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RESEARCH ARTICLE

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Artificial orpiment, a new pigment in Rembrandt's palette

Annelies van Loon^{1,2*} , Petria Noble¹, Anna Krekeler¹, Geert Van der Snickt³, Koen Janssens³, Yoshinari Abe⁴, Izumi Nakai⁴ and Joris Dik²

Abstract

This paper reports on how the application of macro X-ray fluorescence (MA-XRF) imaging, in combination with the re-examination of existing paint cross-sections, has led to the discovery of a new pigment in Rembrandt's palette: artificial orpiment. In the NWO Science4Arts 'ReVisRembrandt' project, novel chemical imaging techniques are being developed and applied to the study of Rembrandt's late paintings in order to help resolve outstanding questions and to gain a better understanding of his late enigmatic painting technique. One of the selected case studies is the Portrait of a Couple as Isaac and Rebecca, known as 'The Jewish Bride', dated c. 1665 and on view in the Rijksmuseum. During the re-installation of the Rijksmuseum in 2013, the picture was scanned using the Bruker M6 Jetstream MA-XRF scanner. The resulting elemental distribution maps made it possible to distinguish many features in the painting, such as bone black remains of the original hat (P, Ca maps), and the now discolored smalt-rich background (Co, Ni, As, K maps). The arsenic (As) map also revealed areas of high-intensity in Isaac's sleeve and Rebecca's dress where it could be established that it was not related with the pigment smalt that also contains arsenic. This pointed to the presence of a yellow or orange arsenic-containing pigment, such as realgar or orpiment that is not associated with the artist's palette. Subsequent examination of existing paint cross-sections from these locations taken by Karin Groen in the 1990s identified isolated, almost perfectly round particles of arsenic sulfide. The round shape corresponds with published findings on a purified form of artificial orpiment glass obtained by dry processing, a sublimation reaction. In bright field, the particles characteristically exhibit a dark cross in the middle caused by internal light reflections. The results of additional non-invasive techniques (portable XRD and portable Raman) are discussed, as well as the implications of this finding and how it fits with Rembrandt's late experimental painting technique.

Keywords: Painting analysis, MA-XRF imaging, Cross-sections, Rembrandt, The Jewish Bride, Artificial orpiment

Background

The production of pigments was the work of specialists in the seventeenth century. There was a lively trade in pigments and other painting materials throughout Europe at the time. Artists bought their materials at an apothecary's shop or at a grocer or colorman [1, 2]. The choice of pigments was limited, as compared to the huge selection of pigments available today. But this limited palette was by no means an obstacle for their creativity. In particular an artist like Rembrandt knew exactly which

materials to combine, in order to achieve his intended painterly effects and pictorial illusion, while manipulating color contrast, texture and translucency of the paint. 'His mixtures attain an almost comical level of complexity', as Philip Ball rightly pointed out in his book in 2003 [3]. Furthermore, Rembrandt deliberately exploited all stages of the painting process in the final image: from ground to painted sketch to underpaint, to the final paint layers. Rembrandt's late works (after 1651) show a fundamental change in the means with which he created pictorial illusion [4]. These works are characterized by their loose, sketchy appearance and unusual surface roughness. To realize these effects, this demanded new ways to apply the paint in order to manipulate its properties. Rembrandt started to use a palette knife to spread his paint,

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modelled his paint to attain texture, and scratched in the paint with the back of his brush or used his finger [5, 6]. The use of thickly impastoed, lead white passages, usually remarkably well preserved, are common throughout his entire oeuvre. In the late works Rembrandt also used lead white paint in underlayers to build up the impasto, which were then toned in the final layers [7]. The dense packing of the pigment particles primarily accounts for the stiffness of the lead white paint that remains standing after application. Groen also identified the addition of a gum in passages of red lakes, thought to have been added to thicken the paint. Another unique feature of Rembrandt's late painting technique is the extensive use of coarse smalt, a blue cobalt glass [8, 9]. He often mixed smalt with lakes, earths and black pigments, not only for its color, but also for its drying properties and to give texture and translucency to the paint. It is not always clear to us what Rembrandt's intentions were, since many of his late pictures have severely changed in appearance over time, as a result of paint alterations and old restorations.

In the NWO *Science4Arts* 'ReVisRembrandt' project, novel chemical imaging techniques are being developed and applied to the study of Rembrandt's late paintings in order to gain a better understanding of his late enigmatic painting technique, and to help resolve outstanding questions regarding attribution, paint alterations, artist's changes and old restorations [6, 10]. Techniques include macro X-ray fluorescence imaging (MA-XRF), reflectance imaging spectroscopy (RIS), macro X-ray powder diffraction (MA-XRPD), as well as optical coherence tomography (OCT). One of the selected case studies is the *Portrait of a Couple as Isaac and Rebecca*, known as 'The Jewish Bride', dated c. 1665 that is on view in the Rijksmuseum (Fig. 1a). The painting owes its name to the Amsterdam art collector Adriaan van der Hoop, who purchased the painting in 1833. He believed that it shows a Jewish father hanging a necklace around the neck of his daughter on her wedding day. Today, the general consensus is that the painting is a wedding portrait, depicting a contemporary couple dressed in historical costumes as characters from the Old Testament. The costumes are based on fifteenth- and sixteenth-century styles. Rembrandt preferred these elaborate costumes over contemporary classical draperies, probably because they gave him more opportunity to live out his rich imagination and taste for colorful decorations [11]. The story of Isaac and Rebecca was a popular theme associated with weddings and portraits of married couples in the seventeenth century. During the re-installation of the Rijksmuseum in 2013, the opportunity was taken to scan the picture using a mobile MA-XRF scanner. This is a recent chemical imaging tool that reveals the elemental distributions on and below the paint surface in a non-invasive manner

[12]. Notably, the resulting arsenic (As) map revealed areas of high-intensity in Isaac's sleeve and Rebecca's dress where it could be established that it was not related with the pigment smalt that also contains arsenic. The data-processing also corrects for overlap of the As-K emission lines with spectral lines of lead and mercury. This pointed to the presence of a yellow or orange-red arsenic-containing pigment, such as orpiment (As_2S_3) or realgar (As_4S_4) that is currently not associated with the artist's palette [13].

