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Amorphous arsenic sulfide pigments and Raman spectroscopy – identifying production processes and characterizing elemental composition

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Abstract

This paper reports the dry and wet synthetic procedures and characterization by Raman spectroscopy of amorphous arsenic sulfide reference pigments. Reference spectra of two amorphous materials obtained by wet process methods and four dry process references of amorphous arsenic sulfide pigments of known composition are presented and discussed.

While all materials present a main band characteristic for the amorphous pigment centered on 341 cm^{-1} , additional small contributions indicate the presence of sulfur, arsenic oxide and crystalline nano phases embedded in the amorphous matrix. While only the main contribution is necessary to identify the arsenic sulfide as an amorphous material, the smaller additional features allow for the characterization of the various manufacturing processes and initial materials used. These small features also enable to assess the elemental composition of the studied amorphous arsenic sulfide pigment based on their relative intensity. In this context, the latter reference spectra were used to characterize the amorphous arsenic sulfide pigments and their arsenic to sulfur elemental composition in four 18th- to 20th-century historical samples and compared to SEM-EDX semi-quantitative analyses. The identification of the amorphous arsenic sulfide used in these historical samples was compared to the description of the manufacturing processes described in historical sources of the time allowing for a better understanding of the evolution of the amorphous arsenic sulfide pigments manufacturing methods.

Key words

Amorphous arsenic sulfide; Raman spectroscopy; Synthesis; Dry process; Wet process

1. Introduction

In the field of heritage science, the identification of artists' pigments found in works of art often requires comparisons with reference material data, especially for spectroscopic techniques.¹⁻⁶ However, due to the very limited number of arsenic-containing pigments, arsenic sulfide pigments (yellow orpiment, As_2S_3 ; and orangey-red realgar, As_4S_4) have often been identified based on the color of the arsenic-containing areas: orpiment was identified in yellow areas while realgar was to be expected in orangey-red zones.⁷⁻⁹ Nevertheless, the identification of pararealgar (As_4S_4), the yellow light-induced degradation product of realgar, made the identification solely based on elemental and color analysis rather difficult. With the presence of such compounds, arsenic-rich yellow areas would

not necessarily correspond to orpiment. Therefore, other analytical techniques such as x-ray diffraction or Raman spectroscopy were applied to the study of such pigments.^{10–12} In that regard, among the other techniques, Raman spectroscopy proved to be a method of choice for a quick and easy differentiation between natural orpiment and pararealgar, thus overriding the limitations of elemental analysis.^{13–15}

Despite being mentioned in artists' treatises as early as the 14th century,^{16,17} arsenic sulfide glasses, the artificial amorphous forms of arsenic sulfide pigments, were not identified in arsenic sulfide pigments characterization studies. Instead, most studies identified orpiment, realgar or pararealgar as being the arsenic sulfide pigments present.^{18–21} All three aforementioned pigments occur to be natural crystalline arsenic sulfide pigments with reference spectra available in spectral databases and scientific literature.^{22,23} Hence, the lack of identification of amorphous arsenic sulfide pigments in works of art may be due to the lack of reference materials to compare the result with as it may appear difficult to differentiate between the crystalline and amorphous forms based solely on microscopic and elemental techniques.²⁴

Nonetheless, in recent technical studies, optical and electronic microscopy allowed for the identification of amorphous arsenic sulfide pigments.^{25,26} The occurrence of such pigments was based on the presence of almost perfectly round bright-yellow particles with a diameter of 2–5 μm interpreted as a purified form of artificial orpiment glass obtained by dry processing as suggested by the pioneering research on amorphous arsenic sulfide by Grundman and Rötter.²⁷ In cases when samples mounted as cross-sections do not exhibit these almost perfectly round particles, Raman spectroscopy proved to be a powerful technique to highlight the presence of the arsenic sulfide amorphous material based on its characteristic vibrational signature, very distinct from its crystalline counterparts.²⁴ Therefore, in the past years, its positive identification was reported several times in art objects.^{24,26,28,29} However, most of these identifications are based on previously published so-called reference spectra for amorphous arsenic sulfides prepared in the laboratory.²⁴ While the amorphous nature of this reference material is not questioned, its purity, homogeneity and exact compositions remain unknown. Consequently, due to the increasing identification of amorphous arsenic sulfide in works of art, reliable reference spectra are becoming a requirement.

In this article, the authors report the Raman spectra and vibrational assignments of four pure homogeneous amorphous arsenic sulfide pigments synthesized by dry process and two amorphous pigments obtained by wet process. Based on the reference spectra obtained, dry-process amorphous arsenic sulfide was identified in four historical samples. While the amorphous arsenic sulfide references given in this paper allow for the identification of amorphous arsenic sulfide pigments in historical paint samples, the identification of the smaller secondary bands also give access to more information regarding the synthesis processes of the pigment identified in the same historical samples such as their composition or the initial materials used for their preparation.

To the best of our knowledge, this article reports for the first time in the field of heritage science the Raman spectra and vibrational assignments of four pure amorphous arsenic sulfide pigments of known compositions. Furthermore, the satellite bands recorded for the four references were used to positively estimate the arsenic and sulfur composition for four 18th-20th-century historical samples.

