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Discovering the evolution of Jacques-Louis David's portrait of Antoine-Laurent and Marie-Anne Pierrette Paulze Lavoisier

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Abstract

Jacques-Louis David's (1748–1825) iconic portrait of *Antoine Laurent Lavoisier (1743–1794) and Marie-Anne Lavoisier (Marie-Anne Pierrette Paulze, 1758–1836)* has come to epitomize a modern couple born of the Enlightenment. An analytical approach that combined macro-X-ray fluorescence with the examination and microanalysis of samples by Raman spectroscopy and scanning electron microscopy-energy dispersive X-ray spectrometry to investigate precise indications of changes to the composition observed by microscopy and infrared reflectography allowed the visualization of a hidden composition with a high level of detail. The results revealed that the first version depicted not the progressive, scientific-minded couple that we see today, but their other identity, that of wealthy tax collectors and fashionable luxury consumers. The first version and the changes to the composition are placed in the context of David's mastery of the oil painting technique by examining how he concealed colorful features in the first composition by using paint mixtures that allowed for maximum coverage with thin paint layers. The limitations of the analytical techniques used are also discussed. To our knowledge, this is the first in-depth technical study of a painting by J.-L. David.

Keywords: Jacques-Louis David, Antoine Lavoisier, Marie-Anne Pierrette Paulze, Underlying composition, IRR, MA-XRF, Raman spectroscopy, SEM-EDS

Introduction

Jacques-Louis David's monumental portrait of *Antoine Laurent Lavoisier (1743–1794) and Marie-Anne Lavoisier (Marie-Anne Pierrette Paulze, 1758–1836)* (Fig. 1A) is a milestone of European portraiture and a cornerstone of The Metropolitan Museum of Art (The Met) since it came into the collection in 1977 [1, 2]. Not only is this painting seen as a stylistic landmark, but also daringly utilizes a full-length format associated with royal sitters to depict an aristocratic couple [2]. Downplaying their privileged role as rich tax collectors and foregrounding their status as progressive scientists, David presents them

as rational thinkers joined in a casual, even affectionate pose that indicates Madame Lavoisier's well-documented role in her husband's scientific practice [3, 4].

On continuous display at The Met for over forty years, this painting has offered an ostensibly crystal-clear declaration of neoclassicism to scholars and to the public but had never been subjected to in-depth imaging or chemical analyses. In fact, to our knowledge, there are no published in-depth technical studies of paintings by this important artist.

An optical microscopy examination carried out in preparation for the removal of a deteriorated varnish provided vague indications of possible alterations to the composition that prompted the application of infrared reflectography (IRR). The reflectogram revealed some changes, however some unclear shapes visible in this reflectogram suggested the possible presence of other

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Fig. 1 **A** Jacques-Louis David, *Antoine Laurent Lavoisier* (1743–1794) and *Marie-Anne Lavoisier* (*Marie-Anne Pierrette Paulze*, 1758–1836), 1788. Oil on canvas, 259.7 × 194.8 cm. Purchase, Mr. and Mrs. Charles Wrightsman Gift, in honor of Everett Fahy, 1977 (MMA# 1977.1). The Metropolitan Museum of Art, New York. **B** Infrared reflectogram (IRR)

changes. Because these features were not fully resolved by this technique, macro X-ray fluorescence (MA-XRF) mapping was used, followed by the microanalysis of paint samples, which assisted the interpretation of the mapping results and answering further questions. The results of this combined analytical approach completely upended our understanding of this painting: beneath its neoclassical solemnity we found an entirely unknown version piled with high excess, with implications for how we understand its place in art history, as well as the stylistic shift synonymous with David: a radical, sudden break between the rococo and neoclassicism [5].

The imaging and chemical analysis performed for the present study revealed significant compositional changes. We could never have known just how closely the first version of this portrait came to following relatively conventional depictions of these wealthy individuals, rather than a progressive, scientific couple we know today.

Results and discussion

The infrared reflectography (IRR) examination of the painting revealed the carbon-based black underdrawing done with a dry drawing medium as well as with black

paint. Vague indications of changes to painted passages appeared in the reflectogram as slightly dark unrecognizable shapes. In this section, these results are discussed first, followed by those obtained by macro-X-ray fluorescence (MA-XRF), which allowed us to clarify these features, explain observations made under magnification on the surface of the painting, and revealed additional changes with a high level of detail. MA-XRF is a powerful method that, in addition to providing maps of the elemental distributions, together with visual and microscopic analysis often allow establishing the location of the mapped elements within the stratigraphy of different areas [6–10]. However, in many cases the sources of some of the elements detected and mapped are multiple and the same element may be present in different layers in the same paint passage [11, 12]. In the study of this portrait, microscopic samples were taken from seven locations in order to help interpret the MA-XRF results and to assess the colors of the sitter's garments, the furniture and its decoration, the background, and other features in the hidden composition (all of which have implications from an art historical perspective). These samples were mounted as cross-sections and analyzed by Raman

spectroscopy and scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDS). One of these samples also helped to better understand the masterful way in which David concealed the extensive and colorful first composition, leaving few clues on the surface of the finished work.

General description of the painting and infrared reflectography (IRR)

The portrait, measuring 259.7×194.8 cm, is painted in an oil medium on fabric prepared with a thickly applied Pb-containing white ground that provided a completely smooth support displaying no canvas texture. SEM-EDS analyses of the ground preparation in the sample cross-sections revealed coarse and finely divided Pb-containing particles and Raman spectroscopy showed that these are lead white, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, by its characteristic bands at *ca.* 415, 680, and 1051 cm^{-1} [13–15]. The full stratigraphy and composition of these samples are discussed in the following section. The painting was lined with an aqueous glue/paste adhesive to a new canvas support and attached to a modern stretcher before it entered The Met's collection.

The full IR reflectogram is presented in Fig. 1B and the locations of the details discussed in this section are indicated in Additional file 1: Figures S1–S4. With IRR, underdrawing as well as painted features containing a carbon-based black pigment were imaged in this painting, as mentioned above. Throughout the composition, IRR revealed the overall feathery brushstrokes, commonly referred to as *frottis* [16], typically used by David to tone down a white ground (see for e.g., [17]) (Fig. 1B and Additional file 1: Figure S1). Examination of the surface of the painting with magnification confirmed the toning is various shades of a reddish-brown color (Additional file 1: Figure S2A, B).

