

ARE COMMERCIAL PIGMENTS RELIABLE REFERENCES FOR THE ANALYSIS OF PAINTINGS?

Laura RAMPAZZI^{1,2*}, Cristina CORTI¹

¹Dipartimento di Scienze Umane e dell'Innovazione per il Territorio, Università degli Studi dell'Insubria, via Valleggio 11, 22100 Como, Italy

²Istituto per la Conservazione e la Valorizzazione dei Beni Culturali, Sezione "G. Bozza", Consiglio Nazionale delle Ricerche, via Cozzi 53, 20125 Milano, Italy

Abstract

When paintings are examined by spectroscopic techniques, building a robust database is of major importance, in order to compare the analyses with reliable references and to correctly understand the results. The database, which is usually homemade, should include carefully chosen commercial pigments, which should be as pure as possible and should correspond to the expected formula or composition of the historical pigments. Unfortunately, sometimes no correspondence between the names of the pigments used by companies and the actual composition of some of the colors is ascertained. In some cases, the composition is in fact made up of different chemical compounds; in others the presence of extenders is revealed, for example gypsum and calcite. In this paper some cases studies are discussed, regarding commercial pigments analysed by infrared spectroscopy, thermal analysis, X-ray diffraction and X-ray fluorescence. The results highlighted the importance of checking the purity of commercial pigments and excluding any extraneous compounds while interpreting the results of analytical survey of paintings.

Keywords: *Painting analysis; Pigments; Infrared spectroscopy; Thermogravimetry; X-ray diffraction; X-ray fluorescence*

Introduction

When analyzing painted artifacts (easel and wall paintings, written and wooden supports) in order to identify the palette used or for conservation and authentication purposes, a database of the reference painting materials is of major importance, irrespective of the technique used. Firstly, original pigments in use when the painting was created need to be identified from artists' handbooks and manuals, if possible in collaboration with art historians or archaeologists. Secondly, the modern commercial pigments used for the database need to be as similar as possible to those used in the past. This is particularly important from an analytical point of view, as the references should be as pure as possible. In other words the references should correspond to the expected formula or composition of the historical pigments. Having characterized the references, the analysts can then decide which analytical techniques are best for the identification of the pigments presumed to be present in the artifacts, taking into account any possible matrix interference, and also evaluating the use of non-invasive instruments.

The support of a robust database ensures reliable results in terms of the artist's palette. It may also be useful in revealing forgeries, if a pigment that does not correspond with the historical period or the painter is identified, and if the recipes described in technical manuals

* Corresponding author: laura.rampazzi@uninsubria.it

have been used. Particular attention should thus be paid to the names of the pigments, as the same term may be used in the past to refer to more than one pigment and conversely the same pigment can be called different names. The technical names of painting materials may have changed considerably over time, depending on the historical period, the painter, the production recipe, location, or simply due to misunderstandings [1]. The names given to materials occasionally referred to the hue, without relating to the composition that would be expected from the terms. Confusion about names has only partially been overcome with a universally recognized vocabulary [1, 2]. The confusion regarding technical terms also makes it complicated to decipher the historical sources, as one-to-one translations are not always easy. In fact as Michel Pastoreau commented “the color of the painter is not that of the physicist, and that of the physicist is not that of the poet”/“*la couleur du peintre n’est pas celle du physicien et que celle du physicien n’est pas celle du poète*” [3]. Thus a bibliographic research needs to include the synonyms used for the same pigments in different historical periods and geographical areas, and all the nomenclatures should be listed in the database.

Commercial brands should include a report on how the pigments have been produced together with their composition, and scientists should opt for those prepared following traditional recipes. This is also important for restorers, who during conservation work often have to fill or replace gaps in the paint and need to know the real composition of the products in order to predict the chemical compatibility with the compounds present in the artifact and prevent unwanted secondary reactions.

Based on our experience and in line with the literature [4–8], the purity of commercial pigments is sometimes doubtful, suggesting that the composition needs to be checked and the signals of the extraneous compounds need to be removed in order to obtain results that only refer to unadulterated compounds. The adulteration and substitution of pigments, the substitution of names, the addition of other materials have also been of major concern for painters, particularly when tube paints came into use in the 19th century and painters no longer prepared colors themselves from raw materials, as demonstrated by an analytical campaign on paintings and sample books of this period [9, 10]. Many artists have noted differences in the painting materials they have used over time, unaware that the suppliers had consciously adulterated the pigments without revealing the real formula and key ingredients [11]. In fact, lower-quality and cheaper ingredients were added or substituted the expected pigments components, also to expand the range of colors for sale.

Here we discuss some significant results of analysis of references [12–15] by infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray fluorescence (XRF), thermogravimetric analysis (TGA).

We also discussed the so-called Mars pigments, i.e. supposedly artificial ochres that have been produced since the 19th century from iron salts, alum and alkali but have never been extensively characterized before [1, 2, 16]. The term Mars comes after the name of the Roman god of war and is associated with iron. Depending on the addition of alum and on the different temperatures and heating times, and the subsequent different hydration levels, the hue ranges from yellow to violet, and from brown to black. All the varieties were produced starting from Mars yellow, which could be turned by heat to orange, red, and violet. Chemically, the Mars pigments possible are goethite (FeOOH), magnetite (Fe₃O₄) and hematite (Fe₂O₃), usually mixed with minerals such as kaolinite, gypsum, calcite and quartz (SiO₂). The aim of the characterization by various techniques was to provide new insights into the different composition of each Mars hue.

Experimental

Pigments

The considered pigments were both traditional and synthetic modern products and manufactured in Italy and Germany from 2015 to 2017. The names refer to the traditional and

most widespread ones, not necessarily considering the brand labels.

Infrared spectroscopy

FTIR spectra were recorded on KBr pellets (Sigma-Aldrich FTIR Grade) in transmission mode, by BioRad Excalibur Series FTS 3000 and Thermo Scientific Nicolet iS10 spectrometer (detector DTGS) in the 4000–400 cm^{-1} range, with a resolution of 4 cm^{-1} . Pellets were prepared by mixing samples and KBr in an agate mortar, pouring the mixture into a press and then applying a pressure of 6 t/cm^2 for 1 minute. Paper-based databases, reference spectra from literature and web databases were used to identify the species in each FTIR spectrum, by comparing experimental peaks with reference patterns.

