Determination of metals in artistic pigments using the optimized GFAAS method and Raman spectroscopy

Tatjana Tripković1 · Ružica Vasić1 · Aleksandar Lolić2 · Rada Baošić2

Abstract
Graphite furnace atomic absorption spectroscopy (GFAAS) was applied to identification of historical pigments. The method is adapted to determine different metals, usually found in pigments. Operating conditions were optimized, such as sample drying step, pyrolysis and atomization temperatures, modifiers, and volume of sample introduced into the atomizer, to reduce interferences due to a complex sample matrix. Using the optimized method pigments in samples from the painting Coronation of the Virgin from the Church of the Shroud of the Holy Virgin in Barić were identified. The samples were analyzed also by Raman microscopy to verify the identification achieved by GFAAS. Raman microscopy confirmed the assumptions made based on GFAAS results. Using the two techniques a variety of pigments have been identified, such as calcite, lead white, goethite, hematite, ultramarine, vermilion, minium, carbon black. Based on GFAAS results the presence of azurite was observed in the blue paint sample, although this finding was not confirmed by Raman microscopy.

Keywords GFAAS · Method optimization · Pigments · Art objects · Raman microscopy

Introduction
Preservation of cultural heritage is an essential task of modern society. Examination of the physical properties and chemical composition of the artifact is helpful and is increasingly being used to place the work in an appropriate historical context, to determine its origin and authenticity, or to test the technology used in the making. People have always used different types of materials, organic and inorganic, natural and synthetic, from their natural environment to create these artifacts. Understanding the chemical and physical properties of the used materials is necessary to protect works of art.

A big part of the world’s cultural heritage are paintings. Typically, the painted surface consists of two or more layers of paint applied above the primer. Paints are colored fluid mixtures of at least three components: pigment, medium, and binder (Goffer 2007). Generally, the pigment is defined as a solid organic or inorganic substance, insoluble in the medium, and does not physically and chemically react with it (Christie 2001). Inorganic pigments are more stable and resistant to light compared to pigments of organic origin (Clark 1964).

Natural inorganic pigments, prepared mainly by mechanical grinding of minerals, have been used since prehistoric times. The roots of the production of synthetic inorganic pigments can be traced back to the ancient Egyptians (Christie 2001), Greeks, and Romans (Feisner and Reed 2014). Through the Middle Ages and the Renaissance, new pigments were introduced as the technique of painting evolved. The number of pigments available to artists has expanded significantly since the Industrial Revolution and most of the metal-based paints were developed by the nineteenth century (Clark 2002). From the type and amount of specific chemical elements in a given paint sample, pigments used by an artist could be deduced. Identification of pigments in paint samples is often difficult due to the presence of organic compounds such as varnishes and binders, strong attachment of the pigment to the substrate, and chemical changes of pigments and other species present in the paint layers.

The application of physics and chemistry to the analysis of cultural heritage materials is almost as old as the scientific documentation of art and archeological objects, dating back
to the eighteenth century (Doménech-Carbó and Osete-Cortina 2016). Instrumental techniques must be sensitive and specific to be applied in the analysis of objects of artistic, historical, and archeological nature (Janssens 2005). Numerous papers dealing with the identification of artistic pigments using different instrumental techniques have been published. A vast number of them applied spectroscopic techniques, such as X-ray fluorescence (XRF) (Fisher et al. 2005; Moens et al. 1994; Klockenämper et al. 1993), scanning electron microscopy (SEM) (Keune and Boon 2005; Agnoli et al. 2007; Mazzocchin et al. 2007; Aliatis et al. 2009; Haswell et al. 2008), X-ray diffraction (XRD) (Rampazzi et al. 2007; Moussa et al. 2009; Mazzocchin et al. 2006), laser-induced breakdown spectroscopy (LIBS) (Mazzocchin et al. 2006; Melessanaki et al. 2001; Burgio et al. 2001) and Fourier-transform infrared spectroscopy (FTIR) (Mazzocchin et al. 2007; Aliatis et al. 2009; Wainwright 2009). Emission spectroscopic techniques, with inductively coupled plasma atomic emission spectroscopy (ICP-AES), have been widely used to determine the chemical composition of inorganic materials (Moussa et al. 2009), such as glass, glazes, and alloys, among other antiques and archaeological materials, as well as pigments in old manuscripts, paintings and old maps (Goltz et al. 2007).

