

Visualization of a Lost Painting by Vincent van Gogh Using Synchrotron Radiation Based X-ray Fluorescence Elemental Mapping

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Vincent van Gogh (1853–1890), one of the founding fathers of modern painting, is best known for his vivid colors, his vibrant painting style, and his short but highly productive career. His productivity is even higher than generally realized, as many of his known paintings cover a previous composition. This is thought to be the case in one-third of his early period paintings. Van Gogh would often reuse the canvas of an abandoned painting and paint a new or modified composition on top. These hidden paintings offer a unique and intimate insight into the genesis of his works. Yet, current museum-based imaging tools are unable to properly visualize many of these hidden images. We present the first-time use of synchrotron radiation based X-ray fluorescence mapping, applied to visualize a woman's head hidden under the work *Patch of Grass* by Van Gogh. We recorded decimeter-scale, X-ray fluorescence intensity maps, reflecting the distribution of specific elements in the paint layers. In doing so we succeeded in visualizing the hidden face with unprecedented detail. In particular, the distribution of Hg and Sb in the red and light tones, respectively, enabled an approximate color reconstruction of the flesh tones. This reconstruction proved to be the missing link for the comparison of the hidden face with Van Gogh's known paintings. Our approach literally opens up new vistas in the nondestructive study of hidden paint layers, which applies to the oeuvre of Van Gogh in particular and to old master paintings in general.

Vincent van Gogh is generally recognized as one of the founding fathers of modern painting.¹ In recent decades his work has undergone extensive art historical and technical study. One

striking feature that emerged is Van Gogh's frequent reuse of paintings in order to recycle the canvas.^{2,3} The artist would simply paint a new composition on top of an existing work. This is usually attributed to the artist's lifelong economic hardship and the rapid, energetic evolution of his artistic ideas. Visualizing such hidden paintings is of interest to both specialists in the field of Van Gogh and the public alike. Covered paintings in general provide an insight into the making of artworks and the underlying conceptual changes. In the case of Van Gogh, they also present a touchstone for comparison with preparatory drawings and the abundant literary record. The extensive correspondence with his brother Theo van Gogh, an art dealer based in Paris, is full of remarks by Vincent on his work.

Nondestructive imaging of such hidden paint layers is usually realized by means of tube-based X-ray radiation transmission radiography (XRR). The absorption contrast in these images is mostly caused by the heavy metal components of pigments employed, such as lead in lead white or mercury in vermilion. Conventional XRR, however, has a number of important limitations. First of all, the observed X-ray absorbance is a summation of all element-specific absorbancies. This implies that the contribution to the overall image contrast due to (low quantities of) weakly absorbing elements will frequently be obscured by heavier elements that are present in higher concentrations. Second, prior to the application of the paint layer, a canvas is usually primed with a homogeneous layer of lead white. This raises the overall background of the absorption image derived from the paint layers. Finally, the polychromatic character of an X-ray tube further reduces the contrast in radiographic images. As a result, conventional XRR imaging of paintings frequently provides only a fragmentary view of their substructure, which can severely hamper the readability of hidden compositions.⁴