The IRR shows a fine underdrawing with a dry carbonaceous medium in many locations along the contours of both figures and reveals that the positions of the figures were established in the early stages and did not change substantially. However, as the composition evolved, there were shifts along contours and slight adjustments in the position of the hands (Additional file 1: Figure S3A). Although it was David's common practice to prepare elaborate study drawings for his history paintings, there are few studies identified for portraits, and none are known for this painting. It seems, based on the evidence from IRR that the composition was worked out directly on the canvas support prepared with the lead white ground. In the face of Lavoisier, the underdrawing includes fine short parallel lines marking in features, such as the deep recesses below the eyebrows. There is fine drawing along the contour of his nose as well as a

line defining the contour of the cheek (Additional file 1: Figure S3B). In Madame Lavoisier, there are contour lines along the chin and two parallel diagonal lines marking the outside corner of the proper left eye (Additional file 1: Figure S3C). Many delicately drawn lines appear along the contours of the hands. For Lavoisier, this includes drawing along the contour of the second, third and small finger of the proper left hand. A significant adjustment was made to the contour of the back of this hand, the reason for which will be discussed later. For Madame Lavoisier, there is underdrawing visible along the palm of the proper right hand and her thumb; no drawing is visible along the contours of her proper left hand (Additional file 1: Figure S3A). However, there are multiple shifts and refinements of the contours and position visible in the IRR due to the use of carbon black-containing paint.

The most remarkable revelations made possible by IRR are that, beneath the scientific instruments and desk cover, Lavoisier was originally depicted seated at a neoclassical writing desk decorated with an ormolu frieze of interlacing trifoliate and round acanthus (Additional file 1: Figure S4). The leg of the desk is columnar with ormolu capital and fluting. The inkwell, two quills and paper were always placed as seen today; however, to their right, three large sheets of paper once unfurled over the desk's edge (Additional file 1: Figure S4). One other object on the desk far right, vaguely defined in the IRR but clearly identifiable through MA-XRF mapping, is discussed later. Beneath the desk, the complicated form of a wicker wastepaper basket was painted and brought to a high degree of resolution (Additional file 1: Figure S4). While the features described above were fully painted, Lavoisier's proper left leg was sketched in with fluid strokes of black paint. The position of this leg, which awkwardly straddles the desk leg, shifted several times before the artist partially painted it from the shoe to just below the knee (Additional file 1: Figure S4). IRR also revealed shifts to the position of his proper right leg.

There are vague suggestions of other details revealed in the IRR. These include a dark shape across Madame Lavoisier's hair and slightly dark passages surrounding the top of her head, as well as indistinct rectangular shapes extending from the canvas's right edge nearly to Lavoisier's proper left wrist (Additional file 1: Figure S4)—all features made clear in the MA-XRF maps discussed in the next section.

The parquet floor was initially drawn to the base of the wall across the entire lower portion of the painting and reinforced with black paint before figures were placed. This is partially revealed in the IRR and more completely in the MA-XRF maps discussed below. In addition to the parquet floor, David had already drawn the dado and pilaster before adding the armchair, portfolio, and shawl.

The parquet floorboards are painted carefully within the confines of the individual boards with directional strokes of brown paint containing a carbon-based black pigment. Similarly, the elaborate meandering contour of Madame Lavoisier's hemline was drawn and reinforced with black paint before the artist finished the costume. David achieved transparency and variation in the thinly gazed white muslin dress by scumbling on top of the reddish-brown *frottis* and dark undermodeling containing a carbon-based black pigment. In the IRR, slightly darker passages surrounding the bustle suggest alterations in this area and perhaps an initial idea for a larger bow.

Macro X-ray fluorescence (MA-XRF) mapping and sample cross-sections

The sitters' garments

Examination of the surface of the grey background surrounding Madame Lavoisier's head with raking light revealed, below the paint, low relief texture of sweeping brushstrokes extending over a large area (Fig. 2A).

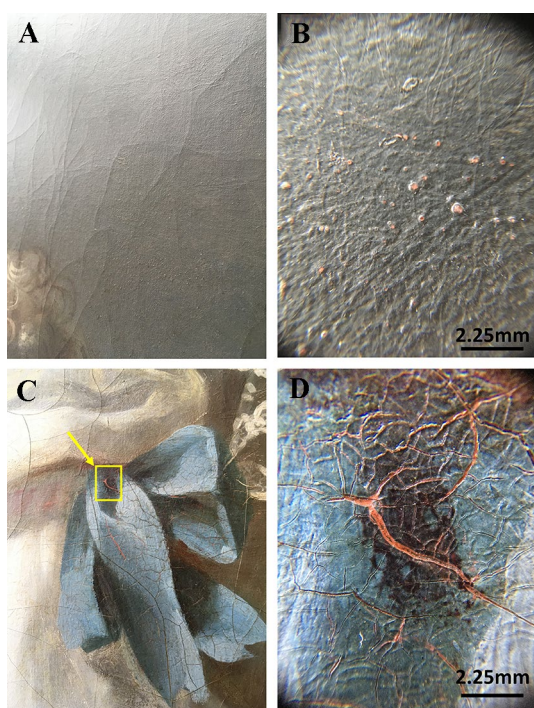


Fig. 2 **A** Photograph taken with raking light illumination in area above Madame Lavoisier's head. **B** Photomicrograph of the protrusions of red underlying paint from the feather of Madame Lavoisier's hat, original magnification x24. The location where this photomicrograph was taken is indicated in Additional file 1: Figure S6C. **C** Photograph of detail of the blue ribbon and sleeve showing the red paint below the final blue. **D** Photomicrograph showing the underlying red paint in the wide drying cracks, original magnification x24. The area where this photomicrograph was taken is indicated with a yellow rectangle and a yellow arrow in C

In addition, points of distinctly red paint are visible throughout, protruding from below and within the cracks (Fig. 2B). While the IRR suggested some significant changes, the Hg and Pb distribution maps obtained by MA-XRF provided a sharply modeled image of features hidden below the warm grey marbleized wall (Figs. 3A, B; 4A). Initially, Madame Lavoisier was wearing a large, feathered hat adorned with ribbons, bows and a sprig of flowers. The Raman and SEM-EDS analyses of samples, discussed in detail below, showed that, in these elemental distribution maps, the presence of Hg is due to vermilion, HgS [13], and the Pb mainly to lead white and, also, to Naples yellow, a lead antimonate with a stoichiometry that varies depending on the recipe and the conditions of the manufacturing process [18]. Lead white was identified in the ground preparation and in some paint layers in the sample cross-sections, and Naples yellow was observed in the grey paint from the background (sample S6), that also contains Pb white, and, in relatively smaller amounts, in the brown paint from Lavoisier's coat in the first composition (sample S4). Since Sb was not detected by MA-XRF it is not possible to discriminate the distributions of these two pigments.

