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Assessing the stability of arsenic sulfide pigments and influence of the binding media on their degradation by means of spectroscopic and electrochemical techniques

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Abstract

In this paper, we used the semiconducting and lightfastness properties of arsenic sulfide pigments to study their stability by means of electrochemical and microfadometric techniques. A combination of these techniques show that in the early stage of the degradation process, amorphous arsenic sulfides are more stable than both crystalline forms, while upon longer exposure time, amorphous pigments will fade more than both natural pigments, making it less suitable. While the stability study was carried out on unbound pigments, the influence of the organic binder on the relative degradation of the arsenic sulfide pigments was investigated through a multi-analytical approach on pigment/binder mock-up paint samples. For this purpose, the formation of arsenic trioxide was assessed by micro Fourier transform infrared (μ -FTIR) spectroscopy while the influence of the binder on the formation of sulfates was studied by means of synchrotron radiation X-ray near edge structure (μ -XANES). Both techniques elucidate a higher stability of all pigments in gum arabic while the use of egg yolk as binder leads to the most degradation, most likely due to its sulfur-rich composition. In the context of the degradation of arsenic sulfide pigments, other binders such as animal glue, egg white or linseed oil show an intermediate impact.

Keywords: Arsenic sulfide pigment; Stability; Pigment degradation; μ -FTIR; XANES; Electrochemistry

1. Introduction

Arsenic sulfide pigments such as natural orpiment (As_2S_3 ; golden yellow), natural realgar (As_4S_4 , As_2S_2 or AsS ; orange-red) or their amorphous forms ($\text{g-As}_x\text{S}_{100-x}$; color varying from bright yellow to red depending on the relative amount of sulfur and arsenic in its composition) have been identified as artists' pigments in works of art from antiquity until the early 20th century [1–6]. Even though only identified in works of arts in the past decades, artificial arsenic sulfides have been known for centuries and their existence has been described as early as the 14th century by Cennino Cennini in his *Libro dell'arte* as well as in other painting manuscripts [7,8].

In art objects, natural and artificial arsenic sulfide pigments have been found mixed in various binding media, ranging from polysaccharide-based gum arabic to protein-based or oil-containing binders [2,4,9,10]. One of their main characteristics, extensively described in manuscripts and

painters manuals, is their light sensitivity leading to the formation of white arsenic trioxide (As_2O_3); the latter being often identified in artworks [8,11–15] and to some extent, to arsenate [9,16]. This chemical transformation leads to a global loss of color and transparency of the pictorial layer [17] and is described as a light fastness phenomenon. While arsenic trioxide and arsenate ions are identified as two of the degradation products of the natural pigments [9,16,18], these products are often not associated with the degradation of the amorphous pigment due to the lack of corresponding contribution with vibrational techniques [3,4,16,19,20]. This lack of reported degradation products leads to the, hitherto unfounded, assumption that the amorphous compounds featured a higher chemical stability than their crystalline equivalents.

Furthermore, in art works, arsenic sulfide pigments appear to behave differently depending on the medium in which they are bound: while degradation products have been mostly observed in oil-based painted artifacts [9,16,18], they are rarely encountered in polysaccharide-based paintings such as in illuminated manuscripts [21–24]. Even though both these types of artifacts may not be subjected to similar aging conditions due to their different support, it would not be unusual to find both type of objects in a museum environment and therefore exposed to similar lightning or relative humidity conditions. Therefore, questions regarding the influence of the binding medium on the degradation of these pigments, both natural and artificial, were raised and it appears then relevant to study the influence of the binding medium on the comparative degradation of both crystalline and amorphous arsenic sulfide pigments. Even though the molecular interactions between the arsenic sulfide pigments and the binders are of great interest, the lack of access to instrumental techniques necessary for such research did not permit to investigate this further. As a result, this research only assessed the relative influence of the binder on the degradation process of the pigments.

This work investigates the stability of pigments to light using electrochemical and spectroscopic methods. In recent years, electrochemistry has proven itself to be a valuable tool to quickly assess the stability of semiconducting pigments such as vermilion (HgS) or minium (Pb_3O_4) by measuring the photocurrent induced by monochromatic light illumination [25–27] and was applied here to arsenic sulfide pigments. The electrochemical study was paralleled with microfadometry, which allows foreseeing the long-term color fate of the pigments. Due to the different color exhibited by the various pigments, it is important to bear in mind that they will absorb different fraction of light. However, in this study, they will be exposed to the same laser and/or Xenon lamp making it possible to compare their stability toward light illumination. Working on unbound powders, the influence of the binder as well as its discoloration during the artificial light-aging is avoided in the first part of the study. Nonetheless, the influence of the binding medium on the degradation of arsenic sulfide pigments has been further investigated. However, the electrochemical technique is not yet optimized for the examination of pigment/binder mixtures due to (a) the lack of intimate contact between binding medium-embedded pigment particles and the electrode and (b) the sensitivity of water-based binders to the aqueous electrolyte. Consequently, in this work, the influence of the binder on the degradation was studied by means of micro Fourier transform infrared spectroscopy (μ -FTIR) and micro x-ray absorption near edge structure (μ -XANES) at the sulfur K-edge on aged pigment/binder mock-up paint samples. Indeed, according to previous research, the expected degradation products for orpiment, realgar and amorphous arsenic sulfide pigments all include sulfate ions (SO_4^{2-}) and As_2O_3 , [9,16,28–30]. Therefore, arsenic trioxide formation was assessed with μ -FTIR while the formation of sulfate ions was followed by means of μ -XANES measurements at the sulfur K-edge.

2. Material and methods

2.1. Reference samples

Natural orpiment (As_2S_3), natural realgar (As_4S_4), both from Kremer Pigmente, Germany, and laboratory-synthesized amorphous arsenic sulfides of known composition (g- $\text{As}_{30}\text{S}_{70}$, g- $\text{As}_{34}\text{S}_{66}$ and g- $\text{As}_{40}\text{S}_{60}$) were used as pigment references in this study. The composition of the commercially available pigments was verified using x-ray diffraction (ref instrument, SI) and small amount of arsenic oxide was found along natural orpiment and natural realgar. Amorphous arsenic sulfide pigments of known composition were synthesized by a melt/quench dry technique [31,32], allowing a complete transformation of the initial materials (5N purified sulfur and arsenic) and therefore to tune the composition of the final material. Their composition was confirmed by semi-quantitative scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX).

