

1st CrysAC Workshop
Cultural heritage authentication and forensic science

6th Meeting
X-ray and other techniques in investigations of the objects of cultural heritage

Celebrating the 100th anniversary of X-ray powder diffraction

Krakow 18-21 May 2016

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Krakow, 18-21 May 2016

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ORGANIZERS

Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Krakow, Poland
www.chemia.uj.edu.pl

National Museum in Krakow
al. 3 Maja 1, 30-062 Krakow, Poland
www.mnk.pl

Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, ul. Niezapominajek 8, 30-239 Krakow, Poland
www.ik-pan.krakow.pl

Faculty of Conservation and Restoration of Works of Art
Jan Matejko Academy of Fine Arts in Krakow, ul. Lea 27-29, 30-052 Krakow, Poland
www.asp.krakow.pl

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Gilberto Artioli
Dipartimento di Geoscienze, Università di Padova, Italy

David Hradil
Institute of Inorganic Chemistry of the Academy of Sciences of the Czech Republic, Academy of Fine Arts in Prague Laboratory ALMA, Czech Republic

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PROGRAMME

1st CrysAC Workshop Cultural heritage authentication and forensic science

18 May, Wednesday, National Museum in Krakow, al. 3 Maja 1

8.00–10.00 am Registration

9.00 am **Opening:** Gilberto Artioli, Chair of the IUCr Commission on Crystallography in Art and Cultural Heritage; Andrzej Betlej, Director of the National Museum in Krakow

Session 1 Chair: Alicja Rafalska-Łasocha, CrysAC, Faculty of Chemistry, Jagiellonian University

9.05–9.30 am **Gilberto Artioli**, Dipartimento di Geoscienze, Università di Padova, ***Introductory lecture***

9.30–10.10 am **Filippo Terrasi**, Department of Mathematics and Physics, Second University of Naples, ***Forensic applications of 14C accelerator mass spectrometry***

10.10–10.50 am **Zuzanna Brożek-Mucha,** Institute of Forensic Research, Krakow, ***Applications of X-ray spectrometry and X-ray diffraction in forensic investigations***

10.50–11.00 am Coffee break

11.00–11.40 am **Sariel Shalev**, University of Haifa, ***Unusual objects in archaeology: genuine or fake?***

11.40 am–12.20 pm **Paul Craddock**, British Museum, London, ***Artificial patinas: methods and motives***

12.20–1.00 pm **Petr Bezdička**, Institute of Inorganic Chemistry of the Academy of Sciences of the Czech Republic (ALMA laboratory) ***Advanced methodology for quantitative X-ray microdiffraction analysis and its use in provenancing clay-based pigments in paints***

1.00–2.00 pm Lunch break

Session 2 Chair: **Petr Bezdička**, CrysAC, Institute of Inorganic Chemistry of the Academy of Sciences of the Czech Republic (ALMA laboratory)

2.00–2.40 pm **Manfred Schreiner**, Institute of Science and Technology in Art, Academy of Fine Arts, Institute of Chemical Technology and Analytics, Vienna University of Technology, ***Application of computational techniques and material analysis for the authentication of our cultural heritage***

2.40–3.20 pm **Koen Janssens**, University of Antwerp, ***Authentication of paintings via non-destructive chemical mapping analysis***

3.20–3.40 pm Coffee break

3.40–4.20 pm **Barbara Łydżba-Kopczyńska,** LANBOZ, Krakow, ***A combined imaging and spectroscopic approach to fine art authentication***

4.20–5.00 pm **Stjepan Prugovečki**, **Jan Gertenbach**, PANalytical B.V, ***Authentication and forensic applications on PANalytical X-ray systems***

5.00–5.30 pm **Round table discussion chaired by Gilberto Artioli**

6th Meeting X-ray and other techniques in investigations of the objects of cultural heritage

19 May, Thursday, National Museum in Krakow, al. 3 Maja 1

8.00–10.00 am Registration

10.00–10.15 am **Opening/welcoming remarks:** Grażyna Stochel, Dean of the Faculty of Chemistry, Jagiellonian University in Krakow; Malgorzata Witko, Director of the Jerzy Haber Institute of Catalysis and Surface Chemistry PAS; Marta Lempart-Geratowska, Dean of the Faculty of Conservation and Restoration of Works of Art, Jan Matejko Academy of Fine Arts in Krakow; Gilberto Artioli, Chair of the IUCr Commission on Crystallography in Art and Cultural Heritage; Andrzej Betlej, Director of the National Museum in Krakow

Session 1 Chair: Wiesław Łasocha, Faculty of Chemistry, Jagiellonian University

10.15–10.55 am Invited lecture: ***High-end PIXEL detectors for fine art investigation: high-performance X-ray radiography, X-ray fluorescence imaging, X-ray microdiffraction*****, David Hradil**, Janka Hradilová, Jan Žemlička, Petr Bezdička, Institute of Inorganic Chemistry of the Czech Academy of Sciences, Academy of Fine Arts in Prague, ALMA Laboratory, Institute of Experimental and Applied Physics, Czech Technical University in Prague

10.55–11.35 am Invited lecture: ***Non-invasive documentation and material analysis using X-ray fluorescence, infrared and Raman spectroscopy*****, Manfred Schreiner,** Institute of Science and Technology in Art, Academy of Fine Arts, Institute of Chemical Technology and Analytics, Vienna University of Technology, Vienna

11.35 am–12.05 pm ***Precipitation and microchemical characterisation of CdS yellow and orange pigments*****, Silvia Pedetti**, Matthias Alfeld, Philippe Walter, Laboratoire d'Archeologie Moléculaire et Structurale, UMR 8220, Université Pierre et Marie Curie, Paris

12.05–12.25 pm **In situ *non-invasive XRF research on the evolution of the use of pigments by Polish painters in the period 1800–1900*****, Mirosław Wachowiak**, Grzegorz Trykowski, Dept. of Conservation and Restoration of Modern Art, Faculty of Chemistry, Nicolaus Copernicus University, Toruń

12.30–1.00 pm Poster session

1.00–2.00 pm Lunch break

Session 2 Chair: Gilberto Artioli, Dipartimento di Geoscienze, Università di Padova

2.15–2.55 pm Invited lecture: ***Micro-XRPD, XRPD tomography, and MA-XRPD: 3 methods to better understand structural changes in cultural heritage materials***, **Koen Janssens**, University of Antwerp

2.55–3.25 pm ***Macro X-ray fluorescence imaging for antique polychromy*****, Matthias Alfeld,** Maud Mulliez, Philippe Jockey, Philippe Walter, Sorbonne Universités, Université Pierre et Marie Curie, Centre National de la Recherche Scientifique, UMR 8220, Laboratoire d'archéologie moléculaire et structurale (LAMS), Aix-Marseille Université, Centre Camille Jullian

3.25–3.45 pm ***Developmental progress of the macro-XRF scanner for the investigation of historical objects,*** **Bartosz Mindur,** Tomasz Fiutowski, Piotr Frączek, Stefan Koperny, Marek Lankosz, Agata Mendys, Anna Sikorska, Krzysztof Świentek, Piotr Wiącek, Paweł M. Wróbel, Władysław Dąbrowski, AGH University of Science and Technology, National Museum in Krakow, Krakow

3.45–4.05 pm ***Comparison of PIXE and XRF in the analysis of silver denarii of the early Piasts,*** **Janusz Lekki,** Marta Matosz, Czesława Paluszkiewicz, Julio M. del Hoyo-Meléndez, Institute of Nuclear Physics, Polish Academy of Sciences, Laboratory of Analysis and Non-Destructive Investigation of Heritage Objects, National Museum in Krakow, Krakow

4.05–4.25 pm ***Optimization of powder diffractometer configuration to achieve the best possible results,*** **Stjepan Prugovečki,** Jan Gertenbach, PANalytical B.V, Almelo

7.00–11.00 pm **Conference dinner in The Bishop Erazm Ciolek Palace, the National Museum in Krakow, ul. Kanonicza 17**

20 May, Friday, National Museum in Krakow, al. 3 Maja 1

Session 3 Chair: Manfred Schreiner, Akademie der Bildenden Künste Wien

10.15–10.55 am Invited lecture: ***'ZOOMING-IN' with compositional XRF analysis: is there a limit? The case of Middle Bronze Age daggers in the Levant***, **Sariel Shalev**, University of Haifa

10.55–11.35 am Invited lecture: ***Experimental evidence of the recipes of Vitruvius and Pliny: the art of mortars,*** **Gilberto Artioli**, Dipartimento di Geoscienze, Università di Padova

11.35 am–12.05 pm ***X-ray mapping of hidden wall paintings: a feasibility study,*** **Piotr Targowski,** Ermanno A. Clerici, Liesbeth Dingemans, Jędrzej Musiela, Robert Rogal, Institute of Physics, Nicolaus Copernicus University, University of Bologna, Technical University of Delft, Restauro Sp. z o.o., Institute for the Study, Restoration and Conservation of Cultural Heritage, Nicolaus Copernicus University

12.05–12.25 pm ***Known unknown: X-ray investigations of selected copper coins from Mount Gromnik, SW Poland*****, Beata Miazga**, Paweł Milejski, Institute of Archaeology, University of Wrocław

12.30–1.00 pm Poster session

1.00–2.00 pm Lunch

Session 4 Chair: Janusz Czop, National Museum in Krakow

2.15–2.55 pm Invited lecture: ***The major Egyptian bronze statuary of the third intermediate period: casting and decoration,*** **Paul T. Craddock**, British Museum, London

2.55–3.25 pm ***X-ray-based imaging and spectroscopy of paintings by Olga Boznańska,*** **Anna Klisińska-Kopacz**, Piotr Frączek, Michał Obarzanowski, Janusz Czop, National Museum in Krakow

3.25–3.45 pm ***Non-destructive analysis of canvas paintings in the Archbishop's Palace of Seville,*** **Anabelle Kriznar,** Kilian Laclavetine, Ana Isabel Gamero González, Miguel Ángel Respaldiza**,** Centro Nacional de Aceleradores (CNA), University of Seville (US), Department of Atomic, Molecular and Nuclear Physics, Faculty of Physics, (US), Department of Sculpture and Art History, Faculty of Fine Arts (US), Archdiocese of Seville, Archbishop's Palace, Seville

3.45–4.05 pm ***An analytical protocol for the isolation and identification of natural organic dyestuffs present in historical artistic paints,*** **Olga Otłowska**, Magdalena Śliwka-Kaszyńska, Dept. of Organic Chemistry, Gdańsk University of Technology, Gdańsk

POSTERS:

Warsaw's Old Market Square: material studies of its decoration, **Sylwia Svorová Pawełkowicz**, Academy of Fine Arts in Warsaw, Faculty of Conservation and Restoration, Warsaw

Instrumental analysis of paper support, **Anna Nowicka**, Academy of Fine Arts in Warsaw

X-ray diagnostics on Caravaggesque paintings: a presentation of research**, Mateusz Jasiński,** Academy of Fine Arts in Warsaw, Faculty of Conservation and Restoration of Works of Art

Text enhancement and examination of traces on documents using hyperspectral imaging combined with the chemometric approach, **Alicja Majda**, Agata Mendys, Renata Wietecha-Posłuszny, Barbara Łydżba-Kopczyńska, Paweł Kościelniak, Laboratory for Forensic Chemistry, Faculty of Chemistry, Jagiellonian University, Laboratory of

Analysis and Non-Destructive Investigation of Heritage Objects (LANBOZ), National Museum in Krakow, Faculty of Chemistry, University of Wrocław, Institute of Forensic Research, Krakow

Optimisation of the geometry of the full-field XRF imaging system based on a gaseous detector, **Paweł M. Wróbel,** Tomasz Fiutowski, Piotr Frączek, Stefan Koperny, Marek Lankosz, Agata Mendys, Bartosz Mindur, Anna Sikorska, Krzysztof Świentek, Piotr Wiącek, Władysław Dąbrowski, AGH University of Science and Technology, National Museum in Krakow

A new methodology for removal of absorption artefacts in the macro-XRF imaging of paint layers, **Pawel M. Wróbel**, Piotr Fraczek, and Marek Lankosz, AGH University of Science and Technology, Krakow, National Museum in Krakow

X-ray computed tomography study of archaeological artifacts**,** **Ewelina Miśta**, Tymoteusz Kosiński, Władysław Weker, National Centre for Nuclear Research, Otwock-Świerk, State Archaeological Museum in Warsaw

The effect of growth ring structure on the response of wood subjected to changing climate conditions, **Leszek Krzemień,** Michał Łukomski, Marcin Strojecki, Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Getty Conservation Institute, Los Angeles, CA

Chemical, structural, and morphological characterisation of metallic objects for forensic purposes, **Zuzanna Brożek-Mucha**, Dariusz Mucha, Institute of Forensic Research, Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow

Composition of gold alloys and degradation of pigments used in Portuguese artworks from the 14th to 17th centuries, **Manuel J. L. Sarmento**, Afonso M. T. Coxito, Francisco P. S. C. Gil, CFisUC – Centre for Physics of the University of Coimbra, Department of Physics, and Molecular Physical-Chemistry R&D Unit, Chemistry Department, University of Coimbra

Animal remains in contemporary art. The use of X-ray and other techniques to obtain a deeper understanding of the technology of atypical contemporary artworks and their care on the basis of 'Pyramid of Animals' by Katarzyna Kozyra and 'Bitch' by Mirosław Bałka, **Anna Kowalik, MA,** Academy of Fine Arts in Warsaw, Faculty of Conservation and Restoration of Works of Arts

A research project on twelve paintings **en grisaille** ***from Janow Podlaski,*** **Marta Zaborowska**, Faculty of Conservation and Restoration of Works of Art, Academy of Fine Arts in Warsaw

Decoration techniques in mediaeval Hebrew Bibles: non-invasive XRF and μ-Raman analysis, **Anna Rogulska**, Barbara Łydżba-Kopczyńska, Faculty of Chemistry, Jagiellonian University, Krakow

Preliminary studies of Katarzyna Kobro's gypsum sculptures**, Marta Grzesiak-Nowak**, Alicja Rafalska-Łasocha, Anna Klisińska-Kopacz, Elżbieta Cieślak, Wiesław Łasocha, Faculty of Chemistry Jagiellonian University, National Museum in Krakow, Muzeum Sztuki in Lodz, Jerzy Haber Institute of Catalysis and Surface Chemistry PAS

Painting materials used by Henryk Siemiradzki in some of his works, **Dominika Sarkowicz**, Alicja Rafalska-Łasocha, Marzena Sieklucka, Anna Klisińska-Kopacz, Marta Matosz, Julio del Hoyo-Meléndez, Marta Grzesiak-Nowak, Wiesław Łasocha, National Museum in Krakow, Faculty of Chemistry Jagiellonian University, Jerzy Haber Institute of Catalysis and Surface Chemistry PAS

Evaluation of various scientific techniques applied to ancient metal objects**, Anna Grzesik,** Marcin Oszajca, Marta Grzesiak-Nowak, Wiesław Łasocha**,** Faculty of Chemistry Jagiellonian University, Jerzy Haber Institute of Catalysis and Surface Chemistry PAS

Hyperspectral imaging investigation of writing traces on paper, **Damian K. Chlebda**, Anna Rogulska, Alicja Majda, Tomasz Łojewski, Jagiellonian University, Faculty of Chemistry, Krakow

21 May, Saturday

Session 5

9.00–10.30 am How we do it: visits to scientific labs carrying out investigations of the objects of cultural heritage

at the Faculty of Conservation and Restoration of Works of Art, Jan Matejko Academy of Fine Arts in Krakow, ul. Smoleńsk 9
or
in the Laboratory of Analysis and Non-Destructive Investigation of Heritage Objects, National Museum in Krakow, ul. Piłsudskiego 14
or
at the Faculty of Chemistry, Jagiellonian University in Krakow, ul. Ingardena 3
or
at the Jerzy Haber Institute of Catalysis and Surface Chemistry PAS,
ul. Niezapominajek 8

11.00 am Visit to the tourist attractions of Krakow and its surroundings

ABSTRACTS

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ORAL PRESENTATIONS



IUCr Commission on Crystallography in Art and Cultural Heritage

1st Workshop

CULTURAL HERITAGE AUTHENTICATION AND FORENSIC SCIENCE

INTRODUCTION

Gilberto Artioli
Chair, IUCr Commission on 'Crystallography in Art and Cultural Heritage'
gilberto.artioli@unipd.it

The IUCr Commission on 'Crystallography in Art and Cultural Heritage' is aimed at identifying and promoting all activities involving cultural heritage which are of interest to the crystallographic community. Crystallography is, of course, naturally and historically linked to symmetry in all its expressions and aspects, both theoretical and applied (Fig. 1). However, crystallographic analyses (diffraction-based and beyond) of artworks and archaeological materials are important tools in the broader context of cultural heritage investigations and the characterisation of materials related to human activities of the past.

