

7th Meeting 'X-ray and other techniques in investigations of the objects of cultural heritage'

Celebrating the Centenary of Regaining Independence of the Republic of Poland

Krakow 17–19 May 2018

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

Krakow, 17–19 May 2018

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PROGRAMME

7th Meeting X-ray and other techniques in investigations of the objects of cultural heritage

17 May, Thursday,
Faculty of Chemistry, Jagiellonian University in Krakow, Gronostajowa 2

8.00−10.00 Registration

10.00−10.15 **Opening – Welcoming remarks**

Session 1. Chair: Wiesław Łasocha, Faculty of Chemistry, Jagiellonian University in Krakow, Poland

10.15−11.00 Invited lecture – SR-XRF AND SR-XRD OF HISTORIC PIGMENTS AND METALS – Manfred Schreiner, Florian Bausch, Klaudia Hradil, Institute of Science and Technology in Art, Academy of Fine Arts Vienna, Institute of Chemical Technologies and Analytics, Technische Universität Wien, X-Ray Center, Technische Universität Wien, Austria

11.00−11.30 WHAT WE KNOW, BUT WHICH CANNOT BE SEEN. HIGHLIGHTS OF NEW RESEARCH ON THE WORKS OF HENRYK SIEMIRADZKI OBTAINED USING ANALYTICAL RADIATION TECHNIQUES − **Dominika Sarkowicz**, Marzena Sieklucka, Michał Obarzanowski, Piotr Frączek, National Museum in Krakow, Poland

11.30−11.50 UTRECHT CARAVAGGISTI PAINTING TECHNIQUE IDENTIFIED BY X-RAY RADIOGRAPHY, XRF AND SEM-EDS ANALYSES − **Mateusz Jasiński**, Academy of Fine Arts in Warsaw, Faculty of Conservation and Restoration of Works of Art, Poland

11.50−12.10 LA INMACULADA UNDER EXAMINATION BY XRF AND OTHER TECHNIQUES − **Anabelle Kriznar**, Auxiliadora Gómez Morón, Lourdes Núñez Casares, Eugenio Fernández Ruíz, Gabriel Ferreras Romero, Lourdes Martín, Miguel Ángel Respaldiza, Centro Nacional de Aceleradores (CNA), University of Seville, Instituto Andaluz de Patrimonio Histórico (IAPH), Seville, Department of Sculpture and Art Theory, Faculty of Fine Arts University of Seville, Spain

12.10−12.30 A MULTI−ANALYTICAL APPROACH TO THE CHARACTERIZATION AND PROVENANCE STUDY OF THE MEDIEVAL PANEL PAINTING "THE FIVE SORROWS OF MARY" IN REFERENCE TO NICOLAUS HABERSCHRACK'S WORKS − **Anna Klisińska-Kopacz**, Piotr Frączek, Michał Obarzanowski, Karolina Budkowska, Agnieszka Patała, Laboratory of Analysis and Non−Destructive Investigation of Heritage Objects, National Museum in Krakow, National Museum in Wrocław, Poland

12.30−13.00 APPLICATION OF NIR SPECTROSCOPY TO WORKS OF ART − **Szymon Stolarek**, Malvern Panalytical B.V., Warsaw, Poland

13.00−14.00 Lunch break

Session 2. Chair: Julio del Hoyo−Meléndez, Laboratory of Analysis and Non−Destructive Investigation of Heritage Objects, National Museum in Krakow, Poland

14.00−14.30 XRD STUDY OF BEHAVIOUR OF Pb AND Zn OXIDE PIGMENTS WITH DIFFERENT OILS − **Eva Kočí, Petr Bezdička**, Silvia Garrappa, Jiří Plocek, Silvie Švarcová, Institute of Inorganic Chemistry of the Czech Academy of Sciences, ALMA Laboratory, Czech Republic

14.30−15.00 DETECTION OF MgO HYDRATION AND CARBONIZATION PRODUCTS IN ALTERED DOLOMITIC BINDERS USING XRD AND DTA − **Inta Kirilovica**, Lauma Lindina, Riga Technical University, Institute of Silicate Materials, Latvia

15.00−15.20 TWO HOARDS OF PRAGUE GROSCHEN FROM LOWER SILESIA: CONFRONTATION OF ROYAL LAW WITH COINAGE PRACTICE BASED ON THE RESULTS OF ARCHAEOMETRIC RESEARCH − **Beata Miazga**, Paweł Milejski, Institute of Archaeology, University of Wroclaw, Poland

15.20−15.40 AUTHENTICATION OF ANCIENT ARROW HEADS USING POWDER X-RAY DIFFRACTOMETRY AND SCANNING ELECTRON MICROSCOPY − **Michał Duda**, Marcin Oszajca, Wiesław Łasocha, Jagiellonian University, Faculty of Chemistry, Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, Poland

15.40−16.00 Coffee break

16.00−17.00 POSTER SESSION

1. USING THE XRF METHOD TO CHARACTERIZATION OF SILVER CROWN HALF-GROSCHEN OF WŁADYSŁAW JAGIEŁŁO − **Ewa Pańczyk**, Joachim Kierzek, Lech Waliś, Michał Zawadzki, Maciej Widawski, Władysław Weker, Institute of Nuclear Chemistry and Technology, Royal Castle in Warsaw, National Archeological Museum, Warsaw, Poland

2. PIXE ANALYSIS OF MEDIEVAL SILVER COINS − **Ewa Pańczyk**, Lech Waliś, Imre Kovács, Zoltán Szőkefalvi−Nagy, Maciej Widawski, Władysław Weker, Institute of Nuclear Chemistry and Technology, Wigner Research Centre for Physics, Hungarian Academy of Science, National Archeological Museum, Warsaw, Poland

3. PALACE OF THE BISHOPS OF KRAKOW IN KIELCE UNDER THE MICROSCOPE − **Sylwia Svorová Pawełkowicz**, Małgorzata Misztal, Barbara Wagner, Biological and Chemical Research Centre, University of Warsaw, Palace of the Bishops of Krakow, Branch of the National Museum in Kielce, Faculty of Chemistry, University of Warsaw, Poland

4. SMELLY MISTERY UNCOVERED. TRACING THE LINK IN THREE HISTORIC MOSAIC MORTARS − **Pavla Bauerová**, Magdalena Kracík Štorkánová, Martin Keppert, Milena Pavlíková, Lenka Scheinherrová, Petr Svora, Alberto Viani, UCEEB and Faculty of Civil Engineering, Czech Technical University in Prague, Institute of Physics ASCR, v.v.i., Art & Craft Mozaika, z.s., ITAM ASCR, v.v.i., Centre of Excellence Telč, Czech Republic

5. PAINTINGS OF MIECZYSŁAW SZYMAŃSKI − ANALYSIS OF PAINT LAYERS − **Anna Nowicka**, Academy of Fine Arts in Warsaw, Poland

6. APPLICATION OF XRPD TO THE STUDY OF PIGMENTS FROM PAINTINGS ON THE MEDIEVAL STAINED-GLASS PANELS IN DOMINICAN MONASTERY IN KRAKOW − **Alicja Rafalska-Łasocha**, Marta Grzesiak-Nowak, Edyta Bernady, Małgorzata Walczak, Wiesław Łasocha, Faculty of Chemistry, Jagiellonian University in Krakow, Faculty of Conservation and Restoration of Works of Art, Jan Matejko Academy of Fine Arts in Krakow, Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, Poland

7. METHODS OF RESEARCH ON PAINTINGS IN THE STATE RESEARCH AND RESTORATION WORKSHOPS IN THE PERIOD OF 1930-1970 − **Daria Petlina**, Monument and Museum Studies Centre of the National Academy of Sciences of Ukraine, Ukrainian Society of Protection of Monuments of History and Culture, Ukraine

8. BIOMINERALIZATION OF $CaCO_3$ FOR THE PROTECTION AND RESTORATION OF HISTORIC STONE MATERIALS − **Barbara Krajewska**, Kinga Raczak, Małgorzata Krzeczkowska, Jagiellonian University, Faculty of Chemistry, Cracow University of Technology, Faculty of Architecture, Poland

9. PDF−4+ DATABASE AS A POWERFUL TOOL IN INVESTIGATION OF OBJECTS OF CULTURAL HERITAGE − **Marcin Kozieł**, Wiesław Łasocha,

Jagiellonian University, Faculty of Chemistry, Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, Poland

10. GUNPOWDER FIREARMS − A PASSION FOR ANCIENT WEAPONS OR FOR CRIMES? − **Zuzanna Brożek-Mucha**, Kacper Jurek, Institute of Forensic Research, Faculty of Law and Administration, Jagiellonian University, Poland

11. THE OLDEST COLOR LAYERS IN THE DOMINICAN CONVENT OF ST. NICHOLAS CHURCH IN KAMIANETS PODILSKYI IN UKRAINE. PRESENTATION OF THE RESULTS OF THE FIRST STAGE OF RESEARCH − **Anna Kudzia**, Academy of Fine Arts in Warsaw, Faculty of Conservation and Restoration of Works of Art, Poland

12. DIAGNOSTIC TECHNIQUES OF ANCIENT EGYPTIAN METALS ARTIFACTS IN THE GRAND EGYPTIAN MUSEUM - CONSERVATION CENTRE (GEM-CC) − **Abdelaziz Elmarazky**, The Grand Egyptian Museum-Conservation Centre (GEM-CC), Egypt

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18 May, Friday,
Faculty of Chemistry, Jagiellonian University in Krakow, Gronostajowa 2

Session 3. Chair: Roman Kozłowski, Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, Poland

9.00–9.45 Invited lecture – NON-INVASIVE CHEMICAL IMAGING OF PAINTING SURFACES: AN OPPORTUNITY FOR NEW INTERDISCIPLINARY RESEARCHES IN ART HISTORY– Philippe Walter, Sorbonne Université, Laboratoire d'Archéologie Moléculaire et Structurale (LAMS), France

9.45−10.15 PERFORMANCE AND APPLICATIONS OF FULL-FIELD XRF IMAGING SYSTEM FOR NON-INVASIVE INVESTIGATION OF ARTWORKS − **Bartłomiej Łach**, Tomasz Fiutowski, Piotr Frączek, Stefan Koperny, Marek Lankosz, Agata Mendys, Bartosz Mindur, Krzysztof Świentek, Piotr Wiącek, Paweł Wróbel, Władysław Dąbrowski, AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, The National Museum in Krakow, Laboratory of Analysis and Non-Destructive Investigation of Heritage Objects, Poland

10.15−10.45 Coffee break

10.45−11.15 COMPREHENSIVE ANALYSIS OF MANUSCRIPTS. SYSTEMATIC STUDY OF COPTIC INKS − **Tea Ghigo**, Zina Cohen, Grzegorz Nehring, Olivier Bonnerot, Oliver Hahn, Paola Buzi, Ira Rabin, University of Rome La Sapienza, Centre for the Study of Manuscript Cultures - University of Hamburg, Bundesanstalt für Materialforschung und –prüfung (BAM), Ecole Pratique des Hautes Etudes (EPHE), Laboratoire SAPRAT, Nicolaus Copernicus University, Department of Paper and Leather Conservation