Thermal analysis

Thermal analysis (TGA/DSC) was performed by means of a NETZSCH STA 409 PC instrument. Samples were placed in alumina crucibles, with the temperature program ranging from room temperature to 600°C, at a heating rate of 20°C min^{-1} under pure nitrogen atmosphere. TG and DSC raw data were corrected on the basis of a background curve.

X-ray fluorescence

X-ray fluorescence analysis was performed by means of a PANalytical Minipal 4 energy-dispersive XRF Bench-Top Spectrometer (30kV, auto-current, no filters, 180 sec of acquisition). Element recognition was achieved by means of an electronic database.

X-ray powder diffraction analysis

X-ray diffraction analyses were conducted using a Rigaku Miniflex 300 diffractometer (30kV, 10mA, Cu-K α radiation ($\lambda = 1.5418\text{\AA}$), 5-55° Theta/2-Theta, step scan 0.02°, scan speed 3°/min). PDXL2 software supporting ICDD (The International Centre for Diffraction Data) PDF2 databases were used to identify the phases in each X-ray powder spectrum, by comparing experimental peaks with reference patterns.

Results and Discussion

The pigments were analyzed by FTIR, XRD and XRF. Mars pigments were also characterized by thermal analysis. The results of the XRD and XRF analyses were interpreted with the instrument databases, and the TG and FTIR determinations were deciphered on the basis of references discussed in the literature.

Figure 1 shows the XRD signals of the pigment Titanium white (German manufacturing) overlapping with the reference of the natural mineral rutile-composed of titanium dioxide-showing a perfect fitting and proving the correspondence between the composition and what stated on the label. IR and XRF results confirmed the purity of the pigment, as no peaks were observed and only the signal of titanium was recorded, respectively.

The same correspondence was observed with Prussian Blue (German manufacturing). The FTIR spectrum showed an intense peak at 2088 cm^{-1} , which is the typical band of CN stretching. In addition, the bending peak at 3257 cm^{-1} and stretching signal at 1611 cm^{-1} , which may be due to HOH and OH signals of interstitial water respectively, the FeC stretching peaks at 1415, 1043, and 605 cm^{-1} , and the FeCN bending modes at 512 and 497 cm^{-1} confirm the compound described by the manufacturer, which is iron(II, III) hexacyanoferrate(II, III) [17]. XRD results confirmed the attribution.

In some cases, some substances possibly associated with natural occurrences of mineral-based pigments or due to intentional additives were determined.

Figure 1 shows the FTIR spectrum of pigment Azurite (German manufacturing). The peaks of carbonate group absorption at 1495, 1464, 1416, 1091, 837, 816, 769, 745 cm^{-1} , OH out-of-plane bending modes at 3426, 1031, 953 cm^{-1} , bending CuO signals at 494 and 459 cm^{-1} are typical of the basic copper carbonate that constitutes this pigment [18, 19]. In addition, we observed signals at 3695, 3620 and 693 cm^{-1} , and a band at 1009 cm^{-1} , which undoubtedly are the typical absorptions of OH and SiO groups contained in clay minerals, respectively [20].

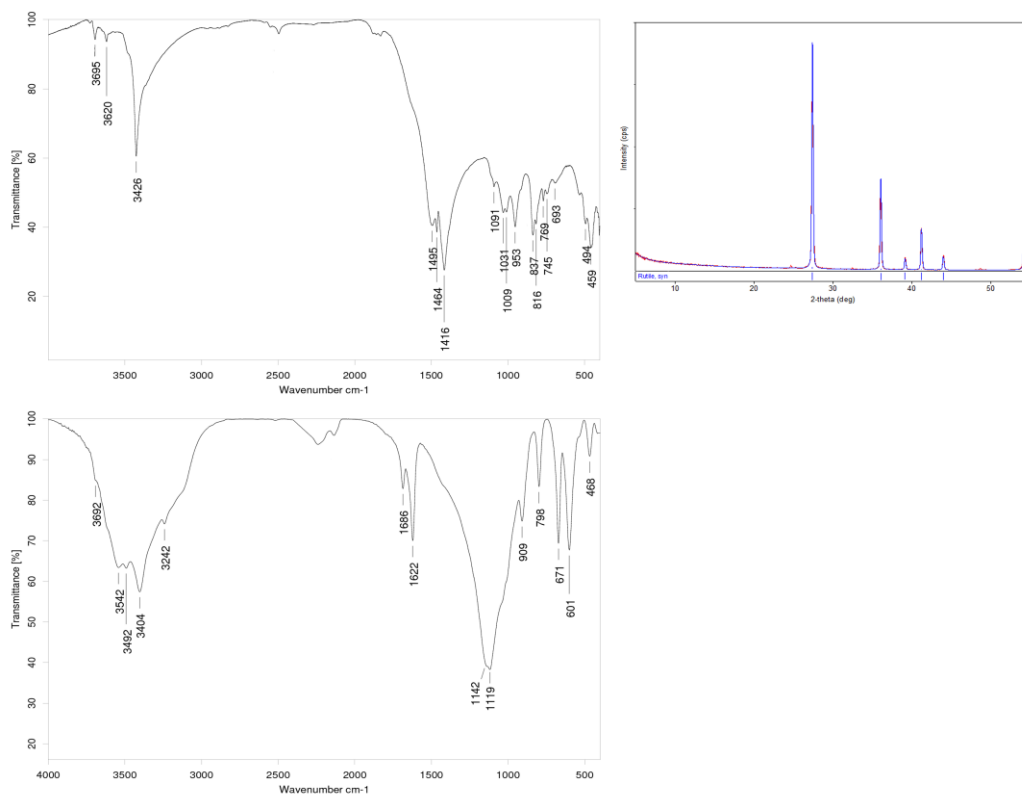


Fig. 1. FTIR transmittance analysis of Azurite (above, left), showing the signals of azurite (3426, 1495, 1464, 1416, 1091, 1031, 953, 837, 816, 769, 745, 494, 459 cm^{-1}) and clay minerals (3695, 3620, 1009, 693 cm^{-1}), and of Yellow ochre (bottom, left), presenting the peaks of kaolinite (3692, 909 cm^{-1}), goethite (798, 468 m^{-1}) and gypsum (3542, 3492, 3404, 3242, 1686, 1622, 1142, 1119, 671, 601 cm^{-1}). XRD analysis (above, right) of pigment Titanium white (red line) compared to the reference of mineral rutile (blue line).