A sample cross-section, taken from the background of the painting, right above Madame Lavoisier's head (Additional file 1: Figure S5), includes red paint from the hat



Fig. 3 Elemental distribution maps acquired by MA-XRF on the portrait of Antoine-Laurent and Marie-Anne Pierrette Paulze Lavoisier. Pb (**A**); Hg (**B**); Fe (**C**); and Ca (**D**) distribution maps



Fig. 4 Details of combined elemental distribution maps for selected areas of the portrait of Antoine-Laurent and Marie-Anne Pierrette Paulze Lavoisier: Pb (white) and Hg (red) (A); Fe (orange) and Ti (purple) (B); Pb (white) and Hg (red) (C); Fe (orange), Ca (green) and Hg (red) (D)

and grey paint from the background, and is missing the ground preparation (sample S6, Fig. 5A–C). Raman analysis of the red paint (layer #1 in Fig. 5B) showed that the main components are vermillion, with main Raman bands at *ca.* 253 and 343 cm^{-1} [14], and lead white. Particles of calcite, CaCO_3 , identified by its main Raman bands at *ca.* 283, 713, and 1087 cm^{-1} [14], and Fe-containing particles, likely an iron oxide, were observed by SEM–EDS in the red paint. These results confirm that Madame Lavoisier’s hat ornaments are red, painted with a mixture containing opaque red pigments mixed with white.

In the grey paint layer in this sample (layer #2 in Fig. 5B), Ca and P were detected by SEM–EDS in the black pigment particles, indicating that these are a bone or ivory black [13, 19], lead white was observed by Raman spectroscopy, and Fe-containing particles were identified as hematite, $\alpha\text{-Fe}_2\text{O}_3$, by its Raman bands at *ca.* 224, 291, 411 and 611 cm^{-1} [20–22]. The yellow particles in this grey layer were found to be composed of Sb and Pb by SEM–EDS, and bands at *ca.* 135, 298 and 512 cm^{-1} in the Raman spectra acquired in these particles indicated that they are Naples yellow [18].

Examination of the surface under magnification confirmed that the brim and crown of the hat are black (Additional file 1: Figure S6A–C). The Hg distribution map revealed that the original colors of the belt and ribbon on the arm were also red before the artist ultimately changed these to blue, features that are also visible when the surface of the painting is examined under magnification (Fig. 2C, D).

MA-XRF showed that Lavoisier’s knee-breeches and coat, as well as the buttons in the coat that extend below the desktop, contain Fe-based pigments (Fig. 3C). Photomicrographs of a paint cross-section taken from the coat (sample S4), photographed with visible and UV illuminations, and an SEM-backscattered electron image (BSE) are presented in Fig. 5D–F. In the ground layer of this sample (layer #1 in Fig. 5E), SEM–EDS showed the presence of coarse and finely divided Pb-containing particles (Fig. 5F), both identified by Raman spectroscopy as lead white, as mentioned above in the IRR section. Ground layers of similar composition and morphology were observed for the rest of the samples taken from this painting, except for sample S6 that is missing the ground.

In sample S4, SEM–EDS analyses of the dark paint layer on top of the stratigraphy (layer #4 in Fig. 5E), revealed that Ca and P are present in the black particles, demonstrating that these are a bone or ivory black, and that particles composed of Fe, Si, and Al, indicative of an ochre [20, 21, 23] and also red lake particles are mixed with the black. In the lighter layer below the top dark layer (layer #3 in Fig. 5E), a mixture composed of a bone or ivory black (identified by SEM–EDS), vermillion (identified by Raman spectroscopy and SEM–EDS), a few particles of lead white (identified by Raman and SEM–EDS) and of Naples yellow (identified by SEM–EDS), and red lake particles was observed. In this study, evidence of the presence of a lake pigment was obtained by the examination and analysis of samples with optical microscopy, under visible and UV illuminations, the latter revealing a pink fluorescence, combined with SEM–EDS which indicated that these fluorescent particles are mainly organic in composition and have relatively small amounts of Al and Pb, or just Al, elements that have been reported in the substrates of lake pigments from the eighteenth and nineteenth centuries [24]. The analysis of layer #2 by a combination of Raman and SEM–EDS showed that the main components are a bone or ivory black, vermillion, a red lake of similar composition to that observed in layer #3, and some particles of lead white.

The microscopic examination and analytical results obtained in sample S4 confirmed that, below the final black coat with only three buttons and the black knee-breeches, Lavoisier was initially depicted wearing a brown costume with a longer coat, achieved by mixing a