11.15−11.45 X-RAY FLUORESCENCE ANALYSIS OF BLACK MEDIEVAL INKS: CHARACTERIZATION AND INTERPRETATION. CASE STUDY OF AN 11TH CENTURY EGYPTIAN CORPUS − **Zina Cohen**, Judith Schlanger, Ira Rabin, Ecole Pratique des Hautes Etudes (EPHE), Laboratoire SAPRAT, Bundesanstalt für Materialforschung und -prüfung (BAM), Universität Hamburg UHH, Germany

11.45−12.10 CAN AN INKWELL LEAK INTO INK? COMPARISON OF THE PERFORMANCE OF VARIOUS XRF SPECTROMETERS AND THE QUALITATIVE AND SEMI-QUANTITATIVE ANALYSIS OF AGED IRON-GALL INK SAMPLES − **Grzegorz Nehring**, Ira Rabin, Piotr Targowski, Nicolaus Copernicus University, Department of Paper and Leather Conservation, Bundesanstalt für Materialforschung und -prüfung (BAM), Department of Analysis of Cultural Artefacts, Nicolaus Copernicus University, Department of Physics, Poland

12.10−12.40 EX SITU AND IN SITU APPROACH TO EVALUATING CHANGE IN CRYSTALLINITY OF *BOMBYX MORI* SILK FIBROIN DURING ARTIFICIAL THERMO-AGEING − **Monika Aksamit-Koperska**, Maciej Sitarz, Joanna Łojewska, Ewa Bulska, Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw, AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Jagiellonian University, Faculty of Chemistry, Poland

12.40−14.00 Lunch break

Session 4. Chair: Petr Bezdička, Institite of Inorganic Chemistry of the CAS, ALMA Laboratory, Czech Republic

14.00−14.30 Invited lecture – MAGRITTE ON PRACTICE: FINDING LOST COMPOSITIONS BY NON-INVASIVE TECHNIQUES – **David Strivay,** Catherine Defeyt, Francisca Vandepitte, Frederik Leen, Elodie Herens, UR Art., Archéologie, Patrimoine, Université de Liège, Belgium, Royal Museums of Fine Arts of Belgium, Belgium

14.30−14.50 SZYMON CZECHOWICZ'S PALETTE IN THE LIGHT OF INTERDISCIPLINARY TECHNICAL INVESTIGATIONS − **Ewa Doleżyńska-Sewerniak**, Faculty of History, Department of the History of Art and Culture, Nicolaus Copernicus University in Torun, Poland

14.50−15.20 TECHNICAL EXAMINATION AND DEVELOPMENT OF A PREVENTIVE CONSERVATION STRATEGY FOR A COLLECTION OF ARTWORKS BY STANISŁAW WYSPIAŃSKI − **Julio M. del Hoyo-Meléndez**, Agnieszka Marecka, Michał Płotek, Joanna Sobczyk, Anna Klisińska-Kopacz, Piotr Frączek, Łucja Skoczeń-Rąpała, Laboratory of Analysis and Non-Destructive Investigation of Heritage Objects, National Museum in Krakow, Paper and Leather Conservation Studio, National Museum in Krakow, Department of Conservation Chemistry and Physics, Jan Matejko Academy of Fine Arts, Poland

16.00−18.00 Visit to the National Museum in Krakow − WYSPIANSKI and Lady with an Ermine by Leonardo da Vinci

18.30−22.00 Conference dinner in Collegium Novum

22.00 − 15th Museum Night in Krakow

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19 May, Saturday,
Faculty of Chemistry, Jagiellonian University in Krakow, Gronostajowa 2

Session 5. Chair: Manfred Schreiner, Institute of Science and Technology in Art, Academy of Fine Arts Vienna, Institute of Chemical Technologies and Analytics, Technische Universität Wien, Austria

9.00−9.40 Invited lecture – SYNCHROTRON-BASED X-RAY AND INFRARED MICRO-ANALYSIS OF ARTISTIC MATERIALS AT THE ID21 BEAMLINE, ESRF – Marine Cotte, ID21, European Synchrotron Radiation Facility, Grenoble, Laboratoire d'Archéologie Moléculaire et Structurale (LAMS), France

9.40−10.00 STUDIES OF METAL ARTIFACTS FROM VARIOUS AGES USING SYNCHROTRON RADIATION AND NEUTRONS − **Roman Senin**, Elena Tereschenko, Ekaterina Yatsishina, Alexandr Blagov and Mikhail Kovalchuk, NRC „Kurchatov Institute", FSRC „Crystallography and Photonics" RAS, Russia

10.00−10.20 COMPREHENSIVE INVESTIGATIONS OF CULTURAL HERITAGE OBJECTS IN THE NRC KURCHATOV INSTITUTE: FROM EGYPTIAN MUMMIES TO MEDIEVAL CERAMICS − **Elena Tereschenko**, Ekaterina Yatsishina, Pavel Kashkarov, Mikhail Kovalchuk, FSRC „Crystallography and Photonics" RAS, NRC „Kurchatov Institute", Lomonosov MSU, Russia

10.20−11.00 Invited lecture − SYNCHROTRON SOLARIS − PRESENT AND FUTURE RESEARCH OPTIONS − Marek Stankiewicz, SOLARIS National Synchrotron Radiation Centre, Jagiellonian University, Poland

11.00 – Coffee break

11.30–13.00 Visit to the National Synchrotron Radiation Centre SOLARIS

13.00−14.00 Lunch

14.00 − Closing of the meeting and free time for an individual walk along the Wyspiański's route in Krakow city centre

ABSTRACTS

ORAL PRESENTATIONS

SR-XRF AND SR-XRD OF HISTORIC COINS AND PIGMENTS

Manfred Schreiner[1,2], **Florian Bausch**[2], **Klaudia Hradil**[3]

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Among the great variety of instrumental techniques, which have been applied for studying the elemental composition of objects of art and archaeology, X-ray fluorescence analysis (XRF) has gained growing interest. The method has the advantage of detecting in principle all elements (except H and He) of the periodic table and handheld instruments are available on the market nowadays, which can be brought into collections or to an archaeological site. Unfortunately, when measurements are taken in air, only elements with an atomic number higher than approx. 16 (sulfur) can be detected. Also for the full quantitative analysis including minor and trace components, which are in many cases indispensable for the determination of the provenance of an artifact, investigations by means of scanning electron microscopy in combination with energy dispersive X-ray micro-analysis (SEM/EDX) or XRF using synchrotron radiation is meaningful.

Using XRF, only the elements present can be determined and no compound specific or crystallographic information is obtained. Therefore, e.g. in the case of calcium carbonate ($CaCO_3$), which was mainly used as ground material in paintings or polychromed sculptures, no differentiation between the three modifications calcite, vaterite or aragonite can be gained. Also mixtures of inorganic pigments can hardly be completely characterized; e.g. the detection of lead (Pb) in a red paint layer indicates the presence of red lead (minium), but mixtures of this red pigment with lead white cannot be clearly identified by just XRF. Therefore, X-ray diffraction techniques are

promising complementary methods, as such investigations are non-destructive, which means that the sample material is preserved for further investigations.

In the presentation, an overview of SY-XRF applied to Roman and Byzantine coins as well as cross-sections of paintings by Peter Paul Rubens will be presented and the application of SEM/EDX, SY-XRF, SY-XRD, and XRD with micro-focused beam in a commercial instrument will be discussed.

References

[1] B. Hochleitner, M. Schreiner, M. Drakopoulos, I. Snigireva, A. Snigirev: *Analysis of paint layers by light microscopy, scanning electron microscopy and sychrotron induced x-ray micro diffraction.* In: R. Van Grieken, K. Janssens: Cultural Heritage Conservation and Environmental Impact Assessment by Non-Destructive Testing and Micro-Analysis, Balkema publishers 2005. pp. 171-182.

[2] M. Rodrigues, F. Cappa, M. Schreiner, P. Ferloni, M. Radtke, U. Reinholz, B. Woytek, M. Alram: *Further metallurgical analyses on silver coins of Trajan (AD 98-117).* Journal of Analytical Atomic Spectrometry, Themed issue: Synchrotron Radiation in Art and Archaeometry 26 (2011) 984-991.

[3] M. Rodrigues, M. Schreiner, M. Melcher, M. Guerra, J. Salomon, M. Radtke, M. Alram, N. Schindel: *Characterization of the silver coins of the Hoard of Beçin by X-ray based methods*. NIM-B: Beam Interactions with Materials and Atoms 269 (2011) 3041-3045.

WHAT WE KNOW, BUT WHICH CANNOT BE SEEN. HIGHLIGHTS OF NEW RESEARCH ON THE WORKS OF HENRYK SIEMIRADZKI OBTAINED USING ANALYTICAL RADIATION TECHNIQUES

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A research project has been underway since 2012 at the National Museum in Krakow. This project intends to increase the understanding of painting techniques used by Henryk Siemiradzki. So far, 67 oil paintings created by the artist have been studied. Each of the works was photographed in different wavelengths of electromagnetic radiation: ultraviolet (UV), near-infrared, and X-radiation. The images provided a great deal of insight into the techniques used to create the paintings, the creative process of the artist, and the materials used. X-ray radiography revealed the stages of creation of the works and the decisions that the artist made while painting, as well as indicating that he often made major or minor changes in the concept while the work was in progress. Thanks to the fact that the artist used lead white, the X-ray images shed light on his brushstroke, methods of building up the paint layers, variety of techniques, and means of expression. A digital X-ray camera system consisting of an Orange 1040HF Portable X-ray unit and a wireless Examion Dix-Ray® Flexible® X-ray detector was used to create the images.

The heterogeneous fluorescence of the painted surface induced by UV radiation, which is characteristic of certain pigments and dyes, made the distribution of these materials visible in the paintings. UV induced fluorescence imaging was conducted using four 40W General Electric F40 Black Light Blue EX lamps, emitting radiation of a wavelength of 368 nm. The use of the ultraviolet radiation in optical microscopy also allowed for a preliminary identification of some pigments in the cross-sections of the samples.

The infrared images taken under radiation of 830-1000 nm wavelength made visible elements of the preparatory drawing and the sketch executed with the use of a brush. This method also revealed traces of the brushstrokes, which helped illustrate the painting technique. In several cases, the infrared images allowed for the discovery of the overpaintings (*pentimenti*) done by the artist. Analytical radiation also revealed a later interference with the structure of the paintings.

The data obtained with the use of non-invasive, analytical radiation not only significantly added to our knowledge of the painting techniques used by Henryk Siemiradzki, but also contributed to the comparative studies of works of uncertain attribution.

UTRECHT CARAVAGGISTI PAINTING TECHNIQUE IDENTIFIED BY X-RAY RADIOGRAPHY, XRF AND SEM-EDS ANALYSES

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In the early 17th century, Catholic artists from the Netherlands travelled to Rome as students and were profoundly influenced by the work of Caravaggio. On their return to the north, this group became known as the "Utrecht Caravaggisti". Caravaggio's painting technique is one of the most investigated of all artists. However, in terms of technique and technology, the analyses of works of his followers look exceptionally poor. The research on Utrecht Caravaggisti paintings was conducted as part of an exploratory project: *Technique and technology of Caravagesques paintings based on Polish museum collections*. The project was financed by National Science Centre (2013/09/N/HS2/02116, PRELUDIUM V).