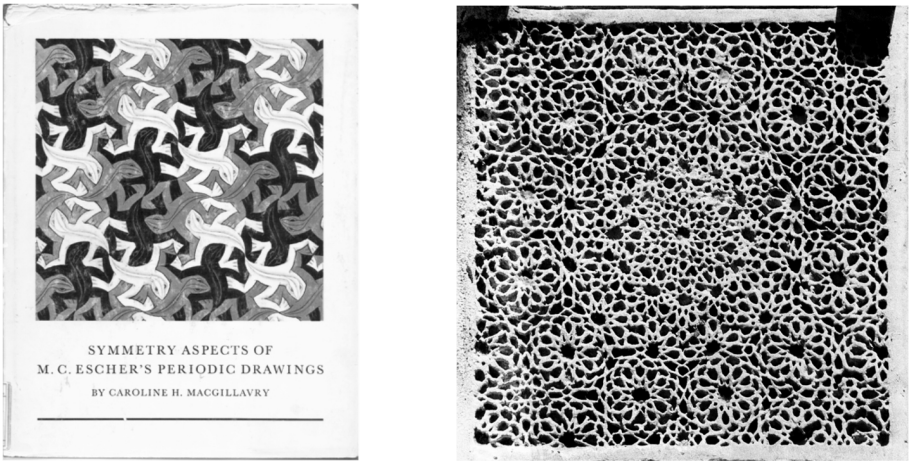


Fig. 1 Symmetry in art and architecture: left, the cover of a historical volume by Caroline MacGillavry on analysis of the symmetry of M. C. Escher's periodic drawings; right, the first identification of dodecagonal quasiperiodic tiling in historical Islamic architecture [1].

This first CrysAC Workshop wishes to emphasise the importance of advanced characterisation techniques in the investigation of materials as diverse as artworks and forensic remains. It is no surprise that state-of-the-art analytical techniques are helpful in art and archaeological authentication [2–3] as well as forensic traceability [4]; the appropriate use of scientific methods may provide clues to a very different kind of unsolved riddle.

References

[1] Makovicky, Emil, and Nicolette M. Makovicky. 'The first find of dodecagonal quasiperiodic tiling in historical Islamic architecture'. *Journal of Applied Crystallography* 44.3 (2011): 569–573.

[2] Craddock, Paul, ed. *Scientific investigation of copies, fakes and forgeries*. Routledge, 2009.

[3] Ragai, Jehane. 'The Scientist and the Forger: Insights into the Scientific Detection of Forgery in Paintings'. *World Scien*tific, 2015.

[4] James, Stuart H., Jon J. Nordby, and Suzanne Bell, eds. *Forensic science: an introduction to scientific and investigative techniques*. CRC Press, 2002.

FORENSIC APPLICATIONS OF 14C ACCELERATOR MASS SPECTROMETRY

Filippo Terrasi
Center for Isotopic Research on Cultural and Environmental heritage – Dept. of Mathematics and Physics, Second University of Naples
filippo.terrasi@unina2.it

Accelerator mass spectrometry (AMS) radiocarbon dating is one of the most powerful analytical tools available for the study of the past evolution of the activities of humankind and its environment. In particular, the ability to date tiny (<1 mg) amounts of organic material has enabled researchers to accurately establish the chronology of various findings of archaeological or art-history interest. In several cases, time-based authentication of such findings proved possible in cases where attribution issues spanned several decades, as compared with experimental uncertainties (typically ±25–30 years). More recently, the so-called 'bomb spike effect' has made it possible to determine the age of recent samples (after 1950 AD) with largely improved precision (<1 year), or at least to ascertain whether they can be dated before or after the beginning of the nuclear era. This information is often sufficient to distinguish false cultural heritage objects from true, and has proven extremely valuable in several forensic applications. A review of certain cases investigated at CIRCE, using both the 'classical' and 'bomb-spike' radiocarbon AMS methods, will be given in the present contribution.

APPLICATIONS OF X-RAY SPECTROMETRY AND X-RAY DIFFRACTION IN FORENSIC INVESTIGATIONS

Zuzanna Brożek-Mucha
Institute of Forensic Research, ul. Westerplatte 9, 31-033 Krakow
zbrozek@ies.krakow.pl

Analytical techniques based on X-rays, known to be non-destructive and requiring small amounts of a specimen, may serve for the chemical, structural, and morphological characterisation of evidential material of interest in forensic and historical investigations.
X-ray spectrometry, alone or in combination with optical and electron microscopy and molecular spectroscopic techniques such as infrared and Raman spectrometry, can be applied to the identification and comparison of fragments of glass, paint, and metal related to car accidents and burglaries [1], residues of gunshots and explosions originating from serious crimes committed with the use of firearms [2, 3] and explosive devices [4], potentially radioactive agents, organic and inorganic poisons, and many other types of materials related to forgeries as well as to historical and cultural questions [5, 6]. A particular role in the identification of a substance may be played by X-ray diffraction, the only method capable of establishing the phase of the substance [6].



Fig. 1 Nicolaus Copernicus (photo: zadane.pl)



Fig. 2 Adam Mickiewicz (photo: krakow.travel)



Fig. 3. Władysław Sikorski (photo: pl.wikipedia.org)

Selected examples of the application of X-ray spectrometry and X-ray diffraction for the examination of materials related to interesting forensic and historical cases will be presented, e.g. the remains of some historical personalities: the femoral bone of the astronomer Nicolaus Copernicus (Fig. 1), hair of the poet Adam Mickiewicz (Fig. 2), and various materials from the exhumation of General Władysław Sikorski (Fig. 3).

References

[1] Z. Brożek-Mucha, *X-ray Spectrometry*, 38(1), 2009, 58–67.
[2] Z. Brożek-Mucha, *Microscopy and Microanalysis*, 2011, 17(6), 972–982.
[3] Z. Brożek-Mucha, *Forensic Science International*, 2014, 237(1), 46–56.
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[5] J. K. Sadlik, Z. Brożek-Mucha, *Archive of Forensic Medicine and Criminology*, LIX, 2009, 41–47.
[6] J. Wąs-Gubała, Z. Brożek-Mucha, *Archive of Forensic Medicine and Criminology*, LIX, 2009, 48–56.

UNUSUAL OBJECTS IN ARCHAEOLOGY: GENUINE OR FAKE?

Sariel Shalev
School of Marine Sciences & Dept. of Archaeology, Univ. of Haifa, Israel
sariel.shalev@univ.haifa.ac.il

Over the last 150 years of data collection in the 'young' field of archaeology, unique objects, whenever they appear, tend to be treated in one of two extreme and opposing ways. Either they are presented with superlatives, such as 'the only one known' or 'the first one in history', which often gains them a place on the front pages of the (archaeological) news, where they are highly desirable and 'eaten up' by an enthusiastic public, or they are placed at the other extreme of 'normative' archaeological treatment of finds and become highly suspect, if not completely ignored, and typically accused of being fakes or forgeries. In this presentation, I will present some cases that occupy the two extreme limits of the 'normative' and the well-accepted distribution patterns of archaeological finds.

On the 'legitimate' end of the spectrum:

1. The case of the oldest metal object in the southern Levant: A corroded copper awl from the late 6th Millennium CalBC from Tel Tsaf, Israel [1], which received the prestigious title of being the first existing evidence of 'the beginning of metallurgy in the Southern Levant'…

2. The case of the earliest archaeometallurgical evidence of the production and utilisation of steel in the Holy Land: The story of an iron pick found in the excavations of D. Davis [2] of the Early Iron Age (12th Century BCE) site of Mt. Adir in Northern Israel and hailed by prominent and well-known archaeometallurgists [3] as the first 'living' evidence of the use of steel in history …

… and on the 'illegitimate' end of the spectrum:

The story of the Dead Sea Scroll book of Deuteronomy found by a Bedouin in a cave near the Dead Sea and presented in 1883 by Moses Wilhelm Shapira, a

well-known antique dealer from Jerusalem, to the British Museum. During the summer of the same year it was decisively and unequivocally declared by the famous French archaeologist Charles Clermont-Ganneau as an out-and-out fraud. An essential part of his argument was that it could not be older than the oldest mediaeval Hebrew Bible text known at that time. Soon afterwards, the identification of this scroll as a fake was widely accepted by the world's archaeological community and museum keepers. Shapira's story ends in March 1884, in a small cheap hotel in Rotterdam, where he committed suicide. Several years later, the allegedly faked scroll disappeared …

Epilogue: in 1947, more than 50 years later, a young Bedouin shepherd looking for a lost sheep found the famous Dead Sea Scrolls of the Second Temple period in a cave near Qumran, in the Judaean Desert ... and the rest is history!

References

[1] Garfinkel, Y., Klimscha, F., Shalev, S., & Rosenberg, D., 2014, The Beginning of Metallurgy in the Southern Levant: A Late 6th Millennium CalBC Copper Awl from Tel Tsaf, Israel. *PLOS ONE 9-3*.

[2] Maddin R., Muhly J.D., & Stech-Wheeler T., 1977. How the Iron Age Began. *Scientific American 237*: 128.

[3] Davis D., Maddin R., Muhly J.D., & Stech T., 1985. A Steel Pick from Mt. Adir in Palestine. *Journal of Near Eastern Studies 44-1*: 41-51.

ARTIFICIAL PATINAS: METHODS AND MOTIVES

Paul T. Craddock
The British Museum, London WC1B 3DG
paulcraddock74@btinternet.com

Artificial patinas: methods and motives

David Lowenthal [1] wrote 'Decay demonstrates and secures antiquity', and as such the patination of antiquities has always generated great interest and raised many questions. Most works of art were probably originally kept brightly polished, so how can something which 'secures antiquity' not be original? This lecture will first consider some of the methods by which convincing and not-so-convincing patinas have been produced. Secondly, the motives for applying an artificial patina will be considered. Many a genuine antiquity which very likely had no patina originally now has a patina very different from the one it had when first discovered. Such patinas were applied for a wide variety of reasons, such as restoration, corrosion treatments, and aesthetic considerations, or to make the fake look ancient as well as to make the genuine appear fake [2]. Thus authenticity examinations are conducted in order to determine not only 'is it genuine/is it fake?' but, as well, 'what is the life history of the object?'

References

[1] Lowenthal, D. (1985) *The Past is a Foreign Country*, Cambridge University Press, Cambridge.
[2] Craddock, P. T. (2009) *The Scientific Investigation of Copies, Fakes and Forgeries*, Butterworth-Heinemann, Oxford.

ADVANCED METHODOLOGY FOR QUANTITATIVE X-RAY MICRODIFFRACTION ANALYSIS AND ITS USE IN PROVENANCING CLAY-BASED PIGMENTS IN PAINTS

Petr Bezdička,[1] **David Hradil,**[1,2] **Janka Hradilová**[2]

[1]Institute of Inorganic Chemistry of the Czech Academy of Sciences, v.v.i, ALMA Laboratory, č.p. 1001, 250 68 Husinec-Řež, Czech Republic

[2]Academy of Fine Arts in Prague, ALMA Laboratory, U Akademie 4, 170 22 Praha 7, Czech Republic

email: petrb@iic.cas.cz

Lack of a suitable methodology is the main reason why individual clay minerals (as a significant part of earth pigments) are not being properly detected, regardless of their often significant content, in the colours and preparatory layers of paintings. None of the microspectroscopic or spectrochemical analytical methods frequently used in the field enables reliable differentiation of clay minerals, due to their variable chemical composition, structural similarities, and low Raman scattering. To identify them it is necessary to employ powder X-ray microdiffraction, the only microanalytical method that enables reliable differentiation of the structures of individual clay minerals in the colours and ground layers of paintings. However, it has not yet been satisfactorily tested for the correct and unambiguous discrimination of clay structures in paint layers or, eventually, for the reliable quantitative analysis of their relative contents. To overcome this lack of knowledge, several sets of laboratory experiments with model mixtures and reference samples imitating real paint layers have been performed and general rules for the proper discrimination of clay structures established. As an integral part of the research, clay-binder interactions were studied to avoid misleading interpretations. It was discovered that various characteristic shifts of basal diffraction lines depend on the type of organic binder and the relative content of expandable layers in the clay structure. The expandable clay structures of smectites and different types of interstratified structures with smectites are modified by interaction with organic binders in

the layer. The experiments showed that proteinaceous binders cause an increase in their basal spacing (relative to the content of smectite layers in the structure), while the presence of fatty compounds (in oils or egg yolk) results in a very slight decrease. In both cases, subsequent dehydration of the structure is prevented.

Apart from the common limitations of micro-pXRD (e.g. poorer resolution, insufficient size of the irradiated area etc.), the accuracy of quantitative microanalysis of clay minerals in mixtures with other minerals in earth pigments is characterised by total bias values in the range of 3–10 wt.%, whereas in the case of conventional Bragg-Brentano geometry, the total bias does not exceed 6 wt.%. However, a more critical issue seems to be the effect of heterogeneity of natural materials, which tends to be more pronounced in small irradiated volumes. In our study, the newly-determined accuracy of quantitative microanalysis was found to be sufficient for the differentiation of red earths from two historical sources in Bavaria and Bohemia, respectively, both in reference samples and in microsamples of Baroque grounds of paintings by e.g. the famous Czech painter Karel Škréta. Further, as a specific indicator of origin, randomly ordered illite-smectite interstratified structures were differentiated from pure smectites in painting grounds used by Baroque Venetian painters. These and other examples demonstrate the practical utility of this methodological approach for comparative studies of paintings focussing on the differentiation of their regional provenance.

APPLICATION OF COMPUTATIONAL TECHNIQUES AND MATERIAL ANALYSIS FOR THE AUTHENTICATION OF OUR CULTURAL HERITAGE

Manfred Schreiner
Institute of Science and Technology in Art, Academy of Fine Arts, Schillerplatz 3, A-1010 Vienna, Austria
Institute of Chemical Technology and Analytics, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria
m.schreiner@akbild.ac.at

In recent decades, a particular collaboration has been developed between historical, philological and cultural studies on one side and natural sciences on the other, while close co-operation between e.g. archaeology, art history, or conservation-restoration and physics, chemistry, or biology seems fairly well established. One reason for this is that art historians, conservators and archaeologists are constantly concerned with the questions of **WHERE**, **WHEN**, and by **WHOM** an object of art or archaeology was made. Increasingly, investigations of physical properties and material composition are used in addition to visual and stylistic analysis to link an object to a particular historic or prehistoric context, to determine the correctness or incorrectness of its claimed provenance, or to explore the technology used to manufacture an object. Thus these investigations are based on discovering when new materials, techniques, or technologies were introduced or others ceased to be used. However, the analysis of a great number of dated or precisely dateable artefacts is necessary, enabling us to set up a ***terminus post quem*** or a ***terminus ante quem*** for e.g. pigments used for paintings or metal alloys for coins, as well as for methods developed or even invented for the processing or fabrication of materials.

The second reason for this close cooperation, which might help to elucidate the authenticity of an artwork, concerns the present state of such objects. Scientists working in the field of art and cultural heritage are confronted more and more often with deterioration and hence the need for restoration

and preservation. As material degradation/corrosion under natural conditions differs in many cases from artificial ageing, the determination of corrosion products and processes can also be used for the identification of an authentic artwork.

In this presentation, a number of case studies will be discussed in which traditional photographic techniques, working in the visible, infrared, ultraviolet, and x-ray ranges, as well as multispectral imaging (MSI), in combination with digital image processing, were applied in order to visualise underdrawings in paintings and watermarks in graphic art objects, or to enhance the readability of palimpsests and damaged manuscripts. For material analysis, so-called non-destructive/non-invasive analytical techniques such as x-ray fluorescence (XRF), UV-Vis, infrared spectroscopy (FTIR), and Raman spectroscopy were employed for the identification of pigments in paintings and determination of the chemical composition of silver coins, glass, and ceramics. These investigations may contribute to proving the authenticity of these objects.

AUTHENTICATION OF PAINTINGS VIA NON-DESTRUCTIVE CHEMICAL MAPPING ANALYSIS

Koen Janssens
University of Antwerp
koen.janssens@uantwerpen.be

In this lecture, via a number of case studies, the use of macroscopic X-ray fluorescence (MA-XRF) analysis and related methods for objectively strengthening or weakening the link between a specific work of art and a (famous) painter will be discussed.

