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# *Adam and Eve* by Lucas Cranach the Elder from the National Museum in Warsaw New Technological Analysis

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**ABSTRACT**

The paper presents the results of the latest technological research on Lucas Cranach the Elder's painting *Adam and Eve* from the collection of the National Museum in Warsaw. The tests were conducted using non-destructive or micro-invasive physical and chemical methods. The painting was analysed under analytical radiation within ultraviolet (UV), visible (VIS), infrared (IR) and X-ray (X-ray, CT) wavelength ranges. To examine the composition of the paint layers, the authors employed X-ray fluorescence spectroscopy (XRF), reflectance Fourier-transform infrared spectroscopy (FTIR), Fourier transform infrared-attenuated total reflectance spectroscopy (FTIR-ATR), gas chromatography coupled with mass spectrometry (GC/MS), liquid chromatography coupled with mass spectrometry (LC/MS), Raman microscopy, as well as microchemical and stratigraphic analyses. These tests enabled a highly detailed identification of the painting technique, facilitated a comparison with Lucas Cranach the Elder's other works and provided a solid basis for a more in-depth argument regarding the painting's creation date.

**KEYWORDS**

Lucas Cranach the Elder, early modern German painting, technological analysis of artworks, physical and chemical analysis of artworks, *Adam and Eve*, National Museum in Warsaw, spectroscopy (XRF, reflectance FTIR, FTIR-ATR), chromatography (GC/MS, LC/MS), Raman microscopy, non-destructive methods

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The painting *Adam and Eve*[1] by Lucas Cranach the Elder, kept at the National Museum in Warsaw, was created during the early period of the master's activity at the court of the Saxon electors in Wittenberg (fig. 1). In 1505 the artist became the court painter of Frederick the Wise and remained in the service of his successors, John the Steadfast and John Frederick I, until the end of his life (d. 1553).

The painting depicts Adam and Eve standing on either side of the tree of knowledge of good and evil. The first parents are portrayed just before committing original sin; Eve raises the apple to her lips, while Adam gazes upwards, perhaps observing the serpent slithering along the trunk. The figures are set against a uniform dark background, which contrasts with their fair, naked bodies.

Scholars offer different botanical interpretations of the tree placed at the centre of the composition. Some have identified it as an oak (*Quercus robur L.*),[2] referencing the ancient Germanic forest described by Tacitus and Julius Caesar (*Silva Hercyniana* – the Hercynian Forest) as well as by early Renaissance German humanists.[3] However, the botanist Artur Zagajewski notes that the structure of the trunk, as well as the type and shape of the foliage, are characteristic of the common fig (*Ficus carica L.*).[4] This would align with the biblical account, in which fig leaves were used to cover the first parents' nudity.[5] In the painting, Adam's genitals are therefore concealed by a fig leaf, while Eve's pubic area is covered by an apple tree branch, whose fruit she holds in her hand. The variety of apple has been identified by Zagajewski as Alant (*Malus domestica Alant*), a subspecies that was popular in sixteenth-century Germany and Switzerland.[6] The fact that the artist depicted the forbidden fruit as an apple (rather than a fig, which would correspond to the species of the depicted tree) suggests that he contaminated – whether consciously or not – various traditions of representing the tree and fruit of paradise. *Fructus paradisi* (*paradiseus*) was most commonly shown as an apple, the most familiar type of fruit in Europe. However, in

**fig. 1** Lucas Cranach the Elder, *Adam and Eve*, National Museum in Warsaw (after conservation treatment)
photo Małgorzata Kwiatkowska

many depictions of the Virgin and Child, or in statuettes of the naked Christ Child, where the infant holds or plays with a fruit, it is sometimes depicted as a fig or a pomegranate – fruits associated with the South, exotic in northern Europe. Less frequently, a pear replaced the apple in these representations. From a botanical and pomological perspective, the iconography of the fall of the first parents, depictions of the Virgin and Child or individual figures of the infant Jesus was not codified. The artist had significant freedom in selecting the botanical motif. It appears that Cranach's choice of tree and fruit species was deliberate. His selection combined the pomological flora of Italy and Germany, bringing together Mediterranean and Hyperborean nature, just as Cranach's art was heavily inspired by Italian models, merging the Italian formula of antiquity revival with German tradition. In the artist's concept, Nature and

Art would thus unite the South with the North. Today, it is difficult to determine whether the artist intended this to symbolize the universality of original sin, encompassing all of humanity. We do not know whether this botanical peculiarity (a fig tree bearing apples) was noticed by contemporary viewers. However, if it was, the observer would have been confronted with an absurd scenario within the representation of Adam and Eve: they would have had to assume that the tree of knowledge of good and evil was actually outside the depicted scene. In that case, Eve would have plucked the apple from an unseen tree along with the branch from which it hung, and whose leaves now cover her nudity. The tree visible in the painting would then be some other, unidentified tree from the Garden of Eden. Perhaps Cranach indeed intended to juxtapose two worlds of art and nature: Italian (and classical) with his native one.

Lucas Cranach the Elder returned to the theme of the first parents several times during the early stages of his career, when his workshop was based at Wittenberg Castle (1505 – circa 1512–1515), and later revisited it in the 1520s. Scholars estimate that over 50 such depictions were produced in Cranach's workshop (including both his original works and workshop variants). The subject of Adam and Eve's nudity, fashionable and particularly appealing due to its erotic dimension, was first developed by Cranach in the more sophisticated and socially liberal courtly environment. He painted for the Prince-Elector and members of his entourage, including Renaissance humanists associated with him. In the later period, when the artist ran a workshop catering to the open market, primarily for the bourgeois, the production of paintings focused on reproducing popular themes, including representations of the first parents. However, rather than simply copying his earlier 'courtly' compositions, Cranach tended to modify them by emphasizing the narrative element, with greater movement of both figures, placing them among various accessories (*Beiwerk*) and animals (deer, squirrels, etc.), which lent the depictions a genre-like character.

Scholars have generally agreed that the Warsaw painting belongs to Cranach's early courtly period, with proposed dating ranging between 1507 and 1512.[7] However, they have differed in determining its place within the chronology of his depictions of Adam and Eve from this period. The compositions closest to this version include: a pair of panels in Besançon (the earliest, currently dated to circa 1508–1510),[8] a panel in the Alte Pinakothek in Munich (circa 1510–1519)[9] and a work in Würzburg (circa 1513–1515).[10] Friedländer and Rosenberg dated the Warsaw painting to circa 1512, later than the Munich version, which they estimated to have been created between 1510 and 1512.[11] However, according to the latest research, the Alte Pinakothek painting was produced in the second decade of the sixteenth century, most likely as a pair of triptych wings, later reassembled into a single panel.[12] The earlier dating of the Warsaw version to circa 1510 – as suggested by Wolfgang Schade[13] and more recently by Gunnar Heydenreich[14] – is supported by the present study. If this dating is correct, the painting represents Cranach's earliest depiction of Adam and Eve within a single pictorial composition, that is, on a single panel.

The influence of Albrecht Dürer is particularly evident in the Warsaw painting. Lucas Cranach the Elder frequently competed with Dürer, and his depiction of the first parents was directly inspired by Dürer's 1504 engraving and his pair of paintings from 1507, now in the Prado (figs 2, 3).[15] In his engraving, Dürer presented Adam and Eve against the backdrop of a dense, dark forest, portraying them as ideal first humans in the *all'antica* tradition. Their nude bodies, modelled after famous Greco-Roman sculptures *Venus de'Medici* and *Apollo Belvedere,* are positioned in contrapposto to highlight the muscular structure beneath the skin. This work reflects Dürer's fascination with antiquity and his scientific pursuit of an ideal proportional system for depicting the perfect human form. To achieve this, he produced countless life drawings, meticulously analysing the human body. In the engraving, Adam and Eve are shown at the very moment before the fall: Eve hands Adam the apple, assisted by the serpent. Their nudity is modestly covered by foliage: a rowan branch (Adam) and a fig-like leaf (Eve), though attached to an apple tree branch. Surrounding them are animals symbolizing the four temperaments, which they

**fig. 2** Albrecht Dürer, *Adam and Eve*, 1504, engraving, Rijksmuseum, Amsterdam
photo public domain

**fig. 3** Albrecht Dürer, *Adam and Eve*, a pair of paintings, 1507, Prado, Madrid
photo © Museo Nacional del Prado

have not yet acquired: a cat – choleric temperament; a rabbit – sanguine temperament; an ox – phlegmatic temperament; a stag – melancholic temperament. In Dürer's Prado paintings, Adam and Eve are set against a uniform dark background, contrasting with their fair bodies. Both are depicted completely nude, with their modesty covered by apple tree foliage. The influence of Dürer's Madrid painting on Cranach's composition is particularly evident in Adam's pose: the positioning of his right hand close to his thigh, with an open palm, as well as the relaxed placement of his right foot, gently touching the ground. Cranach painstakingly replicated Dürer's anatomical models, including the muscular structure of the bodies, but elongated their proportions and modernized their facial features: Adam's curly beard and hairstyle resemble those found in contemporary portraiture. The bodies are modelled with soft light and shadow, subtly contrasting against the black background.

## New Technological Analysis

In 2018 experts from the NMW Laboratory (now the Laboratory for Research and Protection of Museum Collections) – Dr Magdalena Wróbel-Szypula, Justyna Kwiatkowska and Dr Elżbieta Pilecka-Pietrusińska – undertook a study to thoroughly examine the structure and painting technique of *Adam and Eve* and thus contribute to the broader study of Lucas Cranach the Elder and his workshop. This technological analysis was prompted by the painting's comprehensive conservation.[16] Multiple layers of secondary varnishes, which had darkened significantly over time, along with localized retouching, distorted the perception of the work and obscured many compositional details (fig. 4). The removal of the varnishes and retouches revealed the painting's original beauty, along with its precisely rendered details.[17]

## Research method

In the 1990s the painting was examined as part of the collection catalogue project.[18] The present study incorporates the findings from those analyses, which have now been corrected, expanded and refined thanks to the availability of highly specialized instrumental methods.[19]

The new, comprehensive study of the painting employed modern non-invasive or micro-invasive methods, allowing for the collection of very small samples from the paint layers. The painting was first examined using analytical radiation in the ultraviolet (UV), infrared (IR)[20] and X-ray ranges, as well as using computed tomography (CT)[21] (figs 4–7). The surface was also analysed in visible light using a Nikon SMZ 800 stereoscopic microscope with up to 60× magnification. To examine the composition of the technological layers, researchers employed non-invasive X-ray fluorescence spectroscopy (XRF)[22] and reflectance Fourier-transform infrared spectroscopy (FTIR).[23]

A full technological analysis required sampling from the painting, but due to the extensive use of non-invasive methods, the number of samples was minimized to just a few. No samples were taken from the flesh tones of Adam and Eve, only from the background (edges of the painting), green foliage and earth. These samples were used for stratigraphy and microchemical analysis,[24] Raman microscopy,[25] gas chromatography coupled with mass spectrometry (GC/MS), as well as liquid chromatography coupled with mass spectrometry (LC/MS).[26] Selected substances were further examined using microchemical analysis and Fourier-transform infrared attenuated total reflectance spectroscopy (FTIR-ATR).[27]

The pigments used in the paint layers were identified based on spectrometric analyses,

**fig. 4** Lucas Cranach the Elder, *Adam and Eve*, National Museum in Warsaw, photograph in UV radiation (300–400 nm) revealing a veil with blue fluorescence, which indicates the presence of a synthetic resin covering the surface, as well as small retouches from at least two conservation periods: the older retouches appear as black spots, while the more recent ones are seen as dark grey spots; also visible are losses and surface scratches
photo Anna Lewandowska, Piotr Lisowski

including X-ray fluorescence spectroscopy (XRF), Raman microscopy (using stratigraphic samples), Fourier-transform infrared attenuated total reflectance spectroscopy (FTIR-ATR) and microchemical analysis (fig. 8). Binders were identified through Fourier-transform infrared reflectance spectroscopy (FTIR), as well as gas chromatography-mass spectrometry (GC/MS) and liquid chromatography-mass spectrometry (LC/MS) (fig. 9). Stratigraphic analysis conducted on several locations enabled the determination of the structure and thickness of the technological layers. This comprehensive physical and chemical analysis enabled a highly detailed identification of the painting technique and facilitated a comparison with other works by Lucas Cranach the Elder.