In the seventeenth century, lead-tin yellow, yellow ochre and yellow lake were the dominant yellows in Northern European easel painting, whereas vermilion, red ochre and red lake were the dominant reds. Orpiment and realgar were less frequently used, with the exception of still-life painting. Although their rich color was universally praised in treatises, they had well-known disadvantages. Besides their poisonous character, they were poor drying, lacked body, and were difficult to grind and handle. Sources also mention incompatibility with other pigments.

To be able to confirm and identify the arsenic pigment in *The Jewish Bride*, we correlated the results of the MA-XRF scanning with the re-examination of existing paint cross-sections taken during the restoration of the painting in the 1990s. In-situ spot analyses were carried out at the same time in the galleries using portable X-ray diffraction (XRD) and Raman spectroscopy. This paper presents the results of analysis, and discusses the implications of the identification of a new pigment in Rembrandt's palette.

Experimental

Non-invasive techniques

MA-XRF

Macroscopic X-ray fluorescence maps were collected using a Bruker M6 Jetstream instrument [14]. The instrument consists of a measuring head with a Rhodium-target microfocus X-ray tube (30 W, maximum voltage 50 kV, maximum current 0.6 mA), and a 30 mm² XFlash silicon drift detector (SDD) with beryllium window (energy resolution <145 eV at Mn-K α). By slowly moving the measuring head on the XY-motorized stage, the painting was scanned pixel by pixel, line by line. By recording the emitted X-ray fluorescence radiation, the chemical elements present in the paint, which are associated with specific pigments, could be identified. The beam size is defined by means of a polycapillary optic with a focal spot of c. 40 μm . The measuring spot can be varied by changing the distance between the paint surface and the measuring head. A typical distance of c. 1 cm results in a spot of c. 350 μm . An area of maximum 80 $\times$ 60 cm is scanned in one session that typically lasts several hours. Paintings



Fig. 1 Rembrandt, *Portrait of a Couple as Isaac and Rebecca, known as 'The Jewish Bride'*, c. 1665, oil on canvas (lined), 121.5 × 166.5 cm, Rijksmuseum Amsterdam (SK-C-216). Visible light image (**a**), and corresponding MA-XRF maps: arsenic (**b**), cobalt (**c**), nickel (**d**), lead (**e**), mercury (**f**), iron (**g**), calcium (**h**)

of larger dimensions need to be scanned in sections that are then assembled. *The Jewish Bride* was scanned in a total of four scans. X-ray tube settings were 50 kV and 600 mA; a step size of 900–950 μm , and a dwell time of 70 ms/step were used. All data were collected with the Bruker M6 Jetstream software package. The acquired spectra were then exported and processed using PyMca and the in-house developed Datamuncher software [15]. This resulted in element distribution maps of Pb (M- and L-lines), K (K), Ca (K), Sn (L), Mn (K), Fe (K), Co (K), Ni (K), Cu (K), Bi (L), As (K), Hg (L), Sr (K), Ti (K), Cr (K), Ba (L), and Zn (K).

Portable X-ray diffraction (p-XRD)

X-ray diffraction measurements of selected spots of the painting were performed using a portable powder diffractometer (Techno-X Inc., Osaka, Japan) developed for non-invasive, in situ analysis of cultural heritage materials [16]. The diffractometer (dimensions: $29 \times 20 \times 17$ cm/weight: 5.5 kg) was mounted on a tripod and positioned in close contact with the paint surface. The instrument is equipped with a laser beam focus that helps locate the exact measurement spot on the painting. The diffractometer consists of a $\theta - \theta$ goniometer, a Cu X-ray tube (MAGPRO[®] 60 kV, 12 W/200 μA) and an SDD detector; the latter can also be used for XRF. The X-ray beam size is 2 mm in diameter; typical scan range (2θ) 30–70°; step size 0.1°/3 s, minimum 0.02°; FWHM of Si (111) = 0.65° in 2θ ; typical measurement time 40 min. Spectra were smoothed.

Portable Raman (p-Raman)

Raman spectra were collected using a MiniRam[™] portable micro-Raman spectrometer (B&W Tek Inc., Japan). The MiniRam is a light-weight (~2 kg) instrument, suitable for non-invasive, in situ analysis of cultural heritage materials. The instrument is also capable of micro-Raman analysis using a microscopic video system. A 785 nm laser was used, with an output power of 9 mW, and a spot size of 45 μm in diameter. The instrument has a 2048 pixel CCD detector. Spectra were acquired with a 40 $\times$ objective lens, spectral range 2000–100 cm^{-1} (Raman Shift), and spectral resolution of about 10 cm^{-1} FWHM. We also collected reference spectra of As-bearing mineral pigments (orpiment and realgar). We used reference spectra for vermilion from the RRUFF database [17] and for As–S glass from the literature [18].

Cross-section analyses

Samples and sample preparation

We re-examined paint cross-sections taken by Karin Groen during the treatment of the painting in the early 1990s: sample 40/17 from the black belt of Isaac where

it is painted over the yellow sleeve, and sample 40/8 from the red dress of Rebecca. The cross-sections were embedded in Poly-pol PS230, a two-component polyester mounting resin (Poly-Service Amsterdam, The Netherlands). We improved the surface of the cross-sections by dry-polishing with Micromesh sheets grades 6000, 8000 and 12,000 (Micro-Surface Finishing Products Inc., Wilton, Iowa, USA) [19].

Light microscopy

Light microscopy of the embedded paint cross-sections was carried out on a Zeiss Axio Imager.A2m microscope equipped with a Zeiss AxioCam MRc5 digital camera. The cross-sections were analyzed at magnifications up to 500 $\times$, in bright field, dark field, and ultraviolet (UV-A) (LED 365 nm light source; filterset EX G 365, BS FT 395, EM LP 420).