2. Materials and methods

a. Raw materials

Various compounds were considered as starting materials for the syntheses and references for the Raman characterization. These materials include commercially available natural orpiment (Kremer Pigmente GmbH & Co, Aichstetten, Germany) as well as metalloid arsenic, arsenic oxide and sulfur, all from Sigma-Aldrich (St. Louis, Missouri, USA).

b. Raman spectroscopy

Micro-Raman spectroscopy (μ -RS) spectra were acquired with a Renishaw inVia Raman microscope with a Peltier-cooled (203 K), near-infrared enhanced, deep-depletion CCD detector (576×384 pixels) using a high power 785 nm diode laser (Innovative Photonic Solutions, New Jersey, USA) in combination with a 1200 l/mm grating. The instrument was calibrated using a silicon wafer. Samples were analyzed using a 50x objective in a direct-coupled Leica DMLM microscope with enclosure. To avoid degradation or heat induced physical changes, the power on the samples was reduced to 0.3 mW with neutral density filters. A sample exposure time of 10 seconds (1 accumulation) was employed, resulting in an adequate signal-to-noise ratio. Spectra were acquired using the Wire 4 Raman software and were baseline corrected and normalized into the range [0,1] using the OriginPro 8 software.

c. Scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX)

Analyses were carried out using a Zeiss - EVO LS15 SEM equipped with an Oxford EDS detection system, all operated under variable pressure vacuum. Images, elemental maps and semi-quantitative analysis were recorded using an acceleration voltage of 15 kV, and 8 mm working distance. The accuracy of the EDX semi-quantitative analysis was assessed on the pure arsenic sulfide glasses of known composition used as standards. Data was collected and processed using the AZtecEnergy software system, v. 2.1 (Oxford Instruments).

d. Historical samples

For this study, arsenic sulfide pigments from four historical samples were investigated (Fig. 1a-d). One was taken on a French rococo Chinese-inspired oil painting, arbitrary untitled *Chinoiserie* (H1), which represents a couple walking in a garden (Fig. 1a). The arsenic sulfide was mixed with Prussian blue to obtain the desired green color of the landscape from where the sample was taken (Fig. 1e). The second sample (H2) comes from a Japanese leather paper or kinkarakawakami from the musée Charlier in Saint-Josse-ten-Noode in Belgium (Fig. 1b). In this sample, the yellow arsenic layer is found between the leather and metallic layers (Fig. 1f). Samples H3 and H4 were taken on two decorative panels of the Japanese tower found in Laeken, Brussels, Belgium (Fig. 1c-d). These samples present different application processes: sample H3 is found mixed with ultramarine blue in the paint underlayer (Fig. 1g) while sample H4 presents two successive layers of arsenic sulfide pigments of different tone (Fig. 1h). The upper layer, thinner, presents a brighter hue while the thicker deeper layer present a darker yellow tone (Figure 1.e). The four historical samples were prepared as embedded cross-sections in order to be analyzed.

To be cast as cross-sections, the loose samples were first fixed on a 1 cm³ poly(methyl methacrylate) (PMMA) cube using a white poly(vinyl acetate) (PVA) glue, after which the acrylic copolymer resin (Spofacryl[®], SpofaDental, Prague) was poured on the samples and a second PMMA cube placed on top and left to dry. Cross-sections were polished until the sample surface was exposed, first with wet polish and finished dry with Micromesh[®] polishing cloths up to 8 000 mesh (Scientific Instruments Services Inc., MN). Microphotographs were taken with an optical microscope Axio Imager 2 (Carl Zeiss, Oberkochen, Germany) with incident light and dark field with magnification up to 500 (Figure 1e-h).