Raman spectroscopy coupled with a microscope is considered a key technique for identifying pigments in works of art, mainly because of its high spatial and spectral resolution, extreme sensitivity, and selectivity. Raman microscopy is even more effective in combination with other complementary techniques (XRF, XRD, IR, PIXE, LIBS) (Mazzocchin et al. 2006, 2007; Bussotti et al. 1997; Wehling et al. 1999).

Atomic absorption spectrometry (AAS) is a suitable approach for the identification of metals in inorganic pigments due to the small sample requirement and high sensitivity of these instruments. The most significant advance in AAS is the introduction of non-flammable atomizers. AAS can be a reliable method for analyzing major and trace elements in paints. Usually, a sample needs to be dissolved before analysis by microwave digestion in pressure vessels or simple digestion on the oven. Partial acid digestion with incineration in a kiln, with nitric and hydrofluoric acid, is most commonly used (Wehling et al. 1999). However, dissolving the sample requires effort and time, and it could be a major source of error, mainly due to loss of analyte and/or contamination (Bader 2011). The main obstacles to AAS analysis are matrix interferences, sample insolubility, loss of analytes, and contamination during digestion in open vessels. Also, significant losses of volatile elements such as Cd, Hg, As, and Pb can occur. Some of these problems could be avoided by direct sampling techniques which can be used for pigment analysis, direct sampling GFAAS (Bentlin et al. 2007). Direct sampling GFAAS was applied in the rapid mono-elemental determination in various complex materials (Belarra et al. 1997; Dong and Krivan 2001; Vale et al. 2006), including old manuscripts and paintings (Bentlin et al. 2007). Castro et al. (2002) applied AAS for the identification of pink and green colors in decorative wallpapers. Goltz et al. (2004, 2007) published a technique of micro-sampling of painted surfaces using a cotton swab in combination with GFAAS analysis of metals in samples. The absolute limit of detection for GFAAS is usually in the range of 40–60 pg (Barcelo 2000), so 1 μg of the paint sample is sufficient to determine metals in pigments and elements in low concentrations. Wang et al. (2007) applied a GFAAS method with optical temperature control for the determination of Cd traces in painting samples. The linear range, increased sensitivity, as well as the lifetime of the graphite tube was expanded, while the temperature and atomization time was reduced.

This work aimed to identify the different pigments in nineteenth century painting Coronation of the Virgin using GFAAS technique for analysis of metals characteristic of the most common pigments. The pigments are characterized also by Raman microscopy to achieve a more reliable identification.

**Experimental**

**Materials**

**Chemicals**

Deionized water (specific resistivity of 18 MΩ·cm) was used to prepare all the solutions. Calibration solutions were prepared by appropriate dilution of commercial standard solutions of analytes (Ca²⁺, Cd²⁺, Cr²⁺, Fe³⁺, Pb²⁺ from Merck, Darmstadt, Germany; As³⁺, Co²⁺, Cu²⁺, Mg²⁺, Mn²⁺, Ni²⁺ from J.T. Baker, Phillipsburg, USA), 1000 mg/L for all). For all determinations, intermediate solutions of metal cations were made at a concentration of 10 ppm. To all calibration solutions and intermediate solutions, 1 mL of concentrated nitric acid (J.T. Baker, Phillipsburg, USA) was added per 100 mL to prevent hydrolysis. To dissolve samples, concentrated nitric acid 69% (w/w) and hydrogen peroxide 33% (w/w) (p.a. both Zorka, Šabac) were used. Modifier solutions: 2 g/L NaNO₃, 2 g/L LiNO₃, Ni(NO₃)₂ at concentrations of 50 and 100 ppb and Mg(NO₃)₂ at a concentration of 1 g/L were made by dissolving appropriate amounts of solid salts p.a. purity (all Merck, Darmstadt, Germany) in deionized water.