A Leica DM2500 light microscope equipped with a Leica DFC490 digital camera was used to analyze the cross-sections at a magnification of 1000 $\times$, in bright field, with an oil immersion objective.

SEM-EDX

The paint cross-sections were gold coated (sample 40/17) or chrome coated (sample 40/08) (3 nm) on a SC7640 sputter coater (Quorum Technologies, Newhaven, East Sussex, UK) to improve surface conductivity. The samples were analyzed using a FEI Verios 460 high-pressure electron microscope at an acceleration voltage of 20 kV and a beam current of 0.20 nA. The SEM was equipped with an Oxford EDX system to yield elemental composition of the pigments within the paint layers.

Results

MA-XRF scanning

The resulting elemental distribution maps made it possible to distinguish many new features in the painting. Figure 1 presents the visible image of the painting together with distribution maps of selected elements (As, Co, Ni, Pb, Hg, Fe, Ca). The calcium (Ca–K) map, for instance, helps visualize the bone black remains of the original hat—bone black is a calcium phosphate-based black pigment (Fig. 1h). Since the last treatment of the painting in the early 1990s, there has been much debate about the authenticity of the hat [20]. The cobalt (Co–K) map together with the Ni/As/Bi/K maps point to the use of excessive amounts of (now discolored) smalt in the background paint (Fig. 1b–d). Smalt is a blue pigment made of finely ground potassium glass that is colored blue by the addition of cobalt ore. Arsenic, iron, nickel and bismuth, are introduced with the cobalt ore and are associated with its geological source [21]. Unfortunately, smalt is not a stable pigment in oil media and the background now

has a monochrome, translucent brownish color, interspersed with vague dark passages. The presence of smalt, however, in such large quantities, mixed with yellow lakes, bone black and earth pigments, suggests its color was originally different, possibly more greenish and more nuanced. Smalt is also found in parts of Isaac's cloak, and in Rebecca's jewelry, her rings and pearls (or glass beads) in her hair. Interestingly, the arsenic (As–K) map reveals areas of high intensity in Isaac's sleeve and Rebecca's dress that are not related with smalt, which also contains arsenic (Fig. 1b). The Co/Ni/Bi/K signals are low in these areas. The lead (Pb–L) and mercury (Hg–L) distribution maps demonstrate that these elements are also present in high amounts/concentrations: lead in Isaac's sleeve, and mercury and lead in Rebecca's dress (Fig. 1e, f). XRF analysis of arsenic in the presence of lead and mercury presents some challenges. In particular, the most intense arsenic spectral line is the $K\alpha$ peak at 10.56 keV, an emission line that overlaps with the lead $L\alpha$ at 10.54 keV. The arsenic $K\beta$ peak at 11.73 keV, on the other hand, does not interfere with the Pb–L lines but shows overlap with the mercury $L\beta$ peak at 11.82 keV. Nonetheless, the As–K, Pb–L and Hg–L maps shown in Fig. 1 display clear and different signal distributions, suggesting that, for this painting, the peak fitting algorithm of the PymCa software was relatively successful in separating the different elemental contributions to the spectral peaks. However, care must still be taken when interpreting mapping results with high concentrations of both Pb and Hg, as is the case in the red dress.

Figure 2 shows visible images of Isaac's sleeve with corresponding elemental distribution maps of As, Pb, Sn and Fe, which can be related to specific color areas or underlayers. Rembrandt has suggested light and space in a highly sophisticated manner, with the brilliant yellow sleeve as a highpoint. Rembrandt achieved this effect by making use of bright yellow tones, combined with strongly, raised texture, which brings the sleeve literally to the foreground and enhances its brilliance. The uneven surface texture reflects the real daylight, thus reinforcing the effect of light [22]. Under the yellowish and orangey brown brushstrokes of the sleeve there is in fact an underlayer of pure lead white paint that was used to build up the thick impasto, as can be seen in the lead (Pb–L) distribution map (Fig. 2e). The painting has a brownish gray so-called 'quartz' or clay ground rich in ground sand and clay minerals [23]. Therefore, the lead in the Pb–L distribution map is not from the ground, but originates from the paint layers. Groen confirmed the presence of a lead white underlayer in a paint cross-section from Isaac's sleeve, where the compact white layer can be seen underneath a transparent brown paint [7]. Apart from thick daubs and blobs of paint, Rembrandt also used

a palette knife to create surface relief. The patterns of square ridges of paint testify to the use of palette knife, which Rembrandt started to use for this purpose only in the 1650s [5]. Careful comparison of the As map with the visible image reveals that the arsenic high intensity areas correspond with the brownish half-shadow and shadow areas of the sleeve, and not with the bright yellow lit areas of the sleeve (Fig. 2d). The latter show strong signals for both lead (visible in Pb–M and Pb–L maps, but only Pb–L is shown here) and tin (Sn–L) (Fig. 2f). This indicates the use of lead–tin yellow pigment, a lead–tin oxide (Pb_2SnO_4), in the final paint layer. The relatively smooth orangey brushstrokes in the half-shadows, on the other hand, are rich in iron, which points to the use of an earth pigment (Fig. 2c). The As/Pb/Fe maps (Fig. 1) show that the sleeve was originally slightly larger, but is covered by Isaac's black belt in the final composition. The belt is visible in the Ca distribution map, which suggests the pigment is bone black (Fig. 1h).

The mercury (Hg–L) map shows high concentrations of this element almost exclusively in the red dress of Rebecca (Fig. 1f). Hg is associated with vermilion, a mercury sulfide (HgS). The warm red tones of Rebecca's dress are also reflected in her hands and sleeves, as well as those of Isaac. These red brushstrokes of the light reflections show up in the Hg map, but with much lower intensity than the dress itself. The map also visualizes an initial broader expanse of the dress at the lower left in the first lay-out of the composition, now covered by Isaac's clothing. Some tin is detected in the lighter/orangey red passages, in the center of the dress, indicating the addition of lead–tin yellow to the vermilion paint (tin map not shown). The blobs of lead white (under) paint used to build up the impasto are clear to see in the lead (Pb–L) map. Here again, the uneven relief/texture of the paint enhances the brilliance of this passage. The dark red paint areas of the dress reveal a higher signal for potassium, a good marker for the alum substrate of red lake pigment [6] (potassium map not shown).