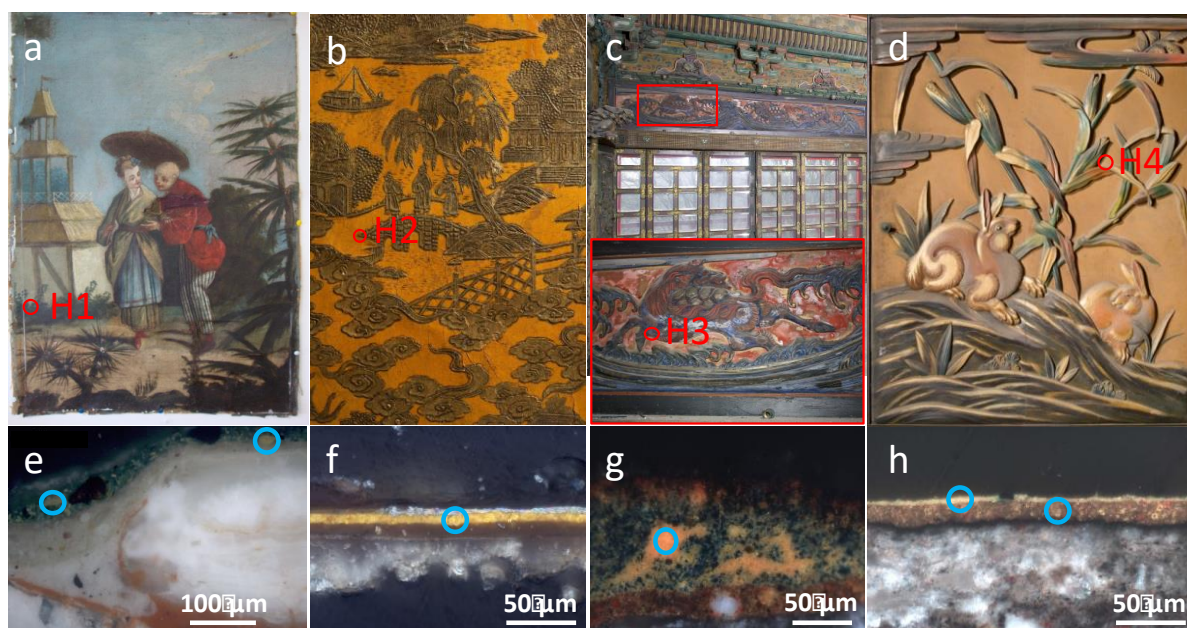


Figure 1. Photographs of (a) “Chinoiserie” (18th century), oil on canvas by an unknown artist (private collection), (b) Japanese wallpaper (ca. 1900), gilt leather paper by unknown artist (Musée Charlier, Brussels), (c-d) decorative panels from the Japanese tower (ca. 1900), mixed medium on wood by unknown artists (Royal Museums of Art and History, Brussels) in which the sampling locations are indicated (H1-H4). (e-f) correspond to the microphotographs of respective cross-sections under visible light showing the arsenic sulfide pigment. Location of Raman analyses are indicated by blue circles.

3. Results and discussion

- a. Synthesis and characterization amorphous reference materials
 - i. Melt/quench dry process

Due to the limited commercial availability and high prices of amorphous arsenic sulfide pigments, the synthesis of reference materials with various composition was undertaken. With the development and use of arsenic sulfide as a semiconducting material in the 20th century, industrial recipes corresponding to a melt/quench of arsenic and sulfur mixture are accessible.^{30–34} The obtained amorphous masses are very homogeneous and their compositions are easily tunable due to a full control of the experimental conditions, quantity and purity of the starting materials.

Following such procedures, four amorphous arsenic sulfides were synthesized: $g\text{-As}_{40}\text{S}_{60}$, $g\text{-As}_{34}\text{S}_{66}$, $g\text{-As}_{30}\text{S}_{70}$ and $g\text{-As}_{25}\text{S}_{75}$. These compositions were chosen for the variety in shades they offer, from bright yellow ($g\text{-As}_{25}\text{S}_{75}$) to orangey-red hues ($g\text{-As}_{40}\text{S}_{60}$) (Fig. 2).

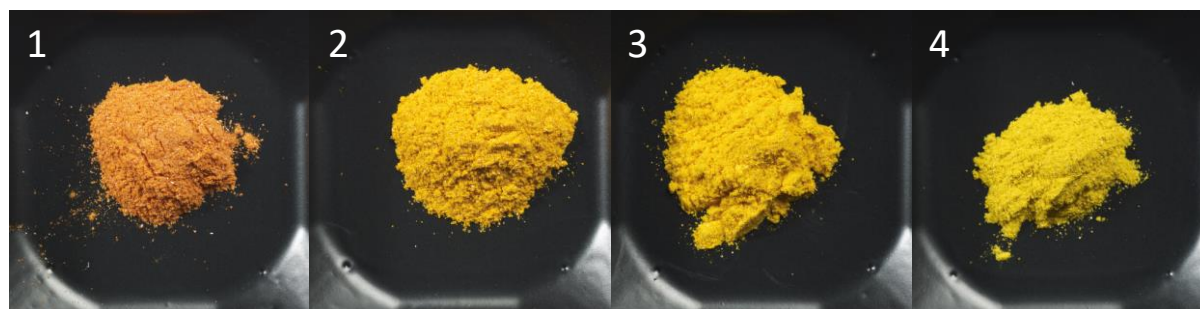


Figure 2. Photograph of ground (1) $g\text{-As}_{40}\text{S}_{60}$, (2) $g\text{-As}_{34}\text{S}_{66}$, (3) $g\text{-As}_{30}\text{S}_{70}$, (4) $g\text{-As}_{25}\text{S}_{75}$ produced by melt/quench dry process, showing the variation of hue from orange/red to bright yellow depending on the As/S ratios.

10 grams of each four chalcogenide glasses were prepared by standard melt-quenching method.^{30,35} High purity (5N) arsenic and sulfur, which amounts were calculated according to Equations 1 and 2, were loaded into a cleaned quartz ampoule. The ampoule was evacuated (~10⁻³ Pa) and sealed. The reagents were melted in a rocking tube furnace at 800 °C for 48 h. Subsequently the ampoule with melted glass was quenched in cold water and the amorphous masses collected.

The required masses of sulfur and arsenic necessary for the synthesis of 10 grams of each glass as well as the final mass of chalcogenide glasses and reaction yields are given in Table 1.

$$m_{As} = \frac{\text{mass of the final product (g)}}{M_{As} \times \%_{As} + M_S \times \%_S} \times \%_{As} \times M_{As} \quad (\text{Eq. 1})$$

$$m_S = \frac{\text{mass of the final product (g)}}{M_{As} \times \%_{As} + M_S \times \%_S} \times \%_S \times M_S \quad (\text{Eq. 2})$$

$M_{As} = 74.9216 \text{ g.mol}^{-1}$; $M_S = 32.06 \text{ g.mol}^{-1}$

$\%_{As}$ and $\%_S$: percentages of arsenic and sulfur in the final products

The Raman spectra obtained of the four amorphous arsenic sulfide glasses are presented in Figure 3 (1-4) along with the Raman spectra of natural orpiment (5), sulfur (6) and arsenic oxide (7) reference materials. The main bands wavenumbers, relative intensities and vibrational assignments for all compounds can be found in Table 2.