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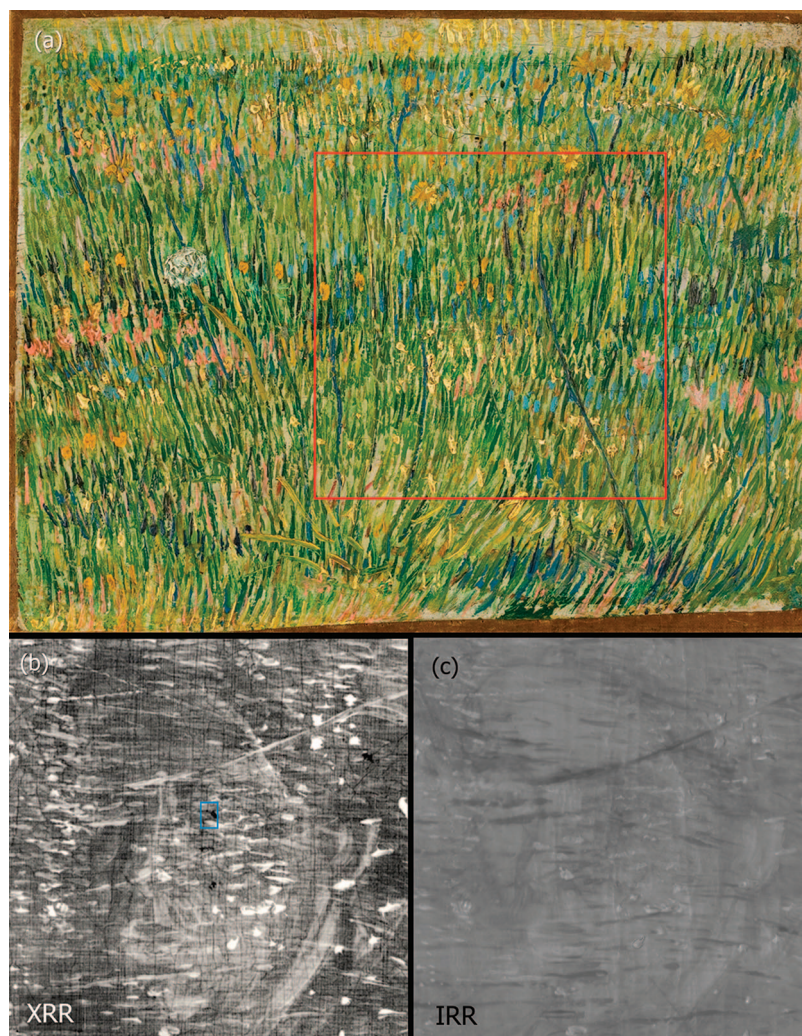


Figure 1. (a) Vincent van Gogh, *Patch of Grass*, Paris, Apr–June 1887, oil on canvas, 30 cm × 40 cm, Kröller-Müller Museum, Otterlo, The Netherlands (KM 105.264; F583/JH1263). The red frame indicates the field of view in images b and c (rotated 90° counter-clockwise). (b) X-ray radiation transmission radiograph (XRR), paint sample location indicated in the blue frame (Figure 4). (c) Infrared reflectograph (IRR).

Figure 1a shows the painting by Van Gogh from his 1886–87 Paris period, *Patch of Grass* (Kröller-Müller Museum, Otterlo, The Netherlands).⁵ Earlier examinations with XRR and infrared reflectography (IRR) vaguely revealed a head under the surface painting (parts b and c of Figure 1). However, due to the limitations of XRR, the facial characteristics could not be clearly read, making the person portrayed far from identifiable.

Instead of using the absorption of primary X-rays as an imaging method, one can also record the intensity of secondary radiation, emitted by the atoms in the painting while a pencil beam of energetic X-rays is scanned over the surface. This fluorescence technique has the added advantage that the emitted X-ray radiation is element specific. The covering surface layers will not significantly attenuate the high-energy fluorescence signals from heavy elements in the hidden layers; in this manner, the distribution of both minor and major components in the painting can be visualized. The use of high intensity X-ray beams reduces the dwell time for data acquisition to such an extent that large, decimeter-sized areas can be scanned.

METHODS AND TECHNIQUES

To carry out the analysis, we transported *Patch of Grass* to the microfluorescence beamline L at DORIS-III, a second-generation synchrotron light source at HASYLAB (Hamburger Synchrotronstrahlungslabor at Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany). A pencil beam ($0.5 \times 0.5 \text{ mm}^2$) of quasi-monochromatic synchrotron radiation with an energy of 38.5 keV was used for primary excitation. With this beam, we scanned a square of approximately $17.5 \times 17.5 \text{ cm}^2$, corresponding to the position of the covered head. The dwell time was 2 s per pixel, so that the total scan time was approximately 2 days. Fluorescence spectra were recorded for each pixel with a high-resolution energy-dispersive Ge-detector. A typical spectrum is displayed in Figure 3a. The resulting spectra were processed using the software package AXIL⁶ to subtract background signal and determine net peak areas for all identified elements. The extracted peak areas were adjusted to account for fluctuations in the current of the synchrotron storage ring, detector dead times, and spectra collection times. Elemental distribution images were then reconstructed from the resulting sets of peak areas. These maps were

