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Welcome

Dear SR2A participant,

Six years after the organisation of the first SR2A in Grenoble, it is a great pleasure to welcome you in Amsterdam. The well-attended SR2A-2004 meeting was the start of the series of bi-annual conferences devoted to the use of synchrotron radiation (and similar types of penetrating probes) for the characterisation and investigation of materials from cultural heritage and archaeological sciences.

The previous conferences have been organized by, in the vicinity of and with the help of scientists from synchrotron facilities. The present edition of SR2A on the other hand is in the hands of cultural heritage professionals and scientists employing synchrotron (and related types of) radiation for their research.

In view of the excellent facilities available at the *Van Gogh Museum* for a conference the size of SR2A and of the interest in the cultural heritage institutes situated near the Museum Square in the use of synchrotron and neutron beams for characterisation of artistic and archaeological artefacts and materials, the choice of Amsterdam as conference venue was obvious.

We gratefully thank Luc Van't dack for his hard work and ever lasting effort. Without his professional organisational skills and unbelievable efficiency it would have been much more difficult to organize this meeting.

Thanks to the active help of all members of the scientific committee we are able to propose you an inspiring scientific programme.

The entire meeting will take place inside the *Van Gogh Museum*, except for the poster session (Tuesday afternoon) for which the meeting rooms and entrance hall of the nearby 'Ateliergebouw' have been reserved. This building houses the laboratories of the Netherlands Institute for Cultural Heritage (ICN), the training programme for conservators at the University of Amsterdam (UvA), and the conservation laboratories of the Rijksmuseum. The posters therefore will only be on display Tuesday afternoon. All posters are to be mounted at the start of the Tuesday afternoon session. During the poster session, several possibilities will be offered to visit some of the laboratories and conservation studios.

On Wednesday afternoon an award for the best poster will be presented; this award is made available by the Royal Society of Chemistry via the *Journal of Analytical Atomic Spectrometry* and by the organisers.

Amsterdam is a very agreeable city and we are delighted to welcome you in the city by means of a reception that will take place in the ‘Felix Meritis huis’, a traditional Amsterdam merchant’s town palace.

Please make use of the possibility to enter both the *Rijksmuseum* and the *Van Gogh Museum* free of charge by showing your conference badge at the respective museum entrances.

We hope that you will enjoy the conference and look forward to meeting you again at the next SR2A conference.

Koen Janssens
Joris Dik
Janneke Ottens
Robert van Langh

Programme overview

	Sunday 7 November 2010	Monday 8 November 2010	Tuesday 9 November 2010	Wednesday 10 November 2010
09:30-10:15		Registration		
10:15-10:35		Welcome / opening	Ph. Walter - Archaeology	M. Dowsett - XEOM
10:35-10:55		G. Weber - Art & science		
10:55-11:15			M. Rodrigues - Silver coins	M. Cotte - Pigments
11:15-11:35		J. Mass - Pigment degradation	S. Leroy - Armour	J. Mirao - Roman glass
11:35-11:55		L. Monico - $PbCrO_4$ degradation	E. Perelli Cippo - Bronze & jewellery	S. Cagno - Glass corrosion
11:55-12:15		L. Samain - Prussian blue degradation	W. Kockelmann - Bronzes	S. Lahlil - Lead antimonate
12:15-13:45		*lunch break*	*lunch break*	*lunch break*
13:45-14:25		J.J. Boon - Paint tomography	M. Spring - Smalt degradation	L. Jansen - van Gogh
14:25-14:45		L. Bertrand - IPANEMA	J.-P. Echard - Varnishes	D. Howard - Maia detector
14:45-15:05		A. Candeias - Roman frescoes	I. Reiche - Bones	M. Radtke - pnCCD detectors
15:05-15:25		S. Reguer - Al corrosion	J. Blaas - THz imaging	M. Alfeld - Rembrandt & Runge
15:25-15:50		*refreshment break*	transfer from van Gogh Museum to ICN	*refreshment break*
15:50-16:10		P. Sciau - Gloss coatings	Poster session (ICN) *incl. refreshments*	L. Glaser - Palimpsest
16:10-16:30	Registration *with welcome cocktail*	D. Vantelon - P-speciation		A. Krekeler - Goya
16:30-16:50		A. Adriaens - Pb-carboxylates		J. Dik - Laminography & XRD
16:50-17:10		F. Kergourlay - Dechlorination		Closing remarks
17:10-17:30		R. van Langh - NWO funded research		
17:30-18:00				

PROGRAMME

Sunday 7 November 2010

Felix Meritis, Keizersgracht 324, Amsterdam

16.00 - 19.00 : Registration
Welcome drink & finger food

PROGRAMME

Monday 8 November 2010

Van Gogh Museum, Paulus Potterstraat 7, Amsterdam (doors open at 09.30)

09.30 - 10.15 : Registration

10.15 - 10.35 : Welcome and opening remarks

SESSION I

Session chairperson: Eric Dooryhee

10.35 - 11.15 : ***Invited lecture 1*: Art and science.** [IL-1]
Gregor J.M. Weber (Rijksmuseum Amsterdam, Department of Fine Arts, Amsterdam, The Netherlands)

11.15 - 11.35 : **Photo-oxidative degradation of yellow pigments in Matisse's *Le Bonheur de Vivre* (1905-6): a comparison of XANES, XPS, Raman, and FTIR methodologies.** [O-1]
Jennifer Mass (Winterthur Museum, Scientific Research and Analysis Laboratory, Winterthur, Delaware, U.S.A.)

11.35 - 11.55 : **The degradation process of a lead chromate pigment studied by means of synchrotron radiation X-ray absorption near edge (SR-μXANES) and X-ray fluorescence spectroscopy (SR-μXRF).** [O-2]
Letizia Monico (University of Antwerp, Department of Chemistry, Micro- and Trace Analysis centre (MiTAC), Antwerp-Wilrijk, Belgium)

11.55 - 12.15 : **Study of the degradation mechanisms of Prussian blue in paint layers by X-ray absorption spectroscopy.** [O-3]
Louise Samain (Université de Liège, Centre Européen d'Archéométrie, Liège, Belgium)

12.15 - 13.45 : Lunch provided by conference organisers in the *van Gogh Museum*

PROGRAMME

Monday 8 November 2010

Van Gogh Museum, Paulus Potterstraat 7, Amsterdam

SESSION II

Session chairpersons: Alberto de Tagle - Ina Reiche

13.45 - 14.25 : ***Invited lecture 2*: Synchrotron-based X-ray tomographic microscopy of paints.** [IL-2]
Jaap J. Boon (Swiss Institute for Art Research, Zürich, Switzerland)

14:25 - 14.45 : **Progress state of the European research platform IPANEMA for ancient materials at the SOLEIL synchrotron.** [O-4]
Loïc Bertrand (Synchrotron Soleil, IPANEMA, Gif-sur-Yvette, France

14.45 - 15.05 : **Integrated study of Roman frescoes from Evora (Southern Portugal).** [O-5]
Antonio Candeias (Evora University, HERCULES Laboratory and Evora Chemistry Centre, Évora, Portugal)

15.05 - 15.25 : **EXAFS contribution to the study of aluminium corrosion layers of air and space museum aircrafts for their preservation.** [O-6]
Solenn Reguer (Synchrotron Soleil, DiffAbs Beamline, Gif-sur-Yvette, France)

15.25 - 15.50 : Refreshment break

15.50 - 16.10 : **X-ray fluorescence microprobe study of the gloss coatings of antique potteries.** [O-7]
Philippe Sciau (CNRS, CEMES, Toulouse, France)

16:10 – 16:30 **Phosphorous speciation in the corrosion products of historical iron artefacts.** [O-8]
Delphine Vantelon (Synchrotron Soleil, LUCIA Beamline, Gif-sur-Yvette, France)

16.30 - 16.50 : **Real time XRD monitoring of lead carboxylate growth in an environmental cell.** [O-9]
Annemie Adriaens (Ghent University, Department of Analytical Chemistry, Ghent, Belgium)

16.50 - 17.10 : **In situ monitoring of dechlorination treatment of marine archaeological artefacts by combination of microbeam synchrotron X-ray diffraction and X-ray absorption.** [O-10]
Florian Kergourlay (C.E.A. Saclay, IRAMAT LMC CNRS UMR 5060 and LAPA; SIS2M UMR 3299 CNRS-CEA, Gif-sur-Yvette, France)

17.10 - 17.30 : **Funded research possibilities by NWO (The Netherlands Organisation for Scientific Research) between sciences and arts.**
Robert van Langh (Rijksmuseum Amsterdam, Department of Conservation, Amsterdam, The Netherlands)

PROGRAMME

Tuesday 9 November 2010

Van Gogh Museum, Paulus Potterstraat 7, Amsterdam (doors open at 10.00)

10.00 - 10.15 : Registration

SESSION III

Session chairperson: Martin Radtke

10.15 - 10.55 : **Invited lecture 3: 14 years of synchrotron radiation for the French museums: back to the Louvre.** [IL-3]
Philippe Walter (CR2MF - Centre Recherche et Restauration des Musées de France, Paris, France)

10.55 - 11.15 : **Further metallurgical analyses on silver coins of Trajan (98 - 117 AD).** [O-11]
Marta Rodrigues (Academy of Fine Arts, Institute of Science and Technology in Art, Vienna, Austria)

11.15 - 11.35 : **Trace element microanalytical study of the provenance of armour samples from the Wallace Collection.** [O-12]
Stéphanie Leroy (C.E.A. Saclay, IRAMAT LMC CNRS UMR 5060 and CEA/CNRS UMR 9956, Gif-sur-Yvette, France)

11.35 - 11.55 : **The *ANCIENT CHARM* project: element sensitive imaging with thermal and epithermal neutrons.** [O-13]
Enrico Perelli Cippo (University of Milan-Bicocca, Department of Physics, Milan, Italy)

11.55 - 12.15 : **Studying Renaissance bronze statuettes by combined neutron imaging and neutron diffraction techniques.** [O-14]
Winfried Kockelmann (STFC - Science and Technology Facility Council, Rutherford Appleton Laboratory, ISIS Neutron Source, Chilton, Great Britain)

12.15 - 13.45 : Lunch break

PROGRAMME

Tuesday 9 November 2010

Van Gogh Museum, Paulus Potterstraat 7, Amsterdam

SESSION IV

Session chairperson: Simona Quartieri

13.45 - 14.25 : ***Invited lecture 4*: Investigation of the degradation of smalt in paintings using multiple synchrotron and laboratory techniques.** [IL-4]
Marika Spring (The National Gallery, London, Great Britain)

14:25 - 14.45 : **Synchrotron analyses of varnishes of historical musical instruments.** [O-15]
Jean-Philippe Echard (Musée de la Musique, Laboratoire de Recherche et de Restauration, Paris, France)

14.45 - 15.05 : **Synchrotron radiation micro-X-ray tomography - a useful tool for the identification of prehistoric bone materials.** [O-16]
Ina Reiche (CR2MF - Centre Recherche et Restauration des Musées de France, UMR 171 CNRS, GdR 3174 ChimARC, Paris, France)

15.05 - 15.25 : **THz imaging.** [O-17]
Jorik Blaas (Delft University of Technology, Faculty of 3ME, Material Science and Engineering, Structure and Change, Delft, The Netherlands)

Rijksmuseum / ICN
Ateliergebouw, Hobbemastraat 22, Amsterdam

15.40 - 19.00 : Poster session / Finger food & drinks

Participants have the possibility to visit the:
- Rijksmuseum conservation laboratories
  (glass/ceramics and metals)
- ICN analytical laboratories

Pre-registration required (before Tuesday lunchtime) using the card enclosed with the conference documents.

PROGRAMME

Wednesday 10 November 2010

Van Gogh Museum, Paulus Potterstraat 7, Amsterdam (doors open at 10.00)

10.00 - 10.15 : Registration

SESSION V

Session chairperson: Joris Dik

10.15 - 10.55 : ***Invited lecture 5*: X-ray excited optical microscopy - a new tool for cultural heritage, spectroelectrochemistry, and wider applications.** [IL-5]
Mark G. Dowsett (University of Warwick, Department of Physics, Coventry, Great Britain)

10.55 - 11.15 : **Synchrotron-based micro X-ray fluorescence and cultural heritage: complex samples and complex spectra.** [O-18]
Marine Cotte (ESRF - European Synchrotron Radiation Facility, Grenoble Cedex, France)

11.15 - 11.35 : **Study of Roman glasses from Southwest Iberia using SR-µ-XRF, external PIXE/PIGE, and variable-pressure SEM-EDS.** [O-19]
José Mirao (Evora University, HERCULES Laboratory and Evora Geophysics Centre, Évora, Portugal)

11.35 - 11.55 : **The browning of stained glass windows: characterisation of Mn-rich bodies and evaluation of cleaning methods.** [O-20]
Simone Cagno (University of Antwerp, Department of Chemistry, Micro- and Trace Analysis centre (MiTAC), Antwerp-Wilrijk, Belgium)

11.55 - 12.15 : **New insight on antimonate-based glass opacifiers by the use of SR-µ-XANES, SR-µ-XRF and TEM.** [O-21]
Sophia Lahlil (CR2MF - Centre Recherche et Restauration des Musées de France, Paris, France)

12.15 - 13.45 : Lunch break

PROGRAMME

Wednesday 10 November 2010

Van Gogh Museum, Paulus Potterstraat 7, Amsterdam

SESSION VI

Session chairpersons: Koen Janssens - Jean Susini

13.45 - 14.25 : ***Invited lecture 6*: Questions about van Gogh.** [IL-6]
Leo Jansen (Van Gogh Museum, Amsterdam, The Netherlands)

14:25 - 14.45 : **Scanning X-ray fluorescence elemental mapping of paintings with synchrotron radiation.** [O-22]
Daryl L. Howard (Australian Synchrotron, Clayton, VIC, Australia)

14.45 - 15.05 : **First images of a colour X-ray camera, a detector with high resolution in energy and space.** [O-23]
Martin Radtke (BAM - Federal Institute for Materials Research and Testing, Berlin, Germany)

15.05 - 15.25 : **Imaging of hidden paint layers in historical paintings by synchrotron-based scanning macro-XRF.** [O-24]
Matthias Alfeld (University of Antwerp, Department of Chemistry, Micro- and Trace Analysis centre (MiTAC), Antwerp-Wilrijk, Belgium)

15.25 - 15.50 : Refreshment break

15.50 - 16.10 : **Recovering erased scripts from palimpsests using the X-ray fluorescence element mapping technique.** [O-25]
Leif Glaser (Hamburger Synchrotronstrahlungslabor HASYLAB at Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany)

16.10 - 16.30 : **In-situ investigation of a hidden portrait by Goya using a mobile scanning macro-XRF set-up at the Rijksmuseum in Amsterdam.** [O-26]
Anna Krekeler (Rijksmuseum Amsterdam, Dept. of Paintings, Amsterdam, The Netherlands)

16.30 - 16.50 : **Laminography and diffraction-based imaging of painting.** [O-27]
Joris Dik (Delft University of Technology, Department of Materials Science and Engineering, Delft, The Netherlands)

16.50 : Conference closing / Concluding remarks / Poster award
Eric Dooryhee

PROGRAMME

Tuesday 9 November 2010

Rijksmuseum / ICN
Ateliergebouw, Hobbemastraat 22, Amsterdam

15.40 - 19.00 : Poster session / Finger food & drinks

POSTER SESSION

1. **Different methods of analysis for the identification of materials dated to different periods in Egypt.**
   Safaa Abd El Salam
2. **Analysis of Safavid and Mughal tiles of 16th and 17th centuries using XRD and EDX.**
   Kamran Ahmadi and K. Marzban Rad.
3. **In-situ investigation of a version of Caravaggio's "*Supper at Emmaus*" with a mobile scanning macro-XRF set-up.**
   Matthias Alfeld, Koen Janssens and Joris Dik
4. **Iron oxidation state in archaeological silicatic glasses: a comparison between XANES and Mössbauer data.**
   Rossella Arletti, Simona Quartieri, L. De Ferri, Ian C. Freestone and F. Wagner
5. **The use of innovative techniques for the study of degradation and alteration products on building stones: a case study.**
   Donatella Barca, C.M. Belfiore, G.M. Crisci, Mauro F. La Russa, A. Pezzino and S.A. Ruffolo
6. **Analysis of charcoal and wood from Czarnówsko site (Pomorskie Province, Poland).**
   Magdalena Benysek, Danuta Nawrocka and Małgorzata Szczepaniak
7. **The alteration processes in stained glasses: a comparison between modern and ancient Italian stained glass windows.**
   R. Bertoncello, B. Dal Bianco, A. Lausi, Luca Nodari, Jasper R. Plaisier, E. Rebello, U. Russo and A. Vezzoli
8. **The portraits of the "*Uomini Illustri*": characterisation of green painted areas using combined µ-SR-XRF and µ-SR-XRD.**
   Irene Bonacini, Myriam Eveno, Giorgia Sciutto, Gema Martinez-Criado, Edith Joseph, Michel Menu, Rocco Mazzeo, Silvia Prati, Letizia Amadori and Marine Cotte
9. **Looking inside! 3D imaging experiments on alum-conserved archaeological wood.**
   S. Braovac, M. Christensen, Hartmut Kutzke, S. Hartmann, R. Mokso and Eberhard H. Lehmann
10. **Microtomography and SEM microanalysis studies of musical instruments from the Correr Museum in Venice.**
    Stefania Bruni, Giuseppe Maino, Emanuele Marconi, Carmela Vaccaro, Lisa Volpe and Franco Zanini

PROGRAMME

Tuesday 9 November 2010

Rijksmuseum / ICN
Ateliergebouw, Hobbemastraat 22, Amsterdam

15.40 - 19.00 : Poster session / Finger food & drinks

POSTER SESSION - continued

11. **SR-μ-XRF on human bones: an aid to reconstruct dietary habits.**
Néstor Caracciolo, Susana Boeykens, O. Palacios, V. Killian Galván, D. Olivera and Cristina Vázquez

12. **Evidence of the role of Zn and Fe cations as dopants in lead antimonite yellow by X-ray absorption spectroscopy (XAS).**
Laura Cartechini, C. Miliani, F. Rosi, V. Manuali, Bruno G. Brunetti, A. Sgamellotti and Francesco D'Acapito