## Description of the Painting's Technique and Technology

### Support and Ground

The artist used a limewood panel as the support, composed of four horizontally butt-joined planks, each 0.5–0.6 cm thick. The planks vary in width, with one cut almost radially, while the other three were cut at an intermediate angle between radial and tangential directions. Due to the thinness of the wood, this cutting method caused significant warping of the top and bottom planks (fig. 5).[28]

The front surface of the wood was carefully smoothed, while the reverse side was chamfered along all four edges.[29] At the time of painting, the panel was already framed; the

**fig. 5** Lucas Cranach the Elder, *Adam and Eve*, National Museum in Warsaw, X-radiograph of the painting revealing the horizontal butt-joints between individual wooden panels of the support and the modelling technique used for the figures of Adam and Eve, with highlights made by using a higher concentration of lead-based pigments; the small white spots, primarily in the lower part of the painting, indicate traces of xylophagous insects
photo Łukasz Kownacki

**fig. 6** Lucas Cranach the Elder, *Adam and Eve*, National Museum in Warsaw, IR photograph revealing the original underdrawing, showing adjustments to Eve's positioning
photo Anna Lewandowska, Piotr Lisowski

artist primed and painted the work within the frame. On the surface of the painting, there are unprimed strips along all edges and thickened paint layers at the junction with the frame.[30] This is also evidenced by the chamfered edges of the support, meaning they were bevelled to reduce thickness towards the outer edges, facilitating the painting's mounting within the frame. The support and frame were primed with a white ground layer composed of calcium carbonate[31] and animal glue.[32]

Once the ground was sanded and smoothed, the artist applied an underdrawing. Infrared (IR) photography reveals compositional changes made by the artist, such as a different original design for the apple branch on Eve's right thigh, a line running along her left side and leg, and an outline of her breast, suggesting that Eve's position was initially different (fig. 6).

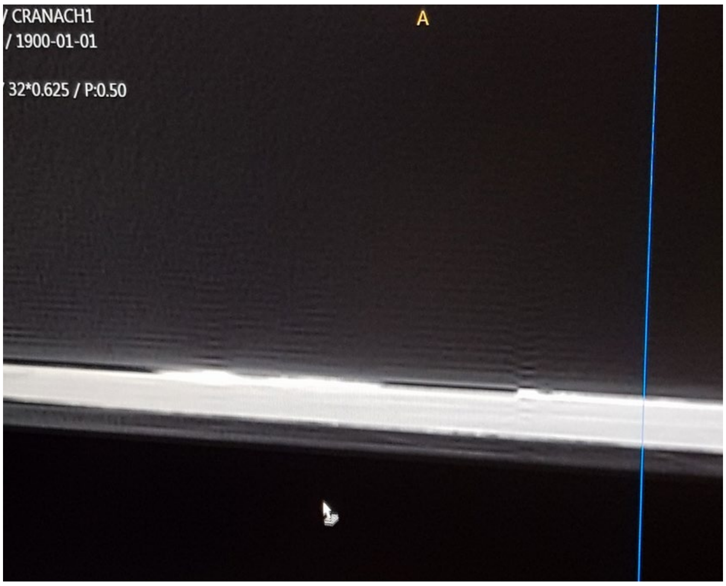



**fig. 7** Lucas Cranach the Elder, *Adam and Eve*, National Museum in Warsaw, detail in CT imaging revealing differences in X-ray absorption between the figures, which contain lead (brighter, thicker layers), and the black background, where lead is present only in the ground layer
photo Łukasz Kownacki

## Paint Layer

On the primed surface with the preparatory sketch, the artist applied an imprimatura: a very thin layer of white paint, composed of lead white and an oil binder, as confirmed by all of the conducted studies.[33] This layer served to protect the absorbent ground from soaking up the oil binder from the upper paint layers, preventing a loss of binding strength and subsequent flaking or detachment of pigments. Stratigraphic cross-sections of the technological layers indicate that this insulation effectively fulfilled its function, although some binder from the imprimatura did penetrate into the ground.[34]

On this prepared surface, the painter applied the colour layers, using oil paints with very small amounts of pigments. He probably also used dyes, as suggested by the local presence of gypsum alongside calcium carbonate, both of which were commonly used as carriers for dyes. However, FTIR analysis did not detect signals of dyes, possibly due to their extremely low concentration. Pigment analysis identified the following colours in Cranach's palette: lead white, lead-tin yellow, yellow ochre, azurite, cinnabar, iron oxide reds, minium, plant-based black and traces of natural ultramarine (lapis lazuli). To elaborate the paint layer, the artist used linseed oil as binder. GC/MS analysis confirmed the absence of egg yolk; the protein revealed through FTIR spectroscopy suggests the localized use (Eve's figure) of an oil-protein mixture, which could be interpreted either as a tempera additive to the oil binder or the result of later overpainting.[35]

The artist mixed the binder with finely ground pigments, achieving the colours and shades necessary for the different elements of the composition (see fig. A1.1). The chemical composition of these areas was established through analyses conducted at NMW (see Annexes 1 and 2).

For flesh tones, Cranach used a limited colour palette. Analysis confirmed the presence of lead white, cinnabar, iron oxide pigments (red) and carbon black.[36] The uniform or highly similar elemental composition of the paint layers in multiple XRF measurement points within the flesh areas[37] suggests that the artist used a three-tone modelling technique. Lighter areas were achieved by increasing the amount of lead white, while shadows were deepened with higher concentrations of iron oxide pigments and plant-based black.[38] This corresponds to the painting technique of Cranach's workshop, as described by Heydenreich.[39]

**fig. 8** Lucas Cranach the Elder, *Adam and Eve*, National Museum in Warsaw, map of XRF measurement points (nos 1-36) and micro-sample locations for microchemical (nos C1, C3, C5, C6) and stratigraphic analyses (nos C7, C8, C11)
photo Justyna Kwiatkowska

**fig. 9** Lucas Cranach the Elder, *Adam and Eve*, National Museum in Warsaw, map of FTIR measurement points (nos 1–26) and micro-sample locations for GC/MS and LC/MS analyses (nos C2, C4, C9, C10)
photo Magdalena Wróbel-Szypula

In constructing Adam and Eve's flesh, the artist made use of the white or pinkish imprimatura or ground layer as a base for applying flesh tones. This first flesh tone layer was often applied quite thickly, followed by the modelling of shadows (greyish or brownish tones) and highlights. Cranach typically worked with a minimal number of colour components, a technique also observed in the Warsaw painting.[40]

Cranach modelled Eve's hair by mixing iron oxide pigments with silicates and lead white in varying proportions.[41] Using a similar technique but with a different pigment ratio, he created the darker shade of Adam's golden curls. Analysis of these areas also detected mercury (Hg) and copper (Cu) signals, likely originating from cinnabar and azurite, respectively. This probably results from the painting technique of Cranach's workshop, as described by Heydenreich.[42] The artist first outlined the heads with flesh-coloured underpainting, before outlining their contours with the colour of the background: black. Finally, he added delicate golden strokes of paint, shaping Eve's flowing hair cascading down to her hips and Adam's finely curled locks.

For the uniform black background surrounding Adam, Eve and the tree, Cranach used plant-based black,[43] with individual grains of iron oxide red and azurite.[44] Observations of this part of the composition revealed two layers of black paint in some areas, raising the question of whether the background was original or overpainted. Physical and chemical analyses of these parts confirmed that the lower black layer lies directly on the ground and imprimatura, meaning that even if the upper layer was applied later, this did not alter the artist's original intent (fig. 7). Cracks observed in certain areas of the black background may have formed during the painting process, due to the properties of oil paint mixed with plant-based black. It was slower to dry,[45] causing cracks on the surface, which is why Cranach may have applied a second black layer.[46] Alternatively, this second layer could have been added later by an unknown artist to even out the cracked surface as a conservation measure. The monochrome dark background enhanced the visibility of the pale figures and tree, creating a strong contrast.[47]

Red areas were painted using cinnabar, lead white and iron oxide pigments. Eve's lips contain cinnabar and lead white. The red of the apple she holds in her right hand was likely enhanced by adding a dye fixed on gypsum to the paint or by applying a glaze containing this dye.[48] In another colour area, on Adam's thigh, gypsum was detected, which could also be linked to a dye or simply be an additive to iron oxide pigments. However, due to the extremely small amount of this substance in the paint layer, it was not possible to identify the specific dye used.

For the earth strip and the main part of the tree, the artist used lead white, copper-based pigments and black, with small amounts of iron oxide pigments: yellow ochre (see Annex 1, fig. A1.1).[49] The green of the leaves was created by mixing two pigments – blue (azurite) and (lead-tin) yellow[50] – combined with lead white and a natural iron-based pigment.[51] Traces of natural ultramarine were also found in the fig leaf.[52] According to Heydenreich, mixing azurite with lead-tin yellow was not a common practice in Cranach's workshop.[53] The only confirmed case of this technique appears in a detail of *Saint Stephen of Hungary* (c.1510, Germanisches Nationalmuseum, Nuremberg), specifically in the grassy part of the foreground.[54]

Cranach painted the serpent winding around the tree trunk – grey-gold with black linear detailing mimicking scales – by taking advantage of the luminosity of lead-tin yellow combined with lead white. He contrasted these tones with grey, achieved by mixing plant-based black and lead white (see Annex 1, fig. A1.2).[55]

## Conclusion

The technique and technology of the discussed painting show significant similarities to Cranach's works created between 1505 and 1512, when he was beginning his career as a court artist to the Saxon electors. During this period, the painter prepared his wooden panels with a white ground layer, composed of calcium carbonate and animal glue.[56] Since the successively applied oil-based paint layers required an insulating layer on the highly absorbent ground, Cranach applied an imprimatura – a pigment ground with oil binder – over the entire surface of the painting. In the Warsaw painting, he used a white imprimatura made from lead white, which he employed wherever he needed to enhance the luminosity of colours. Both the use of lead white and the other pigments identified in this study align with the painting practices of Cranach's workshop.

During his early career, Cranach's workshop was located within Wittenberg Castle. Around 1512 he relocated it to the town, altering the workshop's organizational structure and collaborating with new subcontractors, which influenced, among other things, changes in panel construction. The support for *Adam and Eve* consists of thin limewood planks (0.5 cm thick) of varying widths, some cut radially and others tangentially, forming an irregular shape and joined horizontally. These features confirm that the painting was created during Cranach's early years in Wittenberg. Heydenreich established that limewood was Cranach's preferred support material during this period,[57] as it was supplied as part of his work for the court.[58] The panels were likely prepared by a carpenter working for the castle, particularly since the butt-joining of short planks, cut both radially and tangentially with irregular dimensions, was not a common panel-making technique in the sixteenth century, as it increased the risk of warping due to internal tensions.[59]

This also has implications for *Adam and Eve*'s commissioner. Heydenreich demonstrated that of all the paintings produced between 1505 and circa 1511 – featuring a support made from a different type of wood than limewood and a construction that differs from the one described here – none were commissioned by the Elector of Saxony.[60] This allows for the hypothesis that the Warsaw painting was created on commission for Frederick the Wise. An additional indication supporting this theory is the presence of lapis lazuli in the paint layer. Natural ultramarine, which appears in Cranach's works created shortly after 1508, is linked to his journey to Antwerp, where he acquired this costly pigment from Afghanistan. Cranach later used ultramarine primarily for paintings commissioned by the elector.[61] However, the question of the Saxon prince's potential role in the creation of the Warsaw painting requires further historical and possibly technological research.

Translated by Aleksandra Szkudłapska

## NOTES

1 Lucas Cranach the Elder, *Adam and Eve*, *c.*1510, oil on limewood, 59.3 × 44.5 cm, inv. no. M.Ob.588 MNW. Provenance: until the mid-19th c. in the collection of the princes Hohenzollern-Hechingen, Burg Hohenzollern near Hechingen, Baden-Wirttemberg; then owned by Johann Nepomuk (?) Sepp in Munich; until *c.*1895 in the collection of Roberta Oertl in Munich; then in an unidentified private collection in Paris; in 1925 acquired by the Schlesisches Museum der Bildenden Künste in Wrocław (inv. no. 1309); during the Second World War, in 1942, evacuated to a collection point in Kamieniec Ząbkowicki (Kamenz); included in the NMW collection in 1946.

2 Bożena Steinborn, Antoni Ziemba, *Malarstwo niemieckie do 1600 roku. Katalog zbiorów / Deutsche Malerei bis 1600. Bestandskatalog*, National Musuem in Warsaw (Warsaw, 2000), cat. no. 8, pp. 44–47.

