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Influence of Arsenic Compounds on the Colour Palette of 15th- and 16th-Century Icons from the National Museum in Cracow

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Abstract

The National Museum in Krakow houses a collection of 15th- and 16th-century icons from the territory of the former Republic of Poland, distinguished by the presence of arsenic compounds both in the coloured layers of paintings, lights, as well as on the plain surface of backgrounds – which is rare. In historical treatises on painting, yellow arsenic sulfide – orpiment (As_2S_3) – in combination with indigo was used to obtain greens, and alone or in combination with whites to imitate gilding, including chrysography. Among the oldest Late Byzantine painting treatises, a background made with orpiment appears only in an Armenian manuscript. Mineral and synthetic forms of chemically unstable arsenic pigments, such as orpiment, realgar and para-realgar (As_4S_4 or AsS), degrade to partially transparent arsenic trioxide (arsenolite). The colour changes identified in colour mixtures, especially in the backgrounds of nine icons from the collection of the National Museum in Krakow, together with an analysis of technique and technology based on published research, allow in regard to four of them – the icon of *Christ Pantocrator with Archangels* (MNK XVIII-27) pre-

sented in more detail in the paper, as well as in the form of a supplement to the icons *St John the Baptist and St Paul* (from the *Deesis*, MNK XVIII-26), *The Last Judgement* (MNK XVIII-10), and *The Last Judgement* (MNK XVIII-32) – to assign them to the Armenian and South Balkan painting tradition.

Abstrakt

Wpływ związków arsenu na paletę barw piętnasto- i szesnastowiecznych ikon z Muzeum Narodowego w Krakowie

Muzeum Narodowe w Krakowie posiada w swojej kolekcji piętnasto- i szesnastowieczne ikony z terenów dawnej Rzeczypospolitej, wyróżniające się obecnością związków arsenu zarówno w barwnych warstwach malowidła, światłach, jak i na powierzchni gładkich teł – co należy do rzadkości. W historycznych traktatach malarskich żółty siarczek arsenu – aurypigment (As_2S_3) – w połączeniu z indygiem stosowano do otrzymania zieleni, a samodzielnie lub w połączeniu z bielami do imitacji złoceń, w tym chryzografii. Wśród najstarszych późnobizantyńskich traktatów malarskich tło wykonane aurypigmentem zostało wymienione jedynie w rękopisie ormiańskim. Mineralne i syntetyczne formy niestabilnych chemicznie pigmentów arsenowych, takie jak aurypigment, realgar i pararealgar (As_4S_4 lub AsS), ulegają degradacji do częściowo transparentnego trójtlenku arsenu (arsenolitu). Zmiany kolorystyczne zidentyfikowane w mieszaninach kolorystycznych, a szczególnie tłach dziewięciu ikon z kolekcji Muzeum Narodowego w Krakowie, wraz z analizą techniki i technologii na podstawie opublikowanych badań, pozwalają na przyporządkowanie czterech z nich: ikony *Chrystus Pantokrator z archaniołami* (MNK XVIII-27) – omówionej w niniejszym artykule, a także ikon *Św. Jan Chrzciciel i św. Paweł* (z rzędu *Deesis*, MNK XVIII-26), *Sąd Ostateczny* (MNK XVIII-10) oraz *Sąd Ostateczny* (MNK XVIII-32), do ormiańskiej i południowobałkańskiej tradycji malarskiej.

Introduction

Contemporary methods of analysing artworks facilitate much more than descriptions of technological change to paintings of various historical periods; they also identify materials used in the creation of objects according to strict rules. In the painting of icons, colour symbolism reflects the hierarchy of the universe divine and the colour palette has remained unaltered since Byzantine times as evidenced by an early painting treatise[1] as well as by later ones[2]. The gold of the backgrounds, nimbi, attributes, and garment details

[1] Georgi R. Parpulov, Irina V. Dolgikh, and Peter Cowe, "A Byzantine Text on the Technique of Icon Painting," *Dumbarton Oaks Papers* 64 (2010): 201–216, DOI: 10.2307/41480886.

[2] Dionizjusz z Furny, *Hermeneia, czyli objaśnienie sztuki malarskiej*, ed. Małgorzata Smorąg-Różycka (Kraków: Wydawnictwo Uniwersytetu Jagiellońskiego, 2003), 15–50.

symbolises the purity and sanctity of the celestial kingdom described by Pseudo-Dionysius the Areopagite in his theological treatise *Corpus Dionysiacum* as God's causality to the emanation of light[3]. A similar role is played by the white or purple (blend of red and blue or violet) of Christ's chiton, an attribute of divine or royal legacy, standing in opposition to the azure of the himation, the colour indicative of His human nature[4]. Purple would become the colouristic attribute of baptised temporal sovereigns fulfilling divine will; they also wore deep red and maroon (a mix of red and brown) – symbol of the divine grace they have been blessed with[5]. Madonna's robes – blue or green chiton and purple maphorion – symbolised her elevation as Queen of Heaven[6]. Vibrant red stood for divine energy, vital power and glory, adopted also as the hue of military saints – such as St. George or St. Demetrios – and of martyrs, male and female alike, true followers of Christ, whose robes, their purple replaced with red, emphasised the authenticity of His incarnation, and the blood He spilt to save mankind[7]. The array of icon colours closes with black – symbol of finality and death, visible in representations of caves interpreted as tombs or hell; and the blue of the sky and the green of forests and meadows as an expression of all things natural[8].

Aforementioned colour palette and related symbolism also finds reference to 15th- and 16th-century icons from the territories of the former Republic of Poland[9], collection of the National Museum in Cracow[10]. Nine of these are distinguished by the content of arsenic compounds in the compositional details and especially in the area of backgrounds. Despite dissimilarity of provenance and time of creation the following icons: *Archangel Gabriel and St. Peter* (inv. no. XVIII-111, 1520s–1530s, circle of the painter of the Birth and Dormition of the Mother of God of Terlo)[11], *Christ Pantocrator and Archengels* (inv. no. XVIII-27, 1560s–1570s, the circle of

[3] Ivan Stasûk, "Color as an Expressive Instrument of the Icon," *Historical and Cultural Studies* 2, no. 1 (2015): 93.
[4] Stasûk, "Color," 94.
[5] Stasûk, "Color," 94.
[6] Stasûk, "Color," 94.
[7] Stasûk, "Color," 94.
[8] Stasûk, "Color," 94.
[9] Rafał Czupryk, "Eparchia przemyska na pograniczu polsko-ruskim (XIV–XVIII w.). Rys historyczny," *Prace Historyczno-Archiwalne* 9 (2002): 88.
[10] Mirosław P. Kruk, *Ikony XIV–XVI wieku w Muzeum Narodowym w Krakowie*, vol. 1 *Katalog*, vol. 2 *Badania technologiczne*, vol. 3 *Ilustracje* (Kraków: MNK, 2019).
[11] Kruk, *Ikony*, vol. 1, 118.