X-rays allow looking deeper into the structure of Utrecht Caravaggisti paintings and often confirm attributions. Combined with the historical knowledge about procedures and organization of the workshop, they can provide access to the process of creating works, to the stages of preparation and their changes that have left marks in the structure of the object. Elemental composition of paint-layers was determined by means of XRF (X-Ray Fluorescence Spectroscopy). Also the following non-destructive methods were used in the research work: ultraviolet (UV), infrared (IR), photography in visible light (VIS) and various physico-chemical analysis of binders, pigments and dyes. The samples taken from the paintings were also studied and there were interpreted by visible and UV light microscopy and by SEM-EDS analysis.

One of the most important aspects of the technology used by Caravaggio and his followers was the dark colour of the grounds, which gave a significant tone to particular paintings. Artists of Utrecht used a different way of preparing painting substrates. Generally, they used ground laid in two layers,

orange-brown applied first, then gray or gray-brown as the second. The examinations showed that pigments used by the Utrecht Caravaggisti were typical 17th century earth-based pigments. A very interesting part of the palette of the Caravaggisti is the use of white: they used calcium carbonate or chalk as an extender to lead white.

LA INMACULADA UNDER EXAMINATION BY XRF AND OTHER TECHNIQUES

A. Kriznar[1,3], **A. Gómez Morón**[2], **L. Núñez Casares**[2], **E. Fernández Ruíz**[2], **G. Ferreras Romero**[2], **L. Martín**[2], **M.A. Respaldiza**[1]

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Origin and authorship of la *Inmaculada*, known also as *Tota Pulchra*, are unknown, but according to its style, the date can be situated around 1600. It is probably a copy of a painting made by Giuseppe Cesari (1568-1640), an Italian Mannerist painter, much valued in Rome by the popes and high society [1]. Most of his works are conserved in Italy, however one is in the collection of the „Real Academia de Bellas Artes de Santa Isabel de Hungría" in Seville. It was painted around 1600 in the technique of oil on canvas. Recently, the painting was sent to the „Instituto Andaluz de Patrimonio Histórico" for its restoration and material research.

In general, the conservation state of the painting was very poor, principally due to a fracture in the lower part of the canvas, but also due to natural processes of ageing of the materials and to some unfortunate interventions in the past. Therefore, the restoration was principally directed towards removal and reparation of existing damage but also to return to the painting its aesthetic presentation.

During its restoration, material analyses were carried out, in order to identify pigments and painting preparation used by the artist. For this purpose, invasive and non-invasive techniques were used [2], such as UV luminescence to distinguish later interventions, radiography to see the internal structure of the painting, and X-Ray Fluorescence (XRF), used for the identification of inorganic materials. Besides, three samples of colour layers and one of textile fibres from the canvas were extracted and studied by

optical microscope (OM) and scanning electron microscope (SEM) with energy dispersive X-Ray Spectroscopy (EDS). Organic fibers were studied under OM. For identification of organic materials, such as binders, varnishes and lakes, Gas Chromatography with Mass Spectroscopy (GC-MS) and Fourier Transform Infrared Spectroscopy (FTIR) in transmission and in ATR mode were also applied. The XRF was carried out directly in situ, in the restoration workshop. Different colours and tonalities were selected, in order to get the best overview of the materials applied by the artist. The XRF results revealed the use of Ca-based preparation, probably chalk (identified by Ca peaks) with a thin layer of reddish priming, carried out as a mixture of red ochre (Fe) and vermilion (Hg). In the painter's palette, we can also find lead white (Pb), used also for highlighting, yellow ochre (Fe) and lead-tin yellow (Pb, Sn), azurite (Cu) and smalt (K, Co, Ni, As) for blues and a copper based green pigment which was not possible to identify with more precision by XRF; for dark colours umber and bone black were used. Also later interventions were confirmed with the help of the UV light and XRF, which identified the existence of modern pigments (20th century) as titanium white (Ti), cadmium yellow and cadmium red (Cd).

References

[1] Röttgen, H. 2002. *Il Cavalier Giuseppe Cesari d´Arpino.: Un grande pittore nello splendore della fama e nell´inconstanza della fortuna*. Roma: Ugo Bozzi.
[2] Artioli, G. 2010. *Scientific methods and Cultural Heritage: An introduction to the application of materials science to archaeometry and conservation science*. Oxford, New York: Oxford University Press

A MULTI-ANALYTICAL APPROACH TO THE CHARACTERIZATION AND PROVENANCE STUDY OF THE MEDIEVAL PANEL PAINTING "THE FIVE SORROWS OF MARY" IN REFERENCE TO NICOLAUS HABERSCHRACK'S WORKS

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The use of non-destructive and micro-invasive analytical methods together with the knowledge of historic painting technology are very helpful for provenance studies, dating or confirming authorship of paintings.

This study focused on the medieval pentaptych "The Five Sorrows of Mary" from the collection of the National Museum in Wrocław. These paintings were originally the setting of the altar of St. Stanislaus and St. Vincent in the Wrocław Cathedral. The paintings under investigation can be found in the literature as a work created in Wrocław in 1507. However, the paintings were different from those locally produced at that time. They are characterized by unique formal and stylistic features, as well as different composition patterns. The first and fundamental question concerns the doubts of art historians as to whether or not this work was imported from a non-Silesian workshop or if it was an altarpiece created on the territory of Silesia. A challenging issue was to understand the specific construction of these paintings in terms of their materials and artistic techniques.

X-ray fluorescence spectroscopy, infrared spectroscopy, and scanning electron microscopy analyses were conducted to establish the technique and to characterize the pigments and materials used in the paintings. The identified pigments and the information provided by analytical photography (IR, X-ray images) were compared with the results obtained during a detailed examination of twelve panel paintings authored by Nicolaus Haberschrack.

The paintings by Haberschrack are the remains of a retable from the main altar of St. Catharine's Augustinian Church in Krakow.

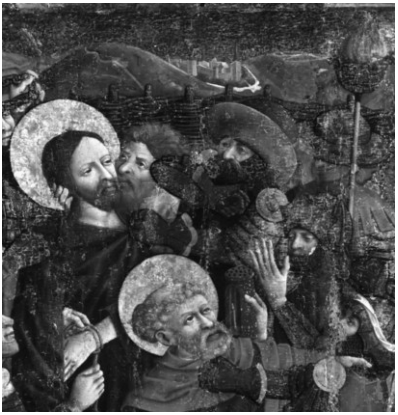
A)  B) 

Fig. 1 Details of two paintings depicting "The Arrest of Christ": A) Wrocław pentaptych B) Nicolaus Haberschrac's retable.

Acknowledgements

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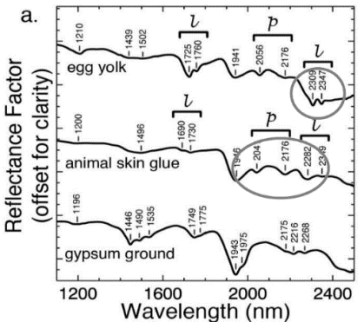
APPLICATION OF NIR SPECTROSCOPY TO WORKS OF ART

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Many different primary analytical methods are used to study properties of artworks or manuscripts. Most are expensive, expert intensive, and time consuming. ASD NIR instruments can be used to transform these primary analytical methods into unified fast and more convenient measurements. For example, there are useful correlations between ASD instrument spectral reflectance measurements and primary analytical techniques for canvas pH and degree of polymerization.

ASD instruments have the added value of being portable and with optimal signal-to-noise design for faster measurements, and wide spectral coverage of 350-2500 nm for a variety of chemical and properties detection possibilities. ASD offers different instrument configurations and many accessory options for a variety of setup and sampling approaches for the most convenient and productive measurement scenarios. ASD NIR instruments are a practical solution to expanding artwork or manuscript analysis opportunities.

One of examples is identifying paint binders on a gypsum ground shown below:



- Egg Yolk: Lipid bands at 2309, 2347, 1725, 1760 nm
- Animal Skin Glue: Amide Protein bands at
- 2056 nm for egg yolk
- 2041 nm for animal skin glue

Fig. 1 Identifying paint binders on gypsum ground

XRD STUDY OF BEHAVIOUR OF Pb AND Zn OXIDE PIGMENTS WITH DIFFERENT OILS

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An oil paint which is composed of pigments, a drying oil and other possible additives has to be initially liquid enough to allow a painter to spread color onto a support. Then it is left to dry. While egg yolk tempera dries by evaporation of water, oil paint "dries" by polymerization of oil into densely cross-linked molecular network. Though it might seem that the system is stable and nothing is happening once a paint has solidified, there are several reactions and interactions under way. One of them is a partial degradation of pigment and leaching of metal ions into the polymer matrix where metal ions can react with fatty acids from oil binder to form metal soaps [1]. These complexes are sometimes considered to play a positive role as anchor points, during paint drying processes on the other hand they are also considered as responsible for many degradation processes (protrusions, efflorescences, loss of color and transparency of a paint layer) [2].

Understanding the mechanism of formation of metal soaps as well as the related degradation phenomena in paint layers is important for evaluation of the risk factors affecting the stability of paintings.

Use of powder X-ray diffraction as a tool for monitoring of early stages of metal soap formation in various model experiments is demonstrated for the model systems of Pb and Zn oxides with several drying oils (linseed, poppy-seed, walnut, linseed standoil). Because of unavailability of suitable structural data in commercial databases, corresponding metal carboxylates were synthesized as reference compounds.

As there is only very limited information on their structural data available in commercial databases, Me (II) carboxylates were synthesized as reference compounds.

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DETECTION OF MgO HYDRATION AND CARBONIZATION PRODUCTS IN ALTERED DOLOMITIC BINDERS USING XRD AND DTA

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Dolomitic binders for mortars have been used since ancient times in the regions where dolomitic rocks are dominant type of carbonates. Dolomitic lime mortars are known to be used in the castles in territory of Latvia [1] (also in Italy, Austria, Spain etc. [2,3]) built till 20th century. Another dolomitic binder produced in such regions as Eastern-Europe, Russia and Northern-America was dolomitic Roman cement, popular in late 19th and early 20th centuries [4,5]. It was a hydraulic binder used in the construction of several significant historical buildings of Latvia [4].

Since the beginning of the 20th century, the manufacturing of dolomitic Roman cement has been stopped. Currently, a dolomitic binder is synthesized that would be suitable for restoration purposes of historical dolomitic Roman cement objects.

The XRD and DTA studies of both historical and newly synthesized binders indicate presence of specific MgO-based crystalline phases. Hydromagnesite and nesquehonite are two characteristic phases found in historic dolomitic binders using XRD. Historic dolomitic binders contain $Mg(OH)_2$ formed as a result of hydration of MgO. The carbonation of $Mg(OH)_2$ is always incomplete due to its low solubility [3]. Formation of magnesium carbonate hydrates (artinite and minerals from hydrotalcite group) are noticed in the newly synthesized binder after 1 year of hardening.

The detection of magnesium carbonate hydrates by XRD is not always possible because of their low state of crystallinity. DTA can be used as an additional method, but it must be taken in account that thermal effects due to dehydration of magnesium carbonate hydrates appear at low temperature range (200-500°C) in which also the dehydration reactions of cement mineral

hydrates and dissociation of clay minerals can occur, leading to overlapping of the effects. Still, chemical analysis and XRD give the most accurate evidence of the dolomitic nature of the binder.