Vine black (Italian manufacturing) should mainly contain carbon from vine wood, and low amounts of organic compounds and silicates [21]. The signals at 3619 and 1031 cm^{-1} of the FTIR spectrum could in fact be ascribed to OH and SiO signals of clay minerals, respectively [20]. Organic compounds were also present, as suggested by the peaks at 1593 and 1660 cm^{-1} , which could be attributed to CO absorption. However, FTIR bands at 1682 and 1617 cm^{-1} could be hydroxyl bending vibrations, while the peaks at 1141, 1119 cm^{-1} and 666 and 601 cm^{-1} could be ascribed to SO asymmetric stretching and bending modes, recalling the pattern of gypsum [22, 23], whose presence was confirmed by XRD analysis.

Regarding Yellow ochre (Italian manufacturing), the interpretation of the XRD results assigned the signals to quartz, kaolinite and goethite (FeO(OH)). The FTIR spectrum in fact showed the peaks at 3692 cm^{-1} and 909 cm^{-1} , which could be attributed to OH stretching and deformation characteristics of kaolinite [20] (Fig. 1). The bands at 798 and 468 cm^{-1} also revealed the presence of goethite, due to the out-of-plane OH deformation and FeO stretching peak. The overall composition was as expected for ochre, i.e. typically clay and goethite [2]. However, both XRD and FTIR spectra presented the signals of at least one other compound. A comparison with the corresponding databases suggested an unexpected compound. The FTIR bands at 3542, 3492, 3404 and 3242 cm^{-1} could be typical of hydroxyl stretching, 1686 and 1622 cm^{-1} may be the related bending vibrations, while the peaks at 1142, 1119 cm^{-1} and 671 and 601 cm^{-1} could be attributed to SO asymmetric stretching and bending modes. The pattern was clearly that of gypsum [22, 23].

In some cases the supposed composition of the pigments on the basis of the commercial names did not match the results of the analytical investigations.

One example was pigment Cinnabar (Italian manufacturing). As cinnabar is composed of mercury sulfide, the infrared spectrum was expected not to have peaks. However the commercial pigment showed intense peaks at 526 and 448 cm^{-1} a comparison with the data in the literature showed a correspondence with the pigment minium and the typical signals of PbO stretching [24]. XRD analysis confirmed the presence of minium, as well as the XRF signals of lead. Conversely, the pigment Vermillion B2 was actually mercury sulfide, as shown by the XRD spectrum in Figure 2.

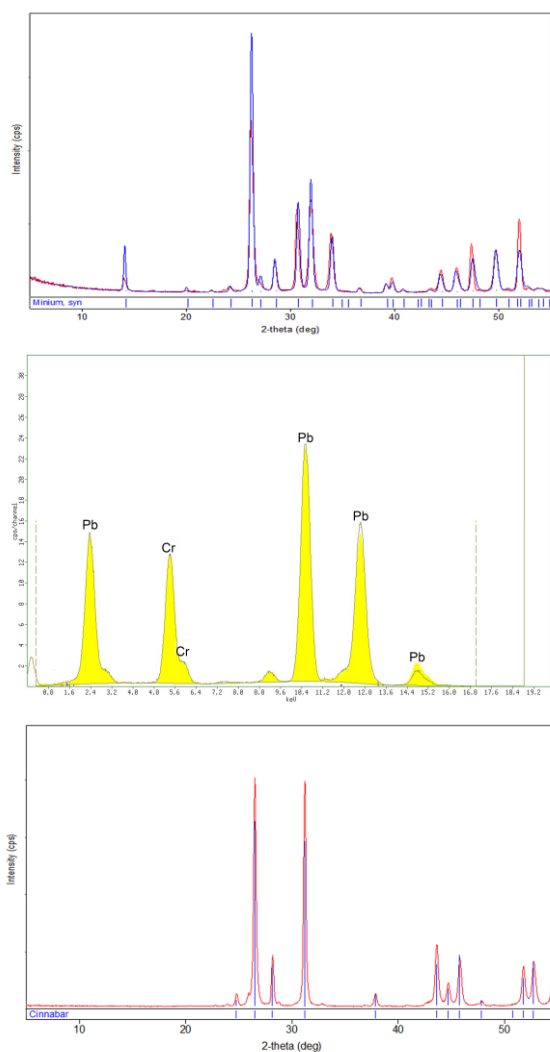


Fig. 2. XRD analysis of Cinnabar (red line) compared to minium reference (blue line) (top) and of Vermillion (red line) compared to cinnabar reference (blue line) (bottom). XRF spectrum of Cinnabar (center). The peaks of chromium, visible in the XRF spectrum, are due to the source used by the instrument.

Barium white (Italian manufacturing) FTIR spectrum did not match the expected absorbance values of barium sulfate, which are supposed to be the main peaks in the SO_4^{2-} group: the symmetric stretching vibration around 1179, 1083 and 982 cm^{-1} , the stretching signal

around 1623cm^{-1} , the out-of-plane bending vibration around 634 and 610cm^{-1} (Fig. 3) [25]. The first attempt at a comparison with the references of barium compounds led to a successful fit with barium carbonate, for the peaks at 2881 , 2822 , 2542 , 2452 , 2093 and 1754cm^{-1} (combination and overtones bands), 1451 and 1060cm^{-1} , asymmetric and symmetric CO stretching modes respectively, 855 and 692cm^{-1} , in-plane and out-of-plane CO_3^{2-} bending respectively [19]. In fact, XRD analysis showed the presence of witherite- BaCO_3 mineral (Fig. 3).

