New scientific investigations on the *Salvator Mundi* from Stanisław Kostka Potocki's Wilanów collection by non-invasive analytical methods

DOI: 10.36135/MPKJIII.01377329.2022.SWXXIX.pp.307–331

Philippe Walter
Sorbonne Université, CNRS, Laboratoire d'archéologie moléculaire et structurale
Paris, France

Dorota Folga-Januszewska
Anna Guzowska
Elżbieta Modzelewska
Museum of King Jan III's Palace at Wilanów

Iwona Szmelter
Faculty of Conservation and Restoration of Works of Art
Academy of Fine Arts in Warsaw

Wilanów Studies
vol. XXIX, 2022 pp. 307–331
Yearbook, E-ISSN: 2720-0116

ABSTRAKT: W artykule przedstawiono wyniki nowych analiz fizykochemicznych obrazu *Salvator Mundi* z kolekcji wilanowskiej. Analizy te pozwoliły poznać materiały użyte do stworzenia obrazu i proces jego powstawania. Istotne zmiany chromatyczne wynikają z przebarwienia smalty, pierwotnie niebieskiej. Pentimento kciuka ręki błogosławiącej, podobne do tego zaobserwowanego na obrazie *Salvator Mundi* znajdującym się obecnie w zbiorach Ministerstwa Kultury Arabii Saudyjskiej (wersja Cooka), może wskazywać, że obraz powstał w pracowni Leonarda da Vinci.

SŁOWA KLUCZOWE: analiza chemiczna, obraz, Leonardo da Vinci, pentimento, smalta, *Salvator Mundi*

ABSTRACT: This article presents the results of new physicochemical analyses undertaken on the *Salvator Mundi* from the Wilanów collection. The analyses make it possible to better understand the nature of the materials used and the process of creating the painting. Important chromatic changes are due to the discoloration of the smalt, originally blue. A *pentimento* on the position of the blessing hand's thumb, similar to the one observed on the *Salvator Mundi* now in the collections of the Ministry of Culture of Saudi Arabia (the Cook version), could indicate that the painting was made in the studio of Leonardo da Vinci.

KEYWORDS: chemical analysis, painting, Leonardo da Vinci, pentimento, smalt, *Salvator Mundi*

The painting of *Salvator Mundi* in the Wilanów collection was bought by Stanisław Kostka Potocki in 1798 in Milan. Potocki wrote just after its purchase: "I am in possession of a painting of his original making, of Christ holding a glass terrestrial orb in his left hand, counted among his most beautiful works by all the Writers of Leonardo's life. His face became the universal model for the dignified heads of Christ".[1] The earlier history of this work is unknown, but many technical aspects suggest features of Leonardo's artistic legacy.[2] In this paper, we would like to discuss the new insights we may gain on these artistic practices thanks to the application of scientific imaging and chemical analyses, allowing to be discussed whether this painting could have been produced in da Vinci's studio, in collaboration with him or by a pupil, or whether it is a copy or a replica belonging to his followers. These aspects have been recently discussed by Dorota Folga-Januszewska and Iwona Szmelter in the book *Leonardiana in Polish Collections*.[3]

Scientific studies were already carried out during the restoration of the painting in 2005 and in 2018–2019.[4] Photographs taken in different radiation ranges (visible, ultraviolet, infrared) and Reflectance Transformation Imaging (RTI) yielded information on the underdrawings and on the restorations carried out on the panel painting in the past. The wooden support was examined and its dating conducted by dendrochronology. Stratigraphic analyses by optical and electron microscopes were carried out on five samples to describe the preparation layers and the painted layers. Gas chromatography-mass spectrometry (GC-MS) and Fourier-transform infrared spectroscopy (FTIR) yielded information on the binders. X-ray fluorescence spectrometry (XRF) made it possible to identify the pigments.

---

1 A. Kwiatkowska, '*Leonardiana* in the archives. Archival inquiry (condition as per 1 January 2019)': AGAD (Central Archives of Historical Records in Warsaw, hereinafter: AGAD), Archiwum Publiczne Potockich (Public Archives of the Potockis, hereinafter: APP), signature 257 S.K. Potocki's manuscript *On the Art of the Contemporaries ... Brouillon corrections ... biographies of Engravers and Painters* [before 1821], p. 250, in: D. Folga-Januszewska, A. Kwiatkowska, E. Modzelewska, I. Szmelter, A. Woźniak-Wieczorek, Leonardiana *in Polish Collections. What's What: Original, Replica, Copy*, vol. 2 (Warszawa, 2020, Series: 'Catalogue of the Wilanów Collection'), p. 28.

2 D. Folga-Januszewska, '*Leonardiana* and Stanisław Kostka Potocki's passion for collecting', in: Folga-Januszewska, Kwiatkowska, Modzelewska, Szmelter, Woźniak-Wieczorek, Leonardiana *in Polish Collections*, p. 33.

3 I. Szmelter, 'Closer to the truth about Leonardo da Vinci's artistic *bottega* – notes and comments on *Salvator Mundi* from Stanisław Kostka Potocki's Wilanów collection', in: Folga-Januszewska, Kwiatkowska, Modzelewska, Szmelter, Woźniak-Wieczorek, Leonardiana *in Polish Collections*, p. 69.

4 E. Modzelewska, '*Salvator Mundi* in the light of the latest research', in: Folga-Januszewska, Kwiatkowska, Modzelewska, Szmelter, Woźniak-Wieczorek, Leonardiana *in Polish Collections*, p. 57.

From the dendrochronological analysis, Tomasz Ważny[5] concluded that the support used for the *Salvator Mundi* was made from the timber of an oak tree which had been cut down after the year 1585, most probably in Central France. However, the documentation on the painting mentions various interventions on the wooden support that had been conducted probably several times. It was also observed on the painting samples that the panel was covered with a bright chalk-and-glue primer (containing also dolomite chalk), covered with a slightly coloured *imprimatura* containing lead white.[6] The materials and the techniques used in the making of the painting could indicate that the work is from the end of the sixteenth century and probably has an origin of the North of Europe. Nevertheless, the nature of the preparation layer, which is characteristic of this region while a *gesso* made with calcium sulphates was preferred in Italy, is not always a decisive argument. We have shown on the *Christ with Singing and Music-Making Angels*, a late fifteenth-century panel painting attributed to Hans Memling and assistants, that both chalk and gypsum are present in the grounds: these materials, probably applied in separate layers, been detected in various locations on all panels.[7] The issue of the painting's dating can, and should be, the subject of further research.

These previous studies have also shown that the cloak was painted with a blue pigment (smalt), today totally discoloured. From all these data, it seems that this painting was deeply retouched in the past, for example on the background and on the globe, which currently seem to be uniformly black. The painting has been restored in 2005 by Iwona Stefańska from the National Museum in Warsaw,[8] and UV fluorescence photographs taken during other investigations in 2018–2019[9] highlight

---

5 T. Ważny, 'Analiza dendrochronologiczna obrazu Salvator Mundi', Laboratory of Dendrochronology, Institute for the Study and Conservation of Cultural Monuments at Nicolaus Copernicus University in Toruń (Toruń, 2005).

6 Authors of the 2005 research: P. Karaszkiewicz, M. Walczak, Faculty of Art Conservation and Restoration, Academy of Fine Arts in Cracow – micro-chemical analyses of the samples, laser micro-analysis; I. Zadrożna, Faculty of Chemistry, Warsaw University of Technology – gas chromatography–mass spectrometry (GCMS) and Fourier--transform infrared spectroscopy (FTIR) analyses; T. Ważny, Laboratory of Dendrochronology, Institute for the Study and Conservation of Cultural Monuments at Nicolaus Copernicus University in Toruń – dendrochronological analysis; E. Rosłoniec, National Museum in Warsaw – preparation of samples for analysis.

7 G. Van der Snick et al., 'Material analyses of "Christ with singing and music-making Angels", a late 15th-century panel painting attributed to Hans Memling and assistants: Part I. Non-invasive *in situ* investigations', *Journal of Analytical Atomic Spectrometry*, vol. 26, 2011, pp. 2216 –29.

8 I. Stefańska, Dokumentacja konserwatorska obrazu "Salvator Mundi", Pracownia Konserwacji Sztuki Nowożytnej, Muzeum Narodowe w Warszawie, 29 VIII 2005 (copy of the documentation conveyed to the Wilanów Palace Museum in 2005).

9 Authors of the 2018–2019 research: P. Targowski, M. Iwanicka – Optical Coherence Tomography (OCT) analyses; J. Bonecka – computer tomography scanning; P. Kozakiewicz – the analysis and interpretation of CT scans; T. Łojewski – multispectral

Fig. 1

Setup for XRF (left) and hyperspectral imaging (right)

the recent repaints visible on the face, the background, the glass sphere, the cloak, etc.