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TWO HOARDS OF PRAGUE GROSCHEN FROM LOWER SILESIA: CONFRONTATION OF ROYAL LAW WITH COINAGE PRACTICE BASED ON THE RESULTS OF ARCHAEOMETRIC RESEARCH

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Prague groschen, as the most accurate realization of the idea of large-size double-sided silver coins in medieval Eastern and Central Europe, which flowed from the Northern regions of Italy, are present also in Silesia. From this region/area, we have over 30 collective finds (hoards) of coins, containing groschen of Charles IV (1346–1378) and Wenceslas IV (1378–1419) [1], among them hoards from Oleśnica (420 coins; *terminus post quem* 1405) and from the area of Walbrzych (1385 coins; *terminus post quem* 1415).

During the long rule of the two rulers from the Luxembourg dynasty – 1346–1419 – new mint laws were implemented. First reform was carried out in the early fifties of the 14th century, the next one in 1378 [2], the following one in 1384 and the last mint regulation dates from 1407 [3]. From the Czech annals, we know the assumptions of all of the mentioned mint ordinances – mint standard and the ratio of silver to copper in the alloy. Thanks to the conducted research of 10% of coins from the hoard from Oleśnica [4] (around 40 groschen) and 10% of coins from the hoard from Wałbrzych (around 140 groschen) we are able to tell, if introduced in the second half of the 14th century and in the first decade of the 15th century mintage regulations were respected in this period in the mint of Kutná Hora, which as the only one at this time was striking Prague groschen.

In realizing this aim, chemical analyses were performed. Due to the huge historic value, the studies of the coin-alloy were done by non-destructive or less invasive analytical methods. The corrosion layers present on the Prague groschen have been studied by spectroscopic tools (Fourier transform infrared spectroscopy and X-ray diffraction). The results pointed to the long-term deposition of the collections/objects in soil and confirmed their

archaeological context. However, the general diagnostic tool was energy-dispersive X-ray fluorescence spectroscopy [5], conducted on the prepared the metallic surface as well as the coin-edge, which allowed the representative areas of the coin's alloy to be analysed.

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AUTHENTICATION OF ANCIENT ARROWHEADS USING POWDER X-RAY DIFFRACTOMETRY AND SCANNING ELECTRON MICROSCOPY

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Powder X-Ray Diffraction (PXRD) is an important technique which allows crystal phase analysis of polycrystalline materials such as historical pigments [1], metals and alloys [2], as well as products of their degradation. Several computer programs connected with crystallographic databases (such as PDF, COD, ICSD) allow performing not only qualitative but also quantitative analysis of crystalline material composition. Results obtained from PXRD measurements can be supported by Scanning Electron Microscopy (SEM) for imaging surface details and elemental composition and distribution [2] using characteristic X-ray radiation generated through the interaction of the electron beam with the studied sample.

In this study, eight ancient metal arrowheads from the Black Sea areas were investigated (Fig. 1). Five of them were assumed (after consulting with a specialist) to be authentic bronze archeological artifacts (Fig. 1b) and the authenticity of the remaining three was disputable (Fig. 1a). To work out the problem of authenticity, X-ray diffraction patterns of all of the objects were collected (PanAlytical X'Pert powder diffractometer) and analyzed (HighScore equipped with PDF-4+ diffraction database) for qualitative and semi-quantitative analysis of the materials that the objects consisted of. To overcome difficulties with phase analysis based on the measured patterns, SEM measurements were carried out. The supplementary technique provided not only confirmation of conclusions from PXRD but also the possibility of surface topography comparison between the samples. Results for the three arrowheads of uncertain authenticity were compared with the results

collected for the ones taken as authentic. Additionally, the research helped to confirm the assumption of originality of the five arrowheads.

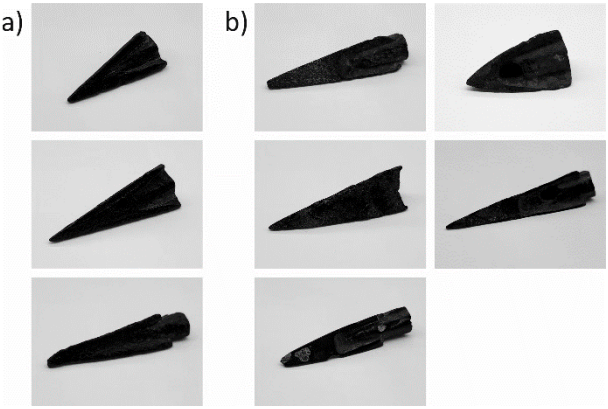


Fig. 1 a) three objects of disputable authenticity; b) arrowheads assumed to be authentic

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NON-INVASIVE CHEMICAL IMAGING OF PAINTING SURFACES: AN OPPORTUNITY FOR NEW INTERDISCIPLINARY RESEARCHES IN ART HISTORY

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The precious character of cultural heritage artifacts and their uniqueness imply particular cautions and require instruments, which may give the maximum of information directly on the objects, in-situ in the museums or in the archaeological sites. The implementation of new analytical tools, including mobile instruments, allows a deep insight into the archaeological and artistic materials. We will show applications of different mobile instruments we built recently in the laboratory to be used in challenging work environments like Egyptian tombs and to allow in situ characterization of artistic materials:

- In the Egyptian, Greek and Roman antiquity, buildings, tombs and statues were often painted in brightest colors. Only few traces of this splendor remain today on marbles, but their study allows gaining insight in this world of antique polychromy. XRF and Visible-NIR hyperspectral imaging techniques allow traces of pigments different in elemental composition from the marble support or surface contaminations to be clearly visualized.
- The impressionists are renowned for their painting technique and their approach to capturing the effects of light in nature through a new use of color. We will show on a Gustave Caillebotte painting that high spatial resolution chemical data measured with a new full field X-ray fluorescence imaging instrument reveal a complex use of pigments and the formation of alteration products, and help to understand the artist's choice of materials and their manipulation with small and thin brushstrokes.

PERFORMANCE AND APPLICATIONS OF FULL-FIELD XRF IMAGING SYSTEM FOR NON-INVASIVE INVESTIGATION OF ARTWORKS

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Analysis of the spatial distribution of elements on the heritage objects, using X-ray fluorescence spectroscopy, has become a very important support for conservators in recent years. Elemental mapping offers possibility to study spatial distributions of pigments on the surface of artworks and in the hidden painting layers.

In this work, we present the design and performance of a novel full-field XRF imaging system developed in a collaboration between the Faculty of Physics and Applied Computer Science of the AGH University of Science and Technology and the Laboratory of Analysis and Non-Destructive Investigation of Heritage Objects of the National Museum in Kraków. Compared to commercially available scanning macro-XRF systems using detectors with no position sensitivity, the full-field XRF technique is based on a pinhole camera and a large area position-sensitive and energy dispersive detector. Thus, XRF radiation from large area of an investigated object is simultaneously projected on the detector and such a technique has a number of advantages:

- it offers shorter measurement times,
- the pine-hole camera can be adjusted to optimise the measurement procedure, making a compromise between the spatial resolution and the measurement time,
- fast-moving measuring head is eliminated, which is an important aspect for safety of the investigated objects,

- the infinite depth of field of the pinhole camera allows one to investigate non-flat objects.

Our system is equipped with two Varian VF-50J low power air-cooled X-ray tubes and employs 10cm × 10cm Gas Electron Multiplier (GEM) detector, custom developed Application Specific Integrated Circuits, and custom developed readout and data acquisition system [1]. Moderate energy resolution of GEM detectors limits elemental selectivity of the system, however, by optimization of the front-end electronics and detector readout significant improvement of the energy resolution has been achieved compared to typical values reported in the literature [2].

Performance of the detection system and results of elemental mapping obtained with the developed apparatus are presented. The imaging measurements have been performed on several phantoms painted with different pigment compositions. Some selected imaging results are presented and discussed, including images of non-flat and spatial objects.

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COMPREHENSIVE ANALYSIS OF MANUSCRIPTS. SYSTEMATIC STUDY OF COPTIC INKS

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While studying the socio-geographic history of inks, division 4.5 of the BAM (Bundesanstalt für Materialforschung und Prüfung) together with the Centre for the Study of Manuscript Cultures in Hamburg has developed a protocol for ink analysis. It consists of a primary screening to determine the type of the ink, and a subsequent in-depth analysis using several spectroscopic techniques. The XRF elemental analysis aims primarily at understanding the fingerprints of inks containing metals, making it possible to distinguish among different inks.

Our own research aims primarily at recreating a socio-geographic history of inks, parchment, and papyrus and includes the comparative analysis of the writing materials of the Dead Sea Scrolls, ink and papyrus in Ancient and Hellenistic Egypt, and inks in documents from various contemporary medieval communities in Fustat (first nucleus of Cairo). During many years of study, we concluded that the continuous production of Coptic manuscripts from late Antiquity to the Middle Ages offers a unique opportunity for historical study of the ink in a large geographic area. Thanks to the collaboration with the ERC project "PAThs" (www.paths.uniroma1.it), based at the University of Rome La Sapienza, and within the activities of a PhD research dedicated to this topic, we therefore created a new branch of our project focused entirely on the analysis of Coptic inks, pigments, and dyes. This pioneering systematic study of writing materials coming from a specific area and time frame (5th-10th century) aims not only at a better understanding of the complex Coptic

multicultural and plurilingual society, but also and mainly at clarifying the links among the Coptic and other societies between the ancient and medieval eras. Finally, it will cast light on the history of the technological development of inks in the eastern world, from Antiquity to the Middle Ages.

X-RAY FLUORESCENCE ANALYSIS OF BLACK MEDIEVAL INKS: CHARACTERIZATION AND INTERPRETATION. CASE STUDY OF AN 11TH CENTURY EGYPTIAN CORPUS

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This study focuses on the analysis of a corpus of manuscripts found in Fustat (medieval Cairo, Egypt) in the biggest medieval "archive" found until now: the Cairo Geniza. The giant collection of mostly Jewish documents has been attracting scholars' attention a lot but so far, the material aspects of these documents seem to have been mainly neglected.

Application of scientific methods of analysis, especially X-Ray fluorescence characterization, contributes to our understanding of the materials used for production of manuscripts during the Middle Ages.

Our corpus of the 11th century manuscripts comprises manuscripts written by scribes belonging to three Jewish communities that co-existed in Cairo during this period: the Karaites, the so-called Jerusalemites (or Palestinian) and the so-called Babylonians (or Iraqi), three different communities with different traditions and different leaders. The differences manifest themselves also in the paleographical properties of the manuscripts produced within each community. Can we extend the differences detected by the paleographical analysis to differences in composition of the writing materials and especially the composition of the inks? Or can we relate the differences in the composition to the manuscript type (legal, private...), or to another criterion. In this presentation, we offer answers to some of the questions using statistical analysis of the measurements results.

CAN AN INKWELL LEAK INTO INK? COMPARISON OF THE PERFORMANCE OF VARIOUS XRF SPECTROMETERS AND THE QUALITATIVE AND SEMI-QUANTITATIVE ANALYSIS OF AGED IRON-GALL INK SAMPLES

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X-ray fluorescence analysis, due to its non-destructive nature and its suitability to work with historic objects *in situ*, quickly became one of the most important methods for the evaluation of iron-gall ink. The main advantage of this qualitative and semi-quantitative method is that it makes it easy to differentiate between inks, based on the assumption that the differences result from the manufacture of the ink.