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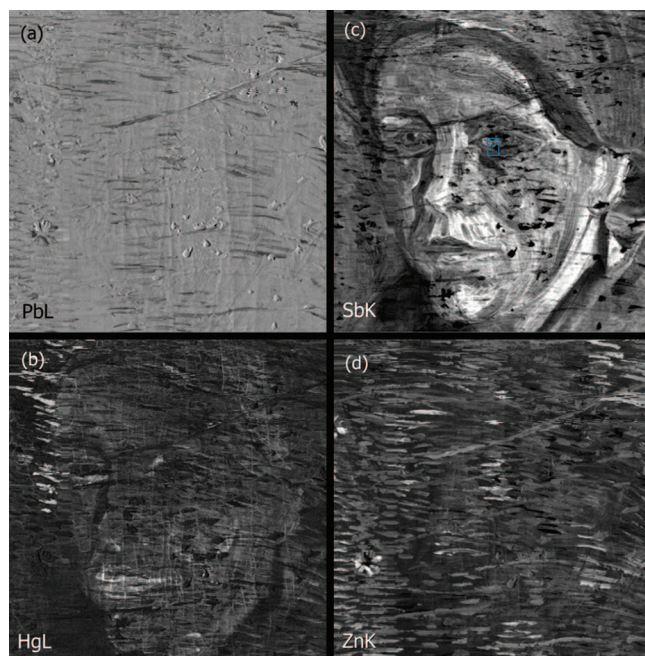


Figure 2. (a) Distribution of Pb L measured with SR-based XRF (black, low intensity; white, high intensity). (b) Hg L showing distribution of vermilion. (c) Sb K showing distribution of Naples yellow, paint sample location indicated in the blue frame (Figure 4). (d) Zn K showing distribution of zinc white, mostly corresponding with surface painting but some overlap with concentrations of SbK (nose, ear, neck).

then compared with features on the surface painting as well as the XRR and IRR images.

From the elemental distribution maps acquired by XRF, antimony could be identified as the most important tracer element of the hidden layer. In order to learn about the chemical binding of the Sb, we performed X-ray absorption near edge structure (XANES) measurements at the Sb K-edge on the most interesting points of the hidden layer. Those measurements were carried out at beamline C of HASYLAB at DESY.^{7,8} The monochromatic beam was generated with a fixed-exit Si double-crystal monochromator. Fine-tuning to 60% and stabilization of the monochromator was realized by a piezoelectric driven microgoniometer mounted below the second crystal. Energy scans were performed with step sizes of 10 eV before the edge, 0.5 eV steps in a 30 eV region around the edge, and equidistant steps in the energy range above the edge. Energy calibration was performed by transmission measurements of an Sb foil and the use of a high-resolution Renishaw optical encoder system mounted on the theta goniometer. The position of the edge was calibrated to 30 491 eV. The XANES spectra were recorded in fluorescence mode in the horizontal plane of the beam in backscattering geometry (50° from the incident beam). This geometry had the advantage that the beam

impinged at 90° to the sample surface thus minimizing its path length in the top layer and therefore also its absorption. A one pixel high-resolution energy-dispersive Ge-detector with an active area of 491 mm² was used for recording of the Sb K α fluorescence signal of the samples. The fluorescence signal was normalized to the intensity of the incoming beam recorded in a 10 cm long ionization chamber installed in front of the sample. Besides the investigations on the painting per se, in order to identify the pigment in the painting, measurements were also performed on reference antimony compounds which are known to have been used as paint pigments at the time of origin of the painting. Among these were Naples yellow (Pb₂Sb₂O₇), valentinite (Sb₂O₃), and kermesite (Sb₂S₂O). Some of the resulting XANES spectra are shown in Figure 3b. The mineral reference samples were provided by the Mineralogical Museum at Earth Sciences Department of the University of Kiel, Germany. For the measurements, parts of the mineral grains were removed and ground to fine powders.

A microscopic sample was taken from the painting in order to study the elemental composition of the upper and lower paint (sample location indicated in Figure 1b). The paint sample was embedded in epoxy resin. The orientation of the sample in the resin was such that the cross section, perpendicular to the original paint surface, could be studied. The surface of the resin was ground flat with corundum paper and polished with fine diamond pastes up to a final diameter of 0.25 μ m. The sample was analyzed by means of a Jeol 6300 electron microprobe system equipped with an energy dispersive Si(Li) X-ray detector (Princeton Gamma Tech). X-ray spectra were collected from the cross-sectioned surface at 20 kV, a beam current of 1 nA, and a live time of 200 s. X-ray maps were recorded to study the spatial distribution of the elements at 20 kV and a beam current of 15 nA during 3600 s.