3 Antoni Ziemba, 'Lucas Cranach starszy, Adam i Ewa' [catalogue entry], in *Das Heilige und der Leib. Schätze aus dem Nationalmuseum Warschau / Duchowość i cielesność. Skarby Muzeum Narodowego w Warszawie*, eds Dorota Folga-Januszewska, Matthias Winzen, exh. cat., Staatliche Kunsthalle, Baden-Baden, National Museum in Warsaw (Ostfildern-Ruit, 2005), p. 90; Hanna Benesz, 'Temat na pokuszenie,' *Art&Business*, no. 11 (262) (2012), p. 82. For more details on the ancient Germanic forest, see Christopher S. Wood, *Albrecht Altdorfer and the Origins of Landscape* (Chicago, 1993); Antoni Ziemba, *The Agency of Art Objects in Northern Europe, 1380–1520* (Berlin, 2021), pp. 245–262.

4 Information from Dr Artur Zagajewski (formerly of the Botanical Garden of the Polish Academy of Sciences in Powsin) dated 26 June 2018. Previously (2005), the identification of the tree as a fig tree was proposed by Prof. Dr hab. Krzysztof Spalik (Faculty of Biology, University of Warsaw) in correspondence with the then curator of the European Painting Collection at the National Museum in Warsaw, Prof. Antoni Ziemba.

5 'And the eyes of them both were opened, and they knew that they were naked; and they sewed fig leaves together, and made themselves aprons' (Genesis 3:7); quoted from the King James Bible.

6 Information from Dr Artur Zagajewski dated 26 June 2018. Alant, a subspecies popular in the 16th century, existed in two subvarieties with different phylogenies: North German (primarily Lower Saxon), Silesian and Swiss. Alant apples are medium to large (approx. 6–8 cm in size), slightly elongated, lemon-yellow with a delicate striped blush. The variety has been recorded since the early 16th century, first appearing in French-language literature (Swiss variety) and in German pomology from 1760. It was known under the following names: *Alantapfel*, *Gestreifter Kaiserapfel*, *Grosser edler Prinzessinapfel*, *Princessinapfel*, *Winteralantapfel*, *Mönchsnase.*

7 Bożena Steinborn, 'Obrazy Cranachowskie', in *Nobile claret opus. Studia z dziejów sztuki dedykowane Mieczysławowi Zlatowi*, eds Lech Kalinowski, Stanisław Mossakowski, Zofia Ostrowska-Kębłowska (Wrocław, 1998), pp. 45–49. Dating: Heinz Braune, Erich Wiese, *Katalog der Gemälde und Skulpturen. Schlesisches Museum der Bildenden Künste Breslau* (Wrocław, 1926), p.17, cat. no. 1309: 1507–1508; *Lucas Cranach d. Ä. und Lucas Cranach d. J. Gemälde, Zeichnungen, Graphik*, exh. cat., Staatliche Museen (Berlin, 1937), no. 19: *c.*1510–1512; Max J. Friedländer, Jakob Rosenberg, *The Paintings of Lucas Cranach* (New York, 1978), cat. no. 44: *c.*1512; Steinborn, Ziemba, *Malarstwo niemieckie*...: *c.*1510.

8 Musée des beaux-arts et d'archéologie, Besançon; panel (limewood?), each panel 139 × 53.9 cm. Dating *c.*1508–1510 – see Gunnar Heidenreich, *Lucas Cranach the Elder. Painting materials, techniques and workshop practice* (Amsterdam, 2007), pt. A, pp. 318–321; *Cranach der Ältere*, ed. Bodo Brinkmann, exh. cat., Städel Museum (Frankfurt, 2007), cat. no. 116, p. 361; Gunnar Heydenreich, 'Adam and Eve in the Making',

in *Temptation in Eden. Lucas Cranach's Adam and Eve*, ed. Colin Campbell, exh. cat., Courtauld Institute and Art Gallery, Somerset House (London, 2007), p. 25.

9 Bayerische Staatsgemäldesammlungen, Alte Pinakothek, Munich, limewood, 47.2 × 35.3 cm. Dating: Friedländer, Rosenberg, *The Paintings*..., cat, no. 43, p. 78: 1510–1512; Claus Grimm, 'Die Anteile von Meister und Werkstatt. Zum Fall Lucas Cranach d. Ä.', in *Unsichtbare Meisterzeichnungen auf dem Malgrund. Cranach und seine Zeitgenossen*, ed. Ingo Sandner (Regensburg, 1998), p. 79: *c*.1512; Martin Schawe, *Cranach in Bayern*, exh. cat., Bayerische Staatsgemäldesammlungen, Alte Pinakothek (Munich, 2011), no. 720, p. 136: *c*.1510–1519.

10 Museum für Franken, Staatliches Museum für Kunst- und Kulturgeschichte, Würzburg, panel, 72 × 62 cm. Dating: *c*.1513–1515: Friedländer, Rosenberg, *The Paintings*..., cat. no. 113, p. 92.

11 Friedländer, Rosenberg, *The Paintings*..., cat. nos 43 and 44, p. 78.

12 Schawe, *Cranach in Bayern*..., no. 720, p. 136.

13 Werner Schade, *Malarski ród Cranachów* (Warsaw, 1980), p. 426, no. 51.

14 Heydenreich, *Lucas Cranach*..., p. 67.

15 Albrecht Dürer, *Adam and Eve*, signed and dated 1507, oil on panel, 209 × 81 cm (*Adam*) and 209 × 80 cm (*Eve*), Museo Naciónal del Prado, Madrid, inv. nos P02177 and P02178.

16 The conservation was carried out by Iwona Maria Stefańska from the Conservation of Sculpture and Painting on Wood Laboratory at the NMW.

17 Iwona Maria Stefańska's conservation documentation is kept in the NMW's conservation archive.

18 Steinborn, Ziemba, *Malarstwo niemieckie*..., cat. no. 8, pp. 44–47, table 8, p. 388. The tables containing the analyses and results of the technological and conservation studies were prepared by a team led by Agnieszka Czubak (Conservation of Sculpture and Painting on Wood Laboratory, NMW). The dendrochronological analysis was conducted by Prof. Dr hab. Tomasz Ważny (then of the Academy of Fine Arts in Warsaw; currently, Nicolaus Copernicus University in Toruń).

19 This was made possible thanks to the support of the Association of Friends of the National Museum in Warsaw, for which we extend our gratitude to its members and president, Paweł Kastory.

20 UV and IR photographs were taken by Anna Lewandowska and Piotr Lisowski, Conservation of Canvas Paintings Laboratory, NMW.

21 X-ray imaging and CT were performed by Dr Łukasz Kownacki, MD, at the European Health Centre in Otwock.

22 Analysis and description: Prof. Dr hab. Barbara Wagner and Dr Olga Syta – Interdisciplinary Laboratory for Archaeometric Research, University of Warsaw.

23 The analysis was performed by Dr Magdalena Wróbel-Szypula, Laboratory for the Analysis and Protection of Museum Collections, NMW.

24 The analysis was performed by Justyna Kwiatkowska, Laboratory for the Analysis and Protection of Museum Collections, NMW.

25 The analysis was performed by Dr hab. Zofia Żukowska, Eng. – Faculty of Chemistry, Warsaw University of Technology.

26 The analysis was performed by Dr Bartłomiej Witkowski and Prof. Dr. hab. Tomasz Gierczak – Faculty of Chemistry, Warsaw University of Technology.

27 The analysis was performed by Justyna Kwiatkowska, Laboratory for the Analysis and Protection of Museum Objects, NMW.

28 Tomasz Ważny, *Analiza drewna obrazu* Adam i Ewa *ze zbiorów Muzeum Narodowego w Warszawie – ekspertyza dendrologiczna*, 1997, conservation and research documentation at the Conservation of Works on Wooden Supports Laboratory, NMW.

29 Steinborn, Ziemba, *Malarstwo niemieckie*..., table 8, p. 388.

30 The original frame has not survived; the current frame is a later addition and dates back to at least the period when the painting was held in the Schlesisches Museum der bildenden Künste. It was displayed there in this frame during the 1935 exhibition *Deutsche Malerei des 16. Jahrhunderts in Schlesien*; see the negative in the Collection of Photographs and Survey Drawings at the

Institute of Art, Polish Academy of Sciences, no. IS PAN 0000031010. We extend our thanks to Michał Przygoda for his assistance in confirming this fact.

31 Previously identified as chalk, but the microchemical analysis, as well as observation in transient light and FTIR- ATR clearly indicate calcium carbonate.

32 Annex 3, GCMS results.

33 X-ray tomography observation.

34 Annex 1 – yellow colour seen in stratigraphy.

35 This is supported by the observation made by conservator Iwona Stefańska, who noted locally varying responses to solvents during the varnish removal process.

36 Microchemical analysis was performed by Justyna Kwiatkowska (2018) and Izabela Kobla (1994).

37 See Annex 2, section *White, pink, red: Adam's figure*. The Zn signal detected on Adam's figure may originate from secondary retouches, as the XRF analysis was conducted before the painting's conservation..

38 Annex 1. See also Izabela Kobla's 1994 analysis; the presence of plant-based black is confirmed by microchemical analysis, which identified carbon black, as well as by XRF analysis, which detected a K signal, characteristic of plant black, while showing no signal for bone black.

39 Heydenreich, *Lucas Cranach*..., p. 194.

40 Ibid.

41 In Cranach's work, iron oxide red was rich in silicates – see Heydenreich, *Lucas Cranach*..., p. 135.

42 Heydenreich, *Lucas Cranach*..., p. 194.

43 Justyna Kwiatkowska's (2018) and Izabela Kobla's (1994) microchemical research.

44 See Annex 2 and Izabela Kobla's 1994 research results.

45 Cennino Cennini, *Treatise on Painting*, tr. Mary P. Merrifield (London, 1844) [online facsimile]: https://archive.org/details/gri_33125009350998/page/n15/mode/2up [retrieved: 10 Mar. 2025].

46 The composition of the layers – pigment + binder – is identical; see Annex 3: GCMS, samples C9, C10; microchemical analysis, samples C5, C6.

47 Microscopic observations confirm that no remnants of other layers (e.g., blue sky) are present beneath overpaint and the black background.

48 This is indicated by the S signal revealed in XRF; see Annex 2.

49 FTIR analysis, Annex 4.

50 FTIR analysis, Annex 4; Raman, FTIR, Annex 1 and Izabela Kobla's 1994 microchemical analysis.

51 Cranach raport_25.08_XRF and Eve's leaf, additionally FTIR, Annex 1, fig. A1.3. (stratigraphy of sample C7).

52 B. Steinborn, A. Ziemba, *Malarstwo niemieckie*..., table 8, p. 388 (Izabela Kobla's 1994 microchemical analysis).

53 Heydenreich, *Lucas Cranach*..., p. 186

54 Ibid., n. 40, p. 350.

55 Annex 1. Stratigraphy of sample C11, fig. A1.2.

56 Heydenreich, *Lucas Cranach*..., pp. 93–103.

57 At least 20 paintings by Lucas Cranach the Elder, created between 1505 and 1515, are made on limewood; see data in the Cranach Digital Archive: www.lucascranach.org [retrieved: 26 Nov. 2014].

58 Heydenreich, *Lucas Cranach*..., p. 47.

59 Ibid., pp. 62–63.

60 Ibid., p. 63.

61 E.g., Lucas Cranach the Elder, *The Holy Kinship*, limewood, 1509, Städel Museum, Frankfurt am Main.

## Annex 1. Methodology and Results of Stratigraphic, Microchemical and Infrared Spectroscopic Analyses

The tests were conducted by Justyna Kwiatkowska (Laboratory for the Analysis and Protection of Museum Objects Collections, NMW) in 2018.

For the stratigraphic analysis, micro-samples were taken and embedded in Premacryl Plus acrylic resin before being examined under Nikon SMZ18 and Nikon SMZ1500 stereoscopic microscopes in reflected light and UV fluorescence at various magnifications (up to 810×). The samples were then subjected to microscopic and microchemical analyses. A significant challenge in obtaining results from these studies was the extremely small size of the samples. A summary of the samples and their locations is provided in table A1.1, while fig. 8 shows the exact locations where they were taken.