masters of Potylich-Drohobych)[12], *St. John the Baptist and St. Paul* (inv. no. XVIII-26, 1560s–1570s, the circle of masters of Potylich-Drohobych)[13], *The Last Judgement* (inv. no. XVIII-10, late 16th c., the circle of masters of Potylich-Drohobych)[14], *Hodegetria Surrounded by Archangels, Apostles, Joachim and Anna* (inv. no. XVIII-28, late 15th-early 16th c., West Ruthenia)[15], *The Last Judgement* (inv. no. XVIII-25, 2nd quarter of the 16th c., the lands of Przemysl, Pol. Stary Sambor)[16], *The Last Judgement* (inv. no. XVIII-32, late 16th c. – early 17th c., the lands of Przemysl)[17], *St. Paraskeva with scenes of Life and Passion* (inv. no. XVIII-57, 1490s, the lands of Przemysl)[18], *St. Nicholas with Scenes of Life and Miracles* (inv. no. XVIII-192, late 15th c., the circle of painters of Żohatyn, Węglówka and Zwierzyn in the lands of Przemysl)[19], have a number of common features. Four of the mentioned icons: *Christ Pantocrator and Archengels* (inv. no. XVIII-27, fig. 1), which is the main issue of the paper, and *St. John the Baptist and St. Paul* (inv. no. XVIII-26, fig. 3), as well as *The Last Judgement* (inv. no. XVIII-10, fig. 4, and inv. no. XVIII-32, fig. 6: a) seem to have most in common.

The use of macro-X-ray fluorescence (MA-XRF) scanner to identify the distribution of elements in technological layers has revealed large-surface arsenic concentrations (fig. 2) in non-invasive and non-destructive manner[20], not exactly representable by point-based techniques as e.g. Fourier--transform infrared spectroscopy (FTIR)[21], Micro-Raman spectroscopy or X-ray powder diffraction (XRPD) for which taking samples are required. Partly similar techniques as macro-X-ray powder diffraction (MA-XRPD)[22]

12 Kruk, *Ikony*, vol. 1, 128.
13 Kruk, *Ikony*, vol. 1, 132.
14 Kruk, *Ikony*, vol. 1, 441.
15 Kruk, *Ikony*, vol. 1, 279.
16 Kruk, *Ikony*, vol. 1, 422.
17 Kruk, *Ikony*, vol. 1, 451.
18 Kruk, *Ikony*, vol. 1, 631.
19 Kruk, *Ikony*, vol. 1, 597.
20 Małgorzata Walczak et al., "MA-XRF Study of 15th–17th Century Icons from the Collection of the National Museum in Krakow, Poland," *X-Ray Spectrometry* 48, no. 4 (2018): 1–8, DOI: 10.1002/xrs.2949.
21 Marc Vermeulen et al., "Visualization of As(III) and As(V) Distributions in Degraded Paint Micro-Samples from Baroque- and Rococo-Era Paintings," *Journal of Analytical Atomic Spectrometry* 31 (2016): 1913–1921, DOI: 10.1039/C6JA00134C.
22 Jonas Simoen et al., "Combined Micro- and Macro scale X-ray Powder Diffraction Mapping of Degraded Orpiment Paint in a 17th Century Still Life Painting by Martinus Nellius," *Heritage Science* 7 (2019): 83, DOI: 10.1186/s40494-019-0324-4.

and Raman mapping[23], also prevent to determine of arsenic pigments in such extensive area.

Arsenic pigments – characteristic and process of degradation

Attempts to follow the technique of creation regarding the discussed icons would chiefly require an analysis of processes occurring in arsenic pigments; in this case have played a fundamental role for a variety of reasons. Mineral orpiment (As_2S_3), realgar and pararealgar (As_4S_4, AsS) have been used as pigments since antiquity. Produced in a process of sulphur sublimating with arsenic in assorted proportions, synthetic arsenic sulphides have been known and applied since the Middle Ages (as described i.a. by Cennini[24]). Chemical instability and considerable photoactivity are typical of all arsenic compounds[25]. When exposed to light especially of wavelengths shorter than 549 and 609 nm, they undergo degradation. Compounds darker in hue as red and orange-red, such as realgar or pararealgar become photoactive at 609 nm; yellow arsenic sulphides, such as orpiment, are activated at 549 nm[26]. This is how realgar transforms into pararealgar, which in turn changes into orpiment. Realgar, pararealgar and orpiment all oxidise, ultimately reaching chemical stability in arsenolite (AsO_3)[27], in use in medicine and cosmetology since antiquity[28].

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[23] Debbie Lauwers et al., "In Situ Raman Mapping of Art Objects," *Philosophical Transactions of The Royal Society A Mathematical Physical and Engineering Sciences* 374 (2016): 20160039, DOI: 10.1098/rsta.2016.0039. See also Polonca Ropret et al., "Advances in Ramanmapping of Works of Art," *Jounal of Raman Spectroscopy* 41 (2010): 1462–1467, DOI: 10.1007/978-3-642-28252-2_6, accessed November 16, 2021.

[24] [Cennino Cennini,] *The Book of the Art of Cennino Cennini*, transl. Christiana J. Herringham (London: Ruskin House, 1899), 39.

[25] Karen Trentelman, Leon Stodulski, and Marc Pavlosky, "Characterization of Pararealgar and Other Light Induced Transformation Products from Realgar by Raman Microspectroscopy," *Analytical Chemistry* 68 (1996): 1755–1761.

[26] Marc Vermeulen et al., "Assessing the Stability of Arsenic Sulfide Pigments and Influence of the Binding Media on their Degradation by Means of Spectroscopic and Electrochemical Techniques," *Microchemical Journal* 138 (2018): 82–91, DOI: 10.1016/J.MICROC.2018.01.004.

[27] Simoen et al., "Combined Micro- and Macro scale," 83, DOI: 10.1186/s40494-019-0324-4, accessed July 20, 2020.

[28] Georgius Agricola, *De Natura Fossilium (Textbook of Mineralogy)*, transl. from the first Latin edition of 1546 by Mark Ch. Bandy and Jean A. Bandy (Special Papers, The Geological Society of America 63) (New York: Geological Society of America, 1955), https://pubs.geoscienceworld.org/ books/book/704/ De-Natura-Fossilium-Textbook-of-Mineralogy, accessed June 17, 2020.

In the process of ageing, arsenic pigments undergo gradual discolouration or become transparent[29], which makes them poorly visible and identifiable in artworks[30]. Furthermore, sulphur and arsenic compounds easily react with copper-[31] and lead-[32] based pigments; as a result, Verdigris – hugely popular in the Middle Ages – turns into chalcocite[33] when reacting with orpiment. In contrast, a stable combination is shown by mixture of orpiment with organic blue (indigo[34], or its less expensive substitute – woad). In terms of stability, about the greens created in this way mention Jehan le Beuge[35] and Cennino Cennini[36]. Reactions of sulphur with copper (Verdigris[37] in particular) and with lead[38] were usually described in most treatises on painting, and by painters themselves as unfavourable combinations. In "The Materials of the Painter's Craft in Europe and Egypt: From Earliest Times to the End of the 17th Century, with Some Account of Their Preparation and Use"[39], the author quotes Cornelis Janssens van Ceulen or Anthony van Dyck, both of whom described the yellow arsenic sulphide as the one "killing" other colours[40].

