Investigation of roman age pigments found on pottery fragments

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Abstract

This work deals with the study of the physico-chemical characteristics of pigments found on pottery fragments from an excavation in Vicenza (Contrà Pedemuro S. Biagio). The examined pigments were: a blue colour on a terracotta fragment; an olive green on a black pot bottom; yellow traces on a red depurated terracotta; an olive green plate bottom with an amaranth “a fresco” test; a deep red on a depurated terracotta; a white trace, again on a depurated terracotta. The techniques used were optical microscopy, scanning electron microscopy (SEM), equipped with an energy dispersive (EDS) microanalysis detector, X-ray powder diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. Most of those techniques were non-destructive and able to provide the required results. All the pigments belonged to the group of basic colours, we did not find “precious” pigments. They have many similarities to those discovered in other European sites in France and Switzerland, witnessing the active trading exchange in which Xth Regio, Venetia et Histria played an important role.

Keywords: Roman pigments, Chemical analysis, Archaeometry, Energy dispersive, X-ray diffraction, Fourier transform infrared spectroscopy

1. Introduction

One of the most important questions in the study of ancient paintings, specially as far as Roman age painting is concerned, is the nature of the pigments used in the painting “atelier” to realize the decorations. The physico-chemical analysis, in fact, gives information useful to define the gamut of pigments available on a local and regional scale and to understand and appreciate the techniques of colour preparation and application. In addition, the study of the provenance of the pigments allows one to discover the communications and trade exchange lines, or even defining the so-called “site taste”.

These kinds of studies have been carried out in France, Switzerland and Spain as one is allowed to verify from the contribution presented in the Proceedings of the International Workshop on Roman Wall Paintings held in Fribourg in 1996 [1].

Three important studies on the nature and on the gamut of Roman pigments appeared in “Germania”, the bulletin of the Romisch-Germanischen Kommission of the German Institute of Archaeology concerning colour fragments found in the archaeological site of Argentomagus, France [2]; in work on the Gallo-Roman wall painting from Durikon [3] and...
in the Proceedings of the International Workshop on Roman Wall Paintings in Switzerland [1].

In Italy physico-chemical analysis is not yet commonly applied to the study of pigments used in the wall decorations as well as those rarely found in the outfit of working shops, which were usually preserved in terracotta, glass or bronze containers [4–8].

The aim of the present work is the study of six pigments found on pottery fragments during an archaeological excavation in a Roman villa in Vicenza (Contrà Pedemuro, S. Biagio) directed by the “Sovrintendenza Archeologica per il Veneto” by Dr. Luigi Malnati and Prof. Gian Pietro Bregaglio of the University of Padova.

All the fragments came from ceramic containers of varied production; these containers are still subject to a systematic study. The correlation between the pigments studied herein and the rich and numerous wall decorations found in the area as a consequence of demolition, will be enhanced through the analysis of the “a fresco” samples, which is ongoing.

The examined pigments, present in small quantity, were: a blue colour on a terracotta fragment; an olive green on a black varnish pot bottom; yellow traces on a red depurated terracotta; an olive green plate bottom with an amaranth “a fresco” test; a deep red on a depurated terracotta trace of white, again on a depurated terracotta.

The most important techniques used in this work were optical microscopy, scanning electron microscopy (SEM), equipped with an energy dispersive (EDS) microanalysis detector, X-ray powder diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy.

Most of those techniques were non-destructive and able to give results useful for the characterisation of the pigment.

2. Materials and methods

2.1. Optical microscopy

The samples were observed by means of an optical microscopy Wild-Leitz M8 with a 19.2–256× zoom. The samples were illuminated using a movable fibre glass system.

2.2. Scanning electron microscopy (SEM)

SEM images were taken using a Jeol (Tokyo) JSM 5600 LV instrument equipped with an Oxford Instruments 6587 EDS microanalysis detector. The images were taken under low vacuum conditions where samples did not show any charging effects; in this way, it was possible to avoid coating the samples with a high conductance thin film (gold or graphite films). EDS microanalysis was made to obtain information on the elemental composition of the sample.