The As map indicates that the entire skirt of Rebecca's red dress is rich in As that is not associated with cobalt (smalt), with slightly higher concentrations in the dark red areas than in the light red areas (Fig. 1b). The areas of high intensity in the As map in the sleeve and dress indicate the use of an arsenic-containing pigment, such as orpiment (As_2S_3) or realgar (As_4S_4), but its use does not seem related to the light-colored areas or final highlights as one might expect. Based on comparison of the XRF maps with the painting, we conclude that the arsenic pigment is used in the mid- and shadow tones, mixed with other pigments, and/or in underlayers. Subsequent analysis using p-XRD and p-Raman ("p-XRD and p-Raman spot analyses") and cross-section analysis ("Cross-section

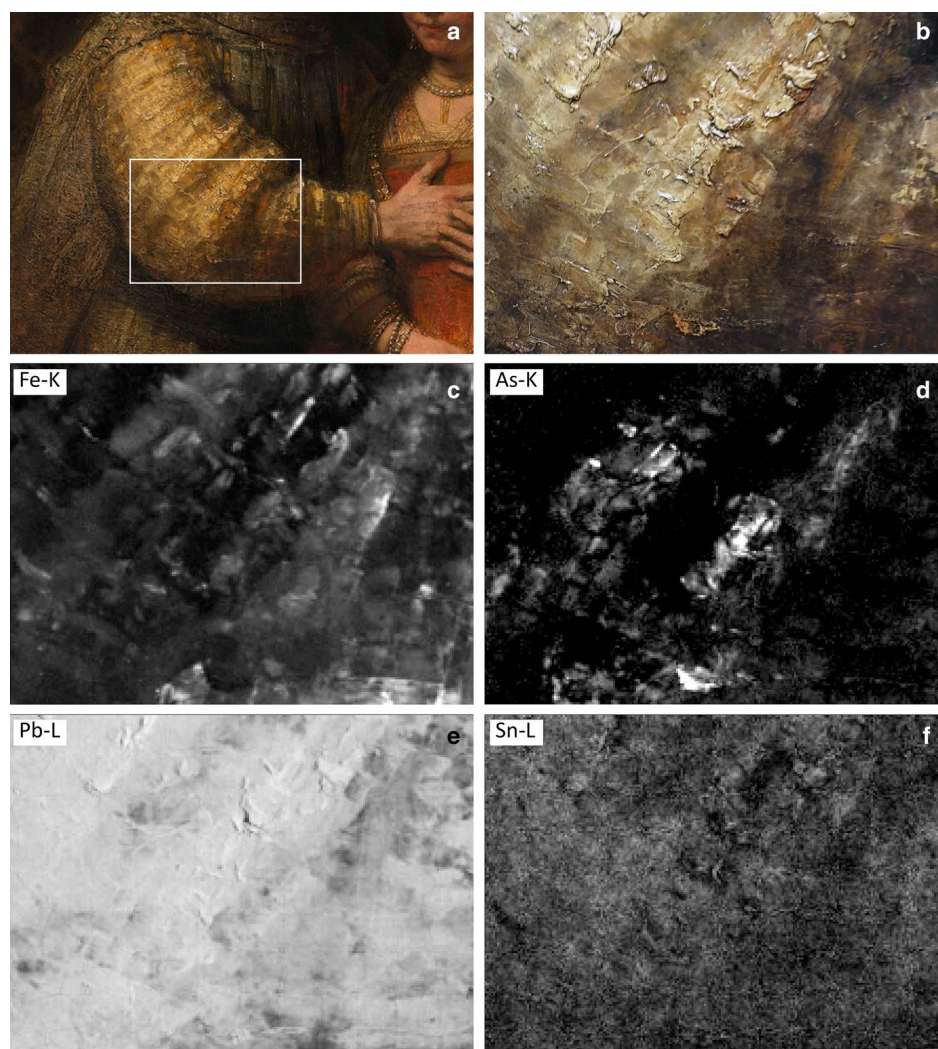


Fig. 2 Sleeve of Isaac. Visible light image (a), with detail showing coarse-textured paint (b), and corresponding MA-XRF maps: iron (c), arsenic (d), lead (e), tin (f)

analyses”) shed further light on the type of arsenic pigment, and how it was applied.

p-XRD and p-Raman spot analyses

Portable XRD and Raman analyses were undertaken to obtain structural information about the arsenic pigment in a non-invasive manner. Measurement spots were selected based on information from the MA-XRF elemental distribution maps. We collected two XRD data sets and nine Raman spectra from different As-containing paint areas of the yellow sleeve of Isaac, as well as a few Raman spectra from As-rich spots of the red dress of Rebecca. Before collecting the XRD data, new XRF spot measurements were made at the same spot using the same instrument (see “Experimental”) to confirm the presence of As. At the first analysis spot of the yellow

sleeve, Fe, As, Pb and Sn were detected. The XRD and Raman spectra both show peak patterns characteristic of lead–tin yellow type 1 (data not shown). XRD also identifies hydrocerrusite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$), as well as palmierite ($\text{K}_2\text{Pb}(\text{SO}_4)_2$). Palmierite is a common degradation product in Old Master paintings, often associated with degraded smalt, lakes or ultramarine in combination with lead white that is present in the same paint layer or an adjacent paint layer [8]. The diffraction data show no indication for the presence of an arsenic compound, suggesting that it is either present below the detection limit or in a non-crystalline form. Similarly, Fe, As, Pb and Sn were detected at the second analysis spot of the yellow sleeve, a thick orangey daub. The XRD data are very comparable to that of the first spot, and also show diffraction patterns of lead–tin yellow type 1, hydrocerrusite

and palmierite (Fig. 3a). The Raman spectrum, however, does not contain peaks for lead–tin yellow, but instead reveals a large broad peak at around 340 cm^{-1} , that corresponds to spectra of amorphous arsenic sulfide glass $\text{g-As}_x\text{S}_x$ (Fig. 3b) [18]. The Raman spectra of other As-rich analysis spots of the yellow sleeve show a similar feature at around 340 cm^{-1} (spectra not shown). Although XRD and Raman were done in the same area, XRD has a much larger spot size (2 mm) compared to Raman ($45\text{ }\mu\text{m}$), and a deeper penetration. This may explain why lead–tin yellow was picked up with XRD, but not with Raman. Raman analysis of the red dress of Rebecca was less successful. The spectra only showed the presence of vermillion, and gave no indication of an As–S species in the As-rich passages as determined by MA-XRF (Fig. 3c).