MA-XRF is a non-destructive method of element-specific imaging analysis based on the collection of element-specific X-ray fluorescence signals from many points on the surface of a work of art.

In addition to oil paintings, other types of artefacts such as illuminated manuscripts, stained glass windows, and ceramic tile tableaus are now being investigated as well. A number of case studies involving oil paintings attributed to the painters Peter Paul Rubens, Anthony van Dyck, Vincent van Gogh, and René Magritte will be discussed.

A COMBINED IMAGING AND SPECTROSCOPIC APPROACH TO FINE ART AUTHENTICATION

Barbara Łydżba-Kopczyńska[1, 2]

[1]National Museum in Krakow, Laboratory of Analysis and Non-Destructive Investigation of Heritage Objects, Piłsudskiego 14, 31-109 Krakow (Poland);

[2]Faculty of Chemistry, University of Wroclaw, Cultural Heritage Research Laboratory, F. Joliot-Curie 14, 50-383 Wroclaw, Poland

blydzba@mnk.pl

Over the last few years the fine arts market has generated more than a billion dollars in the US alone, but there are suggestions that many pieces of art being sold are of questionable authenticity. The number of fakes, forgeries, and copies that have appeared on the art market in Poland in recent years is growing significantly.

Traditionally, decisions about authenticity are based on the opinions of art experts or art historians. However, a true statement of authenticity should include at least three levels of analysis: the verification of the artistic style of work by an art expert, scientific analysis of the object using generally approved methods, and the confirmation of provenance, i.e. of the authenticity of documents supporting the piece's ownership [1]. Detection of forgery in paintings can be an extremely challenging task. Usually, an art expert has to analyse many different types of evidence before reaching a conclusion on the authenticity of a given painting. This evidence may include physicochemical analysis of the pigments, binding media, and substrate; studies of the process of the painting's creation; and tracing all documents that may be related to the painting (e.g. the artist's correspondence, confirmations of ownership). As a consequence, the expert may be overwhelmed with a huge volume of formless data from different sources which have to be combined to yield a result. In order to simplify and speed up the process of data analysis and decision-making by an art expert, a list of attribution markers has been proposed [1]. The use of machine learning

techniques (in particular decision trees) has been proposed to build a prototype of a scoring system which will automatically classify paintings according to the list of attribution markers and which will support the decision-making process [2].

In the Laboratory of Analysis and Non-Destructive Investigation of Heritage Objects (LANBOZ) at the National Museum in Krakow, several projects, devoted to analysis of the painting techniques of famous Polish painters such as Maksymilian Gierymski, Henryk Siemiradzki, and Olga Boznańska, have been carried out. Based on non-invasive physicochemical investigations, a database was created of the significant features which characterises the painting techniques of these masters. Moreover, in the laboratory, investigations have been carried out for private collectors and for court trials concerning paintings whose attributions had been questioned. The prototype for a scoring system is being tested on selected artworks by Gianfrancesco Penni, Tintoretto, Michael Willmann, Jeremias Knechtel, and Artur Grottger being investigated by the Cultural Heritage Research Laboratory at Wroclaw University and selected artworks analysed by LANBOZ at the National Museum in Krakow.

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AUTHENTICATION AND FORENSIC APPLICATIONS ON PANalytical X-RAY SYSTEMS

Stjepan Prugovečki, **Jan Gertenbach**
PANalytical B.V, Twentepoort Oost 26, 7609 RG Almelo, the Netherlands
Stjepan.Prugovecki@panalytical.com

As non-destructive analytical techniques, both powder X-ray diffraction (XRD) and X-ray fluorescence (XRF) are well suited for fast and reliable checks of the authenticity of various materials and products. As the only technique that reveals the structural 'fingerprint' of a crystalline material, XRD can be used for forensic investigations ranging from the identification of soil and paint to that of complex 'street' drugs and counterfeit pharmaceutical products. The sensitivity and speed of modern XRF spectrometers enables the fast qualitative and quantitative elemental analysis of almost any type of material and is ideal for the first screening of investigated subject.

The results and experimental optimisation will be discussed for the following examples:
–analysis and screening of several counterfeit medicines;
–analysis and screening of controlled drug substances and formulations;
–screening of cosmetic and food products.

6th Meeting
X-ray and other techniques in investigations of the objects of cultural heritage

HIGH-END PIXEL DETECTORS FOR FINE ART INVESTIGATION: HIGH-PERFORMANCE X-RAY RADIOGRAPHY, X-RAY FLUORESCENCE IMAGING, X-RAY MICRODIFFRACTION

David Hradil,[1,2] **Janka Hradilová,**[2] **Jan Žemlička,**[3] **Petr Bezdička**[1]

[1]Institute of Inorganic Chemistry of the Czech Academy of Sciences, v.v.i, ALMA Laboratory, č.p. 1001, 250 68 Husinec-Řež, Czech Republic

[2]Academy of Fine Arts in Prague, ALMA Laboratory, U Akademie 4, 170 22 Praha 7, Czech Republic

[3] Institute of Experimental and Applied Physics, Czech Technical University in Prague, Horská 3a/22, 128 00 Praha 2, Czech Republic

email: hradil@iic.cas.cz

In the ALMA laboratory, pixel detectors are used for several distinct applications, all intended to improve the methodology of the non-invasive and non-destructive investigation of fine art, particularly paintings. In the first place must be mentioned current developments in the field of imaging technology conducted in cooperation with the Institute of Experimental and Applied Physics at Czech Technical University in Prague (a member of the international Medipix consortium). Newly-developed devices for X-ray transmission/emission radiography (XRR), equipped with the latest generation of detectors of the Medipix/Timepix family, exhibit advantageous properties such as unlimited dynamic range, absence of integration and readout noise, high spatial resolution, and energy sensitivity, enabling material-sensitive X-ray radiography as well as X-ray fluorescence (XRF) imaging. The system's second important advantage is its portability for *in situ* measurements. High spatial resolution at the level of micrometres enables the acquisition of microradiographic images and the display of surprising details within the framework of a restorer's survey of a painting. X-ray fluorescence detection, on the other hand, does not achieve such high energy resolution as the application of analytical SDD detectors. However, its practical utility is mainly shown by its provision of X-ray fluorescence maps with no need for scanning.

Within cultural heritage research, one of the trendy topics of recent decades is the collection of combined visual and analytical information with the same device, on either a macro- or microscale. The alternative use of gallium arsenide instead of silicon-based sensors for pixel detectors has enabled, for example, the development of a hybrid device (now commercially available) for X-ray microdiffraction and computer tomography (micro-XRD/CT). Despite the higher detection efficiency of GaAs sensors, their use for other applications is limited by their poor spectroscopic properties, stability, and homogeneity of response. The powder X-ray microdiffraction device in the ALMA laboratory is equipped with the position-sensitive detector X'Celerator (PANalytical), a very fast detector based on RTMS (Real Time Multiple Strip) technology, which offers the direct detection of diffracted X-ray photons and can efficiently process input signals with no decrease in resolution quality. These advantages enable savings in measuring time, a crucial factor in all microdiffraction experiments. We have already used the method for the fast distinction of different structural types of pigments in actual paintings (e.g. lead-based yellows, copper- and clay-based pigments), which has proved very useful for determining their origin, the technology of their manufacture, or the process of their formation in nature. Furthermore, the detection of minor phases in microsamples (e.g. the rare pigment vivianite or technological or corrosion by-products) is achieved within a reasonable time frame.

NON-INVASIVE DOCUMENTATION AND MATERIAL ANALYSIS USING X-RAY FLUORESCENCE, INFRARED AND RAMAN SPECTROSCOPY

M. Schreiner,[1,2] F. Cappa,[1] B. Frühmann,[1] W. Vetter,[1] M. de Bardi[1,2]

[1] Institute of Science and Technology in Art, Academy of Fine Arts, Schillerplatz 3, A-1010 Vienna, Austria

[2]Institute of Chemical Technology and Analytics, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria

m.schreiner@akbild.ac.at

Since the very beginnings of the investigation, preservation, and conservation-restoration of our cultural heritage, the documentation of artworks by applying photographic techniques in the visible, infrared, ultraviolet, and x-ray ranges of the electromagnetic spectrum and the determination of their chemical composition have played an important role in studying the styles, ancient production, art technology, and materials used for works of art and archaeology and in understanding degradation processes and developing and evaluating new materials for intervention. The booming development of computer techniques and electronics over the past decades has brought new methods and instruments of great perfection to digital imaging as well as to analytical chemistry, thus opening new horizons not only in material identification but also in the fields of origin or authenticity, technical construction, and preservation. Parallel to the development of instruments, the requirements for material analysis have also changed completely, as nowadays so-called non-destructive or non-invasive methods are preferred, which means that no original sample material can be taken from an object. In many cases the analytical procedure has to be carried out *in situ* in order to avoid climatic changes and high insurance costs due to the transportation of an object to the laboratory.

In the field of photographic documentation, developments such as multispectral imaging (MSI) enable improvements in the readability of palimpsests and damaged manuscripts. Furthermore, certain automated

investigations of the codicology and palaeography of manuscripts such as layout, line structure, or identification of scribes can be carried out.

Among the great variety of instrumental techniques which have been applied to the study of the elemental composition of objects of art and archaeology, x-ray fluorescence analysis (XRF) has attracted growing interest. Its greatest advantage is that, in principle, all elements (except H and He) of the periodic table can be detected. Furthermore, hand-held instruments which can be brought into collections or to an archaeological site are now available on the market. For compound specific analysis, which is indispensable for the identification of the inorganic and organic constituents in artworks, infrared and Raman spectrometry have been employed widely and are in principle also applicable in a non-destructive way.
In this presentation, a short description of the principles of MSI and the associated analytical techniques is given and case studies are discussed, including documentation of damaged manuscripts and palimpsests and identifications of pigments and inks. Furthermore, studies concerning weathering/corrosion occurring on metal and glass surfaces and the effect of sol-gel coatings on such objects are presented. Such coatings protect e.g. glass from further degradation due to serious damage caused by the ambient atmosphere.

PRECIPITATION AND MICROCHEMICAL CHARACTERISATION OF CdS YELLOW AND ORANGE PIGMENTS

Silvia Pedetti, **Matthias Alfeld, Philippe Walter**
LAMS, Laboratoire d'Archeologie Moléculaire et Structurale, UMR 8220, Université Pierre et Marie Curie, UPMC, 5 place Jussieu, 75005 Paris, France
silvia.pedetti@upmc.fr

Following the introduction of the pigment cadmium yellow to artists' palettes around 1840, its use became widely diffused among the most important painters of Impressionism such as Monet, van Gogh and Matisse.[1] The importance of Cd-based pigments relies on several of their physicochemical properties such as a strong absorption coefficient, strong masking power due to their fine-sized particles, and high refractive index. The phenomena of darkening and lightening photodegradation on surfaces containing cadmium yellow paints has been observed on artworks, and a photo-oxidation mechanism has been proposed.[2] Recently the photoluminescence of Cd pigments has attracted much interest, since deep trap emission and band edge emission can be observed and spectroscopic non-invasive techniques can be used for the identification of the pigment.[3]

Considering their colorimetric properties, Cd-based pigments can exhibit several hues ranging from pale yellow to red nuances when they contain selenide. In the present work we investigated the synthesis of cadmium sulphide pigments prepared through precipitation from an aqueous solution of cadmium salts and sulphide precursors. CdS is a II-VI semiconductor material existing in two different crystal structures, hexagonal (α-CdS) and cubic (β-CdS). Unlike HgS, whose colouration depends on its crystal phase (red mineral cinnabar α-HgS or black β-HgS), cadmium sulphide can be synthesised as yellow or orange in both crystal phases.[4]

We focussed on organic sulphide precursors such as thiourea and potassium xanthogenate, on sulphide salts such as sodium sulphide and sodium

hydrosulphide, and finally on H_2S gas, mainly used for the earliest preparation of the pigment in the 19th century. Different experimental conditions, such as the concentration of precursors, reaction temperature, and sulphide precursor addition procedure, were investigated. As-synthesised powders were characterised by means of X-ray diffraction, X-ray fluorescence, infrared spectroscopy, and scanning electron microscopy, while colorimetric characterisation of samples was conducted using diffuse reflectance spectroscopy. Our study helps to determine more precisely the relation between the microstructure of CdS samples and their optical properties and to highlight how synthetic conditions may modify the microstructure of the pigment. We compared our results using historical CdS pigments produced by Winsor and Newton at the beginning of the 20th century.

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IN SITU NON-INVASIVE XRF RESEARCH OF THE EVOLUTION OF THE USE OF PIGMENTS BY POLISH PAINTERS IN THE PERIOD 1800–1900

Mirosław Wachowiak[1], **Grzegorz Trykowski**[2]
[1] Dept. of Conservation and Restoration of Modern Art, N. Copernicus University, Torun, Poland
[2]Faculty of Chemistry, Nicolaus Copernicus University, Torun, Poland
miroszwach@wp.pl

More than 100 certainly-dated objects of various Polish artists from the period 1800–1900 were investigated using a portable XRF spectrometer. The research included works by Józef Szermentowski, Jan Matejko, Wojciech Gerson, Wojciech Weiss, Leon Wyczółkowski and others. Where sampling was possible, complementary research using Raman spectroscopy, SEM-EDX, and XRD was conducted.

The research determined the actual dates of the first appearance in paintings of individual pigments, often significantly shifted in time in comparison to the dates of their invention or implementation of their mass production. Where more paintings by one painter were investigated, some changes were discovered during an individual artist's lifespan; for example, in the case of Wyczółkowski, lead white was replaced by zinc white and chrome yellows by cadmium yellows. Some pigments appeared to be typical for a certain painter, as, for example, Naples yellows containing zinc white as an admixture in five different hues of this pigment found in Matejko's paintings. Tadeusz Pruszkowski preferred synthetic copper blue verditer, as opposed to other painters who mostly used cobalt blue and artificial ultramarine. Rarely-used pigments, such as cobalt violet, found only in some works by Weiss and Jacek Malczewski at the end of the 19th century, and manganese violet in paintings by Wyczółkowski, present different approaches, more open or more conservative, by various artists to the new pigments appearing on the market. A significant number of paintings showed the possibility of

preliminary characterisation of organic-dye-based paints through the identification of their substrates and fillers and through the dates of the early implementation of the Sn-based carrier in red dyes.

The volume and complexity of information expanded our knowledge of studio practice in the second half of the 19th century and enabled the creation of a database for more reliable comparative studies concerning pigments typical of individual painters, the actual date of their manufacture, and their popularity among Polish painters in subsequent periods. These were helpful in certain case studies assessing authenticity, showing possibilities and limits, and establishing the actual times of turning points in the evolution of use of certain pigments by individual painters, enabling the proposal of a wider 'technological panorama' of the 19th century and creating comparative background data for further studies of Polish and European paintings from this period.

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MICRO-XRPD, XRPD TOMOGRAPHY, AND MA-XRPD: 3 METHODS TO BETTER UNDERSTAND STRUCTURAL CHANGES IN CULTURAL HERITAGE MATERIALS

Koen Janssens
University of Antwerp
koen.janssens@uantwerpen.be

In this presentation, the use of three different forms of imaging/scanning X-ray powder diffraction (XRPD) for the characterisation of cultural heritage materials will be discussed.

The first two, 'regular' two-dimensional micro-XRPD and XRPD microtomography, involve the use of (sub)microscopic beams of synchrotron radiation and can be used to visualise the crystal phase composition of complex, multi-layered paint microsamples. The latter usually become available during restoration projects involving historical paintings. Their analysis can reveal relevant information about the original materials employed by the artist, as well as about the spontaneous chemical alteration of these materials since the work's creation. Examples involving paintings by the 15th-century painter Hans Memling and the 19th-century painter Vincent van Gogh will be discussed.

Macroscopic XRPD (MA-XRPD) is a variant of macroscopic X-ray fluorescence (MA-XRD) mapping that enables visualisation, in a highly specific manner, of the distribution of pigments in or below the surface of paintings. In this manner new types of information can be obtained about the use of pigments by specific painters. In selected cases, the secondary products formed during spontaneous alteration of painters' pigments can also be mapped. Examples involving paintings from the circle of Velasquez, de Heem, and van Gogh will be presented.

MACRO X-RAY FLUORESCENCE IMAGING FOR ANTIQUE POLYCHROMY

Matthias Alfeld,[1] Maud Mulliez,[1] Philippe Jockey,[1,2] Philippe Walter[1]
[1]Sorbonne Universités, UPMC Univ Paris 06, CNRS, UMR 8220, Laboratoire d'Archéologie Moléculaire et Structurale (LAMS), 4 place Jussieu, 75005 Paris, France,
[2]Aix-Marseille Université, Centre Camille Jullian, 5 rue du Château de l'Horloge, BP 647,13094 Aix-en-Provence, France
matthias.alfeld@upmc.fr

Today, the rich polychromy on statues and buildings of the ancient Greeks has mostly disappeared. Nonetheless, minute traces of pigments and a few well-preserved objects provide an insight into this lost world of colour.