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29 Elisabeth West FitzHugh, "Orpiment and Realgar," *Artists' Pigments. A Handbook of Their History & Characteristics* 3 (1997): 49.

30 FitzHugh, "Orpiment," 51.

31 Katrien Keune et al., "Analytical Imaging Studies of the Migration of Degraded Orpiment, Realgar, and Emerald Green Pigments in Historic Paintings and Related Conservation Issues," *Heritage Science* 4 (2016): 10, DOI: 10.1186/s40494-016-0078-1.

32 Marc Vermeulen et al., "The Darkening of Copper- or Lead-Based Pigments Explained by a Structural Modification of Natural Orpiment: a Spectroscopic and Electrochemical Study," *Journal of Analytical Atomic Spectrometry* 32 (2017): 1331–1341, DOI: 10.1039/C7JA00047B.

33 Vermeulen et al., "The Darkening," 1331.

34 Dominika Tarsińska-Petruk, "Zestawienie zbiorcze warstw technologicznych ikon," in Kruk, *Ikony*, vol. 2, 194 (MNK XVII-26), 196 (MNK XVIII-27), 188 (MNK XVIII-10), 200 (MNK XVII-32).

35 Mary P. Merrifield, *Original Treatises, Dating from the XIIth to XVIIIth Centuries on the Arts of Painting, in Oil, Miniature, Mosaic, and on Glass; of Gilding, Dyeing, and the Preparation of Colours and Artificial Gems; preceded by a General Introduction; with Translations, Prefaces, and Notes*, vol. 1 (London: J. Murray, 1849), 252, 274, https://hdl.handle.net/2027/yale.39002059304486, accesed March 17, 2020.

36 [Cennini,] *The Book*, 53.

37 Arthur P. Laurie, *The Materials of the Painter's Craft in Europe and Egypt: From Earliest Times to the End of the XVIIth Century, with Some Account of Their Preparation and Use* (Edinburg: T.N. Foulis, 1910), 219.

38 Cyril Stanley Smith and John G. Hawthorne, "Mappae Clavicula: A Little Key to the World of Medieval Techniques," *Transactions of the American Philosophical Society* 64, no. 4 (1974): 27–28.

39 Laurie, *The Materials*, 219.

40 Laurie, *The Materials*, 219.

Orpiment in art works and treatises on painting

In reference sources, orpiment (As_2S_3) presence was confirmed in multiple artworks: ancient Egyptian and Coptic pieces, Pompeiian paintings, painted ornamentation of the Al-Aqsa Mosque in Jerusalem; Armenian (11th until the 16th century) and Arab (14th century) manuscripts; Persian miniatures (early 14th through the 16th century); Japanese artworks (17th until the 19th century); Central Asian murals (between the 6th and 13th century); and Tibetan thangkas[41]. In Europe, brought in from the Orient and employed until the 19th century, it was used in minor quantities from the 9th until the late 19th century, i.a. in Dutch (since the early 15th century) and Venetian (Titian, Tintoretto, Veronese[42]) paintings[43]. Orpiment (As_2S_3) and realgar (As_4S_4 or AsS) were listed in Russian, Armenian, and Azerbaijani writings on painting from the 15th until the 18th century, and in 4th-century Indian writings (duly applied in painting from the early 12th until the 17th century)[44]. In icons, yellow orpiment and red realgar remained in use from the 12th until the 16th century in fold details of Russian (Novgorod, 15th century)[45], Bulgarian and Balkan[46] art. In all probability, regarding orpiment (As_2S_3) identyfied in SEM-EDX[47] and μ-Raman spectroscopy[48] analyses, its occurence could be also attributed to territories of former Galicia and Red Ruthenia, including the lands of Przemyśl, Sambor and Drohobych[49].

In all listed artworks, orpiment was present mainly as an ingredient of colour combinations, containing organic and non-organic pigments. One of the most popular was its mixture with indigo, which gave a deep green. Such

41 FitzHugh, "Orpiment," 47–49.

42 Nicholas Penny, Ashok Roy, and Marika Spring, "Veronese's Paintings in the National Gallery Technique and Materials: Part II," *National Gallery Technical Bulletin* 17 (1996): 40, www.nationalgallery.org.uk/upload/pdf/penny_roy_spring1996.pdf, accessed May 30, 2020.

43 FitzHugh, "Orpiment," 49.

44 FitzHugh, "Orpiment," 50.

45 Olga V. Lelekova and Marina Naumova, "Data on Icons Pigments Composition and Their Attributive Value," *ICOM Committee for Conservation. 6th Triennial Meeting* (Ottava) 4 (1981): 81/24/3–8, https://www.icom-cc-publications-online.org/3767/Data-on-icons-pigments-composition-and-their-attributive-value, accessed February 24, 2021.

46 FitzHugh, "Orpiment," 50.

47 Michał Płotek and Małgorzata Walczak, "Wyniki analizy SEM-EDX," in Kruk, *Ikony*, vol. 2, 76–77, 79–85, 90–91, 94.

48 Kamilla Małek, "Raport z wyników pomiarów techniką spektroskopii rozpraszania ramanowskiego," in Kruk, *Ikony*, vol. 2, 122, 129.

49 Kruk, *Ikony*, vol. 1, 118, 128, 279, 422, 441, 451, 597, 631, 662–666, 667–673, 681–697, 698–702, 708–709.

formula for green can be found in the Armenian manuscript and also in writings by Eraclius, Lomazzo[50], Pacheco, Strassburg, Sloane MSS 1754, Biondo, The Marciana MS[51], Jehan le Beuge[52] or Cennino Cennini[53]. The combination of orpiment and indigo was identified in icon of *The Last Judgement* (inv. no. MNK XVIII-10)[54] and the *Deesis* icons (inv. no. MNK XVIII-26 and XVIII-27)[55], performed by painters of Potelych (Potylicz) and Drohobych (Drohobycz), and *The Last Judgement* (inv. no. MNK XVIII-32)[56] of the lands of Przemyśl. A similar mixture can be found in a number of Greek Epirus paintings (from the 16th until the late 18th century)[57].