13. **Integrated X- and neutron-based analysis on bronze artefacts from the Ligurian settlement of Guardamonte-Monte Vallassa.**
C. Chiaramonte Treré, L. Mordeglia, Enrico Perelli Cippo, Roberta Cattaneo and G. Gorini

14. **A study on gold and copper provenance for Romanian prehistoric objects using micro-SR-XRF.**
Bogdan Constantinescu, A. Vasilescu, Martin Radtke and Uwe Reinholz

15. **Comparison between TOF-ND and XRD quantitative phase analysis of ancient potteries.**
V. Crupi, D. Majolino, V. Venuti, Germana Barone, C.M. Belfiore and Paolo Mazzoleni

16. **Characterisation of ancient findings by means of X-ray fluorescence and Fourier-transform infrared absorbance spectroscopy.**
V. Crupi, Francesca Longo, D. Majolino, V. Venuti, Germana Barone and Paolo Mazzoleni

17. ***esaPROJECT*: user friendly software developed for synchrotron-based heritage science.**
Mark G. Dowsett and Annemie Adriaens

18. **A synchrotron radiation study of copper carboxylate layers on the XMAS beamline.**
Alice Elia, Annemie Adriaens, P. Normile and Mark G. Dowsett

19. **Shedding light on the role of the substrate in Prussian blue discolouration process.**
Claire Gervais, E.P. Vicenzi, M-A. Languille, S. Pelletier, Loïc Bertrand, Solenn Reguer, C. Laulhe, M. Gillet and C. Garnier

20. **From Koto age to modern times. Quantitative characterisation of Japanese swords through time-of-flight neutron diffraction.**
Francesco Grazzi, Laura Bartoli, F. Civita, R. Franci, A. Paradowska, A. Scherillo and M. Zoppi

PROGRAMME

Tuesday 9 November 2010

Rijksmuseum / ICN
Ateliergebouw, Hobbemastraat 22, Amsterdam

15.40 - 19.00 : Poster session / Finger food & drinks

POSTER SESSION - continued

21. **Non-destructive study of antique bronze coins with high lead content using X-ray and neutron tomography.**
    Martina Griesser, R. Traum, P. Vontobel and Eberhard H. Lehmann
22. **Combined neutron and synchrotron X-ray microprobe analysis: attempt to disclose 3600 years-old secrets of a unique Bronze Age metal artefact.**
    Daniel Grolimund, D. Berger, S. Bolliger-Schreyer, C.N. Borca, F. Müller, J. Hovind, K. Hunger, Eberhard H. Lehmann, P. Vontobel and H.A.O. Wang
23. **SRXRF measurements at non-planar objects: automatic determination of the angle of incidence of the exciting X-ray.**
    Christian Grunewald, Martin Radtke, Uwe Reinholz and Heinrich Riesemeier
24. **Optical design of an X-ray excited optical luminescence microscope (XEOM).**
    Matthew Hand, Mark G. Dowsett and Annemie Adriaens
25. **Looking at the infinitively small for a deeper investigation of prehistoric stone tools.**
    Maria Rosa Iovino
26. **Characterisation of iron minerals in the slip layers of Hellenistic ceramic wares from Dorylaion (Eskisehir, Turkey).**
    Ali Issi, A. Kara, A. Raškovska, O. Grupce and B. Minčeva-Šukarova
27. **Analysis of the late 18th - early 19th century creamware - the problem of provenance.**
    Mateja Kos and Z. Smit
28. **MCX: new opportunities in cultural heritage research using X-ray diffraction.**
    A. Lausi, Luca Nodari, Jasper R. Plaisier, U. Russo and G. Zerauschek
29. **Modern pigments and artistic ceramics: the use of oxide based pigments in the Art Nouveau tiles of the *Hungaria Hotel* at Venice Lido.**
    A. Lausi, Luca Nodari, Jasper R. Plaisier and U. Russo
30. **Characterisation of fossil bone composition at micro-scale by synchrotron infrared micro-spectroscopy.**
    Matthieu Lebon, Katharina Müller and Ina Reiche

PROGRAMME

Tuesday 9 November 2010

Rijksmuseum / ICN
Ateliergebouw, Hobbemastraat 22, Amsterdam

15.40 - 19.00 : Poster session / Finger food & drinks

POSTER SESSION - continued

31. **The complementary use of neutrons and X-rays for the non-invasive inspection of objects with cultural heritage value.**
Eberhard H. Lehmann, J. Hovind, S. Hartmann, E. Deschler-Erb, K. Müller and C. Flügel

32. **Composition and morphology of the priming in Hayez paintings.**
Maurizio Mattarelli, S. Gialanella, C. Perazzolli, L. Lutterotti and B. Ferriani

33. **Pre-restoration investigation of floor mosaics from the "*Tretyakov Trade House*" in Moscow.**
Anna Ya. Mazina and S.V. Sokolov

34. **Detecting deterioration of ancient stone material using scanning electron microscopy with X-ray microanalysis and possibilities of conservation: the case of Marina el Alamein archaeological site (Egypt).**
Malgorzata Mrozek-Wysocka and P. Zambrzycki

35. **A study of HgS discolouration in "*The Adoration of the Magi*" by P.P. Rubens.**
Marie Radepont, Koen Janssens, Geert Van der Snickt, Marine Cotte and L. Klaassen

36. **Characterisation of precious metal objects with SRXRF at the BAMline.**
Martin Radtke, Uwe Reinholz and Heinrich Riesemeier

37. **Room temperature study of the degradation of iron gall ink impregnated under various oxygen and humidity conditions – time-dependent monitoring by viscosity and X-ray absorption near-edge spectrometry measurements.**
Veronique Rouchon, Maroussia Duranton, Cédric Burgaud, Eleonora Pellizi, Koen Janssens, Wout de Nolf, Geert Nuyst, Frederik Vanmeert and Kevin Hellemans

38. **Metal production in Israel during the Persian period: archaeometallurgical and geometallurgical research.**
Kamil Sari

39. **Search of improved radiographic methods for paintings by means of state-of-the-art laboratory and synchrotron technology.**
Olivier Schalm, Ana Cabal and Piet Van Espen

40. **Benefits of the complementary use of monochromatic and white-beam X-ray microdiffraction for the investigation of ancient materials.**
Philippe Sciau, Josep Roqué Rosell, Philippe Goudeau, Martin Kunz and Nobumichi Tamura

PROGRAMME

Tuesday 9 November 2010

Rijksmuseum / ICN
Ateliergebouw, Hobbemastraat 22, Amsterdam

15.40 - 19.00 : Poster session / Finger food & drinks

POSTER SESSION - continued

41. **Role of synchrotron radiation in the stones and paintings of *Kalinjar Fort* in India.**
Raj Kishor Shukla, Ved Prakash Shukla, Kumar Arvind and P.C.S. Dwivedi

42. **Portable XRF and LIPS combined characterisation of copper alloy artefacts.**
Salvatore Siano, Juri Agresti, A. Mencaglia, M. Miccio and M. Ferretti

43. **The role of copper on colour of paleo-christian glass mosaic tesserae: a XAS study.**
Alberta Silvestri, Francesco D'Acapito, S. Tonietto and Gianmario Molin

44. **Cultural heritage studies at ANKA FLUO beamline.**
Rolf Simon

45. **Application of cathodoluminescence in mortars selection for ^{14}C dating.**
Małgorzata Szczepaniak and Danuta Nawrocka

46. **SEM-EDS, XRD and petrography in deterioration of sandstone building materials.**
Małgorzata Szczepaniak

47. **Casting technology of Renaissance bronze statuettes: the use of TOF-neutron diffraction for studying afterwork of Renaissance casting techniques.**
Robert van Langh, L. Bartoli, J. Santisteban and D. Visser

48. **Determination of the oxidation and coordination of Co, Mn and Fe in blue glaze studied by XAFS spectroscopy.**
Changsui Wang, Lihua Wang, Jian Zhu, Li Guan, Yuying Huang and Jing Zhang

49. **XAS characterisation of copper in archaeological glasses in Thailand.**
K. Won-in, Y. Thongkam, W. Klysuban and Pisutti Dararutana

50. **Drilling technology research of perforated jades excavated from Xuejiagang site (5000 - 6000 BP) in China through SR-MCT.**
Yimin Yang, Y. Yang, W.H. Hong and Changsui Wang

51. **Scientific analysis of dragonfly-eyed beads in the Late Warring State (476 - 221 BC) excavated from Shenmingpu site, Henan Province, China.**
Yimin Yang, L.H. Wang, G.D. Song, and Changsui Wang

List of sponsors

The conference organizers wish to acknowledge the support of the following organisations and their sponsors:

- Van Gogh Museum Amsterdam
- Rijksmuseum Amsterdam, Migelien Gerritzen Fonds
- NWO - Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Organisation for Scientific Research), The Hague
- Universiteit Antwerpen
- EXSA - European X-ray Spectrometry Association
- Delft University of Technology
- ICN - Instituut Collectie Nederland (Netherlands Institute for Cultural Heritage)

Monday

8 November 2010

Oral Session I

chairperson: Eric Dooryhee

INVITED LECTURE 1.

ART AND SCIENCE

Gregor J.M. Weber*
Rijksmuseum Amsterdam, Department of Fine Arts
Jan Luijkenstraat 1, P.O. Box 74888, NL-1070 DN Amsterdam, The Netherlands
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ABSTRACT

The creation of a work of art involves two parties, the artist and the beholder. Consciously or not, both are dependant on scientific ideas common in their time. Historically, art and science were not seperated, but integral phenomena. Especially in the 17th and 18th centuries artists tried to base their theoretical ideas and their methods on such sciences as physics, optics, logic, rhetoric, etc.

Nowadays – and especially in these days, when we discuss art and science we are primarily concerned with our modern technical methods for physical examining works of art. This will be the focus of much of today's symposium. This paper, however, will look at the two parties – the artist and the beholder – involved in the process of creating art, and the science that informed that process. In doing so, I will try not to forget the questions that arise from the art itself, and, indeed, from the history of art.

ORAL LECTURE 1.

PHOTO-OXIDATIVE DEGRADATION OF YELLOW PIGMENTS IN MATISSE'S *LE BONHEUR DE VIVRE* (1905-6): A COMPARISON OF XANES, XPS, RAMAN, AND FTIR METHODOLOGIES

Jennifer L. Mass[1,*], *B. Buckley*[2], *M. Little*[2], *C. Weiland*[3], *F. Fang*[3] *and K. Finkelstein*[4]
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ABSTRACT

Matisse's iconic and controversial work, *Le Bonheur de Vivre* (The Joy of Life, 1905-1906, The Barnes Foundation) was examined to identify the origin of the fading, discoloration, chalking, and spalling of the yellow paints. Visual comparison of this work with Matisse's painted studies located at the *Statens Museum for Kunst* in Copenhagen, *The Barnes Foundation* in Merion (PA), and the *San Francisco Museum of Modern Art*, reveal substantial colour shifts in the foliage in the upper left corner and fading of the yellow paints below the central reclining figures. An XRF mapping of the work revealed that the painting was executed with both chrome yellow ($PbCrO_4$) and cadmium yellow (CdS) pigments, but that the discoloration and flaking were confined to the cadmium yellow regions. Microsamples of the cadmium yellows were examined by XANES, SEM-EDS, FTIR, XPS, and Raman spectroscopies. Cadmium carbonate ($CdCO_3$) was identified as the major degradation product in all of the samples, but minor phases of cadmium sulphate and cadmium hydroxide [$CdSO_4.xH_2O$ and $Cd(OH)_2$] were detected by XANES. The light and RH levels required to initiate the discoloration and flaking respectively are currently being examined for the work's reinstallation in Philadelphia.

ORAL LECTURE 2.

THE DEGRADATION PROCESS OF A LEAD CHROMATE PIGMENT STUDIED BY MEANS OF SYNCHROTRON RADIATION X-RAY ABSORPTION NEAR EDGE (SR-μXANES) AND X-RAY FLUORESCENCE SPECTROSCOPY (SR-μXRF)

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ABSTRACT

In the 19th century, the pioneers of modern art, such as *V. van Gogh*, *J. Ensor* and *G. Seurat*, benefited greatly from both the invention of the paint tube and the introduction of new painting materials. New pigments were either synthetic, purer equivalents for the traditional pigments or entirely new compounds, yielding brighter colours. The latter provided new stylistic possibilities, intensively explored by the progressive painters of that period. Nevertheless, the incorporation of these innovative materials into the palette did not only create new artistic vistas, it also entailed a significant risk. In contrast with the tried-and-tested materials used by the Old Masters (e.g., *P.P. Rubens*, *Rembrandt*, etc.), the resistance of such modern pigments towards (fluctuating) atmospheric conditions (i.e., light and humidity) was largely unknown. More than one century later, quite a few of the modern pigments employed by the 19th century avant-garde artists appear to discolour as a result of photo-chemically induced reactions and/or reactions with atmospheric gases. In this work, the degradation process of the pigment chrome yellow ($PbCrO_4$) is studied by means of synchrotron radiation X-ray absorption near edge (XANES) and X-ray fluorescence (XRF) spectroscopy. Measurements were carried at beam line ID21 (ESRF, Grenoble) on both artificially aged model samples and historic samples, taken from paintings of *Vincent van Gogh* (van Gogh Museum, Amsterdam). Both XANES point measurements as XRF-maps revealed the presence of a Cr(III) compound in an aged model sample. This degradation product is especially located in the discoloured top layer. The reduction of the original Cr(VI) is demonstrated by a decrease of the intensity of the Cr pre-edge peak at 5.993 keV and by a shift of the absorption edge towards lower energies. XANES point measurements performed on imbedded samples from two different *van Gogh* paintings revealed the presence of Cr(III) in Ba-rich areas. In addition, various Cr(VI) compounds (probably K and Pb chromates) were identified. Although the exact nature of the degradation product has not yet been revealed, the analytical results

suggest a reduction of the original, hexavalent Cr. In this context, IR and Raman studies are in progress. In addition, the possible influence of Ba and other components, such as sulphates and carbonates, on this Cr(VI) reduction process is also in progress.

ORAL LECTURE 3.

STUDY OF THE DEGRADATION MECHANISMS OF PRUSSIAN BLUE IN PAINT LAYERS BY X-RAY ABSORPTION SPECTROSCOPY

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ABSTRACT

Prussian blue was accidentally discovered in Berlin in 1704. Often described as the first synthetic coordination compound, Prussian blue is a hydrated iron(III) hexacyano-ferrate(II) complex that can contain ammonium, potassium or sodium ions. The intense blue colour is due to an intervalence charge transfer between the two oxidation states of iron at 680 nm. Because of its low cost the pigment enjoyed immediate popularity and was widely used by artists until about 1970. However, the permanence of Prussian blue was already questioned by the mid-18th century, as the pigment shows a tendency to fade in the light. The presence of impurities in the pigment was recognized as a contributory factor. The methods of preparation affect thus the permanence of the pigment in the way that they lead to the introduction of a certain amount of impurities. However, the degradation processes of Prussian blue in paintings are not completely understood, although the comprehension of these mechanisms can help for preventive conservation and restoration of paintings.

We report here the synthesis of Prussian blue pigments according to ancient and modern preparation methods and their characterisation before and after accelerated ageing by Fe K X-ray absorption spectroscopy. This technique allows identifying the changes in the local electronic and structural configuration of the iron ions in aged Prussian blue.

Oral Session II

chairpersons: Alberto de Tagle & Ina Reiche

INVITED LECTURE 2.

SYNCHROTRON BASED X-RAY TOMOGRAPHIC MICROSCOPY OF PAINTS

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ABSTRACT

Synchrotron based X-ray tomographic microscopy (XTM) is an innovative way to examine samples from paintings. Minimal preparation or manipulation is required and the paint sample is studied and sectioned in virtual space after X-ray tomographic analysis. Using image processing techniques such as segmentation, the three-dimensional distribution of pigment particles, media and other features can be reconstructed at a voxel resolution of 350 nm. Different paint components interact with a coherent X-ray beam in different ways through scattering and absorption. Features with contrasting X-ray interaction properties are successfully distinguished, imaged and studied with this technique. To overcome limitations in resolution and chemical contrast, correlative analytical microscopy is performed using imaging FTIR and SEM-BSE-EDX on actual hand polished cross-sections using the 3D data and virtual sections for orientation and sectioning of the paint chip in the embedding resin. How XTM is integrated in correlative analytical research of paintings is the main theme in the talk.

Explorative studies have been done on historically accurate paint reconstructions and on samples from paintings by the Swiss painter Cuno Amiet (1868-1961), the American painter F.E. Church (1826-1900), the Dutch painter Johannes Bosboom (1817-1891), the 17th century painters Rembrandt van Rijn (1606-1669) and Johannes Vermeer (1632-1675), and the 16th century painter Herman Tom Ring (1520-1597). These studies address questions related to stratigraphy and paint composition, mechanisms of paint reactivity (e.g., formation of crusts and metal soap aggregates) and the physical properties such as porosity of paint and ground layers. X-ray tomography was crucial in a study of the causes of significant paint loss of the tile floor of *The Art of Painting* (c. 1668) by Vermeer.

ORAL LECTURE 4.

PROGRESS STATE OF THE EUROPEAN RESEARCH PLATFORM IPANEMA FOR ANCIENT MATERIALS AT THE SOLEIL SYNCHROTRON

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ABSTRACT

SOLEIL, with a set of international partners, is currently setting-up IPANEMA, a research platform devoted to ancient and historical materials (archaeology, artwork conservation, palaeontology and past environments). The new building adjoining the SOLEIL synchrotron is due to open in 2012 to French, European and international users, and will comply with conservation and environmental standards. The activities of the platform are centred on two main fields: increased support to researchers on ancient materials and research in specific methodological developments. The organisation of training activities such as the New Lights on Ancient Materials School (2004, 2007, 2010) will be continued.