2.3. X-ray diffraction (XRD)

X-ray powder diffraction was used to identify the different crystalline phases present in the pigments. A Philips X’Pert vertical goniometer with Bragg-Brentano geometry, connected to a highly stabilised generator, was used for XRD analysis. Cu Kα Ni-filtered radiation, a graphite monochromator on the diffracted beam and a proportional counter with pulse height discriminator were used. Measurements in a 5–60° range were taken with a step size of 0.05° and 2 s per point.

2.4. Infrared (FTIR) spectroscopy

Absorption spectra in the IR region were collected using a Nicolet Magna 75 FTIR spectrometer. The spectra were given as an average of 32 measurements. Samples were diluted in KBr pellets (IR grade, Merck, Darmstadt, Germany).

2.5. Procedure

Sample analysis was carried out as follows:

- An optical microscopy examination was used in order to verify the presence of a heterogeneous mixture of components and to evaluate the crystal sizes.
- A FTIR spectroscopic examination gave a quick response to the identification of the anionic groups present in the sample.
- Electron microscopic imaging, was used to evaluate the structure of the sample at high magnification and to evaluate the presence of recognisable crystal phases.
- Elemental microanalysis (EDS) was carried out on the selected point.
X-ray diffraction analysis was used in order to identify crystalline phases, correlating the obtained peaks with those in suitable data bases.

3. Results and discussion

3.1. Blue colour

On the edge of a terracotta pot, a small blue deposit of about 1 cm² was present. The examination of the pigment, by means of the stereomicroscope, allowed one to observe that this was constituted of a whitish basis in which small, intense blue crystals of approximately 10 μm were immersed.

In Fig. 1 the IR spectrum of a small part of the sample is shown. One can see the frequencies (cm⁻¹) of Egyptian blue, as reported by Bruni et al. [9], middle intensity bands at 1070, 1050 and 1005 cm⁻¹ and small intensity bands at 1170 and 1240 cm⁻¹. The spectrum also clearly shows the presence of carbonate, as one can infer from the bands present at 873 and 700 cm⁻¹ and from the large intense band made by two peaks centred at 1430 and 1470 cm⁻¹, which also appear in IR spectra of pure samples of calcium and magnesium carbonates. The presence of carbonates is due not only to the mortar lying beneath, but also to the use of sodium, calcium and copper carbonates; the synthesis of CaCuSi₄O₁₀ is anything but complete, thus the presence of carbonate is rather frequent. The hydroxyl group stretching which appears at 3425 cm⁻¹, can mainly be ascribed to the humidity still present in the sample.

In Fig. 2, the XRD spectrum of the blue sample is shown. It allowed us to identify the crystalline form of cuprorivaite, which constitutes the blue pigment [2,10], as well as the presence of silica. The carbonate phase was identified as dolomite.

Fig. 3 shows an image taken using a scanning electron microscope. One can observe, in the centre of the figure, some crystals of the average size of 10-20 μm surrounded by other, smaller crystals. In Fig. 4 an EDS spectrum of one of the central crystals is shown. One can see a rather intense peak due to the presence of silicon, and the revealing presence of copper, which confirms that this pigment is a double calcium and copper silicate, which constitutes the blue pigment [2,9]. Obviously, the peaks corresponding to oxygen, calcium and magnesium are also present.
Fig. 2. XRD response of the blue sample with the following crystalline phases: cuprorivarcite, dolomite and silica.

Fig. 3. SEM image of the blue sample.
3.2. Green colour

Traces of an olive green pigment were deposited onto four black Campanian vase (a Morel type small amphora [11]) fragments.

Optical microscopy revealed the presence of small, intense blue crystals diluted in a whitish basis. The whole sample was olive green owing to the presence of other green mineralogical components.