The aforementioned *golden pigment* used to emphasise highlights (Jehan le Beuge[58], "Mappae Clavicula"[59]) or imitation gold is an entirely different matter. In this context, pigment was used for the background of the representations, and can be found in one of the Byzantine manuscripts[60], as well as in icons (such as the 16th-century double-sided icon of *The Man of Sorrows*, or the icon of *St. Demetrius* at the Byzantine Museum of Kastoria)[61]. Unpatterned, light-cream-coloured background of the Pskov icon of *The Miracle of St. George and the Dragon* (Il'inski Pogost parish) preserved in the British Museum in London, was performed in this way. The application of orpiment was documented by a restorer and master copier Adolf Ochinnikov of the Grabar Art Institute in Moscow; in 1960, he was responsible for conservation works on the icon prior to its transfer to London: "The nimbus, lance and chrysography on the armour were rendered in gold leaf, the background – in orpiment"[62]. As a substitute for the expensive ore, it appears i.a. in the Lucca

[50] Merrifield, *Original Treatises*, CLIV.
[51] Merrifield, *Original Treatises*, CLV.
[52] Merrifield, *Original Treatises*, 252, 256, 274.
[53] [Cennini,] *The Book*, 39, 43, 199, 256.
[54] Małek, "Raport," 127–128.
[55] Małek, "Raport," 128–129.
[56] Małek, "Raport," 126–127.
[57] Georgios P. Mastrotheodoros, Konstantinos G. Beltsios, and Yannis Bassiakos, "On the Blue and Green Pigments of post-Byzantine Greek Icons," *Archeometry* 62, no. 4 (2020): 777–779, DOI: 10.1111/arcm.12537.
[58] Merrifield, *Original Treatises*, 256.
[59] Smith and Hawthorne, "Mappae Clavicula," 30.
[60] Parpulov, Dolgikh, and Cowe, „A Byzantine Text," 211.
[61] I wish to extend my special thanks to all the Byzantine Museum in Kastoria for kind welcome, patience and permission to take some comparison photos for private use.
[62] I wish to show my appreciation the British Museum in London for the source documents and icons provided as part of the query conducted on 24 and 25 January 2019.

manuscript ("Scripto similis auri")[63], though by far the greatest number of "golden paint" recipes is listed by the Greek-Byzantine 12th-century *Mappae Clavicula*[64]. Reasons for painters seeking substitutes of gold may be sought in poverty and economising as well as the scarcity of bullion resources, either shrinking or exhausted as well as fraud[65]. Synthetic orpiment[66] manufactured since the Middle Ages, its hues wondrous and golden[67], was in all probability conducive to the practice. While "golden paint" was certainly helpful in producing precise chrysography, its application in large areas of backgrounds could have arisen from a wish to economise, scarcity of gold, or the will to cultivate a certain iconographic tradition. The only pre-17th century Greek manuscript, *Vaticanus Palatinus graecus* 209, dated at approximately 1355 and purchased between the years 1550 and 1570 in Venice or Padua[68], describes the practice of painting in greater detail, in a set of instructions regarding the stages of painting complexions and robes in icons, as well as recommended colour combinations. Texts contained therein, describing the creative process of the Greek masters (Panselinos, Palatinus and the Cretan school), once contrasted with other Latin (Theophilus, manuscripts of Lucca and Bologna), Slavic (Nectarius, Kyrkalov), and Armenian formulae, allow the identification of differences in principles concerning painting techniques[69]. In icon painting, which most usually employs a fixed set of oldest pigments, fundamental dissimilarities are identifiable in the shades, thickness and transparency of the primer (Greek: *proplasmos*, Russian: *sanquir*); painting layer, the graphic or painting treatment of facial contours and features, colour tones and distribution of tonal transitions (fluent or stippled), though style tendencies are varied here as well[70]; the nature, number, length and

[63] Srebrenka Bogovic-Zeskoski, "Gold and Not So Real Gold in Medieval Treatises," *Conservar Património* 22 (2015): 53, DOI: 10.14568/cp2015018.

[64] Smith and Hawthorne, "Mappae Clavicula," 28–39, 44, 47, 59, 66.

[65] Bogovic-Zeskoski, "Gold," 54.

[66] Nicholas Walsh Eastaugh et al., *Pigment Compendium. A Dictionary and Optical Microscopy of Historical Pigments* (New York: Routledge, 2008), 23.

[67] [Cennini,] *The Book*, 39.

[68] Parpulov, Dolgikh, and Cowe, "A Byzantine Text," 201–202.

[69] Parpulov, Dolgikh, and Cowe, "A Byzantine Text," 214.

[70] N. I. Miednikova, "Specific Skills of the Formation of the Lessirovochny Layer of the Dolichny Pismo. A Comparative Analizis of the Novgorod Icon-Painting of the 15–16th Centuries," in *Changes in Post-Byzantine Icon Painting Techniques*. *ICOM Committee for Conservation, Interim Meeting of the Icon Research Area*, eds. Nina Jolkkonen and Helena Nikkanen (Uusi-Valamo: Valamo Art Conservation Institute, 2001), 7–14.

colour of highlights and the placement and shape of pink complexion components (or lack thereof), the rendering of eye colour (pupils and whites)[71]. The Greek, Latin, Slavic and Armenian ways of modelling robes and complexions as described in the *Vaticanus Palatinus* were developed in three fundamental layers: the even undercoat, the deepening of shadows, and convex surface highlights[72]. The following colours prevailed in Greek painting: violet (black [possibly obtained from vine] and white), grey (black [charcoal, soot] and white), blue applied in garments (cyan and white), Constantinople ochre and green used to emphasise complexions and cheek contours, white, cinnabar, purple, and blacks (Cappadocian pigment and soot). Theophanes active between 1535 and 1545 on Mt Athos[73], is a good illustration of the approach. In the icon painting instruction by Panselinos, the primer (*proplasmos*) involves the use of white, ochre, *terre verte* (one part of each) with a black additive. The next stage involves the painting of facial features (with violet), lines thin to thick, the use of black to accentuate pupils and nostrils, and black or brown (umber) in eyelids and eyebrows. The subsequent stage of painting is the complexion with a mixture of good white (French or Venetian), ochre (Venetian), cinnabar (one part of each pigment)[74]. In another complexion formula by the same author (Panselinos), white is mixed with yellow-red ochre and a dash of bole; nonetheless, as specified in the formula, Thasos ochre required no bole additive. The mixture was then combined with a little *proplasmos* colour. The complexion colour was used to cover the tops of the cheeks and the chin, taking care for these areas not to stand out from the undercoat; colour would then be applied to the remaining parts of the face (including wrinkles in the elderly and eye sockets in the young). Finally, central parts of the face were illuminated by adding white to the complexion colour apply thinly. Young figures were distinguished by adding a thin layer of pink (cinnabar mixed with flesh colour) in the central part of

[71] Parpulov, Dolgikh, and Cowe, "A Byzantine Text," 215.

[72] Parpulov, Dolgikh, and Cowe, "A Byzantine Text," 214.

[73] Miodrag Marković, "Painters in the Late Byzantine World (1204–1453). Monumental Painting in Byzantium and Beyond: New Perspectives," conference paper: Dumbarton Oaks, Byzantine Studies Colloquium, November 4, 2016, https://www.academia.edu/31058516/Painters_in_the_Late_Byzantine_World_1204-1453_Monumental_Painting_in_Byzantium_and_Beyond_New_Perspectives._Byzantine_Studies_Colloquium_Dumbarton_Oaks_Washington_DC_November_4_2016_full_text_without_footnotes, accesed July 20, 2020.