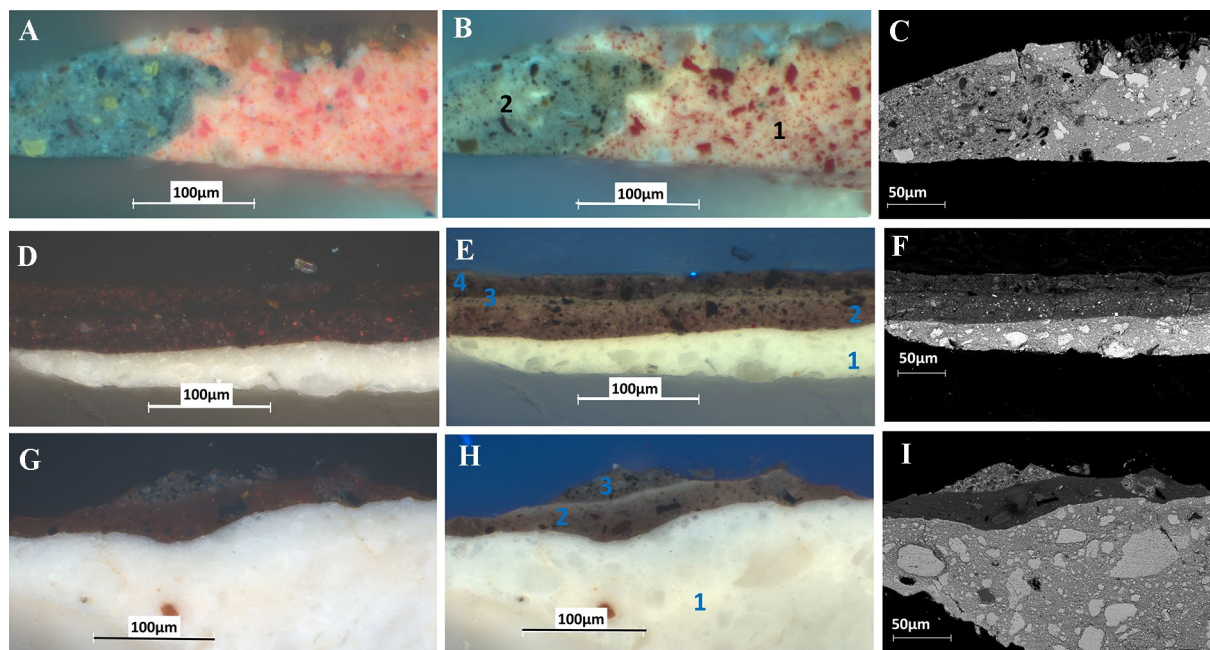


Fig. 5 Cross-sections of paint samples. Sample S6, taken from the background, above Madame Lavoisier's head, photographed with visible (A) and UV illumination (B), original magnification $\times 400$; and SEM-BSE image, $\times 400$ (C). The ground layer is missing in this sample. Sample S4, taken from Lavoisier's coat, photographed with visible (D) and UV illumination (E), original magnification $\times 400$; and SEM-BSE image, $\times 330$ (F). In this sample, layer #1 is the ground, layers #2 and #3 are Lavoisier's brown coat and layer #4 corresponds to the black coat. Sample S5, taken from the black shawl on the chair at left, photographed with visible (G) and UV illumination (H), original magnification $\times 400$; and SEM-BSE image, $\times 400$ (I). The locations where these samples were taken are indicated in Additional file 1: Figure S5

bone or ivory black pigment, vermilion and few particles of lead white, Naples yellow, and red lake, as mentioned above. The Fe distribution map and the examination of areas on the surface of the painting where the black paint is abraded indicate that there were seven plain buttons painted with a yellow ochre and, therefore, meant to appear golden, perhaps brass.

MA-XRF showed the presence of Ti in the coat (Fig. 4B); however only traces of this element were detected by SEM-EDS in the top layer of sample S4, associated with the ochre (layer #4 in Fig. 5E). Similarly, only traces of Ti were observed in the top layer of sample S3, removed from an area of the coat that appears to contain more Ti in the distribution map obtained by MA-XRF (Fig. 4B and Additional file 1: Figure S5) than that revealed in the location of sample S4. Photomicrographs of sample S3, taken with visible and UV illumination, an SEM-BSE image of this sample, and EDS spectra acquired in the top paint layers in samples S3 and S4, respectively, are presented in Additional file 1: Figure S7A–E. Ti is a common component in ochres [20, 23] however, with the trace levels detected for this element in the two samples analyzed, it is not possible to explain the Ti distribution observed by MA-XRF in terms of the artist's technique.

More astonishing perhaps is that Lavoisier was wearing a red mantle that pulled across his shoulders and wrapped around his proper left elbow before falling into his lap and onto the floor (Figs. 3B, 4C). A sample taken from a location where the red mantle is visible in the Hg distribution map (sample S7, Additional file 1: Figure S5) shows the red paint of the mantle beneath the black paint that corresponds to the final black coat. Photomicrographs of this sample taken with visible and UV illuminations are presented in Additional file 1: Figure S8A, B. Raman spectroscopy analysis showed that the red paint of the mantle is mainly composed of vermilion mixed with lead white. When the red mantle was concealed in the final composition, the artist made the adjustments to Lavoisier's proper right wrist that are mentioned above in the discussion of the IRR.

The Hg distribution map also indicates the presence of vermilion in the black shawl draped on the arm-chair (Fig. 3B). Examination of a sample taken from the shawl area under visible and UV illuminations (sample S5, Fig. 5G, H) showed that the deep black color was achieved by underpainting with mixtures of brown, black, and red pigments (layer #2 in Fig. 5H). Raman spectra acquired in the black pigment particles in this underpaint layer present broad bands at *ca.* 1325 and

1580 cm^{-1} , expected for C-based black pigments, but no modes due to PO_3^{3-} at *ca.* 961 cm^{-1} in bone or ivory blacks [25]. SEM–EDS analysis revealed that some of these black particles are indeed composed of Ca and P, indicating a bone or ivory black, while others are a different type of C-based black that does not contain these elements, such as lamp black [19]. Other pigments in layer #2 are vermillion and lead white, identified by Raman spectroscopy, and an ochre composed of Si, Al and Fe, detected by SEM–EDS. In the paint layer on top of the stratigraphy (layer #3 in Fig. 5H), the combined Raman and SEM–EDS analysis revealed a mixture of abundant bone or ivory black, another C-based black pigment with no Ca or P, abundant lead white, an ochre (Si, Al and Fe), some Fe-containing particles, likely an iron oxide, and quartz particles. The relative abundance of lead white in layer #3 can be visualized in the SEM–BSE image (Fig. 5I) by its brighter appearance in contrast to layer #2. A thin layer that fluoresces under UV illumination is present between the layers #2 and #3 in Fig. 5H and appears to be mainly organic in this photomicrograph and in the SEM–BSE image (Fig. 5I). From these observations, it is not possible to indicate the origin of this fluorescent layer with certainty. However, it is a possible indication

that the artist applied an organic medium to the surface before continuing to paint, as was practiced during this period [26, 27].

The use of the pigments mentioned for the shawl area can be visualized in the combined Fe, Hg, and Ca distribution maps presented in Fig. 4D. SEM–EDS results showed that the presence of Ca in the map corresponding to this area is due to bone or ivory black, as mentioned above. David's practice of using admixtures of vermillion to achieve deep blacks and browns has been observed in his painting *The Death of Socrates* [28–30].

The objects on and below the desk

The Hg distribution map also provided a clear image of the object placed at far right on the desk, which appears indistinctly in the IRR image. This feature, which initially balanced the other still life elements on top of the desk in the first composition, is a globe with a red supporting mount, painted with vermillion (Figs. 3B, 6A).