The IPANEMA team supports access for research on ancient materials to all SOLEIL beamlines, but also to other analytical platforms and synchrotron facilities, in the context of a strong increase of the demand at the facility. Over the past 2 years, the team supported research on the identification of rock art painting techniques and alteration, pigment degradation in oil binders, composition of musical instrument varnishes and related data processing, provenance of mediaeval archaeological ferrous artefacts. SOLEIL is already hosting dedicated equipment for sample preparation and complementary characterisations. Access to SOLEIL / IPANEMA for European user groups working on ancient materials is specifically supported through FP7 CHARISMA (European Commission).

Once the platform is fully operational, user support will primarily take place within medium-term research projects – typically 2 to 3 years, adapted to “hosted” PhDs or post-docs. Supported projects will focus on the study of corpuses of samples or collections of objects in order to meet with the needs expressed by the disciplines. In-house methodological developments will focus on 2D and 3D imaging and advanced data analysis of ancient materials. In particular, the IPANEMA project comprises the building, exploitation costs and staff of PUMA, a new full-field and scanning imaging hard X-ray beamline currently in its conceptual design phase.

ORAL LECTURE 5.

INTEGRATED STUDY OF ROMAN FRESCOES FROM EVORA (SOUTHERN PORTUGAL)

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ABSTRACT

Evora, a UNESCO world heritage town, has been inhabited since immemorial times and presents cultural remnants of this intense occupation. In 1988, during renovation works at the Noble House of Rua de Burgos, the ruins of four Roman houses with frescoes that date back from the 1st century AD were found partially overlapped by the Roman City Wall constructed in the 4th century AD. These paintings are excellent examples of Roman paintings and have been exposed since then. Due to the exposure and environmental conditions, the paintings suffered degradation and present several pathologies including white veils, salt efflorescence, biological colonisation and paint detachment. Under the framework of a conservation-restoration intervention that will take place in 2010 a multidisciplinary analytical approach was put together including characterisation of paintings polychromy, binders and mortars, identification of biodeteriogenic microorganism populations and paint pathologies.

Elemental analysis was performed by non-destructive in-situ XRF using an Amptek X-ray source Eclipse II and XR-100CR detector. Microsampling of paint layers was performed on representative areas of the paintings and the cross-sections were analyzed by optical microscopy and SEM-EDS. Complementary analyses of the cross-sections were carried out using the confocal SR μ-XRF setup available at ANKA synchrotron FLUO beamline. The study allowed the identification of the alteration products and revealed the original pigments palette: ochres for the reds, browns and yellows, malachite and green earths for the greens, azurite for the blues, carbon for the blacks and white lead for the whites. Furthermore, the high sensitivity and mapping capacity of FLUO beamline allowed the recognition of elemental associations and segregations.

ORAL LECTURE 6.

EXAFS CONTRIBUTION TO THE STUDY OF ALUMINIUM CORROSION LAYERS OF AIR AND SPACE MUSEUM AIRCRAFTS FOR THEIR PRESERVATION

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ABSTRACT

For 30 years, new metallic materials as Al alloys appear especially in air and space museum collections which preserve a large number of aircrafts. Due to their large dimensions, these latter are often conserved outdoor. These uncontrolled environmental conditions of storage lead to important corrosion processes of the Al alloys surface. Thus, to improve the aircrafts conservation, curators need information on the physico-chemical characteristics of the corrosion layers, especially the phase's structure, and their reactivity under humidity fluctuations. In close collaboration with the French Air and Space museum the study of samples collected on various aircrafts built in the 1930-1980 period was carried out. Nowadays, the composition of the thick corrosion layers formed during long term exposure remains widely unknown because the corrosion products form of very thin marblings of amorphous Al hydroxides. To determine the speciation of Al atoms across the corrosion layers, μ-XANES investigations at the Al-K edge have been performed at the LUCIA beamline (synchrotron SOLEIL). In addition to their amorphous structure, data have shown that corrosion products contain always six-fold coordinated Al but the arrangement of the Al octahedra can differ inside the corrosion layer. These new data obtained for the first time on the corrosion layers of Al alloys are decisive to model the behaviour of such amorphous Al phases during ageing process in cyclic atmospheric conditions and finally to propose new coherent conservation strategies.

ORAL LECTURE 7.

X-RAY FLUORESCENCE MICROPROBE STUDY OF THE GLOSS COATINGS OF ANTIQUE POTTERIES

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ABSTRACT

The ceramic production of the Greek and Roman periods is highly marked by the development of high-gloss surface finishes obtained through the vitrification of an iron oxide-rich clay preparation. Depending on the firing protocol used the surface finishes could be more or less vitrified with a black (reducing condition) or red (oxidising condition) or black and red colour (thermal multi steps process). The mastering of the multi steps process was at the origin of the famous Attic potteries while Terra Sigillata ware comes from the improvement of red gloss coatings through the creation of specific kilns during the Roman time. The mastering of the firing protocol played a significant role in the production of this type of coatings and a key feature to assess the production quality of these antic potteries.

We present results of synchrotron μ-XRF, elemental and valence state mapping and μXANES spectroscopy measurements obtained on cross-sections of pottery specimens previously prepared for scanning electron microscopy. Fe chemical mapping at the micrometer scale revealed an in depth Fe valence distribution in the slip/body set, which is a key factor for inversely getting (reverse engineering) the atmosphere variations during the firing process, and thus allowed us to trace an important part of the firing protocol. Another advantage was the use of the same sample for all type of characterization, which allowed coordinated studies.

ORAL LECTURE 8.

PHOSPHOROUS SPECIATION IN THE CORROSION PRODUCTS OF HISTORICAL IRON ARTEFACTS

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ABSTRACT

Several ancient world heritage iron based structures present quite a good corrosion resistance that is for some authors related to the presence of phosphorus in their metallic substrate. However, the exact protection mechanisms are today not elucidated. The indoor atmospheric corrosion layers are generally mainly constituted of goethite, ferrihydrite and/or maghemite. Some of these phases are very reactive and take part in the metal corrosion processes. The presence of phosphorus could probably modify their chemical reactivity. In order to better understand the role of this element, its distribution and speciation have been investigated, in complement of micro-Raman and meso-XRD investigations, using the combination of micro-XRF and micro-XANES at the P K-edge (LUCIA beamline, SOLEIL Synchrotron) on two types of ancient samples. They contain variable P content in their metallic substrate and are coming from two different geographic sites: beams used as reinforcement in the Amiens Cathedral (France) and Indian built heritage (India). The French samples present a corrosion system mainly constituted by ferrihydrite and goethite with different crystallinities, while the Indian samples possess corrosion layers mainly made of maghemite/magnetite and goethite phases. For both types, two sources of P, global endogenous (in the metal and in fayalite) as well as localised exogenous (in apatite) were revealed. From these two sources, the P diffuses and is heterogeneously distributed in the corrosion layers. Variations of the shape of the XANES spectra evidenced that P is adsorbed as phosphate on all the iron corrosion products present in the layers.

ORAL LECTURE 9.

REAL TIME XRD MONITORING OF LEAD CARBOXYLATE GROWTH IN AN ENVIRONMENTAL CELL

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ABSTRACT

Long-chain lead monocarboxylates have been proposed as corrosion inhibitors for a variety of metals including lead. Using a new and simple deposition process which exploits the fact that long chain carboxylic acids are soluble in ethanol and propanol, we have grown polycrystalline layers of lead carboxylate up to C_{18} simply by soaking the lead in the tincture for a few hours. The growth of these has been monitored in real time in an environmental cell (eCell IV) containing a lead coupon and the tincture on BM28 (XMaS) at the ESRF. X-ray diffraction images were taken at 8 keV using a Mar CCD 165 camera mounted on the Huber goniometer on XMaS the UK CRG at ESRF. S Images were acquired every few minutes over a period of up to 16 hours. Spectra were extracted from the images using our own software esaProject, specially developed to deal with large camera angles and image sets. In some cases grown layers were exposed to acetic acid vapour (a major corrosive agent for heritage lead) at high levels (6 % by volume in air) in eCell to promote attack on a timescale compatible with beam time allocations. We demonstrate the growth of carboxylate layers across the range of chain lengths from C_{10} to C_{18} and show that whilst the lead substrate is coarsely polycrystalline, the carboxylate layers consist of small polycrystals which tend to be randomly oriented from the original aqueous solutions, but have a strong preferred orientation when deposited from alcohol. The acetic acid exposures show that the layers inhibit the formation of lead acetate.

ORAL LECTURE 10.

IN SITU MONITORING OF DECHLORINATION TREATMENT OF MARINE ARCHAEOLOGICAL ARTEFACTS BY COMBINATION OF MICROBEAM SYNCHROTRON X-RAY DIFFRACTION AND X-RAY ABSORPTION

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ABSTRACT

After their archaeological excavation, iron artefacts need to be stabilized by extracting chloride ions from corrosion products to avoid any further degradation. In close collaboration with specialised restoration-conservation laboratories, our work aims to get a better knowledge of the corrosion layout and dechlorination processes occurring during a treatment. To this purpose, a corpus constituted of Roman wrought iron ingots founded on gallo-roman shipwrecks dated from 50 AD has been studied. An original set-up combining X-ray diffraction and X-ray absorption at the Fe K-edge using focused microbeam has been carried out in order to monitor, in situ, the structural evolution of β-$Fe_2(OH)_3Cl$, the main Cl-containing corrosion product of studied samples, during a dechlorination treatment. Moreover, to provide structural information on the chlorinated phases and especially about the environment of the chlorine atom, μ-XANES and μ-EXAFS measurements at the Cl K-edge on a transverse section of the corrosion product layers have been performed using a micrometre beam. It has been highlighted that chloride ions could be adsorbed on iron oxyhydroxides, not only akaganeite but also goethite or ferrihydrite. First results of in situ evolution of β-$Fe_2(OH)_3Cl$ stressed out the usefulness and the complementarity of μ-XRD and μ-XAS to apprehend the dechlorination mechanisms within the corrosion layout.

Tuesday

9 November 2010

Oral Session III

chairperson: Martin Radtke

INVITED LECTURE 3.

14 YEARS OF SYNCHROTRON RADIATION FOR THE FRENCH MUSEUMS: BACK TO THE LOUVRE

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ABSTRACT

We have made since 14 years various synchrotron radiation experiments that were designed to characterize the nature and the mode of preparation of different pigments, both used for paint or makeup (origin of the minerals, chemical synthesis of new compounds, crushing of crystals, mixing of matters, etc.). The combined use of synchrotron X-ray diffraction and X-ray fluorescence spectroscopy offers analytical capabilities of particular interest with various spatial resolutions. These experiments led us to imagine different instruments complementary of synchrotron radiation, namely for the laboratory located in the Louvre Museum or portable, allowing a direct access to the collections in the museums or during excavations. Through examples, we will describe the strength of the association of XRD and XRF and the advantages and limits of the different analytical devices in term of quality of the data, spatial resolution, sensibility and compromise between easiness to use and sophistication.

ORAL LECTURE 11.

FURTHER METALLURGICAL ANALYSES ON SILVER COINS OF TRAJAN (98 - 117 AD)

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ABSTRACT

Within an interdisciplinary project, a group of 65 silver coins (denarii) of Trajan, evenly distributed over the entire span of his reign (2nd to 6th consulate), as well as 3 coins from the reign of his predecessor, the emperor Nerva (96 - 98 AD), were acquired on the coin market. These pieces could be cross-sectioned in order to carry out analyses. Measurements were performed with μ-XRF and μ-SRXRF to check the fineness of the denarius alloy as well as to study if the coins of the different consulates showed distinct traits concerning metal composition which could suggest a change of ore sources.

A clear decrease in the Ag content between the years 99 AD and 100 AD could be observed: while the coins of the Trajan's COS II (98 - 99 AD) contained an average of 88 % Ag, the Ag content was reduced to about 82 % in the coins of his COS III (100 AD). This remained the standard of the Roman mint until the end of Trajan's reign (117 AD). The coins struck from 98 - 102 AD (COS II and COS IV) and the later issues show marked differences in the Au, Bi and Pb concentrations, which indicate a possible change in the sources of metal used. In this context, the problem whether a potential influx of precious metals into the Roman treasury after Trajan's First Dacian Campaign (101/102 AD) could have had any repercussions on the composition of the denarius alloy was also investigated. Documentation of the cross-sections was performed with SEM/EDX in order to clarify details concerning the specific microstructure of the coins. An enrichment of Ag of approx. 100 to 200 μm in the near surface regions of most of the coins due to corrosion effects could be observed.

ORAL LECTURE 12.

TRACE ELEMENT MICROANALYTICAL STUDY OF THE PROVENANCE OF ARMOUR SAMPLES FROM THE WALLACE COLLECTION

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ABSTRACT

Iron-based materials played an essential role in the technical and economical history of past societies, and their circulation generated considerable interest among historians and archaeologists. The present study concerns the trade of iron objects from Lombardy (Italian Alps), a major medieval production area. Most of the regional iron-making industry was dedicated to the production of weapons and armours. However, the latter are not always identified by manufacture marks, and their Lombard provenance is based on stylistic studies. We study here the hypothetical Lombard origin of armours from the *Wallace Collection* (London). This work is part of a wider study on the provenance of steel artefacts from the area.

During the solid-state reduction process of the ore, a large fraction of the iron compounds is not reduced and becomes slag, partly entrapped in final metal artefacts as non-metallic *slag inclusions* (SIs). Recent studies demonstrated that the content ratios in several elements remain constant from the initial ore to the SIs, enabling the study of their provenance from the trace elemental signatures of ore from supplying regions.

SIs in the highly manufactured armours are all very small in dimensions (<40 x 40 μm^2) and need to be studied non-destructively from tiny microsamples. We therefore used the confocal μXRF setup of the FLUO synchrotron beamline (ANKA) to record their trace elemental signatures. As shown from comparisons with a database of Lombardian ores and slag gathered by our team, some armours could have been sold under a counterfeit Italian origin, as the latter was a pledge of quality. In particular, we question the provenance of two Italian helmets, designated by English contemporaries as "Spanish morions", in accordance with doubts expressed by curators.

ORAL LECTURE 13.

THE *ANCIENT CHARM* PROJECT: ELEMENT SENSITIVE IMAGING WITH THERMAL AND EPITHERMAL NEUTRONS

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ABSTRACT

Many elements, especially metals, have a relatively high neutron absorption cross-section in the thermal range. Moreover, some of them (for instance Cu, Zn, Sn, Ag, Au, Sb, As) have neutron absorption resonances in the epithermal energy range (1 eV < E < 1 keV). After neutron absorption, the nuclei are usually left in an excited state and decay with the emission of prompt gamma-ray cascades. Both the gamma-ray emission and neutron transmission spectrum can be measured, either directly (with the use of high-resolution gamma spectrometers) or via the time of flight technique. The aim of *ANCIENT CHARM* was to develop known element-sensitive bulk techniques like prompt gamma activation analysis and neutron resonance capture analysis into space resolved, thus imaging techniques. The new techniques, called prompt gamma activation imaging (PGAI) and neutron resonance capture imaging combined with neutron resonance transmission (NRCI/NRT), were developed both at reactor neutron sources (FRM-II and IKI-HAS) and pulsed neutron sources (GELINA and ISIS), and they were applied to selected samples of importance for cultural heritage (bronze relieves, antique jewels). In fact, such neutron-based techniques are distinctively non-destructive and non-invasive, thus being ideal for cultural heritage applications.

In this study, we present the scientific fundamentals of PGAI and NRCI/NRT and some results obtained with archaeological and artistic samples.

ORAL LECTURE 14.

STUDYING RENAISSANCE BRONZE STATUETTES BY COMBINED NEUTRON IMAGING AND NEUTRON DIFFRACTION TECHNIQUES

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ABSTRACT

The internal features and materials of hollow cast Renaissance bronze statuettes are usually concealed; however, they hold important information relating to the techniques used in the construction of these fine works of art. For this reason we have made these internal structures visible by applying neutron imaging techniques (tomography) at the Paul Sherrer Institute, Villigen, Switzerland. The tomography method allows us to study the exact three-dimensional construction of such bronze sculptures, but the method does not provide direct information on material composition. Since sample taking is not allowed on these precious works of art, additional non-destructive methods have to be used and new scanning techniques developed for further research on the composition of the inner parts. Our approach focuses on analyzing small volumes (2 mm^3) selected with reference to the tomography data. Particular software techniques were used to set-up neutron diffraction measurements on ENGIN-X at the ISIS facility at the Rutherford Appleton Laboratory, UK, which are able to provide compositional information. Using this technique features inside the sculpture could be pinpointed and their material compositions studied. Results from this combined imaging-diffraction technique will lead to a better understanding of the production techniques and greatly assist the archaeometric study of these marvellous bronzes.

Oral Session IV

chairperson: Simona Quartieri

INVITED LECTURE 4.

INVESTIGATION OF THE DEGRADATION OF SMALT IN PAINTINGS USING MULTIPLE SYNCHROTRON AND LABORATORY TECHNIQUES

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ABSTRACT

Smalt is a blue potash glass pigment, with the colour deriving from cobalt. It was most commonly used in paintings between the 16th and 18th centuries, but is not a stable pigment and often degrades causing sometimes dramatic changes in the appearance of paintings. This paper will describe an investigation of this process coupling multiple synchrotron and laboratory techniques. The project was a collaboration between IPANEMA at SOLEIL synchrotron, The National Gallery, and Centre de Recherche et de Restauration des Musées de France. Samples prepared as cross-sections from paintings in the National Gallery and the Louvre that included particles of smalt in varying states of degradation were analyzed, combining synchrotron micro X-ray absorption spectroscopy (μXAS) at the Co K-edge on the LUCIA beamline and synchrotron FTIR microspectroscopy on the SMIS beamline, as well as optical microscopy, SEM-EDX and μ-Raman spectrometry. The results illustrate the specific contribution that each of these complementary techniques makes to our understanding of the deterioration of this pigment, enhanced when used in combination. μ-XAS elucidated the changes occurring in the coordination and environment around the cobalt ion. Differences between degraded and undegraded smalt seen in the FTIR and Raman spectra were indicative of structural changes in the glass. The results from all of these could be correlated with quantitative SEM-EDX analysis carried out on individual particles and on their appearance – degraded or still blue – under the optical microscope.

ORAL LECTURE 15.