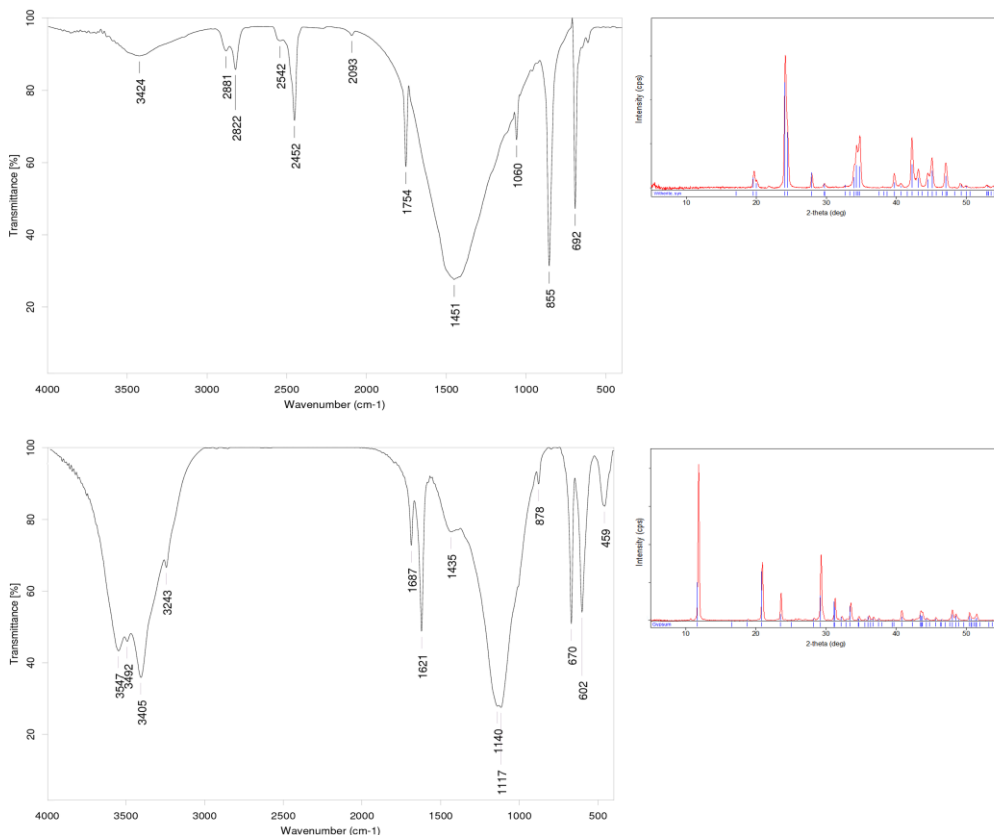


Fig. 3. FTIR transmittance analysis of Barium white showing the peculiar peaks of barium carbonate (2881 , 2822 , 2551 , 2452 , 2093 , 1754 , 1451 , 1060 , 855 , 692cm^{-1}) (above, left) and XRD analysis of the same pigment (red line), compared to witherite reference (blue line) (above, right); FTIR transmittance spectrum of Egyptian blue, showing the signals of gypsum (3547 , 3492 , 3405 , 3243 , 1687 , 1621 , 1140 , 1117 , 670 , 602 , 459cm^{-1}) and calcium carbonate (1435 , 878cm^{-1}) (bottom, left), and XRD analysis of the same pigment (red line) compared to gypsum reference (blue line) (bottom, right).

The analysis of Egyptian blue (Italian manufacturing), which is supposed to be cuprorivaite - sodium aluminum silicate - revealed that the compound that provides the blue color was probably under the detection limit of the three techniques and the matrix may have covered the signals. The FTIR peaks 3547 , 3492 , 3405 and 3243cm^{-1} resembled in fact the signals of the hydroxyl stretching bands observed in gypsum. The bending vibrations (1687 and 1621cm^{-1}), SO asymmetric stretching modes at 1140 and 1117cm^{-1} , and bending modes at 670 , 602 , 459cm^{-1} confirmed the presence of gypsum (Fig. 3) [22, 23]. Weak peaks at 1435 and 878cm^{-1} were also present, suggesting the CO asymmetric stretching band and out-of-plane

bending vibration of calcium carbonate-possibly in low amounts [23]. XRD analysis confirmed the identification of gypsum, as well as the XRF spectrum.

XRD analysis of Cobalt blue (Italian manufacturing) - which should be cobalt alluminate - identified a mixture of cobalt oxide and low amounts of cobalt sulfide, together with the mineral willemite, Zn_2SiO_4 - zinc orthosilicate - (Fig. 4), which is normally white. XRF analysis was then performed, which led to the identification of zinc and cobalt (Fig. 4). Infrared signals at 1091 , 973 , 928 , 867 cm^{-1} were interpreted as SiO_4 stretching modes, and the peaks at 896 and 460 cm^{-1} could be the torsional vibration and bending modes of the SiO group, which are all clues indicating willemite (Fig. 4) [26]. This was confirmed by the ZnO_4 stretching at 613 cm^{-1} and the $ZnOSi$ vibration mode at 576 cm^{-1} . The expected peaks of cobalt aluminate (806 , 680 , 560 , and 523 cm^{-1}) were absent [27].

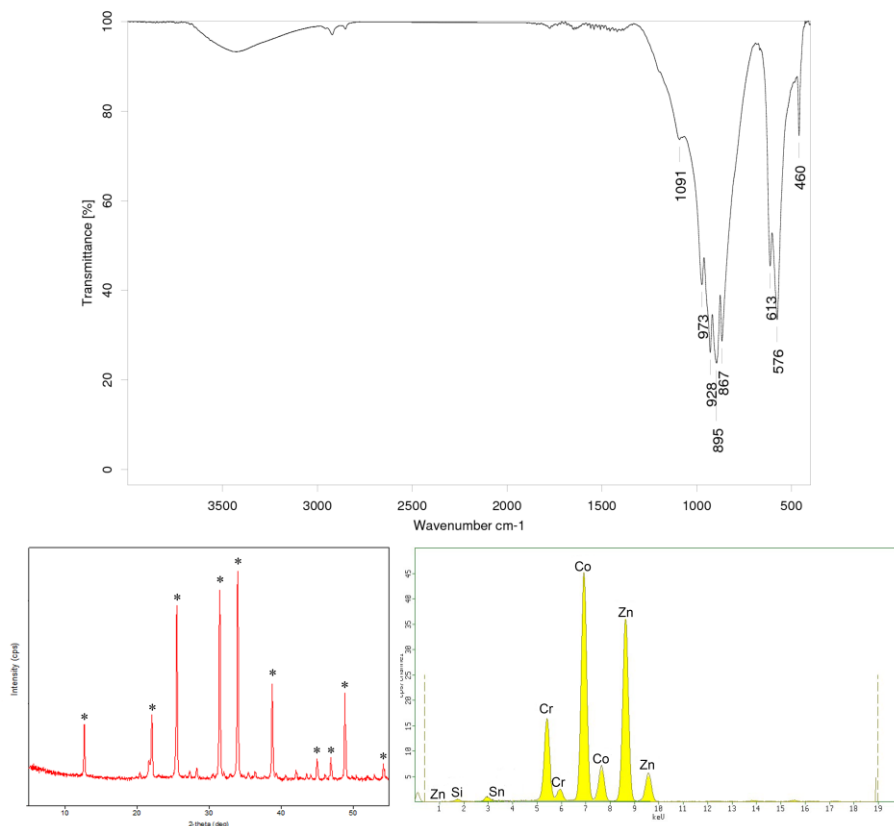


Fig. 4. Cobalt blue: FTIR transmittance spectrum presenting the peaks of willemite (1093 , 973 , 928 , 867 , 895 , 613 , 576 , 460 cm^{-1}) (above), XRD analysis -the signals of willemite cobaltian are marked- (bottom, left) and XRF spectrum (bottom, right), showing the presence of zinc and cobalt. The peaks of chromium, visible in the XRF spectrum, are due to the source used by the instrument.