Mock-up samples were prepared by mixing the ground pigment together with binders such as gum arabic, egg yolk or white, glue or pre-polymerized linseed oil in a 1 to 1 mass ratio. The pigment/binder mixtures were applied on microscope pre-cut polycarbonate slides in 100 μm thickness layers using a ZUA 2000 Universal Applicator (Zehntner GmbH, Switzerland) and let to dry, especially allowing the curing of the linseed oil mock-up paint samples. All mock-ups were prepared in triplicates. After curing, one set was artificially aged for 20 weeks in Atlas Suntest CPS+ aging chamber (Atlas Material Testing Technology LLC, IL, USA) under a 650 W/m^2 and 175000 lux Xenon lamp. Temperature and relative humidity (RH) of the aging conditions were not tunable and were measured to be ca. 35°C and 18% RH. These values appear quite far from real environmental exposure conditions (18-25°C and 45-60% RH) but suitable to assess the influence of light (and temperature) on the formation of degradation products. The two other mock-up paint samples sets were kept in cabinet drawers and were used as unaged references.

2.2. Scanning Electron Microscopy with Energy Dispersive X-ray spectroscopy (SEM-EDX)

Backscattered electron images and elemental semi-quantitative analysis on the aforementioned amorphous reference materials were collected via SEM-EDX, using a Zeiss - EVO LS15 SEM equipped with an Oxford EDS detection system, all operated under variable pressure vacuum. Semi-quantitative analyses were obtained under low vacuum conditions using an acceleration voltage of 15 kV, and 8 mm working distance. No preparatory coating of the materials was required due to the low vacuum analytical conditions. Data was collected and processed using the AZtecEnergy software system, v. 2.1 (Oxford Instruments).

2.3. UV-Vis diffuse reflectance (UV-DR)

Absorption spectra of natural orpiment, natural realgar and amorphous arsenic sulfides were characterized via diffuse reflectance UV-Vis spectrophotometry to define their band gap energies. To avoid saturation of the detector and due to the small quantities of reference materials, 0.02 grams of pigment powder was blended and crushed with 0.98 grams of KBr dried at 200°C. KBr was chosen as it is the most used alkali halide in pellet for Infrared Spectroscopy and solid state UV due to its broad transmission window. The spectra were recorded using a Thermo Electron Nicolet Evolution 500 UV-VIS spectrophotometer equipped with an RSA-UC40 diffuse reflectance cell in the wavelength range of 250–850 nm.

2.4. Electrochemical setup

An amount of 5 mg of the ground pigment was suspended with 1 mL of absolute ethanol; 2 μ L of the orpiment-ethanol suspension was deposited on a screen-printed graphite electrode (DropSens, Llanera (Asturias) Spain). The surface of the prepared electrode was left to dry before the electrochemical measurements. Prior to the beginning of the experiment, 40 to 200 μ L of a 0.01 M NaCl solution was deposited on the surface of the electrode as the electrolyte using an in-house 3D printed cell allowing the use of a larger quantity of electrolyte. Measurements were acquired using a μ -Autolab potentiostat from Metrohm (The Netherlands), controlled by NOVA 1.10 software, allowing measuring a wide range of photocurrent in the micro and nano scale.

While several monochromatic light lasers were available for artificial aging purposes (405 nm blue; 532 nm green; 650 nm red), the electrode was illuminated for up to 90 minutes with an external blue (405 nm) laser with a power of 30 mW (Figure 1). Photocurrent was measured after an initial 5 minutes' illumination, after another 5 minutes' illumination (10 minutes total) and after every extra 10 minutes' illumination until 90 minutes were reached. Extra measurements were taken at 2 and 8 minutes' illumination for the amorphous pigment and after 7 minutes' illumination for natural realgar.

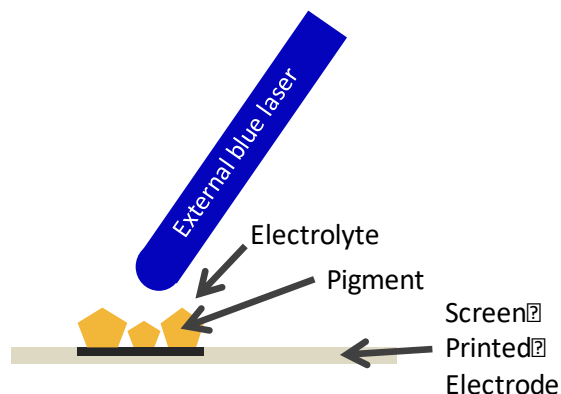


Figure 1. Schematic representation of the pigment's artificial aging under external blue laser irradiation for the electrochemical setup

2.5. Microfadedometry

The microfader employed in this study is based on the design developed by Paul Whitmore [33] except for the 100 micron fiber optic cable (Multimode Inc.) which consists of a bifurcated 6 (fibers to detector) around 1 (fiber from source) design with a 1-2 mm working distance. The light source is an Oriel 75 W Xenon arc lamp (ca. $120 \cdot 10^6$ lux for a 100 micron diameter spot) controlled by a power supply (model 69907) and Digital Exposure Control flux meter (model 68945) both from Newport Corporation, CA, USA. Microfading tests were achieved in 14 minutes. UV and infrared wavelengths were removed with a UV filter, a water filter, and a hot mirror resulting in reflection spectra in visible light only (between 400 nm and 700 nm). After calibration of the instrument on a white Teflon reference and optimization of the reading time, three random spots for each sample were measured. Color differences ΔE were calculated using the CIE 1976 $L^*a^*b^*$ equation [34] for 2° standard observer and standard illuminant C. The CDI Spec32 software (Control Development, USA) was used for data acquisition while its viewing and was performed on the Getty-developed Spectral viewer software.

2.6. Microscopic Fourier transform infrared spectroscopy (μ -FTIR)

For a better sample representativeness, aged mock-up paint samples were taken on their full thickness and flattened in a diamond compression cells prior to measurements. Spectra were recorded in transmission mode on a Hyperion 3000 spectrometer (Bruker Corporation, Germany) equipped with a Mercury Cadmium Telluride (MCT) detector. An average of 64 spectra for both the sample and the background measurement was employed, allowing an adequate signal-to-noise ratio throughout the accumulation range (4000-600 cm^{-1}) with a 4 cm^{-1} resolution. Spectra were acquired using the OPUS 7.2 FTIR software and an atmospheric compensation was performed when necessary. To make sure of the representativeness of the results, all samples (binder + pigment) were analyzed in triplicate and, peak areas were measured using OPUS 7.2 software.