SYNCHROTRON ANALYSES OF VARNISHES OF HISTORICAL MUSICAL INSTRUMENTS

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ABSTRACT

Varnishes on musical instruments are complex multilayer systems. Each of these layers is a few tens of micrometres thick, and is a mixture of natural binding media materials admixed with, possibly, colouring materials. The characterisation of the organic and mineral composition within each layer is essential to understand the instruments-makers' materials and techniques. Such analytical characterisation is challenging by the high spatial resolution necessary to characterize each individual layer's composition on samples, whose dimensions are strictly limited by the instruments' conservation rules.

A dedicated innovative sample preparation protocol has been developed, allowing for a complete characterisation using a single sample of approx. 1 mm^3 containing the wood support and the complete varnish stratigraphy. SR-FTIR (on the SMIS beamline, Soleil Synchrotron) and complementary molecular techniques, have been used on varnish samples from a series of violin- and lute-type instruments. Chemical maps of the cross sections allowed identifying oil- and protein-based layers, discriminating the compositions of adjacent layers at the micrometre-scale, and gave new insights into the diversity of varnishing materials and techniques in Europe between the 16th and the 18th century.

ORAL LECTURE 16.

SYNCHROTRON RADIATION MICRO X-RAY TOMOGRAPHY - A USEFUL TOOL FOR THE IDENTIFICATION OF PREHISTORIC BONE MATERIALS

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ABSTRACT

Prehistoric objects are important witnesses of human occupations. Scientific examinations of these objects contribute to our understanding of ancient societies. Amongst others, the determination of the raw materials used is a key point for archaeological interpretation. This study is focused on the distinction of archaeological ivory, bone and antler in order to identify the raw material used for the manufacture of Palaeolithic objects. Even if the identification of different kinds of osseous material seems to be trivial it can be difficult in the case of ancient objects heavily carved and more or less altered in their chemical and isotopic composition. The high performance of SR micro-CT providing highly resolved 3D information on the micro-structure permitted to establish structural distinction features between modern references of ivory, bone and antler. However, diagenetic structural changes during burial time have to be considered for archaeological objects. As SR micro-CT enables to compare inner and possibly less altered parts of the object the potential of this method for the distinction of archaeological bone materials was tested. Specific structural parameters allowing the distinction of ivory from bone and antler can also be determined for Palaeolithic bone materials. Thus, we provide a new tool to identify non-destructively prehistoric bone objects.

ORAL LECTURE 17.

THz IMAGING

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ABSTRACT

Terahertz imaging is a promising new technique for understanding the stratigraphy of paintings. Pulsed time-domain terahertz measurements can provide us a safe, non-ionising, non-destructive, way to image the layered structure of paintings. The optical pulsed light penetrates the surface up to a depth of several millimetres, even through paint layers which are opaque to infrared light or X-rays. The pulse reflects off surface interfaces, in particular at the transition layers between different paints and materials, giving us thickness information on these layers. We demonstrate our results on imaging thin layers, and show how the sensitivity can be optimized by dedicated hardware modifications and additional signal processing.

Wednesday

10 November 2010

Oral Session V

chairperson: Joris Dik

INVITED LECTURE 5.

X-RAY EXCITED OPTICAL MICROSCOPY - A NEW TOOL FOR CULTURAL HERITAGE, SPECTROELECTROCHEMISTRY, AND WIDER APPLICATIONS

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ABSTRACT

Bombardment of materials by keV X-rays results in broadband (200 - 1000 nm) optical emission due to fluorescence and phosphorescence. When the X-ray energy is swept across core ionisation energies of the atoms, the processes which impose XANES and EXAFS modulation on the fluorescent X-ray emission, also modulate the optical wavelengths, sometimes in a near-identical fashion. In addition, low energy photoelectrons generated by core level ionisation close to the edge energy, can themselves excite narrow-band optical transitions spatially close to the ionized atom. A combination of light-optical imaging and dispersion therefore forms the basis for a spectromicroscopy which has the potential to give both site and state specific information. This technique can give chemical imaging with micron-scale lateral resolution, without the need for a micro-focus beam-line. We describe a new large aperture broadband microscopy system based on the above principles and show results from a proof of concept device deployed on the UK and Dutch-Belgian CRGs (XMaS and DUBBLE) at the ESRF. Test systems were the heritage metals copper, lead zinc and tin and a selection of their corrosion products. The results show the close similarity and information content from XANES and EXAFS data acquired in this way, to that resulting from X-ray fluorescence measurements, with the addition of emission from chemically specific chromophores in particular optical bands. The latter allow the direct mapping of the chemical species responsible, and technique in general will allow mapping of structure and oxidation state.

ORAL LECTURE 18.

SYNCHROTRON-BASED MICRO X-RAY FLUORESCENCE AND CULTURAL HERITAGE: COMPLEX SAMPLES AND COMPLEX SPECTRA

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ABSTRACT

Art objects are usually puzzling materials. For instance, ancient paintings are often a complex mixture of tens of ingredients, inorganic and crystallized products such as pigments and plasters; organic and amorphous ingredients, such as binders, sizers or varnishes. Access to their micrometric heterogeneity requires high spatial resolution micro-analytical techniques, as exemplified by SR-based micro-X-ray fluorescence (μ-XRF) which is increasingly used for elemental analysis of ancient materials.

Beyond the technical challenges of μ-XRF, analysis of art objects involves other methodological issues such as complexity of the XRF spectra. Indeed, these complex samples often contain mixtures of high-Z elements (such as lead or mercury) together with low-Z elements. Overlap of M- or L-emission lines of the former with the K-emission lines of the latter hampers elemental identification with fluorescence analyses. This problem is particularly frequent on the ID21 beamline (ESRF), which is dedicated to micro-spectroscopy in the tender X-ray domain (2 - 7 keV). The overlap between K-lines of low Z elements with M- and L-lines of high Z elements is usually smaller than the energy resolution of classical solid state energy-dispersive X-ray detectors. To tackle this last issue, two parallel strategies have been developed at ID21.

A software solution was offered with the development of a user friendly programme for XRF spectra fitting and semi-quantitative analysis, *PyMca*. Complete description of the M-shell is possible, which is particularly helpful for analysis of data collected at low energy and for the decomposition of overlapping peaks. This programme allows interactive as well as batch processing of large data sets. *PyMca* is now commonly used in the cultural heritage field, primarily for SR-based μXRF, and progressively for an increasing number of types of hyper spectral data sets.

A hardware approach was also considered to complement the software development. For this purpose, a compact high resolution wavelength-dispersive X-ray spectrometer has been especially designed to fit into our microscope. It is based on a polycapillary optic for XRF collection and relies upon a flat-crystal geometry. Energy resolutions of tens of eV can easily be achieved and enable a very good separation of M-, L- and K-lines, hence a more reliable and more sensitive elemental identification. Line selectivity proved to be also a clear asset for background free X-ray absorption spectroscopy.

Assets and drawbacks of the two approaches will be discussed in the specific context of the analysis of complex materials from cultural heritage field and illustrated by examples of studies of paintings and glasses.

ORAL LECTURE 19.

STUDY OF ROMAN GLASSES FROM SOUTHWEST IBERIA USING SR-μ-XRF, EXTERNAL PIXE/PIGE, AND VARIABLE-PRESSURE SEM-EDS

José Mirão[1,*], *N. Schiavon*[1], *A. Carneiro*[2], *M.C. Lopes*[3], *T. Ferreira*[4], *C. Dias*[4], *Rolf Simon*[5], *T. Calligaro*[6] *and Antonio Candeias*[4,7]

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ABSTRACT

During the Roman Empire, the Iberian Peninsula, known as Hispania, was an important region due to the abundance of natural resources including gold, silver, lead, tin and copper ores, rich soils and seas. Monumental towns like Emerita Augusta (Merida, Spain) and Pax Julia (Beja, Portugal) enabled the administration of the southwest territory and the development of important commercial, industrial and agricultural activities. Archaeological excavations are bringing to light evidences of this intense occupation, allowing a deeper understanding about exchange and trade patterns in this Roman region by the differentiation between local and imported goods and the identification of possible local sources.

In this work we present results of a multi-technique methodology for the study of roman glasses from different archaeological sites and ages (from 1st to 5th century) in Southern Portugal using non-destructive and microanalytical techniques namely confocal synchrotron induced X-ray fluorescence spectrometry, proton induced X-ray and gamma ray emission spectrometry (PIXE/PIGE) and variable pressure scanning electron microscopy coupled with energy dispersive X-ray spectrometry (VP-SEM-EDS).

The material characterisation study of the glasses allowed the identification of different technological processes including minor and major elements, fluxes, inclusions and chromophores and the evaluation of degradation processes including leaching patterns and pathologies. Furthermore, the statistical analysis allowed the classification into different clusters and groups according to source, colour and age.

ORAL LECTURE 20.

THE BROWNING OF STAINED GLASS WINDOWS: CHARACTERISATION OF Mn-RICH BODIES AND EVALUATION OF CLEANING METHODS

Simone Cagno[1,*], *Gert Nuyts*[1], *Kristel de Vis*[2], *Joost Caen*[2], *Lukas Helfen*[3], *Simone Bugani*[4] *and Koen Janssens*[1]

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ABSTRACT

Mn-rich bodies can be found in the alteration layer of ancient glass objects and cause the surface to turn brown to black. Historical glass contains a natural quantity of manganese in the Mn(II) or Mn(III) oxidation states. In the Mn-containing bodies, instead, manganese is in the Mn(IV) state. Both internal and external sources of Mn have been hypothesised to explain this phenomenon. In restoration practice, dark surface layers are converted into colourless ones with the application of reducing solutions.

In this work the shape and distribution of the Mn-bodies are studied and the effectiveness of different glass restoration methods is assessed. Fragments of glass windows dated to the 14th century, originating from the Canterbury Cathedral (UK) were examined with high resolution CT, performed with synchrotron radiation at ESRF, beamline ID19. The same samples were analysed before, during and after the treatment with products used in common restoration practice, with different concentrations and application time, in order to have a 'real time' monitoring of the treatment. The results obtained provide useful information in view of a correct conservation approach of glass artefacts.

ORAL LECTURE 21.

NEW INSIGHT ON ANTIMONATE-BASED GLASS OPACIFIERS BY THE USE OF SR-µ-XANES, SR-µ-XRF AND TEM

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ABSTRACT

White calcium antimonate and yellow lead antimonate compounds have a predominant role throughout history as they are found from the 3rd millenium BC in Mesopotamia, until modern times. However, both their technology and provenance remain obscure. Indeed, many difficulties remain on determining the nature and the structure of the crystals because of their small sizes, their high heterogeneity of chemical composition, the effect of the surrounding environment and the variability of the lattice parameters of the crystalline structure. Moreover, in classical X-ray fluorescence (XRF) spectra and X-ray energy-dispersive analyses, elements present in the crystals such as Ca, Sb and Sn, highly interfere with an overlap smaller than the energy resolution of classical solid state energy dispersive detectors.

Through the study of calcium or lead antimonate based opacifiers in three opaque glass productions – Egyptian glass of the 18th dynasty (1570 - 1292 BC), Roman mosaic tesserae from Aquilea and Rome (1st century BC - 4th century AD) and Nevers lampworking glass figures (18th century AD) – this paper aims at showing the necessity of using systematic micro-chemical analyses, high spatial and energy resolution techniques to investigate this type of materials. The synchrotron-based µ-XANES measurements proved to be very well suited to the selective measure of the antimony oxidation state in the vitreous matrix. This latter, combined with the microstructure observations and the crystalline phases identification, is one of the key parameters used as an indicator of the opacification process employed. Besides, synchrotron-based µ-XRF coupled with WDS analyses and cartographies were necessary to identify the phases present in complex aggregates of crystals. This new approach is the first step to getting information on the raw materials used and the technological processes employed to produce antimonite compounds.

Oral Session VI

chairpersons: Koen Janssens - Jean Susini

INVITED LECTURE 6.

QUESTIONS ABOUT VAN GOGH

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ABSTRACT

In recent years Vincent van Gogh's paintings and drawings have been examined in great depth, not just by art historians and conservators but also by scientists. New techniques make it possible to look far below the surface of his paintings and drawings, with astonishing results. This has generated much valuable information about the artist's working process and the materials he used. But we aren't there yet: the complexity of Van Gogh's oeuvre still leaves important questions unanswered. Following an overview of what has been reached so far, this talk will deal with a number of desiderata in the field of Van Gogh studies where physical research will play a crucial role.

ORAL LECTURE 22.

SCANNING X-RAY FLUORESCENCE ELEMENTAL MAPPING OF PAINTINGS WITH SYNCHROTRON RADIATION

Daryl L. Howard[1,*], *Deborah Lau*[2], *David Hay*[2], *Chris Ryan*[2], *Robin Kirkham*[2], *Gareth Moorhead*[2], *John Payne*[3], *Michael Varcoe-Cocks*[3], *Carl Villis*[3], *Martin D. de Jonge*[1], *David J. Paterson*[1] *and David Thurrowgood*[3]

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ABSTRACT

Scanning X-ray fluorescence mapping using synchrotron radiation is a powerful non-destructive technique for the imaging of cultural heritage items such as paintings. One of its unique strengths is the potential to reveal metal distributions in the pigments of underlying brushstrokes, thus providing information critical to the interpretation of a painting. Some preliminary scans at the XFM beamline of the Australian Synchrotron have utilized the prototype event-mode Maia X-ray fluorescence detector, which has the ability to record elemental maps at megapixels per hour.

Test canvases, some with an overlayer of ubiquitous lead white pigment, and an overpainted self-portrait by Australian artist Arthur Streeton were used for a pilot study towards our goal of recording high definition scans of whole artworks. The underlying brushstrokes were successfully revealed, and tritonal colour images were constructed based on metal to pigment associations. The fluorescence mapping technique and the analysis of the test canvases will be discussed.

ORAL LECTURE 23.

FIRST IMAGES OF A COLOUR X-RAY CAMERA, A DETECTOR WITH HIGH RESOLUTION IN ENERGY AND SPACE

Martin Radtke[1,*], *O. Scharf*[1], *Uwe Reinholz*[1], *S. Bjeoumikova*[2], *R. Wedell*[3], *H. Soltau*[4], *S. Ihle*[4], *R. Gubzhokov*[2], *Heinrich Riesemeier*[1] *and N. Langhoff*[2]

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ABSTRACT

A new device for high resolution X-ray imaging, an energy and spatial resolving X-ray camera is presented. The basic idea behind this so called "colour X-ray camera" is to combine an energy-dispersive pn-CCD detector with polycapillary optics. Imaging is achieved using multiframe spectral recording of single photons.

The polycapillary optics allows one to zoom on the objects. The CCD has a frame rate of 400 Hz with framestore technique. The camera measures 69696 spectra with an energy resolution around 155 eV for Mn Kα and a spatial resolution of 48 µm over an active area of 11.9 x 12.3 mm^2 simultaneously. A software calculates and displays the transmission or fluorescence images of the probe.

The suitability for X-ray fluorescence analysis and diffractometry of the camera is demonstrated in experiments. Conventional X-ray tubes as well as synchrotron radiation from BESSY II at the BAMline are used as X-ray sources. Examples for different application fields will be shown.

ORAL LECTURE 24.

IMAGING OF HIDDEN PAINT LAYERS IN HISTORICAL PAINTINGS BY SYNCHROTRON-BASED SCANNING MACRO-XRF

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ABSTRACT

Under the surface of historical paintings often hidden paint layers, remnants of the painting's creation are present. Since they offer a unique insight in the paintings creation process, they bear valuable information for art historians; yet it is very challenging to image these paint layers, as the precious and unique nature of paintings asks for non destructive analysis.

Scanning macro-XRF, in which the sample is scanned by an X-ray beam of some hundreds of micrometres diameter and the fluorescence radiation emitted by the sample is analyzed, allows us to determine the distribution of pigments on the macroscopic scale without damaging the painting. While conventional X-ray radiography only images the density distribution in the painting, so the obtained image is dominated by lead white, scanning macro-XRF allows us to image the elemental distribution and thus obtain a more detailed image of the original or intermediate state of the painting.

In this contribution we will present our results of the analysis of historical paintings by scanning macro-XRF and demonstrate how our imaging of hidden paint layers allows having a look on paintings from artists like Rembrandt van Rijn and Philipp Otto Runge from a different perspective.

RECOVERING ERASED SCRIPTS FROM PALIMPSESTS USING THE X-RAY FLUORESCENCE ELEMENT MAPPING TECHNIQUE

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ABSTRACT

In the Middle Ages, literary texts where frequently copied on parchment before the use of paper prevailed. As the availability of affordable parchment was at times limited, it was not uncommon to reuse parchment from older books to write upon, creating what we call a palimpsest. The original writing was erased by chemical or mechanical means, and the repristined parchment leaves from one or several former books were written upon once more. Today, the erased underlying texts on these palimpsests are often at least as interesting to the scholar as the upper text, and there are even some texts from Classical Antiquity which have only been preserved through such copies.

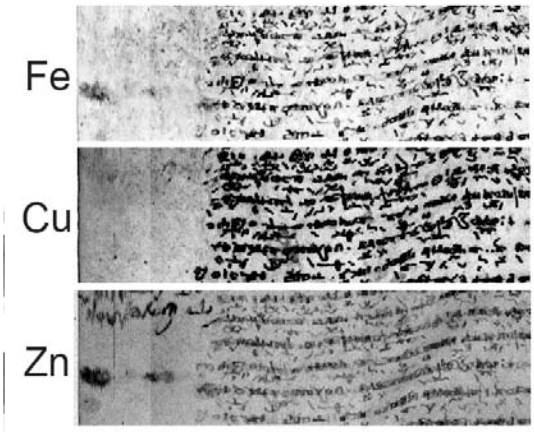

Figure 1: The element maps of iron, copper and zinc show quite different contrast and partially even different layers of the texts.

The inks used where of the iron gall variety, and in those palimpsests created by chemical erasure are often still (or again) partially visible to the naked eye. Various methods have been used to make these better readable. Most recently X-ray fluorescence spectroscopy (XRF) was used in an experiment similar to the one presented here, to map the text on several pages from the Archimedes palimpsest. X-ray techniques pose no significant danger to a parchment's preservation, as radiation damage is negligible.