A cobalt-doped willemite mineral was probably used in which one zinc atom is substituted by cobalt, which is responsible for the characteristic deep blue color of the pigment, in order to minimize the use of toxic cobalt and the production costs. According to a study by Pisareva, in Russia the pigment was named 'cobalt spectral' and was first produced as a painting material in the late 1950s [28]. Pisareva characterized the compound, proving that polarizing microscopy and X-ray diffraction are reliable techniques to distinguish cobalt blue and cobalt spectral. The further comparison with the XRD reference of willemite cobaltian

(International Centre for Diffraction Data PDF file 46-1316) and the XRD data reported by Pisareva for ‘cobalt spectral’ confirmed the co-presence of doped willemite and pure willemite (Fig. 4). On the basis of this result, the attribution of infrared signals of the pigment Cobalt blue also to doped willemite cannot be ruled out. Other references report the use of Co - doped zinc silicate ($Zn_{2-x}Co_xSiO_4$), possibly as a coloring agent for ceramic glazes [29, 30].

The XRD results (Fig. 5) on Lead white (Italian manufacturing) showed a mixture of hydrocerussite $Pb_3(CO_3)_2(OH)_2$, lead oxide carbonate hydroxide $Pb_{10}(CO_3)_6(OH)_6O$ (plumbonacrite), and cerussite $PbCO_3$ versus the expected presence of only hydrocerussite and lead carbonate as minor components [31].

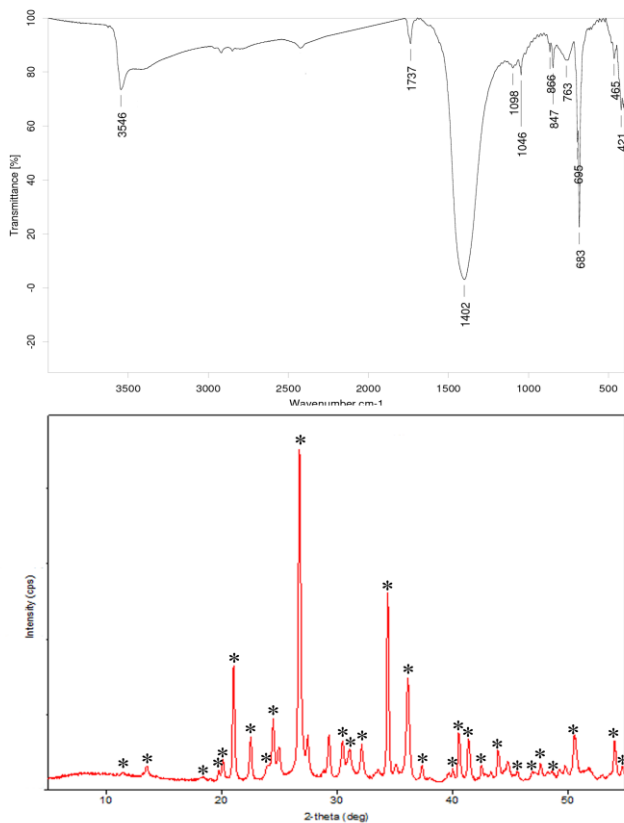


Fig. 5. Lead white FTIR transmittance spectrum, showing the peaks of basic lead carbonate (1737, 1402, 1098, 1046, 866, 695, 683, 465 cm^{-1}), lead carbonate (847 cm^{-1}) and plumbonacrite (3546, 763, 421 cm^{-1}) (above), and XRD analysis - the signals of plumbonacrite are marked - (bottom).

FTIR peaks at 1098 and 1046 cm^{-1} point to OH stretching and bending signals, while the features at 1402, 866, 695, 683 cm^{-1} are typical of CO_3^{2-} stretching, and 471 cm^{-1} recalls the characteristic PbO stretching, the overall pattern-including the peak at 1737 cm^{-1} - resembling hydrocerussite (Fig. 5) [32, 33]. Some of the bands recorded overlapped with those of $PbCO_3$ and $Pb_{10}(CO_3)_6(OH)_6O$, however the signal at 847 cm^{-1} belong to $PbCO_3$, and the OH stretching at 3546 cm^{-1} , PbOH bending at 421 and 763 cm^{-1} could be due to lead oxide carbonate hydroxide [33, 34]. The relative intensity of the bands suggested the prevalence of hydrocerussite.

Corbeil et al. describe a process dating back to 1940 that formed a “new” lead white, whose crystal structure identified the chemical formula as $Pb_{10}(CO_3)_6(OH)_6O$, although some

authors refer to it as $3\text{PbCO}_3 \cdot 2\text{Pb(OH)}_2 \cdot \text{PbO}$ [35]. The XRD reference spectrum of the modern lead white was established and the compound was named ‘plumbonacrite’ due to its nacreous appearance. Pearlescent white lead may in fact indicate a modern forgery. The speculation regarding the XRD data of traditional and new lead white discussed by Corbeil clearly demonstrates the unambiguous identification of the two compounds. Corbeil et al also report the identification of plumbonacrite in a few 20th century paintings and in a pre-tested permanent Artists' Oil Colors paint tube labelled “Flake White” and suggest that the compound may form as a byproduct of the production of traditional lead white. Recently, plumbonacrite was determined in a painting by Vincent van Gogh and considered by the authors as an intermediate degradation product of the whitening of minium [36].