This work explores the question whether the ink 'fingerprint' results strictly from the elemental composition of the basic ink ingredients even if it is stored in vessels made of metals or metal alloys. In addition, we tested and compared the performance of three different XRF spectrometers.

We prepared various lab-grade inks according to historical ink recipes and measured the metal content of the ink deposited on sized cotton linters paper with three types of XRF spectrometers: a simple hand-held device with an interaction spot of 4 mm and two devices equipped with poly-capillary X-ray optics for line scanning and imaging. Since the exact elemental mass composition of the non-aged ink samples was known, we were able to evaluate the accuracy of the research procedure. Lab-grade inks were then aged in the metal jars imitating inkwells. The aging of the inks in the metal containers resulted in the significant change of the primary inks fingerprint as opposed to that of the control inks stored in glass containers. This effect was independently confirmed by the measurements conducted with every instrument we used. We will present a brief comparison of the results

achieved when using different spectrometers and a possible hypothesis explaining the processes that occurred.

EX SITU AND IN SITU APPROACH TO EVALUATING CHANGE IN CRYSTALLINITY OF *BOMBYX MORI* SILK FIBROIN DURING ARTIFICIAL THERMO-AGEING

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Preservation or heritage science combine a great variety of other fields connected with science and art. Decisions on the conservation of artefacts cannot be made without both thorough physicochemical analyses leading to the determination of degradation mechanisms and historic information on composition handling and manufacturing process. A direct motivation of our study was a call for the immediate conservation intervention of precious, 16th century silk banners from the storage resources of the Wawel Royal Castle in Krakow, Poland.

As a semi-crystallite, silk is degraded mainly by hydrolysis and oxidation of peptide bonds, which may lead to a decrease of polymerization degree and formation of new functional groups on the polypeptide chain together with liberation of volatile products and recrystallisation. Accelerated aging tests are the most commonly accepted method for studying the mechanisms of degradation of various materials including silk's fibroin. Therefore light or/and temperature, various gaseous agents and degrees of humidity are found to be used as aging stimuli [1]. Those are supposed to lead to the changes that reflect naturally occurring degradation reactions.

In our previous work [1], concentrated on the details of the degradation estimators change upon thermal-degradation, we have verified FTIR derived estimators by XRD, SEC, and UV-Vis techniques. In this way, 3 verified degradation markers were put forward, amongst which was the crystallinity

estimator (Ec_{FTIR}). These were then used to analyse the condition of 10 historical samples dating from 16th to 19th century [2]. For historical samples, the crystallinity estimator showed incorrelatable with time trends. This raised our suspicion on the nature of the changes provoked during artificial and natural ageing processes and called for further analyses of crystallinity degree upon ageing.

In order to look into fibroin's degradation process, we have concentrated our efforts on analysing the thermo-induced and naturally occurring degradation with the means of XRD and ATR-FTIR. But because we wanted to eliminate irreproducibility of the test-spots on our samples during *ex situ* tests, we have made an attempt at observing degradation *in situ*. Therefore we juxtaposed two methods:

- *ex situ* ageing in ageing chamber and closed vials;
- *in situ* ageing in airflow and argon flow conditions on a hot plate of ATR/FTIR or XRD device.

Detailed analysis of the *ex situ* and *in situ* experiments has revealed differences in the simulated ageing process. *Ex situ* technique of thermo-aging was shown to provoke breaking of β-sheets into networking α-helix arrangements not into the amorphous degradation products as produced naturally. *In situ* experiments were proven to provoke opposite to natural changes. The β-sheet content seems to grow in time and this is compensated with the amorphous domains decrease. FTIR analysis verified that, unlike *ex situ*, in the *in situ* degradation takes place through a decrease of the parallel, in favour of perpendicular amid I crystalline vibrations in the crystalline region of the polypeptide.

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MAGRITTE ON PRACTICE: FINDING LOST COMPOSITIONS BY NON-INVASIVE TECHNIQUES

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The "Magritte on practice" project aims to throw a new light on the oil painting production of René Magritte (1898 - 1967), through the prisms of technical art history and conservation science. Despite the abundant literature devoted to the most famous Belgian surrealist painter, the materiality of the produced works remains poorly documented. Magritte himself was always reluctant to talk about the painting techniques and materials he used. However those practical concerns embody an integral part of his artistic personality and condition the preservation and the transmission his work. The material and technical study of a large panel of Magritte's oil paintings, through scientific tools addresses multiple issues. Indeed, the precarious financial situation of Magritte between 1920 and 1935, had led him to regularly reuse canvases from earlier compositions. One can therefore reasonably assume the presence of overpainted compositions among the works covering this period. This project proposes to investigate, in situ, forty-two Magritte's oil paintings made between 1921 and 1963, from the MRBAB collection, by means of non-invasive scientific imaging and analytical methods. The objective of this research project is to collect all the technical and compositional information, necessary to formulate substantiated conclusions about the art history, technical art history and conservation issues addressed by Magritte's oil painting production.

We will present the methodology used and several case studies that have led to the rediscovery of lost compositions painted by Magritte himself.

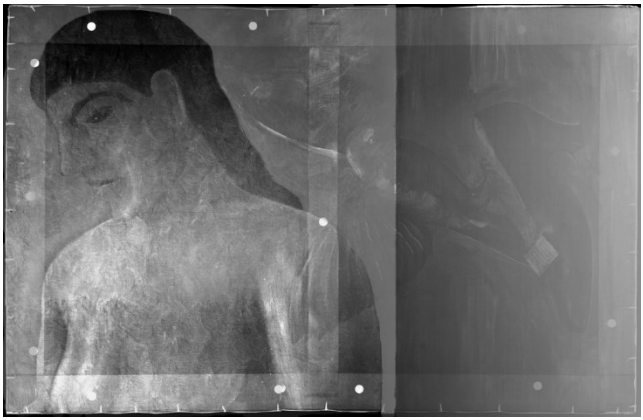


Fig. 1 Rediscovery of "La Pose Enchantée" beneath the painting "Dieu n'est pas un Saint".

SZYMON CZECHOWICZ'S PALETTE IN THE LIGHT OF INTERDISCIPLINARY TECHNICAL INVESTIGATIONS

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The report presents results of research of the Szymon Czechowicz's palette carried out on tens of pictures from Polish, Ukrainian, and Lithuanian museum collections as well as from churches and monasteries in Italy and Poland [1]. Szymon Czechowicz is the most important Polish painter of the 18th century. He commenced his artistic education at the court of Franciszek Maksymilian Ossoliński, who sent him for further studies to Rome around 1711. In 1716, he took part in the prestigious Clementine competition organized by St Luke's Academy, winning the 3rd prize in the second class for the drawing of *Samson Killing the Lion* and *Victorious Return from a Campaign*. In Italy, he also copied works of famous painters, including Raphael, Reni, Rubens or Barocci. He also painted works for Polish St. Stanislas church while staying there. In 1731, after 20 years in Italy, the painter returned to Warsaw. He was a very productive „independent" artist, working for various patrons, both church and lay. He specialized mainly in religious themes but was also able at painting portraits of his patrons and state officials. In his work, he often referred to compositional solutions of various artists, mainly Italian, especially the circle of students and followers of Maratta, Luti, Muratori and Benefial. Szymon Czechowicz had a large studio and taught numerous students who after their master's death copied the composition patterns they learned from him. He left several hundred paintings which are mostly in churches, monasteries and museums in today's Poland, Lithuania and Ukraine.

In the period from 2012 to 2017, the paintings of the artist were subject to invasive and non-invasive tests. Before the chemical analysis, a series of photographs of the paintings were taken in different ranges of electromagnetic radiation: ultraviolet, near-infrared, and X-radiation. Elemental, non-destructive analysis of paint layers was carried out using a

portable X-ray fluorescence spectrometer (XRF). Samples were also taken for specialist examinations such as X-ray fluorescence spectrometry (XRF) [3], X-ray diffraction (XRD) and the ATR infrared (FTIR) tests. In addition, an analysis of the elemental composition was performed for the cross-section samples using Scanning Electron Microscope coupled with an EDS electron microprobe (SEM-EDS). If any of the analyses gave ambiguous results, RS was employed for clarification. In this paper, I present the results concerning only the pigments and the fillers of the paint and ground layers, because these results were the most significant [2].

The conducted research allowed the basic pigments used on the palette of Szymon Czechowicz and in his workshop in the 18th century in the territories of the Polish-Lithuanian Commonwealth to be recognized. The Czechowicz's and his students' palette was limited. The most frequently used pigments were: lead white, Neapolitan yellow, iron based pigments: yellows, reds and browns, cinnabar, Prussian blue (Fig.1-2) and mainly black and coal black.

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A special thanks goes out to Roman Stasiuk for RTG researches, and Rafał Jendrzejewski, Mirosław Sawczak for carrying out the XRF analysis, to Marek Wisniewski for RS and FTIR researches, to Alicja Rafalska-Łasocha and Marta Grzesiak-Nowak for the XRPD tests, to Jakub Kotowski for the SEM-EDS researches, and to Kamilla Małek for FTIR and few samples of RS analyses.

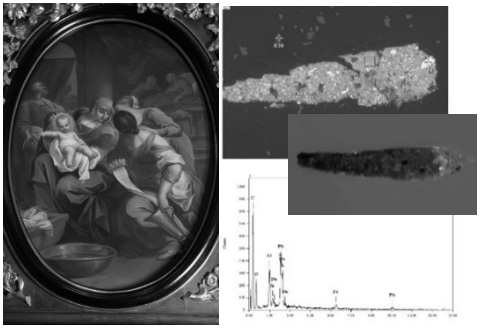


Fig. 1. *Scenes from the life of St Anne*, Kracow, *Energy Dispersive X-ray microanalyses results of the cross-section of the* blue paint layer *sample* using an electron microprobe (SEM-EDS).

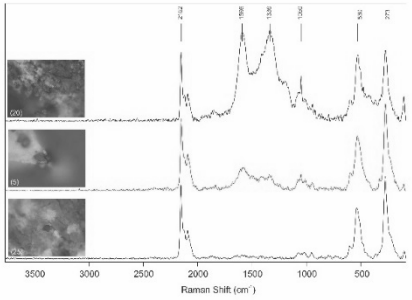


Fig. 2. The Raman spectra of selected blue samples confirming the presence of Prussian blue ($Fe_4[Fe(CN)_6]_3$). (20) *The road to Calvary* (Lviv), (5) *St Anne* from the Missionary Church (Lublin), (25) *St Joseph* (Warsaw).

TECHNICAL EXAMINATION AND DEVELOPMENT OF A PREVENTIVE CONSERVATION STRATEGY FOR A COLLECTION OF ARTWORKS BY STANISŁAW WYSPIAŃSKI

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The year 2017 was the 110th anniversary of the death of Stanislaw Wyspiański, one of the most intriguing and broad-minded Polish artists. The singularity of Wyspiański consisted of his versatile activity and the wide variety of concepts employed during his short 38 years of life. Technological analyses of a representative group of Wyspiański's pastel paintings were conducted using primarily micro- and scanning macro-X ray fluorescence (MA-XRF) spectrometry [1]. XRF analysis was complemented with documentation and evaluation of the state of preservation of the painting materials and the paper supports. For this purpose, several analytical and imaging methods were employed including analytical photography, microfading testing, FORS and pH measurements, and SEM/EDX analysis. Pigments frequently identified in red and yellow areas of the evaluated artworks using XRF included vermilion, lead white, chrome yellow, and iron-based, among others. Qualitative microchemical methods of analysis have revealed the presence of either Prussian or ultramarine blue in samples extracted from blue areas. The results have also revealed that many of the works exhibit a poor state of preservation. In this regard, the research led to the development and implementation of a preventive conservation strategy that takes into account not only the current condition of the artworks, but

also considers the importance of the museum environment and its impact on the degradation of the materials. Microfading testing was also employed to study the responsiveness of materials to light irradiation. A part of the strategy dealing with museum lighting aspects was published in the catalog of the temporary exhibition entitled Wyspiański, which is hosted by the National Museum in Krakow until January 2019 [2].