As a complement to the high energy measurements performed at HASYLAB on the painting itself, the same polished section employed for SEM analysis was used for characterization by means of low-energy synchrotron X-ray microbeam analysis. Measurements were carried out at the X-ray microscopy beamline, ID21, at the ESRF (Grenoble, France).⁹ The objective was to determine the elemental components and the correlation of their distribution within the paint layers. The ID21 scanning X-ray fluorescence microscope operates in an energy range from 2.1 to 7.2 keV. Under vacuum, μ -XRF and μ -XANES measurements were performed at the Sb L-edges (4.8 keV) for a better identification of the pigments. A fixed-exit, double crystal Si(111) monochromator determines the energy of the X-ray beam with a resolution of $\Delta E/E = 10^{-4}$. The beam size was reduced to $\sim 1.1 \times 0.3 \mu\text{m}^2$ (horizontal \times vertical) thanks to Fresnel zone plates by geometrical demagnification of the synchrotron source. The software package PyMca was used to fit fluorescence spectra, in particular to separate the Ca K-lines and Sb L-lines, which strongly overlap.¹⁰ During the μ -XANES scans, the position of the beam footprint was stabilized to within 0.5 μ m.¹¹ The μ -fluorescence signal was collected in the horizontal plane perpendicular to the direction of the incident beam by means of a HPGe solid-state, energy-

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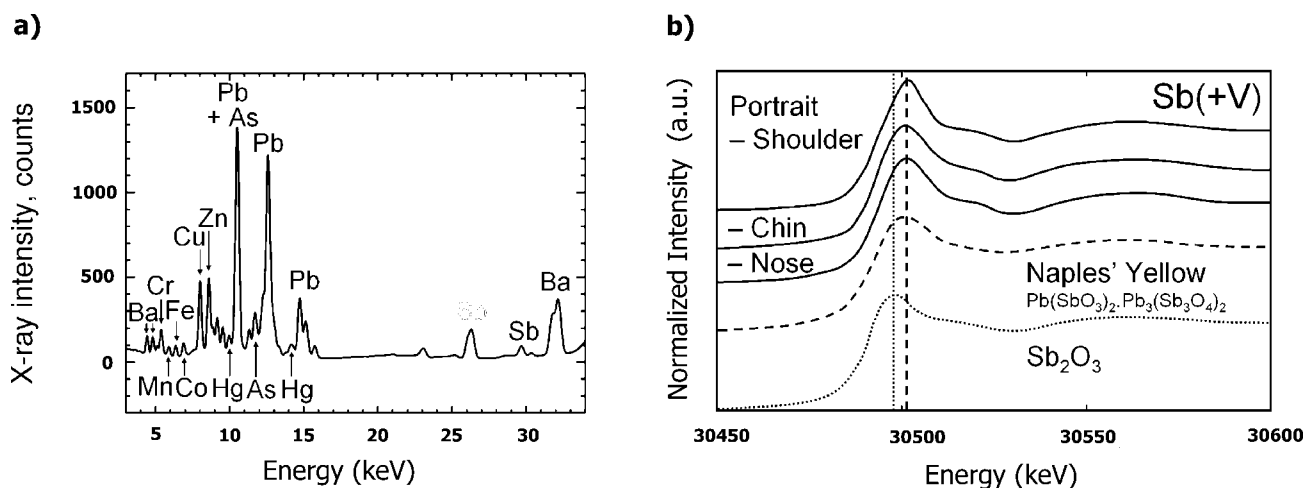


Figure 3. (a) Example of a X-ray fluorescence spectrum, derived from one location on the painting, showing the presence of Sb; (b) Comparison of Sb K-edge XANES spectra from three positions on the painting to reference XANES spectra of Naples yellow [$\text{Pb}(\text{SbO}_3)_2 \cdot \text{Pb}_3(\text{Sb}_3\text{O}_4)_2$] and antimony white (Sb_2O_3). All spectra were recorded in the fluorescent mode.