**Sampling and sample preparation**

For this study, we analyzed 4 samples taken from the painting “Coronation of the Virgin” (dated in 1836) by an
unknown author, which belongs to the iconostasis of the Church of the Shroud of the Holy Virgin in Barič. The Church is built in 1874, while the iconostasis is decorated mostly with icons transferred from the Church of St. Peter and Paul in Topčider, created from 1834 to 1838, commissioned by Prince Miloš Obrenović, Serbian ruler 1815–1839 and 1858–1860. Authors of the icons were painters Konstantin Lekić, who painted the throne icons of Christ and the Virgin, Janja Stergević Moler, who painted the festal and apostolic icons, while Dimitrije Jakšić painted the main and side doors (Popović and Prodanović-Ranković 2005). The Painting “Coronation of the Virgin” was not attributed to any of the three authors mentioned above. During a campaign of iconostasis conservation, samples from the painting are collected and analyzed. Respecting the rules of minimal invasiveness, the samples are taken from the painting edges or damaged areas using a scalpel and tweezers. Locations of the samples are provided in Appendix 1, while sample descriptions are shown in Table 1. Paint samples used for analysis were between 0.2 and 0.5 mg.

Samples were divided and a half of each are used to prepare cross-sections by immersing in cold-curing acrylic resin (ORTOpoli, Polident, Slovenia) and polished. Samples are examined under Olympus BX51 light microscope using reflected visible and UV light with magnification up to ×1000.

To analyze pigments in painting samples by GFAAS, the second part of the sample was weighed in a 5 mL glass beaker, 1 mL of concentrated nitric acid was added and heated at 100 °C until most of the acid evaporated. After cooling, 1 mL of concentrated nitric acid and 0.2 mL of 33% (w/w) hydrogen peroxide were added and the heating process was repeated. Then 0.5 mL of nitric acid and 0.5 mL of hydrogen peroxide were added and evaporated near to dryness. After cooling, the contents were transferred to a 10 mL volumetric flask and, after addition of 0.1 mL of concentrated nitric acid, diluted to the mark using deionized water. The elements in low concentrations were directly determined from this solution. For analysis of macro components, solutions were diluted 100–500 times.

Blank was prepared and analyzed, following the identical procedure applied to the samples. The concentration of metals and metalloids measured in the blank was subtracted from the concentration obtained in the samples. The results shown for the samples represent the final mass fraction of metals.

**Instrumentation and operating conditions for identification of pigments by GFAAS**

Metals in pigments were determined using a Perkin-Elmer 2380 atomic absorption spectrometer equipped with a graphite furnace HGA-400 and a deuterium lamp background correction. Hollow cathode lamps were used for all metals whose operating conditions are listed in Appendix 1. For all determinations, the peak area was measured while argon was used as the inert gas at a flow of 220 mL/min. During atomization, the flow of argon was reduced, while for the determination of arsenic and nickel it was stopped to increase the sensitivity. Pyrolytic graphite cuvettes were used. Optimized graphite furnace heating programs are given for each element individually in Appendix 1. The samples are weighted using a microbalance (Sartorius M500P) with a precision of 0.001 mg.

**Instrumentation and operating conditions for Raman spectroscopy**

Samples were analyzed as paint cross-sections using a DXR Raman microscope (Thermo Scientific) equipped with a 10 × and 50 × objective and a high precision x, y, z motorized stage. For excitation, a frequency-stabilized single-mode diode laser was used operating at 780 nm, and output power of a maximum of 24 mW. Spectra were collected with a resolution of 2 cm⁻¹ from 50 to 3400 cm⁻¹ using 2 accumulations of 20 s integration time per spectrum. The aperture was 50 µm, while the signal-to-noise ratio was adjusted by manual focusing. A long working distance 50 × objective was used for spectra collection. If the collected spectrum has low intensity, 4 accumulations of 20 s integration time were applied. The power on the samples was 0.2–8 mV, depending on signal intensity and spectrum appearance. All data were processed using OMNIC for Dispersive Raman 9.3.32 software, while samples were observed using OMNIC Atlus 9.3.435.