The mineral chrysocolla (*chrysos* and *kolla* mean gold and glue in Greek, respectively) is a bright to bluish green basic copper silicate $(\text{Cu}, \text{Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n(\text{H}_2\text{O})$, occurring in copper deposits and often associated with malachite [1]. It was used as a pigment up to the 17th century and has been identified in various paintings. The investigation of Chrysocolla (German manufacturing) by XRD revealed a mixture of malachite, quartz and muscovite. Infrared spectrum showed peaks at $1497, 1400, 1034, 820, 798, 751\text{cm}^{-1}$ which are the typical carbonate group absorptions of malachite, as well as 3405cm^{-1} OH out-of-plane bending and $\text{CuO } 570\text{cm}^{-1}$ bending modes [18]. Alternatively, the artificial basic copper carbonate green, also called green verditer, may be present. In fact, the XRD and FTIR signals of natural and synthetic versions of the pigments agree very well and differentiation may be possible by only observing the particles' features, using SEM or polarization microscopy [31].

Conversely, the particular absorbance peaks of chrysocolla are likely to be OH stretching at 3618cm^{-1} , intense stretching vibration of Si-O at 1010cm^{-1} , and 770 and 660cm^{-1} [37, 38]. According to the literature, chrysocolla can be considered as a substitute or an impurity of malachite, although with a bluer green hue [1]. Many misattributions between malachite and chrysocolla are thought to have occurred since ancient Rome, since they are both copper minerals.

Investigation into the Mars pigments

The pigments (Italian manufacturing) were analyzed by TG (Fig. 6), FTIR and XRD and the composition is described in Table 1. XRD confirmed the expected presence of iron oxides and oxy-hydroxide, supported by the typical goethite peaks revealed by FTIR (out-of-plane OH deformation band at 794cm^{-1} , FeO stretching peak at 468cm^{-1}) [20]. Mars red also contained gypsum.

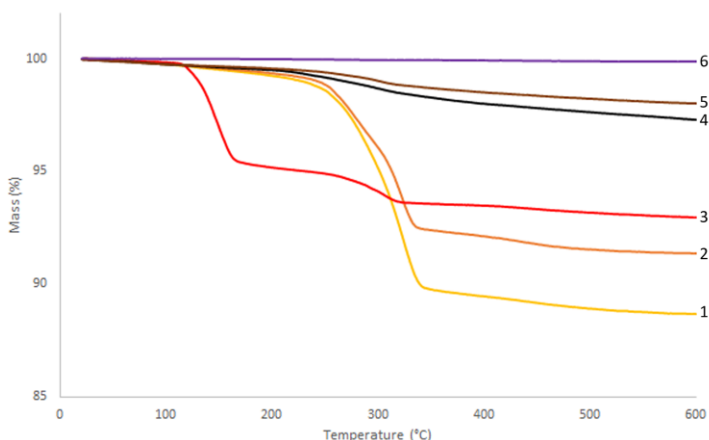


Fig. 6. TG curves of Mars pigments: yellow (1), orange (2), red (3), black (4), brown (5), violet (6).

Table 1. Composition of Mars pigments and loss of water around 300-330°C, as weight percentage, as determined by TG analysis.

Pigment	Composition	Loss of water (weight %)
Mars yellow	Goethite FeOOH	9,52
Mars orange	Hematite Fe ₂ O ₃ (32,41%), goethite FeOOH (67,59%)	6,85
Mars red	Hematite Fe ₂ O ₃ (64,06%), goethite FeOOH (13,91%), gypsum CaSO ₄ 2H ₂ O (22,03%)	1,41
Mars violet	Hematite Fe ₂ O ₃	-
Mars black	Goethite (10,85%), hematite Fe ₂ O ₃ , magnetite F ₃ O ₄	1,10
Mars brown	Goethite (9,28%), hematite Fe ₂ O ₃ , chromite Cr ₂ O ₃	0,94

Considering the literature data and the composition determined by XRD and FTIR analyses, the water content observed in the TG curves around 300-330°C was probably only due to the reaction of goethite which produces hematite [39].

Regarding Mars black and brown, although goethite was not revealed by XRD and FTIR analysis, the weight loss points to the presence of goethite, probably in an amount under the detection limits of the aforementioned techniques. The curve of Mars red (Fig. 6) also shows a weight loss at 155°C, due to the decomposition of gypsum which produces CaSO₄ [40].

Table 1 shows the percentage estimates of components based on the TG curves and FTIR and XRD results, when possible.

Mars violet contained only hematite and no water, as clearly shown by the TG curve (Fig. 6). The hue was probably obtained from hematite with larger particles than those used for Mars red, as suggested in the literature [16].

Conclusions

We have presented the analysis of some commercial pigments, in order to determine their composition. We have discussed the analytical results both in terms of the composition according to the literature and from the descriptions on the labels. The use of complementary techniques led to a reliable determination of the actual composition, in terms of both the molecular and elemental content. The results confirm the conclusions of recent publications regarding a few reference pigments [5, 7, 8, 41–43].

In many cases, the active principle was present, mixed with compounds: calcium carbonate, gypsum, baryte and titanium dioxide. Calcium carbonate was the most common. Such compounds do not contribute to the final hue, but are just traditionally used as an extender, which is a colorless or white inert used to dilute pigments with a high hiding power [2]. In these cases the addition of such compounds could be considered as legitimate for the use of the pigment, but challenging from an analytical point of view.

The addition may have been justifiable in the past because the materials were not available or more durable materials were preferred, and substitutions with more easily obtained materials were necessary. Today, this could be done for financial reasons, or to expand the range of colors for sale. The addition of low-cost materials to increase the weight of genuine pigments has been a common practice since the 19th century, for example the use of gypsum as an adulteration of yellow ochre [11]. In some cases, bright and cheap adulterants were added to enhance genuine dull colors, which thus became more attractive to the painters.

Conversely, we found that in some cases the name of the pigment was completely misleading in relation to its real composition. For example, the Cinnabar (Italian manufacturing) sample was supposed to be HgS but was actually composed of minium. This may be a legacy from Ancient Rome, in fact Pliny the Elder applied the name *minium* to cinnabar and *minium secundarium* to lead tetraoxide, which is minium [44]. After this practice, the name minium referred both to the pigment cinnabar-HgS and red lead-Pb₃O₄. In fact, the term minium remained confusing for a long time up to the Middle Ages, although later translations of the name were still unclear [45]. The cost of cinnabar is higher than minium, thus the confusion of terms also had economic implications. Cennino Cennini described cinnabar as being often produced in a mixture with minium, and suggests: “*Compera sempre cinabro intero, e non pesto nè macinato. La ragione? Chè le più volte si froda o con minio, o con matton pesto*” (“Always buy vermilion unbroken, and not pounded or ground. The reason? Because it is generally adulterated, either with red lead or with pounded brick”) [46]. Adulteration has been demonstrated by analyzing medieval paint samples [45].