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SYNCHROTRON BASED X-RAY AND INFRARED MICRO-ANALYSIS OF ARTISTIC MATERIALS AT THE ID21 BEAMLINE, ESRF

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The ID21 beamline is a multi-modal platform at the European Synchrotron Radiation Facility offering micro-analytical techniques such as micro X-ray fluorescence (μXRF), micro X-ray absorption spectroscopy (μXAS) and micro X-ray diffraction (μXRD) (and previously micro infrared spectroscopy, μFTIR). This beamline has an important activity in the field of cultural heritage [1]. Instruments can be efficiently used to gather information about the ways works of art were manufactured (origin of ingredients, being natural or synthetic, firing conditions, etc). Besides, many analyses are dedicated to artwork conservation and preservation through a better understanding of the composition of degradation products formed with time, through the assessment of effects of external parameters (humidity, light, pollutants etc) and internal parameters (material initial composition) on degradation processes and possibly through the evaluation of the efficiency of conservation treatments.

The current X-ray energy range (2.0-9.1keV) gives access not only to low Z elements such as S (present in many sulfide pigments), but also to most of the 3d transition metals (in particular Mn, Fe, Cr, Co, Cu, responsible for the colour of many pigments, in paints, inks, glasses etc). Heavier metals such as Sn, Sb, Pb can also be analysed, through their L or M edges. Elements can be identified and localized with a submicrometric resolution thanks to μXRF. Their chemical and structural environment can then be further determined using spectroscopy and diffraction techniques. The μFTIR microscope is a very efficient instrument for the characterization of molecular groups, in particular in organic materials.

The complementarity of the different instruments permits to study almost all types of materials, from hard matter (pigment, glass, ceramics) to soft matter (papyri, plastics) and also mixtures of these different materials (e.g. paint [2], photographs [3]). Analyses are usually carried out on tiny fragments from historical artworks (e.g. fragments from Van Gogh's paintings [2]; from first photographs in colour [3]) which can be completed by the analysis of model samples, mimicking historical ones, and possibly artificially aged. Different recent applications and perspectives related to the upgrade of the beamline will be presented.

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STUDIES OF METAL ARTIFACTS FROM VARIOUS AGES USING SYNCHROTRON RADIATION AND NEUTRONS

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The study of cultural heritage objects is widely developing all over the globe. It significantly expands the information that humanities had about different artifacts and their state of preservation, by exploring their elemental and phase composition, internal structure etc. The investigations are very effective in supporting the traditional methods of extracting historical information from written and archaeological sources, which didn't lose relevance. The research is also crucially important for the determination of the optimal methods for restoration, preservation, storage and demonstration of museum exhibits.

A comprehensive instrumentation base including both sources of synchrotron and neutron radiation provides good opportunities for studies of the archaeological and arts objects – X-ray and neutron tomography, elemental and phase analysis. The NSciTeCH laboratory (Natural Sciences Techniques for Cultural Heritage) was established in 2015 at the NRC Kurchatov Institute especially to conduct the comprehensive studies of the artifacts.

In this report, we present the results of research of metal artifacts from the State Historical Museum, the Pushkin Museum of Fine Arts and the Institute of Archaeology RAS, which were carried out at the Kurchatov Institute: spear and beads from the Bronze Age, medieval crosses, etc. [1,2]

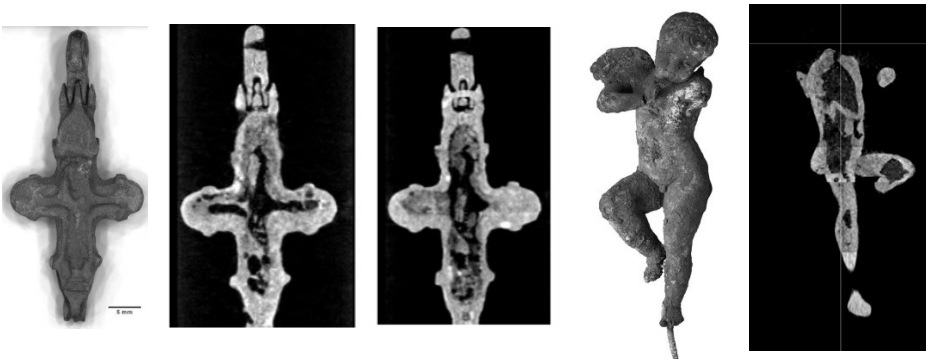


Fig. 1 Samples of studied artifacts: cross-reliquary (IA RAS) and "Amorino" (Dancing Cupid, Pushkin Museum of Fine Arts).

Work was supported by Russian Scientific Foundation –RScF №17-18-01399

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COMPREHENSIVE INVESTIGATIONS OF CULTURAL HERITAGE OBJECTS IN THE NRC KURCHATOV INSTITUTE: FROM EGYPTIAN MUMMIES TO MEDIEVAL CERAMICS

E. Tereschenko[1,2], **E. Yatsishina**[2], **P. Kashkarov**[2,3] **and M. Kovalchuk**[1,2,3]
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The convergence of the natural-scientific approach with the humanities allows us to obtain new data and applications, especially in historical research. Therefore, throughout the world museums, historical and archaeological institutions are increasingly cooperating with physicists, biologists, geologists, physicists, etc. The Kurchatov Institute, since 2015, has been working closely with the State Historical Museum, the Pushkin State Museum of Fine Arts, the Institute of Archeology of the Russian Academy of Sciences and other organizations.

The list of studied artifacts includes: a collection of mummies, metal and ceramic artifacts, organic components of various exhibits and much more. For each type of samples, certain kinds of studies were arranged.

The most complicated study was carried out for mummies. Nine ancient Egyptian mummies from the collection of the Pushkin State Museum of Fine Arts have been studied at the Kurchatov Institute using a set of NBICS technologies. Tomographic scanning is performed using a hybrid positron emission tomography/computed tomography (PET-CT) scanner. Three-dimensional reconstructions of mummies and their anthropological measurements are carried out. Some medical conclusions are drawn based on the tomographic data. In addition, the embalming composition and tissue of one of the mummies are preliminarily analyzed.

This report will present the results of comprehensive studies of mummies from the collection of the Pushkin Museum, organic decoration on the Bronze Age artifact, organic traces in the ceramic pots, and antique ceramics from the Crimea [1, 2].



Fig. 1. Some of studied artifacts: textile from mummies cover (Pushkin Museum of Fine Arts), sphero-conical vessel with organic residue inside (IA RAS) and organic decoration – seeds on the clay disk (State Historical Museum).

The studies were partially supported by Russian Foundation of Basic Research: grants 17-29-04201 (in part of ceramic study) and 17-29-04144 (in part of mummies study).

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SYNCHROTRON SOLARIS – PRESENT AND FUTURE RESEARCH OPTIONS

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National Synchrotron Radiation Centre SOLARIS in Krakow is the most modern and largest multidisciplinary research facility in Poland. The Centre was built between 2010 and 2015. The investment was co-financed by the European Union with funds from the European Regional Development Fund, as part of the Innovative Economy Operational Programme for 2007-2013.

As a strategic investment for the development of science, SOLARIS has been included on the Polish Roadmap for Research Infrastructures.

SOLARIS has been built using the groundbreaking design of magnetic double bend achromats developed at MAX-lab facility in Lund, Sweden, resulting in outstanding properties of generated synchrotron light which places SOLARIS firmly at the cutting edge of devices of this type. SOLARIS synchrotron operates at 1.5GeV energy with up to 500mA stored electron beam. It is powered by 600MeV S-band linac.

SOLARIS can provide synchrotron radiation for up to 18 beamlines from bending magnets and insertion devices. Within the scope of the project budget already two state of the art beamlines (PEEM/XAS and UARPES) have been constructed. On the 9th of April this year SOLARIS opens the first call for the external users for measurements at these beamlines.

The presentation will provide a brief history of the project and describe configuration and key parameters of the SOLARIS facility. However, the presentation will focus on the current status and plans for the future development of SOLARIS and its offer for researchers.

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ABSTRACTS

POSTER PRESENTATIONS

USING OF THE XRF METHOD TO CHARACTERIZATION OF SILVER CROWN HALF-GROSCHEN OF WŁADYSŁAW JAGIEŁŁO

Ewa Pańczyk[1], **J. Kierzek**[1], **Lech Waliś**[1], **Michał Zawadzki**[2], **Maciej Widawski**[3], **Władysław Weker**[3]

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The objective of the current work was to research the history of medieval coinage in Poland during the reign of Władysław Jagiełło. The object of the study were silver coins constituting an important element of the preserved heritage from the era of the multi-national Polish Republic.

The study covered Władysław Jagiełło crown half-groschen made by the mint in Krakow in 1394-1434. Typology criteria and the chronology of the relevant types presented in Stanisław Kubiak's monograph [1] are seriously questioned by numismatists pointing to significant stylistic differences between coins of the same type, suggesting that they might have been made at different time. Trace elements alloy analysis would shed a new light on the origins of silver used in Jagiełło's coins.

In total, 181 Władysław Jagiełło crown half-groschen were examined originating from the Łódź and Biela treasures. In addition, 15 Prague groschen were tested as reference: 4 coins minted during the reign of Charles IV (1346-1378) and 11 during the reign of Wenceslas IV (1378-1419).

The composition of the coins was analyzed using X-ray fluorescence. This method meets all basic requirements of historical artifact analysis: it is non-destructive, does not require samples to be taken, and makes no permanent change to the surface of the objects tested. The studies were performed using an X-ray spectrometer with Si(Li) detector with active area of 80 mm^2, 5 mm thick, with resolution of 180 eV for Mn K_α line of 5.9 keV. Analysis of the spectrum of secondary X-ray radiation recorded with the was performed using AXIL – QXAS software developed and distributed by the International Atomic Energy Agency in Vienna [2].

The measuring setup with a ^{238}Pu source ensures analysis of the relevant elements present in silver coins: primary - Ag and Cu, secondary - Zn and Pb and trace - Au, Hg and Bi. Within the analyzed crown half-groschen and Prague groschen, it is possible to specify three well-defined groups of coins differing in analyzed elements content.

The Charles groschen have a significantly higher silver contents ranging from 77% to 83% percent. The Wenceslas groschen were made of alloys containing between 64% and 74% silver.

The Władysław Jagiełło crown half-groschen were made in Kraków according to other weight and quality standards than in Prague. In these coins, the concentration of Ag varies from 31% to 51%. Only five coins have revealed a significantly lower silver content (ranging between 17% and 22 %). Three of them had been previously deemed counterfeit due to certain properties of the die.

A summary analysis of data was performed using a multivariate statistical analysis method.