The project presented here is a collaboration of Teuchos – Zentrum für Handschriften- und Textforschung (Universität Hamburg, DFG), Universitätsbibliothek Leipzig and HASYLAB, showing the possibilities of X-ray fluorescence element mapping to enhance the contrast of upper and lower writing concentrating not only on the dominant iron signal, but on the impurities of the iron vitriol used in the manufacture of the iron gall ink. Element maps as shown in Fig. 1 for iron, copper and zinc have been recorded for various trace elements in regions of visible and erased writing. While reproduction of part

of the text is often possible using the iron contrast only, additional information can be obtained from the contrast maps based on the iron impurities. In the measurements shown in Fig. 1 the hidden writing could not be identified by mapping of the dominant iron signal, but by the trace element maps.

Studies to optimize this XRF element mapping technique for text recovery are ongoing. The long term goal is to set up a mobile system in order to access objects that may not travel to a storage ring facility.

ORAL LECTURE 26.

IN-SITU INVESTIGATION OF A HIDDEN PORTRAIT BY GOYA USING A MOBILE SCANNING MACRO-XRF SET-UP AT THE RIJKSMUSEUM IN AMSTERDAM

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ABSTRACT

The Rijksmuseum owns one of the few paintings by Goya in Northern Europe and the only one in the Netherlands. Conventional radiography of this painting revealed vague outlines of a second figure below the surface portrait. This figure seems to be wearing a military uniform, including a sash, decorations and epaulettes. However, due to the poor image quality of conventional radiography, the identity of this enigmatic second figure could not be established so far. Using X-ray fluorescence elemental imaging, we examined the painting in-situ in the Rijksmuseum. We obtained large, decimeter-scale, megapixel-sized elemental distribution maps of a large section of the painting. The latter revealed the use of various pigments in both surface and subsurface layers, visualizing the hidden portrait in greater detail. We will discuss these images of the hidden portrait within their art historical context.

ORAL LECTURE 27.

LAMINOGRAPHY AND DIFFRACTION-BASED IMAGING OF PAINTINGS

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ABSTRACT

Over the past years synchrotron-based X-ray fluorescence has been applied successfully to visualize hidden paint layers. Case studies have includes works by Teniers, Rembrandt, van Gogh and others. One of the disadvantages of SR-XRF scanning is the fact that it is mostly surface-sensitive. Low-Z pigments buried within the paint stratigraphy may not be charted by their fluorescence signal, which is easily absorbed by lead containing surface layers. Here, we present two new methods to visualize the substructure of paintings. First, we will discuss laminography, which is an absorption-based tomographic method to spatially visualize the stratigraphy of layered artwork.

Second, we will present diffraction scanning, which allows to collect phase distribution images of paintings. The 3d imaging capability of laminography and chemical specificity of X-ray diffraction are therefore interesting additions to the visualisation toolbox for painting studies.

ABSTRACTS OF THE POSTER PRESENTATIONS

POSTER CONTRIBUTION 1.

DIFFERENT METHODS OF ANALYSIS FOR THE IDENTIFICATION OF MATERIALS DATED TO DIFFERENT PERIODS IN EGYPT

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ABSTRACT

Different questions may be raised during the course of analysis concerning in particular the characterisation of materials used, their preparation and application techniques. The different methods used to identify the materials of mud brick, limestone, plaster, mortar and pigments, collected from different sites and periods from Egypt, in order to identify and characterize the materials; their structure, composition and their mineralogical compounds were: (Op): optical microscopy, which was used to examine and to identify the structure of; the plaster, mud building, limestone and mortars as well as the pigments.

Methods used in initial examination were:

- (MCA): Micro-chemical analysis, to identify the nature of the materials and for water-soluble salts, to identify sulphates, chlorides, carbonates, nitrites and nitrates.
- (SM): Standard methods of wet chemical analysis were used to identify the quantitative and qualitative nature of the, mud building, mortars and their mixtures.
- (SEM & EDS): Analytical scanning electron microscope with energy-dispersive X-ray analysis system was used to examine the micro-morphology and determine the chemical composition of the different materials.
- (X-RD & X-RPD): X-ray diffraction to identify the mineralogical compound of the plaster, limestone, mortars and pigments used.

From all the results obtained, it was possible to establish the nature of the mortars and their binders as well as some other inclusions. In addition to the identification of the stratigraphy of the layers applied in some samples, the examination and analysis gave details of the materials and the approximate ratio of the amount of additives used. Furthermore, the mineralogical analysis provided information on the main mineralogical phases present in the materials analyzed from the different periods.

POSTER CONTRIBUTION 2.

ANALYSIS OF SAFAVID AND MUGHAL TILES OF 16th AND 17th CENTURIES USING XRD AND EDX

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ABSTRACT

This paper attempts to understand the technology employed in fabrication of glazed bricks and tiles used in the historical buildings of Delhi region in India and Isfahan region in Iran. The composition of these tiles are compared with the tiles from Isfahan in 16th and 17th centuries. The study also provide information if these tiles are manufactured at one site and transported to the construction region or were fabricated locally. The study focuses on chemical composition study and X-ray diffraction analysis of glazed bricks and tiles which came from the great Mughal construction like Humayun's tomb, the tomb and mosque of Isa Khan, Tour of the tomb known as Sabz Burj (Persian: sabz, green; burj, dome), Atgah Khan's Tomb and The Jamali Kamali mosque in Delhi and China Ka Roza tomb in Agra. The tomb of Humayun was built in 1562. The architect of the edifice designed it in a Persian 'charbagh' or four-garden square style. The style was introduced in India by Babur, the first Mughal emperor.

Five groups of tiles from the tomb of Humayun and China Ka Roza in Dehli and Agra are studied and compared with three groups of tiles from construction of Naghsh-i Jahan Square in Isfahan.

The differences and similarities between these two series of tiles are explained on the basis of X-ray diffraction (XRD), optical microscopy, scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS) analysis. The results obtained by XRD of samples showed that the quartz, calcite, nantokite, tridimite, diopside, acromanite, lazurite, hematite, cristobalite and feldspar phases were present and SEM/EDX studies revealed the presence of K, Na, Cu, Si, Fe, Al, Ca in both sets of samples and the presence of Pb was found only in Persian tiles from Isfahan.

Comparing typological and analytical data it is conclude that:

1) The bulk part of samples from Isfahan are made from the same type of minerals. Similarly, materials for samples from India are the same. Thus, the analysis showed that the samples from India are formed a class of minerals and the samples from Iran are formed another class. Therefore, it is concluded that these tiles were not fabricated at one site.
2) Quartz, diopside, acromanite, hematite,cristobalite and feldspar phases are common phases in bulk part of the samples from Isfahan.
3 XRD results showed that in samples from Mughal construction, the bulk and the glaze parts of the sample are made of the same type of minerals. However, the bulk and the glaze parts of the samples from Safavid period are different.
4 The element Pb is used only in tiles from Naghsh-i Jahan Square in Isfahan.

POSTER CONTRIBUTION 3.

IN-SITU INVESTIGATION OF A VERSION OF CARAVAGGIO'S *"SUPPER AT EMMAUS"* WITH A MOBILE SCANNING MACRO-XRF SET-UP

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ABSTRACT

"*Supper at Emmaus*" is one of the iconic masterpieces of Caravaggio (1571-1610). While the original is the collection of the National Gallery in London, many other versions of this painting are known to exist. Quite often, the relationship between the original and copy is poorly understood. Here, we investigate such an early, possibly contemporary, copy. Our aim was to characterize the working method and materials for eventual comparison with the original painting in London. The copy was transported to the Gerlach Art Packers & Shippers storehouse and analyzed there in situ for several weeks using a mobile scanning macro-XRF set-up. In doing so, we obtained large, meter-scale, megapixel-sized elemental distribution maps of large sections of the painting. The latter revealed the use of various pigments in both surface and subsurface layers. Cross-sections showed the use of a Cu pigment in the underpainting, which was also visualized at the brush-stroke level in the macro-XRF Cu map. This underpainting seems to have been followed meticulously in the final execution of the painting. The observations render a possible future in-depth comparison with the London original, in particular regarding its underpainting, very interesting.

POSTER CONTRIBUTION 4.

IRON OXIDATION STATE IN ARCHAEOLOGICAL SILICATIC GLASS: A COMPARISON BETWEEN XANES AND MÖSSBAUER DATA

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ABSTRACT

The furnace oxygen fugacity is one of the parameters which had to be carefully controlled by the ancient glass workers, being this variable extremely important in the control of final colour of the glass. It is well known, in fact, that the colour of glass is largely controlled by the oxidation state and the coordination geometry of the metal ions dispersed in the glass matrix – being their presence either intentional or unintentional.

A useful tool in the determination of the oxygen fugacity present in a furnace at the moment of the glass production is represented by the Fe^{2+}/Fe^{3+} ratio in the glass matrix, being this ratio particularly sensitive to the fO_2. Moreover, iron is a suitable element to be considered since it is always present in the glass composition, either as unintentional component (when it is present as an impurity in the sands employed) or as intentionally added colouring element (conferring in its reduced state a typical green colour).

In this contribution we report the preliminary results of a quantitative evaluation of iron oxidation state in a series of ancient roman glass. The Fe^{2+}/Fe^{3+} ratios were determined on each sample by both XANES (very sensitive and non-destructive) and Mössbauer (very accurate) techniques. The preliminary data indicate a good agreement between the results of the two methods.

POSTER CONTRIBUTION 5.

THE USE OF INNOVATIVE TECHNIQUES FOR THE STUDY OF DEGRADATION AND ALTERATION PRODUCTS ON BUILDING STONES: A CASE STUDY

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ABSTRACT

The degree and distribution of the main types of observable rock deterioration in an urban environment are related to different kinds of wetting and particularly to the exposure of the stone surface to rain. In a polluted environment, two kinds of crusts are usually developed on calcareous rocks, the so-called white and black crusts.

The aim of this study is to characterise some black crusts appearing on buildings of the historical centre of Catania. Traditional techniques, consisting of polarising optical microscopy (OM), scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDS), and Fourier-transform infrared spectroscopy (FTIR) analysis, were used in combination with innovative techniques, such as laser ablation inductively coupled mass spectrometry (LA-ICP-MS) and micro-FTIR. LA-ICP-MS micro-analytical technique allows determining the chemical composition of black crusts in terms of trace elements and to monitor their variability from stones to black crusts thus permitting to evaluate the thickness of contamination. The qualitative distribution map of degradation products can be obtained by means of micro-FTIR operating in ATR mode.

The results of this research highlight the benefits of the innovative application of these two recent techniques in providing useful insights on the appropriate choice of cleaning and consolidation methods for preserving the stone materials.

POSTER CONTRIBUTION 6.

ANALYSIS OF CHARCOAL AND WOOD FROM CZARNÓWKO SITE (POMORSKIE PROVINCE, POLAND)

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ABSTRACT

Charcoal it is commonly used material in radiocarbon dating and in authentication and provenancing research. The problem with radiocarbon dating of charcoal may be connected with origin of analyzed fragment and also with e.g., pH conditions in the sediments. Identification of analyzed fragments may give additional information about cultures, technology and provenance. The paper present results of samples analysis from Czarnówko site. 36 samples of charcoal, wood and textile were collected in 2008 during archaeological excavation. 13 samples have been chosen to radiocarbon dating. Macro- and microscopic observations of Czarnówko samples have been made. Photographs taken using a scanning electron microscope show the microstructure and preservation of the charcoal and wood specimen. Czarnówko is an archaeological site in northern Poland. It was using by over 800 years by populations of different cultures. From 7th to 3rd century BC it was a settlement with indefinite boundaries. Then, similar area was using from 1st century BC to 3rd century AD as a cemetery by populations of *Oksywska* and *Wielbarska* cultures. Czarnówko have been exploring from many years, but presented radiocarbon dates are first for this site. It is important because of its extension and riches of artefacts. Samples were collected from different objects, most of them from graves. Charcoal was collected in crematory graves. Wood was come from coffins drilled in logs from skeletal burials. The results of radiocarbon dating have been compared with the relative chronology. The dates obtained by AMS measurements are in agreement with the established archaeological stratigraphic sequence.

POSTER CONTRIBUTION 7.

THE ALTERATION PROCESSES IN STAINED GLASSES: A COMPARISON BETWEEN MODERN AND ANCIENT ITALIAN STAINED GLASS WINDOWS

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ABSTRACT

As it is well known, the alteration of glass in natural environments is a very complex process, involving numerous factors. It depends both on the chemico-physical characteristics of the glass and on external conditions such as micro-climate, temperature, time, pH, aqueous solution composition, etc. For these reasons two sets of samples, coming from different environments and times, were analyzed by using various non destructive techniques. The first set of samples belongs to the 15th century Santi Giovanni and Paolo Basilica (Venice, Italy), while the second one belongs to the San Giovanni church in Polegge (Vicenza, Italy) dated to ca. 1930. XRF, ESEM and XPS analyses fully characterized the elemental composition of the sample surface. Furthermore, the possibility to collect diffraction patterns in grazing angle geometry, using MCX facility, allows the non destructive characterisation of the crystalline phases on the sample surface. The present poster deals with a preliminary description of the alteration products and the proposal of possible alteration mechanisms.

POSTER CONTRIBUTION 8.

THE PORTRAITS OF THE "*UOMINI ILLUSTRI*": CHARACTERISATION OF GREEN PAINTED AREAS USING COMBINED µ-SR-XRF AND µ-SR-XRD

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ABSTRACT

The collection of the Uomini Illustri (second half of the 15th century) was originally painted for the Studiolo of Federico da Montefeltro in Urbino. The attribution of the paintings, even though not yet confirmed, has already been the subject of extensive research and this is part of a wider project aimed at better clarifying the attribution of the 28 portraits. This paper is aimed at presenting the results collected by synchrotron radiation X-ray fluorescence (µ-SR-XRF) and X-ray diffraction (µ-SR-XRD) and applied to the characterisation of the green painted areas where differences in terms of pigments and painting technique have been observed. µ-SR-XRF and µ-SR-XRD analyses have been performed at ID18F of the European Synchrotron Radiation Facility (ESRF), in transmission mode for XRD, at 28 keV X-rays. The combination of the micrometer size of the techniques together with the simultaneous analysis µ-SR-XRF and µ-SR-XRD has proved to be very effective in the compositional mapping of the paint layers in the cross section as well as identification of the different structures of imprimitura and green paint layers. From the µ-SR-XRF analysis, an elemental mapping has been obtained from each of the thirteen green samples, these maps showed the same elements and allowed us to obtain an averaged diffractogram for each layer. The results allowed the differentiation of the green paint samples into two groups characterized by a different imprimitura: hydrocerussite, cerussite, gypsum, calcite and dolomite, with variable intensity, are the main component of the first group, whereas the second is characterized by the diffractograms which show many picks that do not match any mineral references. These picks which are still under investigation are probably ascribable to the green pigments or to the copper and/or lead carboxylates.

POSTER CONTRIBUTION 9.

LOOKING INSIDE! 3D IMAGING EXPERIMENTS ON ALUM-CONSERVED ARCHAEOLOGICAL WOOD

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ABSTRACT

Excavations of the Oseberg burial mound near Oslo in 1904 revealed an extraordinary collection of Viking Age wooden objects dating from about 800 AD. After excavation, the artefacts were treated with a hot (80 - 100 °C), concentrated alum solution. The solution penetrated the waterlogged wood, replacing the water, and the re-crystallized alum stabilized the wood. Unfortunately, today many of these objects are threatened by a slow, active deterioration caused by this conservation method.

Advanced imaging techniques were applied to study the internal structure on macroscopic and microscopic levels, the distribution of alum salts in the wood and the effect of various impregnation materials on the inner structure of the wood. Investigations were undertaken at the Paul Scherrer Institute (Villigen, Switzerland). Neutron and X-ray radiography and tomography experiments were carried out at the neutron imaging stations NEUTRA and ICON. Later, synchrotron-based X-ray tomographic microscopy was performed at the TOMCAT beamline, SLS.

Samples of alum-conserved wood from the Oseberg find were also compared with samples treated with a combination of alum and glycerol from the Hjortspring find, Denmark, untreated archaeological and fresh wood and that recently treated with synthetic resins. Although data processing and evaluation is not yet completed, preliminary results demonstrate the application of the various imaging techniques used to study archaeological and alum-conserved wood.

POSTER CONTRIBUTION 10.

MICROTOMOGRAPHY AND SEM MICROANALYSIS STUDIES OF MUSICAL INSTRUMENTS FROM THE CORRER MUSEUM IN VENICE

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ABSTRACT

In the Correr Museum in Venice (Italy) is conserved the only existing organ with paper pipes, dated 1494, made by Lorenzo Gusnasco. In order to better understand its state of conservation, the Direzione Regionale per i Beni Culturali e Paesaggistici of Lombardia Region, decided to analyze some pipes and to define the state of conservation, aiming to identify the materials and to investigate the techniques used by the maker.

A collaboration with the Synchrotron Elettra Research Center in Basovizza (μ-CT analysis) and with ENEA (Italian Agency for new technologies, energy and sustainable economic development) in Bologna (SEM microanalysis), allowed to achieve a great deal of information.

Feasibility studies have been carried out at the SYRMEP beamline of the Elettra synchrotron laboratory in Trieste with the aim of demonstrating the advantages and evaluating the effectiveness of synchrotron radiation X-ray microtomography as a suitable technique for non-destructive analysis of musical instruments. The particular geometry of the X-ray beam and the use of a novel detector allowed structural evaluation of the main details of the instruments with unprecedented richness of details. This, in turn, will allow precise dendrochronological investigation of historical stringed instruments.

Computed tomography (CT) provides the modern luthier and acoustic scientist with a unique tool for characterisation of normal structure, defects, and repair and for accurate measurements of wood thickness and density. In this case it has been possible to obtain extremely detailed information on the techniques used to manufacture the pipes, and to evaluate the kind of wood and its present condition, especially regarding presence and activity of larvae.

The scanning electron microscope (SEM), with respect to traditional optical microscopes, can provide three-dimensional images, with higher magnification. Moreover, SEM analysis,

once combined with an EDXRS (energy-dispersive X-ray spectrometry) system, can be used to catch X-rays from the atoms of the elements and to yield the chemical composition of the sample. Samples of the paper used for the pipes has been investigated with stereomicroscope and then with SEM. The SEM and microanalysis studies have contributed to define the kind of paper used by the maker, thus complementing the μ-CT approach.