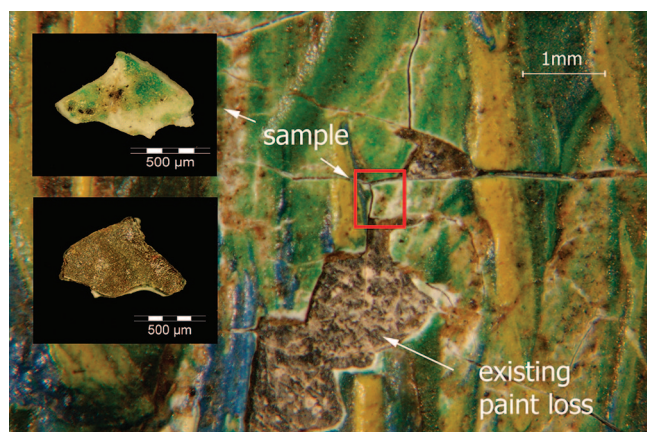


Figure 4. View on sample location indicated in Figures 1b and 2c (rotated 90° counter clockwise). The red frame indicates the location of the sample before removal. The insets show photographs of both sides of the unembedded sample before cross-sectioning.

dispersive detector. The sample surface was oriented vertically, making an angle of 60° relative to the incident beam. A sketch of the setup is given elsewhere.¹² XANES spectra were acquired at both the Sb L_{III} -edge (4.12–4.24 keV) and the Sb L_{I} -edge (4.68–4.77 keV), with energy increments of 0.25 and 0.20 eV, respectively. Reference spectra were acquired on pure powders, in transmission mode, with a broad beam of 200 μm cross section.

Reference antimony compounds were purchased from Alfa Aesar ($\text{KSbO}_3 \cdot 3\text{H}_2\text{O}$ and $\text{NaSbO}_3\text{OH} \cdot 3\text{H}_2\text{O}$), Aldrich (Sb_2O_4), and Kremer (Naples yellow) or lent from museums [valentinite (Sb_2O_3), reference RA1170, senarmontite (Sb_2O_3), reference RC4421, and stibiconite ($\text{Sb}_3\text{O}_6\text{OH}$), reference RC3374, from the Koninklijk Belgisch Instituut voor Natuurwetenschappen/Institut des Sciences Nationales de Belgique, Brussels, Belgium; and kermesite ($\text{Sb}_2\text{S}_2\text{O}$), reference R188, from the Museum National d'Histoire Naturelle, Paris, France].

Finally, XRF measurements were carried out on several portraits painted by V. van Gogh of the same period in the Kröller-Müller Museum (Otterlo, The Netherlands) by means of a

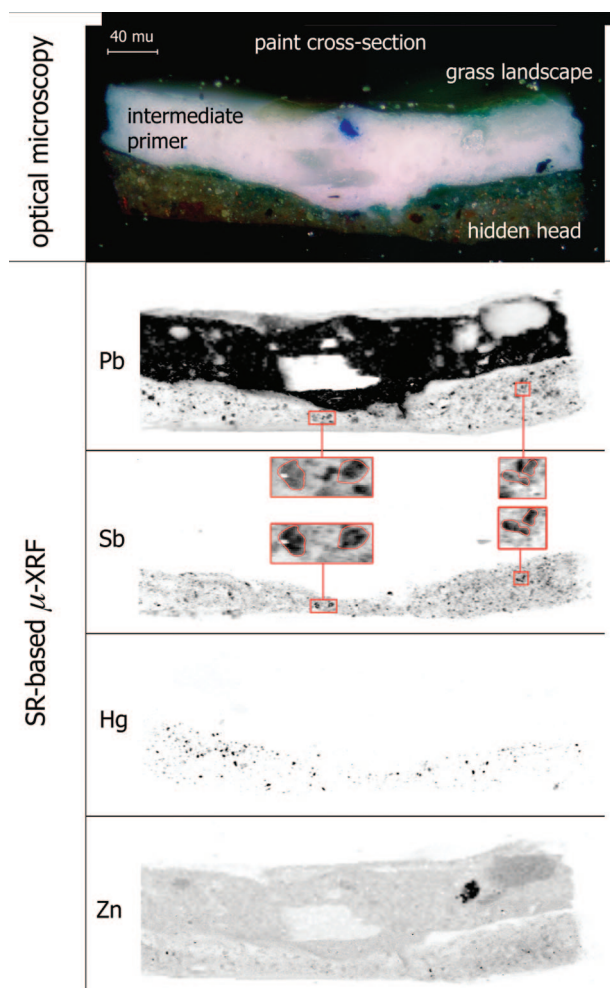


Figure 5. Cross section of paint sample measured with SR-based μ -XRF showing elemental distributions of Pb, Sb, Hg, and Zn (black, high intensity; white, low intensity). Insets show the correlation of Sb and Pb on the pigment grain level.