The aim of the analytical approach we developed is not limited to the identification of materials, but also concerns their relationships to one another with the aim to assess the various influences on the artists and the technical innovations that this work displays.[10] We carried out various types of non-invasive analyses (Fig. 1) by combining visible/near infrared (400–1000nm) reflectance imaging spectroscopy and X-ray fluorescence imaging spectroscopy. We used imaging techniques as well as point analyses with quantitative data treatment in order to go deeper into the understanding of the different materials, with a particular emphasis on the study of the mixtures and superimposed colours, and then to give new insights into their making. Samples taken from the painting and prepared as cross-sections had already provided a uniquely detailed insight into the stratigraphy, which we used for the interpretation of our data. However, sampling provides only local information, which might be misleading, and so it is useful to combine such investigations with imaging techniques, which provide more representative results over a larger surface area.

imaging; S. Svorová Pawełkowicz – stratigraphic analyses on microsection samples and identification of pigments, fillers (SEM EDS), and composition of the ground in the board supporting the underpainting (spectrum measurements in FTIR infrared); K. Załęska – measurements of the X-ray fluorescence (XRF) with a portable spectrometer; A. Tomkowska – HIROX microscope analyses; R. Stasiuk – IR reflectography and digital radiography; E. Bunsch, W. Storoż, K. Radomski – 3D documentation of the painting's fragments with structured lighting imaging and RTI.

10 P. Walter, L. de Viguerie, 'Materials Science Challenges in Paintings', *Nature Materials*, vol. 17, no. 2, 2018, pp. 106–09.

The X-ray Fluorescence spectroscopy (XRF)

For the XRF investigation, two in-house built instruments were used, consisting for the first one (named ScanniX), of an Pd-anode transmission X-ray tube operated in air (without purge or helium) at 30 kV, 100 µA Moxtek MAGNUM (Orem, UT) with a 0.8 mm Pd collimator, and for the second one (named MicroScaniX), of a MCBI Pd-anode source from RTW Gmbh (Germany) combined with a polycapillary optics and developed through a collaboration between the Laboratoire d'archéologie moléculaire et structurale (France), NASA (USA) and the company ExaminArt (CA, USA). MicroScaniX allows collecting spatially resolved XRF data down to 100 µm resolution.

The X-ray detector is a SDD-detector (70 mm^2 active area, collimated to 50 mm^2, X-123FAST SDD, Amptek, Bedford, MA). The instruments were also used as a scanner to acquire elemental distribution images (chemical maps), making use of two motorized stages with a 30 cm travel range (Thorlabs, Newton, New Jersey, USA). The raw spectral data were evaluated by the software packages PyMCA.[11] This setup is optimized in its geometry for the detection of light elements, allowing observation of aluminium and good detection for silicium and phosphorus (and above).

Eighty measurements were carried out by X-ray fluorescence spectroscopy with ScaniX on the face, the hand, the orb, the robe, the cloak and the background. Six XRF-mappings were realized with MicroScaniX on the eye, the mouth, the fingers, the hair, the face and the hand with the orb.

Hyperspectral analyses

Visible and near infrared (VNIR) hyperspectral images were acquired from selected areas with the hyperspectral camera IQ by Specim (Oulu, Finland). The spectral range is 400nm to 1000nm with 204 wavelength channels with a spectral resolution of 7nm and a spatial sampling of 512 × 512 pixels. The field of view of the IQ camera is 31 × 31 degrees. The working distance was about 20 cm. During the investigation, diffuse illumination was provided by two 100 W halogen lamps, placed at 0.5 m away. Dark and white references were acquired for normalization of the data. A *Spectralon* diffuse reference standard was used as white reference.

The dedicated ENVI software (Harris Corporation, Melbourne, Florida, USA) was used for data treatment. The data was normalized with dark and bright field images using the Specim plug-in in ENVI. The spectral angle mapper (SAM) algorithm of ENVI was used to obtain reflectance

11 V.A. Solé, E. Papillon, M. Cotte, P. Walter, J. Susini, 'A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra', *Spectrochim Acta B*, vol. 62, 2007, pp. 63–68.

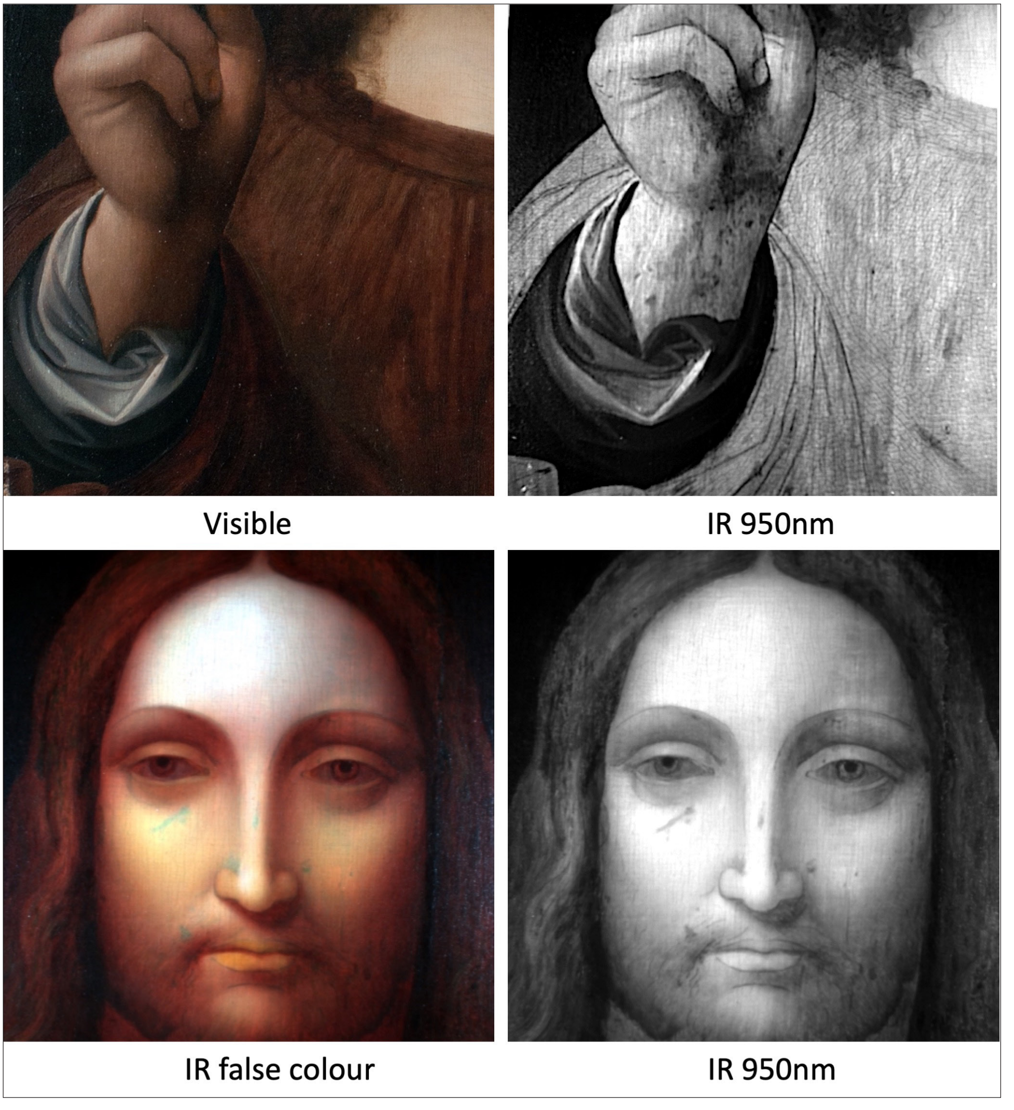

Fig. 2

Infrared reflectography obtained from hyperspectral imaging at 950nm, in two areas showing the underdrawings, and IR false colour image

map considering only a portion of the spectral range that contained the key spectral feature/s characteristic of the material to be mapped. Spectra from selected areas were used to identify the pigments by comparing them with a database of pigments built at LAMS and a software developed at LAMS.

A total of 8 areas were recorded by hyperspectral imaging. Due to the limited time for the acquisitions, the whole surface of the painting was not scanned.

Macrophotography

Macrophotographs of the analyzed areas were recorded with an Olympus camera OM-D E-M5 Mark II, featuring 16.1 or 40 Mpixels images, using an Olympus macro lens M. Zuiko Digital ED 60mm 1:2.8 Macro.