This vast body of experimental material enabled development of a database which represents a significant achievement and will facilitate continued work on coins from the relevant period. It also demonstrates how difficult it is to analyze coins found after centuries in an uncontrolled environment.

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PIXE ANALYSIS OF MEDIEVAL SILVER COINS

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An overall aim was to determine the provenance and dating of a few groups of the early medieval Central European silver coins. An attribution and chronology of them often constitute a serious problem for historians and numismatists. A material research of the historical artifact constitutes an important additional factor that helps us to choose the proper conservation methods. Denarii which were struck approximately from 10th century till 11th century in Central Europe were found in great number in hoards excavated in Poland. Individual characteristic of these coins is cross picture and legend on obverse and reverse sides. Iconography of denarii has not included information about mints [1]. On the iconography criterion, differentiation of eight main types of denarii is possible. For comparison, Otto and Adelheid denarii (991 - 995 A.D.) [5], dirhams (11th century), Hungarian and Czech denarii as well as Polish coins of Bolesław Chrobry, Bolesław Śmiały and Kazimierz Wielki were examined. Totally, 48 coins were selected which is important especially for debasement analysis.

As the Saxon denarii are particularly rare and therefore of high value, it was intended to perform analysis without sampling or with very small interference. Particle-induced X-ray emission spectroscopy (PIXE) is a non-destructive elemental analytical technique. This method is especially useful for the non-destructive study of unique and valuable cultural heritage objects (e.g. archaeological findings and artworks).

The PIXE measurements were performed at the 5MV Van de Graaff accelerator of the Institute of Particle and Nuclear Physics, Wigner Research

Centre, Hungarian Academy of Sciences. Characteristic X-ray spectra were taken by an AMPTEK X-123 X-ray spectrometer. The net X-ray peak intensities and the concentration calculations were made by the off-line GUPIX program package [2].

Twelve elements were determined in each silver coin (Cu, Ag, Mn, Fe, Zn, As, Se, Sn, Au, Hg Pb and Bi). The content of silver found in the investigated coins was between 30% to 98% and that of copper was found to be from 2% to 60%.

The twelve elements were selected for multi-parameter statistical analysis aimed at identifying the degree of similarity of the analysed samples. The STATISTICA 8 (StaSoft) programme was carried out to identify the similarity degree of the analysed coins. The statistical analysis was performed for standarised and logarithmic variables.

In spite of surface analysis, important information was obtained about the major and trace elements in early medieval silver coins minted in Central Europe. The results of these investigations are significant for our knowledge of the history of Central European coinage, especially of Polish coinage. An interpretation of the results of statistical methods allowed us to differentiate the artefacts in relation to the various production centers (mints), various recipes as well as various raw materials and methods of their purification.

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PALACE OF THE BISHOPS OF KRAKOW IN KIELCE UNDER THE MICROSCOPE

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Palace of the bishops of Krakow (the principal seat of the National Museum in Kielce) is the best preserved residence from the age of Vasa dynasty in Poland. The Palace was erected in the years 1637-1644 for bishop Jakub Zadzik, and served as a temporary residence of the bishops of Krakow until 1789. Tommaso Poncino, builder of Ujazdów Castle in Warsaw, was probably the architect.

In 2017, the painted decoration of beamed ceilings and friezes in two rooms of the *piano nobile* (Second Prelates' Room and the Upper Dining Room) was studied.

The Second Prelates' Room is one of the guest rooms. Its beamed ceiling is covered with geometrical, vegetal and genre decoration. In the frieze, that runs around the top of the walls, one may see allegories of agriculture, beekeeping, and hunting, as well as cartouches with coats of arms. Both, the beamed ceiling and the frieze, were strongly repainted at the beginning of the 20th century.

The Upper Dining Room is the most magnificent room in the palace. The beamed ceiling is decorated with geometrical and vegetal motifs, as well as with allegories, genre and moralistic scenes. The upper row of the frieze shows founder's predecessors, portraits of the kings Zygmunt III and Władysław IV, the founder himself and his numerous successors. In the lower row, painted by Aleksander Rycerski in 1863, one may admire portraits of subsequent bishops of Krakow. The decoration was repainted several times and repeatedly restored – the last major conservation took place in 1966-67.

The aim of the present work is to determine the extent of the repaints and to unveil the mysteries of the technology of the original decoration. Portable X-ray fluorescence spectrometer (p-XRF) was used for *in situ* measurements, as well as for the analysis of micro-samples at the laboratory. The cross-sections were further analysed by optical and scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDS).

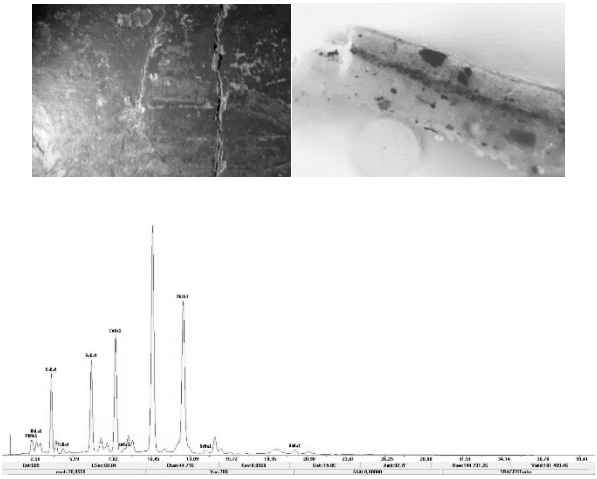


Fig. 1 Sample 13 – sampling site, cross-section and, XRF spectrum.

Acknowledgement
Research project funded by the Polish National Science Centre (NCN) (2015/19/N/HS2/03503).

SMELLY MISTERY UNCOVERED.
TRACING THE LINK IN THREE HISTORIC MOSAIC MORTARS

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The beginnings of a systematic Czech mosaic tradition are closely associated with an Austrian company Neuhauser from Innsbruck which supplied rich mosaic decoration to many famous monuments in the Czech Lands (e.g. Municipal House and St. Wenceslas Church in Prague) and also small-scale mosaic panels to numerous sepulchers. The Neuhauser origin is supposed for many of sepulcher mosaic artworks of that time but in most cases a hundred percent evidence is missing.

This paper presents the first results of an investigation of mortar beds taken from three mosaics ascribed to Neuhauser Innsbruck coming from two different locations in Prague (Sladkovský and Beneš family sepulchers in Olšany Cemetery and Peluněk sepulcher from Malvazinky). The mosaics date back to 1880s (Sladkovský, Beneš) and early 1900s (Peluněk). The Peluněk mosaic depicting Resurrected Christ is listed in an archival Neuhauser company catalogue which confirms its origin. The aim of our study was to characterize the three mortars and to analytically confirm their similarity which was evident at first sight. All mortars looked similar and had a very characteristic smell.

The mortars were studied by a combination of analytical methods - optical microscopy, scanning electron microscopy (SEM-EDX) and thermal analysis (DTG). Mineralogical composition of the aggregates was studied by X-ray

powder diffraction (XRPD). Fourier transformed infrared spectroscopy (FTIR) was employed to identify the “smelly” organic compound.

All mortar binders contain hydraulic compounds and a large amount of unreacted portlandite $Ca(OH)_2$ – a sign of an incomplete carbonation, unexpected in mortars of this age. The FTIR spectra of an extracted organic compound fit well with the reference spectrum of stand oil (Fig. 1). The presence of oil in the mortars explains the high amount of portlandite as linseed oil is known to slow down the carbonation process. Similar chemical and mineralogical composition of the three mortars studied as well as the presence of oil in all samples support the restorers´ and art historians´ hypothesis that the two anonymous mosaics were also the works of Neuhauser´s masters.

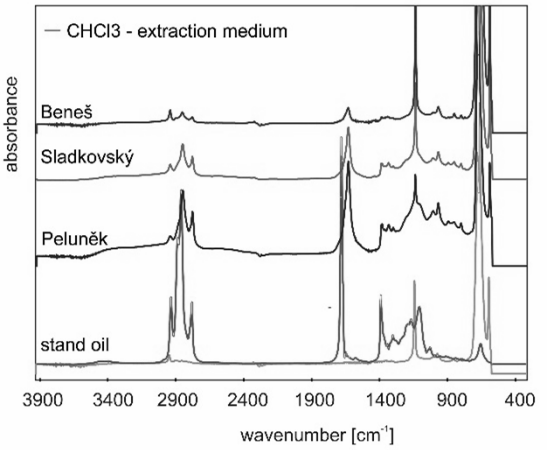


Fig. 1. FTIR spectra of oil extracted from mosaic mortars and reference spectra (stand oil, chloroform).

Acknowledgement

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PAINTING OF MIECZYSŁAW SZYMAŃSKI – ANALYSIS OF PAINT LAYERS

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This poster presents part of the results of a research project *Investigations of the use of the Bookkeeper method for the deacidification of oil paintings on a paper support*. The project was carried out in 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 Polish National Centre for Science (number of grant application 2011/01/N/HS2/02308).

One of its stages was the restoration of five paintings of Mieczysław Szymański (1903-1990), the artist, who was not only painter but also illustrator and fabric designer. In the years 1949 – 1974, he was in charge of the Textile Studio at the Faculty of Painting of the Academy of Fine Arts (ASP) in Warsaw. The Museum of Academy of Fine Arts in Warsaw is the owner of about 650 his works -watercolours, gouaches, drawings and oils.

The paintings chosen for project are geometric abstractions created in the 80s of the last century, painted on paper using a mixed technique with a predominance of an oil technique. The examination of the paintings involved the identification of the substrates, pigments as well as paint layer binders. The pigments identified in paint layers were as follow:
zinc white, lithopone (zinc sulphide + barium sulphate), titanium white; Prussian blue and synthetic ultramarine; cadmium red, iron oxide red and organic red; iron oxide yellow; bone black, lampblack; manganese violet; viridian.
The methodology of testing the paintings:

- Identification of the **pigments** - microscopic methods, SEM-EDS, XRD, Raman spectroscopy;
- Identification of the **binders** - microscopic methods, FTIR, GC-MS.

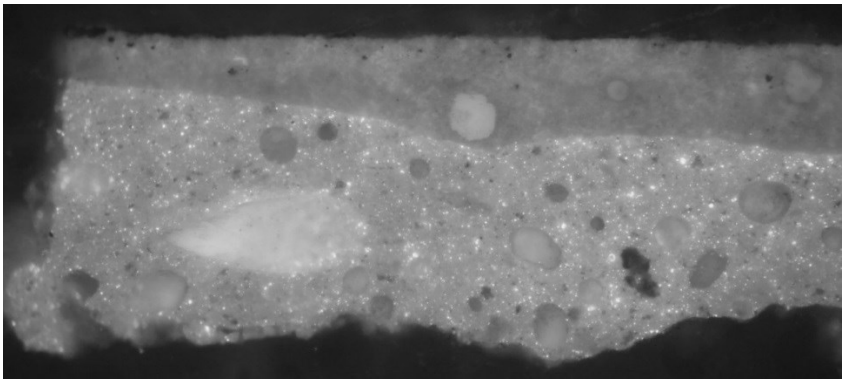


Fig. 1 Cross-section in UV light. Mieczysław Szymański, untitled picture; inventory number: MASP 6713. Photo – Anna Nowicka.