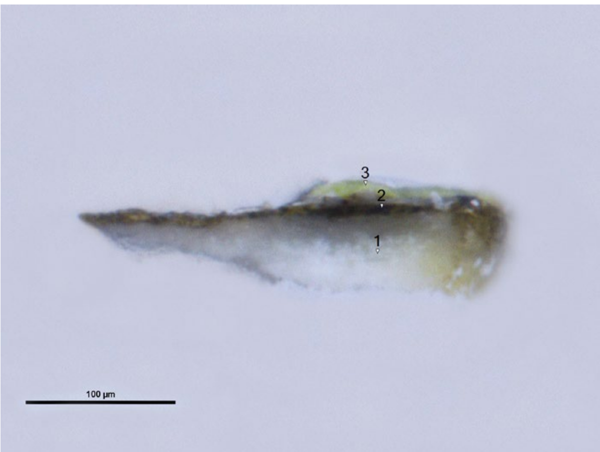
| **Sample ID and location** | **Description of location** | **Type of analysis** | | |
|---|---|---|---|---|
| | | microchemical | stratigraphic | FTIR-ATR |
| C1 (x = 17.5 cm. y = 1.0 cm) | strip of earth along the lower edge of the painting | × | | |
| C3 (x = 42.5 cm. y = 1.0 cm) | strip of earth | × | × | × |
| C5 (x = 43.4 cm. y = 53.0 cm) | background near the upper edge of the painting – paint layer with ground | × | × | |
| C6 (x = 43.5 cm. y = 55.4 cm) | background near the upper edge – upper black layer | × | | |
| C7 (x = 20.0 cm. y = 58.5 cm) | leaf near the tree trunk | | × | |
| C8 (x = 15.5 cm. y = 59.0 cm) | tree near the upper edge of the painting | | × | |
| C11 (x = 20.0 cm. y = 47.0 cm) | serpent | | × | |

**Table A1.1.** Summary of sample locations and types of analysis conducted

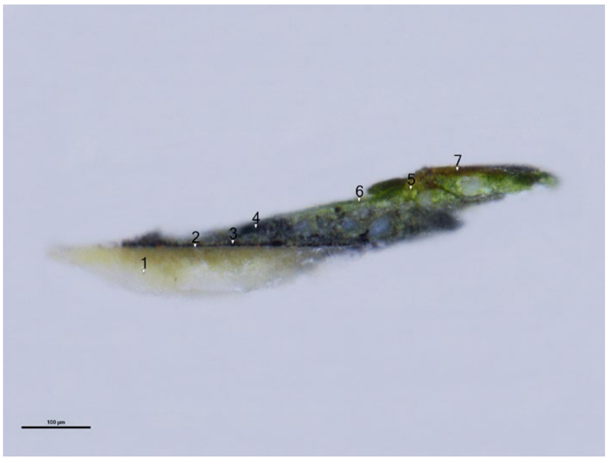
Comparison of the stratigraphy of samples C3, C5, C7 and C11 revealed variations in the number of paint layers. All samples exhibited a standard layer structure: a thick white ground layer covered by a thin white isolating layer (imprimatura), followed by successive chromatic paint layers (underpainting and modelling) of varying thickness. In the earth section from which the tree grows and where the figures of Eve and Adam stand (C3 – fig. A1.1), a single paint layer was identified: a white layer with individual pigment grains. The stratigraphy shows that the imprimatura binder seeped into the more absorbent ground, manifesting as yellowish streaks. Nevertheless, the imprimatura effectively fulfilled its insulating function. Stratigraphic samples taken from other compositional elements show: one paint layer (C5: black background; C8: upper part of the trunk), two layers (C11: serpent) and three layers (C7: leaf near the tree trunk) (figs A1.2 and A1.3).

In the stratigraphy of sample C7, pigment agglomerates – specifically lead white – were clearly visible. These agglomerates formed over time due to aggregation (clumping of solid particles into aggregates and larger agglomerates) under the influence of the oil binder (the average size of primary particles is 10–100 nm, aggregates: 50–500 nm and agglomerates – observed here – more than 500 nm). This process affects the light absorption coefficient (and thus colour intensity), opacity and pigment density in the paint (i.e., the necessary amount of solvent in which the colour particles are dispersed). As aggregation progresses to the agglomerate stage, it causes colour dulling, increased transparency, as well as reduced pigment density and cohesion in the paint.


**A1.1** Lucas Cranach the Elder, *Adam and Eve*, National Museum in Warsaw, stratigraphy of sample C3: 1) white ground layer, 2) white imprimatura, 3) paint layer with individual grains of red and black pigments
photo Justyna Kwiatkowska




**A1.2** Lucas Cranach the Elder, *Adam and Eve*, National Museum in Warsaw, stratigraphy of sample C11: 1) white ground layer, 2) white imprimatura, 3) two paint layers: lower dark grey (black), upper discontinuous white-yellow layer
photo Justyna Kwiatkowska




**A1.3** Lucas Cranach the Elder, *Adam and Eve*, National Museum in Warsaw, stratigraphy of sample C7: 1) white ground layer, 2) white imprimatura, 3) underlayer for dead colouring, black, 4) underpainting layer – dead colouring, dark grey, 5) modelling layer, green, 6) discontinuous green layer, 7) discontinuous light brown layer
photo Justyna Kwiatkowska

Microscopic and microchemical pigment analyses was conducted on four selected samples, two from the earth section and two from the background near the upper edge of the painting. The samples were observed under a Nikon SMZ1500 stereoscopic microscope and a Nikon ECLIPSE E200 laboratory research microscope at various levels of magnifications (up to 400×). The analysis assessed colour, shape, homogeneity, optical properties of crystals, as well as microcrystalline and droplet chemical reactions of pigments.[1]

These reactions clearly confirmed that the black pigment examined was not – as could be expected – bone black, which was commonly used in underpainting for dead colouring (a monochromatic sketch of light and shadow using flat colour patches, over which modelling layers were applied). The absence of bone black was determined by the lack of the pigment's partial solubility when exposed to hydrochloric acid and nitric acid (V). Instead, the presence of plant black was indicated by its distinctive granulation, observable under the microscope as large, varied and sometimes elongated particles.

Observation of sample C3 revealed two white layers. The upper imprimatura contained lead white ($PbCO_3$), while the lower ground layer contained calcium carbonate ($CaCO_3$) as a filler. Solubility reactions and microscopic examination of the sample smear in transmitted light confirmed the absence of gypsum admixtures or remnants of microorganisms (coccoliths and foraminifera) typical of chalk. Chalk is a form of calcium carbonate derived from fossilized marine organisms. In this case, we are still dealing with a chalk-glue ground, but the material used was of exceptionally high purity.

To further investigate sample C3, FTIR-ATR spectroscopy was performed using a Bruker Alpha spectrometer with a DTGS detector and a QuickSnap ATR attachment with a diamond crystal. The ATR/FTIR spectrum was recorded in the 4000–400 $cm^{-1}$ range, with a resolution of 4 $cm^{-1}$, averaging 24 scans and applying automatic ATR correction.[2] The analysis confirmed the presence of calcium carbonate, previously identified through microchemical testing.

## NOTES

1 Piotr Rudniewski et al., *Pigmenty. Analiza mikrochemiczna i instrumentalna*, Academy of Fine Arts in Warsaw (Warsaw, 2018).

2 Signe Vahur et al., 'ATR-FT-IR spectral collection of conservation materials in the extended region of 4000-80 $cm^{-1}$', *Analytical and Bioanalytical Chemistry*, 408 (2016), pp. 3373–3379.

## Annex 2. Report on the Paint Layers Elemental Composition Analysis

The analysis was conducted by Dr Olga Syta and Professor Barbara Wagner (InterLaBAr – Interdisciplinary Laboratory for Archaeometric Research, Biological and Chemical Research Centre, University of Warsaw) on 18 August 2018 at the Painting Conservation Studio of the National Museum in Warsaw.

### Project Description

The aim of the study was to non-invasively establish, the chief elemental composition of the work's paint layers via portable X-Ray Fluorescence Spectrometry (p-XRF).

### Measurement System

The Bruker TRACER III-SD portable XRF spectrometer enables elemental analysis in the range from Mg to Pu, using a Rh X-ray tube as the excitation source. The Rh anode X-ray tube operates at a maximum voltage of 45 kV and a beam current ranging from 2 to 25 µA. The analysis can be performed in field conditions at ambient temperatures between –10°C and 50°C. The use of an additional continuous vacuum pump system (vacuum measurement from 1 Tr) enhances analytical sensitivity for light elements. The conditions for XRF spectrum recording during the elemental composition analysis of the painting are presented in table A2.1.

| Parameter | Value |
|---|---|
| X-ray tube voltage | 40 kV |
| beam current intensity | 11.1 µA |
| spectrum recording time | 60 s |
| continuous-action vacuum pump system | approx. 2 Tr vacuum |

**Table A2.1.** XRF spectrum recording conditions

The recorded X-ray fluorescence signals (measurement locations shown in fig. 8) were processed using S1PXRF and Excel. The final results are presented in table A2.3. XRF spectrum graphs for the specified positions are included in the technological and conservation documentation, stored at the NMW Laboratory under the painting's inventory number: M.Ob.588 MNW. The spectra were recorded from areas previously analysed using infrared spectroscopy (FTIR) (see Annex 4). During XRF spectrum recording, signals could have been excited not only from the surface but also from deeper layers of the painting.

| measurement number and location | coordinates [cm] | XRF analysis results – detected elements with signal intensity (a.u.) |
|---|---|---|
| 01 Eve's arm | x = 33.7; y = 33.5 | **Pb**, Al, Sr, K, Ca, Ti, Fe, Cu, **Hg**, Zr |
| 02 Eve's breast, shadow | x = 33.5; y = 30.0 | **Pb**, Al, Sr, K, Ca, Ti, **Fe**, Cu, Zn, **Hg**, Zr |
| 03 Eve's thigh | x = 35.5; y = 19.3 | **Pb**, Al, Sr, K, Ca, Ti, Fe, Cu, **Hg**, Sr, Zr |
| 04 Eve's knee | x = 31.0; y = 12.5 | **Pb**, Al, Sr, K, Ca, Ti, Fe, Cu, **Hg**, Zr |
| 05 Eve's elbow | x = 27.0; y = 31.0 | **Pb**, Al, Sr, K, Ca, Ti, Fe, Cu, **Hg**, Zr |
| 06 Eve's cheek | x = 31.0; y = 30.3 | **Pb**, Al, Sr, K, Ca, Ti, Fe, Cu, **Hg**, Zr |