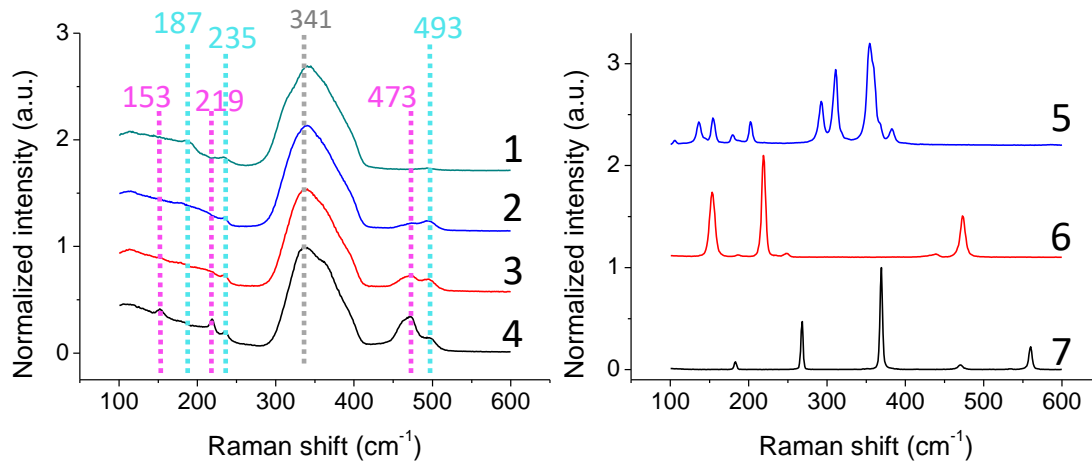


Figure 3. Raman spectra of (1) $g\text{-As}_{40}\text{S}_{60}$, (2) $g\text{-As}_{34}\text{S}_{66}$, (3) $g\text{-As}_{30}\text{S}_{70}$, (4) $g\text{-As}_{25}\text{S}_{75}$, (5) natural orpiment, (6) sulfur and (7) arsenic oxide references and the photographs of all four ground arsenic sulfide glasses analyzed (1-4). For the arsenic sulfide glasses (1-4), Raman bands characteristic for sulfur are indicated in magenta while the bands characteristic for realgar-like nano phases are indicated in cyan color.

From the Raman spectra, it appears clear that the amorphous arsenic sulfide pigments (1-4 in Fig. 3) present vibrational signatures different from the natural orpiment (5 in Fig. 3). All spectra are

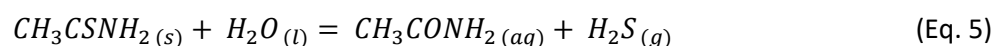
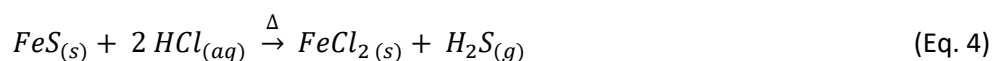
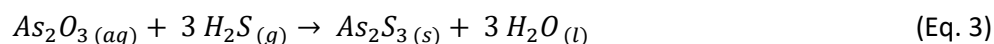
characterized by a broad band centered around 341 cm⁻¹ corresponding to the symmetric stretching vibration mode of AsS_{3/2} structural units.³⁶ Additional minor bands are found at 153, 187, 219, 235, 473 and 493 cm⁻¹. The bands at 153, 219 and 473 cm⁻¹ increase when larger amounts of sulfur are found in the final glass products and, as suggested by the Raman spectrum of sulfur reference (6 in Fig. 3), these bands correspond to free sulfur present in the non-stoichiometric materials. However, the bands at 187, 235 and 493 cm⁻¹ do not depend on the material composition and cannot be associated with excess free sulfur. The contribution at 187 cm⁻¹ is only visible for the g-As₄₀S₆₀ (1 in Fig. 3) while similar contribution intensities at 235 and 493 cm⁻¹ are observed for the three other compositions (2-4 in Fig. 3) but not in spectrum 1. These three contributions are attributed to As-As bending modes in realgar-like nano phases, the latter being crystalline structures included in the glassy matrix.^{31,36,37} These bands are often related to the experimental setup such as the raw materials used, the temperature program or the quenching temperature.³⁸ The differences observed for the reference materials can be explained by the use of different raw materials for g-As₄₀S₆₀ whereas the same materials were used for the three other amorphous glasses.

In characterization study of arsenic sulfide pigments, the satellite bands described here can be used as indicators regarding the composition and intended color of the amorphous pigment found in works of art. They can also be used to differentiate different batches of amorphous pigments used in the same artwork or series. However, conclusions can be difficult when the amorphous arsenic sulfide is found in small quantity or mixed with other pigments.

ii. Wet process

In the 19th and later in the early 20th century, several sources describe the preparation of amorphous arsenic sulfide materials through wet process chemistry.^{39,40} This novel method was made available through the development of wet chemistry in the end of the 19th century. For this synthesis process, a hydrochloric solution of arsenic trioxide is treated with a stream of hydrogen sulfide. The result will be a bright yellow amorphous precipitate that can be used as an artist pigment (Eq. 3).