portable X-ray fluorescence spectrometer (PXRF). Spectra were recorded with a Keymaster Tracer III-V equipped with a rhodium X-ray tube and a peltier cooled SiPIN diode detector. The PXRF

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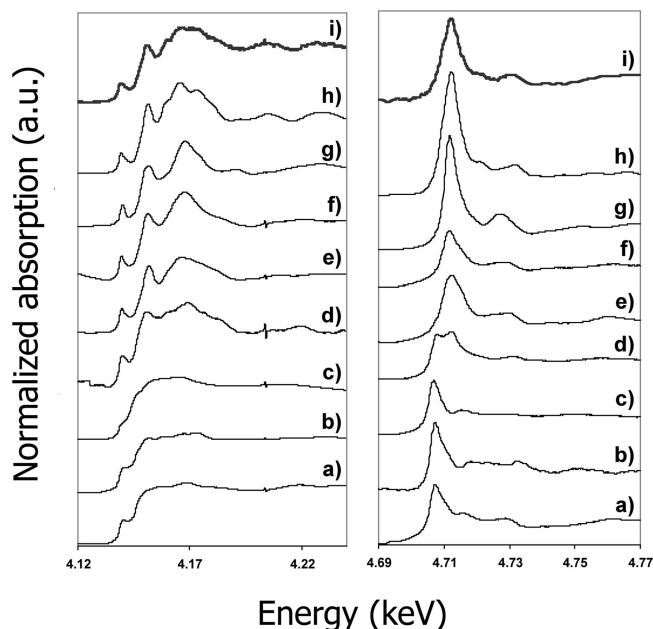


Figure 6. XANES spectra at the Sb-L_{III} edge (upper spectrum) and at the Sb-L_I edge (lower spectrum). Reference antimony compounds: Sb₂O₃ as (a) valentinite and as (b) senarmonite; (c) Sb₂S₂O₆, kermesite; (d) Sb₂O₄; (e) Sb₃O₆OH, stibiconite; (f) KSbO₃·3H₂O; (g) NaSbO₃OH·3H₂O; (h) Naples yellow; and (i) Sb pigment in the cross section of the Van Gogh painting (Figure 5).

instrument was operated at a tube voltage of 40 keV, a current intensity of 2.3 mA, and a measuring time of 200 s (live time). The diameter of the X-ray spot was approximately 1 cm. The instrument was mounted on a mobile XYZ stage. In this way it was possible to position and move the PXRF along the paint surface, in a stable and accurate way, without ever touching the object.

In conclusion, the analytical techniques above nicely complement each other. Portable XRF allows for nondestructive elemental analysis but has a rather large footprint on the painting (1 cm). Its acquisition time per pixel is high (200 s), so that scanning is fairly impossible. Synchrotron sources have a high brightness and energy range compared to classical sources. SR-based XRF therefore allows one to quickly scan large, decimeter-scale areas with submillimeter spatial resolution, but the painting needs to be transported to an SR facility. The laboratory vs synchrotron microimaging techniques of the paint sample compare as follows. SEM has an easy access, has a higher lateral resolution, and probes a thinner superficial layer than SR- μ XRF. Vice versa, μ XRF has a higher sensitivity, notably for heavier elements. In addition, polychromaticity is essential for μ XANES, which complements elemental identification with their chemical characteristics.

RESULTS

The XRF scan of the painting revealed a number of elemental distributions that mostly correspond with the surface painting. Its main elemental components include transition metals such as Mn, Cr, Co, Fe, Cu, Zn, As, and Ba. The pigments used in this landscape painting appear to be chrome green, schweinfurth green, earth pigments, and zinc white, mixed with barium sulfates. Interestingly, Pb showed a more or less homogeneous distribution (Figure 2a), indicating the presence of a lead white priming layer. The maps of two elements directly relate to the covered head,

Hg and Sb (parts b and c of Figure 2), with very weak correspondence in the Zn-map (Figure 2d).