POSTER CONTRIBUTION 11.

SR-µXRF ON HUMAN BONES: AN AID TO RECONSTRUCT DIETARY HABITS

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ABSTRACT

The purpose of this work is to investigate the suitability of synchrotron radiation X-ray micro-fluorescence to study the distribution of trace elements in human bones.

The bones mineral component has a well-defined chemical composition, but several trace elements can substitute for the major constituents. These trace elements in fossil bone depend, in part, on diet and have been used to reconstruct paleodiet.

µ-XRF induced by synchrotron radiation was selected as the analytical technique due the advantages of high sensibility and low detection limits.

The analyzed samples are belonging to human individuals found in the seventies at the archaeological locality of Docellas, Jujuy, Argentina. They belong to a collection placed at the museum of the Instituto Nacional de Antropología y Pensamiento Latinoamericano.

The analysis show the presence of Ca, Cr, Mn, Fe, Cu, Zn, As, Br, Sr, Ba and Pb. Levels of trace elements in bones are reported as the ratio of the concentration of the element to that of Ca (e.g., the Sr/Ca ratio) as it usually done in these cases. Results evidences an omnivora diet taking into account similar values for Zn, Sr, Cu and Ba.

POSTER CONTRIBUTION 12.

EVIDENCE OF THE ROLE OF Zn AND Fe CATIONS AS DOPANTS IN LEAD ANTIMONATE YELLOW BY X-RAY ABSORPTION SPECTROSCOPY (XAS)

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ABSTRACT

Naples yellow ($Pb_2Sb_2O_7$) is one of the oldest known synthetic pigments. It shows a cubic pyrochlore structure, obtained by roasting mixtures of Pb and Sb oxides. Recent studies demonstrate that Naples yellow may exist also in a modified form obtained from a ternary mixture of Pb, Sb and Sn oxides ($Pb_2Sb_{2-x}Sn_xO_{7-x/2}$).

X-ray diffraction and Raman spectroscopy investigations of standard doped yellow pyroantimonates provided evidence that, in general, doping cations (such as Sn^{4+}, Zn^{2+}, Fe^{3}+ or exceeding Pb^{4+}) induce significant structural modifications of the pyrochlore lattice of the pigment, suggesting that ternary cations enter the octahedral sites replacing Sb^{5+} ions.

Here we report on the results obtained by XAS investigations carried out at the GILDA beam-line of ESRF (Grenoble, FR) on the role played by Zn and Fe cations in modified Naples yellow, characterising the ions' local properties (interatomic distances, coordination number and oxidation state). The XAS study has been non-destructively carried out on different standard yellow pyroantimonates, as well as on Renaissance ceramic shards from the collection of the Musei Civici di Pesaro (Italy). XAS measurements at the Zn-K and Fe-K absorption edges evidenced that the chemical environment of the Zn and Fe ions is different from that of the oxides originally present in the pigment preparation. Experimental XAS data have been compared with ab-initio structural simulations, which found that the doping metal occupies the site of Sb. The same structure has been also observed for Zn cations in the yellow pigment of a Renaissance ceramic shard.

The study has been carried out within the joint research activities of the CHARISMA project supported by the 7th F.P. of EU.

POSTER CONTRIBUTION 13.

INTEGRATED X- AND NEUTRON-BASED ANALYSIS ON BRONZE ARTEFACTS FROM THE LIGURIAN SETTLEMENT OF GUARDAMONTE-MONTE VALLASSA

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ABSTRACT

Significant archaeological findings from the pre-Roman Ligurian settlement of Guardamonte-Monte Vallassa (Italy) were made available for a series of material analysis measurements based on X-ray as neutrons radiation. These findings are from different archaeological strata (ascribed from V to III century BC) and are the object of discussion about their origin and the level of technology to which they can be ascribed. Being the objects not yet cleaned and restored, the XRF analysis obtained into a standard low-power spectrometer were limited to the surface of the objects, covered of patina and concretions layers. Time-of-flight neutron diffraction (TOF-ND), however, is widely recognized as one of the most promising techniques for non-destructive analysis of the bulk of archaeological findings and cultural heritage objects allowing to access depths of a few centimetres in metallic objects. Moreover, the INES beamline of the ISIS neutron source offered the unique possibility of performing TOF-ND measurements and, neutron resonance transmission (NRT) measurements. NRT is a complementary technique, developed in the *ANCIENT CHARM* project, to TOF-ND, allowing for a very complete understanding of the components of ancient artefacts and their construction technology. We present XRF and neutron-based results on selected samples, showing how the use of integrated techniques can get information on the physical nature of both the patina layers and bulk of the object, and in some cases giving indications about the way of production of some objects, for instance casting or hammering.

POSTER CONTRIBUTION 14.

A STUDY ON GOLD AND COPPER PROVENANCE FOR ROMANIAN PREHISTORIC OBJECTS USING MICRO-SR-XRF

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ABSTRACT

The main goal of this study is to clarify the metal provenance of Romanian gold archaeological items using the variation of the Au-Ag ratio and the presence of trace elements as Sn, Sb, Te, Pb. We concentrated on several small fragments of gold Dacian coins (Kosons) from a hoard recuperated (September 2009) by Romanian Police. We also tested the possibility to start a new study concerning the copper provenance of Bronze Age items (axes, sickles, daggers, swords, celts). The studies were performed by micro-SR XRF in the maximum energy 32.5 keV SR beams at BESSY Berlin, using respectively the spatially resolved set-ups mounted for analyses at the BAMline. Very small fragments (less than 200 micrometre diameter) from Kosons (20 without monogram and 20 with monogram) were analyzed. The monogram coins are made from refined gold (3 - 5 % Ag, less than 0.5 % Cu). The without monogram coins are made from native Transylvanian gold (5 - 20 % Ag, 0.5 - 2 % Cu). The native gold is mainly alluvial, because we detected Sn and Al, Si, Fe impurities embedded in the gold native alloy. The problem of provenance for prehistoric copper and bronze objects (found in Romania) consists in their classification from the copper provenance Bronze Age regional mines point of view – Ai Bunar (Bulgaria), Rudna Glava and Majdanpek (Serbia), or Transylvania (e.g., Baia-Mare). We analyzed 20 very small samples (less than 500 micrometre diameter) from different archaeological sites in south Romania – especially axes and sickles. The majority presents relevant traces of arsenic and antimony, suggesting the use of copper from North Bulgaria.

POSTER CONTRIBUTION 15.

CHARACTERISATION OF ANCIENT FINDINGS BY MEANS OF X-RAY FLUORESCENCE AND FOURIER TRANSFORM INFRARED ABSORBANCE SPECTROSCOPY

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ABSTRACT

As is well known, X-ray fluorescence (XRF) can be considered as the first step for the chemical characterisation of archaeological artefacts. Hence, in the present study the approach we used was to carry out, first of all, an extensive non-destructive surface investigations using a handheld XRF analyzer, and only the problems not resolved by this method were further analyzed using micro-destructive laboratory equipment, so suggesting a possible general analytical protocol to use in this field.

In particular, the elemental mapping obtained by XRF acted as a valuable guideline for subsequent targeted sampling actions, thus minimising sampling damage. Hence, some questions not answered by XRF (identification of organic pigments, preparation layers, etc.) were subsequently resolved using Fourier-transform infrared absorbance spectroscopy (FT-IR). The combined employment of XRF and FTIR allowed us to characterize findings of ancient buildings located in Sicily (Italy), providing useful information to establish the production technique used by the craftsmen.

POSTER CONTRIBUTION 16.

COMPARISON BETWEEN TOF-ND AND XRD QUANTITATIVE PHASE ANALYSIS OF ANCIENT POTTERIES

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ABSTRACT

A non-invasive time-of-flight neutron diffraction (TOF-ND) analysis has been performed on seven archaeological pottery fragments from the excavation sites in the "Strait of Messina" area (Sicily, Southern Italy). The revealed quantitative information on the mineralogical composition have been compared, in the case of two samples representative of coarse and fine grained pottery, with the weight fractions of the phases as obtained from X-ray diffraction on powders (XRPD), for different amounts of extracted powder. From the results, the consistency of these micro-destructive and non-invasive approaches has been checked.

POSTER CONTRIBUTION 17.

esaPROJECT: USER FRIENDLY SOFTWARE DEVELOPED FOR SYNCHROTRON-BASED HERITAGE SCIENCE

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ABSTRACT

In 2006 we obtained over 600 images of time-dependent processes using the Mar CCD 165 camera on the XMaS beam line at ESRF. With our geometry, the diffraction cones from surface powder diffraction measurements intersected the camera face as a sheaf of ellipses whose eccentricity depended on the diffraction angle. We could find no software for extracting spectra from this data. We had also acquired sets of many hundreds of time-dependent spectra from the RAPID II detector on station MPW 6.2 at the SRS, Daresbury UK. Although the processing was not actually impossible with existing packages, the long chain involved in converting file formats and processing through several packages was irksome and could not be automated. We therefore wrote an integrated suite of user friendly Windows® software which would: read raw image and spectrum formats directly, allow the integration of spectra into two-theta or d- space from any camera angle, batch process an indefinitely large number of images or spectra, implement data mining for the automatic extraction of peak parameters over time, include any arithmetic manipulation of a spectrum or image we could envisage being useful, extract and use ancillary data such as epoch, beam monitor output, from SPEC and other files, remove background, smooth, etc. All operations are invoked through a GUI displaying the image(s) or spectrum (spectra) concerned. This is esaPROJECT, named after its initial function of using geometrical mapping to reproject the XRD images into a linear two-theta or d- space. The package now encompasses XAS data preparation and is being developed to include other spectroscopies.

POSTER CONTRIBUTION 18.

A SYNCHROTRON RADIATION STUDY OF COPPER CARBOXYLATE LAYERS ON THE XMAS BEAMLINE

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ABSTRACT

Long chain copper carboxylates $(CH_3(CH_2)_{n-2}COO)2Cu$ (hereinafter abbreviated to $Cu(C_n)_2$) deposited on copper from an aqueous solutions of the corresponding sodium carboxylate have been proposed as corrosion inhibitors for heritage copper and its alloys. Whilst it has been shown that copper heptanoate $Cu(C_7)_2$ affords some protection in solutions containing both a corrosive medium and sodium heptanoate as the inhibitor, for samples in air there is considerable doubt as to whether it is a coating of a sodium carboxylate, or the formation of the copper salt which has (minor) beneficial effects. Moreover, the exposure of cupreous objects to water after a desiccating conservation treatment is unacceptable. Here, we report a new method of producing a copper carboxylate coating from alcoholic solutions. Chain lengths up to the octodecanoate $Cu(C_{18})_2$ can be deposited with this method, whereas anything above the decanoate is insoluble in water. Such coatings should be both more water resistant and have superior inhibition properties to those with shorter chain lengths. The layers and growth mechanism were characterized using real time synchrotron XRD on copper coupons in an environmental cell (eCell IV) on the UK CRG beam line XMaS at the ESRF. The growth of layers was observed in-situ during soaking and subsequent drying. The corrosion resistance was investigated using electrochemical methods, principally polarisation measurements. We show that the deposition method produces a copper carboxylate coating as intended, and that the long chains improve the corrosion resistance. However, coatings are (unsurprisingly) blue-green and strongly modify the appearance of an artefact, rendering them unsuitable as a conservation treatment. They may, nevertheless, have an application in the deliberate patination of new artworks.

POSTER CONTRIBUTION 19.

SHEDDING LIGHT ON THE ROLE OF THE SUBSTRATE IN PRUSSIAN BLUE DISCOLOURATION PROCESS

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ABSTRACT

Prussian blue (PB, iron(III)hexacyanoferrate(II)) is a pigment that has been widely used in Europe in the 18th and 19th centuries. Exposed to light or to anoxic treatments, some PB-containing artefacts discolour due to a photo-reduction of iron(III) into iron(II). Although several experiments on light induced degradation of PB have been done in the past, the oxido-reduction process related to the fading and particularly the role of the substrate remains poorly understood.

Synchrotron experiments have been performed on Prussian blue laid on paper, textile and gelatin substrates selected according to their oxidation properties. The Fe K-edge of PB was investigated in order to correlate the variation of the Fe(III) / Fe(II) ratio by XANES with discoloration processes. In addition, the crystalline structure at different stages of the discoloration was monitored by X-ray diffraction measurements.

POSTER CONTRIBUTION 20.

FROM KOTO AGE TO MODERN TIMES. QUANTITATIVE CHARACTERISATION OF JAPANESE SWORDS THROUGH TIME-OF-FLIGHT NEUTRON DIFFRACTION

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ABSTRACT

The study of sword forging techniques, and their evolution with time, is one of the most interesting topics in the analysis of the Japanese blade-forging methodology. The investigation about the evolution of shape and manufacturing techniques of Japanese swords is a very well established field of study. However, this has been mostly based on standard punctual analytical techniques, like for example metallography, while this field is still lacking an experimental technique allowing to characterize, quantitatively and in a non-invasive way, the various crystal phases present in the artefacts. Thermal neutron diffraction, thanks to the high penetration power of neutron, can overcome this limit. Six fragments of blades, pertaining to the five Koto Age (10th - 11th century AD) forging traditions, and two more recent ones have been measured by this technique. In addition, the investigation was extended to two intact Japanese long swords again from Koto Age. All measurements were carried out through time of flight neutron diffraction to quantitatively analyze the phase composition. The carbon content, the martensite presence, the conservation status and the amount of the crystalline parts in the slag inclusions were determined. Moreover, experiments aiming to determine stress and strain distribution in selected parts of the blades were performed on the two intact Japanese swords to evidence possible similarities and differences between the two forging traditions.

POSTER CONTRIBUTION 21.

NON-DESTRUCTIVE STUDY OF ANTIQUE BRONZE COINS WITH HIGH LEAD CONTENT USING X-RAY AND NEUTRON TOMOGRAPHY

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ABSTRACT

The *Coin Cabinet of the Kunsthistorisches Museum* (KHM), Vienna, holds a large collection of ancient Greek bronze coins. Among them also a number of highly leaded bronze objects showing progressive corrosion as a result of unfavourable storage conditions within the historic wooden cases. In connection to a research programme concerning the conservation of these objects the causes for the sometimes severe corrosion were studied by radiography and tomography using neutrons and X-rays at the Paul Scherrer Institute. For 20 selected ancient Greek coins (1 - 3 century AD) – varying in their state of corrosion and already investigated for their bulk composition using neutrons at the Rutherford Appleton Laboratories, ISIS, Oxfordshire, Great Britain – the study of the enrichment of lead or lead-based corrosion products in the interior of the objects was performed at the neutron source SINQ, NEUTRA beamline, in a non-destructive manner.

To get a first overview of the inhomogeneity of the coins X-ray and neutron radiographies were taken from all the objects. Following this first examination the coins were investigated by neutron tomography overnight, enabling the further study of the distribution of lead containing inclusions in the core of the objects. The tomography results obtained show that in addition to the lead rich areas on the obverse and reverse of the coins (often already clearly visible on the surface due to the formation of white corrosion products) a varying number of lead containing inclusions could be detected within the antique bronze coins. Also the assumption that some of the corrosion spots seen on one side of the coins correspond to corrosion spots on the opposite side (so by corrosion the formation of holes is possible) could be proven. As the lead containing inclusions are often enriched in certain areas of the coins, information on the casting technique – so far not studied for this type of coins – could also be gained.

POSTER CONTRIBUTION 22.

COMBINED NEUTRON AND SYNCHROTRON X-RAY MICROPROBE ANALYSIS: ATTEMPT TO DISCLOSE 3600 YEARS-OLD SECRETS OF A UNIQUE BRONZE AGE METAL ARTEFACT

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ABSTRACT

Over the most recent years, micro-analytical facilities based on neutron beams as well as synchrotron X-ray beam advanced to indispensable instruments in the context of investigating artwork and archaeological artefacts. Both types of beams are nowadays used for multi-dimensional structural micro-analysis (physical imaging) as well as chemical and crystallographic micro-imaging. Advantageously, based on their characteristic (and generally non-destructive) interaction with matter, neutrons and X-rays yield complementary analytical contrast mechanism. Synchrotron X-ray radiation is predominately used to examine chemically complex samples with high spatial resolution and sensitivity as well as chemical and molecular specificity. Complementary, neutrons exhibit a unique penetration power and a particular sensitivity for lowest Z elements.

By a combined approach using neutron and X-ray microbeam facilities we investigated a unique flanged axe dated into the Early Bronze Age (2200 - 1500 BC). This famous object is decorated with distinctive double inlays of stripes of pure copper and 198 rhombi of gold by a seldom used damascene technique. The focus of the present micro-analytical investigations lies on [i] the reconstruction of the damascene technique (neutron tomography), [ii] the analysis of alloy compositions (2D μ-XRF), and [iii] the elucidation of historical patination and corrosion during burial (2D μ-XRD).

POSTER CONTRIBUTION 23.

SRXRF MEASUREMENTS AT NON-PLANAR OBJECTS: AUTOMATIC DETERMINATION OF THE ANGLE OF INCIDENCE OF THE EXCITING X-RAY

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ABSTRACT

At the hard X-ray beamline of the BAM, the BAMline at BESSY II in Berlin, it is possible to measure large non planar samples under atmospheric conditions. For quantitative synchrotron radiation induced X-ray fluorescence analysis (SRXRF) the angle of incidence of the exciting beam is one of the fundamental parameters. Determination of the angle is difficult, especially for round or ornate objects like in archaeological analysis.

In the experimental setup at the BAMline the X-ray beam hits the sample at a well-defined spot, which lies in the focus of a long-range microscope. Hence, a flat sample appears to be fully sharp whereas a non-planar sample only has sharp regions in the region of interest.

The distance between the microscope and the sample may be varied by a linear stage. Driving the sample from the distance where the deepest areas are sharp to the distance where the highest areas are in the focus, the collected data allows the creation of an elevation profile. The sharpness of an image is defined by the standard deviation of the pixel values.

POSTER CONTRIBUTION 24.