Cross-section analyses

The archives of the RCE (Amsterdam, Netherlands) have 15 paint cross-sections of *The Jewish Bride* taken by Karin Groen during the treatment of the painting in the early 1990s. The sample forms contain detailed descriptions of the build-up and composition of the paint layers as well as schematic drawings of the samples. They also include the results of SEM-EDX analyses of the cross-sections performed at the DSM Laboratories (Geleen, Netherlands) at the time. There is no mention of the presence of an arsenic-containing pigment in the paint layers. During re-examination of the cross-sections with the light microscope, however, we observed unusual, almost perfectly round bright-yellow particles with a diameter of $2\text{--}5\text{ }\mu\text{m}$ in two cross-sections (Figs. 4, 5). These particles looked very familiar to those we encountered several years before when examining paint cross-sections from Rembrandt (workshop?), *Man in a Red Cap*, c. 1660 (Museum Boijmans van Beuningen, Rotterdam) (Fig. 6) [24]. In bright field, the particles characteristically exhibit a dark cross in the middle caused by internal light reflections. EDX detects exclusively the elements As and S with an atomic ratio of 2:3 in the particles, which corresponds with orpiment (As_2S_3). The particles are interpreted as a purified form of artificial orpiment glass obtained by dry processing, a sublimation reaction (further discussed in “Discussion”). They are isotropic and X-ray-amorphous, which corresponds with the Raman results from the previous section (“p-XRD and p-Raman spot analyses”) and explains why portable XRD did not pick up a diffraction pattern [24]. The particles are not a degradation product of the natural form [25]. In fact, this artificial form of orpiment is more stable than the natural product, which is very vulnerable to degradation when exposed to light [18].

Figure 4 presents the light microscopic and SEM-EDX analyses of the cross-section from Isaac's yellow sleeve,

visible under the black paint of the belt (sample 40/17), a later revision by the artist. The black paint layer (layer 3) contains bone black, with minor additions of yellow and red organic lake pigments. Underneath the black paint layer is the yellow–brown paint of the sleeve, which appears as two layers in the UV image (layer 2a and 2b). The yellow–brown paint (layer 2) is a rich mixture of pigments, in which we identified lead–tin yellow, lakes, a little earth, a single particle of smalt and some black pigment. Several bright yellow, ball-shaped particles of artificial orpiment, varying in diameter between 2 and $5\text{ }\mu\text{m}$, are visible throughout the layer. They exhibit medium-gray contrast in the backscattered electron (BSE) image. The middle yellow arrow in the BSE image points to a conglomerate of three of these particles. The high intensity areas in the arsenic EDX distribution map correspond to areas with the bright yellow ball-shaped particles. These areas are also rich in sulfur, as shown by the sulfur map. Apart from the orpiment, sulfur is also associated with the lake pigments, which explains its distribution/presence throughout all paint layers. No other arsenic-containing particles or traces of arsenic were found in the paint, apart from the spherical particles. The cross-section is incomplete as the quartz ground is not present, and the bottom part of the yellow–brown paint layer shows what appears to be remnants of the lead white underlayer (layer 1), as described earlier (“MA-XRF scanning”).

In the cross-section from Rebecca's red dress (sample 40/08), bright yellow ball-shaped particles of orpiment can be noticed in a thin orangey brown underpaint or undermodeling (layer 2) (Fig. 5). Like the previous cross-section, no other arsenic-containing particles or traces of arsenic were found in this layer, apart from the ball-shaped particles. This layer further contains lead–tin yellow, vermillion, significant amounts of lake, and a little earth. The orangey brown underpaint is applied over a thick blackish sketch layer (layer 1), and further worked up with two opaque red paint layers consisting of mostly vermillion (layers 3, 4) and a thick red glaze (layer 5). Interestingly, Groen identified the addition of gum here to thicken the glaze [7].

Discussion

A most interesting aspect with regard to the discovery of orpiment in *The Jewish Bride* is the previous identification of the same/similar purified form of artificial orpiment glass in Rembrandt (workshop?), *The Man in a Red Cap*, c. 1660 (Rotterdam) (Fig. 6). Although Rembrandt's authorship of the Rotterdam painting is still questioned by many scholars, the picture is dated to around the same period as *The Jewish Bride*. Moreover the quartz ground in *The Man in a Red Cap* demonstrates that the painting must have been produced in Rembrandt's studio.