---

**Table 1 Analyzed samples taken from the painting “Coronation of the Virgin”**

| Sample no | Sample description       | Sample location                          |
|-----------|-------------------------|------------------------------------------|
| 1         | Blue paint from the background | The lower-left corner of the painting       |
| 2         | White paint layer        | Robe of the Virgin lower-left quadrant of the painting |
| 3         | Brown paint layer        | The wooden cross on the top left quadrant of the painting |
| 4         | Red paint layer          | Gown of the Virgin lower-left quadrant of the painting |
Results and discussion

Cross-section analysis

Cross-section analysis of samples immersed in synthetic resin provided important information about the layered structure of analyzed paint samples and the ground layer. Samples contain 1–2 paint layers and particles of different pigments are noted within the layers (Fig. 1). The ground is brownish in appearance due to the presence of ochre and umber pigments. On the paint surface, a protecting layer of varnish is present, which exhibits fluorescence under UV illumination.

GFAAS method for identification of pigments

Parameters such as sample drying, pyrolysis and atomization temperatures, modifiers, and volume of samples introduced into the atomizer were optimized using aqueous solutions of analytes standards. These factors are important, especially pyrolysis and atomization temperatures because they greatly influence the signal of the analyte of interest (Ávila et al. 2005). Quantification was achieved using calibration curves obtained by measuring the series of aqueous standard solutions. External calibration using aqueous standard solutions is successfully applied due to the peak area integration, instrument improvement, and chemical modifiers (Resano et al. 2004; Vale et al. 2006). Samples were dissolved as described in a previous section by digestion with nitric acid and hydrogen peroxide in an open vessel.

Taking into account the characteristics of analyzed samples, 11 elements were selected in this experiment to optimize conditions for pigment identification using GFAAS. It was found drying temperature of 90 °C provides the most efficient drying for the sample volume of 20 µL during 15 s. Only for determination of arsenic drying conditions were different. The drying is performed in three stages: 90 °C, 110 °C, and 130 °C for 15, 11, and 45 s respectively. A step before pyrolysis, at 250 °C, was introduced into the temperature program for all analyzed elements, except arsenic, to remove the organic matter from the sample matrix. The addition of chemical modifiers allowed an increase of pyrolysis temperature for arsenic was from 1300 to 1500 °C. Atomization temperatures proposed by the instrument manufacturer were applied for all analyzed metals. The only exception was arsenic and despite the application of 2 g/L sodium nitrate as a modifier, atomization temperature has to be decreased from 2300 to 2100 °C to obtain reproducible signals. The optimized temperature programs have successfully been applied for the analysis of the dissolved painting samples. The operating conditions for measurements, temperature programs, and calibration graphs are all summarized in Appendix 1.

Matrix modifiers were applied only for the determination of arsenic and manganese. Appropriate amounts of modifier solutions are added directly into the graphite tube before a standard or sample was introduced. Several modifiers have been tested, but the best repeatability for arsenic was achieved by the addition of 5 µL of 2 g/L sodium nitrate for manganese, Perkin-Elmer recommends the application of 5 µL of magnesium nitrate solution (1000 mg/L). By using magnesium nitrate, pyrolysis temperature is raised from 1200 to 1400 °C with almost a double signal increase. Also, a wider linear range of the calibration line was achieved.

Analytical characteristics of the method

Analytical characteristics of the optimized GFAAS methods for the determination of metals in pigments and paint samples are summarized in Table 2. The table encompasses parameters of the linear regression analysis and its statistical results, as well as the linear correlation coefficients of the calibration lines, measured using aqueous standard solutions. The linear range and characteristic concentration for each element were determined. The detection limit (LOD) and quantification limit (LOQ) of the method are based on the values of the standard deviation of y-intersection (Sy) and it is calculated as LOD = 3Sy/a and LOQ = 10Sy/a, where a is the slope of the calibration line (Shrivastava and Gupta 2011).