[74] Parpulov, Dolgikh, and Cowe, "A Byzantine Text," 212.

the face, all shadows, contours and wrinkles accentuated with bole (?)[75]. According to Panselinos, all garments (chitons and himations) were to be painted by starting with a transitional shade (combining the selected pigment with white) applied to the entire garment surface, then highlighting, all shaded surfaces omitted. Garment folds were highlighted by a deeper hue of the transitional shade, thin glaze of indigo or reds layers applied. These general rules were practiced by multiple Greek painters, with a few exceptions. Black would be occasionally added to violet, the colour used to paint facial features or shadows. Black was used to paint pupils, eyelids, eyebrows and nostrils[76]. According to Panselinian, eyebrows and other parts of the face were to be painted in umber mixed with bole or pure umber, pupils and nostrils accentuated in black. In the Panselinian complexion painting technique – considerably simpler than that Panselinos – the initial layer of complexion tinting is entirely omitted, all colour applied directly to the *proplasmos*. Typical for Cretan painting, this is a feature distinguishing it from the older, "classic" Panselinos technique. According to Dionysius, Cretan icons were developed on the dark undercoat, with underdrawing and two relatively three colour and illumination layers. Facial features were drawn with a mixture of black and red on darker complexions based on ochre and black with a dash of white, prominent lines and pupils accentuated with pure black. Faces, hands and feet were painted in pale pink (white with small amounts of ochre and cinnabar), edges avoided. Whiter shades of pink were used to pick out the highlights. Hair of the young would be rendered in black, on a dark violet undercoat with added *proplasmos* and flesh colouring, as the grey hair and beards of the elderly were painted in grey directly on the undercoat with no primer, and thinly highlighted. Theophanes applied the same colouring as Dionysius in the undercoat and drawing. The lifeless body of the Christ Crucified would be painted on a dark violet undercoat with flesh and *proplasmos* colouring outlined in black. All colouring and highlights would be painted in pale pink. Robes and hands were left dark, highlighted in central areas only. Within the rules of painting, a 18th-century Russian-language copy of the earliest South Slavic painting manual, created according to Greek paradigm – "The Rule (Типик)", penned by Bishop Nectarios of the Serbian city of Veles were also preserved[77]. In all probability, the manuscript was penned by

[75] Parpulov, Dolgikh, and Cowe, "A Byzantine Text," 207.
[76] Parpulov, Dolgikh, and Cowe, "A Byzantine Text," 207.
[77] Parpulov, Dolgikh, and Cowe, "A Byzantine Text," 209.

the author of the 1557 murals at the Orthodox church in Supraśl, albeit no icon has ever been ascribed to him[78]. The painting technique described in "The Rule…" greatly differs from Greek prototypes. Drawings were transferred to a primed polished panel, "pressing them firmly thereto"[79], all contours outlined in ink. Prior to applying colour, the scene and figures would be glaze-shaded in ink, then filled with the desired colours, nimbi included. The background was to be painted "with ochre or something else"[80]. Complexions were rendered in two shades, applied to a dark undercoat (*sanquir*) of ochre and a little black, and a light-coloured one (ochre with a dash of cinnabar), covered in three layers: a) 3 parts ochre + 1 part cinnabar, b) 3 parts ochre + 1 part cinnabar + dash of white, c) second ochre mix (b) + white – the layer used to paint eyebrows, cheeks, nose, and lips. Finally, all shadows would be glazed in ochre, and highlights applied. A comparable Russian text from the 30s of the 16th-century, known as the "Kyrkalov Handbook"[81], lists an analogous set of pigments recommended for complexion painting (ochre, cinnabar, black, white). Yet there are distinct differences in paint thickness and working with the adhesive – egg tempera, applied in alternating layers – cover and glazing. A slightly thicker layer would be applied to a thin undercoat in dark ochre, contours of the underlying drawing remaining visible and covered again with a layer of thick, light-coloured ochre. Subsequent glazing would offset the differences between the dark undercoat and light-coloured facial areas; violet would then be used to outline the face then enhance shadows and finally selected facial parts in cinnabar blush. All aforementioned layers were gently covered in lighter-coloured ochre in all shaded areas then highlighted by adding a little white, all wrinkles accentuated and transitions evened out. Grey hair was painted in white directly on the undercoat without *sanquir* and shades in black; blond hair was painted by adding flesh pigment and outlines accentuated with light-coloured ochre. For hair chrysography, the handbook author suggests the use of moderate egg binding media amounts only; should an excess amount of egg adhesive binding be added inadvertently, the surface in question should be sprinkled with silica clay. Binding media should be mixed with cinnabar and gold leaf applied to all surfaces requiring intricate gilding. All gold leaf ornamentation was to be

[78] Parpulov, Dolgikh, and Cowe, "A Byzantine Text," 209–210.
[79] Parpulov, Dolgikh, and Cowe, "A Byzantine Text," 209.
[80] Parpulov, Dolgikh, and Cowe, "A Byzantine Text," 209.
[81] Parpulov, Dolgikh, and Cowe, "A Byzantine Text," 210.

pressed with a fingerbone, any excess gilding brushed off with a feather or sponge[82]. In "Kyrkalov's Handbook", the colour palette was slightly warmer than in other instructive writings and lists: golden (orange and yellow), light red (ochre and cinnabar or pink and cinnabar), azure (blue and white), light azure (one part blue, two parts white), green (blue and yellow), dark green (black and yellow), complexion undercoat (ochre and black with a dash of cinnabar), light ochre (ochre and two parts yellow), violet or ordinary purple (two parts cinnabar, one part black), and дикун (ochre and blue with white). Folds and shadows on white garments were rendered in green, on ochre-coloured robes – in violet with green. While practically no Armenian icons were created[83] or rather preserved to the present day, among the painting manuals an Armenian manuscript was preserved as a 1618 copy. It contains a number of curious entries, especially regarding orpiment in the backgrounds and egg yolk as the binding media. This is the only text I am aware of which mentions the use of arsenic sulphide in the background. According to the formula, the panel was covered with thick and liquid glue mixed thrice (the first layer thick, the second one – thinner, the final one the thinnest) with borax ($Na_2B_4O_7$). Once the panel had dried the surface was scraped smooth and the drawing was applied. The entire background surface was covered with orpiment, representations then rendered in the desired colours. Violet was obtained from a mixture of black and red, light red from white and red, light and medium violet was made of aquamarine with red and indigo, dark green – indigo with yellow, or light green as a indigo with yellow and aquamarine composition. Indigo was also recommended to outline blue garment folds. Green garments was to be rendered in basic green, red robes in cochineal, the brushstrokes light and transparent. In the Armenian description, the colour of the complexion was described differently than in other instructions. All faces, hands and feet were painted with an egg tempera with ochre, dark pigment, and gypsum additive. Violet ("apricot")[84] would be used to accentuate the eyes, hands and feet. Red would be added to half the violet mix then used to paint the face, eyebrows, hands and feet; eyes, nose, lips, ears, feet, hands and neck would then be re-accentuated with the contour used before. Eyes and eyebrows were to be outlined lightly in

[82] Parpulov, Dolgikh, and Cowe, "A Byzantine Text," 210.

[83] Dickran Kouymjian, "Armenian Art: An Overview," *Chemins d'Arménie* (paper for a project in Paris of 1995): 5, https://www.academia.edu/37170915, accessed January 14, 2021.