One of the source of hydrogen sulfide is the mineral pyrite (FeS). The latter decomposes into the iron (II) chloride brown solid (FeCl₂) and gaseous hydrogen sulfide when placed in a 6N hydrochloric solution and heated over a Bunsen burner (Eq. 4). However, the H₂S gas produced need to be transported through the delivery tube of a Kipps' apparatus to the arsenic oxide solution in order to form the yellow sublimate (Eq. 3). Therefore, other hydrogen sulfide sources can be used. Thioacetamide (CH₃CSNH₂), an organosulfur compound, has been used due to the easy production of hydrogen sulfide when present in aqueous solutions (Eq. 5). It offers the advantage of producing the hydrogen sulfide gas directly in the 6N hydrochloric solution of arsenic trioxide and form *in situ* the bright yellow amorphous arsenic sulfide according to Eq. 3.



The yellow precipitate produced in both procedures corresponds to fine amorphous arsenic sulfide particles which require filtering and rinsing to eliminate traces of residual arsenic oxide. This latter operation may explain the observation made in the 19th century which reported the wet chemistry arsenic sulfide to be purer than the one obtained by melt or sublimation for which the arsenic oxide was considered to be the colorless matrix.^{25,41}

When analyzing the final product of both preparation methods with Raman spectroscopy, it appears clear that both compounds are amorphous arsenic sulfide materials based on their broad Raman scattering band centered on 341 cm⁻¹ (Fig. 4). However, when obtained with pyrite, small bands at 185,

269, 371 and 562 cm^{-1} (spectrum 1) suggest the presence of arsenic oxide remnants. Such presence is most likely due to an incomplete purification and elimination of the arsenic oxide excess by means of filtration. However, due to the preparation process which does not require the intervention of high temperature or quenching, no realgar-like nano phases are observed for the amorphous arsenic sulfide pigment obtained as suggested by the lack of Raman bands at 187, 235 and

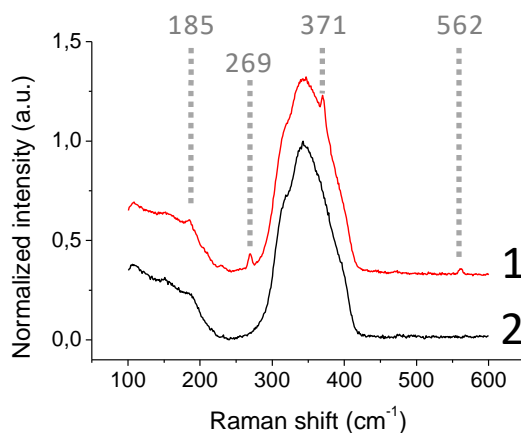


Figure 4. (a) Photograph of amorphous arsenic sulfide produced through bubbling of FeS-induced H_2S in an arsenic oxide solution and (b) Raman spectra of amorphous arsenic sulfide produced by wet chemistry using 1) FeS and 2) thioacetamide as source of H_2S .

b. Historical samples

Arsenic sulfide pigments were identified and localized in various historical samples based on the presence of arsenic and sulfur in elemental analysis (Fig. 5). Due to the yellow color of the pigment particles, natural orpiment is expected. However, it remains difficult to conclude on the nature of arsenic sulfide pigments based on microscopic and elemental analyses only as the simultaneous presence of arsenic and sulfur may correspond to several arsenic sulfide pigments. Therefore, due to the distinctive vibrational signatures of arsenic sulfide pigments,^{21,24,42–44} Raman measurements on the arsenic sulfide particles were undertaken (Fig. 6).

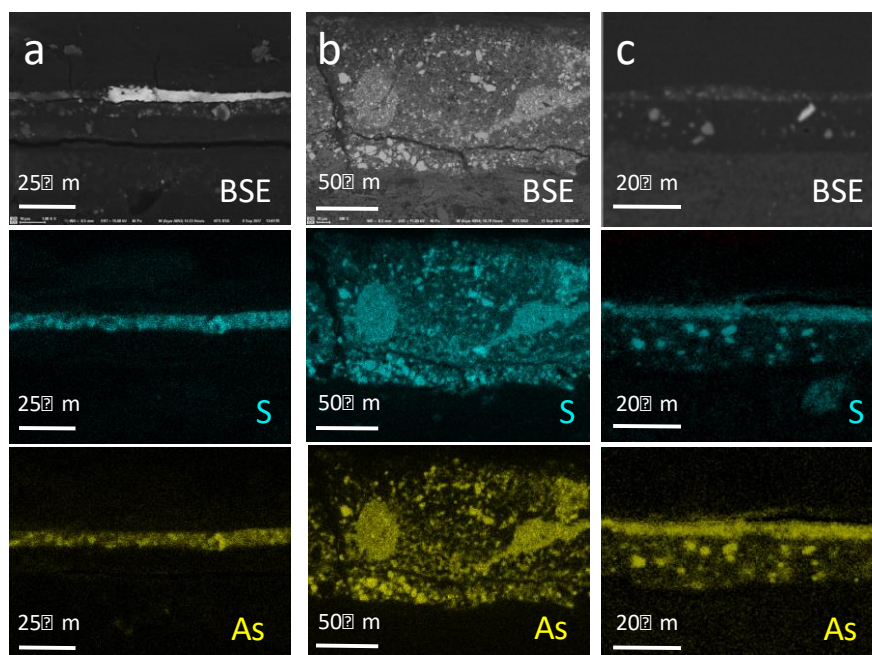


Figure 5. Backscattered electron images of (a) H2, (b) H3 and (c) H4 samples and their respective SEM-EDX analysis highlighting the use of arsenic sulfide pigments in the yellow-containing areas.