2.7. Microscopic X-ray absorption near edge structure (μ -XANES)

μ -XANES (at the S K-edge) experiments were performed at the Phoenix Beamline of the Swiss Light Source (Villigen, CH). A non-focused beam was used for this experiment (beam size of ca. 1 m x 1 m) allowing a greater and more representative amount of sample to be measured. XANES spectra were recorded twice and average in the energy range 2 385-2 668 eV with energy increments of 1 eV. The Athena software package [35] was used to fit the XANES spectra.

3. Results

3.1. Determination of the band gaps for arsenic sulfide pigments

UV-Vis diffuse reflectance spectra of arsenic sulfide materials (Figure 2) clearly reflect their semi-conducting properties. Their onset wavelengths were determined by drawing a tangent line over the most vertical part of the spectra [26,27] and a conversion formula (Equation 1) between wavelength and band gap energy was employed to calculate the band gap of the materials. The onset wavelengths and calculated band gap energies are given in Table 1.

$$\lambda \text{ (nm)} \leq \frac{1241}{E_g \text{ (eV)}} \quad (\text{Eq. 1})$$

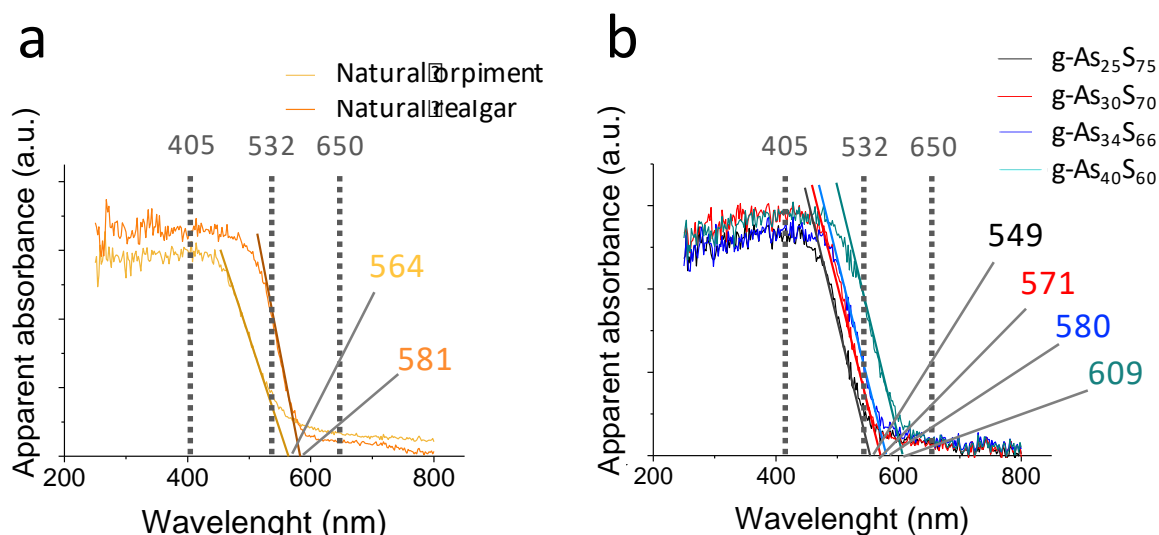


Figure 2. UV-Vis diffuse reflectance (UV-Vis DR) spectra expressed in apparent absorbance of (a) natural orpiment (yellow) and natural realgar (orange) and (b) amorphous arsenic sulfides of known composition ($g\text{-As}_{25}\text{S}_{75}$ in black, $g\text{-As}_{30}\text{S}_{70}$ in red, $g\text{-As}_{34}\text{S}_{66}$ in blue and $g\text{-As}_{40}\text{S}_{60}$ in green). The onset wavelength (in nm) for each compound is indicated. The grey dotted lines indicate the three available lasers considered for the electrochemical setup (405 nm blue; 532 nm green; 650 nm red)

Table 1. Onset wavelengths and calculated band gap energies for natural orpiment, natural realgar and amorphous arsenic sulfides of known compositions.

	λ (nm)	E_g (eV)	Color
Natural orpiment	564	2.20	Golden yellow
Natural realgar	581	2.14	Orangey-red
$g\text{-As}_{25}\text{S}_{75}$	549	2.26	Bright light yellow
$g\text{-As}_{30}\text{S}_{70}$	571	2.17	Bright yellow
$g\text{-As}_{34}\text{S}_{66}$	580	2.14	Dark yellow
$g\text{-As}_{40}\text{S}_{60}$	609	2.04	Orangey red

From the UV-DR measurements, it can be concluded that all pigments become photoactive when exposed to wavelengths shorter than 549 to 609 nm depending on their color (549 nm corresponding to the lighter yellow shade of arsenic sulfide studied here and 609 to the darker orange-red shade). All pigments are barely photoactive at longer wavelengths. Regarding the amorphous pigments, it appears that the band gap is influenced by the amount of sulfur contained in the structure: the higher the amount of sulfur the higher the band gap.

It also appears that the composition is not the only factor influencing the band gap energy as two compounds of similar atomic composition can have different band gap energies. In that regard, natural orpiment (As_2S_3), which is composed of 40 atomic% As and 60 atomic% S, has a band gap of 2.20 eV while the amorphous material of similar composition (40% As, 60% S) has a band gap of 2.04 eV; it is therefore slightly more conductive. Similar observations can be drawn regarding realgar (AsS or As_4S_4 , 50 atomic% As, 50 atomic% S) and $g\text{-As}_{34}\text{S}_{66}$ which appear to have the same band gap energy (2.14 eV) while having different elemental compositions and color. It appears from these

observation that, amorphous arsenic sulfide is generally more conductive/has a smaller band gap than the crystalline form of comparable composition. The conflict between band gap and composition highlighted here may point toward different physical properties between crystalline and amorphous compounds.

3.2. Assessment of the pigments' relative stability

The semiconducting properties of arsenic sulfide pigments were exploited to monitor their photodegradation by measuring the evolution of the laser-induced photocurrent over 90 minutes' exposure. Three lasers were available in order to conduct the analysis: a blue 405 nm laser, a green 532 nm laser and a red 650 nm one. According to Figure 2, the greatest and most stable photo-induced signal is expected for the 405 nm laser while almost no signal and thus virtually no pigment degradation will result from red laser (650 nm) illumination on any arsenic sulfide pigments. Therefore, a blue 405 nm laser was used for the rest of the experiment even though, as seen from the absorption spectrum given in Figure 2, the pigment will absorb broadly but it is unknown how the pigment will degrade at longer wavelengths. Figure 3a presents the typical evolution of the photocurrent for natural orpiment while Figure 3b plots it depending on the illumination time. Natural orpiment initially produces a high oxidation photocurrent, which latter decreases exponentially within the first few minutes of light exposure before stabilizing, showing few changes until the end of the experiment. The same procedure is followed for natural realgar and the amorphous arsenic sulfide and their evolution over a 90-minute time-period is presented in Figure 4.