In Fig. 5, the principal recorded IR bands are reported. One can observe the characteristic carbonate bands at 870 and 1458 cm$^{-1}$, and the silicate bands from 1000 to 1100 cm$^{-1}$. At about 3450 cm$^{-1}$, the large band related to the hydroxyl stretching of water together with the small bands at 3555 and 3600 cm$^{-1}$, due to the hydroxyl stretching of glauconite and celadonite are present.

In the SEM image (Fig. 6), one observes the presence of various materials, with different structures and characteristics, which confirms the complex nature of the mixture.

The EDS spectrum in Fig. 7 shows intense peaks corresponding to Si and O and the presence of Cu, Ca, Mg, Al, K and Fe. Also in this case, XRD (Fig. 8) confirms the presence of the cuprorivaite and dolomite crystalline phases, as well as the green glauconite and celadonite, which both play an important role in giving the olive green colour to the mixture.

3.3. Yellow colour

On the bottom of a large depurated red terracotta pot, with the wall outwardly inclined and found in 10 tallying fragments, one can see, by means of the stereomicroscope, traces of a very fine and dusty yellow pigment gathered in the cracks of the surface. In the IR spectrum of the yellow pigment (Fig. 9), one can observe the characteristic peaks of silicate around 1070 cm$^{-1}$ and a series of bands distributed between 470 and 600 cm$^{-1}$, which can be related to iron oxides [10]. The large band present around 3400 cm$^{-1}$ can be related to the stretching of an OH group. Middle intensity bands, related to carbonate and centred at 873 and 1450 cm$^{-1}$, are also present.

The SEM image confirms that the pigment is very fine-grained and also confirms the presence of different kind of crystals. From the EDS spectrum, Fig. 10, one can see the presence of Si, Fe, Al, Ca and K, as expected from the presence of iron compounds, clay minerals and small quantity of carbonates.

The XRD spectrum (Fig. 11) clearly confirms the presence of four crystalline phases: goethite, dolomite,
Fig. 5. FTIR spectrum of the green colour.

Fig. 6. SEM image of the green sample.
Fig. 7. EDS spectrum of the green colour.

Fig. 8. XRD response of the green sample with the following crystalline phases: cuprorivinite, dolomite, glauconite and celadonite.
Fig. 9. EDS spectrum of the yellow colour.

Fig. 10. FTIR spectrum of the yellow colour.
quartz and kaolin, which discriminate yellow ochre from all the other iron pigments [12].

3.4. Amaranth colour

Among the others, a black Campanian varnish goblet bottom with a ring foot [11] was found. On the surface, a whitish mortar with intense blue crystals was deposited. On this deposit, an amaranth layer, in which blue as well as silica and calcite crystals appeared on the surface, was present. In Fig. 12, the IR spectrum of a sample from the amaranth layer is shown. Two zones with rather intense bands are visible: the first, around 1080 cm\(^{-1}\), related to the O–Si–O group (silicate); the other, between 480 and 600 cm\(^{-1}\), showed peaks related to iron oxides [10].

The IR spectrum of the whitish layer beneath the amaranth shows the bands related to the stretching of the hydroxyl group around 3450 cm\(^{-1}\), the presence of carbonate (around 1430 cm\(^{-1}\)) and of silica as expected by the observation of a mortar IR spectrum.

From the SEM image, one can appreciate the heterogeneity of the sample.

EDS analysis (Fig. 13) showed the presence of O, Fe, and Si as major components and of Al, K, Mg, and Cu as minor components. This leads one to suppose that the whitish mortar is mainly constituted of dolomite and that, besides iron oxides and hydroxides, clay minerals, e.g. kaolin, are also present.

The presence of small quantities of copper is due to the cuprivate crystals immersed in the whitish mortar. In Fig. 14 the image of one of those crystals is shown. In the central part one is allowed to observe a sort of concretion, different from the crystal below. EDS analysis indicates that the main crystal contains Si, Ca and Cu and the spectrum obtained, similar to the one already reported by Bruni et al. [9], allows one to identify the crystal as Egyptian blue.