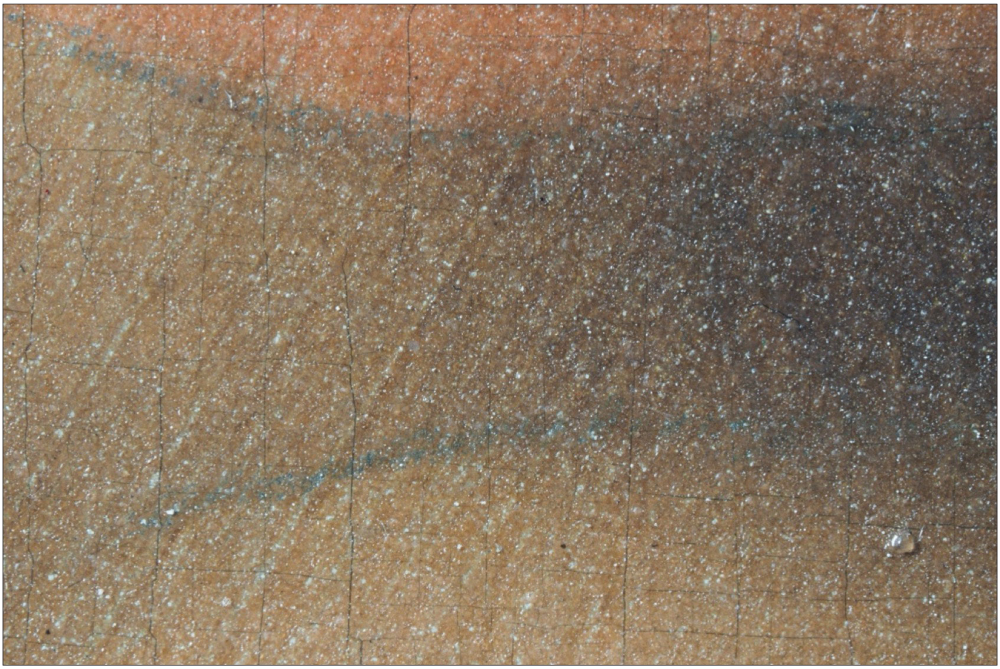

Fig. 3

Macrophotograph showing the underdrawings for the lips and the chin

General considerations on the drawing and repainted areas

The hyperspectral imaging data are allowing to ‘see’ the painting in the visible and near infrared domains. By selecting a wavelength in near infrared (NIR), it is possible to obtain images similar to those of reflectography, showing drawings, restorations, and the spatial distribution of a highly absorbent pigments like carbon black. The results are similar to those obtained by IR reflectography, already carried out by Roman Stasiuk during the research in 2018–2019. Examples of images obtained with our instrument are given in Fig. 2. We observe the drawing probably made on the primer: it looks like a precise copy of lines, probably transferred from a cartoon. There is no evidence of pouncing and it has been suggested that it was probably transferred from a cartoon by tracing the lines on it when its other side was covered with black pigment.[12] Strong contours for the eyebrows, the eyes, the nose and the lips are observed, as are in the copies of the *Mona Lisa* in the Prado Museum and of the *Sainte Anne* from Los Angeles, UCLA,[13] and in paintings by Leonardo, such as *La Belle Ferronière* or the *Ginevra de' Benci*. Interestingly, in the areas where the painting has suffered from abrasion, this drawing is directly visible in the macrophotographs (Fig. 3). It looks discontinuous, probably due to the irregularities of the ground layer surface. The black

12 Modzelewska, ‘*Salvator Mundi*’, p. 60.

13 A. González Mozo, ‘The copy of the Gioconda, and Bruno Mottin, Leonardo’s Monna Lisa in the light of its Madrid copy’, in: *Leonardo da Vinci’s technical practice: paintings, drawings and influence* (Roma, 2014), pp. 194–220.

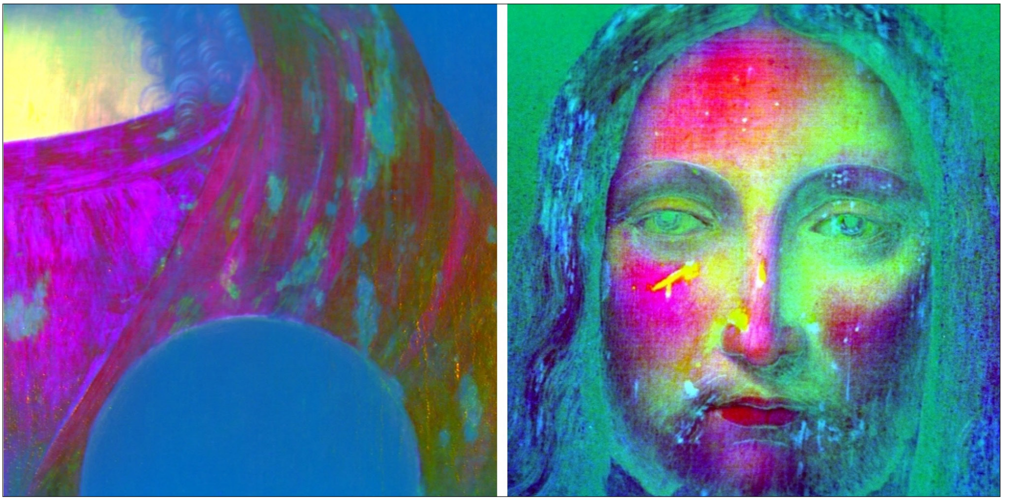

Fig. 4

False colours images obtained with the Minimum Noise Fraction Transform. The different colours are corresponding to the different classes calculated with this procedure

lines appear to have not been done with a liquid medium but with a dry one; this confirms the possible transfer from a cartoon.

Because millions of spectra are collected, we can use the data to carry out statistical treatments and to highlight the heterogeneities in the painted film. We calculated false colour image with a procedure called the Minimum Noise Fraction Transform. This procedure is used to determine the inherent dimensionality of image data, to segregate and equalize the noise in the data, and to reduce the computational requirements for subsequent processing. The calculated images help to quickly uncover dominant spectral materials. This procedure is thus well suited to the painting under analysis as combinations of various components correspond in our case to mixture of pigments creating optical effects. By combining these components, it is possible to create false colour images that highlight the repaints. Examples of images produced by this method are given in Fig. 4: repainted areas on the robe, the cloak and the face are easily visible on false colour images.

The *pentimenti*: modifications in the composition of the painting

Infrared reflectography at 950nm obtained with the hyperspectral camera, XRF mapping and hyperspectral imaging reveals that the blessing hand is showing one or two possible changes on the thumb (Fig. 5). These *pentimenti* are covered by the black paint of the background or by the flesh paint. Nevertheless, they are still visible in infrared or by combination of specific wavelengths to produce a false colour image that takes into account the possible presence of vermilion under the final representation. They are also visible on transformed data, i.e. on the first or second derivative of the Kubelka-Munk transformation of the

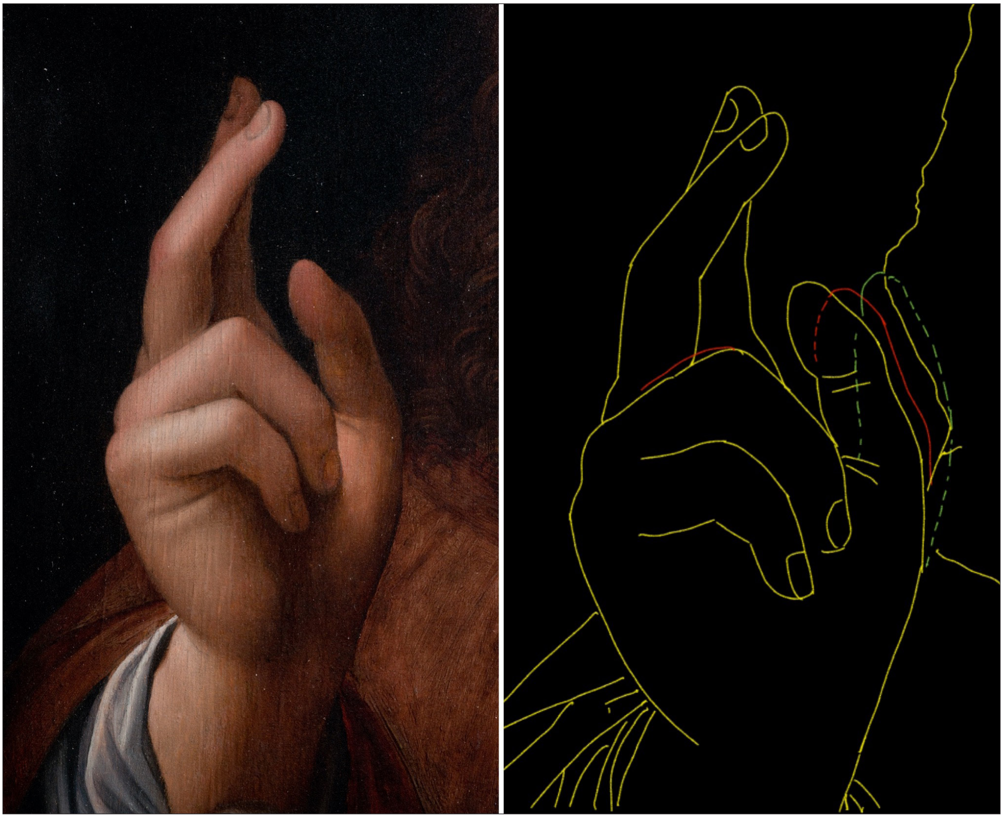

Fig. 5

(left) Photograph of the painting. (right) Drawing of the *pentimenti* observed on the underdrawing and on the layers of painting containing vermilion. The green dotted line corresponds to a modification in the composition that is impossible to determine with certainty on the basis of the existing data

reflectance spectra, as shown in Fig. 6a. This calculation can help to visualize location of pigments: it is showing here a negative peak at 580nm that is linked to the presence of vermilion. This modification is not clearly visible on X-ray image of the painting. To verify this *pentimento*, we have carried out an XRF mapping of this area. We clearly observe on the map of mercury (Hg), corresponding to the pigment vermillion, the presence of a first thumb painted before the final version (Fig. 6b).

During the restoration of the *Salvator Mundi* now in the collections of the Ministry of Culture in Saudi Arabia (also known as the Cook version), Dianne Dwyer Modestini discovered a similar *pentimento*, which shows the blessing hand's thumb in a straight rather than curved position. She added that "it is only a small adjustment, but it was evidently of great importance for the painter to make a major change at such a late state in the development of the final composition".[14] In fact, she observed that the final position of the thumb may have been painted on top of the opaque black background colour and not just the thin initial wash. We have not enough data on this area to verify if the same assumption

14 D. Dwyer Modestini, salvatormundirevisited.com/Pentimenti (accessed 29 March 2022); id., 'Leonardo da Vinci's Salvator Mundi Rediscovered', in: *Leonardo da Vinci's Technical Practice: Paintings, Drawings and Influence* (Paris, 2014), pp. 139–52.