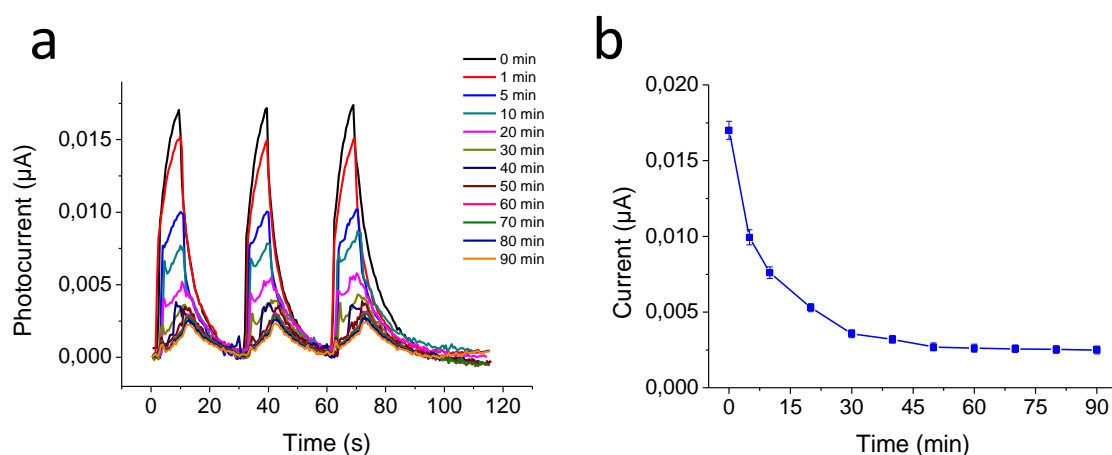


Figure 3. (a) Raw data for the time-dependent blue laser (405 nm) illumination of natural orpiment and (b) evolution of its light-induced photocurrent as a function of cumulated illumination time.

Figure 4 clearly shows that the laser-induced photocurrent for all pigments gradually decreases upon illumination. Nonetheless, clear variations are observed between the three pigments. Over the period of 90 minutes, natural realgar (Figure 4a) presents a uniformly decreasing photocurrent and no stabilization whereas the photocurrent for both natural orpiment and g-As₄₀S₆₀ decreases drastically and already appears to stabilize after 20 minutes of light exposure (Figure 4b). The lack of stabilization observed for natural realgar might be due to the formation of light-induced pararealgar,

another arsenic sulfide semi-conducting pigment. As a result, during the illumination process, photocurrent will be induced by both realgar and pararealgar. The decrease in photocurrent observed is consequently not as drastic as the other two forms, which do not produce another semi-conducting product during their degradation process, but last longer due to the two-step degradation process. The light-induced photocurrent for realgar would be expected to stabilize for longer exposure times, when both realgar and pararealgar would be both transformed into arsenic oxide. From the slopes of the curves, it can be concluded that the initial speed of the degradation reaction is almost 4 times as high for orpiment and the amorphous material (respectively -0.039 and -0.043) than for natural realgar (-0.012).

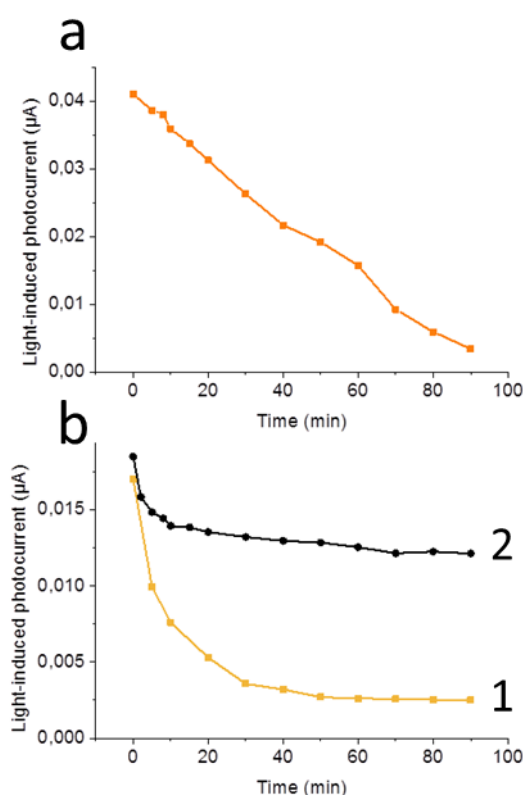


Figure 4. Evolution of the photocurrent obtained during illumination of (a) natural realgar, (b-1) natural orpiment and (b-2) amorphous $\text{As}_{40}\text{S}_{60}$ with blue (405 nm) laser light.

Hypothetically, the different stabilities observed for the various forms of arsenic sulfide pigments could be linked to the amount of weak interactions (Van der Waals bonds) in each pigments' structure. Indeed, while the stoichiometric artificial forms, as an amorphous material, only contains covalent As-S bonding [36–38] (Figure 5a), more Van der Waals interactions are observed in both crystalline forms (orpiment and realgar). In both crystalline forms, sulfur and arsenic atoms are bound to one another by covalent bonds arranged in a ruffled sheet structure for the case of orpiment (Figure 5b) and in molecular cage-like units in case of realgar (Figure 5c). The As_4S_4 molecular cage-like units are connected by Van der Waals forces and arranged in a zigzag way resulting in a layered structure. In both structures, the layers are held together by Van der Waals

interactions. No such weak interactions are involved in the structure of the amorphous form whereas they represent most atoms interactions in the layered structures of both crystalline forms.