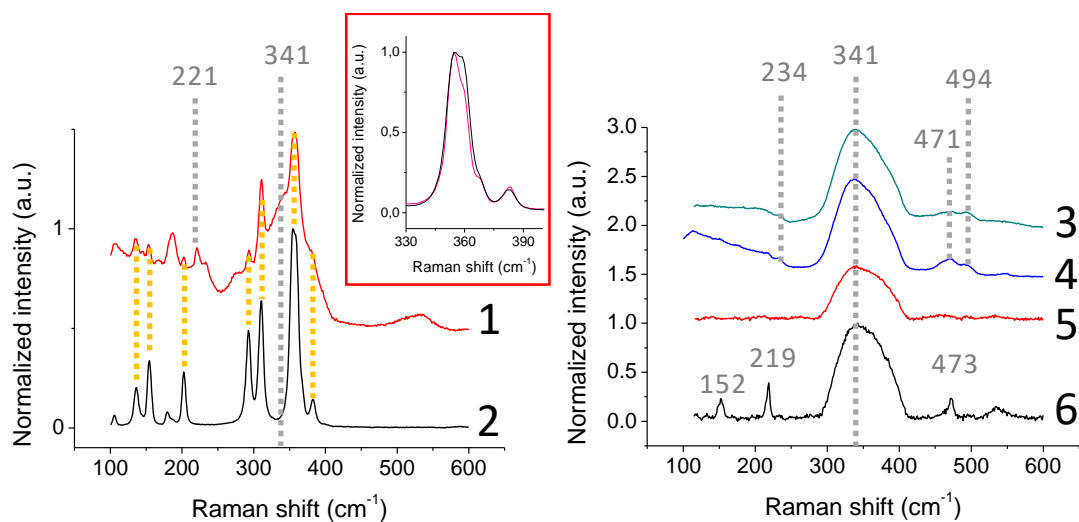


Figure 6. Raman spectra of the arsenic sulfide particles from (1 and 2) the French Chinoiserie (H1), (3) the Japanese wallpaper (H2), and (4, 5 and 6) the decorative panels from the Brussels's Japanese tower (H3 and H4). Insert corresponds to the 330-400 cm^{-1} area of spectrum 2 presenting the increased 359 cm^{-1} contribution compared to unaltered natural orpiment (black spectrum).

Sample H1 distinguishes itself from the other three analyzed samples by the presence of sharp bands characteristic for crystalline arsenic sulfides (yellow dotted lines in spectra 1 and 2 in Fig. 6). However, if spectrum 2 presents the unambiguous signal of natural orpiment, spectrum 1 appears more complex. In addition to the sharp bands of crystalline orpiment, the spectrum looks broaden around 341 cm^{-1} , which indicates the presence of amorphous arsenic sulfide along with crystalline orpiment. The simultaneous presence of both compounds in H1 may suggest an incomplete melt or sublimation of crystalline natural orpiment into the amorphous form of the pigment. Such sublimation processes

were known in medieval time for the preparation of artificial pigments such as vermilion, for which mercury and sulfur were heated together.^{45–47} However, vermilion was not the only pigment produced by sublimation processes.⁴⁸ The dry process preparation of amorphous arsenic sulfide pigments has been described in several artists' treatises such as *Experimenta de coloribus* (Jehan Le Begue, 15th century) or the *Paduan Manuscript* (author unknown, 16th century).^{17,45,48} In these manuscripts, the authors often describe how to melt natural orpiment alone or mixed with a sulfur source (described as "powdered red sulfur" in Jehan Le Begue's manuscript) in order "to make a most beautiful orange yellow color".¹⁷ The sulfur added to the mix is most likely used to modify the hue of the final product as a greater amount of sulfur will lead to a brighter yellow tone (Figure 2) or allowing a purer orpiment to be produced.⁴⁹ Once cooled down, the amorphous material can be conserved and ground when needed. The occurrence of sulfur in H1 (band at 221 cm⁻¹) tends to indicate that sulfur was most likely added to the crystalline pigment to brighten its hue as described in the medieval recipes.

Similar Raman results have previously been observed for arsenic sulfide pigments identified on 13th-century Portuguese illuminated manuscripts.⁵⁰ While the authors identified the amorphous arsenic sulfide as a degradation product of the orpiment, the heat required to transform orpiment into amorphous arsenic sulfide tends to suggest a similar uncomplete sublimation of natural orpiment rather than a degradation product. A similar process has previously been identified in 18th-century Dutch painting in which the artificial arsenic sulfide was identified by Raman spectroscopy as partially sublimed pararealgar.⁵¹

Arsenic oxide, a common degradation product of natural orpiment,^{48,52,53} was not identified by means of Raman spectroscopy in the pigments particles of H1. However, a broadening of the main band of orpiment due to an increase of the 359 cm⁻¹ band contribution (Figure 6 insert) suggests that the natural orpiment has been subjected to light alteration.⁵⁴ Nonetheless, such modification is not observed for the natural orpiment contribution found along the amorphous arsenic sulfide. This further strengthens the greater stability of amorphous arsenic sulfides compared to the natural crystalline forms – at least in the initial degradation phase – as already highlighted in previous research.^{42,55}