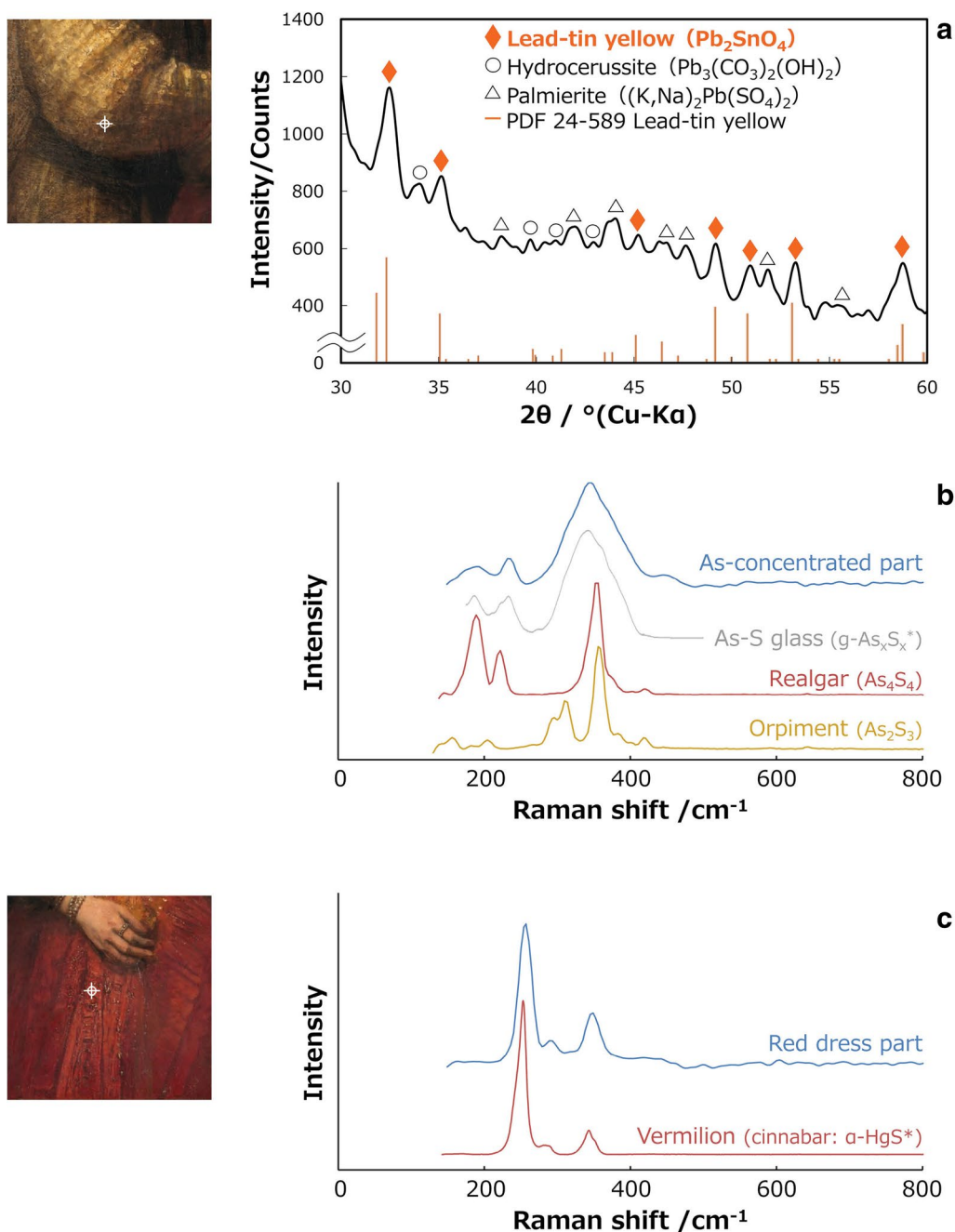
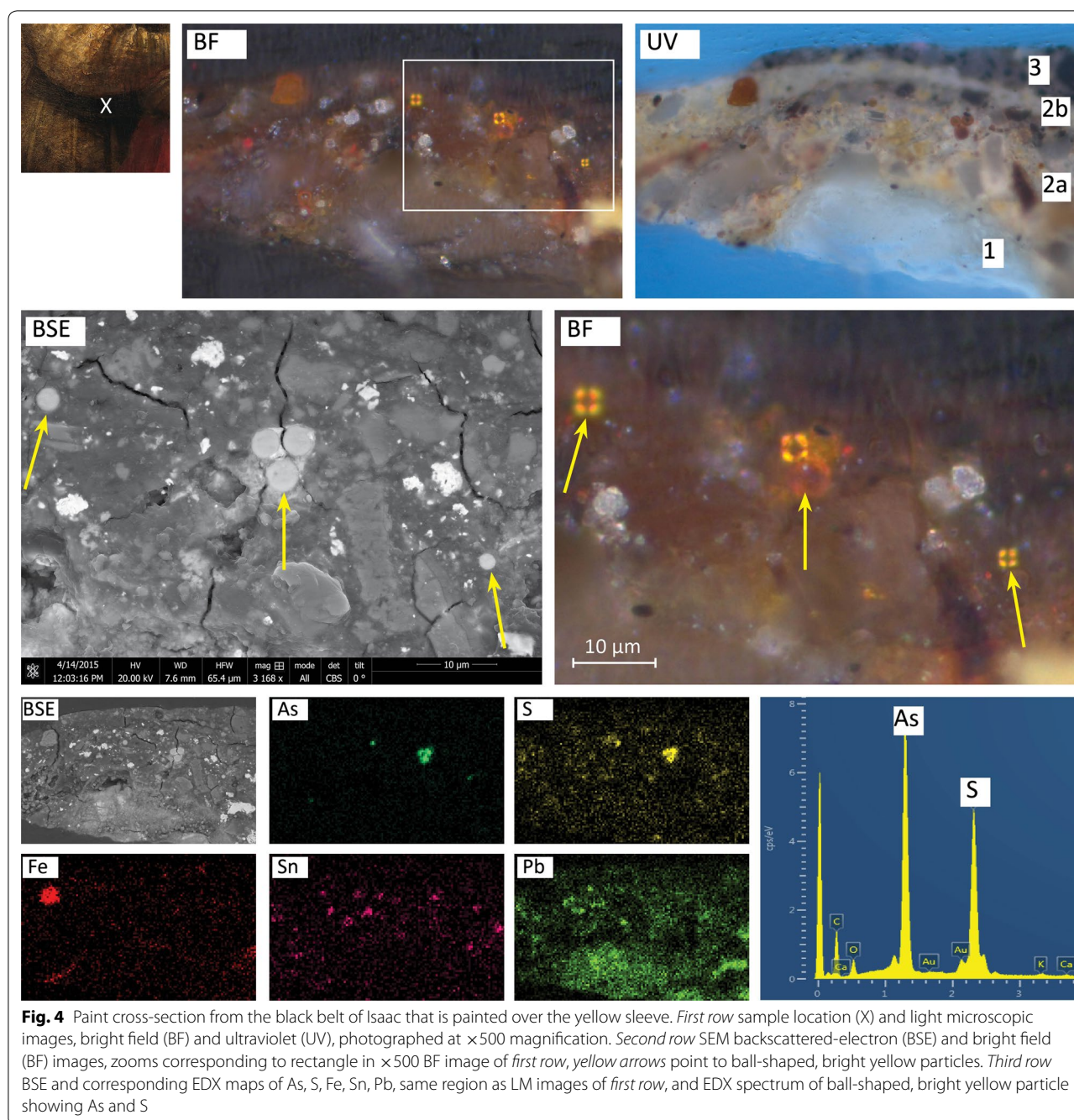