To the best of our knowledge, the so-called Mars pigments have never been extensively characterized until now, and our results have better identified the components and estimated the relative weight percentages, which are responsible for the different hues.

Our results of course do not establish whether substitutions or adulterations occur routinely in commercial products. The conclusions highlight however that the composition should always be monitored and that the signals of extraneous compounds should be eliminated or not considered in the comparison with the actual data from paintings. The compositional data clearly points to the need (although time-consuming) for a multi-analytical campaign, as one technique alone is often insufficient for a complete identification. Checking the purity of pigments before their use in conservation works should be good practice in order to prevent the problems of turning different colors, drying problems or decreasing stability.

Acknowledgements

The authors heartily acknowledge the Fondazione Banca del Monte di Lombardia for support, prof. Norberto Masciocchi, prof. Simona Galli, Sveva Colombo, and Elena Lissoni for suggestions and helpful discussions.

References

- [1] N. Eastaugh, V. Walsh, T. Chaplin, R. Siddall, **Pigment Compendium: A Dictionary and Optical Microscopy of Historical Pigments**, Butterworth-Heinemann, Oxford, 2008.
- [2] R.J. Gettens, G.L. Stout, **Painting Materials: A Short Encyclopaedia**, Courier Corporation, New York, 1966.
- [3] M. Pastoureau, *La couleur et l'historien*, **Pigment. Color. l'antiquité Du Moyen Age** (Editor: B. Guineau), Paris, 1990, pp. 21–40.
- [4] K. Castro, M. Pérez, M.D. Rodríguez-Laso, J.M. Madariaga, *FTIR Spectra Database of Inorganic Art Materials*, **Analytical Chemistry**, **75**(9), (2003) pp. 214A–221A. doi:10.1021/ac031320e.
- [5] A. Vila, N. Ferrer, J.F. García, *Colored inks analysis and differentiation: a first step in artistic contemporary prints discrimination*, **Analytica Chimica Acta**, **588**(1), 2007, pp. 96–107. doi:10.1016/j.aca.2007.01.071.
- [6] C. Miliani, A. Daveri, B.G. Brunetti, A. Sgamellotti, *CO₂ entrapment in natural ultramarine blue*, **Chemical Physics Letters**, **466**(4–6), 2008, pp. 148–151. doi:10.1016/j.cplett.2008.10.038.
- [7] E.L. Kendix, S. Prati, R. Mazzeo, E. Joseph, G. Sciutto, C. Fagnano, *Far Infrared*

- Spectroscopy in the Field of Cultural Heritage, Infrared and Raman Users' Group (IRUG)*, **7**, 2010, pp. 8–13.
- [8] E.P. Tomasini, E.B. Halac, M. Reinoso, E.J. Di Liscia, M.S. Maier, *Micro-Raman spectroscopy of carbon-based black pigments*, **Journal of Raman Spectroscopy**, **43**(11), 2012 pp. 1671–1675. doi:10.1002/jrs.4159.
- [9] J.H. Townsend, L. Carlyle, N. Khandekar, S. Woodcock, *Later nineteenth century pigments: Evidence for additions and substitutions*, **The Conservator**, **19**(1), 1995 pp. 65–78. doi:10.1080/01410096.1995.9995096.
- [10] M. Clarke, *A nineteenth-century colourman's terminology*, **Studies in Conservation**, **54**(3), 2009, pp. 160–169.
- [11] L. Carlyle, *Authenticity and adulteration: what materials were 19th century artists really using?*, **The Conservator**, **17**, 1993, pp. 56–60. doi:10.1080/01410096.1993.9995075.
- [12] C. Corti, L. Rampazzi, P. Visoná, *Hellenistic mortar and plaster from Contrada Mella near Oppido Mamertina (Calabria, Italy)*, **International Journal of Conservation Science**, **7**(1), 2016 pp. 57–70.
- [13] A. Sansonetti, J. Striova, D. Biondelli, I. Aliatis, L. Rampazzi, *Hidden colours in stuccowork damaged by fire: A multi-analytical investigation for revealing the original decorative pattern*, **Journal of Cultural Heritage**, **22**, 2016, pp. 1055–1060. doi:10.1016/j.culher.2015.11.002.
- [14] R. Bugini, C. Corti, L. Folli, L. Rampazzi, *Unveiling the Use of Creta in Roman Plasters: Analysis of Clay Wall Paintings From Brixia (Italy)*, **Archaeometry**, **59**(1), 2017, pp. 84–95. doi:10.1111/arc.12254.
- [15] L. Rampazzi, V. Brunello, C. Corti, E. Lissoni, *Non-invasive techniques for revealing the palette of the Romantic painter Francesco Hayez*, **Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy**, **176**, 2017 pp. 142–154. doi:10.1016/j.saa.2017.01.011.
- [16] K. Helwig, *Mars colours: preparation methods and chemical composition*, **Studies in Conservation**, **43**, sup2, 1998 pp. 23–23. doi:10.1179/sic.1998.Supplement-2.023.
- [17] S.N. Ghosh, *Infrared spectra of the Prussian blue analogs*, **Journal of Inorganic and Nuclear Chemistry**, **36**, 11, (1974) pp. 2465–2466. doi:10.1016/0022-1902(74)80454-9.
- [18] J.A. Goldsmith, S.D. Ross, *The infra-red spectra of azurite and malachite*, **Spectrochimica Acta Part A: Molecular Spectroscopy**, **24**(12), 1968 pp. 2131–2137. doi:10.1016/0584-8539(68)80273-9.
- [19] G.C. Jones, B. Jackson, **Infrared Transmission Spectra of Carbonate Minerals**, Springer Netherlands, 1993.
- [20] M.J. Wilson, **Clay Mineralogy: Spectroscopic and Chemical Determinative Methods**, Chapman & Hall, London, 1994.
- [21] T. Gatta, L. Campanella, C. Coluzza, V. Mambro, P. Postorino, M. Tomassetti, G. Visco, *Characterization of black pigment used in 30 BC fresco wall paint using instrumental methods and chemometry.*, **Chemistry Central Journal**, **6**, Suppl 2:S2, 2012, pp. 1–10. doi:10.1186/1752-153X-6-S2-S2.
- [22] M. Hass, G.B.B.M. Sutherland, *The Infra-Red Spectrum and Crystal Structure of Gypsum*, **Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences**, **236**(1207), 1956, pp. 427–445. doi:10.1098/rspa.1956.0146.
- [23] M.R. Derrick, D. Stulik, J.M. Landry, **Infrared Spectroscopy in Conservation Science**, The Getty Conservation Institute, Los Angeles, 1999.
- [24] R.L. Feller, ed., **Artists' Pigments. A Handbook of Their History and Characteristics - Vol. 1**, National Gallery of Art, Washington, 1986.
- [25] B. Prameena, G. Anbalagan, V. Sangeetha, S. Gunasekaran, G.R. Ramkumaar, *Behaviour of Indian natural baryte mineral*, **International Journal of ChemTech Research**, **5**(1), 2013, pp. 220–231.