Samples H2, H3 and H4, do not present the characteristic bands for crystalline arsenic sulfide. Instead, they present a main broad band centered on 341 cm⁻¹, very similar to the Raman signatures of the pure reference materials presented in Figure 3. Spectra 3 and 4 (samples H2 and H3, Fig. 1f and 1g) present satellite bands at 234, 471 and 494 cm⁻¹, while spectrum 6 (upper bright yellow layer in sample H4, Fig. 1h) presents sharp bands at 152, 219 and 473 cm⁻¹. No significant satellite bands are observed in spectrum 5 (darker layer in sample H4, Fig. 1h). While the 234 and 494 cm⁻¹ satellite bands in spectra 3 and 4 suggest realgar-like nano phases, their 471 cm⁻¹ band and the sharp contributions observed for spectrum 6 correspond to sulfur remnants. All bands indicate amorphous arsenic sulfide obtained by dry process. The presence of sulfur in these samples indicates the use of sulfur in the dry process synthesis. However, it remains difficult to conclude on the nature of the arsenic source used as being metalloid arsenic or arsenic oxide. Nevertheless, similar dry processes involving sublimation or melt/quench of arsenic oxide and sulfur are found in 18th-century historical literature.^{56,57} In these treatises, it was advised to mix together sulfur with a powder arsenic (also described as white arsenic, which could correspond to arsenic oxide but or small pieces of metalloid arsenic) and sublimate the mixture. The achieved materials are described as never as perfect and beautiful as the crystalline form found in nature.⁵⁷ From these treatises, it appears that pigments manufacturer were aware that the quantity of sulfur contained in the final material had an influence on its hue as observed during the dry process manufacturing procedure. The absence of satellite bands observed for spectrum 5 may indicate a different synthetic process than the ones used for the other samples. A similar profile – without realgar-like nano phases or sulfur remnants – is also observed for the amorphous arsenic sulfide obtained by wet process (spectrum 2 in Fig. 4). This may represent the first occurrence of wet-process arsenic sulfide in works of art. However, all amorphous arsenic sulfide obtained by wet process is described as very fine (0,4-1 μm in diameter)^{27,52}, which does not appear to be the case for H4 (Fig.

5.c). The lack of realgar-like nano phases may just inform that this particular amorphous arsenic sulfide was obtained following different experimental procedures than the other pigments analyzed.

If the satellite bands can inform on the experimental conditions and starting materials, they can also be used to roughly extrapolate the composition of the pigment materials. To do so from the Raman spectrum, it is required to calculate the band intensity ratios of sulfur contribution at 471 cm^{-1} (I_{471}) to the intensity of the main Raman contribution at 341 cm^{-1} (I_{341}). Because $g\text{-As}_{40}\text{S}_{60}$ is the stoichiometric material, no sulfur band at 471 cm^{-1} is observed and can therefore not be used in this calculation method. The ratios values for the three other reference materials are calculated to be 0.336, 0.190 and 0.079 respectively for $g\text{-As}_{25}\text{S}_{75}$, $g\text{-As}_{30}\text{S}_{70}$ and $g\text{-As}_{34}\text{S}_{66}$. These results support the previous observation that the more sulfur the greater the 471 cm^{-1} contribution. A calibration curve and its linear regression equation are calculated and presented in Figure 7. The simple regression equation and 0.99979 R^2 coefficient also demonstrate that the intensity of the sulfur band at 471 cm^{-1} is proportional to the proportion of arsenic contained in the final material and that it can therefore be used to extrapolate the composition of the amorphous arsenic sulfide pigments found in historical samples.

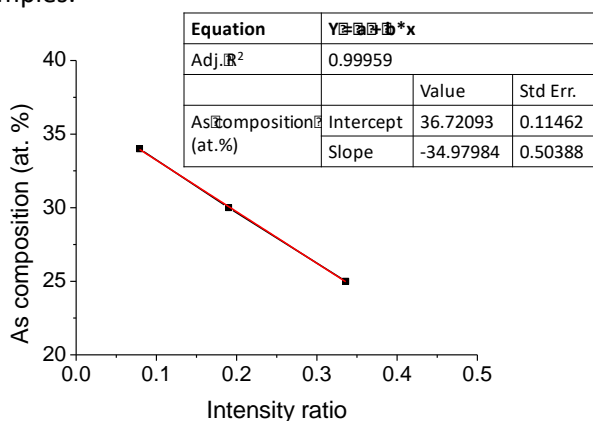


Figure 7. Arsenic composition as a function of I_{471}/I_{341} ratio intensity for amorphous arsenic sulfide reference materials (black line) and its linear regression (red line).

The I_{471}/I_{341} ratios for H2, H3 and H4 (both in the superior and inferior layers) have been calculated (respectively 0.161, 0.183, 0.082 and 0.201) and, combining them with the linear regression equation obtained from the reference materials (Figure 7), the atomic percentage of As and S are deduced. Through this methodology, the amorphous arsenic sulfide contained in H2, H3 and H4 should respectively be around 31.09 at.%, 30.32 at.%, and 33.85 at.% (for the dark bottom layer) and 29.69 at.% (for the bright upper layer). These values compared well with the SEM-EDX semi-quantitative analyses performed on the same samples, which reads respectively 30.14 ± 1.79 , 29.35 ± 2.36 , 34.82 ± 1.79 and 29.23 ± 1.85 . All I_{470}/I_{340} ratios, corresponding compositions and SEM-EDX quantifications are summarized in Table 3. This clearly show that Raman analysis of amorphous arsenic sulfide pigments can also give information on the elemental composition of the materials, without necessarily using SEM-EDX semi quantitative analyses. However, it is important to keep in mind that clean Raman spectra are needed to extrapolate the material composition as an important background/distorted spectrum may induce a wrong I_{471}/I_{341} ratio and *de facto* a wrong composition calculation.