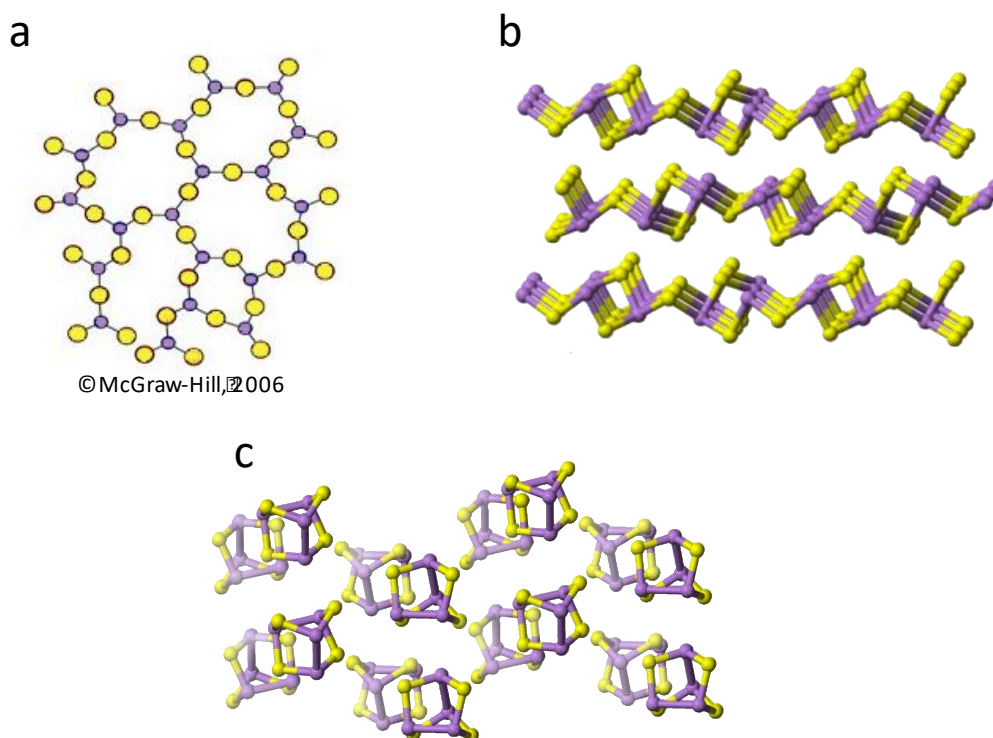


Figure 5. Schematic representation of (a) amorphous arsenic sulfide (b) natural orpiment and (c) natural realgar. Arsenic atoms are represented in purple and sulfur atoms in yellow.

The electrochemical setup highlighted different pigment photochemical behavior. However, due to the need of focused light beam to illuminate the working electrode where the deposited pigment is present, the study was realized with monochromatic light which is not representative of the light to which the pigments is exposed in realistic conditions. Therefore, the light fastness of all three unbound forms of the pigment was investigated by microfadometry, in which the $L^*a^*b^*$ color space coordinates are followed to assess changes in perceived color (ΔE) for each material. The International Commission on Illumination (CIE) introduced the world to the concept of ΔE which is a metric for understanding how the human eye perceives color difference. Because the color change (ΔE) of each sample is not important by itself but rather in comparison to each other, and because the ΔE value to which perceptible color change can be seen by human eyes is not a set value [34], the color variation of all three samples will be compared regardless of whether or not the color change is considered perceivable.

The results of the experiment on the three unbound pigments are given in Figure 6.

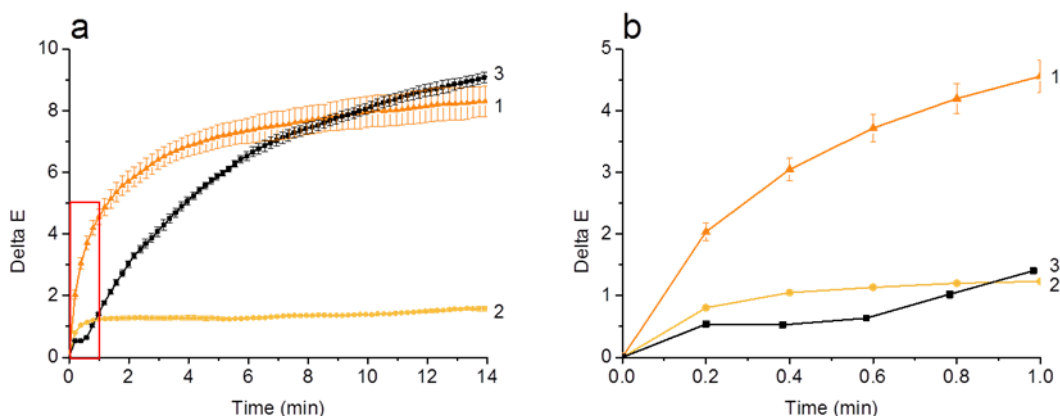


Figure 6. (a) ΔE values recorded during the microfadometry study in presence of oxygen of (1) unbound natural realgar, (2) unbound natural orpiment and (3) g-As₄₀S₆₀ when exposed to a 75 W Xe arc lamp; (b) ΔE values corresponding to the first minute of illumination.

Figure 6 clearly illustrates the differences in light fastness of the three arsenic sulfide compounds. While natural orpiment presents a light fastness clearly lower than realgar (ΔE respectively equal to 1 and 8 after 14 minutes of illumination, Figure 6a), the light fastness for the amorphous material presents a peculiar pattern. Indeed, the light fastness of the amorphous material is lower than the one of orpiment and stabilizes around $\Delta E = 1$ for the first minute of the experiment (Figure 6b). It then increases drastically for the remaining time and finally reaches ΔE values higher than those observed for the realgar (ΔE up to 10 after 14 minutes' illumination (Figure 6a). The results of the full 14 min exposure experiment differ quite drastically from the electrochemical results presented in Figure 4. However, when considering only the first minute of the microfadometric test, their findings appear quite similar: the amorphous form is more stable than the orpiment which is itself more stable than the realgar. By analogy with the microfadometric test, a decrease in photo-induced current for amorphous arsenic sulfide pigment can then be expected if it is exposed for a longer time to a weaker (30 mW) monochromatic or polychromatic light source. These two experiments clearly show that amorphous arsenic sulfide can be considered more stable in the initial period of illumination but will degrade more extensively and lose its vibrant color, even more than the crystalline forms, during longer light exposures.

3.3. Influence of the binding medium on the pigments' degradation

According to literature [9,16,28–30] and the Pourbaix diagrams of dissolved As- and S-species presented in Figure 7, arsenic trioxide and various sulfate compounds are expected to be formed as degradation products for all the arsenic sulfide pigments. Aging of arsenic sulfide-containing painting systems often leads to whitening or increased transparency due to the formation of water-soluble white arsenic trioxide and/or arsenate species [9,16,17]. As illustrated in Figure 8a-b, it appears that this phenomenon greatly depends on the binder used. This figure presents natural orpiment bound in either (a) egg yolk or (b) egg white, artificially aged for 20 weeks.