| | | |
|---|---|---|
| 07 Eve's lips* | x = 30.0; y = 32.5 | **Pb**, Al, Sr, K, Ca, Ti, Fe, Cu, **Hg**, Zr |
| 08 Eve's hair below the ear | x = 32.0; y = 37.5 | **Pb**, **Fe**, Al, Si, Sr, K, **Ca**, Ti, Cu, Zn, Hg, Zr |
| 09 Eve's hair | x = 29.5; y = 26.5 | **Pb**, **Fe**, Al, Si, Sr, K, **Ca**, Ti, Cu, Zn, Hg, Zr |
| 10 fruit | x = 29.0; y = 34.5 | **Pb**, Al, Sr, **S**, K, Ca, Ti, Fe, Cu, **Hg**, Zr |
| 11 leaf, Eve** | x = 32.0; y = 22.0 | **Pb**, **Cu**, Al, Si, Sr, K, **Sn**, Ca, Ti, Fe, Zn, Hg, Zr |
| 12 Adam's chest | x = 09.5; y = 32.5 | **Pb**, Al, Sr, Ca, Ti, Fe, Cu, **Hg**, Zr |
| 13 Adam's armpit | x = 09.0; y = 30.0 | **Pb**, Al, Si, Sr, K, **Ca**, Ti, **Fe**, Cu, Zn, **Hg**, Zr |
| 14 Adam's arm | x = 06.0; y = 24.0 | **Pb**, Al, Sr, K, Ca, Ti, Fe, Cu, Zn, **Hg**, Zr |
| 15 Adam's thigh | x = 10.0; y = 18.0 | **Pb**, Al, Sr, K, Ca, Ti, Fe, Cu, **Hg**, Zr |
| 16 Adam's ankle | x = 13.0; y = 6.0 | **Pb**, Al, Sr, K, Ca, Ti, Fe, Cu, Zn, **Hg**, Zr |
| 17 Adam's hair | x = 10.5; y = 40.0 | **Pb**, **Fe**, Al, Si, Sr, K, **Ca**, Ti, Cu, Zn, Hg, Zr |
| 18 Adam's lips* | x = 12.0; y = 38.0 | **Pb**, Al, Si, Sr, P, K, Ca, Ti, Fe, Cu, Zn, **Hg**, Zr |
| 19 leaf, Adam* | x = 11.5; y = 22.0 | **Cu**, **Pb**, Al, Si, Sr, K, **Sn**, Ca, Ti, Fe, Zn, Hg, Zr |
| 20 earth, v. light | x = 27.0; y = 2.0 | **Pb**, Sr, K, **Sn**, Ca, Ti, Fe, **Cu**, Zn, Hg, Zr |
| 21 earth, v. dark* | x = 40.0; y = 5.5 | Pb, Al, Sr, P, K, Ca, Ti, Fe, Cu, Zn, Hg, Zr |
| 22 earth, near Adam's foot* | x = 06.0; y = 4.0 | **Pb**, Si, Sr, K, Ca, Ti, Fe, Cu, Zn, Hg, Zr |
| 23 tree, root | x = 18.0; y = 5.5 | **Pb**, Al, Sr, K, Ca, Ti, Fe, **Cu**, Hg, Zr |
| 24 background, sifted, original | x = 18.5; y = 12.0 | **Ca**, Al, Si, **S**, K, Ti, Mn, Fe, Cu, Zn, Hg, **Pb**, Sr, Zr |
| 25 background | x = 41.0; y = 11.5 | **Ca**, Al, Si, **S**, K, Ti, Mn, Fe, Cu, Zn, Hg, **Pb**, Sr, Zr |
| 26 background, edge* | x = 04.0; y = 7.0 | **Ca**, Al, Si, **S**, K, Ti, Mn, Fe, Cu, Zn, Hg, **Pb**, Sr, Zr |
| 27 leaves, tree | x = 36.0; y = 45.5 | **Cu**, **Pb**, Al, Si, S, K, **Sn**, Ca, Ti, Fe, Zn, As, Sr, Zr |
| 28 leaves at the branching | x = 16.8. y = 50.5 | **Cu**, **Pb**, Al, Si, K, **Sn**, Ca, Ti, Fe, Zn, Sr, Zr |
| 29 leaf 1, v. light* | x = 17.3. y = 50.5 | **Cu**, **Pb**, Al, Si, K, **Sn**, Ca, Ti, Fe, Zn, Hg, Sr, Zr |
| 30 leaf 2, v. dark* | x = 17.0. y = 50.0 | **Cu**, **Pb**, Al, Si, K, **Sn**, Ca, Ti, Fe, Zn, Hg, Sr, Zr |
| 31 tree, bark | x = 17.0. y = 56.5 | **Pb**, Si, Sr, K, Ca, Ti, Fe, Cu, Zn, Hg, Zr |
| 32 background, black | x = 3.0. y = 56.5 | **Ca**, **Pb**, Al, Si, S, K, Ti, Mn, Fe, Cu, Zn, Sr, Zr |
| 33 serpent, yellow | x = 20.5. y = 44.0 | **Pb**, Sr, **Sn**, Ca, Ti, Fe, Cu, Zn, Hg, Zr |
| 34 serpent | x = 22.0. y = 41.5 | **Pb**, Sr, K, Ca, Ti, Fe, Cu, Zn, Hg, Zr |
| 35 tree, trunk | x = 20.0. y = 32.0 | **Pb**, **Cu**, **Sn**, Ca, Ti, Fe, Zn, Hg, Sr, Zr |
| 36 tree, trunk | x = 20.5. y = 38.0 | **Pb**, **Sn**, Ca, Ti, Fe, **Cu**, Zn, Hg, Sr, Zr |
| 37 back of the painting, metal* | | **Sn**, Si, **Sb**, Fe, Cu, Zn, **Pb**, Hg, Sr |
| 38 back of the painting, red* | | **Fe**, Al, Si, **P**, **S**, K, **Ca**, Ti, Mn, Cu, Zn, Hg, **Pb**, Sr |

* no measurement using infrared spectroscopy (FTIR)
** different coordinates of the measurement location than in the infrared spectroscopy (FTIR) analysis

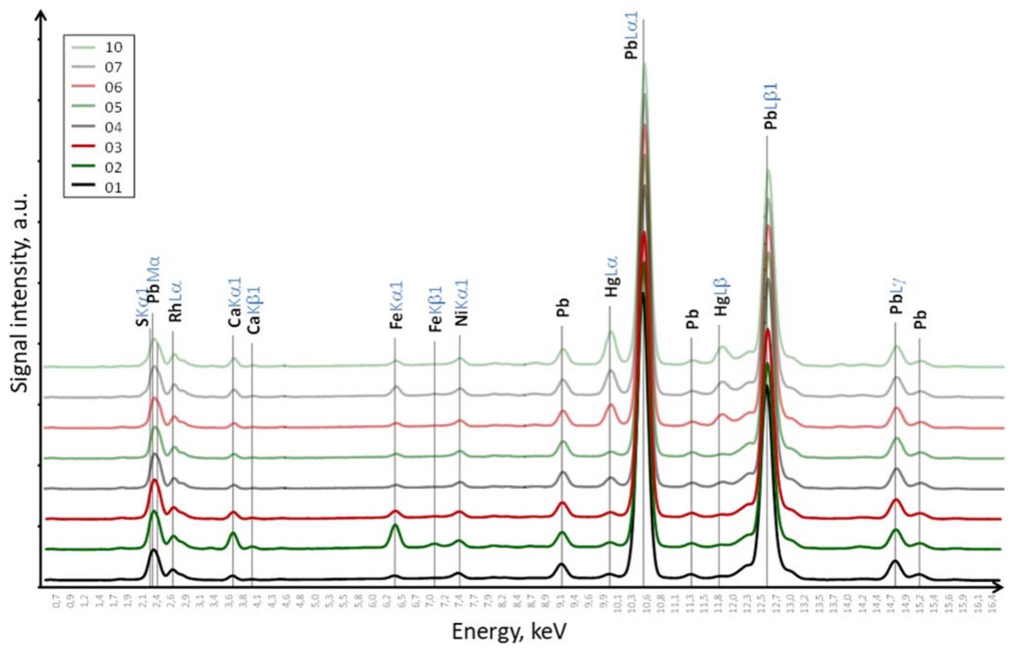
**Table A.2.1.** Registered X-ray fluorescence signals

Based on the recorded data, an attempt was made to assess the chemical composition of the individual measurement locations on the surface of the analysed object.

In all examined areas of the painting, Pb was detected, which may indicate the use of lead white $(PbCO_3)_2 \cdot Pb(OH)_2$, applied as a ground layer and/or as an additive in other pigments. The Pb signal in each spectrum could also be related to the presence of siccatives.

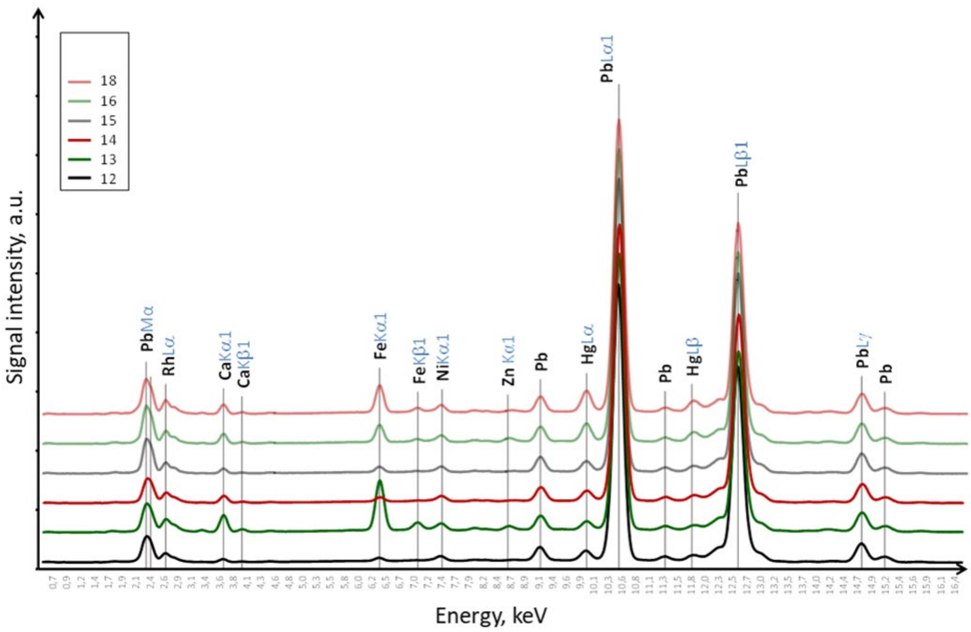
**XRF Spectra Recorded for Areas of Similar Colour**

**White, pink, red: Eve's figure**




Measurement points 01, 02, 03, 04, 05, 06, 07 and 10 (listed in table A2.1) show a similar elemental composition (Pb, Hg). The presence of Pb suggests the use of lead white $(PbCO_3)_2 \cdot Pb(OH)_2$, while the presence of Hg indicates the use of cinnabar (HgS). In spectrum 10 (fruit), an S signal was also detected, despite the low sensitivity of the measurement for this element. In the XRF spectrum recorded for the area beneath Eve's breasts (measurement 02), the Fe signal intensity is higher than in the other measurement points, which may suggest the presence of an iron-based pigment.

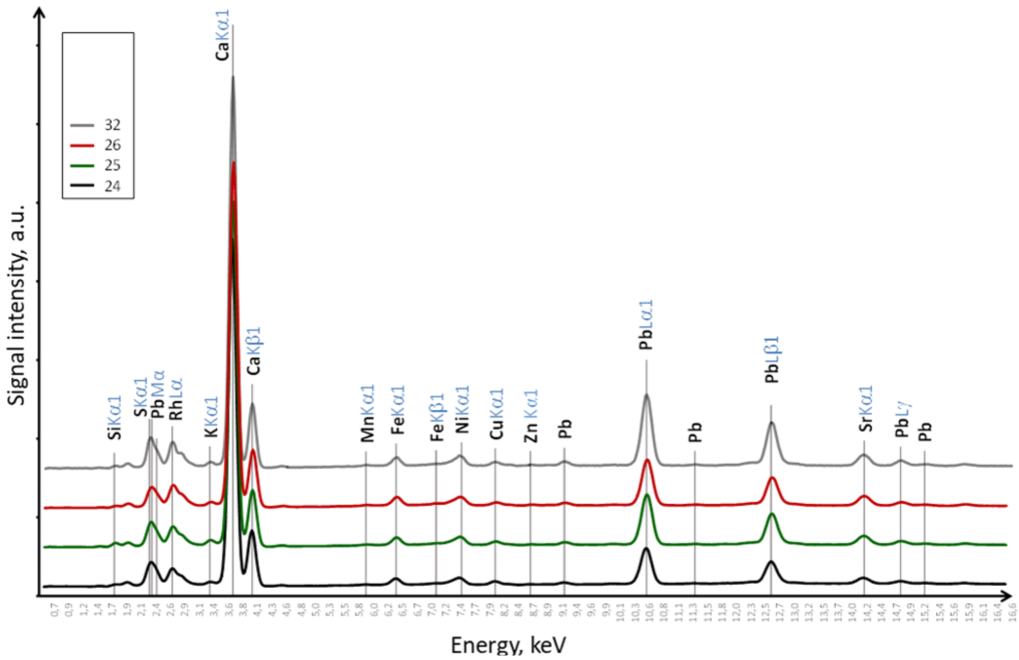
**White, pink, red: Adam's figure**



Measurement points 12, 13, 14, 15, 16 and 18 show a similar elemental composition (Pb, Hg) and share characteristics with measurement points 01, 02, 03, 04, 05, 06, 07 and 10 from Eve's figure. The presence of Pb suggests the use of lead white $(PbCO_3)_2 \cdot Pb(OH)_2$, while the presence of Hg indicates the use of cinnabar (HgS). In the XRF spectra recorded for areas 13 (Adam's armpit), 16 (Adam's ankle) and 18 (Adam's lips), the Fe signal intensity exceeds that detected in other measurement points, indicating the presence of an iron-based pigment accompanied by elements such as Al, Si and K. In spectrum 18, a P signal is also visible.

The XRF spectra recorded for Adam's figure show the presence of Zn signals, which are absent in the spectra recorded for Eve's figure, except for measurement 02 (below Eve's breast, shadow).