These traces of pigments are commonly found with microscopic methods employing visible light and the neighbouring wavelengths, infrared and ultraviolet. Subsequently the traces are studied by spot analysis with X-ray fluorescence analysis (XRF) and UV/VIS spectroscopy [1]. This approach is limited to the remnants of pigments on the surface of the marble which are not covered by encrustations; it is oblivious to faint traces of pigments left in rough areas on stone surfaces.

XRF imaging, in which the surface of a sample is scanned with a focussed X-ray beam to obtain elemental distribution images, has been established in recent years for the investigation of large areas (several hundred to one thousand square centimetres) of historical paintings [2]. It has enabled new insights into a number of historical paintings, providing information on sketches, pigment use, and the artistic composition of overpainted works.

We used our self-built mobile XRF scanner in the investigation of the polychromy of the frieze of the Siphnian Treasury in the Delphi Archaeological Museum (Delphi, Greece). This frieze from the archaic period, dedicated to Apollo in 525 BC, was excavated by the French School of Archaeology in Athens (Ecole Française d'Athènes) in 1894 [3]. Since then, it has been subjected to thorough investigation [4]. Nevertheless, XRF imaging enabled

the revelation of new information by identifying, among others, the largest area of original Cu, containing pigments present on the frieze but hidden under encrustations, enabling the reconstruction of the polychromy of a crucial feature of the frieze. Furthermore, several traces of pigment, previously unknown and faded to a degree undiscernible by microscopic investigation, were identified.

In addition to illustrating the value of the method using the results from the Siphnian Treasury, we will provide an outlook on how modern scientific methods can support the understanding of antique polychromy.

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DEVELOPMENTAL PROGRESS OF THE MACRO-XRF SCANNER FOR THE INVESTIGATION OF HISTORICAL OBJECTS

B. Mindur,[1] T. Fiutowski,[1] P. Frączek,[2] S. Koperny,[1] M. Lankosz,[1] A. Mendys,[2] A. Sikorska,[1] K. Świentek,[1] P. Wiącek,[1] P. M. Wróbel,[1] W. Dąbrowski[1]

[1]AGH University of Science and Technology, Krakow, Poland

[2]The National Museum in Krakow, Krakow, Poland

bartosz.mindur@agh.edu.pl

The principle of operation of the X-ray fluorescence imaging system of cultural heritage painting has been confirmed and presented previously. The pilot experimental setup, equipped with a large area (10×10cm^2) Gas Electron Multiplier (GEM) detector combined with dedicated readout electronics, a pinhole camera, and a wide-field X-ray beam is fully operational and provides satisfactory results. The technique is suitable for rapid imaging of the paintings and other objects, including small 3D objects. Key features of the system include the safety of the investigated objects, infinite depth of field, and the capacity for recording images with variable magnification and adjustable spatial resolution (affording a balance between measurement time and accuracy of obtained images).

The experimental setup is now undergoing significant refurbishment in order to make it suitable not only for laboratory measurements but also for operation within the museum. The present series of construction and design changes involves practically all of its components. The optimisation process involves further improvement in the performance of the GEM detector (especially to obtain improved energy resolution), pinhole camera parameterisation (size and magnification), front-end electronics enhancement (better signal-to-noise ratio and dynamic range), and, finally, irradiation X-ray source types and handling geometries (to obtain more intensive and uniform illumination of the investigated object).

In this paper the design and performance of the existing pilot experimental system will be compared to that expected using the new or modified

components. Various aspects of how to make the system much more comprehensive and suitable, not only for laboratory measurements but also for the investigation of actual historical objects, will be discussed.

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COMPARISON OF PIXE AND XRF IN THE ANALYSIS OF SILVER DENARII OF THE EARLY PIASTS

Janusz Lekki,[1] Marta Matosz,[2] Czesława Paluszkiewicz,[1]
Julio M. del Hoyo-Meléndez[2]

[1] Institute of Nuclear Physics, Polish Academy of Sciences, Radzikowskiego 152, 31-342 Krakow, Poland

[2] Laboratory of Analysis and Non-Destructive Investigation of Heritage Objects, National Museum, Piłsudskiego 14, 31-109 Krakow, Poland
Janusz.Lekki@ifj.edu.pl

The rule of Mieszko I and his son Bolesław Chrobry was characterised by the creation of a modern state through the unification of Polish tribes, political influence on the European level, and the development of trade. The scarcity of coins from this time period is remarkable, as there are only about two hundred items currently above ground. The major elements detected in these coins are Ag and Cu, while minor elements such as Pb, Fe, Au, Bi, and Zn may also be present. Twenty-three of these coins were studied using micro-X-ray fluorescence (XRF) spectrometry and particle-induced X-ray emission (PIXE) spectroscopy, with the aim of determining their elemental composition and conducting a cross comparison of the results obtained with both techniques. Evaluation of the results generally shows a slightly higher Ag content determined by PIXE relative to XRF, in the range 90–97% Ag. This preliminary assessment of the data suggests that the majority of the analysed coins are characterised by Ag surface enrichment, a common process observed in archaeological silver-copper alloys. This finding is plausible when one considers the lesser penetration depth of the protons used in the PIXE analysis relative to that of the primary X-rays generated by the Rh tube used in the XRF examination. Although the data obtained from both techniques offer information about the composition of the base alloy, it is important to consider that deposition of corrosion products on the surface of the coins may also account for the observed variations due to the use of different

microsampling locations with each of the two instruments. The two evaluated techniques offer a promising tool for numismatic studies, since they provide a way to conduct non-destructive quantitative analysis of the silver-copper alloys used in historical coinage.

OPTMIZATION OF POWDER DIFFRACTOMETER CONFIGURATION TO ACHIEVE THE BEST POSSIBLE RESULTS

Stjepan Prugovečki, **Jan Gertenbach**
PANalytical B.V, Twentepoort Oost 26, 7609 RG Almelo, The Netherlands
Stjepan.Prugovecki@panalytical.com

Modern powder diffractometers are in fact multipurpose experimental platforms, equipped with a variety of optical modules and detectors. The PANalytical Empyrean is truly an open and modular platform, enabling virtually any type of application on any type of sample, with no compromise on analytical results for a particular experiment. The recent addition of a Bragg-Brentano^{HD} incident beam optical module and a GaliPIX 2D detector has further expanded the range of applications.

The Bragg-Brentano^{HD} module significantly improves the peak/background ratio and thus system sensitivity in classical Bragg-Brentano mode, but can also be used for identification of thin layers and SAXS experiments. Examples of measurements and comparisons with classical optical setups will be shown. The GaliPIX detector is the first 2D detector with CdTe sensor material, enabling very high detector efficiency for a wide range of energies, especially for 'hard' radiation such as MoKα and AgKα. Using 'harder' radiation for diffraction experiments enables deeper penetration into the sample, eliminates sample fluorescence, and reduces the required 2θ scanning range. The high efficiency, combined with a very small pixel size, enables diffraction and imaging experiments that were almost impossible on a laboratory diffractometer. Examples of diffraction and imaging experiments and comparisons with other detectors and setups will be shown.

‘ZOOMING-IN’ WITH COMPOSITIONAL XRF ANALYSIS: IS THERE A LIMIT? THE CASE OF MIDDLE BRONZE AGE DAGGERS IN THE LEVANT

Sariel Shalev
School of Marine Sciences & Dept. of Archaeology, Univ. of Haifa, Israel
sariel.shalev@univ.haifa.ac.il

Hundreds of copper-based objects dated to the Middle Bronze Age II (MB II; ca 2000–1500 BCE) have been unearthed all over the Levant, most of them in burials. In this period, the development of more complex weapons (decorated daggers, swords, complex battle axes, etc.) was made possible by alloying copper either with arsenic (As) or tin (Sn), to produce, respectively, arsenical copper and tin-bronze [1].

Owing to the archaeometallurgical history of the region, in which arsenical (As) copper preceded the appearance of alloys with tin (Sn) and, often, lead (Pb), it is usually assumed that the MB copper-based objects alloyed with arsenic are probably ‘older’ than similar objects which are perceived as part of a ‘newly-arrived fashion’.

A recent synthetic summary of the state of research dealing with MBII metallurgy [2], based upon all available analyses of weaponry, showed that all possible alloys could be found region-wide; over time and in identical objects, extreme quantitative variability is apparent.

In order to move forward and try to better understand the possible causes for such great variability in the quantities of the major elements detected in different objects of the same type and identical shape, a new group of 68 MBII daggers from all major types were submitted for XRF surface analysis. All of the analysed daggers derive from a single vast MBII cemetery, excavated by Y. Levi of the Israel Antiquities Authority, in Rishon Lezion (RL), south of Tel Aviv on the Mediterranean coast of Israel, and the only way to analyse them all was to use an on-site, non-destructive, hand-held ED-XRF.

To this end, systematic ED-XRF compositional analyses were conducted, in an effort to optimise the method’s advantages thanks to the total non-destructive, easy, and quick operation of the analyser: namely, the ease of

producing quantities of on-site, and therefore more representative and statistically valid, results. At the same time, this approach sought to minimise the well-known disadvantages of the method due to the corrosion effect on surface-only measurements, consisting mainly of changes in absolute quantities and ratios of major elements and loss or amplification in both cases, leading to results, which do not represent the original states or quantities of minor elements.

These 'simple', ample, on-site and non-destructive 'crude' ED-XRF surface analyses enable us, for the first time, to obtain the optimal available statistical representation for the exploration of a possible correlation between the metal compositions of the different major types. Thus, a better understanding of the production method and available alloys of the metal industry in the southern Levantine Middle Bronze Age was achieved.

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EXPERIMENTAL EVIDENCE OF THE RECIPES OF VITRUVIUS AND PLINY: THE ART OF MORTARS

Gilberto Artioli
Università di Padova
gilberto.artioli@unipd.it

Roman mortars and concrete binders rightly acquired, even in antiquity, the reputation of being durable materials with optimised technical properties. In time they became standard examples of ancient technical abilities and assumed the status of 'reference' binders before the advent of modern Portland cement. It proves a very interesting exercise to compare the results obtained by the experimental characterisation of Roman mortars and binders according to the 'standard' recipes described by ancient literary sources [1–2]. Examples are shown of binder materials used in different architectural components, such as floors, mosaics, cisterns, plasters, etc., from the Republican to Imperial ages.



Fig. 1 Examples of Roman age binders. Left: part of a Roman tower incorporated in the Torba Monastery (Varese). Right: the 'Casa del Bicentenario', Herculaneum (Napoli).

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X-RAY MAPPING OF HIDDEN WALL PAINTINGS: A FEASIBILITY STUDY

Piotr Targowski,[1] Ermanno A. Clerici,[2] Liesbeth Dingemans,[3] Jędrzej Musiela,[4] Robert Rogal[5]

[1]Institute of Physics, Nicolaus Copernicus University, [2]University of Bologna, [3]Technical University of Delft, [4]Restauro Sp. z o.o., [5]Institute for the Study, Restoration and Conservation of Cultural Heritage, Nicolaus Copernicus University

ptarg@fizyka.umk.pl

It is quite common for wall paintings in historical buildings to be hidden behind layers of limewash or plaster. It would be desirable to detect their presence and evaluate their state of preservation in a non-invasive way, without conducting traditional uncovering trials by means of a scalpel. Given the penetration of X-rays through many materials, X-ray induced fluorescence could, in principle, be used for this purpose. The major limitation is imposed by the absorption of emitted X-ray fluorescence by covering layers. This effect is especially pronounced for emission from light elements such as iron (Kα: 6.4 keV). The aim of this preliminary study was to assess the applicability of available XRF instruments to this task, especially in the context of fluorescence mapping.

To accomplish this, two instruments were used: a portable Tracer III-SD and a transportable M6 JetStream [2], both manufactured by Bruker GmbH. The former is a point-wise hand-held instrument used in this case to manually collect data from a grid of spots; the latter is designed especially for automatically collecting data from large areas to provide maps of distribution of elements with sub-millimetre resolution.

The test were performed on mock-ups prepared at ISRCCH NCU which, after reference scanning with the M6, were covered with limewash layers of various thickness and scanned again with the same instrument as well as on-site in the medieval courtroom of The Old City Hall in Torun, Poland (at present: The District Museum). According to historic records [1], one of the

walls has remained in its original condition since the end of the 14th century, though it is at present covered with layers of limewash and white paint. On this wall, no uncovering trials were performed, but those performed on other, less interesting walls may suggest some paint layers below the limewash.

The experiment with the Tracer was performed on a grid of 224 points placed every 10 cm (150 × 130 cm^2) with an acquisition time of 29 s/point; the experiment with the M6 covered an area of 75 × 90 cm^2 with 0.65 mm resolution and an acquisition time of 30 ms/point. Both approaches have shown general consistency, but a 10 × 10 cm^2 grid seems insufficient. In the report, detailed results will be given and the advantages and disadvantages of both approaches will be discussed in detail.

Acknowledgement
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KNOWN UNKNOWN: X-RAY INVESTIGATIONS OF SELECTED COPPER COINS FROM MOUNT GROMNIK, SW POLAND

Beata Miazga, **Paweł Milejski**
Institute of Archaeology, University of Wroclaw
beata.miazga@uwr.edu.pl, pawel.milejski@uwr.edu.pl

Archaeological research on Mount Gromnik was started in 2005 and is being continued by Professor Krzysztof Jaworski and his interdisciplinary team, including archaeologists, art historians, architects, chemists, physicists, and archaeozoologists [1]. The most interesting and characteristic object at the site is a building in the form of a rotunda with two apses. After a decade of investigations, several thousands of artefacts have been found. The older finds, flint tools, are dated back to the Neolithic and constitute strong evidence of human activities on the mountain. The site also yielded objects from other periods, e.g. fragments of Lusatian culture pottery. The largest group of artefacts are medieval finds from the 9th century and later (especially from the 15th century, connected with the ruins of the rotunda).

Among medieval artefacts excavated from the Gromnik site is a group of coins, of which the copper coins are especially interesting. Some of them have been identified as imitations of the Polish silver pennies of Vladislaus III of Varna. Other specimens, especially hellers of the municipality of Legnica or Jagiellonian pennies, were made from interesting raw materials atypical for such coins. The presence of the copper coins initiated a discussion of their provenance and even of the possible presence of a forger's workshop on Mount Gromnik. This question is still unanswered.

The numismatic investigations are supported by X-ray investigations (X-ray fluorescence and diffractions). XRF is the main tool which could be very helpful in solving this problem. At the same time, we should consider the limitations of the analytical process for archaeological finds, which are often in need of conservation and/or badly preserved. Corrosion layers and patinas render investigations using analytical methods which penetrate the surface of

the objects difficult. Therefore, when planning and carrying out the investigations, the most significant factor is the appropriate preparation of each archaeological coin.

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THE MAJOR EGYPTIAN BRONZE STATUARY OF THE THIRD INTERMEDIATE PERIOD: CASTING AND DECORATION

Paul T. Craddock
The British Museum, London WC1B 3DG
paulcraddock74@btinternet.com

The Third Intermediate Period saw many technical innovations through the first half of the first millennium BC. Not least of these were major developments in bronze technology. Examination of some of the large hollow bronze statues in the collections of the British Museum has established that they were cast by both the direct and indirect lost wax processes. This, the earliest evidence of the indirect process, was almost certainly ancestral to the bronze casting technology of the Archaic Greeks.

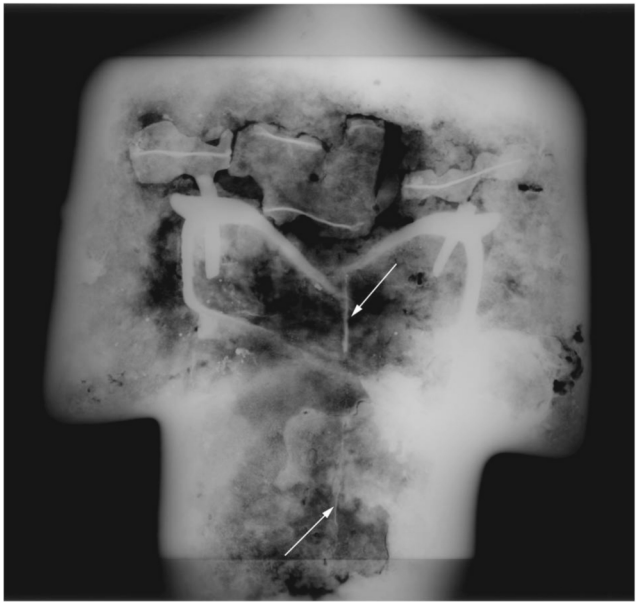


Fig. 1 Radiograph of major hollow bronze figure of Osiris in the British Museum reveals (arrowed) straight lines of thickening where wax-to-wax joins were made assembling the wax sections taken by the indirect method of bronze casting.