4. Conclusions

Identification of amorphous arsenic sulfide in works of art is not as straight forward as it may seem. It often requires a multi-analytical approach, which includes microscopic and spectroscopic techniques.

However, in recent studies, Raman spectroscopy has allowed to characterize amorphous arsenic sulfide pigment based on its As-S-As stretching vibration in $\text{AsS}_{3/2}$ structural units. Most studies used a previously published reference spectrum for amorphous arsenic sulfide as reference materials and Raman spectra that can be used to compare the historical samples remain scarce. Even though the amorphous nature of this reference material is not contested, its unknown composition and homogeneity make it non-fully trustworthy for further investigations. Therefore, more homogeneous and reliable references were required due to the steady Raman-based identification of amorphous arsenic sulfide pigments in works of art. This article fills this gap by reporting the Raman spectra of four dry-process homogeneous amorphous arsenic sulfide pigments of known composition along with the Raman spectra of two wet-process pigments. The article also investigates the various dry- and wet-process synthesis procedures available through times to better understand the possible preparation of arsenic sulfide pigments found in works of art, applying it to amorphous arsenic sulfide found in three 18th to 20th-century decorative objects.

While the main Raman broad band at 341 cm^{-1} is enough to conclude on the amorphous nature of the arsenic sulfide pigment, the satellite bands provide information on the materials used and the preparation conditions, such as the use of sulfur or arsenic oxide in excess or the dry-preparation when realgar-like nano-phases are found in the amorphous material.

Furthermore, when working on high signal-to-noise ratio, well-baselined Raman spectra, the ratios for the sulfur contribution at 471 cm^{-1} to the amorphous pigments $\text{AsS}_{3/2}$ contribution at 341 cm^{-1} provide information regarding the As/S ratios without requiring access to SEM-EDX semi-quantitative analyses. This can be very useful to explain various shades of arsenic sulfide pigments within one object as well as to potentially differentiate between various manufacturers or pigment batches.

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Tables

Table 1. Summary of the arsenic and sulfur masses used for the preparation of the arsenic sulfide glass, the mass of the final products and the yields of the reaction.

Glass	m_{As} (grams)	m_S (grams)	m_{g-AsS} (grams)	Yield (%)
g-As ₂₅ S ₇₅	4.3785	5.6215	9.76	97.6
g-As ₃₀ S ₇₀	5.0035	4.9965	9.71	97.1
g-As ₃₄ S ₆₆	5.4625	4.5375	9.88	98.8
g-As ₄₀ S ₆₀	6.0906	3.9094	9.86	98.6

Table 2. Raman shifts and vibrational assignments for natural orpiment, arsenic sulfide glass, arsenic oxide and sulfur.

Raman shift (cm ⁻¹)	Intensity	Vibrational assignment
Arsenic sulfide glass ³⁷		
233	w	Realgar-like nano phase
341	vs, br	As-S-As stretching vibration in AsS _{3/2}
495	w	Realgar-like nano phase
Natural orpiment (As ₂ S ₃) ²²		
106	vw	Unknown
136	w	Bending pyramids AsS _{3/2}
154	m	Skeletal deformation
179	w	Bending pyramids AsS _{3/2}
203	m	Symmetric stretching of As-S-As bridges
293	s	Symmetric stretching of pyramids AsS _{3/2}
311	vs	Asymmetric stretching of pyramids AsS _{3/2}
355	vs	Stretching of pyramids AsS _{3/2}
384	m	Asymmetric stretching of As-S-As bridges
Sulfur		
152	w to vw	
218	w to vw	
471	w to s	
Arsenic (III) oxide (As ₂ O ₃)		
183	sm	As-O-As bending vibration
268	s	As-O-As wagging vibration
369	vs	As-O-As bending vibration
470	s	As-O stretching vibration
560	m	As-O stretching vibration

w, m, s = weak, medium, strong; v = very, sh = shoulder, br = broad

Table 3. I_{471}/I_{341} ratios (references and historical samples) and associated Raman-based extrapolated arsenic and sulfur compositions (for historical samples only) compared with the SEM-EDX semi-quantitative composition (in atomic %) of the same particles identified in historical samples (H2, H3 and H4).

	Raman			SEM-EDX	
	I_{471}/I_{341}	Extrapolated As (at. %)	Extrapolated S (at. %)	Measured As (at. %)	Measured S (at. %)
References					
g-As ₃₄ S ₆₆	0.079	-	-	34	66
g-As ₃₀ S ₇₀	0.190	-	-	30	70
g-As ₂₅ S ₇₅	0.336	-	-	25	75
Historical samples					
H2	0.161	31.09	68.91	30.14 ± 1.79	69.86 ± 1.79
H3	0.183	30.32	69.68	29.35 ± 2.36	70.65 ± 2.36
H4 – lower dark layer	0.082	33.85	66.15	34.82 ± 1.79	65.18 ± 1.79
H4 – upper bright layer	0.201	29.69	70.31	29.23 ± 1.85	70.77 ± 1.85