Analysis of paint samples by GFAAS technique

Content of the elements determined by analysis of four paint samples from the painting “Coronation of the Virgin” is summarized in Table 3. The elements with the highest contents in all samples are calcium, lead, and iron. Magnesium and manganese are natural companions of calcium and iron. The content of cadmium is very low, while cobalt was below the detection limit. Based on these findings, cadmium yellow (cadmium sulfide, CdS) and red (cadmium zinc sulfoselenide CdS-CdSe) pigments, as well as cobalt blue (cobalt(II) oxide-aluminum oxide, CoO-Al2O3), are not present in analyzed samples. Contents of copper and chromium are lower compared to the main components.

Based on the cross-sections of the samples (Fig. 1), a brownish ground layer with particles of different pigments is observed in all analyzed samples. Based on the results presented in Table 3, for the ground layer the artist probably used a mixture of chalk (calcium carbonate), lead white (basic lead(II) carbonate, 2PbCO3·Pb(OH)2), and ochre (iron(III) oxide, Fe2O3).
Fig. 1 Cross-sections of the samples under the light microscope with reflected visible and UV light

Sample 1, x100, visible and UV light

Sample 2, x200, visible and UV light

Sample 3, x200, visible and UV light

Sample 4, x200, visible and UV light
White lead (its natural form is mineral cerussite) was also used as the white pigment on this painting, according to sample number 2. The content of lead in sample 2 is several times higher than in other samples. Lead white was in use from antique times until the nineteenth century and was prepared from metallic lead and vinegar (Gettens et al. 1967). White lead was used until the nineteenth century as the only white pigment, which corresponds to the time frame when the analyzed icon is dated. Calcium and lead contents in sample 1 are also quite high, but based on the cross-section and the sampling spot, the artist mixed a blue pigment with white to achieve a light blue tone. Contents of iron and copper in this sample are slightly above the average in other analyzed samples. Several blue pigments contain iron (Prussian blue) and copper (ultramarine, azurite, Egyptian blue, Han blue). Therefore, based on the presence of these two elements in this sample was not possible to identify the blue pigment. The identity of blue pigment was further investigated utilizing Raman spectroscopy.

The content of iron in sample 3 is similar to calcium and lead. In the cross-section of sample 3, the ground layer and the paint layer look very similar, but the paint layer has a slightly more intense tone. According to the results and observations, the paint layer probably consists of lead white and ochre, similar to the ground layer.

According to the cross-section observations, sample 4 has three layers of paint which can contain possibly three different pigments. The paint layer applied directly over the ground layer contains the highest concentration of red pigment, while the other two layers are less pigmented. Identification of red pigments in this sample is not straightforward. Based on elements identified in the sample and its relative concentrations, the presence of red pigments based on iron (hematite), lead (minium), mercury (vermilion), and organic pigments such as alizarin (Madder Lake) should be investigated further. Cadmium red can be excluded because the content of cadmium is below the detection limit in this sample. Individual layers were further investigated by Raman microscopy.

### Identification of pigments by Raman microscopy

After optical microscopy, the samples immersed in synthetic resin were analyzed using Raman microscopy. The Raman spectrum of blue pigment grains in sample 1 from the painting "The Coronation of the Virgin" unequivocally indicates the pigment lazurite (ultramarine blue, $Na_3Ca_2Al_6Si_6O_{24}[(SO_4)_2(S, Cl, (OH))]$.). Lazurite was a very
popular, but rare and expensive pigment extracted from the mineral lapis lazuli, whose largest deposit is in Afghanistan, the Hindu-Kush mountains (Schumann 2013). This mineral, as well as its synthetic equivalent ultramarine blue, in the Raman spectrum can be recognized by the symmetric stretching vibration at 548 cm\(^{-1}\) of its blue chromophore, \(S_3^-\) ion (Osticioli et al. 2009), entrapped within the aluminosilicate cage. The overtone of this band usually appears at 1096 cm\(^{-1}\) (Tomasini et al. 2016). The bending vibration of \(S_3^-\) at 258 cm\(^{-1}\) is identified in this spectrum also. In the blue paint layer of sample 1, two white pigments are identified—calcite (CaCO\(_3\)) by symmetric stretching mode of CO\(_3^{2-}\) at 1088 cm\(^{-1}\) and white lead also by symmetric stretching mode of CO\(_3^{2-}\) at 1049 cm\(^{-1}\). Based on this find, the blue pigment was mixed with white lead and chalk to achieve the desired color hue (Fig. 2). Also, in one of the spectra collected at the blue paint layer, a peak at 988 cm\(^{-1}\) appeared due to symmetric stretching of SO\(_4^{2-}\), indicating the presence of Alum K (aluminum potassium sulfate, KAl(SO\(_4\))\(_2\)·12H\(_2\)O) in the sample and suggesting the natural origin of lazurite. Bearing in mind the fact that Prince Miloš Obrenović ordered these icons, the use of precious pigments was expected.