[84] Parpulov, Dolgikh, and Cowe, "A Byzantine Text," 211.

black, whites of the eyes slightly highlighted, all shaded surfaces rendered in green; finished by applying white highlights wherever required, and finally varnished thrice[85]. The 15th-century Bologna Manuscript in Latin reaches for Greek exemplars in details as well, albeit it describes the complexion as painted in red and white only; drawings in black, and all highlights in white. Brown produced with the use of red and black was used in eyebrows, pupils black with no white highlights. It was proposed that cheek shadows should be painted in deep red (*sinopia rubea*). The lifeless body of Christ Crucified was performed with ochre, white, and a small amount of green earth (*terre verte*) mixture, hair and facial features was painted in charcoal black and red, and finally highlights applied in white. Another 15th-century manuscript (Lucca) in Latin, "De coloribibus opus" recommends the use of pure colours mixed with white, and applied as the first layer. All folds were to be shaded in pure pigments i.e. red in shadows and white in highlights. A reverse procedure would occasionally be used as well, pure pigments used as the first layer, then shaded in red diluted with white, and highlighted with white. As the authors of the paper point out, other West European mediaeval manuals of painting, vastly differ from the *Palatinus* manuscript[86].

Discussion of the *Christ Pantocrator with Archangels* (MNK XVIII-27) and related icons

With regard to the oldest late Byzantine painting treatises the technique and materials used in the four out of nine ostensibly different icons from the Cracow collection, combined with arsenic pigment background show the greatest similarities to Armenian and South Slavic exemplars with slight Greek paradigms reminiscences. Yet a full analysis for all objects extends beyond the scope of this publication therefore only the icon of *Christ Pantocrator with the Archangels* shall be presented extensively.

The analysis of research documentation, including photographs, macrophotographs, elemental distribution maps obtained by macro X-ray fluorescence technique (MA-XRF) as well as cross-sectional studies allow to confirm this assumption. Research methods presented on the icon with the representation of *Christ Pantocrator with the Archangels* (inv. no. MNK

[85] Parpulov, Dolgikh, and Cowe, "A Byzantine Text," 211.
[86] Parpulov, Dolgikh, and Cowe, "A Byzantine Text," 213.

XVIII-27, fig. 1) example, illustrate the similarities in the construction of paint layers, visible also in other icons – *St John the Baptist and St Paul* (inv. no. MNK XVIII-26, fig. 3) likely originate from the same *Deesis* and the icon of *The Last Judgement* (inv. no. MNK XVIII-32, fig. 6), all of them a work by the masters of the Potelych and Drohobych circle, as well as the icon of *The Last Judgement* (inv. no. MNK XVIII-10, fig. 4) of the lands of Przemyśl. To clearly understanding the correlation of materials and painting layers structure, image processing software, such as Photoshop 22.5.2/2021 used in this case, allow to merge distribution elements maps (MA-XRF)[87] with photography of the original and transformed by ageing processes paint layers taken in the visible light (VIS). The resulting visualisation of fragment *The Christ Pantocrator with Archangels* icon (MNK, Inv. no. XVIII-27) (fig. 7: b–g)[88] shows areas of individual element occurrence and therefore pigments feasible to application of the painting.

Calcium (Ca), fragmentarily visible in the background, hair, nimbi, the blue-and-green himation and pink wing of the Archangel Michael as well as chiton of the Archangel Gabriel, points to the presence of chalk primer (fig. 7: c) confirmed in cross-section 27.6, and in analysis of the assemblages of calcareous nannoplankton from the ground layers originating probably from Chełm[89]. Similar structure represents cross-section 26.2 taken from icon of *St John the Baptist and St Paul* (from the Deesis) (MNK, Inv. no. XVIII-26).

The Christ Pantocrator with Archangels (from the Deesis) (MNK, Inv. no. XVIII-27) icon also includes lead (Pb), covering the greatest part of the icon's area, characteristic for lead white, red lead or massicot (fig. 7: d). Its vast quantities tie in with the use of lead white in complexions, highlights, white pages of the Holy Scripture, chrysography (of the throne) and garment details; lead white, red lead or massikot was used also to render the wings of the Archangel Gabriel, chiton of the Archangel Michael, throne and *klaw* (golden belt, a symbol of the dignity of the High Priest[90]), as well as nimbus

[87] Elemental distribution maps were generated using Bruker's dedicated software, see: Walczak et al., "MA-XRF Study," 303–3305.

[88] Kruk, *Ikony*, vol. 3, 96–97.

[89] Mariusz Kędzierski, "Analysis of the Assemblages of Calcareous Nan Oplankton from the Ground Layers of Icons from the Collection of the National Museum in Krakow," in Kruk, *Ikony*, vol. 2, 33, 36.

[90] Sławomir Fałek, "Wizerunek Zbawiciela w malarstwie ikonowym," on-line, fig. 17, https://www.muzeumtomaszow.pl/wp-content/uploads/2021/06/Sl.-Falek-Wizerunek-Zbawiciela-w-malarstwie-ikonowym.-Czerwiec-2021.pdf87, accesed July 9, 2021.

inscriptions (fig. 7: d). Element distribution maps for calcium (Ca), lead (Pb) and arsenic (As) as well as the photography taken in VIS prove that no lead pigments were applied to paint the Archangel Michael's wings (except for highlight lines), as opposed to the Archangel Gabriel rendering; in case of the latter, the lead (Pb) map allows a conclusion that the wing surface was fully covered with lead pigment(s), less intense in the background (mixtures with other pigments), more intense in the highlights. It is highly probable that wings were originally to be covered with orpiment and white highlights, as in case of the icon of *The Last Judgement* (MNK, Inv. no. XVIII-10) (fig. 4, 5). The original intent of rendering wings in gold may be suggested by an analysis of the cross-section 27.6 collected from the Archangel Gabriel's left wing, near the defect close to the silver-plated framing. A protective layer executed with glue adhesive binding, orpiment with chalk filler and silicon one, and lead white containing animal black were applied to a three layers of chalk primer developed in different thicknesses, bodies – two lower as a ground layer with a large grain size, the upper – with a fine one. Looking at the VIS photograph, the pink colouring of Archangel Michael's left wing which covers the *golden* layer visible on the map for arsenic (As) elements (fig. 7: b), one would be hard-pressed to declare beyond reasonable doubt whether what is at hand constitutes an extensive underpainting with orpiment or intentional *auteur* change in the colour of the wing. Aforementioned lead white has also been identified in Christ's blue himation; the absence of copper (Cu), cobalt (Co) or even iron (Fe) signals in indicated area would suggest that it had been mixed with an organic blue (indigo /woad /?). In careful observation of himation underpainting visible on the lead (Pb) map (fig. 7: d), allows a conclusion that once the composition had been delineated on the ground, that section was covered with top-to-bottom and slightly transverse brushstrokes, not always aligned with the outline of the folds. It proves that a large surface had been painted swiftly and efficiently in one colour with a flat, soft brush. The tri-stage paint application: darker shade of blue; whitening; and topmost highlights is illustrated by varied white intensity visible on lead (Pb) map.