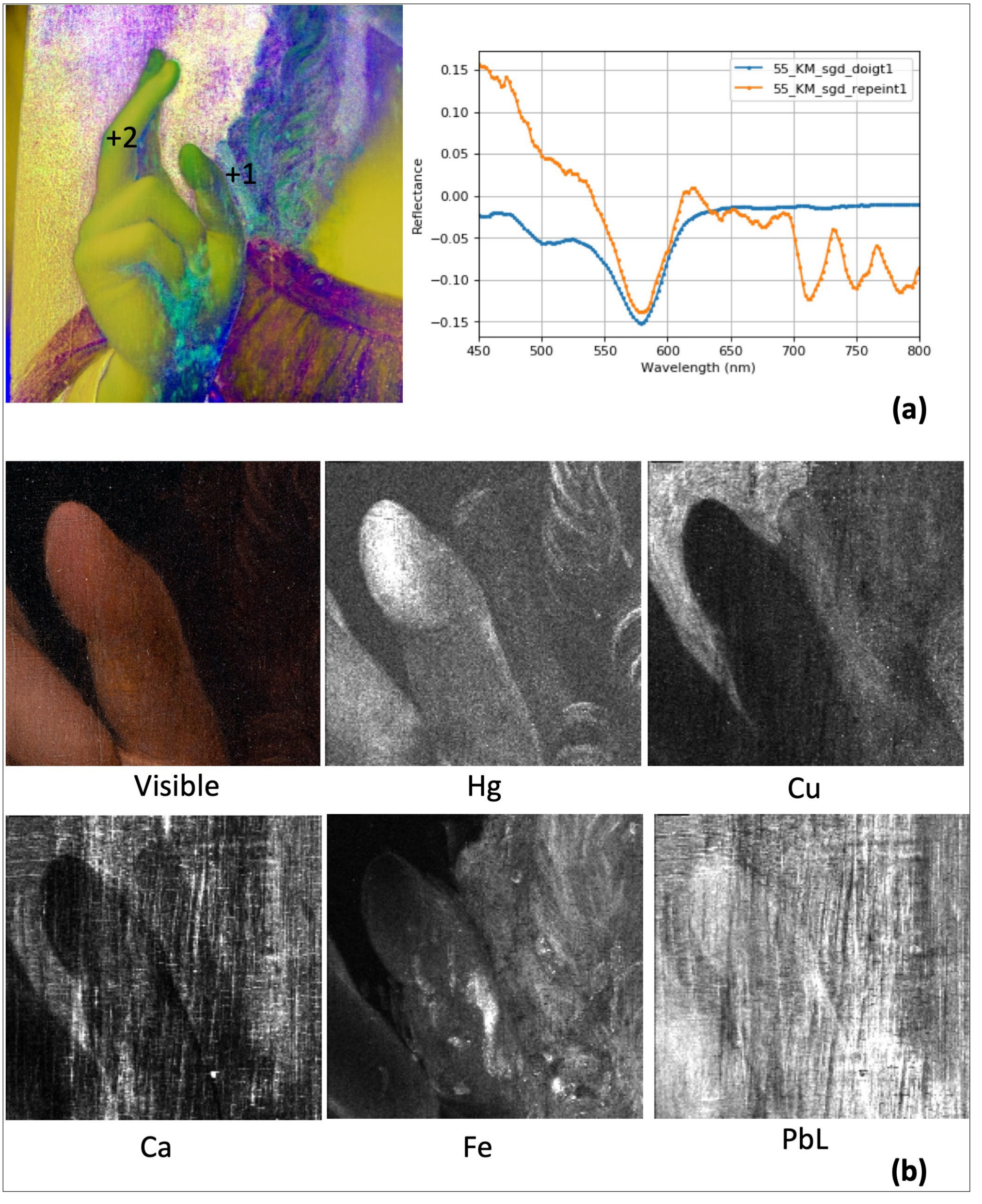

Fig. 6

(a) First derivative of the Kubelka-Munk transform of the reflectance spectra on the right on two points located on the image in false colour (left) and corresponding to the pentimento and the hand. The negative peak at 580nm corresponds to vermilion. (b) XRF mapping of the area of the thumb showing the distribution of chemical elements characteristic to the main pigments present in this area: vermilion (for Hg), azurite (for Cu), probably bone black and impression layer (for Ca), earth (for Fe) and lead white (for Pb) can be made regarding the *Salvator Mundi* from the Wilanów collections, but the presence of a first thumb painted before the final version is demonstrated in the two paintings.

Diane Dwyer Modestini observed also a shift in the position of the hand holding the orb which it is not a *pentimento* as such, but rather a freely brushed sketch made by the artist at the *abbozzo* stage. XRF mapping on this area of the painting from Wilanów does not show any trace of a previously painted composition in this area.

To sum up, this is a turning point for suppositions regarding the provenance and dating of the Wilanów's *Salvator Mundi*. The *pentimento* shows the artist had a second thought about the positioning of the thumb. This is commonly considered to constitute evidence that a given painting is not a copy made after the completion of the original, since copiers would have no doubts about composition. It seems that we have a comparable modification in the composition of the painting under analysis here; the two paintings were, then, probably being painted simultaneously.

The pigments

In 2005, five samples of the painting layers were taken.[15] The identified pigments were lead white, copper pigments, organic red, earth pigments of the Renaissance colour palette, and later additions: Prussian blue and lead chromate, present in the repainted and retouched areas. Here, we focused our XRF analyses on a non-restored area, paying attention to UV and X-ray documents when choosing the areas to be analysed. The palette of observed pigments is classical for the sixteenth century. We have identified lead white, smalt, azurite, vermillion, several earth pigments, carbon black, and probably bone black. Dyes used for the preparation of lake pigments cannot be observed by XRF and were not observed by reflectance spectrometry because of the presence of a thick and unusual varnish that interferes with the reflectance signals. Considering only a limited number of measurements on the representative areas of the painting were carried out by XRF on this painting, it is possible that other pigments have been used and are not described here. Different data suggest a possible use of minium (red lead).

Lead white

Lead white (lead carbonates) is present in a large quantity in the whole painting, as shown also by the radiography. A primer containing a large amount of lead white was applied over the whole surface. Its thickness is at least 8µm, according to the calculation in particularly thin areas (for example in the background).[16] Lead white was also used for the flesh

15 Modzelewska, '*Salvator Mundi*', p. 62.

16 This estimate was obtained thanks to a methodology developed in L. de Viguerie, V.A. Sole, and P. Walter, 'Multilayers quantitative X-ray fluorescence analysis applied to easel paintings', *Analytical and Bioanalytical Chemistry*, vol. 395, 2009, pp. 2015–20.

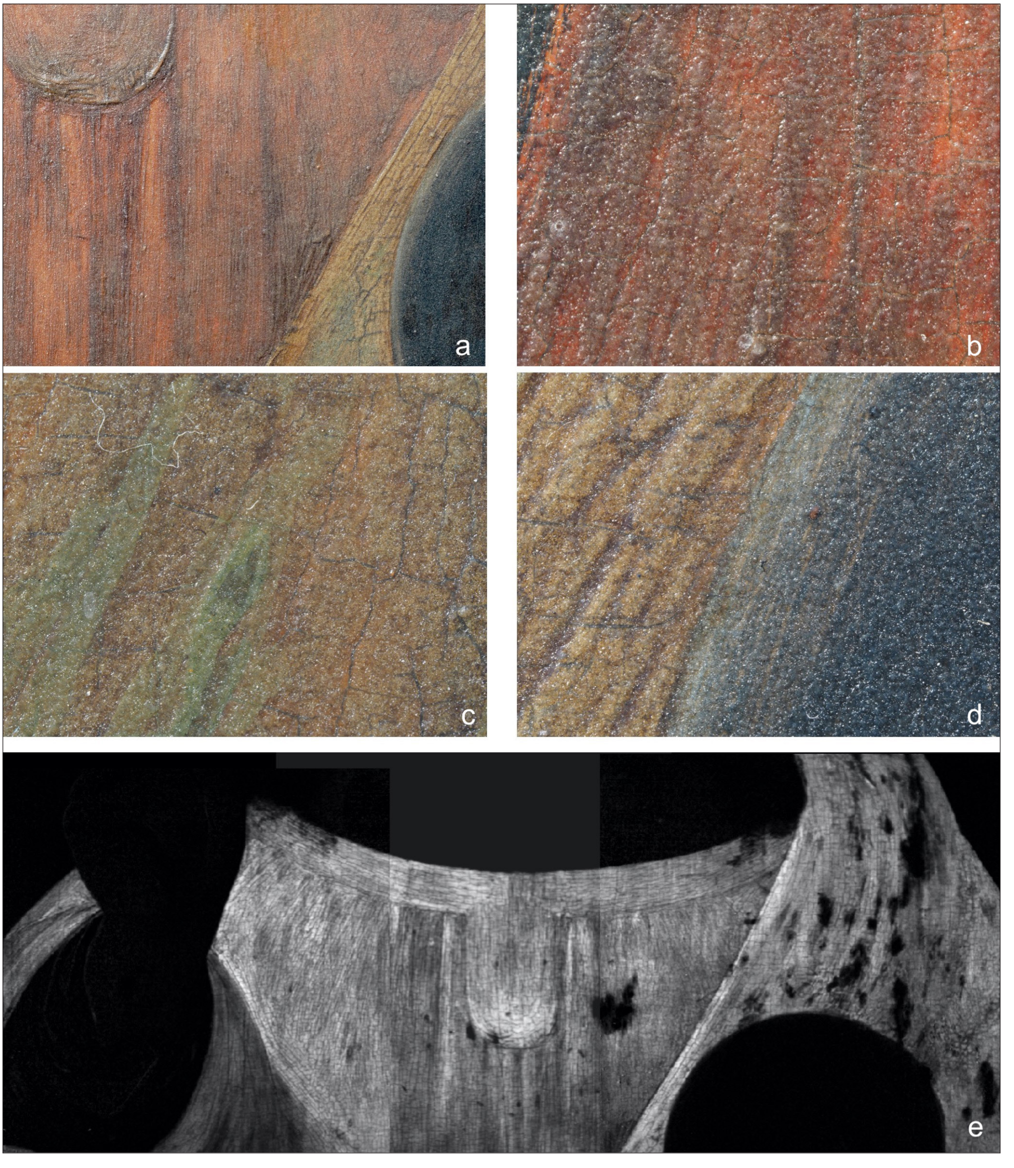

Fig. 7

(a-d) Detail and macrophotograph of the robe and the cloak; (e) Map of smalt in grey level (semi-quantitative) calculated by fitting the peak at 677nm on the first derivative of the reflectance spectra tones and for the white shirt. This thickness increases to about 60 µm in the lightest areas on the forehead.