Mercury is associated with vermillion, i.e., the red pigment mercury sulfide. As expected, this pigment was found predominantly in the lips and cheek. A good candidate for the zinc signal is zinc white (ZnO), a typical pigment used by Van Gogh in that period.¹³ Given its use in both the upper and lower painting, and the fairly low fluorescence energy of the Zn-K α line (8.6 keV), the Zn distribution predominantly corresponds to the landscape painting. However, we observed a weak overlap with Sb concentrations in the light parts of the nose, ear, and collar of the head, strongly suggesting the use of zinc white in these lighted areas.

The chemical origin of Sb was less obvious. At first, lead antimonate (Pb₂Sb₂O₇), also known as Naples yellow, seemed to be a plausible source, notably in view of Van Gogh's frequent use of this pigment in his Dutch years.¹⁴ However, the distributions for Pb detected by Pb L-shell emission lines and Sb detected by K-shell emission lines did not show any correlation. This could be explained by the difference in fluorescence energy and thus detection depth. Yet, we scanned a fairly large surface with many brushstrokes and a correspondingly irregular topography. Given that heterogeneity, one might expect to still find areas in which both elements would be detected together. The total lack of correlation between Pb and Sb therefore appeared puzzling.

In order to examine further the chemical Sb-compound in the lower portrait, XANES K-edge measurements were performed at selected positions on the head (Figure 3b). This indicated that valentinite (Sb₂O₃), a white pigment introduced in the 1920s can be excluded as a possible Sb source. Instead, the acquired XANES spectra were rather similar to that of Naples yellow (lead antimonate). Apart from indicating that Sb is present as an antimonate [Sb(+V) valence state], the XANES did not provide additional information on the molecular compound within which Sb is present.

A paint sample was taken in order to verify the identification of the pigments, to determine their distribution within the paint stratigraphy, and to correlate this to the lateral elemental distributions. A suitable sample location was found near an existing area of paint loss (Figure 4). The sample area is situated on the white of the left eye of the hidden face; at this location, a fairly strong Sb-K α intensity was observed (Figure 2c). The cross section nicely revealed the buildup of paint layers in this area. The thin green layer on top relates to the greenish glaze of the surface landscape painting. Underneath, we find a 50 μ m thick white layer. This served as a (secondary) priming layer for the landscape painting, as shown by the uniform lateral distribution of Pb in Figure 2a. The two dark, greenish layers underneath correspond to the painting of the covered head. Elemental examination with SEM/EDS and synchrotron-based μ XRF on the paint sample confirmed the presence of Zn, Sb, and Hg in the lowest two layers and also showed significant amounts of Ca, P, and Fe. Moreover, we noted that the distributions of Pb and Sb are partially correlated on the level of individual pigment grains in the two lowest layers (Figure 5, see insets). Indeed, the correlation is not perfect: in each Sb-containing grain, Pb is also observed; yet, lead grains are

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(14) Personal communication by Ella Hendriks, head of conservation, Van Gogh Museum.



Figure 7. (a) Tritonal color reconstruction of Sb (yellowish white) and Hg (red) representing the flesh color of the hidden face. (b) Detail from Vincent van Gogh, *Head of a Woman*, Nuenen, winter 1884–85, oil on canvas, 42 cm × 33 cm, Kröller-Müller Museum, Otterlo (KM 105.591; F154/JH608). (c) Detail from Vincent van Gogh, *Head of a Woman*, Nuenen, winter 1884–85, oil on canvas, 42 cm × 34 cm, Van Gogh Museum, Amsterdam (F156/JH569).

additionally present without Sb, possibly as lead white. Besides, this internal layer is covered with a $\sim 50 \mu\text{m}$ -thick layer of a lead white priming layer that completely hampers any colocalization of Pb and Sb while acquiring X-ray fluorescence data from the painting directly.