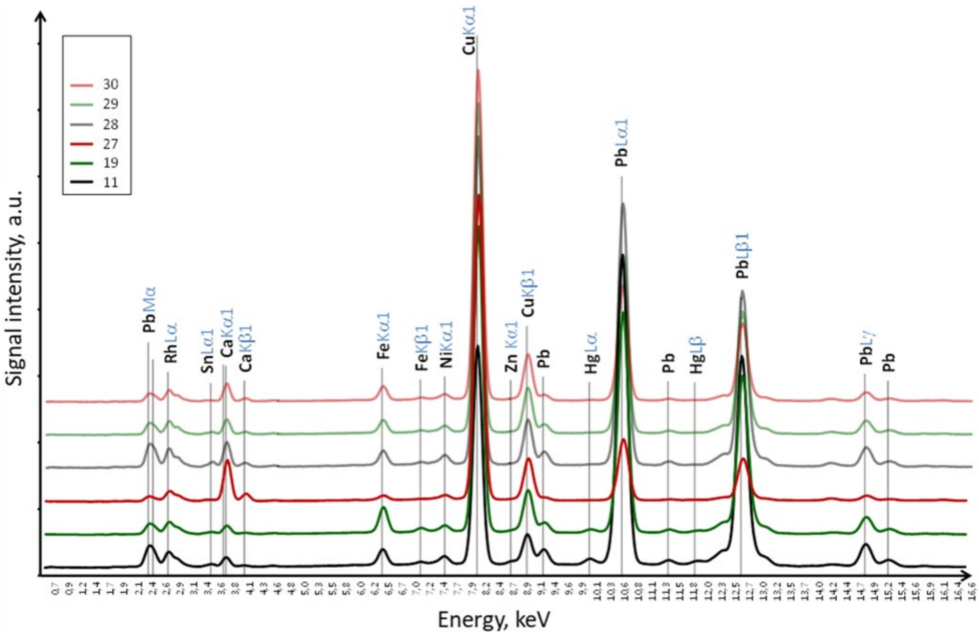
Black: background




The XRF method does not allow for the detection of C, making the identification of organic blacks challenging and often reliant on indirect reasoning. The results of the measurements indicate a high probability that an organic black pigment was used for painting the dark areas of the work. If the XRF spectrum had shown a strong K signal, it could have been interpreted as evidence of the use of plant-based black. However, in this case, the K signal is relatively weak. Strong signals for Ca and P would suggest the presence of bone black, but P was not detected in the analysis.

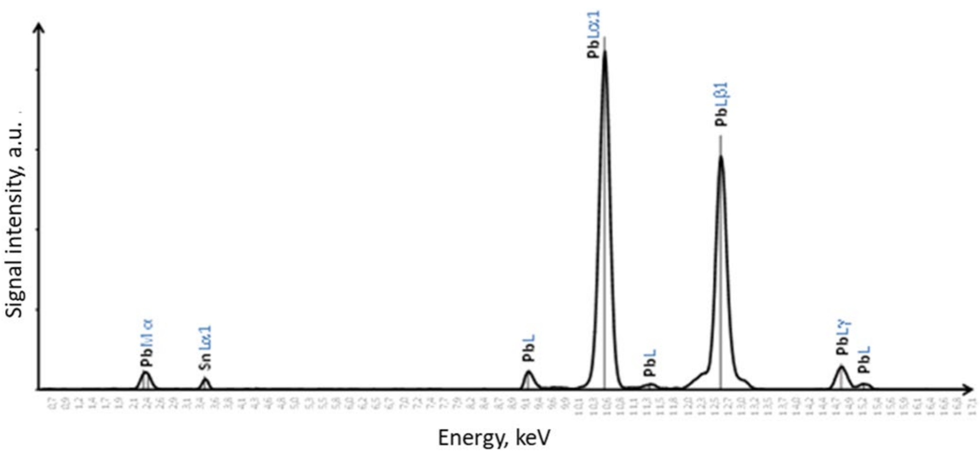
A distinct Ca signal may indicate the presence of calcium compounds, such as chalk ($CaCO_3$), in the underlying layers. The simultaneous presence of Ca and S signals in the spectrum could suggest the presence of gypsum ($CaSO_4 \cdot 2H_2O$). Conservation studies conducted in 1994 confirmed the presence of both chalk and gypsum in samples taken from the painting, identified using microcrystalline methods: chalk was found beneath the upper layer of carbon black in the background, while gypsum was identified in the tree area [*Raport Pracowni Konserwacji Sztuki Średniowiecznej Muzeum Narodowego w Warszawie: Cranach, Adam i Ewa* (1994), NMW conservation documentation archive, samples no. 2 and 3].

### Green: leaves




Strong signals for Cu, Pb, Sn and Fe appear in the spectra recorded for the green leaf areas (11, 19, 27, 28, 29 and 30), suggesting the presence of a copper-based pigment and iron compounds with traces of other elements (e.g., Al and Si), meaning a natural iron-based pigment. Without additional analysis, it should also be considered that the green colour may be a mixture of yellow and blue pigments. In this case, the presence of Pb and Sn could indicate the use of lead-tin yellow ($Pb_2SnO_4$) and a copper-based blue pigment such as azurite $2CuCO_3 \cdot Cu(OH)_2$. Conservation research conducted in 1994 using microcrystalline methods confirmed the presence of azurite in the green layer of a sample taken from the painting (*Raport*..., sample no. 3).

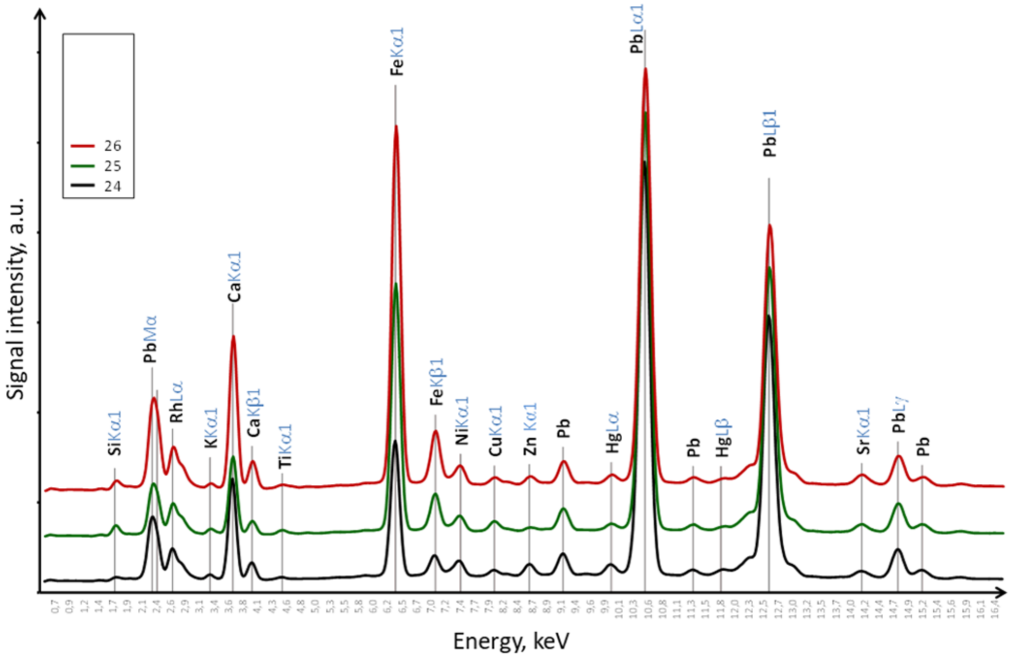
The measurement window of the spectrometer used in the analysis was approximately 0.8 × 0.5 cm, making it difficult to automatically obtain selective elemental composition data for small details located within the analysed area along with the background. To isolate data specific to a lighter detail within the leaves (measurement 29), an additional spectrum was recorded for a darker section of the leaf (measurement 30). By subtracting the intensity of spectrum 30 from spectrum 29, a differential spectrum (29–30) was obtained, as presented in the graph below.



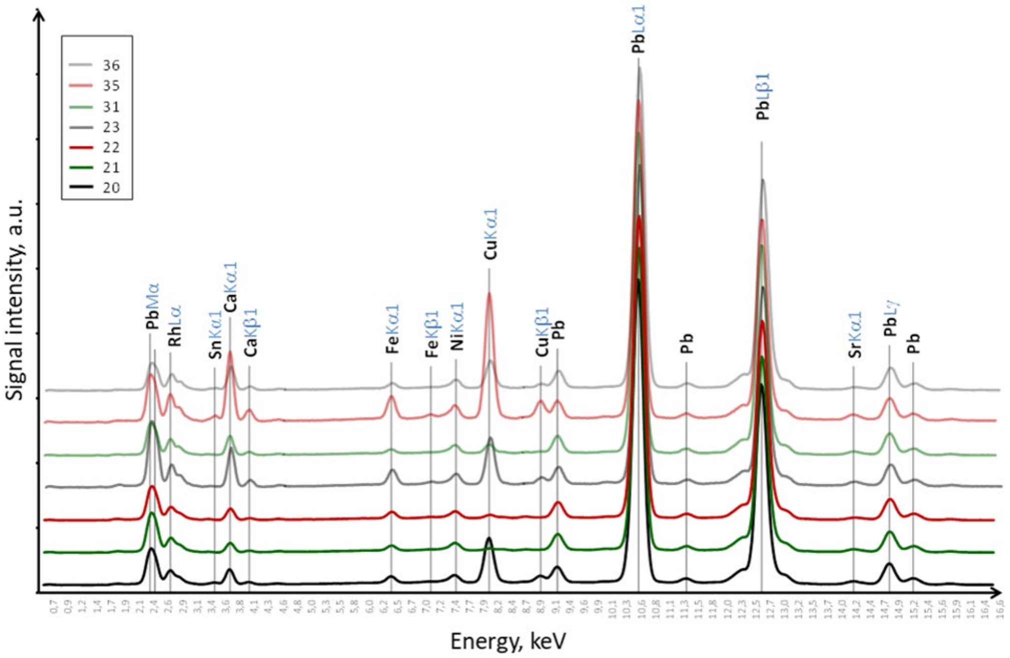

Differential spectrum 29 (v. light leaf) – 30 (v. dark leaf)

The differential spectrum represents the approximate elemental composition of the paint used for the lighter leaf. It is characterized by increased levels of two primary elements: Pb and Sn, which strongly suggest the presence of lead-tin yellow. However, confirming this identification would require the application of a molecular analysis method such as Raman spectroscopy or infrared spectroscopy (FTIR).

Brown: hair

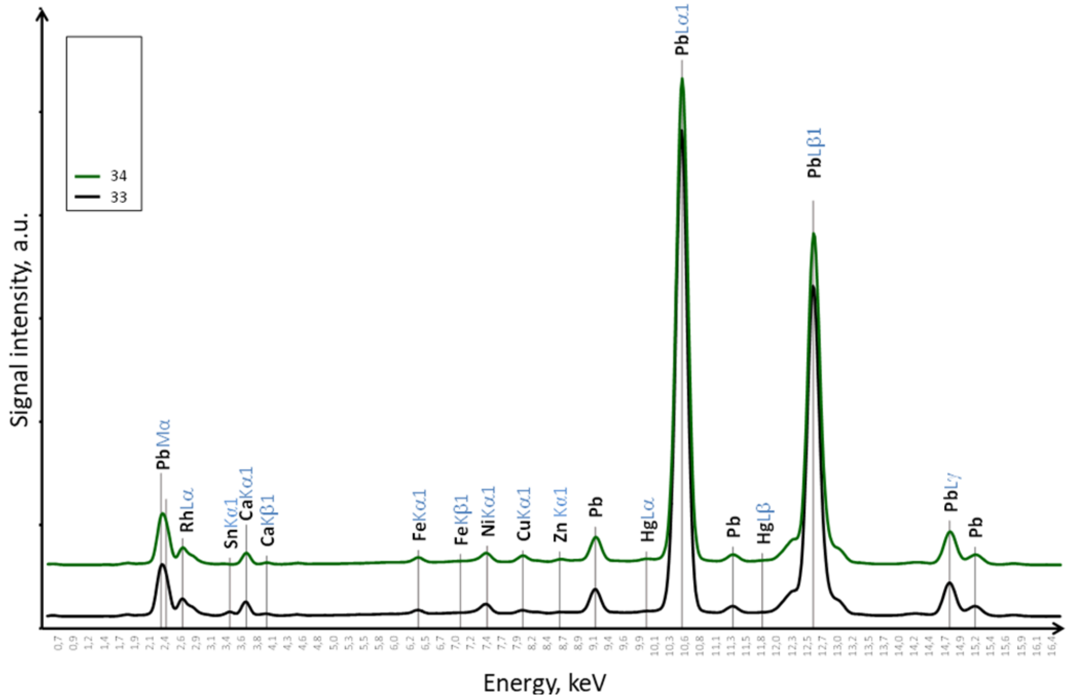


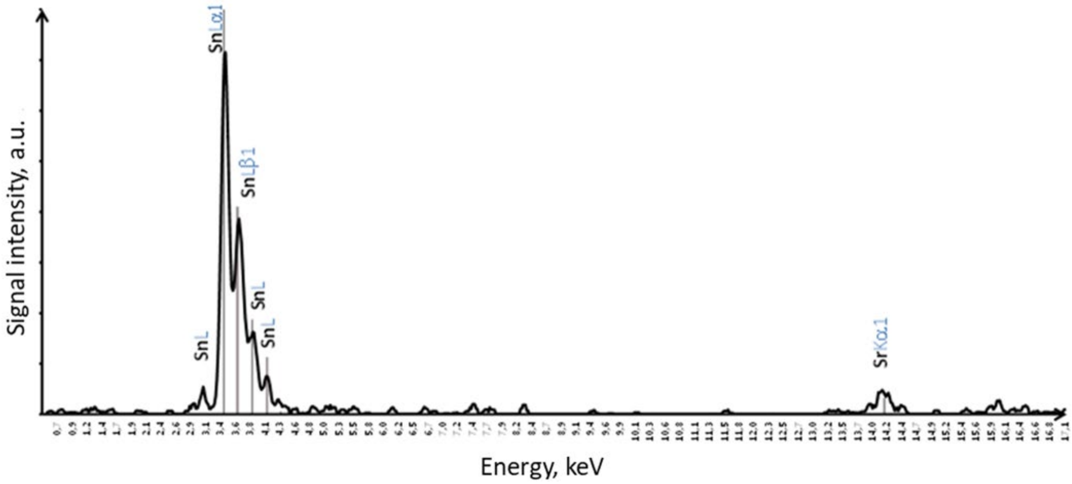

Brown: tree, earth




The individual measurement points exhibit a similar elemental composition. In the recorded spectra, the dominant signals in the hair areas (24–26) originate from the presence of Pb and Fe, whereas in the tree and earth areas (20–23, 31, 35–36), the presence of Fe decreases, while Cu appears with varying intensity.