3.5. Deep red

The interior side of a pot fragment, probably used as a colour container, in depurated ceramic with a light exterior hump, was covered by a deep red colour. At the stereomicroscope, we observed deep red stains containing whitish crystals approximately 20–30 μm across. The deep red colour is constituted of red crystals of smaller dimensions; in some areas, there were intense red crystals and other brilliant orange ones.

The IR spectrum (Fig. 15) showed a large, intense band around 3450 cm\(^{-1}\), related to the stretching of the hydroxyl group; a low intensity band at 1637 cm\(^{-1}\)
Fig. 12. FTIR spectrum of the amaranth layer.

Fig. 13. EDS spectrum of the amaranth colour.
Fig. 14. SEM image of a cupronivaite crystal from the amaranth layer.

Fig. 15. XRD response of the deep red colour with the following crystalline phases: quartz, hematite, dolomite, kaolin, goethite and gypsum.
Fig. 16. FTIR spectrum of the deep red colour.

Fig. 17. FTIR spectrum of the white colour.
that could be related to the presence of sulphate; a band at 1440 cm\(^{-1}\) related to carbonate; a large intense band around 1040 cm\(^{-1}\) related to O–Si–O and sulphate; and a band between 570 and 470 cm\(^{-1}\) corresponding to the peaks of iron oxides [10]. The SEM image shows the sample to be fine-grained and rather homogeneous. EDS analysis made at different points of the sample showed the presence of Fe, Si, Al, O as

![](image)

**Fig. 18.** (a) EDS spectrum of the white pigment; (b) EDS spectrum of the back of the white pigment.
major components and Ca and Mg as minor components.

The XRD response (Fig. 16), confirms the previous results since those elements constitute the crystalline phases quartz, hematite, dolomite, kaolin, goethite and gypsum.

3.6. White colour

On some vase fragments, traces of a very intense white pigment were found. It seemed to be constituted of every small crystals among which we found some orange crystals.

The white colour can be easily removed from the vase and showed on the back a brown-orange colour, probably due to the colour of the pot.

Fig. 17 shows the IR spectrum of a small amount of this colour, which seems to be constituted of carbonate with a small quantity of silicate (1080 cm$^{-1}$).

EDS analysis (Fig. 18a) confirms that calcium is nearly the unique component of the white pigment, which can be defined as calcium carbonate. This was also confirmed by XRD data.

EDS analysis carried out on the back of the sample (Fig. 18b) showed the presence of silicon, aluminium and iron, components of the surface of the pot, hence confirming that the brown colour was absorbed from the contact area.

4. Conclusions

The techniques used for the chemical and physical characterisation of the pigments were shown to be satisfactory for obtaining the required results.

The use of EDS microanalysis gave punctual qualitative data and allowed us to avoid the use of other techniques (e.g. X-ray fluorescence) and tedious, complicated conventional chemical analysis.

XRD gave all the required structural information even using a quite small angular width, 5–60° range, and rather short measurement times.

All the pigments belong to the group of basic colours, which were usually chosen by the artist, whereas we did not find "precious" pigments.

This was one of the first opportunities to examine a sample of a Roman age Egyptian blue from an Italian excavation, besides the Aosta one [13]. It is worth noting that, in many cases, Egyptian blue was added in small amounts to enhance the brilliance of other colours.

The use of the celadonite in the examined olive green is rather interesting. Celadonite, in fact, is a mineral, which came either from Cyprus or from Monte Baldo, rather close to the villa in Vicenza.

FTIR spectroscopy, even if it is a relatively poorly-sensitive technique, was quick and simple to use for identification of the anionic groups in inorganic pigments.

Optical microscopy, the lack in FTIR spectra of clear bands related to organic ligands and the presence of carbonates, led us to think that the colours were applied “a fresco” or that they were just attached to the interior walls of their container (e.g. deep red and yellow).

The studied pigments have many similarities with those discovered in other European sites [2,14] witnessing the active trading exchange that took place in Roman times.

Last, this study gave a contribution to the knowledge of the materials used during the Roman age in the X$^{5}$ Regio, Venetia et Histria.

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References