Discovering its original appearance can be difficult, as Egyptian statuary is sometimes found in an extremely corroded condition, but the pieces were certainly often heavily gilded and incorporated a variety of polychrome decorative techniques including deliberate patination. Establishing whether the present minerals derive from original deliberate patination, corrosion products resulting from long burial, or post-excavation 'restoration' treatments is not easy. Detailed examination, especially using XRD and XRF, has helped to resolve some of these issues, though some questions remain unresolved.

X-RAY-BASED IMAGING AND SPECTROSCOPY OF PAINTINGS BY OLGA BOZNAŃSKA

Anna Klisińska-Kopacz, Piotr Frączek, Michał Obarzanowski, Janusz Czop
National Museum in Krakow, al. 3 Maja 1, 30-062 Krakow
aklisinska@mnk.pl

The scientific examination and comparative investigation of pigments is fundamental to the further understanding and analysis of historic and artistic works, and particularly useful for conservators. In fine art authentication, investigations focus strongly on identification of the painting materials used by the artist. This study focusses on the use of non-invasive analytical techniques to enhance our knowledge of the painting technique of Olga Boznańska and for the further comparative analysis of objects attributed to the painter with works of questionable attribution.



Fig. 1 Olga Boznańska's palette and Kwiaciarki*, from the collection of the National Museum in Krakow.*

Olga Boznańska (1865–1940), considered one of the greatest European female artists, showed her paintings at prestigious exhibitions, salons, and renowned art galleries [1]. In 1904 she joined the Société Nationale des Beaux Arts in Paris. Boznańska's art was greatly influenced by the refined paintings of James McNeill Whistler and the free painting style of Edouard Manet, both of whom combined realism with impressionism. During her

Munich period she defined the range of her palette, narrowing it down to dark colours dominated by browns, greens, greys, and black, with white and pink serving as counterpoints.

The aim of this study was to assess the technology, painting technique and materials used by Olga Boznańska. Pallets, tubes of paint, and several oil paintings were studied. For each painting, a series of images were recorded using various ranges of electromagnetic radiation including near-infrared, visible light, ultraviolet, and X-rays. In order to characterise the pigments present in the paint layer, measurements of their elemental composition were carried out using X-ray fluorescence spectroscopy (XRF). This enabled the identification of the artist's painting technique and the discovery of how she executed her paintings, how she applied paint, and which pigments she used. It turned out that paintings which had seemed to be limited to shades of silvery greys were in fact painted with rainbow-coloured paints which the artist mixed on her palette while working on the painting and applied onto the substrate with gentle brushstrokes.

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NON-DESTRUCTIVE ANALYSIS OF CANVAS PAINTINGS IN THE ARCHBISHOP'S PALACE OF SEVILLE

Anabelle Kriznar,[1,3] Kilian Laclavetine,[1,2] Ana Isabel Gamero González,[4] Miguel Ángel Respaldiza[1,2]

[1]Centro Nacional de Aceleradores (CNA), University of Seville (US), [2]Department of Atomic, Molecular and Nuclear Physics, Faculty of Physics, (US), [3]Department of Sculpture and Art History, Faculty of Fine Arts (US), [4]Archdiocese of Seville, Archbishop's Palace, Seville, Spain

akriznar@us.es

The Archbishop's Palace holds one of the richest art collections of Seville, composed of nearly 300 paintings [1]. Several of these artworks require urgent restorative intervention, as recently supported by analytical research on the materials applied and the damage sustained. Among the first artworks selected for this interdisciplinary approach were two paintings on canvas by two of Seville's most important painters of the 17th and 18th centuries: *The Presentation of the Virgin* (1680–90) by Matías de Arteaga, and *Christ Crucified* (1778–81) by Juan de Espinal.



Fig. 1. In situ XRF analysis of *Christ Crucified* by Juan de Espinal

The principal objectives of the analysis were to obtain information on the painting and preparation materials used and to discern later interventions to the original parts in order to assist the restoration process. For both works the same procedure was selected in which only non-destructive techniques

were used [1]. First, general and detailed images were taken in visible and UV light before and after the cleaning of the surface, in order to observe the condition of the paintings. Then, infrared reflectography (IRR) was used to discover possible underdrawings. As the last step, X-ray fluorescence (XRF) was applied to identify the pigments and preparation used.

UV images discovered wide areas of later interventions, the number and size of which decreased significantly after the surface had been cleaned. The IRR images highlighted certain other interventions, not visible under the UV light, and showed several *pentimenti*. The results obtained by XRF revealed that both painters used a calcium-based preparation (identified by Ca peaks), probably gypsum, which was typical of Spanish painting of the time. Arteaga also added some ochre (Fe) to obtain a darker preparation suitable for faster colour modelling. The pigments applied were characteristic of the 17th and 18th centuries, and both painters applied the same pigments, with the exception that Arteaga's palette was wider due to the more colourful *Visitation*. The results were helpful at the last step of the reintegration of the painting layers. *Christ Crucified* represented a special restoration challenge, because it was necessary to recreate Christ's hands, a task carried out magnificently by the restorer. Further interventions and non-destructive analyses of paintings in the Archbishop's Palace are being scheduled in the near future.

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AN ANALYTICAL PROTOCOL FOR THE ISOLATION AND IDENTIFICATION OF NATURAL ORGANIC DYESTUFFS PRESENT IN HISTORICAL ARTISTIC PAINTS

Olga Otłowska, **Magdalena Śliwka-Kaszyńska**
Dept. of Organic Chemistry, Gdansk University of Technology, Narutowicza 11/12, Gdansk, Poland
olgotlow@student.pg.gda.pl

Organic dyestuffs are natural components of many objects of cultural heritage. The identification of colouring substances present in historical artistic paints provides relevant information for a wide range of specialists dealing with works of art and in the field of conservation science. Analysis of natural dyes in historical objects is fundamental to the development of effective and appropriate conservation strategies, as well as to determine the origin of a given artefact and to obtain historical information necessary to document a given artwork and its authenticity.

Hyphenated techniques (high-performance separation techniques coupled with extremely sensitive and selective spectrometric detectors) seem to be the most efficient tools for the analysis of very small samples of materials characterised by complex matrices [1]. Among them, reversed phase liquid chromatography with electrospray mass spectrometric detection offers solutions for difficult problems encountered in the analysis of real samples of unknown composition where there is a lack of proper standards.

The sample preparation procedure is apparently of great importance, as it can have crucial effects on the analytical results obtained by HPLC [2]. Most natural dyestuffs are of the mordant type in lake form obtained by co-precipitation with an inorganic substrate, in which the dyes are chemically bound by chelate bonds which are difficult to dissociate.

The aim of the research project is the identification of organic colouring substances of natural origin which are components of artists' paints used in

the second half of the 19th century by the most famous Polish painters (Jan Matejko, Leon Wyczółkowski, and Jacek Malczewski). This paper presents an analytical protocol for the identification of natural organic dyes using liquid chromatography-mass spectrometry with atmospheric pressure electrospray ionisation, which was successfully applied to identification of the main components of the historical red, yellow, and blue lakes.

The methods used to extract the dyes were critical for these analyses. The use of HF to extract intact colourants from lakes ensures non-destructive extraction of acid-labile components, while the strong mineral acid HCl not only hydrolyses the metal-dye complex but also decomposes the glycosidic dye into the parent aglycon and causes formation of many undesirable by-products which may hinder proper identification of the dye [3].

Acknowledgements:
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ABSTRACTS

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POSTER PRESENTATIONS

WARSAW'S OLD MARKET SQUARE: MATERIAL STUDIES OF ITS DECORATION

Sylwia Svorová Pawełkowicz
Academy of Fine Arts in Warsaw, Faculty of Conservation and Restoration, Wybrzeże Kościuszkowskie 37, 00–379 Warsaw, Poland
email: s.pawelkowicz@labko.pl

The Warsaw Old Town is known as an example of meticulous post-war reconstruction and as such is listed as a UNESCO World Heritage Site.

The earliest references to the houses of the Warsaw Old Town date back to the first half of the 15th century [1]. The most prosperous period of the city's development took place during the 17th century, after the capital of Poland was relocated there in 1596. Few people know that, in fact, the Old Town Market Square had already become depopulated and had fallen into ruin at the beginning of the 19th century. In the 1920s, it underwent serious refurbishment. In 1944, during the Warsaw Uprising, over 80% of the buildings were levelled to the ground.

After World War II, the communist government decided to officially celebrate the reconstruction of the Old Town Square on 22 July 1953, the anniversary of the communist PKWN Manifesto and, at that time, the National Day of Poland's Revival. Artists were invited to prepare projects and to decorate the facades of the buildings. They were given three months to complete the task (8 May–22 July 1953). At the very beginning of the work, they sent a letter to the Ministry of Culture explaining that because of the intensity and pace of work they were unable to take responsibility for the quality and durability of their work.

In 2015, as part of the project 'Modernisation, Conservation and Digitisation of Historical Facilities of the Museum of Warsaw's Principal Seat at the Old Market Square in Warsaw', researchers studied plaster from the northern part of the Old Town Square. The following techniques were used: optical microscopy, petrographic studies, scanning electron microscopy with energy

dispersive X-ray spectrometry (SEM-EDS), X-ray powder diffraction (XRD), matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry (MALDI-TOF).

The facades were mostly decorated with tinted plaster, sgraffiti and some fresco ornaments. According to the literature, samples of colours were prepared and tested by Helena Grześkiewiczowa [2]. However, in order to obtain intensive and dark hues, such as dark grey or dark brown, too much pigment was added and the binder-to-aggregate ratio was distorted. On the cross sections and thin sections of the samples, the poor state of conservation of the original plaster from the 1950s could be seen. Casein glue was most probably used to make this system more durable.

During the recent work, it also became obvious that a few remnants of the former decorations dating back to 1920s had survived the war, including the paintings of Zofia Stryjeńska. In addition, inside the Moor House the researchers discovered remnants of late Renaissance decoration.

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INSTRUMENTAL ANALYSIS OF PAPER SUPPORT

Anna Nowicka
Academy of Fine Arts in Warsaw
ananow@wp.pl

This poster presents part of the results of a research project entitled 'Investigations of the use of the Bookkeeper method for the deacidification of oil paintings on a paper support. The project was carried out at the Department of Conservation and Restoration of Works of Art of the Academy of Fine Arts in Warsaw from 2011 to 2015 and was fully financed by the National Centre for Science in Krakow (grant application no. 2011/01/N/HS2/02308).

One of its stages was the restoration of five paintings of Mieczysław Szymański from the Museum of Academy of Fine Arts in Warsaw.

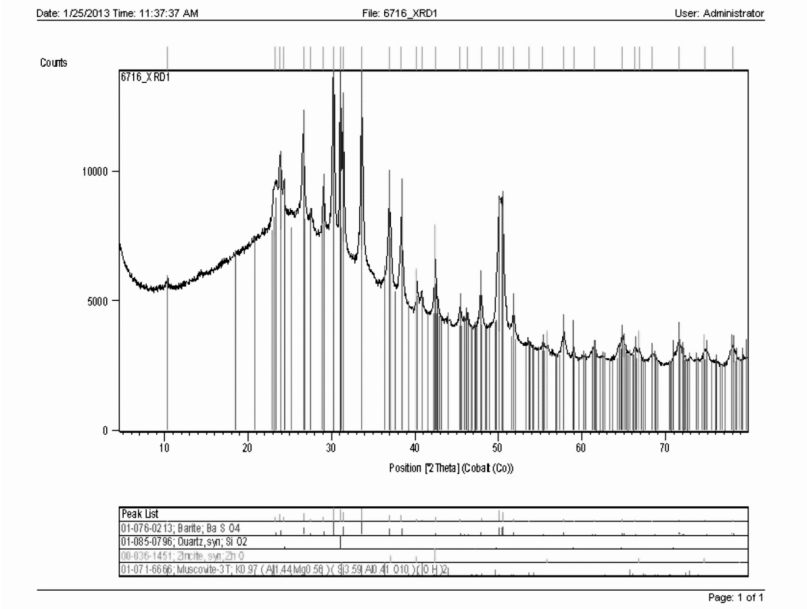


Fig. 1 XRD analysis of fillers and coating. Made by Grzegorz Kaproń (Warsaw University).

Prior to the conservation, an analysis of the artist's studio was carried out. The supports and paint layers were examined.

In light of the aim of the project, the composition and condition of the paper was particularly interesting to researchers. Traditional analysis, SEM-EDS, XRD, and other instrumental tests were performed. Not only were fibres, fillers, and coating identified, but pH, brightness and yellowness index changes were also measured.

X-RAY DIAGNOSTICS ON CARAVAGGESQUE PAINTINGS: A PRESENTATION OF RESEARCH

Mateusz Jasiński
Academy of Fine Arts in Warsaw, Faculty of Conservation and Restoration of Works of Art
jasinskimateusz@poczta.fm

Research on Caravaggesque paintings was conducted as part of an exploratory project: *Technique and technology of Caravaggesque paintings based on Polish museum collections*. The project was financed by the National Science Centre (2013/09/N/HS2/02116, PRELUDIUM V) and is the subject of a doctoral thesis carried out under the guidance of Professor Jerzy Nowosielski.

The research was based on paintings in the collections of Polish museums and concentrates mainly on the collection of the National Museum in Warsaw, which includes a group of 15 Caravaggesque paintings. The project also includes two paintings from the National Museum in Poznan, two from the Lublin Museum, two from the Museum of King Jan's III Palace at Wilanów and one from the National Museum in Wroclaw. Most of the paintings have not yet been examined.



Fig. 1 Cecco del Caravaggio, Martyrdom of Saint Sebastian, inventory no. M.Ob. 645 MNW

X-rays enable us to look more deeply into the structure of Caravaggesque paintings and often to confirm attributions. Combined with historical knowledge about the procedures and organisation of a painter's studio, they can provide access to the process of creation, the stages of preparation, and changes that have left their traces in the structure of the artwork. Based on this information, preferences concerning applied materials will be defined, as well as support in dating works and establishing the relationships between Caravaggio and his followers.

The following non-destructive methods were also used in this research: ultraviolet (UV), infrared (IR), photography in visible light (VIS), and various physicochemical analyses of binders, pigments and dyes.

TEXT ENHANCEMENT AND EXAMINATION OF TRACES ON DOCUMENTS USING HYPERSPECTRAL IMAGING COMBINED WITH THE CHEMOMETRIC APPROACH

Alicja Majda,[1] Agata Mendys,[2] Renata Wietecha-Posłuszny,[1] Barbara Łydżba-Kopczyńska,[2,3] Paweł Kościelniak[1,4]

[1]Laboratory for Forensic Chemistry, Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow

[2]Laboratory of Analysis and Non-Destructive Investigationof Heritage Objects (LANBOZ), National Museum in Krakow 3 Maja 1, 30-062 Krakow

[3]Faculty of Chemistry, University of Wroclaw, F. Juliot-Curie 14, 50-383 Wroclaw

[4]Institute of Forensic Research, Westerplatte 8, 31-033 Krakow

ala.majda@doctoral.uj.edu.pl

In recent years, the hyperspectral imaging (HSI) technique has gained a great deal of attention in the fields of forensics and cultural heritage analysis. A non-destructive reflection spectroscopy technique, it does not cause contamination of samples. HSI enables the acquisition of an image of the object with full spectral information within every pixel of the image, creating a three-dimensional data cube, or so-called 'hypercube'. The spectral characteristics included in every pixel can be extracted from an image and analysed externally using statistical methods. The statistical approach, applied directly to the full hypercube, enables classification of different regions and analysis of the spatial distribution of characteristic features.

This paper presents an analysis of documents written in inks and gel-pen inks which have been subsequently flooded, charred, or treated with biological substances. Studies were performed using a SPECIM Photonfocus VIS-NIR camera with 1312 × 1082 pixels, within a spectral range of 400–1000 nm. Typical scanning parameters were as follows: image recording frequency, 10 Hz; exposure time, 75 ms; scan speed, 0.9 mm/s. Following acquisition, the data was corrected for dark current and normalised using recordings obtained for white standard under the same conditions used during the sample scanning. A Spectralon plate was used as a white reference, yielding maximum reflectance value along the scanned line.