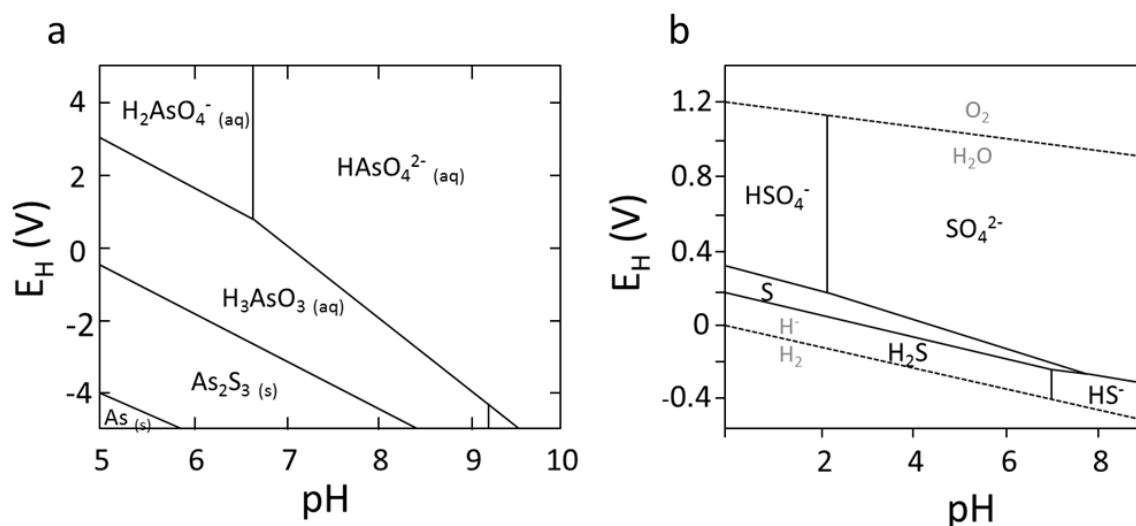


Figure 7. Pourbaix diagrams of a) the arsenic system and b) the sulfur system, both showing the potential oxidation products than can be expected in case of the degradation of arsenic sulfide pigments.

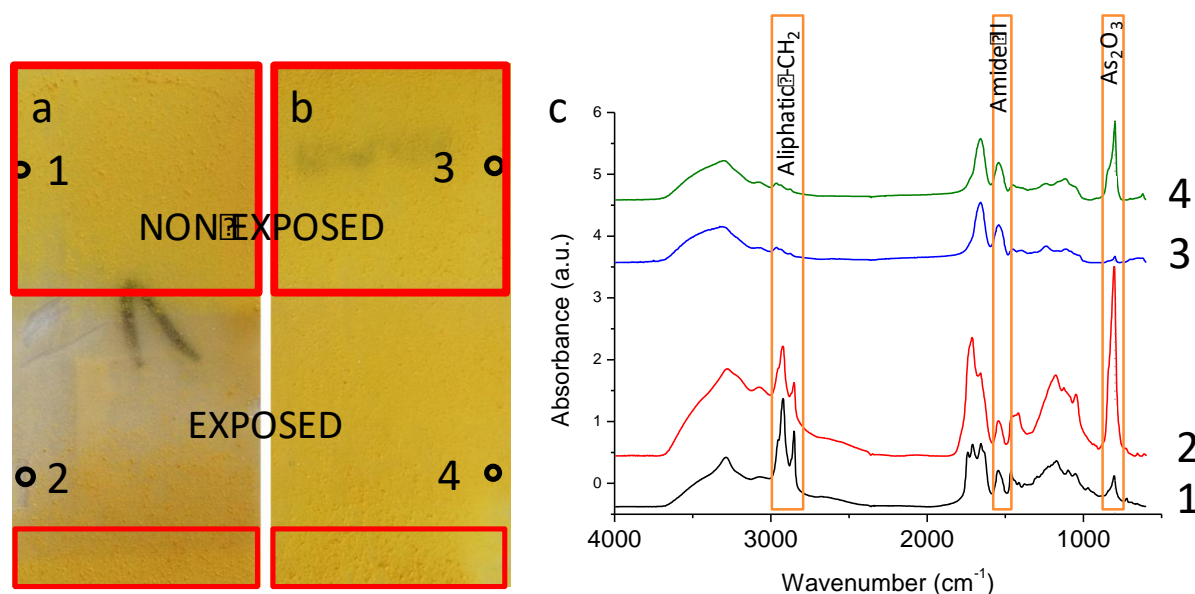


Figure 8. Partially exposed mock-up samples of natural orpiment bound in (a) egg yolk and (b) egg white; (c) transmission μ -FTIR spectra obtained from the non-exposed (1 and 3) and light-exposed areas (2 and 4).

As Figure 8 shows, the exposed parts of the orpiment/binder system clearly present discoloration which appears more pronounced in the case of orpiment/egg yolk (Figure 8a). This discoloration can be linked to the transformation of the pigment into soluble arsenic trioxide, as identified by its specific AsO vibration band (804 cm^{-1}) by means of μ -FTIR (Figure 8c). Significantly lower amounts of arsenic trioxide were detected in the covered areas of the orpiment/binder systems (Figures 8c-1 and c-3), which clearly demonstrates the light-induced phenomenon described in literature [9,16,29,39,40]. Because the pigment jars were not sealed under an oxygen-free environment, the

As₂O₃ detected in the covered areas could correspond to the initial amount present when preparing the mock-up paint samples due to the high light and oxygen sensitivity and rapid transformation of the pigment.

Even though arsenic trioxide was identified in exposed areas for both samples, the clear difference in their visual appearance along with the higher AsO signal obtained in the egg yolk (Figure 8c-2), compared to egg white (Figure 8c-4) while aged in the same conditions, demonstrates the influence of the binder on their degradation.

To explore this phenomenon further, a wider study was undertaken on both natural pigments and three of the amorphous artificial forms of known composition (g-As₃₀S₇₀, g-As₃₄S₆₆ and g-As₄₀S₆₀), bound in five different common artists' media (animal glue, gum arabic, egg yolk, egg white and linseed oil). The pigment/binder systems were also aged for 20 week under the experimental conditions previously described.

The formation of arsenic trioxide was assessed by calculating the ratio of the area of the AsO vibration band (908 to 754 cm⁻¹) to that of the area of the amide II band (1594 to 1494 cm⁻¹) for the proteinaceous binders (glue, egg yolk and egg white), and to that of the area of the aliphatic CH₂ band (3038 to 2810 cm⁻¹) for the oil, gum arabic and egg yolk binders. These bands were chosen due to their apparent stability over the aging process and in view of the lack of other inert internal standards. The results are given in Figure 9.