Smalt

Smalt is a cobalt-coloured blue potash glass, well known for its fugitive nature when used with oil. XRF measurements carried out on Christ's cloak and robe show high peaks for cobalt, potassium and arsenic, strongly suggesting the presence of smalt, even if the pigment is now totally discoloured. It is well known that over time its blue colour turns to a light grey hue, as the potassium migrates out of the glass.[17] The layer containing smalt is thick and the paint was probably applied thickly, as observed on the macrophotographies (Fig. 7a-d). This presence of smalt was already described during the previous study of the painting, on a cross-section of a paint sample obtained from the cloak at the painting's edge. It shows visible grains of considerably degraded smalt, with single, sharp-edged, blue particles.[18]

The presence of smalt is confirmed by hyperspectral images showing features that may be considered to be linked to this pigment: for well-preserved smalt, the first derivative of the reflectance spectrum is showing peaks at 711, 605 et 549nm. Here, it seems these values are slightly shifted for degraded smalt. By considering the peak at 677nm in the image, it is possible to extract the mapping of smalt from the data (Fig. 7e). We must, then, consider that the cloak and the robe, previously described as golden and red, were originally painted in other colours (blue/purple/green depending on the relative quantities of the other pigments in the final tint). We can compare these results with the *Salvator Mundi* from the Saudi Arabia collections, showing an intense blue colour for the robe, and the Detroit Institute version with a green colour for the coat. Another *Salvator Mundi*, in the collections of the Pushkin Museum, attributed to Giampietrino, also has a green coat.

Because no contrast is visible in the infrared at 950nm of the robe, the shadows on the robe were probably painted with differences in the thicknesses of the paint layer or by variations of the qualities of smalt in this layer: more intense blue smalt pigments were prepared with higher cobalt contents, according to ancient preparation techniques and darker shades can be obtained by the admixture of the other pigments. The cobalt content in smalt can give an indication of the original strength of colour; Spring et al. have shown that with 4.8 wt% CoO content, the pigment would originally have been a strong blue, but its intensity can

17 M. Spring, C. Higgitt, D. Saunders, 'Investigation of Pigment-Medium Interaction Processes in Oil Paint Containing Degraded Smalt', *National Gallery Technical Bulletin*, vol. 26, 2005, pp 56–70.

18 Modzelewska, '*Salvator Mundi*', p. 62.

also depend on the particle size (finely ground pigment being paler).[19] The hue of smalt usually resembles that of ultramarine, even if it is a little less intense. To characterize the original colour of the smalt used for this painting, other measurements would be necessary to quantify cobalt in the pigment grains (for example by scanning electron microscopy on a samples). It is the only way to try to evaluate the original colour of the cloak and the robe.

Gettens and Stout[20] suggested that the earliest occurrence of cobalt-coloured glass in Europe may have been in the early fifteenth-century Venetian glass industry, but it seems it was used only rarely before the beginning of the sixteenth century[21] and it became extremely common in the second half of the sixteenth century. This pigment was observed both in oil and fresco paintings.

By X-ray fluorescence, it is possible to measure the impurities in smalt that are characteristics of the cobalt ore and of its treatment before the synthesis of the pigment. The smalt used for this painting contains strong impurities of iron (Fe), copper (Cu), bismuth (Bi), nickel (Ni) and arsenic (As) because most of the cobalt ores combine cobalt with iron, nickel, bismuth and/or arsenic. Copper is more unusual and may be due to some admixture of blue azurite to the smalt.

We observe a strong correlation between the intensity of the different elements and we can assume that only one quality of smalt was used. Here is an estimate of the composition in metallic impurities from a measurement carried out on the cloak, if we consider the concentration of Co as 5%, and we use the fundamental parameters method to interpret the XRF data with the software PyMCA:

Co 5%, Ni 1%, As 6.5%, Bi 2.5%, Fe 4.3%, Mn 0.07%, Cu 0.5%

We note that the smalt used for this painting is very rich in arsenic, nickel and bismuth. We can compare these data with the composition of smalt in other paintings as described in different publications:

– smalt with same impurities was also observed by XRF and in samples taken on the robe and cloak of the *Salvator Mundi* in the collection of the Detroit Institute of Art;[22]

19 M. Spring, 'New insights into the materials of fifteenth- and sixteenth-century Netherlandish paintings in the National Gallery, London', *Heritage Science*, vol. 5, no. 1, 2017, pp. 5–40.

20 G.L. Stout, *Painting Materials* (New York, 1966), pp. 57–59.

21 M. Spring, C. Higgitt, D. Saunders, 'Investigation of pigment-medium interaction processes in oil paint containing degraded smalt', *National Gallery Technical Bulletin*, vol. 26, 2005, pp. 56–70.

22 J.F. Mansfield, B.M. Vyletel, C. Selvius DeRoo, 'SEM and STEM Microstructural and Microchemical Analysis of Pigments Contained in a *Salvator Mundi* in the Collection of the Detroit Institute of Art', *Microscopy and Microanalysis*, vol. 19, 2013 (Suppl. 2), pp. 20–21.

- similar compositions were observed in paintings by Gerolamo Romanino and Parmigianino dating from 1524;[23]
- a study of smalt in paintings by Titian and Veronese in the National Gallery showed similarly all are very rich in arsenic;[24] the arsenic content is considerable in most cases, exceeding that of cobalt;
- the paintings by Raphael in the Villa Farnesina, dating from 1518, also contain smalt with impurities of Ni, As and Bi;[25]
- a similar smalt was observed by XRF spectrometry in the *Madonna and Child* (1510– 1520?), by Bernardino Luini, in the Museo e Real Bosco di Capodimonte.

We have found in the literature only few measurements of smalt with impurities of As-Ni-Bi for the period before 1520. To highlight possible changes in composition during the first decades of the sixteenth century, we can also consider elemental compositions of cobalt blue glazes on terracotta sculptures from the Florentine della Robbia school. They should be produced with the same cobalt ores. The work carried out by Zucchiatti et al. demonstrated a substantial change in the materials used in Florence marked by the presence of arsenic and bismuth in the glaze, and by reduced amounts of iron and nickel just before 1520,[26] probably between 1515 and 1520. The authors supposed that this evolution was due to procedures introduced to industrialize the production of the blue pigment.

Azurite and other copper-based pigments

Azurite is a blue copper carbonate. Whereas copper is observed in many XRF measurements, it is difficult to demonstrate that its presence is always due to this pigment. It may be also linked with its siccative property (and then added in the form of a salt, like vitriol) or to the use of other green pigments (verdigris, copper resinate or malachite).

For the white shirt, a copper-based pigment is visible by XRF in the shadows. Grains of azurite are not visible in the macrophotographs and the reflectance signal is difficult to interpret because the pigment is mixed with carbon black or because the blackening of azurite has occurred.

---

23 Spring, Higgitt, Saunders, 'Investigation of pigment-medium interaction processes'.

24 J. Dunkerton, M. Spring, with contributions from R. Billinge, H. Howard, G. Macaro, R. Morrison, D. Peggie, A. Roy, L Stevenson., N. von Aderkas, 'Titian after 1540: Technique and Style in his Later Works', *National Gallery Technical Bulletin*, vol. 36, 2015, pp. 6–39.

25 C. Seccaroni, J.-P. Haldi, *Cobalto, zaffera, smalto dall'antichità al XVIII secolo* (Roma, 2016).

26 A. Zucchiatti, A. Bouquillon, I. Katona, A. D'Alessandro, 'The Della Robbia Blue: a case study for the use of cobalt pigments in ceramics during the Italian Renaissance', *Archaeometry*, vol. 48, no. 1, 2006, pp. 131–52.