The hyperspectral image data were analysed using ENVI 5.0, and the extracted spectral information analysed further with Statistica 12. A region of interest (ROI) including at least 100 pixels was defined for each of the ink traces, stains, and paper substrates. Chemometric analysis based on minimum noise fraction (MNF), principal component analysis (PCA), and cluster analysis (CA) was performed.

First, MNF was applied to reduce the Poisson noise of the hyperspectral image. In the next step, CA and PCA were applied to reflectance spectra extracted from ROI. Hierarchical cluster analysis with Ward's method and Euclidean distance was used to determine the relationship between the analysed ink traces. The PCA algorithm based on the correlation matrix was used to plot the scatterplot and loading plot for the principal component, containing information about the correlation between loading and variables. According to this analysis, the samples could be divided into groups of traces depending on their correlation with principal components.

As a result, the aforementioned analysis enabled the enhancement of text on damaged documents as well as the establishment of distinctions between different traces. Future research will enable the development of standardised procedures for dealing with damaged documents of high value which cannot be read with the naked eye.

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OPTIMISATION OF THE GEOMETRY OF THE FULL-FIELD XRF IMAGING SYSTEM BASED ON A GASEOUS DETECTOR

P. M. Wróbel,[1] T. Fiutowski,[1] P. Frączek,[2] S. Koperny,[1] M. Lankosz,[1] A. Mendys,[2] B. Mindur,[1] A. Sikorska,[1] K. Świentek,[1] P. Wiącek,[1] W. Dąbrowski[1]

[1]AGH University of Science and Technology, Krakow, Poland

[2]The National Museum in Krakow, Krakow, Poland

pawel.wrobel@fis.agh.edu.pl

X-ray fluorescence imaging has become a very powerful tool for the non-destructive imaging of inorganic pigments in historical paintings, affording an opportunity to study the distribution of pigments – not only those visible to naked eye but also hidden ones. This method enables investigation of the age and provenance of a given object as well as study of the artist's techniques. In contrast to scanning macro-XRF imaging, the full-field XRF technique enables the simultaneous imaging of several irradiated areas of the sample. The image of the analysed area is created by the optic element (usually a pinhole camera) on the surface of a position-sensitive and energy-dispersive detector. Thanks to the infinite depth of view of the pinhole camera, the sample need not have a flat surface.

The new full-field XRF imaging system is based on a Gas Electron Multiplier 10×10 cm^2 detector currently under development as part of the DET-ART project. The system is equipped with two low- power air-cooled X-ray tubes (Mo anode). The image of the irradiated area is projected onto the surface of the detector by a pinhole camera. The prototype of the measuring head, developed in house, enables adjustment of the geometry of the measurement in order to optimise the excitation conditions for chosen projection parameters. There are three adjustable parameters: the incidence angle of primary radiation, the distance from the X-ray tubes to the object, and the distance from the object to the detector plane.

This paper presents an algorithm for semi-quantitative calculation of the distribution of the photon irradiance on the sample surface for different excitation geometries. It also enables the estimation of irradiance on the detector surface for different projection geometries and targets. In the calculations, the absorption of primary and secondary radiation in air was taken into account. The algorithm was implemented in the form of MATLAB scripts supporting optimisation of the measurement geometry. The results of the calculations were compared with the results of the measurements of real samples at different detection geometries.

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A NEW METHODOLOGY FOR REMOVAL OF ABSORPTION ARTEFACTS IN THE MACRO-XRF IMAGING OF PAINT LAYERS

Pawel M. Wróbel,[1] Piotr Frączek,[2] Marek Lankosz[1]
[1]AGH University of Science and Technology, Krakow, Poland
[2]The National Museum in Krakow, Krakow, Poland
pawel.wrobel@fis.agh.edu.pl

The macro-XRF technique enables the imaging and identification of hidden paint layers, making it much more versatile than X-ray radiography. One of the main disadvantages of this method is that characteristic X-rays from deeper paint layers are absorbed in covering layers. This effect manifests itself in the form of artefacts that impede the proper interpretation of acquired images. Recently [1] some fundamental parameter-based methods of correction, suitable only for monochromatic excitation, were presented. Here we prove that those methods can be also extended to the case of polychromatic excitation [2]. Moreover, a new methodology is presented for the selection of correction parameters based on minimisation of the correlation coefficient between fluorescence signals from the covering and covered layers. This approach overcomes the problem of empirically chosen correction parameters, which introduce a human factor capable of distorting the correction results.

The method was tested with the use of test and mock-up paintings measured with a tabletop setup equipped with a low-power X-ray tube [3]. For all samples, an area 5×5 cm^2 was scanned. An example of correction results is shown in Fig. 3. In the case of the mock-up painting, the ground layer was created using lead white. Lead white was also used at the base of the mountains. The bluish-grey landscape in the background was prepared using azurite.



Fig. 1 The investigated area of the mock-up painting



Fig. 2 The original Pb-La image



Fig. 3 The corrected Pb-La image

Fig. 1 shows the Pb-Lα intensity map acquired during the macro-XRF experiment. The fluorescence signal from the lead-white layer is strongly affected by absorption effects from the azurite layers. Fig. 2 shows the Pb-Lα intensity map after absorption correction, in which the proper shape of the base of the mountains was revealed. The presented approach affords very promising results and opens up the possibility of automation of the correction of absorption effects.

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X-RAY COMPUTED TOMOGRAPHY STUDY OF ARCHAEOLOGICAL ARTIFACTS

E. A. Miśta,[1] T. Kosiński,[1] W. Weker[2]

[1]National Centre for Nuclear Research, Otwock-Świerk, [2]State Archaeological Museum in Warsaw

Ewelina.Mista@ncbj.gov.pl

Tymoteusz.Kosinski@ncbj.gov.pl

wweker@poczta.onet.pl

Modern archaeology and conservation science use imagining techniques such as X-ray and neutron radiography, as well as tomography, to obtain information about an object's structure. All of these methods are used in NCNR for archaeological research [1].

Non-invasive imagining shows the original shapes of objects, especially when they are damaged by corrosion. Moreover, it can reveal the techniques used to produce and decorate the object. X-ray examination of closed shapes, such as filled dishes, shows what is inside the structure. A researcher using this information can follow separate all of possible forms existing inside the object without damaging it. In the case of X-ray radiography, imaging is possible due to the different degrees of absorption of X-rays caused by the variation in density of the internal structure of the object.

X-ray computed tomography (X-ray CT) was used to study ancient artefacts, e.g. swords, fibulas, and clay burial pottery. The research was conducted in collaboration with the State Archaeological Museum in Warsaw and the Institute of Archaeology at Warsaw University (P. Szymański, DSc).

In the research, the Nikon XT H 225 ST Computed Tomography system at NCNR was used with a 225 kV reflection target source. Below are examples of the study results.

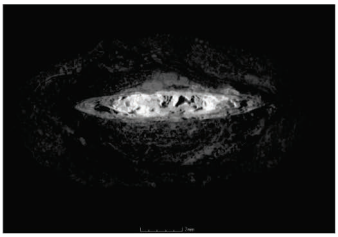


Fig. 1 Cross section of an iron sword in a wooden scabbard (Czersk castle)

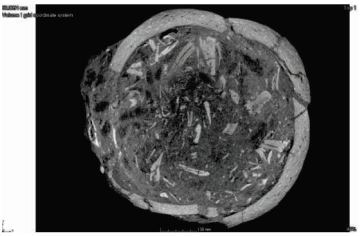


Fig. 2 Cross section of burial pottery (Czerwony Dwór)

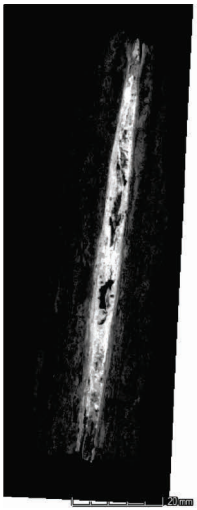


Fig. 3 Longitudinal cross section of a sword from Czersk castle

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THE EFFECT OF GROWTH RING STRUCTURE ON THE RESPONSE OF WOOD SUBJECTED TO CHANGING CLIMATE CONDITIONS

Leszek Krzemień,[1] Michał Łukomski,[2] Marcin Strojecki[1]

[1]Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek 8, 30-239 Krakow

[2]Getty Conservation Institute, 1200 Getty Center Drive, Los Angeles, CA

e-mail: nckrzemien@cyf-kr.edu.pl

The variability of wood structure leads to its inhomogeneous response to external factors and thus to complex deformation of wood-containing objects. It is particularly important to understand the complex response of decorated wooden objects exposed to variations in temperature and relative humidity, as such deformation can result in damage to both the wood structure and the decorative layers. The position and extent of damaged areas on the surface of decorated wood is strongly correlated with the growth ring structure of the wooden substrate. Therefore, measuring the spatial distribution of moisture-induced strain on the growth ring scale is crucial to establishing a safe range of climatic fluctuation in the environment of wooden art objects such as panel paintings or furniture.

Two independent measuring techniques used in this study enabled the acquisition of complementary information about the deformation of the investigated material. The strain distribution on the wood surface was analysed in real time using in-plane digital speckle-pattern interferometry for various amplitudes and durations of relative humidity variations. The shapes and structures of the same wooden samples in equilibrium with different relative humidity levels were recorded with the help of a second technique, X-ray microtomography [1].

The applied experimental approach, which obtained exact information on the dynamic response of the wood surface to variations in environmental

parameters, represents a step forward in defining critical conditions leading to damage of decorated wood.

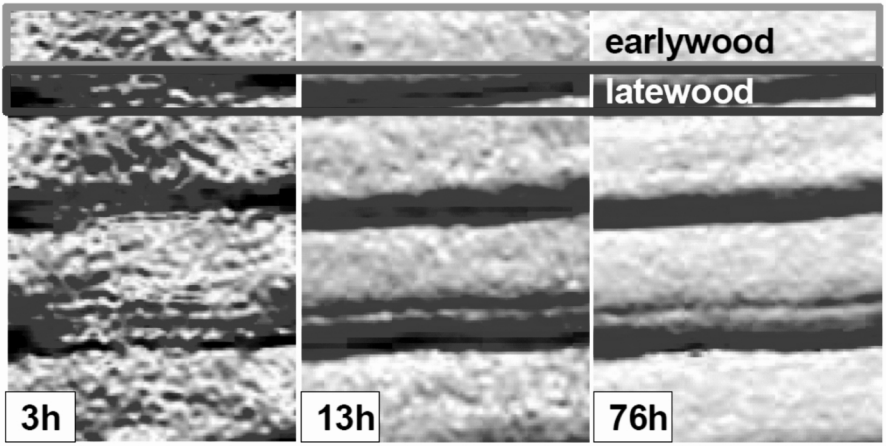


Fig. 1 Shrinkage distribution inside a pine specimen measured using X-ray microtomography 3, 13, and 76 hours after a relative humidity change from 75 to 40%

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CHEMICAL, STRUCTURAL, AND MORPHOLOGICAL CHARACTERISATION OF METALLIC OBJECTS FOR FORENSIC PURPOSES

Zuzanna Brożek-Mucha,[1] **Dariusz Mucha**[2]
[1]Institute of Forensic Research, ul. Westerplatte 9, 31-033 Krakow, Poland
zbrozek@ies.krakow.pl
[2]Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences,
ul. Niezapominajek 8, 30-239 Krakow, Poland
ncmucha@cyf-kr.edu.pl

Various metallic objects may constitute evidence which can be examined by a forensic chemist in order to establish certain circumstances concerning a crime, or to reconstruct it. The size of such an object may vary from submicrons to several metres, e.g. microscopic gunshot residue (GSR) originating from ammunition primer, currency coins, jewellery, or a submarine mine.

To identify GSR particles, their chemical content and morphology, reflecting melting and fast cooling, must be established [1–2]. Post-blast or gunshot residues are thought to be amorphous in their spherical morphology [3–5]. However, detailed analysis of their images revealed some crystalline domains. The presence of high-pressure and high-temperature phases of lead, antimony, and barium alloys in residues present inside cartridge cases was confirmed by means of X-ray diffraction.

In investigations of the authenticity of coins and jewellery, quantitative analysis by means of X-ray fluorescence and X-ray microanalysis can be useful in establishing the chemical content, and thus the origin, of the objects.

Dating of a World War II submarine mine was accomplished by means of elemental analysis and metallographic examinations of fragments of the aluminium alloy parts of the mine and their welding joints. It was established that some parts of the mine originated from post-war times; thus the mine had not been present in the port since World War II.

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COMPOSITION OF GOLD ALLOYS AND DEGRADATION OF PIGMENTS USED IN PORTUGUESE ARTWORKS FROM THE 14TH TO 17TH CENTURIES

Manuel J. L. Sarmento, Afonso M. T. Coxito, Francisco P. S. C. Gil
CFisUC – Center for Physics of the University of Coimbra, Department of Physics, and Molecular Physical-Chemistry R&D Unit, Chemistry Department, University of Coimbra, Portugal
fgil@fis.uc.pt

Many works of art show, within their polychrome, gold layers in more or less extension among various pigments. The composition of the gold polychrome may be gold alloy leaf or another kind of material with a golden appearance, depending on the epoch and the artist's preference. The analysis of these materials determines the history of the artwork itself and its condition over time while subjected to various stages of restoration or alteration. The pigments used may also undergo several degradation processes.

This study is focussed on stone carvings with one or more pictorial layers with a golden appearance. The chosen artworks represent major Portuguese artists from the 14th to 17th centuries: the tomb of Queen Elizabeth's granddaughter (14th century), the tomb of Isabel of Urgell, Duchess of Coimbra (15th century), the altarpiece of João Afonso 'God Corps' (15th century), the 'Lactation of St. Bernard' sculpture of Jean de Rouen (16th century) and the arch of the Chapel of St Michael at the University of Coimbra (17th century).

In an attempt to clarify the differences and similarities between the painting in the studied artworks, including the possibility that the painting may have been made at a later time than the execution of the artwork itself, the composition of the gold leaf was analysed (in all present layers). Subsequent to this study, the changes undergone by each type of pigment found in the studied works of art were monitored, using commercial pigments in various binders (oil- or water-based), artificially aged, using a single accelerated ageing chamber, by controlling temperature and, in particular, exposure to ultraviolet light in two different spectral areas [1,2,3].

In the context of the present study and for the identification of the composition of the gold alloy used by the artists, the following experimental techniques were used: optical microscopy (OM), X-ray fluorescence (XRF) [4], and scanning electron microscopy with X-ray dispersive energy spectroscopy (SEM-EDS) [5].

For the identification of the pigments used by the artists, the following experimental techniques were used: optical microscopy (OM), X-ray fluorescence (XRF), micro-Raman spectroscopy (μ-Raman) [6], and scanning electron microscopy with X-ray dispersive energy spectroscopy (SEM-EDS).

Some of the studied cases showed the existence of different gold alloy compositions, such as gold, silver, and copper; gold, silver, and tin; or gold, silver, copper, and iron. The compositions of these alloys will be compared with those of other gold alloys found in artworks of known origins and compositions.

Most of the studied cases showed the existence of azurite or lazurite (natural and artificial ultramarine blue) for the blue pigments; lead red, hematite (red iron oxide), or vermilion for the red; chrome yellow, yellow ochre (yellow iron oxide), or lead tin yellow for the yellow; malachite or chrome oxide for the green; and lead white, gypsum, or titanium oxide for the white.

To study the effect of ultraviolet radiation on the ageing of the identified pigments in the artworks under consideration, an accelerated ageing chamber with exposure to ultraviolet radiation was used, where samples of commercial pigments applied on glass slides oil mixtures, diluted in aqueous media, were introduced. X-ray diffraction (XRD) and reflectance spectroscopy (RS) were used to monitor the development of changes undergone by the pigments subjected to this ageing treatment.

We thank the National Museum of Machado de Castro and the Queen Elizabeth Confraternity in Coimbra, for access to the studied artworks. We thank TAIL (Trace Analysis and Imaging Laboratory) – University of Coimbra for access to and use of existing experimental techniques.

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ANIMAL REMAINS IN CONTEMPORARY ART. THE USE OF X-RAY AND OTHER TECHNIQUES TO OBTAIN A DEEPER UNDERSTANDING OF THE TECHNOLOGY OF ATYPICAL CONTEMPORARY ARTWORKS AND THEIR CARE ON THE BASIS OF 'PYRAMID OF ANIMALS' BY KATARZYNA KOZYRA AND 'BITCH' BY MIROSŁAW BAŁKA.