Examination of the surface of the painting under magnification confirms that the assembly of the three scientific instruments and green leather document box placed on the desk, as well as the two instruments on the floor lower right, are painted on top of the red velvet desk

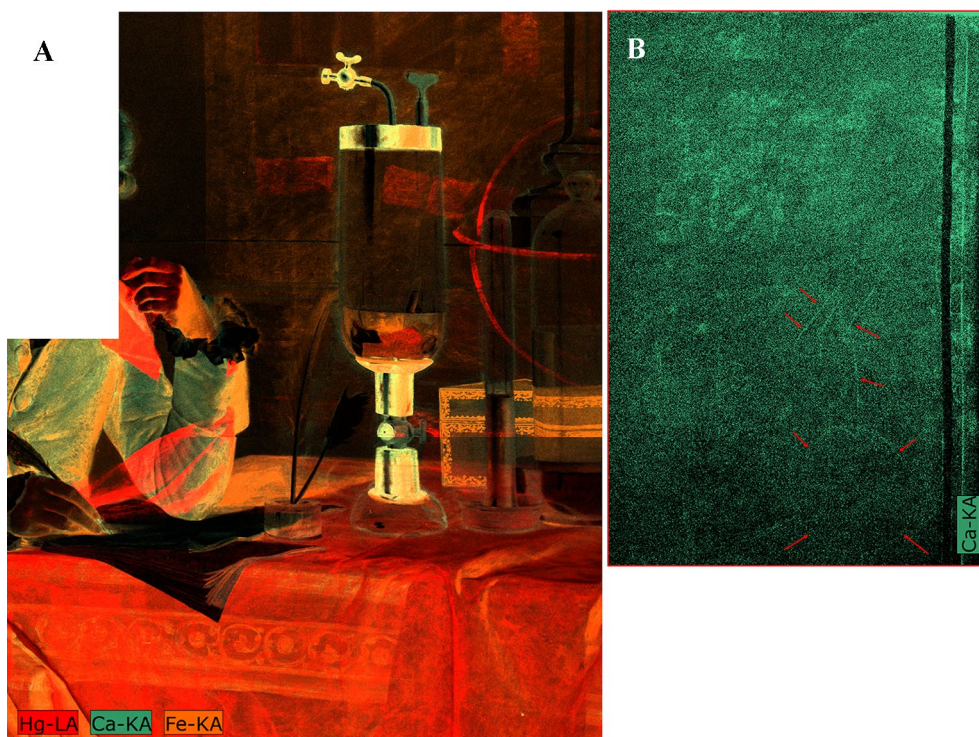


Fig. 6 Details of elemental distribution maps for two selected areas. **A** Hg (red), Ca (green), and Fe (orange) maps of the objects and scientific instruments on the desk. **B** Ca distribution map acquired in the upper right of the painting where red arrows indicate what appears as a relatively large scientific instrument with globular glass containers. The location of this detail of the Ca distribution map in the overall painting is indicated in Additional file 1: Figure S9A



Fig. 7 Details showing the assembly of scientific instruments and green leather box on the table, and instruments on the floor, painted on top of the red tablecover

cover (Fig. 7). However, the Ca distribution map reveals that initially David intended to include a much larger instrument with what appears to be a globular glass container (Fig. 6B). Although such an elaborate contraption would have been in keeping with Lavoisier's latest methods and impressive laboratory [3], it may have been considered too distracting and, subsequently, he abandoned the idea for the series of smaller instruments visible today [5]. Surely, it was an artistic choice to scale down the instruments. The discovery of the larger instrument is important because it is an indication that David was not only engaged with transforming the depiction to focus on the scientific work, but that he was also well aware of the range and development of the instruments used by Lavoisier.

Revealed too in the Ca distribution map are fragments of concentric circles, which indicate that David considered multiple sizes and positions for the glass balloon in the foreground lower right (Additional file 1: Figure S9B).

The Ca distribution map also shows the pattern of the parquet floor extending beneath the figures.

The background, desk and tablecover

The Pb, Hg, and Fe distribution maps revealed that the indistinct rectangular shapes in the background at right are tall shelves filled with bound books and/or cardboard boxes containing papers, each of similar width but animated by combining upright and leaning volumes (Fig. 3A–C). The bands running across each volume, most likely a shade of red, as indicated by the Hg distribution map, have unclear inscriptions. This entire feature was painted out when other significant changes to the first composition were introduced.

The Pb and Fe distribution maps show two vertical lines in the background approximately 16 and 33 cm from the painting's left edge, running from the floor up toward the ceiling. This feature suggests perhaps an abandoned plan for the background architecture that might have included a pilaster that extended to the floor (Fig. 3A, C).

Photomicrographs and SEM-BSE images of samples S1 and S2, taken from the red velvet tablecover (Additional file 1: Figure S5), which concealed the writing desk and elaborate features below revealed by IRR and described above, are presented in Fig. 8A–F. The SEM-BSE images of these two samples (Fig. 8C, F) feature, in the ground layers, coarsely and finely divided Pb-containing particles identified as lead white by Raman spectroscopy and also observed in the samples presented in Fig. 5. The examination of samples S1 and S2 under magnification revealed that the red paint of the tablecover is composed of mixtures of opaque pigments and a transparent red lake that shows a characteristic pink fluorescence under UV illumination (layers# 3 and #4 in Fig. 8B, E). In both samples, Raman analysis showed that the opaque pigment is vermilion in the layers labeled as #3 and that there is lead white in the layers labeled as #4. The SEM-EDS analysis of these layers consistently showed Pb- and Hg-containing particles, and that the red lake pigment consists of an organic colorant precipitated on a substrate composed of Pb and Al, or just Al in some particles. The Pb- and Hg-containing particles in these paint layers appear brighter in the SEM-BSE images in Fig. 8C, F in contrast to the lake pigment that appears darker due to its organic content. These results indicate that, to build the tablecover, David applied first the mixture of transparent red lake and opaque vermilion followed by scumbling with lead white mixtures and glazing with a red lake.

In the top red layer in sample S2, a brownish-red particle containing Fe, As, Si, Ca, Al, and Pb was observed by SEM-EDS, although, in this case, it cannot be ruled out that the presence of Pb in the EDS spectrum is the result of scattering from the abundant finely divided lead white