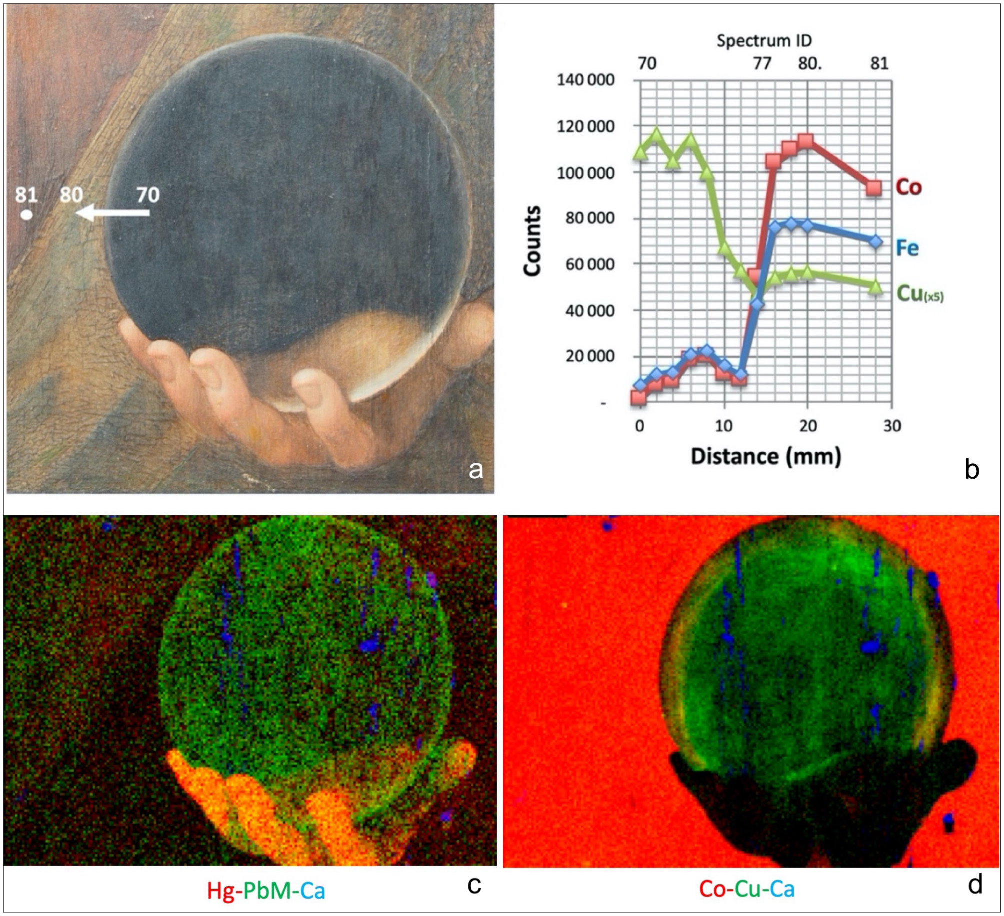

Fig. 8

(a–b) XRF measurements on the orb and the cloak showing evolution of the signals of Co, Cu and Fe. The signal of Cu was multiplied by 5 to show the three elements on the same scale; (c–d) XRF mapping in false colours showing at left: vermillion (Hg), lead white (PbM) and restoration fillers (Ca) and, at right: smalt (Co), azurite (Cu) and restoration fillers (Ca)

A copper-based pigment was also used for the orb. Again, the interpretation of its nature is difficult because of the presence of the black pigments, but azurite is plausible. At the limit between the cloak and the orb, blue grains are visible and should correspond to the azurite pigment (Fig. 8). This difference in composition between the area with the orb and the cloak shows the orb was not painted directly over the blue of the cloak. Unfortunately, the orb was repainted with a black pigment that prevents any other observations. It is interesting to see that a lower content of copper is also visible in the cloak, with a concentration much lower than the one of smalt. Grains of azurite are visible in this area, as on the face (see the section dedicated to the painting of the face) and in the white of the eye (Fig. 9a).

Some areas of the coat are green (Fig. 7c). No green grains of pigment are visible. This colour may be the effect of the presence of a diluted green copper-based pigment (like verdigris) or of a green earth. This can be also due to varnish and/or painting binder which has yellowed.

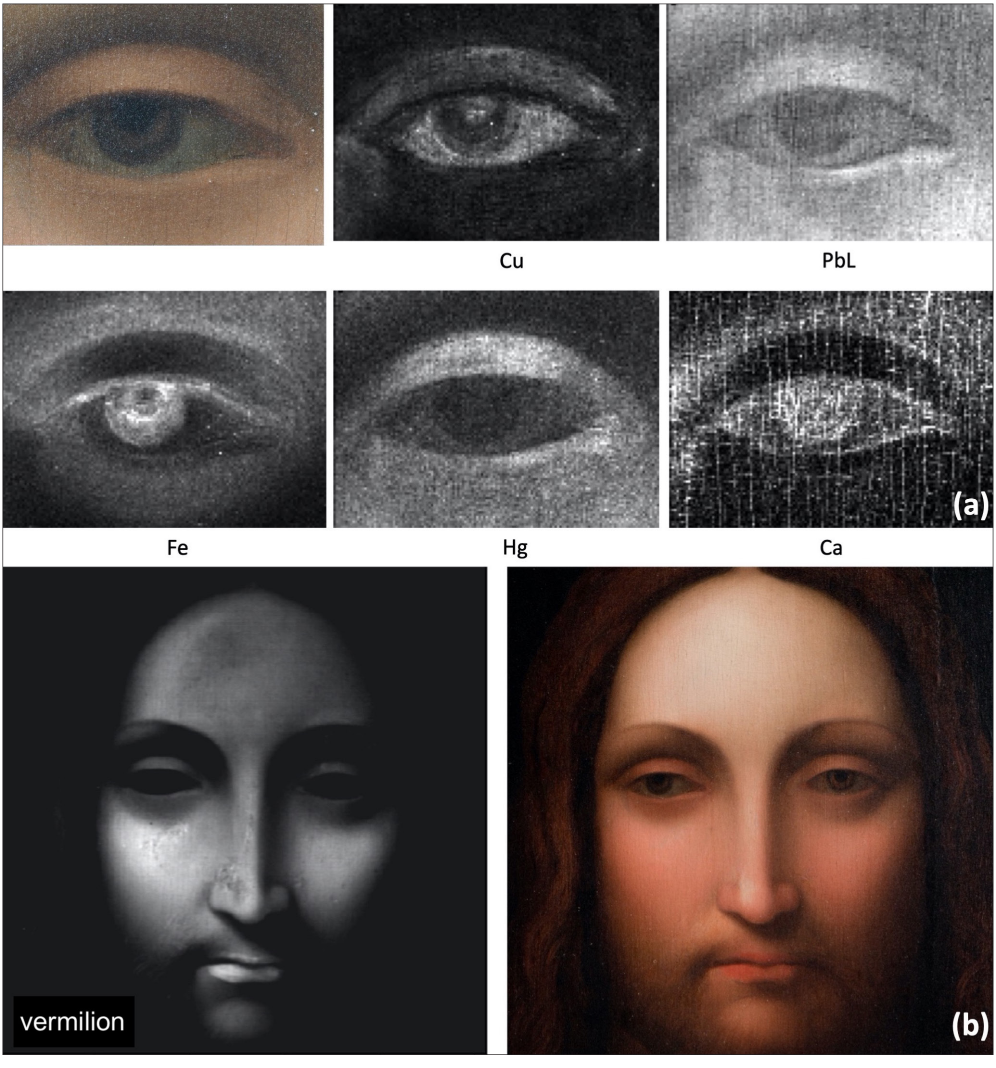

Fig. 9

(a) XRF mapping of the left eye; (b) Map of vermilion (left) from hyperspectral data (peak between 575–589nm) and picture of the face

Vermilion

Vermilion was used for the flesh tones and for the lips. Its reflectance signal in hyperspectral imaging is characteristic, but it can interfere with the signal from hematite. In our case, according to the XRF measurements, vermilion (identified with the presence of Hg) is the origin of almost all the variations of red on the face, but it is possible that a lake pigment is also associated and not detected by our techniques as previously explained: the presence of the varnish does not affect identification of Hg but it does affect identification of lake pigments by hyperspectral imaging.

By calculating the evolution of reflectance signal of vermilion, it is possible to produce a map of its contribution to the colour (Fig. 9b). When it is covered by black pigments, it is not well observed by this technique because its signal is absorbed.