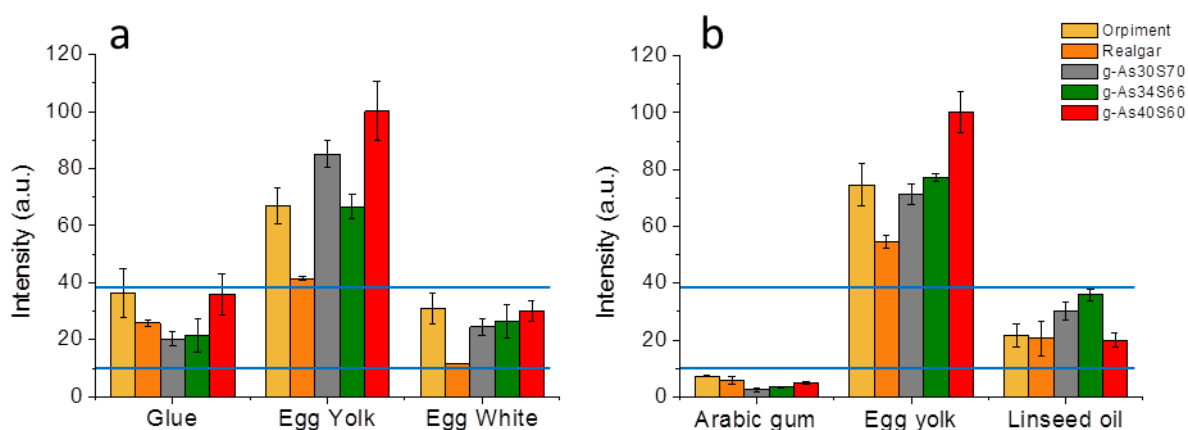


Figure 9. Plot representing (a) the As₂O₃/Amide II and (b) the As₂O₃/aliphatic CH₂ band area ratios in a various binding media for natural orpiment, natural realgar and three amorphous arsenic sulfide pigments of known composition (30/70, 34/66 and 40/60 As/S atomic%) determined by transmission μ -FTIR.

Figure 9 clearly shows that the formation of arsenic oxide differs greatly depending on the medium. The graphs can be divided according to several distinct zones, indicated by the blue horizontal lines: ratios below 10, ratios between 10 and 40 and ratios above 40. Given how the samples were analyzed and the ratios calculated, the higher the ratio, the greater the presence of arsenolite. Only the pigments bound in egg yolk show ratios above 40, indicating a more important or faster degradation process compared to other binders. The formation of arsenolite when gum arabic is used as binder is almost non-existent while glue, egg white and oil have an intermediate influence.

From the μ -FTIR results, the gum arabic binder appears to be the most appropriate for arsenic sulfide pigments. These findings can be corroborated by the various studies realized on illuminated manuscripts, in which arsenic sulfide is often bound with gum arabic but with no sign of alteration and no indications of the present of arsenic trioxide [41–43].

It is interesting to note that for all binding media, the formation of arsenolite is more important when starting from orpiment than from realgar. This suggests a difference in kinetics, with a higher reaction speed for the orpiment. The same observation was made during the initial stage of the degradation in the electrochemical experiment presented in Figure 4.

When it comes to the amorphous arsenic sulfide, Figure 9 suggests that, for all the binders studied except the oil, more arsenic oxide is formed from g-As₄₀S₆₀ than from g-As₃₄S₆₆ or g-As₃₀S₇₀, the latter containing the least arsenic trioxide after 20 weeks of aging. It then appears that the more arsenic is present in the original structure; the more arsenic trioxide will be formed. In other words, the more As atoms that are available for oxidation, the more As₂O₃ is formed.

Along with the formation of arsenic trioxide, the influence of the binder on the degradation of arsenic sulfide pigments was assessed with XANES at the sulfur K-edge by following the formation of sulfate species upon aging. Orpiment, realgar and one of the amorphous arsenic sulfide pigments bound in glue, oil, and egg yolk were analyzed with this technique. To compare the formation of sulfate compounds between different samples, ratios of the intensity of the sulfate band (2482 eV, En₂) over the intensity of the sulfide band (2471 eV, En₁) were calculated. The higher the I(En₂)/I(En₁) ratio, the more degraded is the sample. Given the fact that all samples were aged in the same conditions, a high value for the ratio would indicate a negative influence of the binder on the degradation of the pigments. The calculated intensities ratios are given in Table 2 and the XANES spectra recorded in Figure 10.

Table 2. Ratio values for the sulfate over sulfide intensity at the respective white line energies [I(En₂)/I(En₁)] measured before aging (natural pigments in egg yolk binder) and after artificial aging for natural orpiment, natural realgar and amorphous arsenic sulfide bound in egg yolk, linseed oil and glue. No ratios were calculated for the pigments in oil and glue due to the lack of sulfate signal.

	Egg Yolk <i>Before aging</i>	Egg yolk <i>After aging</i>	Oil	Glue
Natural orpiment	1.31	8.64	1.15	0.75
Natural realgar	1.07	3.98	0.89	0.73
Amorphous	-	-	0.79	0.72