Anna Kowalik, MA
Academy of Fine Arts in Warsaw, Faculty of Conservation and Restoration of Works of Arts
ania_kowalik@gazeta.pl

Animal remains, whether preserved taxidermically or otherwise, pose a variety of issues as an artistic medium, making their use a highly distinctive choice on the part of the artist. The problems which accompany taxidermy and the use of animal remains in general are numerous.

Research work on the basis of 'Pyramid of Animals' by Katarzyna Kozyra and 'Bitch' by Mirosław Bałka presented issues of protection of the integrity of atypical contemporary artworks and how it affects artistic practice. The use of X-rays and other techniques is essential for the identification of materials present in these atypical contemporary artworks to obtain a deeper understanding of the technology.

The research focussed on analysing material structure and internal construction in order to identify the construction, meaning, and main idea of these works of art, and subsequently to devise an optimal programme for their protection.

The research offered new insight into various material specimens of animals and the importance of their protection and conservation, in a country where previously no particular attention had been paid to the educational process for conservators. Accumulated knowledge in this field has been helpful in understanding the techniques and technology of the preparation of animals and their consequences within the field of conservation.

A RESEARCH PROJECT ON TWELVE PAINTINGS *EN GRISAILLE* FROM JANOW PODLASKI

Marta Zaborowska
Faculty of Conservation and Restoration of Works of Art
Academy of Fine Arts in Warsaw
zabor.mart@gmail.com

This group of twelve paintings on canvas is probably part of the original furnishings of the Holy Trinity Collegiate Church in Janów Podlaski (eastern Poland). This collection, unique in Polish art, has not been the subject of any scientific studies to date.

The church was built in the first half of the 18th century. The compositions, depicting the Apostles' deaths as martyrs, were painted on octagonal canvases in a black and white colour scale, in a very professional, high-quality manner. Neither the author, studio, exact date, nor place of origin are known.

The programme was financed by the Ministry of Culture and National Heritage from the Fund for the Promotion of Creativity. It was carried out between October 2015 and the end of March 2016. The aim of the programme was to prepare a project for the conservation and restoration of these paintings, consisting of activities such as photographic documentation, non-invasive investigation, and sampling to prepare cross sections for their use in further chemical analyses. In addition to VIS photographic documentation, UV-radiation-induced luminescence, and infrared reflectography, other tests, including X-ray analysis of selected objects and chemical analyses of the elements under an energy-dispersive (EDS) detector electron microscope, were conducted. All of these enabled us to gather information about the technique, technology, and state of preservation of the paintings. The result will include documentation, with a catalogue and specifications of the knowledge acquired, as well as, of course, the main outcome, a proposal for a programme of conservation.

The paper presents problems concerning the examination of this group of paintings created on a very limited colour scale and the results of non-invasive studies and chemical analyses on samples.

DECORATION TECHNIQUES IN MEDIEVAL HEBREW BIBLES: NON INVASIVE XRF AND μ-RAMAN ANALYSIS

Anna Rogulska,[1] Barbara Łydżba-Kopczyńska[2,3]

[1]Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow

[2]Faculty of Chemistry, University of Wroclaw, F. Joliot-Curie 14, 50-383 Wroclaw, Poland

[3]National Museum in Krakow, Laboratory of Analysis and Non-Destructive Investigation of Heritage Objects, Piłsudskiego 14, 31-109 Krakow, Poland

rogulska@chemia.uj.edu.pl

It is well known that the method of preparing a Torah scroll for use in a synagogue is extremely strict and has become kind of a ritual. The text plays a major role in such a manuscript, but there are certain beliefs concerning miniatures as well, such as the avoidance of depictions of the human form resulting from a strict interpretation of the second commandment (*'You shall not make for yourself a sculptured image or any likeness of what is in the heavens above […]'*[1]). However, it is not clear whether the technological aspect of this kind of sacred book is somehow unique in comparison to religious Western manuscripts. An important factor in developing knowledge about the work methods of Jewish medieval illuminators is access to the objects themselves, which are rare among European museum collections and often inaccessible to scientists.

Therefore, we decided to use this opportunity to join the conservation team from the Ossoliński National Institute in Wroclaw, Poland, and to examine an outstanding codex from their collection. The object of our study was a fourteenth-century illuminated manuscript of German origin. The entire codex is very well preserved. The text is written in Hebrew in Ashkenazi square script, in two columns; Masoretic notations and comments are written in Aramaic. The *masorah magna* notations are often written in micrography, in the form of animal, floral, or geometrical motifs. The text is decorated with 23 illuminations with a predominance of blue, pink, and gold, presenting fantastic creatures, animals, and people. Identification of pigments or dyes in

the miniatures was carried out with the use of a Raman microscope and hand-held XRF spectrometer. All of the measurements were performed *in situ* directly on the codex pages.

As a result of our study, the palette of pigments used in the Hebrew Bible was established. Although the miniatures were full of various vibrant colours, the palette turned out to be fairly limited, containing lead white, red lead, ivory black, lapis lazuli, vermillion, red ochre, and a copper-based green pigment yielding no Raman spectrum, but confirmed by XRF. The initials were decorated with gold leaf, except for one decorated with silver. Silver, now completely black in appearance, was also detected on one miniature. The illuminations were prepared with the use of both pure and mixed colours.

The study is of great importance for understanding the preparation of Hebrew religious manuscripts, especially since there is no comprehensive analytical study in the literature to date of a mediaeval Hebrew Bible of German provenance. It also highlights the need for the application of complimentary analytical techniques in the comprehensive investigations of cultural heritage objects.

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Sculpture appeals to everyone
and speaks to them in the same way.
Its speech is form and space.

PRELIMINARY STUDIES OF KATARZYNA KOBRO'S GYPSUM SCULPTURES

Marta Grzesiak-Nowak,[1] Alicja Rafalska-Łasocha,[1] Anna Klisińska-Kopacz,[3] Elżbieta Cieślak,[2] Wiesław Łasocha[1,4]

[1]Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, [2]National Museum in Krakow, al. 3 Maja 1, 30-062 Krakow, [3]Muzeum Sztuki in Łódź, Więckowskiego 36, 90-734 Łódź, [4]Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, Niezapominajek 8, 30-239 Krakow
rafalska@chemia.uj.edu.pl

Katarzyna Kobro was an avant-garde sculptor of the interwar period. Her early works (e.g. *Hanging Constructions or Abstract Sculptures, from the first half of* 1920s) were created under the influence of Constructivism and Suprematism, which gave priority to the materials used and the artwork's form rather than to the subject matter. She started her artistic work in Soviet Union and during this early period Kobro was in touch with Wassily Kandinsky, Marc Chagall, and Kazimir Malevich. At the turn of 1921/1922 she left Russia together with Władysław Strzemiński to became a part of an avant-garde circle in Poland [1].

In the late 1920s, Kobro started to teach the 'aesthetics of the interior'; she formulated theoretical statements about sculpture, which she published along with her husband Władysław Strzemiński in the book *Spacial Composition* in 1931. They believed that, contrary to painting (related to flat surfaces), sculpture is the art of space. The structure of sculpting space is determined by the rhythms of shapes and colour surfaces, not by solids and their mass. Along with her colleagues, she helped also found International Collection of Modern Art in the Museum of Art in Lodz, first opened to public

in 1931.

After WWII, in 1940s and 1950s, Kobro's works were forgotten due to their novel formula and their creator's misfortunes. Some of her sculptures were lost; some ended up in rubbish heaps. Many of them are known nowadays only from iconographic records [2].

The presented study was performed on samples from three gypsum sculptures by Katarzyna Kobro realized in 1920s. The sculptures belong to the Museum of Art in Lodz. The investigations were performed using X-ray powder diffraction and X-ray fluorescence techniques. XRPD measurements were performed at the Faculty of Chemistry, Jagiellonian University, with the use of an X'Pert PRO MPD diffractometer, CuKa radiation operating at 40kV and 30mA, a graphite monochromator, and a PIXCEL PSD detector. The phase analysis was carried out with the use of the PDF-4+ database. Obtained results will be presented during the conference.

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PAINTING MATERIALS USED BY HENRYK SIEMIRADZKI IN SOME OF HIS WORKS

Dominika Sarkowicz,[1] Alicja Rafalska-Łasocha,[2] Marzena Sieklucka,[1] Anna Klisińska-Kopacz,[1] Marta Matosz,[1] Julio del Hoyo-Meléndez,[1] Marta Grzesiak-Nowak,[2] Wiesław Łasocha[2,3]

[1]National Museum in Krakow, [2]Faculty of Chemistry Jagiellonian University, [3]Jerzy Haber Institute of Catalysis and Surface Chemistry PAS

domisar@o2.pl

Henryk Siemiradzki (1843–1902), a prominent artist and one of the most famous Polish painters of the 19th century, is among the best-known representatives of academic art. His works mainly depict scenes from the life of the ancient Romans, the history of Rome, and the history of the first Christians, as well as illustrations of ancient myths and biblical scenes. His work *Nero's Torches* (1876), exhibited in many cities of Europe, initiated the collection of the National Museum in Krakow, Poland's oldest national museum [1].

Investigations of Siemiradzki's works were conducted within the project 'Analysis of Henryk Siemiradzki's workshop based on works from the collection of National Museum in Krakow and other collections' and are now being continued as a part of a vast new research project aimed at publishing a catalogue of all Siemiradzki's paintings [2]. The goal of the original project was to identify the painting techniques of the artist's studio, including the technological and technical aspects of selected paintings, their history, the painting technique and materials used, and the painter's palette. The research included microscopic and microchemical analysis, spectroscopy (XRF, FTIR, SEM/EDS), and powder diffraction (XRPD) studies [3]. The measurements were performed at the Laboratory of Analysis and Non-Destructive Investigation of Heritage Objects at the Faculty of Chemistry, Jagiellonian University, in Krakow and in other scientific labs.

In the conference presentation we will concentrate on nine of Siemiradzki's paintings: *View of the Świsłocz River* (ca 1873), *Apollo and Muses* (before 1883), *Ruins of a Roman Villa* (ca 1885), *Portrait of Mother* (1885), *Portrait of Father* (1887), *Portrait of the Artist's Son Leoś* (1892), and *Self-portrait with a Palette* (ca 1900) from the National Museum in Krakow, and *Portrait of the Artist Alexander Stankiewicz* (before 1892) and *Roman Rural Woman* (*Fishing*) (the 1890s) from the National Museum in Warsaw.

XRPD measurements were performed by the Structure-oriented Powder Diffractometry Group at Faculty of Chemistry, Jagiellonian University, with the use of an X'Pert PRO MPD diffractometer, using CuKa radiation, operating at 40kV and 30mA, with a graphite monochromator and a PIXcel PSD detector. The phase analysis was carried out with the use of the PDF-4+ database.

During the '6th Meeting: X-ray and other techniques in investigations of the objects of cultural heritage', the Gallery of 19th-Century Polish Art in the Cloth Hall will house an exhibition of Siemiradzki's paintings from the Lviv National Art Gallery. All of the exhibited pictures have undergone thorough examination. This exhibition is a great opportunity to expand scientific interest in Siemiradzki's works.

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EVALUATION OF VARIOUS SCIENTIFIC TECHNIQUES APPLIED TO INVESTIGATIONS OF ANCIENT METAL OBJECTS

Anna Grzesik,[1] Marcin Oszajca,[1] Marta Grzesiak-Nowak,[1] Wiesław Łasocha[1,2]
[1]Faculty of Chemistry Jagiellonian University, Ingardena 3, 30-060 Krakow,
[2]Jerzy Haber Institute of Catalysis and Surface Chemistry PAS,
Niezapominajek 8, 30-239 Krakow
lasocha@chemia.uj.edu.pl

In recent years the Structure-oriented Powder Diffractometry Group at the Faculty of Chemistry, Jagiellonian University in Krakow, have studied several historical metal objects, establishing their chemical composition, provenance, and authenticity, as well as the methods used in their production. Among the applied techniques we can mention:

– X-ray powder diffractometry (XRPD) in classical Bragg-Brentano or DSH geometry as well as microdiffraction,

– Scanning electron microscopy (SEM/EDS) for material morphology, element distribution, and concentration,

– Laser ablation inductively coupled plasma mass spectrometry (LA ICPMS),

– Particle-induced X-ray emission (PIXE),

– X-ray fluorescence (XRF) methods, supported by chemical analysis, spectroscopy techniques, and density determination.

With the use of the above methods we have investigated silver coins (antique, mediaeval, and dating from the 19th century), stamps, seals, jewellery, ornaments, pieces of armour, and everyday objects [1]. The main technique we have applied in our work is X-ray powder diffractometry. Diffraction measurements were performed on an X'Pert PRO MPD diffractometer with CuKa radiation, operating at 40kV and 30mA, equipped

with a graphite monochromator and PIXcel PSD detector. The phase analysis was carried out with the use of the PDF-4+ database.

In the conference presentation we will discuss the obtained results, as well as the advantages and disadvantages of the applied techniques in investigations of ancient metal objects.

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HYPERSPECTRAL IMAGING INVESTIGATION OF WRITING TRACES ON PAPER

Damian K. Chlebda, **Anna Rogulska**, **Alicja Majda, Tomasz Łojewski**
Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Krakow, Poland
damian.chlebda@uj.edu.pl

Imaging technology enables us to see much more than traditional methods of analysis do. Hyperspectral imaging (HSI) has recently emerged as an efficient non-destructive tool for the detection, enhancement, and identification of forensic traces. Recently, it has been successfully applied to the analysis of cultural heritage objects. Hyperspectral imaging, or so-called 'reflection imaging spectroscopy', collects data across a broad range of practical wavelengths (the UV-VIS-NIR regions), providing sufficient data for detailed analysis in the data cube form. Hyperspectral imaging is of critical value in supporting ink examination. Selected applications can be used to read old scripts by enhancing the contrast between text and background or between under- and overwriting [1], extracting the spectral characteristics of the selected area, calculating its colour values, and monitoring changes in state caused by various factors [2,3].

The application of hyperspectral imaging to the assessment of conservation treatments for paper documents using modern techniques will be presented. Plasma treatment is one of the most efficient methods of surface modification, affecting its physical and chemical properties such as wettability and adhesion. The application of low-temperature plasma to sensitive objects, in particular those based on natural polymers, requires non-destructive workflow. The state of the documents can be also monitored after accelerated ageing to provide an excellent overview of their properties. Optical techniques are often used for the documentation and study of cultural heritage objects because of their most valuable features.

The hyperspectral setup used in this study consists of a Headwall Photonics camera (Hyperspec VNIR), an optically stabilised halogen lamp equipped with a cylindrical lens which emits a uniform light-line on scanned samples (SOL-R from Fiberoptics), and a motorised stage (Conix Research), all working under the control of the LabVIEW software suite. Photometrically normalised data cubes were analysed using ENVI and Spectronon software.

The analysis includes various documents (containing modern and historical inks) imaged by the hyperspectral camera before and after cold plasma treatments as well as after accelerated ageing.