Fig. 3 XRD and Raman spectra of arsenic-rich spots from Isaac's sleeve (**a**, **b**), and Rebecca's dress (**c**)

It is noteworthy that approximately eight years ago, Rötter and Grundmann published an extensive, pioneering study about artificial orpiment and realgar [26]. Up until then, it was thought that only the natural form of orpiment and realgar were used in Old Master paintings, and that the synthetic form was not introduced until the end of the nineteenth century when wet-process methods were introduced using hydrogen sulfide

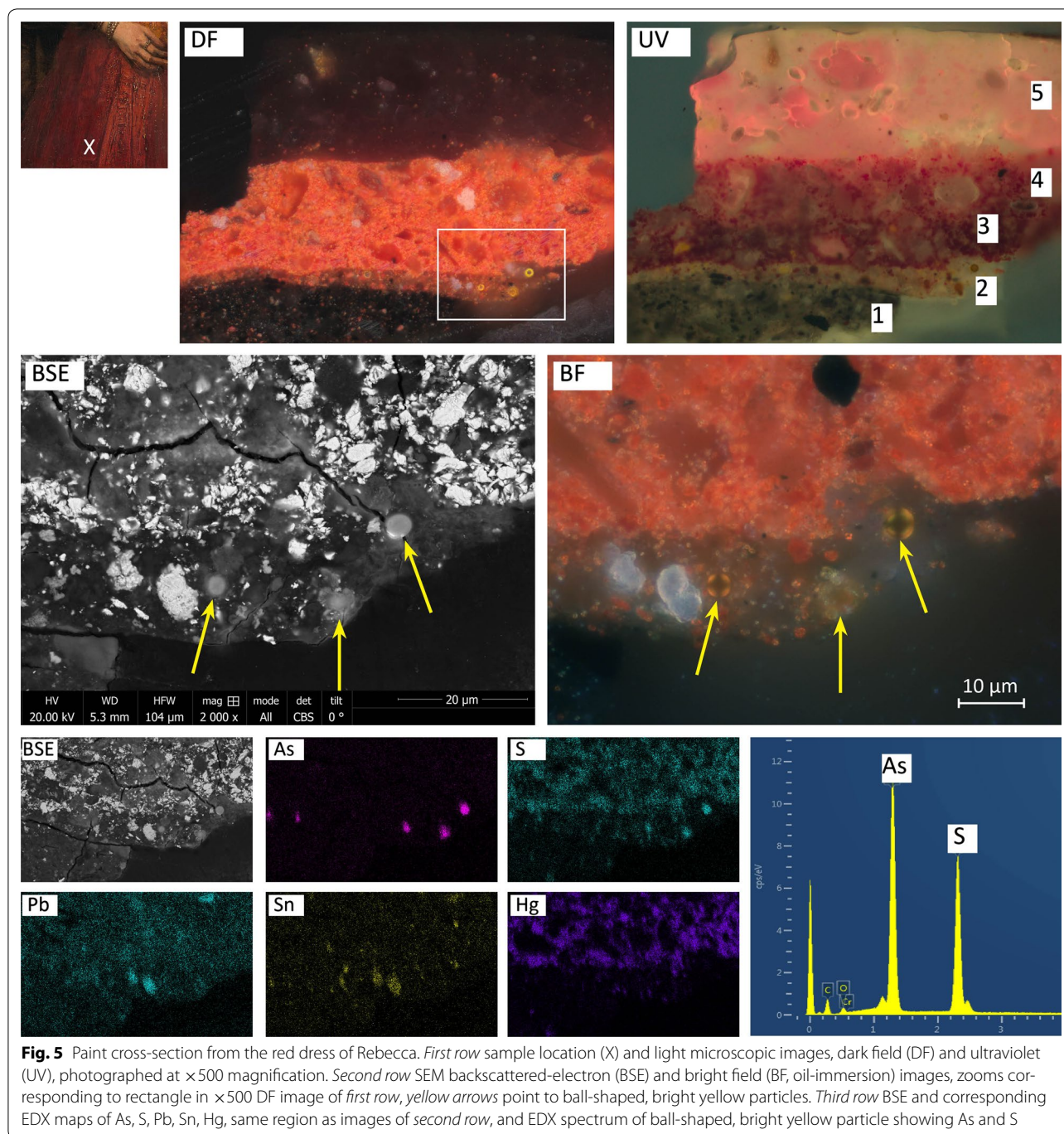
or thioacetamide. Rötter and Grundmann prepared synthesis products, which they analyzed, together with historical arsenic smelters, and historical samples of natural and artificial arsenic sulfide. Supported by historical sources (Cennino Cennini, Willem Beurs), they came to the conclusion that dry-process methods (burning/roasting and sublimation) were already used in the sixteenth century to refine the pigment,



starting from the natural product, the natural product and sulfur, or arsenolite and sulfur. Since then, artificial orpiment and realgar have been identified on several occasions in polychrome sculpture and Old Master paintings (see Table 1).