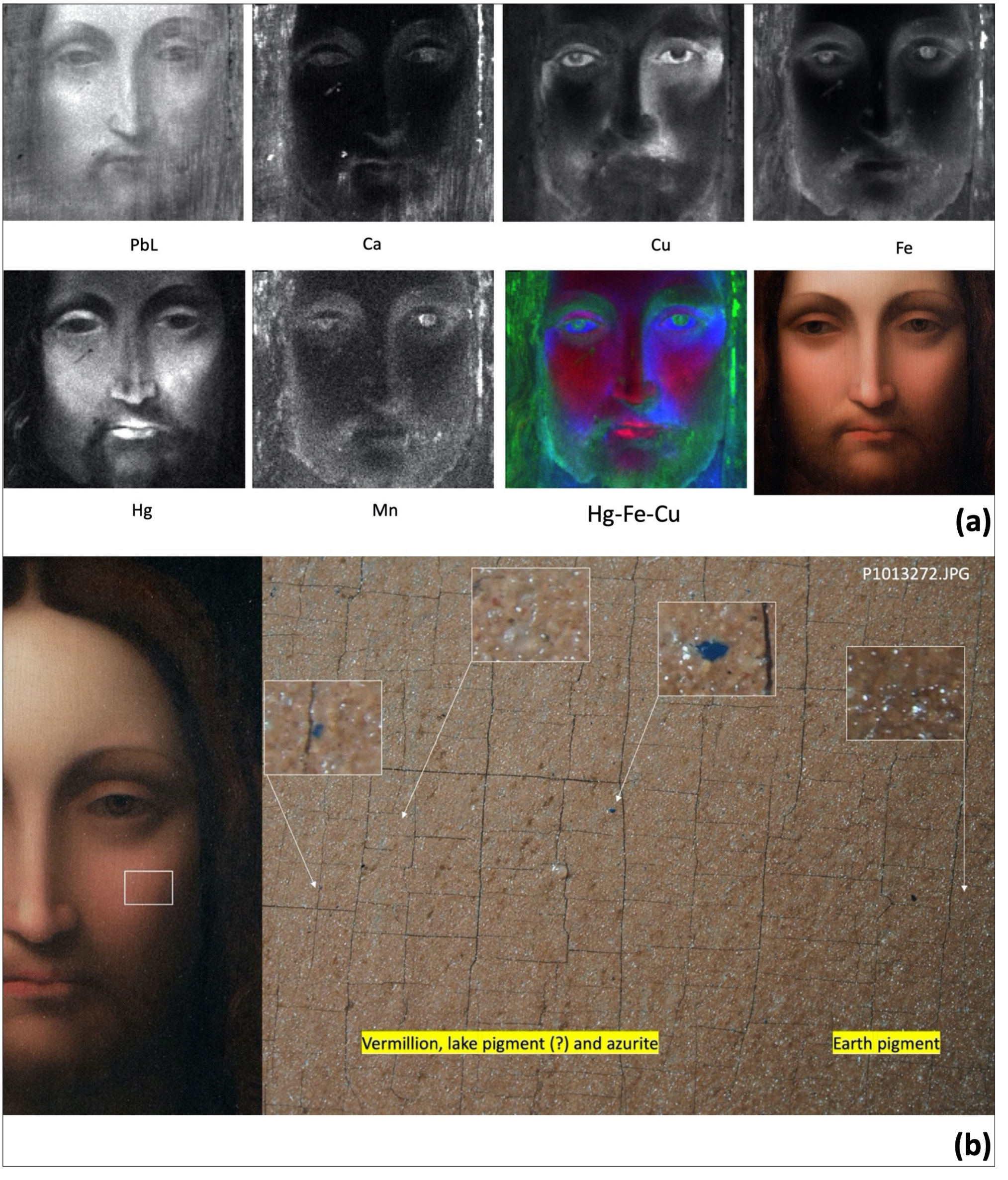

Fig. 10

(a) XRF mapping of the face; (b) macrophotograph of the cheek showing grains of azurite, vermillion and red lake pigments

Earth

It is usually possible to discriminate by XRF different earth pigments from the ratios between iron (Fe) and manganese (Mn), titanium (Ti) or potassium (K). Here, if only the measurements without smalt are considered, we observe a good correlation between Fe and Mn and a low content of K and Ti. We can infer that only one earth is present, with about 8% of Mn relatively to Fe. This kind of earth is usually considered an umber. It was used in the hair and for the shadows on the flesh.

A noticeable impurity of zinc is observed and can be related to the pigment or to some additions to the binder (as white vitriol used in dryers).

Carbon black and bone black

Carbon black cannot be identified by our techniques, whereas bone black (or ivory black) can be observed by XRF with the presence of calcium and phosphorus. Nevertheless, the varnish absorbs the X-rays produced by low energy X-rays. Between the lips, we observe a high content of calcium that can be interpreted as due to the presence of bone black. This pigment was also probably used in the shadows, associated with earth pigments, as will be described below.

For the black background of the painting, XRF measurements show the presence of Fe, Cu, Pb and Ca in various quantities. This colour is also very opaque in infrared, showing the presence of carbon black. It is very difficult to understand what had been done here without taking one or several samples of this area. If lead is as in lead white, it can be assumed that this pigment is only in the priming, because its equivalent thickness is estimated to be 8μm.

The examination of flesh tones on the cheek

We have analysed by XRF a series of points along a line through the cheek, going from the lightest area to the right of the nose to the darkest area, close to the ear (length of the line = 42 mm, number of measurements = 22). This method can give quantitative access to the composition and thickness of the different layers by using appropriate hypotheses on the multilayered material and following the evolution of each chemical element X-ray lines.

Direct examinations of the flesh tones, of the complexion colours and of XRF data, as well as the large XRF mapping on the face (Fig. 10a) suggest that the flesh was painted by superimposing four layers:

(a) the priming layer made of lead white, possibly with a copper-based pigment;
(b) a pink layer based on a mixture of lead white, vermilion, azurite, and probably lake pigments;
(c) a shadow layer made with an earth pigment (probably umber) and possibly bone black;
(d) a varnish.

In the macrophotographs, we observe grains of azurite in the flesh colour, but also red-brown grains with irregular shapes that are probably lake pigments (Fig. 10b). A noticeable quantity of copper is present everywhere: some copper-based pigments may have been included in the priming.

From a qualitative point of view, the XRF spectra show that the Pb-L lines emitted by layers (a) and (b) and Hg lines emitted by layer (b) decrease in the shadows, whereas the Fe and Ca lines, which originate from layer (c), increase. These Pb-L lines are coming from all the layers and are not absorbed by the upper layers. In the darkest areas, the signal of vermilion is close to zero, but a very small amount is still present.

It can be inferred from this information that the thickness of the shadow layer increases with the darkening of the shadow and, simultaneously, the thickness of the pink layer decreases. We can estimate that the total thickness of lead white (the priming and pink layer) grows from 10 µm in the shadow to 22 µm in the light. This is a technique usually used at the beginning of the sixteenth century and observed in paintings by Leonardo da Vinci, Raphael, Bernardino Luini and Andrea del Sarto.

The low energy Pb-M lines (around 2.3 keV) are strongly submitted to the absorption of the upper layers, i.e., in the case of this painting, by the varnish and the shadow. Their signal is here relatively constant. All these observations are confirmed by the XRF mapping of the face. We deduce that the painter used an opaque paint (dark earth with binder) instead of translucent glazes (with a more important amount of binder and no opaque pigment like earth) for the shadow effects, just as in such paintings as *Mona Lisa* and *Saint John the Baptist* by Leonardo da Vinci. This is confirmed by the painting's appearance in macrophotographs and in infrared.

The correlations between iron and manganese, calcium and potassium emphasize the presence of impurities in umber. An estimate of the quantity of calcium makes it impossible to perceive its presence only as an impurity in the earth, and the signal is too strong to be coming only from the primer or from calcite impurities in the lead white. This means that a part of the layer of the shadow is a compound rich in calcium. What is contributing to the black colour is probably bone black. This hypothesis is supported by the fact that the infrared reflectography is not very highly contrasted in this area, showing that carbon black is not present in important quantities.

Conclusion

The results of these analyses show the use of pigments and of a high-quality technique. The presence of totally discoloured smalt, of a varnish that considerably scatters the light, and of numerous restorations, as those in the orb, alter the perception of the quality of the work which we have today: it is very difficult to imagine it with the colours and glazing effects that had to be present just after its making. The blue and green tones of the robe and cloak have disappeared. The very fine work of materialising the orb on the garment is hidden by black repaintings, while a remarkable use of two blue pigments, azurite and smalt, seems to make it possible to take into account the tint differences produced by the transparent sphere.

From the point of view of the painting's dating, the impurities of arsenic and bismuth contained in the smalt indicate a work which could not have been carried out before the years 1510–1515, if we consider that these impurities are related to the cobalt ores used for its preparation and that smalt followed the same evolution in its chemical composition than the blue glazes of sculptures from the della Robbia workshop.

The most interesting new discovery arising from this study is the observation of the first-painted version of the blessing hand with its thumb in a straight position. This modification is very similar to the one described by Dianne Dwyer Modestini during the restoration of the Cook version of *Salvator Mundi*. This means that the painter who executed the painting now in the Wilanów collection had observed the first step of the painting now attributed by experts to Leonardo da Vinci. A copyist could not have noted this change when the original painting was finished, since by then it had been covered by the painting showing the curved position of the thumb. Thus, the painting studied here must have been started before the Cook version reached its final state. We can therefore assume that the Wilanów version was produced by a pupil or a follower of Leonardo who had seen the Cook version at its first stage, probably in the studio of the artist, and in its final state. It is a different version of the model, as was described for the *Mona Lisa* copy in the Prado Museum, for which underlying drawings displaying corrections similar to the ones in the Louvre model have been shown.[27]

BIBLIOGRAPHY

Delieuvin V., González Mozo A., Walter P., *Leonardo y la copia de Mona Lisa del Museo del Prado. Nuevos planteamientos sobre las prácticas del taller vinciano*, exhibition catalogue, Museo del Prado (Madrid, 2021).

Dunkerton J., Spring M., with contributions from R. Billinge, H. Howard, G. Macaro, R. Morrison, D. Peggie, A. Roy, L. Stevenson, N. von Aderkas, 'Titian after 1540: Technique and Style in his Later Works', *National Gallery Technical Bulletin*, vol. 36, 2015, pp. 6–39.

Dwyer Modestini D., 'Leonardo da Vinci's Salvator Mundi Rediscovered', in: *Leonardo da Vinci's Technical Practice: Paintings, Drawings and Influence* (Paris, 2014), pp. 139–52.