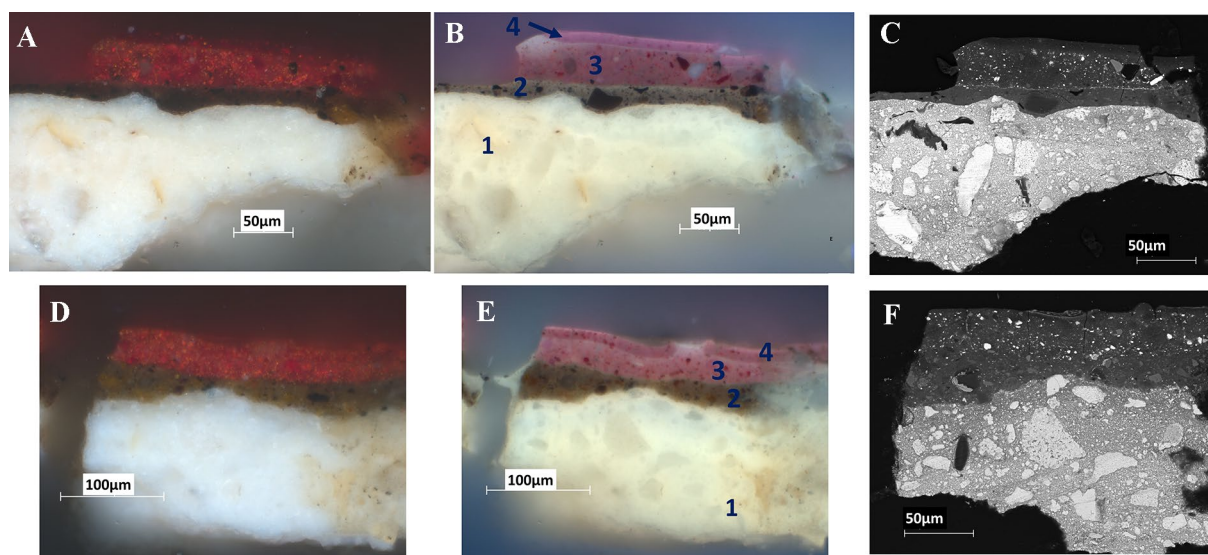


Fig. 8 Cross-sections of paint samples. Sample S1, taken from the red tablecover, at the right perimeter of the painting, photographed with visible (A) and UV illumination (B), original magnification $\times 400$; and SEM-BSE image, $\times 400$ (C). Sample S2, taken from the red tablecover in an area where the desk below is decorated with gilt ormolu, photographed with visible (D) and UV illumination (E), original magnification $\times 400$; SEM-BSE image, $\times 460$ (F). The locations where these samples were taken are indicated in Additional file 1: Figure S5

particles in the surroundings; a particle with a similar composition was identified in the sample taken from the shawl, in the underpaint layer. EDS spectra acquired in these particles, along with details of the SEM-BSE images indicating the locations of the particles, are presented in Fig. 9A, B. Based on their elemental composition, these particles are interpreted as As-containing Fe (hydr) oxides, such as those found in certain earth pigments [31, 32]. Notably, traces of As were detected in association with the ochre pigment in the top layer of sample S4. However, in this case, the As-containing particles are more finely divided than those in samples S2 and S5.

In sample S1, the SEM-EDS analysis of the dark paint layer applied over the ground preparation and below the red paint (layer #2 in Fig. 8B) showed particles containing Si, Al and Fe, indicating that an ochre is present [23], a bone or ivory black (Ca and P), and some Ca-containing particles, further identified as calcite by its characteristic Raman bands at *ca.* 283, 713, and 1087 cm^{-1} . These results indicate that the wood of the writing desk was a shade of brown.

The lighter layer applied over the ground in sample S2 (layer #2 in Fig. 8E) corresponds to the ormolu frieze that decorates the writing desk, which can also be clearly visualized in the Fe distribution map (Fig. 3C). The SEM-EDS analysis of this paint layer showed that it is mainly composed of an ochre, with particles containing Fe, likely an iron oxide, [Si, Al, and Fe], [Si, Al, and Ca], or just Si, possibly as quartz (SiO_2), along with particles

of the following pigments: a bone or ivory black (Ca and P), another C-based black not containing Ca or P (SEM-EDS), and a lake on a substrate with Al and Pb or only Al. Ca-containing particles were also detected in this layer and were identified as calcite by Raman spectroscopy.

The yellow tone of layer #2 in sample S2, compared to the darker brown of the wood paint (layer #2 in sample S1), further supports the hypothesis that it was intended to depict gilded decoration.

The compositions of the paint samples discussed demonstrate that several pigments contribute to the Ca observed in the elemental distribution map obtained for this painting: bone or ivory black, calcite, and ochre(s), such as the one used to paint the ormolu decoration. In fact, the presence of variable amounts of Ca has been reported for ochres and other Fe-based earth pigments from different sources [20, 23].

Other aspects of the technique

The painting is fully signed and dated 1788 and was completed before the Salon of 1789 [2]. Madame Lavoisier's hat was particularly fashionable in the fall of 1787, suggesting work begun that year [5]. There is no evidence of having been reworked by another hand. Therefore, it is safe to assume that the changes were made by David between 1787 and 1788. It is remarkable, in consideration of the extensive changes, that *pentimenti* did not develop as the paint layers aged. A visual hint of one underlying feature is in the red tablecover, where the large document