**Yellow: serpent**




Differential spectrum 33 (serpent, yellow) – 34 (serpent)

The differential spectrum comparing measurement 33 (yellow, lighter area of the serpent) and 34 (darker area of the serpent) shows that tin (Sn) is the distinguishing element. The interpretation of this result is not entirely clear, as the presence of Sn could indicate the use of lead-tin yellow ($Pb_2SnO_4$) but in that case, an increased Pb content would also be expected, which was not observed in this analysis.

## Annex 3. Identification of Organic Substances Using Gas Chromatography coupled with Mass Spectrometry (GC/MS) and Liquid Chromatography coupled with Mass Spectrometry (LC/MS)

The GC/MS and LC/MS analyses, conducted by Dr Bartłomiej Witkowski and Prof. Dr hab. Tomasz Gierczak (Faculty of Chemistry, University of Warsaw), aimed to identify natural organic substances – drying oils, waxes, resins and proteins – in micro-samples taken from Lucas Cranach the Elder's painting *Adam and Eve*[1] (see fig. 9).

### Research Method

**Sample preparation**
Before analysis, the samples required appropriate preparation to ensure high-quality results. Each sample was first extracted twice using trichloroethene to remove secondary conservation materials that could hinder the identification of original components. The samples were then divided into two fractions: a protein fraction, separated from the remaining sample ingredients using an aqueous ammonia solution, and a lipid fraction, which remained after protein extraction.

**Protein identification method: LC/MS**
Amino acid analysis of the protein fraction was performed using a Shimadzu LC20 liquid chromatograph coupled with a QTRAP 3200 tandem mass spectrometer (Applied Biosystem/MDS SCIEX). The results provided detailed information on the amino acid composition and protein content in the examined samples.

**Analysis of natural oils, waxes and resins: GC/MS**
The analysis of drying oils, waxes and resins was conducted using a Shimadzu GCMS-QP2010 Ultra gas chromatograph connected to a Shimadzu QP-5000 quadrupole mass spectrometer. The results allowed for the identification of these substances in the examined samples.

**Reference analysis**
LC/MS and GC/MS are comparative analysis methods, meaning that the identification of a substance in a sample must be preceded by prior analysis of appropriate reference materials.[2] Consequently, before analysing the samples from the painting, a series of proteins, waxes, drying oils and resins commonly used in late medieval and early Northern Renaissance painting techniques were examined. This enabled the identification of these materials in the samples taken from Cranach's painting.

### Analysis of Samples from the Painting

| Sample no. | Mass (mg) |
|---|---|
| C2 | 0.77 |
| C4 | 0.10 |
| C9 | 0.11 |
| C10 | 0.19 |

**Table A3.1.** List of samples analysed using GC/MS and LC/MS

The samples listed in the table were prepared and analysed using GC/MS and LC/MS following the procedure described above. The results of the identification of drying oils, waxes and resins, as well as the detection of proteins, are detailed in the following sections.

### Identification of Oils, Waxes and Resins (GC/MS)

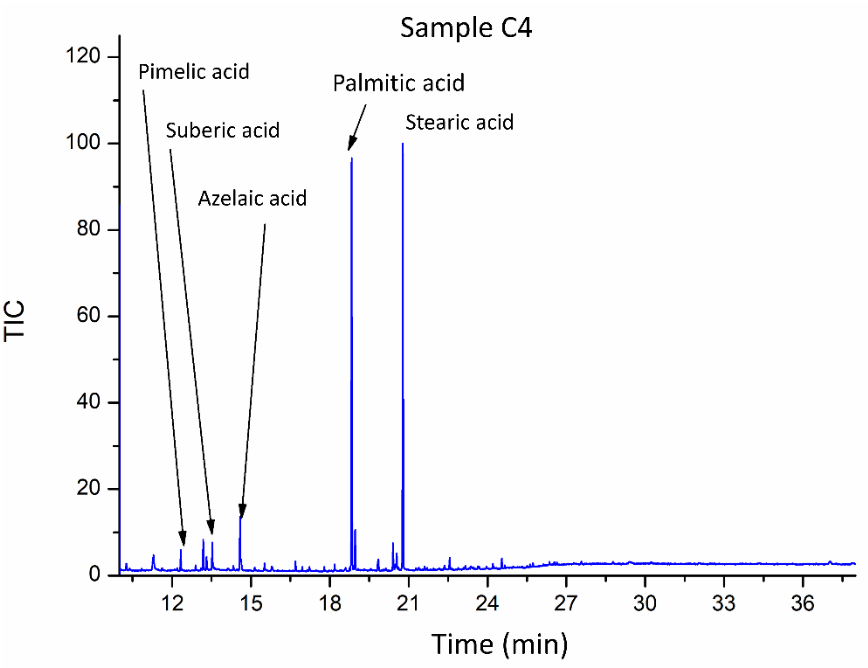



**Fig. A3.1.** Chromatogram of the lipid fraction of sample C4

Sample C4 revealed azelaic, palmitic and stearic acids (fig. A3.1). Very similar results were obtained for the remaining samples, except for C2, in which the fatty acid content was very low. These data indicate the presence of a degraded oil binder in samples C4, C9 and C10.

| Sample no. | P/S | A/P | Dicarboxylic acid content (%) | Identified oil |
|---|---|---|---|---|
| C2 | – | 0.1 | 8 | No drying oil identified |
| C4 | 1.0 | 0.3 | 20 | Linseed oil |
| C9 | 1.0 | 0.5 | 35 | Linseed oil |
| C10 | 0.8 | 0.4 | 31 | Linseed oil |

**Table A3.2.** Results of the quantitative analysis of fatty acids

Each drying oil is characterized by a different P/S coefficient – the relative content of palmitic and stearic acids.[3] Additionally, degraded (dried) drying oils typically have a high azelaic acid content relative to palmitic acid (A/P ≥ 0.3). The P/S values for the most common natural oil-based binders traditionally used in historical painting techniques are as follows: 1–2 for linseed oil, 2–3 for walnut oil, 3–8 for poppy seed oil and approximately 2.5–3.5 for egg yolk. This method allows for the identification of natural drying oils and tempera binders traditionally used in painting.[4] As shown in table A3.2, linseed oil was detected in the examined samples.[5] The data also exclude the presence of egg yolk as a binder – P/S < 2.

### Protein Analysis Results (LC/MS)

Analysis of sample C2 revealed the presence of protein, whereas no protein was detected in the other samples. The relative amino acid content was used to identify the protein found in C2. A similarity analysis was performed using principal component analysis (PCA). In the PCA plot (fig. A3.2), proteins with a similar amino acid composition form separate clusters of closely positioned points. If the point corresponding to the analysed sample is located near or within the cluster of a reference protein, it indicates the presence of that protein in the sample. If the point lies on the boundary between multiple reference clusters, it may suggest the presence of a mixture of proteins.

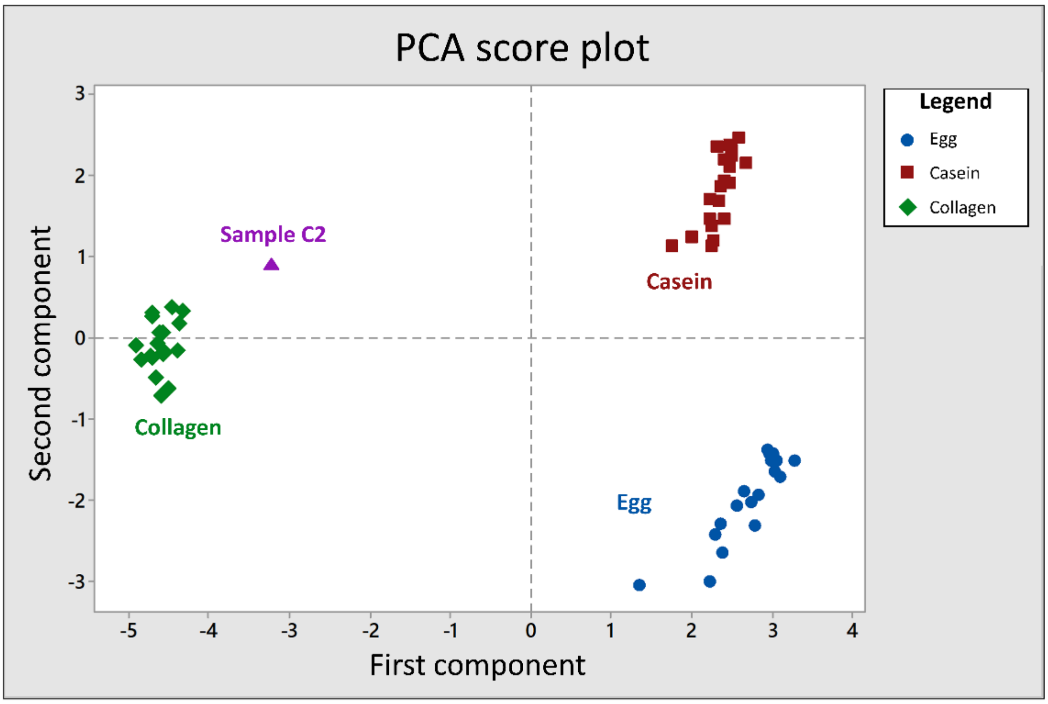



**Fig. A3.2.** PCA plot showing similarity analysis of the amino acid content of proteins detected in sample C2

In the PCA plot (fig. A3.2), sample C2 is located closest to the cluster corresponding to collagen, which is the main component of connective tissues. This result clearly indicates that the sample contains animal glue, which is further confirmed by the presence of hydroxyproline.

### Conclusion

| Sample no. | Identified materials |
|---|---|
| C2 | Animal glue |
| C4 | Linseed oil |
| C9 | Linseed oil |
| C10 | Linseed oil |

**Table A3.3.** Summary of results

As shown in table A3.3, linseed oil was identified in three samples, while animal glue was found in one. The results do not indicate the presence of tempera binders containing egg yolk.

## NOTES

1 Bartłomiej Witkowski et al., 'Identification of proteins, drying oils, waxes and resins in the works of art micro-samples by chromatographic and mass spectrometric techniques', *Journal of Separation Science*, vol. 41, no. 3 (2018), p. 630.

2 See *Organic Mass Spectrometry in Art and Archaeology*, eds Maria Perla Colombini, Francesca Modugno (Chichester, 2009).

3 Ibid.

4 Ibid.

5 Ibid.; Alessia Andreotti et al., 'Combined GC/MS Analytical Procedure for the Characterization of Glycerolipid, Waxy, Resinous, and Proteinaceous Materials in a Unique Paint Microsample', *Analytical Chemistry*, vol. 78, no. 13 (2006), p. 4490; Maria Perla Colombini et al., 'Analytical strategies for characterizing organic paint media using gas chromatography/mass spectrometry', *Accounts Chem. Res*, vol. 43, no. 6 (2010), p. 715.

## Annex 4. Non-Invasive Analysis of Organic Substances Using Fourier-Transform Infrared Spectroscopy (FTIR)

The analysis was conducted by Dr Magdalena Wróbel-Szypula (Laboratory for the Analysis and Protection of Museum Objects, National Museum in Warsaw).