- [26] C.-C. Lin, P. Shen, *Sol-gel synthesis of zinc orthosilicate*, **Journal of Non-Crystalline Solids**, **171**(3), 1994, pp. 281–289. doi:10.1016/0022-3093(94)90197-X.
- [27] B.H. Berrie, ed., **Artists' Pigments. A Handbook of Their History and Characteristics**, Vol. 4, National Gallery of Art, Washington, 2007. <https://books.google.it/books?id=1kE-PgAACAAJ>.
- [28] S. Pisareva, *A note on cobalt spectral*, **Studies in Conservation**, **50**(3), 2005, pp. 190–192. doi:10.2307/25487744.
- [29] D. de Waal, *Micro-Raman and portable Raman spectroscopic investigation of blue pigments in selected Delft plates (17-20th Century)*, **Journal of Raman Spectroscopy**, **40**(12), 2009, pp. 2162–2170. doi:10.1002/jrs.2389.
- [30] E. Ozel, H. Yurdakul, S. Turan, M. Ardit, G. Cruciani, M. Dondi, *Co-doped willemite ceramic pigments: Technological behaviour, crystal structure and optical properties*, **Journal of the European Ceramic Society**, **30**(16), 2010, pp. 3319–3329. doi:10.1016/j.jeurceramsoc.2010.08.013.
- [31] A. Roy, ed., **Artists' Pigments. A Handbook of Their History and Characteristics - Vol. 2**, National Gallery of Art, Washington, 1993.
- [32] J. Bessière-Morandart, V. Lorenzelli, J. Lecomte, II. — *Détermination expérimentale et essai d'attribution des vibrations actives en infrarouge de quelques carbonates basiques métalliques à l'état cristallin*, **Journal de Physique**, **31**(4), 1970, pp. 309–312. doi:10.1051/jphys:01970003104030900.
- [33] J. Van der Weerd, A. van Loon, J.J. Boon, *FTIR studies of the effects of pigments on the aging of oil*, **Studies in Conservation**, **50**(1), 2005, pp. 3–22. doi:10.2307/25487713.
- [34] M.H. Brooker, S. Sunder, P. Taylor, V.J. Lopata, *Infrared and Raman spectra and X-ray diffraction studies of solid lead(II) carbonates*, **Canadian Journal of Chemistry**, **61**(3), 1983, pp. 494–502. doi:10.1139/v83-087.
- [35] M.-C. Corbeil, P.J. Sirois, *A Note on a Modern Lead White, also Known as 'Synthetic Plumbonacrite'*, **Studies in Conservation**, **52**(4), 2007 pp. 281–288.
- [36] F. Vanmeert, G. Van der Snickt, K. Janssens, *Plumbonacrite Identified by X-ray Powder Diffraction Tomography as a Missing Link during Degradation of Red Lead in a Van Gogh Painting*, **Angewandte Chemie**, **127**(12), 2015, pp. 3678–3681. doi:10.1002/ange.201411691.
- [37] M.-S. Sun, *The nature of chrysocolla from Inspiration mine, Arizona*, **The American Mineralogist**, **48**, 1963, pp. 649–658.
- [38] R.L. Frost, Y. Xi, *Is chrysocolla $(\text{Cu,Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ related to spertiniite $\text{Cu}(\text{OH})_2$?—A vibrational spectroscopic study*, **Vibrational Spectroscopy**, **64**, 2013, pp. 33–38. doi:10.1016/j.vibspec.2012.10.001.
- [39] S. Goñi-Elizalde, M.E. García-Clavel, *Thermal behaviour in air of iron oxyhydroxides obtained from the method of homogeneous precipitation. Part II. Akaganeite sample*, **Thermochimica Acta**, **129**(2), 1988, pp. 325–334. doi:10.1016/0040-6031(88)87348-9.
- [40] J. Adams, W. Kneller, D. Dollimore, *Thermal analysis (TA) of lime- and gypsum-based medieval mortars*, **Thermochimica Acta**, **211**, C, 1992, pp. 93–106. doi:10.1016/0040-6031(92)87010-8.
- [41] U. Casellato, P. A. Vigato, U. Russo, M. Matteini, *A Mössbauer approach to the physico-chemical characterization of iron-containing pigments for historical wall paintings*, **Journal of Cultural Heritage**, **1**(3), 2000, pp. 217–232. doi:10.1016/S1296-2074(00)01088-8.
- [42] C. Montagner, D. Sanches, J. Pedroso, M.J. Melo, M. Vilarigues, *Ochres and earths: Matrix and chromophores characterization of 19th and 20th century artist materials*, **Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy**, **103**, 2013, pp. 409–416. doi:10.1016/j.saa.2012.10.064.
- [43] M.C. Caggiani, A. Cosentino, A. Mangone, *Pigments Checker version 3.0, a handy set for*

- conservation scientists: A free online Raman spectra database*, **Microchemical Journal**, **129**, 2016, pp. 123–132. doi:10.1016/j.microc.2016.06.020.
- [44] K.C. Bailey, ed., **The Elder Pliny's Chapters on Chemical Subjects, Part 1**, E. Arnold & Company, London, 1929.
- [45] H.G.M. Edwards, D.W. Farwell, E.M. Newton, F.R. Perez, *Minium; FT-Raman non-destructive analysis applied to an historical controversy*, **The Analyst**, **124**(9), 1999, pp. 1323–1326. doi:10.1039/a904083h.
- [46] C. Cennini, **Il libro dell'arte - The Craftsman's Handbook**, Dover Publications, New York, 1933.
-

Received: May 29, 2018

Accepted: May 20, 2019