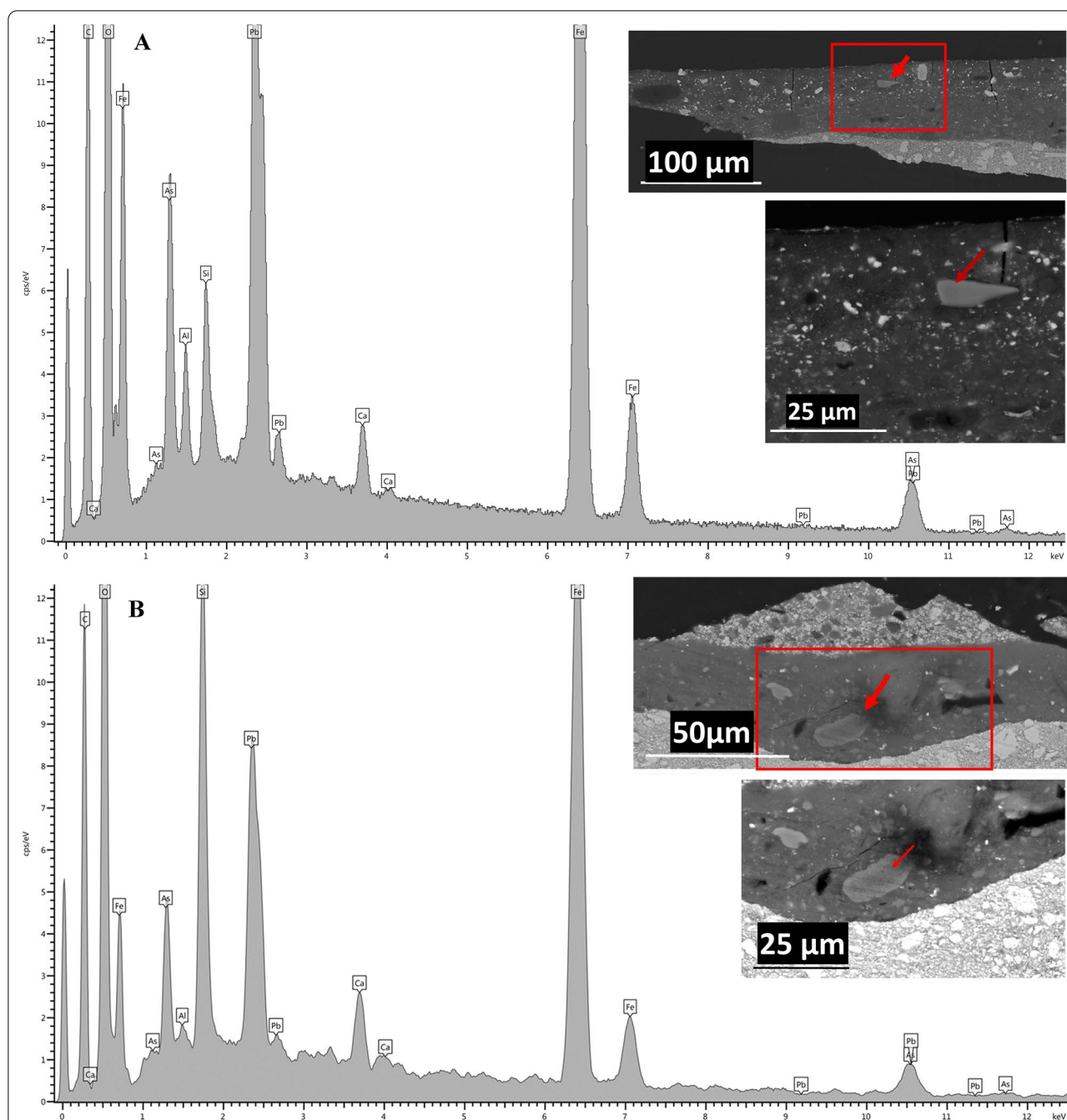


Fig. 9 EDS spectrum acquired in a brownish-red particle in the top red layer in sample S2, and details of SEM-BSE images of this sample ($\times 400$ and $\times 1600$) where the red arrows indicate the location of this particle (A). This is an additional fragment of sample S2, it differs from that shown in Fig. 8D–F. EDS spectrum acquired in a particle in the underpaint layer in sample S5 showing a similar composition to that presented in A and details of SEM-BSE images of this sample ($\times 900$ and $\times 1600$) where the red arrows indicate the location of this particle (B)

presents as a light shape because some barely perceptible drying cracks have formed in the upper paint layer. Another area where drying cracks reveal the first composition is in the ribbons of Madame Lavoisier's garment (Fig. 2C, D).

The admixtures skillfully chosen by the artist for maximum coverage with thinly applied paint resulted in a painting that is remarkably well preserved. David also demonstrated his mastery of painting technique by the way in which he concealed the fully modeled and

strongly colored red and black hat, with a result that is a *tour de force* of the optical use of the oil medium and sound artistic practice. By thinly scumbling over this feature with a combination of a bone or ivory black and lead white pigments, along with some dark red hematite particles, warmed and made more opaque with an admixture of Naples yellow, the artist achieved the perfect color and tone, and efficiently solved the problem of matching the adjacent grey background. As discussed above, this paint mixture was identified in the grey paint layer in sample S6 (Fig. 5A–C) by Raman spectroscopy and SEM–EDS analysis. Sb, that would have indicated the presence of Naples yellow in the paint passage above Mme. Lavoisier's head, was not detected by MA–XRF, as mentioned above. The distribution of this yellow pigment would have further informed how David masterly covered the hat with all its red decorations leaving so few clues on the surface of the finished work.

The light, tawny-grey color of the pilasters is painted delicately, in subtle contrast to the grey marbled wall. This was achieved in an economical fashion, made visible in the IRR image, by scumbling with thin strokes of mixtures containing lead white over the reddish-brown *frottis*, taking advantage of the warm tone below, before adding the final thin light and dark lines to model the columns. By contrast, the balance of the wall, painted with a mixture containing more C-based black, has slightly more optical density.

Conclusions

The analytical approach combining MA–XRF imaging with elemental and molecular analysis of microsamples to scrutinize imprecise indications of changes to the composition observed by microscopy and IRR allowed us to visualize an early composition with a level of detail that would not have been possible only ten years ago, before the development of XRF mapping. However, in this study, the combination of MA–XRF and microscopy alone did not reveal with certainty where, in the paint stratigraphy, some elements were located. When crucial for determining the color of garments and other features in the first composition, such as the hat and its decoration, Lavoisier's coat and mantle, the wooden desk and its gilt decoration, the combined Raman and SEM–EDS analysis of paint samples provided the answers. David's skills were made evident not only in how he built these and other paint passages, but also in how he concealed fully painted features in the early composition leaving so few clues behind by carefully choosing the components of the paint mixtures to ensure full coverage with thin applications. The study also raised questions that remain to be answered, such as the details in the inscriptions

on the books and/or cardboard boxes in the painted out shelves; the distribution of Naples yellow that would give insight into how David matched the grey paint covering the hat to that in the rest of the background; and how he used the Ti-containing pigment, likely an ochre, in Lavoisier's coat.

David's portrait of Antoine Lavoisier and his wife Marie-Anne Pierrette Paulze is a work that responded to the quickly changing historical circumstance in which the artist and his sitters found themselves on the brink of the French Revolution. Although Madame Lavoisier survived the reign of terror, Lavoisier's genius did not save him from the guillotine in 1794, only 6 years after the completion of the portrait. Beyond deepening our understanding of the Lavoisiers' shifting social identity, these findings also reframe an artist as he embraced and helped formulate French neoclassicism.

This latest episode in the portrait's story brought up by the scientific discoveries and the subsequent art historical reevaluation, made some forty years after the painting entered The Met, attests to the richness of these interdisciplinary endeavors. It is tempting to consider that the father of modern chemistry would be pleased with the discoveries made possible through modern imaging techniques and chemical analysis using instruments specifically designed and manufactured for collaborative studies of works of art—as he did by designing the instrumentation for his historically important and fruitful experiments that led to fundamental discoveries in science.

Methods

Infrared reflectography (IRR)

Infrared reflectography was done using an OSIRIS InGaAs near-infrared camera with a 6-element, 150 mm focal length, $f/5.6$ – $f/45$ lens, and 900–1700 nm spectral response. A total of 24 captures were made, each 23.5×23.5 inches and 4096×4096 pixels.