Due to the increased content of copper in sample 1 compared to other samples, azurite in the sample was likely to be encountered. However, azurite was not identified by any of the Raman spectra recorded on the cross-section of this sample. Azurite cannot be excluded from the artist’s palette, but may not be localized in a fragment of a sample analyzed by Raman spectroscopy. Therefore, we can observe the presence of azurite in the sample based on the results of GFAAS analysis of the whole sample, but it has not been unambiguously identified using Raman microscopy. This demonstrates one of the advantages of whole sample analysis over cross-section analysis.

Using Raman spectroscopy, lead white (2PbCO\(_3\)·Pb(OH)\(_2\)), gypsum (CaSO\(_4\)·2H\(_2\)O), calcite (CaCO\(_3\)), red and yellow iron oxides are identified in the ground layer of all samples. These results completely correlate to the results of GFAAS analyses. In Raman spectra of white lead usually appear two peaks at 1050 cm\(^{-1}\) (very sharp and intense) and 1054 cm\(^{-1}\) (less intense) due to C–O symmetric stretching. This pigment, consisting of a mixture of two crystalline phases, cerussite (PbCO\(_3\)), and hydrocerussite (Pb\(_3\)(CO\(_3\))\(_2\)(OH)\(_2\)) (Gettens et al. 1967), can be applied in combination with aqueous media such

Fig. 2 Raman spectra of blue pigment grains in sample 1 indicate presence of a lazurite and calcite, b lazurite and white lead
as egg tempera, gum Arabic, and animal glue. In combination with drying oils lead white dries fast compared to other known white pigments (Kostadinovska et al. 2013). It can be encountered mixed with other white pigments, chalk, or gypsum, especially in the priming layer (Gettens et al. 1967). Gypsum and calcite are identified in the priming layer of analyzed samples by their respective intensive bands at 1008 cm\(^{-1}\) (symmetric stretching of SO\(_4^{2−}\)) and 1086 cm\(^{-1}\) (symmetric stretching of CO\(_3^{2−}\)) in Raman spectra (Fig. 3). In the white paint layer of sample 2 pigment white lead was identified by its Raman band at 1050 cm\(^{-1}\) due to C–O symmetric stretching.

In sample 3, in the yellow paint layer, mineral goethite (α-FeOOH) is identified using Raman microscopy (Fig. 4). Goethite is identified by its characteristic Fe–O vibrations at 547, 485, 393, 298, and 250 cm\(^{-1}\) (Bouchard and Smith 2002) in the sample spectrum. The position of the peaks may vary if substitution of the Fe\(^{3+}\) cation with other cations, such as Al\(^{3+}\), in the crystal of goethite occurs (Zorba et al. 2007). Goethite is the chromophore of yellow ochre (Froment et al. 2008), a natural earth pigment that contains also aluminosilicates (Zorba et al. 2007). The yellow ochre pigment has been widely used from the earliest history (Gettens and Stout 1966) and it is a common pigment in Orthodox iconography. In the spectrum of goethite, wide Raman bands of carbon black, at 1308 and 1606 cm\(^{-1}\) (Bicchieri et al. 2008) due to C–C vibrations, are also recognized. In the same sample, hematite is identified by its Raman bands at 225, 292, 410, 498, 612, and 1322 cm\(^{-1}\) (de Faria et al. 1997) resulting from Fe–O vibration. In the spectrum of hematite, a peak characteristic for calcite at 1086 cm\(^{-1}\) is noticed.