Further analysis of the antimony pigment was performed with μ -XANES at both the Sb L_{III} and L_{I} -edges. Spectra obtained on reference powders are displayed in Figure 6. The Sb L_{III} -edge is more sensitive to the coordination number of antimony while the Sb L_{I} -edge will allow direct identification of the antimony oxidation state.¹⁵ As shown in Figure 6b, a shift of about 4.5 eV is observed between Sb(+III) and Sb(+V) compounds. The white line position is therefore a powerful tool for determining the antimony oxidation state. Additionally, the spectral shape above the white line is sensitive to the chemical environment of antimony. Spectra acquired on Sb–Pb grains, highlighted in Figure 5, are plotted in Figure 6. As was concluded earlier from XANES at the K-edge, performed directly on the painting, Sb(+V) is identified in the painting. In addition, the best agreement of spectra at the two L-edges corresponds to the Naples yellow spectra. The positions of the various peaks are similar. The main difference is related to signal intensity. This point may be attributed to the fact that spectra were acquired in transmission mode from thin layers of the reference powders while they were collected in fluorescence mode from the painting fragments. In that particular case, self-absorption may explain the lowest intensity of the white line. We therefore conclude that Sb is present as lead antimonate, also known as the pigment Naples yellow.

In addition, we performed a number of XRF analyses of similar heads by Van Gogh in the Kröller-Müller Museum, among which

was the *Head of a Woman* (Figure 7a). Point measurements were carried out with a portable XRF unit to determine the elemental composition of the flesh tones, without any sampling. This confirmed the presence of Zn, Hg, Pb and, importantly, Sb, as well as Ca, Fe, and Mn. Red areas, such as the lips, proved to be rich in Hg, while the strongest signals for Pb, Sb, and Zn were found in the lighted parts of the face.

DISCUSSION AND CONCLUSION

On the basis of the analyses described above, we conclude that the distribution of Hg in the hidden face corresponds to vermillion, the red component of pinkish flesh tones. The distribution of Sb relates to Naples yellow, which seems to have been mixed with zinc white and lead white in the lighted parts of the painting. Figure 7c shows a tritonal reconstruction of the covered portrait in which the maps for Hg and Sb have been colorized accordingly. This approximate reconstruction presents a significantly clearer and more detailed image of the hidden composition than the XRR and IRR images (parts b and c of Figure 1) taken earlier. The brushstrokes and all physiognomic details, such as eyes, nose, mouth, and chin could be visualized. In addition, the reddish intensity of the flesh tones of the lips, cheek, and forehead adds to the readability of the head.

Besides the pigments above, we suspect the presence of additional colors that will have remained undetected in the surface XRF scan. A comparison with similar, existing heads of women showed that Van Gogh's palette was fairly dark. His palette contained various black and brown pigments, including earth colors (Fe, Mn), bone black (Ca), and carbon black (C). A combination of these elements was found in the *Head of a Woman* with portable XRF analysis as well as in the hidden layers of the cross section with μ -XRF analysis. Moreover, the IRR image

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(Figure 1c), sensitive to carbon, shows broad contour lines of the head's profile, indicating the use of carbon black. The low-energy K-line fluorescence of these elements, however, will have been absorbed by the intermediate Pb-rich ground layer. Thus, our reconstruction does not include all color components and in particular misses browns and blacks. These dark colors would have given additional modeling to the face both in terms of spatial illusion and the rural, earthy atmosphere that Van Gogh was so keen to express. This is illustrated by comparing the colors visible in the paint cross section with the colors assumed to be present in the reconstruction (Figure 7b) at the sampling location. The greenish dark color of the lowest layers does not entirely match the white of the left eye of the hidden face. The reconstruction, therefore, shows approximate and selected color distributions and should not be considered to show absolute color values.

Nevertheless, the reconstruction proved to be the missing link in comparing the hidden face with the artist's known oeuvre. The hidden painting dovetails with an extensive series of heads from the artist's period in Nuenen (The Netherlands). Between October 1884 and May 1885 he painted the heads of peasant models in the dark settings of their huts, in the neighborhood of the village of Nuenen.¹⁶ Van Gogh did not intend to render lifelike portraits but rather meant to train his control over form, color, and light effects. More specifically, the present head must belong to a smaller group of studies that Vincent gave to his brother Theo in Paris, as mentioned in his letters (*Some of the heads I promised you are finished, but they are not quite dry yet*, Nuenen, mid-March 1885; *I should like to hear whether those rolled-up things arrived safely*, April first, 1885).¹⁷ After 2 1/2 years, Vincent went to join Theo in Paris and may very well have found the woman's head

hopelessly old-fashioned by then. This, together with his uncomfortable financial situation, can explain the presence of a colorful, Parisian style floral painting on top of a dark and sombre head of a provincial Dutch woman.

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