OPTICAL DESIGN OF AN X-RAY EXCITED OPTICAL LUMINESCENCE MICROSCOPE (XEOM)

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ABSTRACT

The production of photoelectrons within a sample caused by the absorption of synchrotron X-rays gives rise to a range of secondary processes which result in the emission of visible photons (X-ray excited optical luminescence (XEOL)). This light has the same information (XANES and EXAFS) as X-ray fluorescence encoded in it, with additional band-specific features due to radiative transitions excited by low energy electrons propagating through the material. In principle, it is relatively straightforward to form images of the light using broadband optics. This gives a method for obtaining micrometre-scale resolution chemical maps with image areas up to several millimetres square and a surface specificity of ~ 200 nm. These characteristics make XEOL microscopy ideally suited to the analysis of corrosion products formed on the surface of heritage artefacts. Following proof-of-concept experiments, a low-aberration optical system capable of forming such images has been designed using OSLO (Optics Software for Layout and Optimisation), an optics ray-tracing package. The design utilizes four custom lenses manufactured from UV-grade fused silica; this has been chosen as the optical glass because of its transmission properties and low X-ray luminescence. The detector is a broadband CCD camera. Possible imaging modes include full image spectra, imaging of the edge shift (i.e., the oxidation state), and imaging of narrow band emission (i.e., electronic structure). The paper will describe the optical design, and present XEOL and conventional XANES data collected in parallel on corrosion products relevant to the conservation of heritage metals.

POSTER CONTRIBUTION 25.

LOOKING AT THE INFINITIVELY SMALL FOR A DEEPER INVESTIGATION OF PREHISTORIC STONE TOOLS

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ABSTRACT

Stone tools may develop texture surface modification known as micro and macro use wear and indeed they can also, on the lithic surface, preserve residue of the material once processed. When the whole or some of these conditions are attested, through the analysis and the recording of these data by optical microscopes and their comparison with a reference collection, it is possible to contribute to the reconstruction of human past activity. This paper will focus on: the formation of polished areas on volcanic glassy materials and will give new insights on tool function through the potentiality of combining data obtained by optical and electron scanning microscopes and XRF characterisation to make possible higher magnification images and chemical determination and further detail the information previously observed on tool surface by the other optical systems.

POSTER CONTRIBUTION 26.

CHARACTERISATION OF IRON MINERALS IN THE SLIP LAYERS OF HELLENISTIC CERAMIC WARES FROM DORYLAION (ESKISEHIR/TURKEY)

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ABSTRACT

Anatolia has a rich cultural heritage from several civilisations like Hatti, Hittite, Urartu, Phrgyia, Hellenistic, Roman, Seljuk and Ottoman from different historical periods of time. There have been considerable numbers of excavations carried out in order to enlighten cultural heritage from them. Amongst those, Dorylaion is one of biggest mounds located in the west of middle Anatolia, in the city of Eskişehir. Nowadays, this mound is called as Şarhöyük. Many artefacts belonging to different historical periods were found during the excavations carried out by the collaboration of The Culture and Tourism Ministry and Anadolu University since 1989. Hellenistic period Megarian bowls and West Slope wares are the main parts of those findings. The sherds of 20 Megarian bowls and 23 West Slope wares were representatively selected. These wares were the fashion cups around the east Mediterranean basin during Hellenistic period. The technological parameters (such as raw materials used in body and slip layers, firing temperatures and atmosphere, microstructural features) of manufacturing were attempted to be enlightened in a frame of an archaeometric work. This study focuses on investigation of the slip layers of those Hellenistic wares. They are in different colours of orange, red, brownish and black. Scanning electron microscopy (SEM) with energy-dispersive X-ray spectrometry (EDX) and μ-Raman spectroscopy were performed for characterisation and determination of components of the slip layers, respectively.

POSTER CONTRIBUTION 27.

ANALYSIS OF THE LATE 18th - EARLY 19th CENTURY CREAMWARE - THE PROBLEM OF PROVENANCE

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ABSTRACT

Cream coloured earthenware (creamware) was invented in Staffordshire, England in mid-18th century. It is made with special clay; its body is of white (or cream) colour. It became very popular, being also much cheaper substitute for porcelain. It was also very suitable for industrialized production.

Because of the advantages the production of creamware spread through Europe very quickly. In the last decade of the 18th century, there were dozens of factories all over Europe.

In Ljubljana, three creamware factories were established in late 18th and early 19th centuries. Their products were well designed and even highly elaborate. All the producers in Europe, also in Ljubljana, used very similar decorative schemes based on English patterns, and similar material.

As many of the objects in the collection of the National Museum of Slovenia are unsigned and there is almost impossible to establish the provenance, we decided to apply scientific non-destructive analytic methods. Firstly, we made several attempts to analyze the objects by XRF, which proved unsuccessful. After that we decided to use in-air PIXE combined with PIGE, since our scientific team has a great deal of experiences on X-rays analysis of glass. With combined methods, we determined the composition of Na, Mg, Al, K, Ca, Ti, and Fe. We used 80 objects, both signed and unsigned, with various (and also dubious) provenance. We grouped our objects accordingly to the results. The groups show rather clearly the producers and thus provide us with efficient tool for provenancing.

POSTER CONTRIBUTION 28.

MCX: NEW OPPORTUNITIES IN CULTURAL HERITAGE RESEARCH USING X-RAY DIFFRACTION

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ABSTRACT

A new bending magnet beamline for Material Characterisation by X-rays – MCX – has been implemented at ELETTRA, the Italian National Synchrotron Radiation facility in Trieste. The beamline has been designed to work in the range 6 - 12 keV, exploiting the high brilliance of ELETTRA bending magnets in this spectral region. Photon flux values of interest for specific experiments are available up to 18 keV and will be available in the range 2.3 - 6 keV.

The spectrum of possible applications is very broad and covers all the characteristics of X-ray diffraction applied to the study of materials (e.g., phase identification, structural solution and refinement, reticular defects and domains, texture analysis). The beamline is furthermore equipped with a furnace that allows in-situ diffraction experiments to follow reactions and transformations during heat treatments.

As a first application in the field of cultural heritage the crystallographic nature of the pigments used in the glazed ceramic tiles was studied, and oxide based pigments were successfully identified under a lead glaze. This study highlights the potential opportunities in research in this field at the MCX beamline at ELETTRA.

POSTER CONTRIBUTION 29.

MODERN PIGMENTS AND ARTISTIC CERAMICS: THE USE OF OXIDE BASED PIGMENTS IN THE ART NOUVEAU TILES OF THE HUNGARIA HOTEL AT VENICE LIDO

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ABSTRACT

In order to understand the crystallographic nature of the pigments used in the glazed ceramic tiles deriving from *Hungaria Hotel*, Lido (Venice), 20 fragments were studied by using the MCX facility. These polychrome tiles were fired under oxidizing conditions, then covered by a frit and, finally, re-fired, to deposit a lead glaze, with thickness around 200 micrometre. Exploiting the possibility of varying the energy of the incident beam, it was possible to overpass the lead glaze and thus analyze the pigment layer, performing in this way a non-destructive analysis of the fragments. The high concentration of lead in the glaze, together with its large thickness, forced a grazing angle experimental setup using a λ of 0.827 nm. An accurate interpretation of the diffraction patterns allows the detection of phases belonging to both the ceramic body and the chromophore oxides. Yellow and brown hues may be ascribed to "modified" Naples yellow, namely $Pb_2SnSbO_{6.5}$, mixed with $CaSnO_4(SiO_4)$ doped with Cr. This compound, know as malayaite, is also responsible of the pinkish hue. The green-turquoise hue is attributable to the presence of $CoCr_2O_4/Cr_2O_3$ while the blue of $CoAl_2O_2$. Some fragments showed also the presence of $CaSO_4 \cdot 2(H_2O)$, $PbCO_3$, and $NaNO_3$. The presence of these compounds has to be ascribed to deterioration processes involving both glaze and ceramic body.

POSTER CONTRIBUTION 30.

CHARACTERISATION OF FOSSIL BONE COMPOSITION AT MICRO-SCALE BY SYNCHROTRON INFRARED MICRO-SPECTROSCOPY

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ABSTRACT

Different post-mortem processes may deeply affect the structure and the composition of bones once their exposition on soil surface and in their burial environment, limiting the usefulness of fossil bones as a source of biochemical information.

Different analytical methods have thus been used to characterize composition changes induced by these alteration processes and to evaluate conservation states. Unfortunately, these analyses are generally performed on bone powder. As bone is a highly hierarchical tissue, the diagenetic processes induce heterogeneous modifications at the histological scale, classically organized in compact bone by osteons surrounding haversian pores.

In this study, Fourier-transform infrared microscopy using synchrotron light sources (SR-FTIR) was applied to investigate the composition of histological structures in Neolithic and Palaeolithic bones. T his method has allowed obtaining highly spatially resolved quantitative and qualitative information on organic and mineral components of archaeological bones. The results obtain by SR-FTIR imaging demonstrate the usefulness of this method for the knowledge of the complex evolution of bone material properties over geological time, and a better localisation of well preserved areas likely to contain un-altered biogenic signal.

POSTER CONTRIBUTION 31.

THE COMPLEMENTARY USE OF NEUTRONS AND X-RAYS FOR THE NON-INVASIVE INSPECTION OF OBJECTS WITH CULTURAL HERITAGE VALUE

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ABSTRACT

There are many objects from cultural heritage which are hidden by corrosion, the excavation remains or contain unknown content. In most cases a destructive approach for getting information about structure and provenance is forbidden for cultural, monetary and ethic reasons.

Non-destructive and non-invasive investigations have been performed mostly by using X-ray methods with conventional (often medical) devices. Nowadays, also synchrotron radiation and dedicated X-ray tomography facilities become more and more common. These techniques fail in cases where metals are involved in certain amounts and thickness. In particular, samples with high content in lead, gold or even uranium are more or less non-transparent.

In such cases, there is the opportunity to use neutron imaging instead. It is the great advantage to use the higher penetrability of thermal neutrons for most of the metals, while a high contrast for all organic material occurs.

This contribution provides a direct comparison of either X-ray inspection or neutron transmission radiography for four very different objects: a block excavation from the Zug region (CH), the example of a Buddha with hidden organic holy content, a Roman sword (Gladius) from the Vindonissa camp (CH), and a belt buckle (DE). These comparisons give an excellent impression how complementarily the both kinds of radiation can be combined.

POSTER CONTRIBUTION 32.

COMPOSITION AND MORPHOLOGY OF THE PRIMING IN HAYEZ PAINTINGS

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ABSTRACT

Primings and ground layers of a painting have several roles and should satisfy both artistic and conservation issues. During the 19th century, a major change in the field of the primings for canvas paints occurred. What was made until then in small workshops or directly by the artist became an industrial product and several recipes were developed. Francesco Hayez (1791-1882), one of the leading artists of Romanticism in Italy, lived just during this period of transition, so that the study of the primings he used allows evidencing such aspects, as their structure and conservation state. Occasionally, degradation aspects of the priming and canvas were also observed.

In this work, we present an in depth characterisation of the priming of several paintings by Hayez, chosen over a time span (1812-1879) covering most of his career. The analyses were carried on by vibrational spectroscopy techniques (FTIR, Raman), XRD, ESEM and EDXS. The study shows the extreme variety in the primings used by the artist. While the main components of the layers making up each priming are usually white lead, barite and calcite: their concentration along the thickness (between 100 and 500 μm) may change considerably. According to the number of layers, composition and microstructure at least five different preparation methods were recognized. Their effect on the conservation of the paintings is discussed.

POSTER CONTRIBUTION 33.

PRE-RESTORATION INVESTIGATION OF FLOOR MOSAICS FROM THE "TRETYAKOV TRADE HOUSE" IN MOSCOW

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ABSTRACT

Complex of analytical methods, which are based on various types of radiation, were used in the pre-restoration investigation of the multi-coloured floor mosaics from the "*Tretyakov Trade House*" located in Moscow's historic centre.

For restoration purposes, the elemental and phase compositions of blue-grey, yellow, and red fragments were determined by means of X-ray fluorescence spectral analysis, X-ray phase analysis, and laser-induced photoluminescence method.

Blue-grey fragments consist of calcite (it has a red luminescence). Yellow fragments contain Fe-dolomite and only single calcite inclusions. Red fragments have the following composition: dolomite, calcite grains and admixture of hematite.

The results of X-ray fluorescence spectral analysis (relative %) are listed in the table below:

Colour of sample	**Ca**	**Mn**	**Fe**	**Sr**	**Total**
Blue-grey	99.91	0.00	0.09	0.00	100.00
Yellow	87.17	0.52	11.24	1.07	100.00
Light-red	94.66	0.43	4.03	0.88	100.00
Dark-red	92.11	0.34	7.32	0.23	100.00

The results of our investigation of mosaic fragments were used during restoration.

POSTER CONTRIBUTION 34.

DETECTING DETERIORATION OF ANCIENT STONE MATERIAL USING SCANNING ELECTRON MICROSCOPY WITH X-RAY MICROANALYSIS AND POSSIBILITIES OF CONSERVATION: THE CASE OF MARINA EL ALAMEIN ARCHAEOLOGICAL SITE (EGYPT)

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ABSTRACT

Excavations at Marina el Alamein (northern Egypt) unearthed a remains of Greco-Roman town. The state of limestone, which was used as main building material for construction purposes, is variable. Different forms of alteration and degradation are observed, like powdering, exfoliation, pitting, granular degradation. The main aim of this research was to establish the reasons of limestone's susceptibility to weathering and to undertake proper conservation methods to prevent progressive deterioration of the objects. Analysis included petrographic observation on thin section and SEM-EDS morphological and micro-chemical analyses. Samples were collected from various parts of the houses and tombs. The results of the present research are due to be applied in the future conservation and restoration works.

POSTER CONTRIBUTION 35.

A STUDY OF HgS DISCOLOURATION IN "*THE ADORATION OF THE MAGI*" BY P.P. RUBENS

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The blackening of the red pigment vermillion or of the corresponding mineral cinnabar (α-HgS) is a phenomenon that is occurring in various mural and oil paintings of different periods. While in some papers, this colour change has attributed to a phase change from red α-HgS (cinnabar) to black β-HgS (meta-cinnabar), a transformation that can take place under intense laser illumination, recent evidence has demonstrated that other factors and transformations are responsible for or related to the colour change.

E.g., in a 17th century painting [1] the presence of calomel and of Cl-containing compounds were found and a degradation mechanism proposed. In Pompeian wall paintings and in a strongly discoloured Catalonian painting of the 16th century, Cotte et al. [2, 3] demonstrated respectively the presence of oxidized sulphate and of the mixed Hg-S-Cl compound corderoite ($Hg_3S_2Cl_2$), present in very thin superficial layers on top of the original red HgS paint. All these findings highlight the role of chlorine- or of chloride-containing compounds as agents involved in the degradation of the HgS paint. The exact nature and role of these compounds (e.g., NaCl, Cl_2, NaOCl, …), however, is not fully understood.

In this contribution, the results of analysis by microscopic X-ray diffraction and microscopic X-ray absorption near edge spectroscopy of paint samples from "*The Adoration of the Magi*" by P.P. Rubens will be discussed. In this monumental altarpiece, the discolouration of the bright red coat of one of the depicted figures from red to black can be observed. On top of the black areas, also a white precipitate has formed. The X-ray based micro-analytical techniques were employed to identify the Hg- and S-compounds present and study their co-localisation. Next to α-HgS, calomel and corderoite were shown to be present near the surface of the altered paint.

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POSTER CONTRIBUTION 36.

CHARACTERISATION OF PRECIOUS METAL OBJECTS WITH SRXRF AT THE BAMLINE

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ABSTRACT

Synchrotron radiation (SR) is useful for all X-ray techniques, whereas for the analysis of ancient metal objects X-ray fluorescence (XRF) is prominent. All examples of this presentation have been measured with the SR-XRF setup at the BAMline at BESSY II. A superconducting wavelength shifter with a maximum field of 7 Tesla is the X-ray source. The useable energy ranges from 5 up to 80 keV. Thus nearly all elements can be detected by measurement of their K-shell flourescence. A W/Si Double-Multilayer-Monochromator (DMM) and / or a Si [111] Double-Crystal-Monochromator (DCM) monochromatise the SR. To achieve higher fluxes it is possible to focus the beam to a size of approximately (300 x 300) μm^2 by bending one multilayer resp. one crystal. If smaller beam sizes are necessary, compound refractive lenses (CRL) can be used to achieve spot sizes in the order of 1 μm^2. For the detection of the fluorescence signal different types of solid state detectors are available.

In this contribution measurements at different ancient gold objects are presented. Questions of provenance, authenticity and technology are raised. Examples from our actual work are shown.

POSTER CONTRIBUTION 37.

ROOM TEMPERATURE STUDY OF THE DEGRADATION OF IRON GALL INK IMPREGNATED PAPER UNDER VARIOUS OXYGEN AND HUMIDITY CONDITIONS - TIME-DEPENDENT MONITORING BY VISCOSITY AND X-RAY ABSORPTION NEAR EDGE SPECTROMETRY MEASUREMENTS

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ABSTRACT

A great part of occidental manuscripts are written with iron gall inks. These inks can damage the paper via two major mechanisms: (a) acid hydrolysis, favoured by the presence of humidity, and (b) oxidative depolymerisation favoured by the presence of oxygen and free iron(II) ions. The degradation of Whatman paper impregnated with different combinations of iron sulphate, gallic acid, and gum Arabic was studied at room temperature in order to assess the relative importance of each mechanism. The samples were stored in various environments including a dry and/or oxygen-free atmosphere. The cellulose depolymerisation was monitored by viscosimetry, and related to changes in the oxidation state of iron, determined by X-ray absorption near-edge spectrometry. The results show that residual amounts of oxygen (less than 0.1 %) promote cellulose depolymerisation, whereas relative humidity levels below 97 % do not have a significant impact. The cellulose depolymerisation also appears closely correlated to oxidative mechanisms. Regarding the oxidation of iron, it is favoured by the simultaneous presence of oxygen and moisture, suggesting the occurrence of rust-like oxidative mechanisms. Finally, the presence of gallic acid has a strong influence, which is only partly explained by its capacity to reduce iron(III) into iron(II).

POSTER CONTRIBUTION 38.