In sample 4, two red painting layers have been identified. The lower thinner layer contains a higher concentration of red pigment, while the upper thicker layer contains less red pigment in a mixture with a white. The red pigment in the lower paint layer yielded bands in the Raman spectrum characteristic of mercury sulfide—a strong band at 254 cm\(^{-1}\) and two weaker ones at 289 and 343 cm\(^{-1}\) (Scheuerman and Ritter 1969; Cosano et al. 2019). Cinnabar, a mineral consisting of mercury sulfide (α-HgS) was used as a pigment since ancient times. Production of the artificial form of this pigment, vermilion, dates back to medieval times in Europe. It was produced by heating a mixture of mercury and sulfur (Clark 2001). The absence of bands at 465 cm\(^{-1}\) typical of α-quartz, and 1085 cm\(^{-1}\) typical of calcite, in the Raman spectrum of pigment grain in the lower red paint layer, suggests that the identified HgS was not natural, but synthetic (Miguel et al. 2014). The spectra for the red pigments in sample 4 are shown in Fig. 5.

In the upper paint layer, Raman analysis revealed the presence of two red pigments—red ochre (hematite, Fe\(_2\)O\(_3\)) and red lead (minium, Pb\(_3\)O\(_4\)). Hematite is a natural mineral widely used as a red pigment since antique times (Burgio et al. 2008). Red lead or minium is a bright red pigment, one of the first artificially prepared pigments by oxidation of litharge (PbO) (West Fitzhugh 1986). Hematite (α-Fe\(_2\)O\(_3\)) was identified in sample 4 by its vibrational bands of Fe\(_2\)O\(_3\) at 226, 295, 410, 615, and ca. 1320 cm\(^{-1}\) (de Faria and Lopes 2007; Hernanz et al. 2012). Minium

---

**Fig. 3** Raman spectra of white pigments in a priming layer—calcite and gypsum, b white paint layer—white lead
characteristic bands at 121, 150, 390, and 547 cm\(^{-1}\) (Miguel et al. 2009) are identified in the same Raman spectrum as hematite. A band of vermilion at 254 cm\(^{-1}\) is also noticed in this spectrum. It is not uncommon to use vermilion and minium in the mixture because of their visual similarity (Kleist and Korter 2019; Egel and Simon 2013), but it is unusual to use hematite together with the two pigments in the same paint layer. The artist did this probably to achieve the desired shade of red. The lower paint layer contains only vermilion. The white pigment in this layer was white lead, identified in all other samples, too.

Conclusions

This paper demonstrates the potential of GFAAS in the quantitative and qualitative determination of metals in paint samples, in micro and macro concentrations. Detection limits for GFAAS are low and the preparation of samples is quite simple with low reagent consumption and waste generation. Aqueous standards can be used for calibration, despite the very complex matrix of paint samples. The technique could be applied to different types of samples—oil, tempera, or fresco paintings. Required sample amounts are very small (a few micrograms, up to 0.5 mg), but may vary, depending on the type of sample, the analyzed element, and concentration of pigment. Carefully optimized temperature programs and the addition of modifiers in this experiment reduced interference in metal analyses. The results obtained here indicate the potential of the developed method in archaeometry for measuring trace elements in small samples. The samples cross sections were analyzed by Raman microscopy to verify the pigment identification achieved by GFAAS. All results obtained here using the two methods were consistent. Additionally, in the sample of the blue paint layer presence of copper was observed using GFAAS, although azurite was not identified by Raman microscopy. Azurite was not excluded from the artist’s palette, probably it was not localized in the fragment of blue sample analyzed by Raman spectroscopy. A certain advantage of the whole sample

Fig. 4 Raman spectra of pigments in the yellow paint layer in sample 3 where a goethite and carbon black, b hematite and calcite are identified
analysis in GFAAS over a cross-section analysis in Raman microscopy could be emphasized because some pigments in the sample can be assumed based on the presence of metals characteristic of these pigments, although conclusive evidence in the form of Raman spectra was not recorded.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11696-022-02110-6.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