A recent, comparative study with MA-XRF and neutron activation autoradiography of Rembrandt's *Susanna and the Elders* from 1647 in Berlin indicated the presence of an As pigment in lower layers of Susanna's red cloak located at the right side of the painting [27]. In this

case no sample analysis was carried out and the passages of As-rich paint have been interpreted as part of a later revision by Joshua Reynolds [28]. During the same MA-XRF scanning campaign as *The Jewish Bride*, As-rich passages in the red tablecloth of Rembrandt's *The Syndics*, 1662 (Rijksmuseum Amsterdam) were encountered. This needs to be further researched, but it would appear at least that the presence of orpiment in *The Jewish Bride* is not a single case, but that artificial orpiment was used more frequently by Rembrandt.



Since arsenic sulfides do not have good drying properties in oil, that could not have been the reason for Rembrandt to add them to his paints. He also seems to have used the pigment exclusively in yellowish brown mixtures—for midtones, shadows and underlayers. It

must therefore have been the reflecting ability of orpiment to lift and brighten translucent brown mixtures that Rembrandt wished to exploit, similar to his use of yellow lake in brown mixtures. This is in keeping with the way Rembrandt uses other pigments to construct

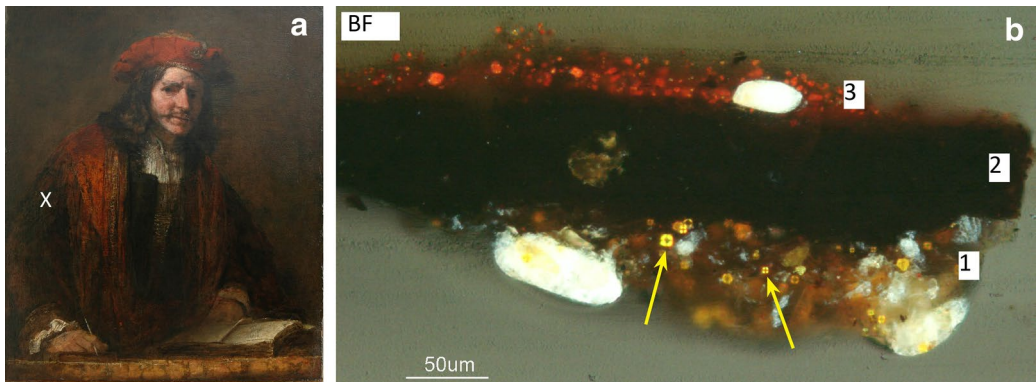


Fig. 6 Rembrandt (workshop?), *Man in a Red Cap*, c. 1660, oil on canvas (lined), 80 × 102 cm, Museum Boijmans van Beuningen, Rotterdam. Visible light image showing the sample location X (a), and light microscopic image of paint cross-section from the left sleeve (as seen from the front) (X) showing the presence of spherical particles of orpiment in the lower, yellowish brown paint layer (1), mixed with (discolored) smalt, lead-tin yellow and yellow earth (b)

Table 1 Identified occurrences of artificial orpiment or realgar in Old Master paintings/polychrome sculptures

Painting/sculpture	Sample location	References
Polychrome recumbent figure of St Alto, 16/17th C, Parish and Abbey Church St Alto, Altomünster, Bavaria	Orange–yellow ground of the gilding	Richter et al. [24]
Domenico Tintoretto, <i>Entry of Philip II into Mantua</i> (from the ‘Gonzaga Cycle’), 1579/80, Alte Pinakothek, Munich	Orange-colored clothing of the figure at the lower right of the painting	Grundmann et al. [33]
Jan Davidsz. de Heem (1606–1684), <i>Still life of Flowers and Fruit with Tazza and Birds</i> , Private Collection	Warm yellow of an orange	Wallert and Dik [34], Sheldon et al. [31]

warm translucent mixtures. In Rebecca’s red dress, however, the thin orangey brown underpaint containing orpiment was subsequently covered with two layers of vermilion (Fig. 5). His use of orpiment in fact goes against the numerous warnings at the time as according to the sources, orpiment was recommended exclusively for the final highlights, only to be applied after all paint had completely dried [29, 30]. And indeed orpiment is often found in highlights, for instance in still life paintings. Despite the warnings, there are a few occurrences of other artists, such as Aelbert Cuyp who employed natural orpiment or realgar in brown mixtures for shadows or half-shadows [31, 32]. Van Eikema Hommes and Van de Wetering in their essay about ‘Light and color in Caravaggio and Rembrandt, as seen through the eyes of their contemporaries’ mention that Rembrandt tried to reduce too strong contrasts in his paintings, in order to enhance the power of light by placing the strongest lights next to slightly less light colors and the deepest shadows to slightly less deep tones [22]. Adding orpiment to his half-shadow and shadow hues may have been a way to

harmonize the darker passages with the sparkling light areas to achieve a convincing overall light effect.

Conclusion

Combined MA-XRF, p-XRD, p-Raman, and cross-section analysis has led to the discovery of artificial orpiment glass pigment in *The Jewish Bride*: in the yellow sleeve of Isaac and the red dress of Rebecca. The use of a purified form of artificial orpiment glass in *The Jewish Bride* is not a single case, as the same pigment was already identified in paint cross-sections from Rembrandt (workshop?), *Man in a Red Cap* (Rotterdam).

MA-XRF imaging of *The Syndics* also demonstrated As-rich passages in the tablecloth, although this needs to be confirmed by cross-section analyses. We hope to encounter more examples of the use of artificial orpiment or realgar in works by Rembrandt or contemporaries in order to find out how widespread its use was. It may also help resolve questions of attribution. Its use is in keeping with Rembrandt’s experimental painting technique and his highly sophisticated use of materials to obtain his painterly effects.

Authors' contributions

AVL microscopic paint analysis, data interpretation related to Rembrandt's materials and painting technique, drafting manuscript; PN data interpretation related to Rembrandt's materials and painting technique; AK, GVDS, KJ, JD collection of MA-XRF data, MA-XRF data processing; YA, IN collection of portable XRD and RAMAN data, XRD and RAMAN data processing. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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