APPLICATION OF XRPD TO THE STUDY OF PIGMENTS FROM PAINTINGS ON THE MEDIEVAL STAINED-GLASS PANELS IN DOMINICAN MONASTERY IN KRAKOW

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Stained-glass panels: *The Holy Trinity (The Throne of Grace),* the Virgin Mary at *The Annunciation,* and Christ with an angel at *The Coronation of the Virgin* belong to the group of 21 medieval stained-glass windows (from 13th to 15th century) preserved in the Dominican Monastery in Krakow. Severe corrosion of glass and numerous losses of paint layers have led to the loss of readability of the paintings. The performed research was focused on the thorough examination of paint layers, their technology and causes of damage. At the beginning, the samples were analyzed by means of XRF, and SEM-EDX [1]. XRPD technique was applied to determine precisely the pigments used in the paintings. Locations of samples taken from the paint layers are indicated by means of red ellipses in Fig. 1-3 *(Photo: P. Gąsior).*

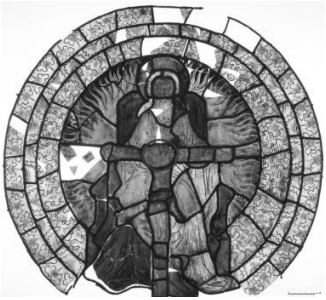


Fig. 1 The Throne of Grace



Fig. 2 The virgin Mary at *The Annunciation*



Fig. 3 Christ with an angel at *The Coronation of the Virgin*

XRPD measurements were performed with the use of an Panalytical X'pert pro MPD laboratory diffractometer, Bragg-Brentano geometry, in 4.0-60° 2θ range, with 0.026° step size. Phase analysis was done with the use of the PDF4+ database. The results will be presented during the conference.

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METHODS OF RESEARCH ON PAINTINGS IN THE STATE RESEARCH AND RESTORATION WORKSHOPS IN THE PERIOD OF 1930-1970

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Since the foundation of the State Research and Restoration Workshops (Ukraine, Kiev) in 1938, the organisation operated a chemical and technological laboratory.

Before the Second World War, Varvara Lokhanko a chemist-technologist worked there. From 1946 to 1949, Tatyana Florova, the chemist, joined the team. Later, Roza Kaganovich was the chief of the laboratory.

The main methods used to study the objects of art were visual research, optical research, spectroscopy in invisible radiation range (non-destructive methods), and microchemical qualitative analysis (associated with sampling).

The visual inspection allowed attributing the objects of art to a certain era and region, and the state of conservation to be revealed.

The inspection with the help of a binocular microscope was called ''more accurate'', which made possible a more accurate conclusion about the state of conservation, the features of painting and material technology, and also identification of craquelure imitations, as evidence of falsification or historical restoration at the beginning of the 20th century.

The studies of ultraviolet luminescence in painting (''luminescent analysis'') made it possible to establish the degree and shade of luminosity of varnish, its uniformity, the location of the interventions, the authenticity of the signature, and also to recognize some pigments. Photography in reflected UV radiation made it possible to detect uneven varnish and restoration interventions. This method was used even before the Second World War.

Examination in reflected infrared radiation allowed the researcher to see the preparatory design on a light ground, traces of changes made by the

artists and restoration interventions. The first mention of the use of this method refers to 1962.

During our study, we identified special methods and various research approaches that were used in the expert practice of the State Research and Restoration Workshops. It should be noted that in the 1960s these methods and approaches were quite diverse. The expert activity of the workers of the State Research and Restoration Workshops in 1930-1970 helped to clarify the attribution of the majority works of painting from the museums of Ukraine.

BIOMINERALIZATION OF $CaCO_3$ FOR THE PROTECTION AND RESTORATION OF HISTORIC STONE MATERIALS

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Construction materials undergo progressive deterioration due to physical, chemical and biological weathering [1-4], today tremendously accelerated by atmospheric pollution. The weathering brings about the weakening of the stability and durability of the construction, be it a building or a statue, be it made of stone (calcareous), bricks or cement. Several chemical treatments are in use to protect and restore the materials [1-3], yet not fully recognized as satisfactory. Organic treatments with polymers and resins frequently form surface films and pore fillings with mechanical properties different from those of the material. They also require large amounts of organic solvents. Inorganic treatments by contrast, e.g. the lime-water technique, end in the formation of fragile crusts. The treatments also suffer from irreversibility and limited durability.

In response to these circumstances, biomineralization of $CaCO_3$ has been proposed as a benign, eco-friendly technique of cementation and deposition, operative under mild conditions *in situ* [1-4].

Biomineralization is a common natural phenomenon that consists of the formation of minerals by living organisms, $CaCO_3$ being among its major products [1-4]. One of the biological pathways of $CaCO_3$ mineralization is the hydrolysis of urea catalyzed by the enzyme urease [5]. The process takes advantage of the supply of carbonate ions derived from urea hydrolysis and of an increase in pH generated by the reaction, the effects that in the presence of Ca^{2+} ions lead to the precipitation of $CaCO_3$:

$$H_2N\text{-}CO\text{-}NH_2 + 2H_2O + Ca^{2+} \xrightarrow{\text{urease}} 2NH_4^+ + CaCO_3(s)$$

Further to its importance in nature, if performed in a biomimetic manner the urease-aided $CaCO_3$ mineralization offers enormous potential in innovative engineering applications as a strengthening/ cementing and surface protection agent, among others for construction materials. In view of the potential of this newly emerging interdisciplinary branch of engineering, this presentation summarizes the principles of the process and reviews its advantages and limitations together with the future perspectives for the application in the sector of the protection and restoration of stone artworks and historic buildings, compared to the conventional techniques presently in use.

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GUNPOWDER FIREARMS − A PASSION FOR ANCIENT WEAPONS OR FOR CRIMES?

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Parallel to modern trends in firearms constructions as well as lead-less and toxic-less ammunition production [1], recently one can observe an increase in black powder arms trade in Poland. A special interest is paid to replicas of old rifles and revolvers that can be seen as attention of collectors to technical and aesthetic details of certain milestone constructions such as Colt Walker .44 (Fig. 1) by Samuel Colt. The revolving-cylinder pistol was produced at his factory in Paterson New Jersey since 1836. Colt's new pistol was enthusiastically received by the Rangers of the newly independent Republic of Texas and in 1844 Colt's pistol made history when sixteen Rangers held off 80 Comanche warriors with their new revolvers. Sam Walker, who had been in the Comanche fight in 1844, became a firm believer in Colt's pistols. He ordered 1 000 of them and rode off to Mexico. The Walker's reputation assured Colt's future success.



Fig. 1 A replica of revolver Colt Walker .44 (http://czarnoprochowce.pl).

On the other hand, the possibility of purchasing a replica of such an old weapon, without the need of obtaining the license, creates the danger of misuse and accidents. Thus, such old-fashioned firearms as well as other related evidence, e.g. gunshot residue, are the subjects of forensic examinations [2]. Examples of forensic opinions as well as the results of necessary background examinations related to gunpowder weapons will be presented.

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THE OLDEST COLOR LAYERS IN THE DOMINICAN CONVENT OF ST. NICHOLAS CHURCH IN KAMIANETS PODILSKYI IN UKRAINE. PRESENTATION OF THE RESULTS OF THE FIRST STAGE OF RESEARCH

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Church of St. Nicholas with the monastery was considered for centuries as the most beautiful temple in Podolia. This is a monument of undeniable value for the Polish cultural heritage. The Dominicans were brought to this land in the 14th century. At that time, in Kamianets, the first wooden monastic church was erected, which was destroyed in a huge fire at the beginning of the 15th century [1]. A stone temple was erected in this place - which differed significantly from that seen today. However, it is not known what it looked like originally.

From the end of the 16th century, the Potocki family became the patrons of the Dominicans [2]. At the beginning of the 17th century, two Renaissance chapels were added to the nave - Our Lady of the Rosary and Christ Crucified [3]. In the middle of the 18th century, Michał Franciszek Potocki funded the reconstruction of the church in the Baroque style [4]. The whole interior has been designed with a uniform stucco decoration in the form of rich ornamental and floral decorations, which on this area was at that time a sensation. In the literature, the figure of Kamianets architect and commander of the local fortress Jan de Witte is associated with these works, but it is not confirmed in scientific studies [5].

In the face of very poor archival materials, which almost entirely burned in fires or were stolen, the interior of the church is the most important source about its history. During the conservation works on the 18th century stucco decoration carried out in recent years, unusual fragments of the history of the temple were found, such as plant decorations, ornaments, fragments of curtains, probably depiction of the Dominicans and St. Catherine of Siena. They are usually placed under a thick layer of Baroque decorations, so the only way of their investigation was to make stratigraphy of technological layers and take samples for analytic research. The following techniques were used: optical microscopy, scanning electron microscopy with energy

dispersive X-ray spectrometry (SEM-EDS) and Raman spectroscopy. The following non-destructive methods were also used in this research: ultraviolet luminescence (UV), infrared reflectography (IR), photography in visible light (VIS).

The test results confirmed the use of such pigments as malachite, smalt, azurite and posnjakite in painting layers. Drawing the conclusions from the research, we managed to compare individual fragments of paintings from various places in the church. Their similar stylistics and technological design indicate a consistent interior design at the time. The research allowed finding common features, defining the chronology of changes in the church and linking particular layers. Thanks to the pictures in visible light, also in raking light, the painting content in the paintings, the texture of the surface or various types of damage were read. Comprehensive documentation and inventory of paintings was created. Due to the inability to remove the 18th century decorations of the entire interior, the most bothersome issue is to find a research technique that will allow looking into the plaster and reading the painting compositions in their full form.



Fig. 1 Depiction of St. Catherine of Siena, discover under plaster in renaissance chapel of Our Lady of the Rosary in St. Nicholas church in Kamianets Podilskyi in Ukraine.

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DIAGNOSTIC TECHNIQUES OF ANCIENT EGYPTIAN METALS ARTIFACTS IN THE GRAND EGYPTIAN MUSEUM – CONSERVATION CENTRE

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It is expected that the Grand Egyptian Museum will be partially inaugurated in 2018. Many ancient Egyptian collections have been transported from different Egyptian museums to the Grand Egyptian Museum – Conservation Centre (GEM-CC) for restoration, conservation and preparation for exhibition. On the other hand, Japan International Cooperation Agency (JICA) provided the Conservation Centre with several examination and analytical techniques such as Stereo Microscopes, Scanning Electron Microscope with Energy Dispersive X-ray (SEM-EDX), X-ray Diffraction (XRD), X-ray Fluorescence (XRF), X-Ray Radiography and Fourier Transform- Infra Red (FTIR).

In order to make an appropriate plan for remedial conservation, it is significant to understand the chemical composition of the metal object, its condition and deterioration mechanism. These techniques played an active role to reveal new secrets about manufacture technology and to identify some deterioration aspects such as unusual corrosion products on copper artifacts, bronze disease, micro cracks and previous treatments. This poster aims to highlight the role of different examination and analysis techniques to grasp the ancient Egyptian metal objects prior to selection the most appropriate approach for remedial conservation.

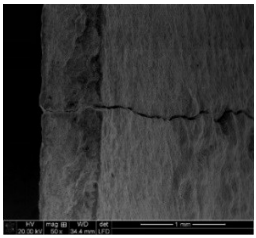


Fig. 1 SEM image shows propagation of micro crack in copper miniature hoe of Tutankhamun

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