Agnoli F, Calliari I, Mazzocchin G-A (2007) Use of different spectroscopic techniques in the analysis of roman age wall paintings. Ann Chim 97(1–2):1–7

Aliatis I, Bersani D, Campani E, Casoli A, Lottici PP, Mantovan S, Marino I-G, Ospitali F (2009) Green pigments of the pompeian artists’ palette. Spectrochim Acta A Mol Biomol Spectrosc 73(3):532–538
Ávila AK, Araujo TO, Couto PRG, Borges RMH (2005) Experimental design applied to the optimization of pyrolysis and atomization temperatures for As measurement in water samples by GFAAS. Metrologia 42(5):368
Bader N (2011) Sample preparation for flame atomic absorption spectroscopy: an overview. Rasayan J Chem 4(1):49–55
Barcelo D (2000) Sample handling and trace analysis of pollutants: techniques, applications and quality assurance, 1st edn. Elsevier Science, Amsterdam
Belarra MA, Crespo C, Martinez-Garbayo MP, Castillo JR (1997) Direct determination of metals in solid samples by graphite-furnace atomic absorption spectrometry: does sample mass influence the analytical results? Spectrochim Acta Part B Spectrosc 52(12):1855–1860
Bentlin F, Pozebon D, Mello P, Flores E (2007) Determination of trace elements in paints by direct sampling graphite furnace atomic absorption spectrometry. Anal Chim Acta 602(1):23–31
Bicchieri M, Monti M, Piantanida G, Sodo A, Tanasi MT (2008) Inside the parchment. Presented at 9th international conference on NDT of art, Jerusalem Israel
vaporization-inductively coupled plasma mass spectrometry and solid sampling-graphite furnace atomic absorption spectrometry for the direct determination of Cr in various materials using solution-based calibration approaches. J Anal Spectrom 19:958–965

Scheuerman W, Ritter GJ (1969) Raman spectra of cinnabar (HgS), realgar (As4S4) and orpiment (As2S3). Z Naturforsch A 24:408–411

Schumann W (2013) Gemstones of the world: newly revised, 5th edn. Sterling, New York

Shrivastava A, Gupta VB (2011) Methods for the determination of limit of detection and limit of quantitation of the analytical methods. Chron Young Sci 2:21–25

Tomasini EP, Marte F, Cureaga VP, Landa CR, Siracusano G, Maier MS (2016) Virtuous colours for mary identification of lapis lazuli, smalt and cochineal in the andean colonial image of our lady of Copacabana (Bolivia). Philos Trans A Math Phys Eng Sci 374:2082

Vale MGR, Oleszczuk N, dos Santos WNL (2006) Current status of direct solid sampling for electrothermal atomic absorption spectrometry—a critical review of the development between 1995 and 2005. Appl Spectrosc Rev 41(4):377–400

Wainwright NM, Moffatt EA, Sirois PJ (2009) Occurrences of green earth pigment on Northwest Coast First Nations painted objects. Archaeometry 51(3):440–456

Wang Z, Wang S, Cai M (2007) Determination of cadmium in paint samples by graphite furnace atomic absorption spectrometry with optical temperature control. Talanta 72:1723–1727

Wehling B, Vandenabeele P, Moens L, Klockenkämper R, von Bohlen A, Van Hooydonk G, de Reu M (1999) Investigation of pigments in medieval manuscripts by micro Raman spectroscopy and total reflection X-ray fluorescence spectrometry. Mikrochim Acta 130:253–260

West Fitzhugh E (1986) Red lead and minium in artists’ pigments: a handbook of their history and characteristics, ed. Feller RLF, National Gallery of Art, Washington, ch.6

Zorba T, Andrikopoulos KS, Paraskevopoulos KM, Pavlidou E, Popkonstantinov K, Kostova R, Platnyov V, Daniilia S (2007) Infrared and Raman vibrational spectroscopies reveal the palette of frescos found in the medieval monastery of Karaach Teke. Ann Chim 97:491–503

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.