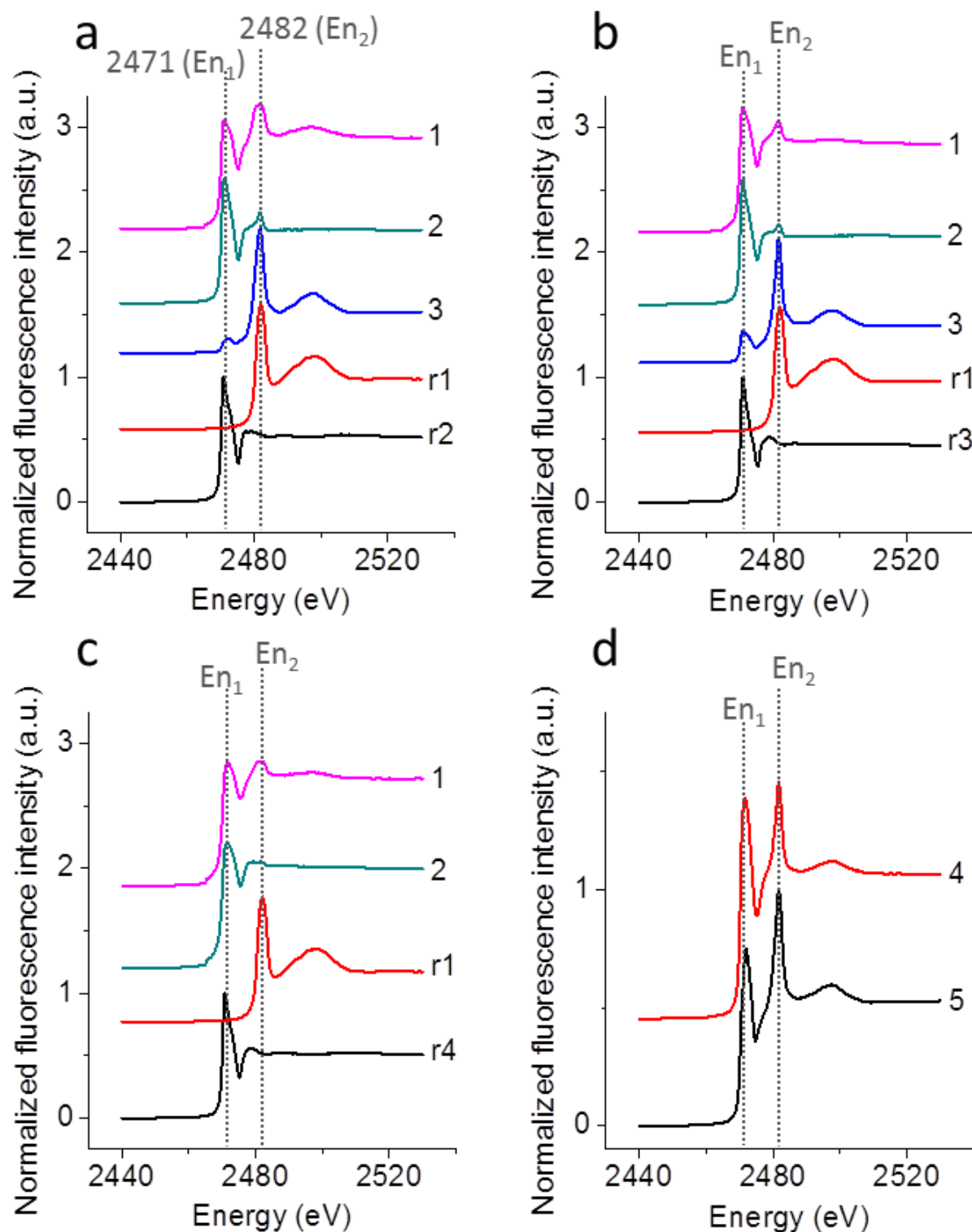


Figure 10. XANES spectra at the S K-edge for a) natural orpiment, b) natural realgar and c) amorphous As₄₀S₆₀ bound in 1) linseed oil, 2) glue and 3) egg yolk after artificial aging and d) XANES spectra at the S k-edge for 4) non-aged orpiment and 5) non-aged realgar in egg yolk. References are indicated in each quadrant: r1) aluminum sulfate, r2) natural orpiment, r3) natural realgar and r4) g-As₄₀S₆₀.

The sulfate/sulfide ratios calculated after aging, reported in Table 3, present significant differences depending on the binder. While the presence of sulfate in the pigment/egg yolk systems allowed for the calculation of $I(\text{En}_2)/I(\text{En}_1)$ ratios, no ratios were calculated for the pigments in oil and glue due to the lack of sulfate signal. It appears that a glue binder induces the formation of less sulfates than an oil binder. Egg yolk gives rise to the formation of 4 to 11 times more sulfates than the other binders. This undoubtedly indicates a larger influence of the egg yolk binder on the degradation of the pigments compared to the two other binders studied. However, as suggested by the presence of sulfates in the XANES spectra measured on non-aged natural orpiment and realgar bound in egg yolk binder (Figure 10d), some of the sulfate observed in the aged samples are most likely already present in the egg yolk. Nevertheless, the important increase in the $I(\text{En}_2)/I(\text{En}_1)$ ratios calculated in the egg yolk binder before and after aging (Table 3) suggests a large transformation of the sulfide into the sulfate during the aging process.

Note that the ratios calculated are always higher for the natural orpiment than for the natural realgar (8.64 vs 3.98 in egg yolk; 1.15 vs 0.89 in linseed oil; and 0.75 vs. 0.73 in glue). A similar observation can be made with respect to the formation of arsenolite assessed in μ -FTIR (Figure 9). This may be explained by a slower degradation kinetic of realgar compared to orpiment as the implied by the slower degradation speed measured in electrochemistry (Figure 4). This phenomenon may be attributed to the structural rearrangement of realgar into pararealgar prior to the formation of arsenic trioxide and sulfates as demonstrated in previous studies [15,39,44,45]. Due to the intermediary light-induced structural modification of realgar, the formation of arsenic oxide will be diminished compared to what is observed for the natural orpiment, where arsenic trioxide is directly and solely formed [11,12].

4. Conclusion

In recent years, electrochemistry had proven to be a valuable tool for predicting the stability of semiconducting pigments. Here, this technique had been used to compare the stability of crystalline arsenic sulfides (orpiment and realgar) and one of their amorphous analogues ($\text{g-As}_{40}\text{S}_{60}$) when exposed to a monochromatic light. In this way, it has been shown that in the initial stage of aging, the amorphous form is more stable toward degradation than the crystalline forms. Within the crystalline forms, natural orpiment appears to degrade more quickly than natural realgar in the initial degradation stage but, overall, less when considering longer exposure times. Therefore, realgar appears less stable towards formation of soluble oxidized species such as arsenic trioxide compared to natural orpiment or amorphous arsenic sulfide. This could be explained by the type of bonding present in the different pigments, the amorphous form being more stable because mainly composed of strong covalent bonds, while weaker Van der Waals bonds are found in orpiment and even more in realgar. However, a microfadometric study exposing the unbound pigments to the entire visible light spectrum has shown that, from a color change point of view, amorphous arsenic sulfide will only be the most stable form during a short period of time. It will quickly present a color loss comparable to that observed for realgar when exposed to light for a longer period of time. Color changes in arsenic sulfide pigments are therefore likely influenced by other factors than the interplanar bonding forces in the different subtypes of pigment.

The influence of the binder on the degradation of arsenic sulfide pigments was studied through a multi-analytical approach by assessing the formation of arsenic trioxide and of sulfate species, two degradation products expected to be formed during the degradation process of all arsenic sulfide pigments. It is concluded that all binders are not equal in this respect. Egg yolk binder clearly has the most negative influence on the degradation process while gum arabic appears to be most suitable binding, inducing the formation of only very limited amounts of arsenic trioxide. Other binders such as glue, egg white or linseed oil have an intermediate influence on the degradation of the pigments.

This multi-analytical study also showed that in all media natural realgar does not degrade as fast as natural orpiment, most likely due to the intermediate conversion of realgar to pararealgar while orpiment is directly converted to arsenic trioxide. However, with time, more degradation products and discoloration are expected for the orangey-red pigment.

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