Arsenic (As) is visible in the form of large and irregular background concentrations, in the Archangels' blue-and-greenish robes (Michael's himation – as confirmed in cross-section 27.3 (fig. 8) and Gabriel's chiton), partly in the Archangel Michael's pink wing, the ornamentation of chitons, and the lips and cheeks (fig. 7: b). The absence of arsenic pigment in the hair, complexion, and nimbi area may suggest that it had not been used throughout the icon's

entire surface – just in the background, in an analogy to classical gilding with gold leaf. Decoration to the neckline and sleeve edging of Christ's chiton and other patterns (of four dots in a diamond shape in this case) carried out gold-mimicking pigment, were typical and frequent in 15th- and 16th-century panel painting equally lines of chrysography. The four dots motive is also identifiable in the Archangels' robes. The absence of points on the arsenic map and visible lead map signal would suggest they have been painted in lead white, making Christ and His Divine Brilliance (expressed of golden pigment) distinctive in comparison with the Archangels.

It is worth mentioning, in the group of nine icons of the Cracow collection, orpiment (As_2S_3) was used in mixtures with copper-[91], ferrous-[92] and lead-based pigments[93] (*The Last Judgement*, inv. no. MNK XVIII-25; *Hodegetria Surrounded by Archangels, Apostols, and Joachim and Anne*, inv. no. MNK XVIII-28; *Archangel Gabriel and St. Peter and the*, inv. no. MNK XVIII-111; *St. Nicholas with Scenes from His life and Miracles*, inv. no. MNK XVIII-192 and *St. Paraskeva with Scenes from Her Life*, inv. no. MNK XVIII-57)[94], as well as with indigo or woad. In combination with lead white, it was mainly present in the highlights, chrysography and details, whereas in combination with read lead and massicot, it produced red- and orange-coloured layers, as well as with copper-based pigments[95] and organic blue pigments[96] – various hues of green. Multiple colour changes visible in aforementioned areas are the consequence of mutual degrading pigment influence.

The iron (Fe) noticeable in the visualisation (fig. 7: f), pointing to areas where ochre (of varied hues) or iron red had been used, and manganese (Mn), an umber-identifying element, are visible in the complexion and hair undercoats, in Christ's purple chiton. The colour of the primer (Greek: *proplasmos*,

[91] Tarsińska-Petruk, "Zestawienie," 210 (MNK XVIII-111), 194 (MNK XVIII-25), 196 (MNK XVIII-28), 202 (MNK XVIII-57), 216 (MNK XVIII-192).

[92] Tarsińska-Petruk, "Zestawienie," 210 (MNK XVIII-111), 194 (MNK XVIII-25, MNK XVIII-26), 196 (MNK XVIII-27, MNK XVIII-28), 188 (MNK XVIII-10), 200 (MNK XVIII-32), 2002 (MNK XVIII-57), 216 (MNK XVIII-192).

[93] Tarsińska-Petruk, "Zestawienie," 210 (MNK XVIII-111), 194 (MNK XVIII-25, MNK XVIII-26), 196 (MNK XVIII-27, MNK XVIII-28), 188 (MNK XVIII-10), 200 (MNK XVIII-32), 202 (MNK XVIII-57), 2016 (MNK XVIII-192).

[94] Tarsińska-Petruk, "Zestawienie," 194, 196, 210, 216.

[95] Tarsińska-Petruk, "Zestawienie," 194 (MNK XVIII-25, MNK XVIII-26), 196 (MNK XVIII-27, MNK XVIII-28), 188 (MNK XVIII-10), 202 (MNK XVIII-57), 216 (MNK XVIII-192).

[96] Tarsińska-Petruk, "Zestawienie," 194 (MNK XVIII-26), 196 (MNK XVIII-27), 188 (MNK XVI-II-10), 200 (MNK XVIII-32).

Russian: s*anquir*) – ochre with an admixture of umber and black (as suggested by the undercoat) – seems to be, as aforementioned (*Vaticanus Palatinus)*, close to Armenian and South Slavic primers (ochre combined with black).

Titanium (Ti) has been identified (fig. 7: e) in the exact ferrous area, a phenomenon suggesting additives typical for terrestrial deposits[97].

Mercury (Hg), element present in cinnabar (or vermillion) has been detected in surfaces described by authors of treatises as areas of whitening, or of the colour pink applied to prominent features of the face, hands and feet – the forehead, nose, cheeks, lips, chin, neck, and palms (fig. 7: g). Transitional tints and complexion completions in ochre with cinnabar additives in each of the three progressively whitened layers (as proven by high mercurial intensity in indicated areas) and white highlights point to the artwork's South Slavic provenance or painting method. Black outlines visible in the icon in intense black, recorded also in an infrared (IR) photograph (IR 830 nm filter), present in signature, contour and hair areas[98], are typical charcoal black traces. On the other hand, the practice of accentuating facial features, pupils, eyelids, eyebrows and nostrils in black has been described in the Panselinian painting technique, and mentioned in the manuscript of Bologna.

An additional issue is the greasy adhesive binding used in the icons, visible as strong, spatial impastos, characteristic of yolk tempera. This binder, causing a faster degradation of arsenic pigments[99], was particularly recommended in Armenian paintings as the most appropriate, protecting the completed painting during the threefold protection with a layer of varnish (lacquer).

In order to illustrate the impact of colour changes resulting from the degradation of the orpiment in the icon of *Christ Pantocrator with Archangels* (from the *Deesis*) (MNK, Inv. no. XVIII-27), the present publication has been enriched with the visualisation of the original colour range of the work (fig. 9). The simulation was created in the Photoshop 22.5.2/2021 graphic programme, taking into consideration all the data obtained as a result of the material analysis. In this way, the intense yellow background imitating gold, the deeper greens of the archangels' robes and the "golden" ornaments illustrate the lost beauty of the *Deesis* fragment. The visualisation does not take into account colour changes resulting from dirt on the surface of the painting.

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97 Kate Helwig, "Iron Oxide Pigments, Natural and Synthetic," *Artist's Pigments. A Handbook of Their History and Characteristics* 4 (2007): 60, 61, 88.

98 Kruk, *Ikony*, vol. 3, 91.

99 Vermeulen et al., "Assessing," 82–91.

Summary

While the presence of orpiment has not been unambiguously identified in all the above nine icons, its original and intentional application as imitation of gold in unpatterned backgrounds and in garment ornamentation is highly probable. The analysis of cross sections of samples taken from the backgrounds of the icons would probably explain unambiguously the colour transformations that took place in the painting layers, however, the above interpretation based on many premises may be significant evidence trace in the history of all paintings in question; primarily, it may serve as an example proof of the enormous difference between the current look of these artworks and their original appearance. A comparison of how the paintings were produced, on the example of *Christ Pantocrator with Archangels* (from the *Deesis*) (MNK, Inv. no. XVIII-27) and related icons, with formulae described in the oldest preserved Byzantine treatises on the art of painting allows the potential origin of the masters to be pinned down through the traces they had left in their works; the latter seem to point to their Armienian and South Slavic rather than Russian or Greek roots, albeit the occasional Greek echo, in all probability embedded in the painters' DNA, continues to be unquestionably present. I hope that pointing to the seemingly invisible pigments will encourage alertness to colour combinations, a subject worth many an academic and expert paper.