### Methodology

Spectra were recorded at 26 measurement points (see fig. 9) with a diameter of 4 cm using Fourier-transform infrared spectroscopy (FTIR). The analysis was performed with a Bruker Alpha FTIR spectrometer equipped with an external reflectance accessory and a DLaTGS detector (deuterated L-alanine-doped triglycine sulphate). Each measurement was preceded by a calibration process, which involved recording a spectrum of a gold plate placed in an interchangeable holder. The spectral resolution was 4 $cm^{-1}$ and measurements were taken in the 4000–400 $cm^{-1}$ range. The collected data were transformed from reflection parameter values into pseudo-absorbance values = log(1/R). The identification of organic compound groups was based on literature sources and reference spectra created from reagents supplied by Kremer.

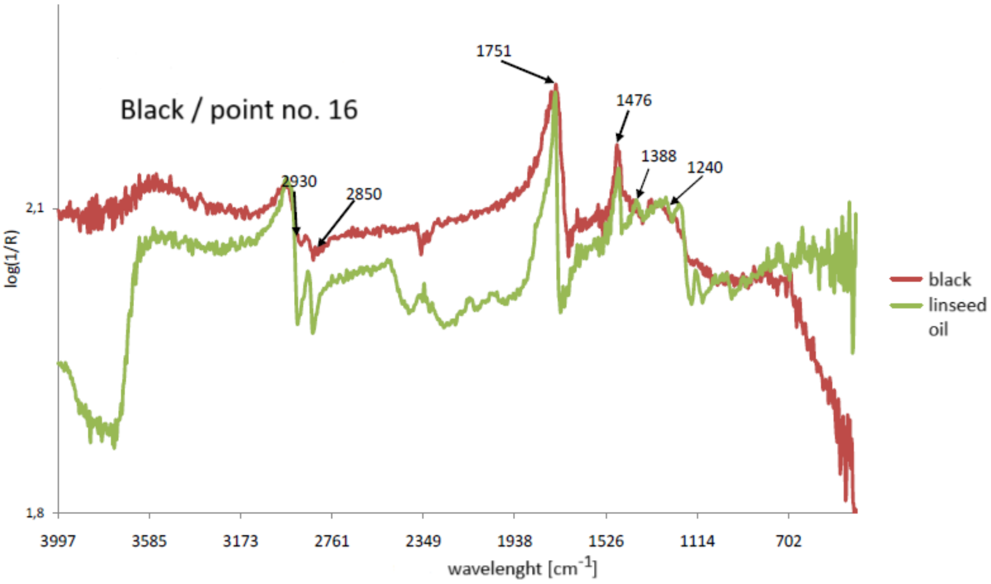
### Results

| Measurement point | Organic compounds | In addition |
|---|---|---|
| **1.** Adam, leg (x = 13 cm, y = 6 cm) | oil | lead white |
| **2.** Adam, arm (x = 6 cm, y = 24.5 cm) | oil | lead white |
| **3.** Adam, chest, right (x = 9.5 cm, y = 32.5 cm) | oil | lead white |
| **4.** Adam, right armpit (x = 9 cm, y = 30 cm) | oil | lead white |
| **5.** Adam, right thigh (x = 10 cm, y = 18 cm) | oil, traces of protein | lead white |
| **6.** Adam, hair (x = 10.5 cm, y = 40 cm) | oil, traces of protein | vermilion, lead white |
| **7.** Eve, leg (x = 35.5 cm, y = 19.3 cm) | oil, traces of protein | lead white |
| **8.** Eve, knee (x = 31 cm, y = 12.5 cm) | oil | lead white |
| **9.** Eve, arm (x = 33.7 cm, y = 33.5 cm) | oil | lead white |
| **10.** Eve, arm 2 (x = 27 cm, y = 31 cm) | oil, traces of protein | lead white |
| **11.** Eve, cheek (x = 31 cm, y = 36.3 cm) | oil | lead white |
| **12.** Eve, breasts, shadow (x = 33.5 cm, y = 30 cm) | oil, traces of protein | lead white |
| **13.** Apple (x = 29 cm, y = 34.5 cm) | oil | lead white |
| **14.** Eve, hair (x = 29.5 cm, y = 26.5 cm) | oil | |
| **15.** Eve, hair 2 (x = 32 cm, y = 37.5 cm) | oil | vermilion |
| **16.** Black (x = 41 cm, y = 11.5 cm) | oil | |
| **17.** Background, black 2 (x = 18.5 cm, y = 12 cm) | oil, traces of protein | yellow ochre |
| **18.** Leaves (x = 16.8 cm, y = 56.5 cm) | oil | |
| **19.** Leaf Eve (x = 35 cm, y = 23 cm) | oil, traces of protein | lead white |
| **20.** Leaf 2a (x = 36 cm, y = 45.5 cm) | oil, traces of protein | |
| **21.** Background, tree (x = 3 cm, y = 56.5 cm) | oil | |
| **22.** Tree (x = 16.8 cm, y = 56.5 cm) | oil, traces of protein | |
| **23.** Earth, tree (x = 18 cm, y = 5.5) | oil, traces of protein | |

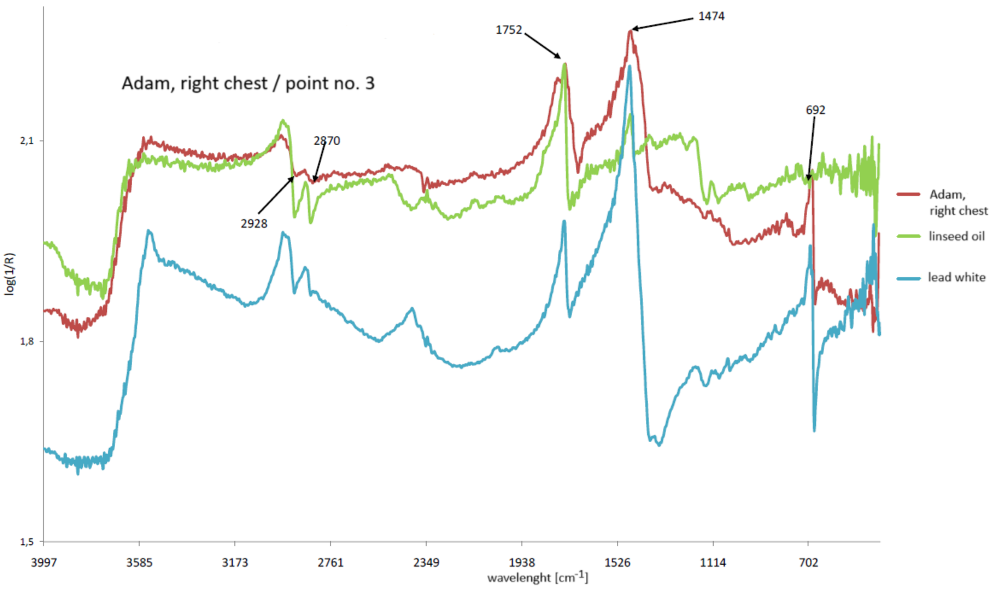
| | | |
|---|---|---|
| **24.** Earth (x = 27 cm, y = 2 cm) | oil | yellow ochre |
| **25.** Serpent, blue (x = 22 cm, y = 41.5 cm) | oil | lead white |
| **26.** Serpent, yellow (x = 20.5 cm, y = 44 cm) | oil | lead-tin yellow |

**Table A4.1**. Results of FTIR spectral analysis

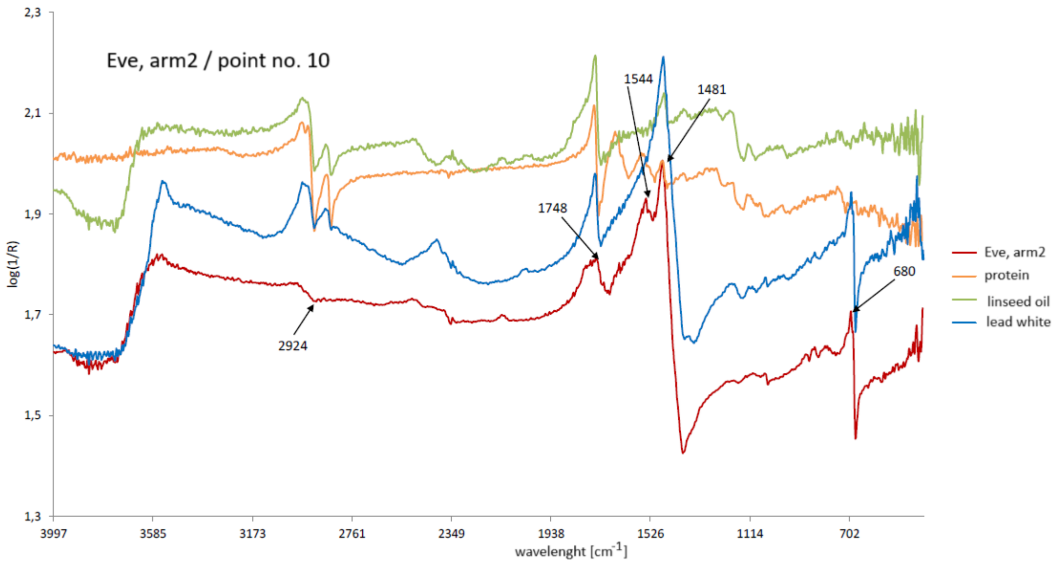
Oil was detected at all measurement points, as evidenced by characteristic spectral peaks at 2930, 2850, 1751, 1476, 1388 and 1240 $cm^{-1}$, such as those observed in spectrum no. 16 below. This confirms that the painting was primarily executed using an oil-based technique. A similar result was obtained in the analysis of samples using gas chromatography (GC/MS) (see Annex 3).



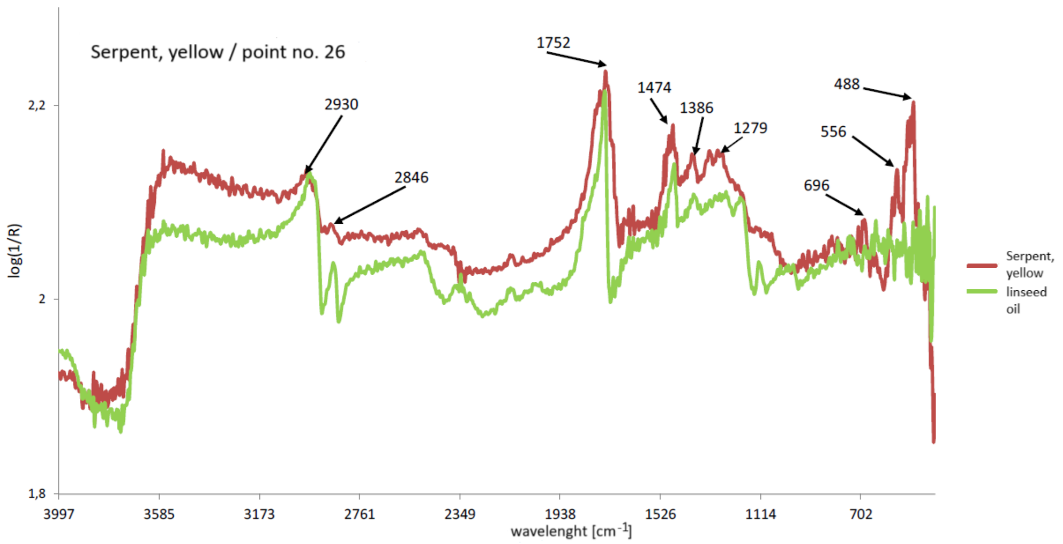

Many measurement points also show peaks indicating the presence of lead white, as illustrated by spectrum no. 3. In this regard, the FTIR spectroscopy results are consistent with the XRF spectroscopy findings (see Annex 2). Both analyses confirm that lead white was used by the artist in the painting.



Additionally, in certain points – 5 (Adam, right thigh), 6 (Adam, hair), 7 (Eve, leg), 10 (Eve, arm 2), 12 (Eve, chest, shadow), 17 (background, black 2), 19 (leaf, Eve 2), 20 (leaf 2a), 22 (tree) and 23 (earth, tree) – there are characteristic peaks at 1748, 1544 and 1481 $cm^{-1}$. In particular, the peak at 1544 $cm^{-1}$ indicates the presence of a substance containing C-N and N-H bonds, which are found in protein-based compounds, including egg yolk. The attached spectrum from measurement point 10 (Eve, arm 2) highlights peaks also associated with oils and lead white.




Another point where FTIR spectroscopy results align with those from XRF and Raman spectroscopy (see Annex 2) is measurement point 26, where the yellow serpent is painted (spectrum no. 26). Along with peaks confirming the presence of oil and lead white, peaks at 556 and 488 $cm^{-1}$, characteristic of lead-tin yellow, were also identified.




Translated by Aleksandra Szkudłapska

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