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LIST OF AUTHORS AND PARTICIPANTS

Matthias Alfeld
Sorbonne Universités, UPMC Univ Paris 06, CNRS, UMR 8220, Laboratoire d'archéologie moléculaire et structurale (LAMS), 4 place Jussieu, 75005, Paris, France
matthias.alfeld@upmc.fr

Gilberto Artioli
Università di Padova, Dipartimento di Geoscienze, V Gradenigo 6, I-35131, Padova, Italy
gilberto.artioli@unipd.it

Mariana Balitska
National Reaserch Restoration Center of Ukraine, Lviv Branch, st. L. Ukrainky 10, 79008 Lviv, Ukraine
mariana908@ukr.net

Monica de Bardi
Academy of Fine Arts, Institute of Science and Technology in Art, Schillerplatz 3, A-1010 Vienna, Austria
Vienna University of Technology, Institute of Chemical Technology and Analytics, Getreidemarkt 9, A-1060 Vienna, Austria

Andrzej Betlej
National Museum in Krakow, Al. 3 Maja 1, 30-062, Krakow, Poland
abetlej@muzeum.krakow.pl

Petr Bezdička
Institute of Inorganic Chemistry of the Czech Academy of Sciences, v.v.i, ALMA Laboratory, č.p. 1001, 250 68 Husinec – Řež, Czech Republic
petrb@iic.cas.cz

Barbara Bożek
Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Niezapominajek 8, 30-239 Krakow, Poland
ncbozek@cyf-kr.edu.pl

Zuzanna Brożek-Mucha
Institute of Forensic Research in Krakow, Westerplatte 9, 31-033 Krakow, Poland
zbrozek@ies.krakow.pl

Federica Cappa
Academy of Fine Arts, Institute of Science and Technology in Art, Schillerplatz 3, A-1010 Vienna, Austria

Damian Chlebda
Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Krakow, Poland
damian.chlebda@uj.edu.pl

Elżbieta Cieślak
Muzeum Sztuki in Łódź,
Więckowskiego 36, 90-734 Łódź,
Poland

Ermanno A. Clerici
University of Bologna, Bologna, Italy

Afonso Coxito
University of Coimbra, Coimbra,
3030-076 Coimbra, Portugal

Paul Craddock
British Museum,
London WC1B 3DG, UK
paulcraddock74@btinternet.com

Janusz Czop
National Museum in Krakow,
Al. 3 Maja 1, 30-062 Krakow, Poland
jczop@muzeum.krakow.pl

Władysław Dąbrowski
AGH University of Science and
Technology, Al. Mickiewicza 30,
30-059 Krakow, Poland

Liesbeth Dingemans
Technical University of Delft, Delft,
The Netherlands

Michał Duda
Jagiellonian University, Faculty of
Chemistry, Ingardena 3,
30-060 Krakow, Poland
michalduda2@gmail.com

Tomasz Fiutowski
AGH University of Science and
Technology, Al. Mickiewicza 30,
30-059 Krakow, Poland

Annette Foelske-Schmitz
Technische Universität Wien,
Analytical Instrumentation Center,
Getreidemarkt 9, 1060 Vienna,
Austria
annette.foelske-schmitz@tuwien.ac.at

Piotr Frączek
National Museum in Krakow,
Al. 3Maja 1, 30-062 Krakow, Poland

Bernadette Frühmann
Academy of Fine Arts, Institute of
Science and Technology in Art,
Schillerplatz 3, A-1010 Vienna, Austria

Ana Isabel Gamero González
Archdiocese of Seville, Archbishop's
Palace, Seville, Spain

Jan Gertenbach
PANalytical B.V Twentepoort Oost 26,
7609 RG, Almelo, The Netherlands

Francisco Gil
University of Coimbra, Department of Physics, Center for Physics of the University of Coimbra and Chemistry Department, Molecular Physical-Chemistry R&D Unit, Coimbra, Portugal
fgil@fis.uc.pt

Tadeusz Glenc
TESTCHEM sp z o.o.
ul. Niepodległości 82D,
44-370 Pszów, Poland
biuro@testchem.pl

Anabel Gonzalez
Jagiellonian University, Faculty of Chemistry, Ingardena 3,
30-060 Krakow, Poland

Sofiia Gorditsa
Lviv National Art Gallery,
st. Stefanyka 3, 79000 Lviv, Ukraine
gordica@bk.ru

Marta Grzesiak-Nowak
Jagiellonian University, Faculty of Chemistry, Ingardena 3,
30-060 Krakow, Poland
marta.grzesiak@uj.edu.pl

Anna Grzesik
Jagiellonian University, Faculty of Chemistry, Ingardena 3,
30-060 Krakow, Poland
anna_g92@o2.pl

Julio M. del Hoyo-Meléndez
National Museum in Krakow, Laboratory of Analysis and Non-Destructive Investigation of Heritage Objects, Piłsudskiego 14,
31-109 Kraków, Poland

Klaudia Hradil
Technische Universität Wien, X-ray center, Getreidemarkt 9, 1060 Wien, Austria
klaudia.hradil@tuwien.ac.at

David Hradil
Institute of Inorganic Chemistry of the Czech Academy of Sciences, v.v.i, ALMA Laboratory, č.p. 1001,
250 68 Husinec – Řež, Czech Republic
Academy of Fine Arts in Prague, ALMA Laboratory, U Akademie 4,
170 22 Praha 7, Czech Republic
hradil@iic.cas.cz

Janka Hradilová
Academy of Fine Arts in Prague, ALMA Laboratory, U Akademie 4,
170 22 Praha 7, Czech Republic

Koen Janssens
University of Antwerp, Department of Chemistry, Groenborgerlaan 171, B-2020 Antwerp, Belgium
koen.janssens@uantwerpen.be

Mateusz Jasiński
Academy of Fine Arts in Warsaw, Faculty of Conservation and Restoration of Works of Art, Wybrzeże Kościuszkowskie 37, 00-379 Warsaw, Poland
jasinskimateusz@poczta.fm

Grzegorz Jezierski
Opole University of Technology, Prószkowska 76, 45-758 Opole, Poland
g.jezierski@po.opole.pl

Philippe Jockey
Sorbonne Universités, UPMC Univ Paris 06, CNRS, UMR 8220, Laboratoire d'archéologie moléculaire et structurale (LAMS), 4 place Jussieu 75005 Paris, France
2Aix-Marseille Université, Centre Camille Jullian, 5 rue du Château de l'Horloge, BP 647,13094 Aix-en-Provence, France

Zofia Kaszowska
Jan Matejko Academy of Fine Arts in Krakow, Faculty of Conservation and Restoration of Works of Art, Smoleńsk 9, 31-108 Krakow, Poland
zekaszow@cyfronet.pl

Anna Klisińska-Kopacz
National Museum in Krakow, Laboratory of Analysis and Non-Destructive Investigation of Heritage Objects, Piłsudskiego 14, 31-109 Krakow, Poland
aklisinska@mnk.pl

Stefan Koperny
AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Krakow, Poland

Tymoteusz Kosiński
National Centre for Nuclear Research, Otwock-Świerk, Poland
Tymoteusz.Kosinski@ncbj.gov.pl

Paweł Kościelniak
Jagiellonian University, Faculty of Chemistry, Laboratory for Forensic Chemistry, Ingardena 3, 30-060 Krakow, Institute of Forensic Research in Krakow, Poland

Anna Kowalik
Academy of Fine Arts in Warsaw, Faculty of Conservation and Restoration of Works of Arts, Wybrzeże Kościuszkowskie 37, 00-379 Warsaw, Poland
ania_kowalik@gazeta.pl

Roman Kozłowski
Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Niezapominajek 8, 30-239 Krakow, Poland
nckozlow@cyf-kr.edu.pl

Anabelle Kriznar
University of Seville, Centro Nacional de Aceleradores (CNA) - Faculty of Physics, Faculty of Fine Arts (US), Department of Sculpture and Art History, Avda. Thomas A. Edison 7, 41092 Seville, Spain
akriznar@us.es

Leszek Krzemień
Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Niezapominajek 8, 30-239 Krakow, Poland
nckrzemi@cyf-kr.edu.pl

Arkadiusz Kupczak
Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Niezapominajek 8, 30-239 Krakow, Poland
nckupcza@cyf-kr.edu.pl

Kilian Laclavetine
University of Seville (US), Centro Nacional de Aceleradores (CNA), Faculty of Physics, (US), Department of Atomic, Molecular and Nuclear Physics

Marek Lankosz
AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Krakow, Poland

Janusz Lekki
Institute of Nuclear Physics, Polish Academy of Sciences, Radzikowskiego 152, 31-342 Krakow, Poland
Janusz.Lekki@ifj.edu.pl

Marta Lempart-Geratowska
Jan Matejko Academy of Fine Arts in Krakow, Faculty of Conservation and Restoration of Works of Art, Smoleńsk 9, 31-108 Krakow, Poland
marta.geratowska@interia.pl

Wiesław Łasocha
Jagiellonian University, Faculty of Chemistry, Ingardena 3,
30-060 Krakow, Poland
Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Niezapominajek 8,
30-239 Krakow, Poland
lasocha@chemia.uj.edu.pl

Tomasz Łojewski
Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Krakow, Poland

Michał Łukomski
Getty Conservation Institute, 1200 Getty Center Drive, Los Angeles, CA, USA

Barbara Łydżba-Kopczyńska
University of Wroclaw, Faculty of Chemistry, F. Joliot-Curie 14,
50-383 Wroclaw
National Museum in Kraków, Laboratory of Analysis and Non-Destructive Investigation of Heritage Objects, Piłsudskiego 14,
31-109 Kraków, Poland
barbara.lydzba@chem.uni.wroc.pl

Alicja Majda
Jagiellonian University, Faculty of Chemistry, Laboratory of Forensic Chemistry, Ingardena 3,
30-060 Krakow, Poland
ala.majda@doctoral.uj.edu.pl

Marta Matosz
National Museum in Kraków, Laboratory of Analysis and Non-Destructive Investigation of Heritage Objects, Piłsudskiego 14,
31-109 Kraków, Poland

Agata Mendys
National Museum in Kraków, Laboratory of Analysis and Non-Destructive Investigation of Heritage Objects, Piłsudskiego 14,
31-109 Kraków, Poland

Beata Miazga
University of Wrocław, Institute of Archaeology, Szewska 28,
50-139 Wrocław, Poland
beata.miazga@uwr.edu.pl

Paweł Milejski
University of Wrocław, Institute of Archaeology, Na Polance 10/17,
51-109 Wrocław, Poland
pawel.milejski90@gmail.com

Bartosz Mindur
AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Krakow, Poland
bartosz.mindur@agh.edu.pl

Ewelina Miśta
National Centre for Nuclear Research, 05-400 Otwock, Poland
ewelina.mista@ncbj.gov.pl

Dariusz Mucha
Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Niezapominajek 8, 30-239 Krakow, Poland
ncmucha@cyf-kr.edu.pl

Maud Mulliez
Sorbonne Universités, UPMC Univ Paris 06, CNRS, UMR 8220, Laboratoire d'archéologie moléculaire et structurale (LAMS), 4 place Jussieu 75005 Paris, France

Jędrzej Musiela
Restauro Sp. z o.o., Torun, Poland

Anna Nowicka
Academy of Fine Arts in Warsaw, Warsaw, Poland
ananow@wp.pl

Michał Obarzanowski
National Museum in Krakow, Al. 3Maja 1, 30-062 Krakow, Poland

Marcin Oszajca
Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Krakow, Poland
oszajcam@chemia.uj.edu.pl

Olga Otłowska
Gdansk University of Technology, Chemical Faculty, Department of Organic Chemistry, Narutowicza 11/12, 80-233 Gdansk, Poland
olgotlow@student.pg.gda.pl

Czesława Paluszkiewicz
Institute of Nuclear Physics, Polish Academy of Sciences, Radzikowskiego 152, 31-342, Krakow, Poland
Czesława.Paluszkiewicz@ifj.edu.pl

Ewelina Pawlak
Muzeum Sztuki in Łódź, Więckowskiego 36, 90-734 Łódź, Poland

Silvia Pedetti
Sorbonne Universités, UPMC Univ Paris 06, CNRS, UMR 8220, Laboratoire d'archéologie moléculaire et structurale (LAMS), 4 place Jussieu 75005 Paris, France
silviapedetti@mac.com

Michał Płotek
Jan Matejko Academy of Fine Arts in Krakow, Faculty of Conservation and Restoration of Works of Art, Smoleńsk 9, 31-108 Krakow, Poland
mplotek@asp.krakow.pl

Maria Poksińska
Nicolaus Copernicus University, Faculty of History, Department for the History of Art and Culture, W. Bojarskiego 1, 87-100 Toruń, Poland
mpoks@umk.pl

Stjepan Prugovečki
PANalytical B.V Twentepoort Oost 26, 7609 RG Almelo, The Netherlands
Stjepan.Prugovecki@panalytical.com

Alicja Rafalska-Łasocha
Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Krakow, Poland
rafalska@chemia.uj.edu.pl

Miguel Ángel Respaldiza
University of Seville (US), Centro Nacional de Aceleradores (CNA), Faculty of Physics, (US), Department of Atomic, Molecular and Nuclear Physics
respaldiza@us.es

Robert Rogal
Nicolaus Copernicus University, Institute for the Study, Restoration and Conservation of Cultural Heritage

Anna Rogulska
Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Krakow, Poland
a.rogulska@uj.edu.pl

Łukasz Sadowski
Devmatech (STOE), Grodkowska 6/109, 01-461 Warszawa, Poland
l.sadowski@devmatech.pl

Steffen Sandner
STOE & Cie GmbH, Hilpertstrasse 10, 64295 Darmstadt, Germany
sandner@stoe.com

Dominika Sarkowicz
National Museum in Krakow, Al. 3 Maja 1, 30-062 Krakow, Poland
domisar@o2.pl

Manuel Sarmento
University of Coimbra, Coimbra, 3030-076 Coimbra, Portugal
sarmento93@sapo.pt

Manfred Schreiner
Academy of Fine Arts, Institute of Science and Technology in Art, Schillerplatz 3, A-1010 Vienna
Vienna University of Technology, Institute of Chemical Technology and Analytics, Getreidemarkt 9, A-1060 Vienna, Austria
m.schreiner@akbild.ac.at

Sariel Shalev
University of Haifa, School of Marine Sciences & Department of Archaeology, Haifa, Israel
sariel.shalev@univ.haifa.ac.il

Anna Sikorska
AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Krakow, Poland

Anna Sobesto
National Museum in Krakow, Al. 3 Maja 1, 30-062 Krakow, Poland
asobesto@muzeum.krakow.pl

Zbigniew Sojka
Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Krakow, Poland
sojka@chemia.uj.edu.pl

Grażyna Stochel
Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Krakow, Poland
stochel@chemia.uj.edu.pl

Szymon Stolarek
Panalytical B.V. Sp. z o. o. Oddział w Polsce, Patriotów 303, 04-767 Warszawa, Poland
szymon.stolarek@panalytical.com

Marcin Strojecki
Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Niezapominajek 8, 30-239 Krakow, Poland

Sylwia Svorová Pawełkowicz
Academy of Fine Arts in Warsaw, Faculty of Conservation and Restoration, Wybrzeże Kościuszkowskie 37, 00-379 Warsaw, Poland
s.pawelkowicz@labko.pl

Magdalena Śliwka-Kaszyńska
Gdansk University of Technology, Chemical Faculty, Department of Organic Chemistry, Narutowicza 11/12, 80-233 Gdansk, Poland

Krzysztof Świentek
AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Krakow, Poland

Piotr Targowski
Nicolaus Copernicus University in Toruń, Institute of Physics, Grudziądzka 5, 87-100 Toruń, Poland
ptarg@fizyka.umk.pl

Filippo Terrasi
Second University of Naples, Department of Mathematics and Physics
filippo.terrasi@unina2.it

Grzegorz Trykowski
Nicolaus Copernicus University, Faculty of Chemistry, Torun, Poland

Wilfried Vetter
Academy of Fine Arts, Institute of Science and Technology in Art, Schillerplatz 3, A-1010 Vienna, Austria

Mirosław Wachowiak
Nicolaus Copernicus University in Torun, Department of Conservation and Restoration of Modern Art, Gagarina 11, 87-100, Torun, Poland
miroszwach@wp.pl

Małgorzata Walczak
Jan Matejko Academy of Fine Arts in Krakow, Faculty of Conservation and Restoration of Works of Art, Smoleńsk 9, 31-108 Krakow, Poland
mwalczak@asp.krakow.pl

Philippe Walter
Sorbonne Universités, UPMC Univ Paris 06, CNRS, UMR 8220, Laboratoire d'archéologie moléculaire et structurale (LAMS), 4 place Jussieu, 75005, Paris, France
philippe.walter@upmc.fr

Władysław Weker
State Archaeological Museum in Warsaw, Długa 52, 00-241, Warsaw, Poland
wweker@poczta.onet.pl

Piotr Wiącek
AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Krakow, Poland

Renata Wietecha-Posłuszny
Jagiellonian University, Faculty of Chemistry, Laboratory of Forensic Chemistry, Ingardena 3,
30-060 Krakow, Poland

Małgorzata Witko
Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Niezapominajek 8,
30-239 Krakow, Poland
ncwitko@cyf-kr.edu.pl

Paweł Wróbel
AGH University of Science and Technology, Al. Mickiewicza 30,
30-059 Krakow, Poland
Pawel.Wrobel@fis.agh.edu.pl

Marta Zaborowska
Academy of Fine Arts in Warsaw, Faculty of Conservation and Restoration of Works of Art,
Wybrzeże Kościuszkowskie 37,
00-379 Warsaw, Poland
zabor.mart@gmail.com

Jan Žemlička
Czech Technical University in Prague, Institute of Experimental and Applied Physics, Horská 3a/22,
128 00 Praha 2, Czech Republic

Anna Żurek
GOREK RESTAURO sp. z o. o. spółka komandytowa, Ruskowy Bród 79a,
03-289 Warszawa, Poland
akeruza@gmail.com

Graphic design
and print preparation:
Marta Grzesiak-Nowak
marta.grzesiak86@gmail.com



Organized by:

Faculty of Chemistry Jagiellonian University

National Museum in Krakow

Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences

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