Macro-X-ray fluorescence (MA–XRF)

Macro-X-ray fluorescence (MA–XRF) was carried out using a Bruker M6 Jetstream instrument equipped with a 30 mm² XFlash[®] silicon drift detector (SDD) and an air-cooled micro-focus Rh-target X-ray tube operated at 50 kV and 0.5 mA. A selected area of the painting was mapped in fifteen sections, each with a 580 μ m spot size, a 700 μ m step size, and a dwell time of 80 ms/pixel. The scans of all areas were performed in an air atmosphere, using unfiltered radiation, and took, approximately, a total of 270 h. Calibration of the instrument is checked periodically using a set of NIST standards. The spectra were processed using the Bruker M6 Jetstream[®] software and, for the images presented in Figs. 3, 6A, the maps of the individual areas were stitched using Photomerge[®].

Samples and optical microscopy

Samples were taken using a scalpel under magnification and were mounted as cross-sections in Technovit® resin and polished using Micromesh® cloth. With the preservation of the integrity of the work of art as our main goal, only seven samples were taken, which was the minimum number that would help us answer the questions that we considered relevant in the context of the study. The locations where these samples were taken are indicated in Additional file 1: Figure S5. For the examination of the sample cross-sections, a Zeiss Axio Imager M2m microscope was used, with 50×, 100×, 200×, 400× and 500× magnifications, an Axiocam HRc digital camera and AxioVision 4.X.X software. Photomicrographs of the painting surface were taken with an Apexel APL-24XMH 24× macro lens attached to an iPhone®.

Raman spectroscopy

Raman spectroscopy measurements were done on the sample cross-sections using a Renishaw System 1000 coupled to a Leica DM LM microscope. All the spectra were acquired using a 785 nm laser excitation focused on the samples using a 50× objective lens, with integration times between 10 and 120 s. A 1200 lines/mm grating and a thermoelectrically cooled CCD detector were used. Powers at the sample were set between 0.5 and 5 mW using neutral density filters.

SEM-EDS

SEM-EDS analyses were performed on the carbon-coated cross-sections with a FE-SEM Zeiss Sigma HD, equipped with an Oxford Instrument X-Max^N 80 SDD detector. Backscattered electron (BSE) images, energy-dispersive spectrometry (EDS) analysis, and X-ray mapping were carried out with an accelerating voltage of 20 kV in high vacuum.

Abbreviations

IRR: Infrared reflectography, infrared reflectogram; MA-XRF: Macro-X-ray fluorescence or XRF mapping; UV: Ultraviolet; SEM-EDS: Scanning electron microscopy–energy dispersive X-ray spectrometry; SI: Supplementary information; BSE image: Backscattered electron image.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40494-021-00551-y>.

Additional file 1: Figure S1. Details of the infrared reflectogram (IRR) showing the *frottis*—thin, rapid smearing of the reddish-brown paint used to tone down the white ground preparation. In the detail to the left, the vertical stripes are the flutes from the column in the background of the painting. **Figure S2. A.** Photomicrograph of the surface of the painting showing the reddish-brown toning (*frottis*) of the white ground preparation beneath the grey upper paint layer, original magnification x24. **B.** Photomicrograph of a loss in the surface at top right, in an area

where the bookshelf is painted beneath the grey background, showing reddish-brown paint on top of the thick white ground preparation, original magnification x24. The blue arrows in **C** indicate the locations where the photomicrographs **A** and **B** were taken. **Figure S3.** Details of the IRR showing adjustments to the contours of the hands and positions of the fingers with red arrows (**A**), and to the facial features (**B** and **C**) with blue arrows. **Figure S4.** IRR indicating features in the first composition discussed in the main text: desk decoration, sheets of paper unfurling on the desk edge, and wicker wastepaper basket. The blue arrows indicate the dark shape across Madame Lavoisier's hair, the yellow arrows the slightly dark passages surrounding the top of her head, the green arrows the changes to the positions of Lavoisier's legs, and the blue rectangle the indistinct rectangular shapes extending from the canvas's right edge.

Figure S5. Portrait of Antoine-Laurent and Marie-Anne Pierrette Paulze Lavoisier, by Jacques-Louis David, showing the locations where the samples S1–S7 were taken. **Figure S6. A and B.** Photomicrographs of areas in the black hat brim beneath Madame Lavoisier's hair, original magnification x24. **C.** The blue arrow and blue square indicate the area where photomicrographs **A** and **B** were taken, and the green arrow shows the approximate location where photomicrograph **B** in Figure 2 (main text) was taken. **Figure S7. A and B.** Photomicrographs of sample **S3**, taken from Antoine Lavoisier's coat, photographed with visible and UV illuminations, respectively, original magnification x400. In **B**, layer #1 is the ground preparation, layers #2, #3, and #4 correspond to Lavoisier's brown coat in the first composition; and layer #5 to the black coat; **C.** SEM-BSE image of sample **S3**, x400. **D.** EDS spectrum acquired in layer #5 in sample **S3**. **E.** EDS spectrum acquired in the top layer of sample **S4** (layer #4 in Figure 5E, main text), corresponding to Lavoisier's black coat. **Figure S8. Sample S7**, taken from Antoine Lavoisier's coat in an area where paint from the red mantle in the hidden composition is visible in the Hg distribution map, photographed with visible (**A**) and UV illumination (**B**), original magnification x400. In **B**, layer #1 is the ground, layer #2 corresponds to the red mantle in the first composition, the black layer #3 to the coat visible in the present version, and #4 to an organic layer, possibly a varnish. The location where this sample was taken is indicated in Figure S5, in this Additional file. **Figure S9. A.** The blue rectangle indicates the location of the Ca distribution map detail shown in Figure 6B. **B.** Detail of the Ca distribution map where red arrows indicate the locations of the concentric circles as J.-L. David tried out different scales for the glass balloon in the foreground.

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Authors' contributions

DM provided the conservation perspective and insights into David's technique, took and prepared the samples, and contributed to their examination by optical microscopy. SAC acquired and interpreted the MA-XRF and Raman spectral data, and contributed to the examination by optical microscopy. FC performed the SEM-EDS analyses of paint cross-sections and interpreted the data. DM and SAC interpreted the data in the context of the painting technique. DP contributed with the art historical perspective. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets acquired at The Met are available from the corresponding author on reasonable request.

Declarations

Competing interests

The authors declare that they have no competing interests.

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