Folga-Januszewska D., '*Leonardiana* and Stanisław Kostka Potocki's passion for collecting', in: D. Folga-Januszewska, A. Kwiatkowska, E. Modzelewska, I. Szmelter, A. Woźniak-Wieczorek, Leonardiana *in Polish Collections. What's What: Original, Replica, Copy*, vol. 2 (Warszawa, 2019, Series: 'Catalogue of the Wilanów Collection'), pp. 33–56.

Gettens R.J., Stout G.L., *Painting Materials* (New York, 1966).

González Mozo A., 'The copy of the Gioconda, and Bruno Mottin, Leonardo's Monna Lisa in the light of its Madrid copy', in: *Leonardo da Vinci's technical practice: paintings, drawings and influence* (Paris, 2014), pp. 194–220.

27 V. Delieuvin, A. González Mozo, P. Walter, *Leonardo y la copia de Mona Lisa del Museo del Prado. Nuevos planteamientos sobre las prácticas del taller vinciano*, exhibition catalogue, Museo del Prado (Madrid, 2021).

Kwiatkowska A., '*Leonardiana* in the archives', in: D. Folga-Januszewska, A. Kwiatkowska, E. Modzelewska, I. Szmelter, A. Woźniak-Wieczorek, Leonardiana *in Polish Collections. What's What: Original, Replica, Copy*, Series: 'Catalogue of the Wilanów Collection', vol. 2 (Warszawa, 2019), pp. 11–31.

Mansfield J.F., Vyletel B.M., Selvius DeRoo C., 'SEM and STEM Microstructural and Microchemical Analysis of Pigments Contained in a *Salvator Mundi* in the Collection of the Detroit Institute of Art', *Microscopy and Microanalysis*, vol. 19, 2013 (Suppl. 2), pp. 20–21.

Modzelewska E., '*Salvator Mundi* in the light of the latest research', in: D. Folga-Januszewska, A. Kwiatkowska, E. Modzelewska, I. Szmelter, A. Woźniak-Wieczorek, Leonardiana *in Polish Collections. What's What: Original, Replica, Copy*, vol. 2 (Warszawa, 2019, Series: 'Catalogue of the Wilanów Collection'), pp. 57–68.

Seccaroni C., Haldi J.-P., *Cobalto, zaffera, smalto dall'antichità al XVIII secolo* (Roma, 2016).

Solé V.A., Papillon E., Cotte M., Walter P., Susini J., 'A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra', *Spectrochim Acta B* 62, 2007, pp. 63–68.

Spring M., Higgitt C., Saunders D., 'Investigation of Pigment-Medium Interaction Processes in Oil Paint containing Degraded Smalt', *National Gallery Technical Bulletin*, vol. 26, 2005, pp. 56–70.

Spring M., 'New insights into the materials of fifteenth- and sixteenth-century Netherlandish paintings in the National Gallery, London', *Heritage Science*, vol. 5, no. 1, 2017, pp. 1–20.

Stefańska I., Dokumentacja konserwatorska obrazu „Salvator Mundi", Pracownia Konserwacji Sztuki Nowożytnej, Muzeum Narodowe w Warszawie, 29 VIII 2005 (copy of the documentation conveyed to the Wilanów Palace Museum in 2005).

Szmelter I., 'Closer to the truth about Leonardo da Vinci's artistic *bottega* – notes and comments on *Salvator Mundi* from Stanisław Kostka Potocki's Wilanów collection', in: D. Folga-Januszewska, A. Kwiatkowska, E. Modzelewska, I. Szmelter, A. Woźniak-Wieczorek, Leonardiana *in Polish Collections. What's What: Original, Replica, Copy*, vol. 2 (Warszawa, 2019, Series: 'Catalogue of the Wilanów Collection'), pp. 69–88.

Van der Snick G. et al., 'Material analyses of "Christ with singing and music-making Angels", a late 15th-century panel painting attributed to Hans Memling and assistants: Part I. Non-invasive in situ investigations', *Journal of Analytical Atomic Spectrometry*, vol. 26, 2011, pp. 2216–29.

Viguerie L. de, Solé V.A., Walter P., 'Multilayers quantitative X-ray fluorescence analysis applied to easel paintings', *Analytical and Bioanalytical Chemistry*, vol. 395, 2009, pp. 2015–2020.

Walter P., Viguerie L. de, 'Materials Science Challenges in Paintings', *Nature Materials*, vol. 17, no. 2, 2018, pp. 106–09.

Ważny T., *Analiza dendrochronologiczna obrazu Salvator Mundi*, Report, Laboratory of Dendrochronology, Institute for the Study and Conservation of Cultural Monuments at Nicolaus Copernicus University in Toruń (Toruń, 2005).

Zucchiatti A., Bouquillon A., Katona I., D'Alessandro A., 'The Della Robbia Blue: a case study for the use of cobalt pigments in ceramics during the Italian renaissance', *Archaeometry*, vol. 48, no. 1, 2006, pp. 131–52.

LIST OF ILLUSTRATIONS

PHILIPPE WALTER

ORCID: https://orcid.org/0000-0002-1804-8374

PhD, the Director of the Laboratory of Molecular and Structural Archaeology (CNRS-Sorbonne Université), director of research at the CNRS, and scientific director of the startup LUMETIS. He is developing new analytical tools adapted to the study of ancient materials. His main research interests focus on the use of analytical chemistry to understand the development of chemistry for health and beauty in Antiquity as well as the elaboration of new painting materials, for instance during the Renaissance. He has written about 300 scientific publications and organized two exhibitions in the Egyptian Museum in Cairo (2002) and in the Musée National du Moyen Age in Paris (2009). He received an MS degree in Physics at the École Normale Supérieure de Saint-Cloud, Lyon, and a PhD in Geochemistry from Paul Sabatier University, Toulouse, in 1993. He was awarded the CNRS silver medal in 2008 and received the Franklin-Lavoisier Prize from the Chemical Heritage Society and the Maison de la Chimie in Philadelphia (USA) in 2010. He was appointed as Professor at College de France for the academic year 2013–2014, with the chair Liliane Bettencourt of Innovative Technology.

The study was conducted as part of the statutory work of the Laboratory of Molecular and Structural Archaeology.

Contact: philippe.walter@sorbonne-universite.fr

DOROTA FOLGA-JANUSZEWSKA

ORCID: https://orcid.org/0000-0002-9865-3792

PhD (habil.), former President of ICOM Poland (2002–2008 and 2012–2018) and President of MOCO ICOM. She chaired the Resolutions Committee at the 31st General Conference of ICOM in Milan in 2016. She is a member of SAREC ICOM and member of AICA. From 2005 she has been a member of the independent group of museum experts of European Council. As a professor at the Academy of Fine Arts in Warsaw, she heads the Theory Department at the Faculty of Graphic Arts. She is also a Deputy Director at the Museum of King Jan III's Palace at Wilanów. In the years 1979–2008, she worked at the National Museum in Warsaw, starting as assistant and terminating as general director. She was the founder and creator of Museum Studies at Wyszyński University in Warsaw (2008–2012) and director of the Institute of Museology. She curated 56 exhibitions in many countries and museums in Europe and the USA. Her works have appeared in more than 300 publications.

Contact: dfolgajanuszewska@muzeum-wilanow.pl

IWONA SZMELTER

ORCID: https://orcid.org/0000-0002-9557-6509

PhD (habil.), art researcher and art conservator, affiliated at the Faculty of Conservation of Academy of Fine Arts in Warsaw. She completed post-graduate studies in Museology at the University of Warsaw and the Nicolaus Copernicus University in Toruń. She is a Polish heritage science and conservation specialist with extensive international/multicultural experience. Her research focuses on identifying artworks and developing new ways of working and new conceptual frameworks that respond to the changing needs of collections.

The study was conducted as part of the statutory work of the Academy of Fine Arts in Warsaw.

Contact: iwona.szmelter@asp.waw.pl

ELŻBIETA MODZELEWSKA
ORCID https://orcid.org/0000-0001-9543-0043

An art conservator, a graduate of the Academy of Fine Arts in Warsaw and post-graduate studies in Management at the Faculty of Management of Warsaw University. She was the head of the Prevention and Conservation Department at the Museum of King Jan III's Palace at Wilanów for 18 years. Since 2004 she has been the curator of conservation and research projects carried out in the framework of the European Union and Ministry of Culture and National Heritage programmes. The focus of her research is the easel painting and wall painting oeuvre of King Jan III's court artists. In the recent years, her research has centered on the artistic workshop of Michelangelo Palloni. She is the author of scholarly papers and popular-science articles, as well as the scientific editor of museum publications related to research on and conservation of museum objects and historical interior decoration.

Contact: emodzelewska@muzeum-wilanow.pl

ANNA GUZOWSKA
ORCID https://orcid.org/0000-0001-6692-6672

A certified art conservator and restorer with special interest in the fields of painting and polychrome sculpture, the head of the Painting Conservation Atelier of the Museum of King Jan III's Palace at Wilanów. Her specialism are the study, conservation and restoration of paintings on various types of support (canvas, wooden and metal supports). Since 2008 she has been broadening her expertise regarding European varnishing techniques, and since 2015 also regarding Oriental lacquer. In 2019 she has opened doctoral proceedings at the Chair of the Conservation and Restoration of Paintings and Polychrome Sculpture at the Academy of Fine Arts in Warsaw under the supervision of Prof. Aleksandra Krupska PhD (habil).

The study was conducted as part of the statutory work of the Museum of King Jan III's Palace at Wilanów.

Contact: aguzowska@muzeum-wilanow.pl