Fig. 1. *Christ Pantocrator with Archangels* (from the *Deesis*), MNK, Inv. no. XVIII-27. MA-XRF mapped area. Photo: P. Frączek, M. Obarzanowski, Central digital repository of the National Museum in Krakow

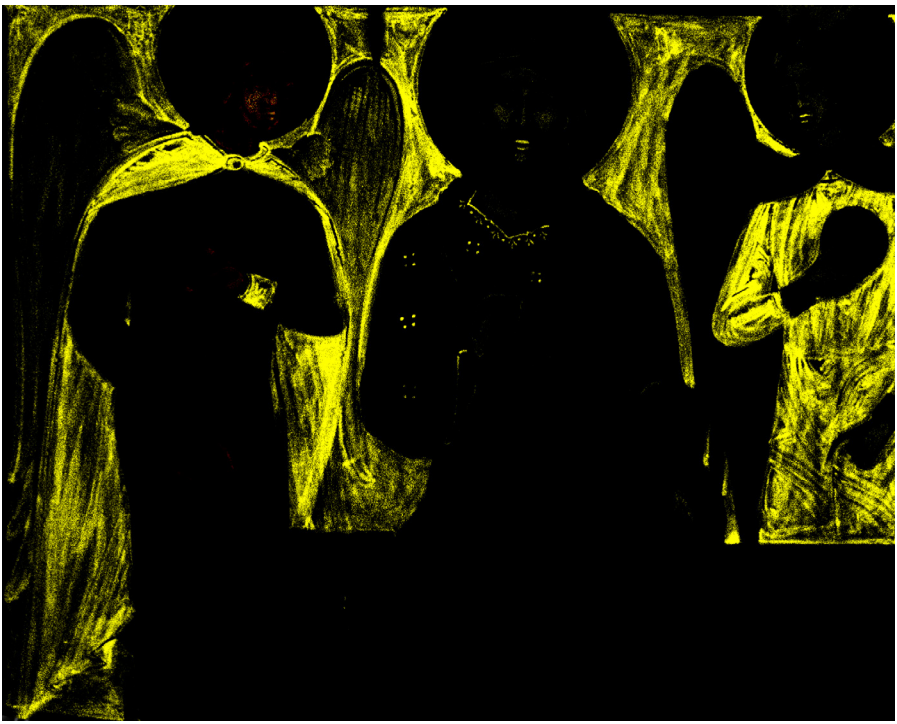

Fig. 2. *Christ Pantocrator with Archangels* (from the *Deesis*), MNK, Inv. no. XVIII-27, section. Distribution map of arsenic (As). Author of MA-XRF map: M. Płotek, Academy of Fine arts in Krakow, after: M. P. Kruk, *Ikony XIV–XVI wieku w Muzeum Narodowym w Krakowie*, vol. 3 *Ilustracje* (Kraków: Muzeum Narodowe w Krakowie, 2019), 96

Fig. 3. *St John the Baptist and St Paul* (from the *Deesis*), MNK, Inv. no. XVIII-26. Photo: P. Frączek, M. Obarzanowski, Central digital repository of the National Museum in Krakow

Fig. 4. *The Last Judgement*, MNK, Inv. no. XVIII-10, section. The layer of orpiment under historical painting layers. Photo: P. Frączek, M. Obarzanowski, Central digital repository of the National Museum in Krakow

Fig. 5. *The Last Judgement*, MNK, Inv. no. XVIII-10, section. Traces of yellow orpiment on the bottom layers of overpainted angels wings. Photo: D. Tarsińska-Petruk

a b

Fig. 6. *The Last Judgement*, MNK, Inv. no. XVIII-32. Painting layer (green grass) performed with a mixture of orpiment and indigo. Photo: P. Frączek, M. Obarzanowski, Central digital repository of the National Museum in Krakow
a – fragment of an icon, general view, b – section

Fig. 7. *Christ Pantocrator with Archangels* (from the *Deesis*), MNK, Inv. no. XVIII-27, detail. Visualisation of the occurrence an individual elements in the painting layers of icon perfomed based on MA-XRF maps and VIS photography. Author of the MA-XRF maps: M. Płotek, after: Kruk, *Ikony*, vol. 3, 96–97. Collage, visualization and graphic processing: D. Tarsińska-Petruk
a – VIS, b–h – distribution of: b – arsenic (As), c – calcium (Ca), d – lead (Pb), e – iron (Fe), f – manganese (Mn), g – mercury (Hg), h – titanium (Ti) elements

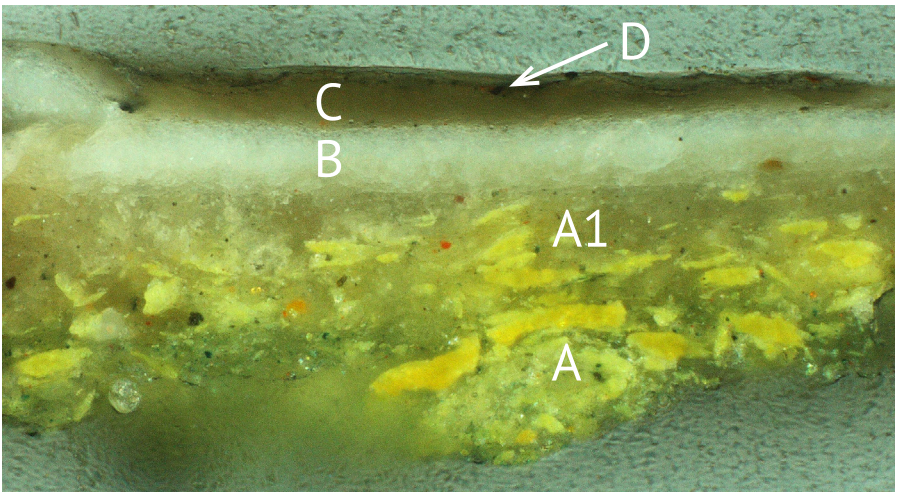

Fig. 8. *Christ Pantocrator with Archangels* (from the *Deesis*), MNK, Inv. no. XVIII-27. Cross-section 27.3. Photo M. Goryl, after: M. Walczak, D. Tarsińska-Petruk, M. Płotek, M. Goryl, and M. P. Kruk, "MA-XRF Study of 15th–17th Century Icons from the Collection of the National Museum in Krakow, Poland," *X-Ray Spectrometry* 48, no. 4 (2018): 303–310, DOI: 10.1002/xrs.2949
Layout of technological layers: A and A1 – orpiment with chalk filler and silicon, B – lead white, C – organic compounds, D – silicon, chalk, earth pigment, possibly vegetable black

Fig. 9. *Christ Pantocrator with Archangels* (from the *Deesis*), MNK, Inv. no. XVIII-27. Visualisation of an icon before colour transformations caused by degradation of pigments and binders. Collage, visualization and graphic processing D. Tarsińska-Petruk

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