METAL PRODUCTION IN ISRAEL DURING THE PERSIAN PERIOD: ARCHAEOMETALLURGICAL AND GEOMETALLURGICAL RESEARCH

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ABSTRACT

The material culture as expressed in the archaeological finds, divides the country into two spheres of influence comprising of the mountainous area of Judea and Transjordan, which were influenced by the Assyrian, Babylonians and Egyptians on the one hand and the Galilee and the coastal plain which were subjected to Phoenician influence on the other. The major goal of this research is to define the difference between the shore area and the inland parts, using chemical analysis and metallographical tests. To achieve this goal, I tried to define the metal objects according to: typology, archaeometallurgical and geometallurgical research, by answering some key questions:

1. Is there a set of metal-objects (types of tools, weapons and ornamentals – according to typological analysis) that we could define as typical to the coastal plain of Israel during the Persian period (586 - 333 BC)?
2. What were the technological affinities of the defined set of metals: what source material was used (XRF = chemical analysis) for the production of each type of objects and how (= metallographic analysis) each of these types was manufactured. Is there any kind of correlation between the typological (shape size and colour) variables, the chemical composition, and their mechanical and thermal properties.
3. Trying to date metal objects by XRF, a group of metal objects from Naharia Excavations (in June 2005), which have been dated to the 4th and 6th century BC by the excavators, went under chemical analysis. The results well be introduced for the first time in the conference.

POSTER CONTRIBUTION 39.

SEARCH OF IMPROVED RADIOGRAPHIC METHODS FOR PAINTINGS BY MEANS OF STATE-OF-THE-ART LABORATORY AND SYNCHROTRON TECHNOLOGY

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ABSTRACT

It is generally known that radiographic inspection of 15th - 17th century paintings can easily be done with a polychromatic X-ray source using a voltage between 20 and 40 kV in combination with classic X-ray films. Unfortunately, with this technology it is not straightforward to study the spatial structure of 19th - early 20th century paintings. Radiographic images are blurred or worse, they do not contain the picture of the painting. By analysing the same test painting but with different stratigraphies, we could identify the main causes for these radiographic problems such as the presence of high absorbing pigments such as lead white in the ground layer.

During the last decades, many technological innovations have been introduced in the field of radiography but their possibilities in cultural heritage have not been explored in full detail. In our investigation we used phosphor imaging plates, line detectors, energy dispersive detectors and synchrotron radiation in order to improve the quality of radiographic images. Several promising techniques were identified that could improve the quality of radiographs of paintings.

POSTER CONTRIBUTION 40.

BENEFITS OF THE COMPLEMENTARY USE OF MONOCHROMATIC AND WHITE-BEAM X-RAY MICRODIFFRACTION FOR THE INVESTIGATION OF ANCIENT MATERIALS

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ABSTRACT

In many cultural heritage related field studies the structural information at micron scale is often needed. X-ray microdiffraction (μXRD) at third generation synchrotrons is one of the most reliable techniques to obtain significant structural information on most of the archaeological remains. However to obtain all the benefits from the increase in spatial resolution using a sub-micrometre beam and obtain reliable structural information, monochromatic μXRD measurements needs to be complemented with white-beam μXRD. Scanning μXRD consists on rastering the sample with a highly focussed white or monochromatic X-ray beam. At each step a 2D diffraction pattern (resp. a Laue and a Debye-Scherrer pattern) is recorded and structural maps of the sample such as phase distribution, grain orientation and/or strain maps can be generated. In our approach, we used monochromatic patterns to identify the nature of nanocrystalline grains, and white beam to identify microcrystalline ones. These techniques have been applied in the present work on lithic bladelets to understand their improved mechanical properties after firing by obtaining stress maps from micron sized quartz and identifying nanosized iron oxide impurities. They have been deployed on antic decorated ceramics to understand the development of pigments in well-sintered thin layers obtained from iron oxide rich clays. They have been deployed also on a Roman iron spike to elucidate the texturation from its core and the development of iron carbide nanograins giving important hints about its metallurgy. In all three examples white-beam μXRD unveiled valuable structural information from highly complex ancient materials.

POSTER CONTRIBUTION 41.

ROLE OF SYNCHROTRON RADIATION IN THE STONES AND PAINTING OF KALINJAR FORT IN INDIA

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ABSTRACT

The historical "*Kalinjar Fort*" was built in seventh century. It was constructed by King Kedar the ruler. The material used in this fort is a unique one and we have collected the sample of the material of different parts of fort and we have observed that this fort was built by the ruler keeping in the view the aspects of security and provision of all essential facilities. The material used in the construction was synthesized and separated by the available techniques and identified by the spectral techniques.

This paper concentrates on the use of synchrotron radiation to understand the atomic structure of the material. Normally it has been observed that some metal in the form of copper is mixed in the material used. After collecting the material from the fort we have synthesized and found that it has got a very nice scope to find out the structure of the different constituents which are available in the stones of the fort. The ability to accurately follow the evolving structure of material from precursor to the final product in consumption with its performance as a working material is critical in developing and optimizing desirable properties. We focus our attention in this paper on material specially stones, wood, glasses, paintings with specific example of structure property relationship. The synchrotron radiation has its unique optical property has open the doors to the study of all material used in the construction of the fort, many of which are less than perfectly crystalline. We have observed the data which will be displayed in the presentation.

The results of observation during the process and the product found have been identified by the different spectral techniques using X-ray method, spectroscopy, IR, UV, etc. All our findings will be presented in detail with the structure of the stable compounds.

POSTER CONTRIBUTION 42.

PORTABLE XRF AND LIPS COMBINED CHARACTERISATION OF COPPER ALLOY ARTEFACTS

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ABSTRACT

XRF is a recognized non-destructive archaeometallurgical tool for achieving semi-quantitative chemical compositions of metal alloys. It is often used for comparing set of objects or independent parts of a given artefact through multivariate data elaborations. Besides problems due to the morphology of the area under analysis, the quantitative data provided by XRF are mainly affected by compositional gradients associated with selective corrosion phenomena. The use of portable laser induced plasma spectroscopy (LIPS) in archaeometallurgical studies is relatively recent with respect to XRF. It is a micro-destructive technique (typical ablation spots of 50 - 100 μm), which can provides reliable quantitative depth profiles. Both small measurement volumes and ablation effects can represent limitations of this approach whenever encountering strong compositional variability and/or very deep corrosion effects, whose thorough investigation would require unacceptable invasiveness. Here, we report a systematic investigation on combined XRF and LIPS characterisation of copper alloy artefacts. Extensive comparative tests were carried out on laboratory samples and figurines from Florence's National Museum of Archaeology. The study showed that preliminary XRF compositional mapping can drastically reduce the invasiveness and reliability of LIPS for achieving representative bulk and depth profile analyses by means of a small set of measurements suitably addressed. Archaeometallurgical implications of the methodology related with the interpretation of the manufacturing processes, authentication, and conservation of the artefact investigated are thoroughly discussed.

POSTER CONTRIBUTION 43.

THE ROLE OF COPPER ON COLOUR OF PALEO-CHRISTIAN GLASS MOSAIC TESSERAE: A XAS STUDY

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ABSTRACT

This work reports the results of an X-ray Absorption Spectroscopy (XAS) study carried out on thirteen copper coloured glass mosaic tesserae from the disrupted paleo-christian glass mosaic of *St. Prosdocimus* (Padua, Italy) and aimed to clarify how the different local structure, oxidation state and quantity of this element could influence the colour. The analyses of high-resolution Cu-Kedge XANES (X-ray Absorption Near Edge Structure) and EXAFS (Extended X-ray Absorption Fine Structure) spectra suggest that copper is present as cuprite (Cu_2O) in orange samples and as metallic copper in red and brown ones. These phases are responsible both of colour and opacity of samples. In addition, Cu^{+}-ions linked to the oxygen atoms of the glass framework were also identified in ratios equal to 60 % and 30 % of the total copper in orange and red samples, respectively. In blue and green samples copper is dispersed in the glass matrix as a mixture of Cu^{+}- and Cu^{2+}-ions, and no peaks relative to crystalline phases are visible. In this context, the Cu^{+}- and Cu^{2+}-contents in glass were also quantified for the first time thanks to suitable standards, demonstrating that the colour intensity of tesserae is directly correlated to Cu^{2+}-content of glass, which is the real chromophorous ion. In particular, in blue and green samples the Cu^{2+}-content varies from 26 to 55 % of the total copper and the higher contents of the above ion are shown by more intensely coloured samples. It should be stressed here that the green colour of the analysed Padua tesserae is due the physic interaction of blue colour due to Cu^{2+}-ions and the yellow colour due to Pb antimoniates used as opacifiers.

POSTER CONTRIBUTION 44.

CULTURAL HERITAGE STUDIES AT ANKA FLUO BEAMLINE

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ABSTRACT

In the recent years various studies on the field of cultural heritage were performed at the FLUO beamline at ANKA synchrotron radiation facility.

The ANKA FLUO beamline is a bending magnet beamline with a multilayer monochromator dedicated to scanning X-ray fluorescence measurements with collimated or focussed X-ray beam of 3 - 35 keV. The beamline allows sampling spatially resolved volume information on chemical composition by confocal XRF or tomographic scanning XRF. By combining the latter technique with powder diffraction tomography or scanning phase contrast absorption tomography complementary data is obtained.

A brief overview over the beamline and its experimental possibilities is given as well as several examples of recent user and in-house experiments, like the study of protrusions in a painting of Max Beckmann. Three-dimensional elemental imaging based on XRF in combination with Raman scattering revealed a very high concentration on zinc in this blister like alterations.

POSTER CONTRIBUTION 45.

APPLICATION OF CATHODOLUMINESCENCE IN MORTARS SELECTION FOR ^{14}C DATING

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ABSTRACT

Cathodoluminescence microscopy is a very popular method applied in geosciences, especially in carbonate rocks studies, but also in analysis of feldspars and quartz grains. It can be very helpful in describing diagenetic processes of quartz sandstone or genesis of quartz crystals. CL microscopy was applied during research into provenance of sandstones used in Romanesque architecture of Poland. The investigation allowed recognizing the source of the stone, what will be very important during future renovation works of the objects studied.

The CL method can also be very helpful during mortars selection for radiocarbon dating. Radiocarbon dating of mortar is based on setting the present ^{14}C concentration from the air by carbonates during the hardening process. To obtain the age of a building construction it is necessary to date the carbonate binder, and exclude the source of re-crystallisation or „dead carbon" from the aggregate.

The analysis and identification of different kind of carbonate particles in mortars is very important. Verification of additional application of CL characterisation beside the standard petrographical procedure can be very helpful. The mortar carbonate ingredients can have different luminescence intensities which depend on many different features like pH condition or proportion between Mn^{2+} and Fe^{2+} during mortar hardening (this proportion can be examined by using SEM-EDS microscopy). Knowledge of this proportion and detailed characterisation of samples may allow avoiding the rejuvenation or over-aging effect in mortars dating. During the analysis, experimental and historical mortars are examined to verify the methods applied.

POSTER CONTRIBUTION 46.

SEM-EDS, XRD AND PETROGRAPHY IN DETERIORATION OF SANDSTONE BUILDING MATERIALS

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ABSTRACT

Deterioration of stone building material used as a panel or stone blocks has different reasons. Usually it depends on the localisation of the building – industrial or village area. Condition of stone material, its damages depend on samples composition, climate in the region, position of sample in monument and human influence (wrong conservation work or environmental pollution).

In Poznań (capital of Greater Poland) in 2010 renovation works were started on two important buildings for the city – Collegium Minus and Collegium Juridicum of Adam Mickiewicz University. In both of these buildings sandstone was used as a panel and material in architectonical details. This stone comes from similar quarry, like stone used in 13th - 16th century in Romanesque churches in southern part of Greater Poland (Lubiń or Krobia). The performed analysis of sandstone deterioration allow to compare: type of degradation, secondary minerals crystallized in the effect of air pollution, etc. It should be noted that university buildings are much younger (built in the beginning of the 20th century) then mentioned churches.

At the moment studies are in progress. The analysis are performed by using XRD, SEM-EDS, optical microscope and chemical analysis, which are helpful in recognition of different type of stone deterioration (for example crystallisation of sulphur or gypsum).

POSTER CONTRIBUTION 47.

CASTING TECHNOLOGY OF RENAISSANCE BRONZE STATUETTES: THE USE OF TOF-NEUTRON DIFFRACTION FOR STUDYING AFTERWORK OF RENAISSANCE CASTING TECHNIQUES

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ABSTRACT

Three Renaissance bronze statuettes belonging to the collection of the Rijksmuseum Amsterdam were examined on their finishing technique using time-of-flight Neutron Diffraction (TOF-ND) on the diffractometer ENGIN-X at the ISIS neutron spallation source, Rutherford Appleton Laboratory in Chilton. The research focused on the hypothesis that a bronze sculpture that seems meticulously finished, could have been cast and no afterworking of the surface using chasing tools had to take place. The examined statuettes on this specific feature are Willem van Tetrode's '*Hercules Pomarius*' (BK-1954-43) and a bust of Pope Gregory XIV presumably manufactured by Bastiano Torrigiani (BK-16937). Both of these sculptures date to the second half of the 16th century. A study of contemporary treatises indicated that casting without chasing was possible. For comparative results a bronze figure from the beginning of the 16th century, doubtlessly cast and chased, representing Paris by Severo da Ravenna (BK-1959-4) was equally analyzed. Reference samples reproducing the techniques involved were manufactured to compare the results with the original objects. We could proof that both the bust of Pope Gregory XIV and Hercules Pomarius were cast and not chased and Paris is cast and chased.

POSTER CONTRIBUTION 48.

DETERMINATION OF THE OXIDATION AND COORDINATION OF Co, Mn AND Fe IN BLUE GLAZE STUDIED BY XAFS SPECTROSCOPY

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ABSTRACT

Colour of glaze is usually determined by the oxidation and coordination state of transition elements, because these elements can absorb characteristic frequencies of visible light as a result of d-d electronic transitions. In this study, SR-XAFS was used to obtain the information about oxidation and coordination state of Co, Mn and Fe in glaze aiming to investigate the colouring mechanism of blue colour porcelain. Samples were mainly from Longzhuge site (Jingdezhen, Jiangxi Province) manufactured by Guan kiln during Qing dynasty. Co K-edge XAFS spectra were collected at BSRF (Beijing, China) and Mn K-edge XAFS spectra and Fe K-edge XANES spectra were collected at SSRF (Shanghai, China). The analysis of Co K-edge showed that Co was mainly present as divalent cations with little amount of Co^{3+} and coordinated with oxygen atoms and located at both octahedral and tetrahedral sites, so $[Co^{2+}O_4]$ was mainly responsible for the colour of blue glaze. The analysis of Mn K-edge revealed that Mn was present as divalent cations coordinated with oxygen atoms in tetrahedral site. Fe K-edge XANES analysis showed that Fe^{3+} was the main constituent, with a small amount of Fe^{2+}. Considering the ability of absorbing the characteristic frequencies, both Mn^{2+} and Fe^{3+} made little contribution for the colour of blue glaze.

POSTER CONTRIBUTION 49.

XAS CHARACTERISATION OF COPPER IN ARCHAEOLOGICAL GLASSES IN THAILAND

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ABSTRACT

In ancient time, glasses have been used in ornaments and decorations in Thailand for several hundred years as seen by archaeological evidences such as glass beads and decorative glasses. Cu K-edge XANES of the blue and red coloured glass bead samples from Hor-Ek, historical site (central Thailand) that affected from copper was collected in fluorescent mode using a 13 element Ge detector. It was found that the blue tonality due to divalent copper, whiles the red one was affected from monovalent copper. SEM was used to characterize their microstructure.

POSTER CONTRIBUTION 50.

DRILLING TECHNOLOGY RESEARCH OF PERFORATED JADES EXCAVATED FROM XUEJIAGANG SITE (5000-6000 BP) IN CHINA THROUGH SR-μCT

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ABSTRACT

Drilling is one of the important methods used to make jade artefacts. Because of rare records or discovery of ancient drilling tools, drilling research depends mainly on interpreting tool marks on the inner wall of perforations and the forms. For smaller perforations, it is hard to observe drilling marks by optical microscope or SEM, so virtual 3D reconstruction by using μCT could be the exclusive method to clearly disclose drilling marks. Many jade tubes were excavated from Xuejiagang Site, and some of them were examined by SR-μCT in Shanghai. Scan data were imaged and analyzed using Mimics12 (Materialise, Belgium). Virtual 3D positive and negative models were constructed to better observe drilling marks and perforation forms. Because the cross-sections of the perforations are perfectly circular, so rotation tools were used. And the characters of drilling were summarized according to virtual models – for solid drilling, the perforation looks like cone; and for core drilling, the perforation looks like cylinder. On one core drilled perforation, the diameter of perforation is 1.89 mm, and the diameter of remained core is 0.65 mm; so the drilling bit may be quill, bamboo tube or bone tube of small vertebrate. Therefore, SR-μCT has great potential in drilling research.

POSTER CONTRIBUTION 51.

SCIENTIFIC ANALYSIS OF DRAGONFLY-EYED BEADS IN THE LATE WARRING STATE (476-221 BC) EXCAVATED FROM SHENMINGPU SITE, HENAN PROVINCE, CHINA

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ABSTRACT

In 2008 field excavation of Shenmingpu Site, Henan Province in China, two intact and two fragmentary dragonfly-eyed beads were excavated from a small tomb with style of the Chu Kingdom in China. In one intact bead, the clay core remained in the perforation; so it was deduced that these beads were produced locally. This speculation was testified by chemical analysis by SEM-EDS. In the monochrome glass surface (green or brown) and convex glassy eyes, K, Pb and Ca are main flux, Fe and Cu are colour-generating elements. In one concentric circle composed of white glass, Ba (7.42 %) and Ti (4.53 %) are detected. These chemical characters are of particular glass in China. Through SR-XRF, line scan were made on the natural cross-section of fragmentary beads, it was found that the beads are not totally composed of glass, they are more similar to glazed pottery. Through SR-μCT, it was also found that glassy phase just covered the surface of the porous pottery body of beads and the convex glassy eyes were added later to the fired beads. Therefore, SR-μCT is a good non-destructive tool to understand the manufacture technology of eye beads.