Pigments of the Campania region (Italy): a first overview for ancient wall paintings

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ABSTRACT

A first overview on the ancient pigments used in Campania region was carried out from some study on ancient wall paintings located both in residential and funerary contexts. The technological skills in the individual use or mixing of pigments from the ancient painters is related to four archaeological contexts of Campania region, dated back from the 6th century BCE to the 1st century CE. The pigments were analysed by means of in-situ spectroscopic techniques and micro-destructive laboratory analyses. The multi-analytical approach revealed the use of pure (natural and synthetic) pigments and some admixtures, created by the ancient painters to obtain assorted colour shades. The same mixtures were found in different chronological contexts and made by a different manufacturer, suggesting an evident transmission of technological knowledge over time.

1. INTRODUCTION

The study of wall paintings represents a valuable tool for tracing the knowledge and technological skills of the ancient painters over time. In fact, humans began the first cave paintings by using readily available raw materials, although recent research indicates that such materials were transported over significant distances during early human history [1]. Subsequently, they began blending pigments to formulate new colouring compounds until their artificial making.

Already at the beginning of the 19th century, the interest in ancient pigments was aimed at characterising them and verifying those recipes passed down by ancient writers [2], [3], [4]. At the time, this interest was justified by the recovery of materials from Pompeii which gave us back the broadest evidence of ancient painting, such as to constitute material of comparison in order to date other wall paintings on the basis of typology. But still today, along with Pompeii, other sites in Campania are the subject of various characterisation studies aimed at the recovery and sometimes the restoration of the extraordinary ancient decorations [5], [6].

The preciousness of the paintings often does not allow for studies involving the use of destructive techniques. As with most materials of artistic or archaeological interest, the archaometric approach must preserve the integrity of the paintings. Therefore, non-destructive analyses such as spectroscopic techniques with portable equipment have been used; these results could be then integrated by micro-destructive analyses in the laboratory. Moreover, the complex matrix constituting the original wall paintings poses challenges in ascertaining the original compounds through a singular analytic approach; thus, a multi-analytical approach is preferred to obtain information that together make up the entire puzzle.

This paper aims to bring together some of the latest studies on ancient wall paintings in Campania region, to make a first overview of the pigments found in different archaeological
contexts and belonging to different chronological phases from the 6th century BCE to the 1st century CE. For this purpose, four studies on two funerary and two residential contexts are discussed.

The wall paintings were investigated in-depth and information on the types of pigments, the painting technique, and the mortar-based supports were obtained. The results of four different diagnostic campaigns carried out in cooperation with other research groups [7], [8], [9], [10] are here reviewed and discussed for a critical comparison of the materials (and technology) used by the ancient painters in Campania region in a time span ranging from the 6th century BCE to the 1st century CE.

2. EXPERIMENTAL

2.1. Materials

The present paper is based on data obtained by multi-analytical studies carried out in situ and in the laboratory. The oldest one is the well-known funerary context of Tomb of the Diver (5th century BCE) a chest tomb that takes its name from the note pictorial representation placed on the covering slab and located 2 km south of Paestum (Figure 1a). Along with the Tomb of the Diver, other tombs recovered at Paestum and belonging to different chronological phases (dated between 6th century BCE and 4th century BCE) were analysed [7], [11].

The other investigated funerary context is the Tomba del Bandello per l’Eternità recovered in the Roman necropolis of the ancient Cumae, dated back to the first decades of the 1st century BCE. It is an extraordinary hypogeeum chamber tomb entirely decorated with a figurative representation on the upper part of the walls, which makes it exceptional in the contemporary panorama of Campania region (figure 1b) [8], [12]. The tomb has returned a wide palette of colours, suggesting an elite membership of the deceased who lay there.

The other investigated wall paintings are referred to Roman residential contexts, namely the patrician domus attributed to Marcus Vipsanius Primigenius, identified in the site of Abellinum (the ancient Atripalda) near to Avellino, and dated back to the 1st century CE decorated in 3rd and 4th Pompeian style (figure 1c) [9], [13]; and the domus of Octavius Quartius in Pompeii (figure 1d), located in the Insula 2 of the Regio II and decorated by frescoes in 4th Pompeian style, restored after the earthquake of 62 CE [10], [14].

The wall paintings of Paestum and Pompeii contexts were analysed in situ with the portable equipment to carry out spectroscopic analyses. Colours analysed on the frescoed walls of the domus of Pompeii encompassed both the red and yellow backgrounds as well as the smaller-scale central pictorial decorations and details in pink, green, and blue; additionally, analysis were also carried out on the black basal section. In the diagnostic campaign at Paestum, the measurements were conducted on tomb slabs, covering both the background whites and the green and blue pictorial decorations, along with figurative patterns primarily rendered in shades of red, yellow, and black.

By contrast, representative samples of decorated plasters from Cumae and Abellinum contexts were collected to investigate the colour palette, studied through micro-destructive analyses by lab techniques. A total of 13 samples were examined from the Cumae hypogeeum tomb, including 3 red samples from the lower sections of the walls. The selection also comprised individual samples of white, pink, purple, 4 different shades of brown, 2

Figure 1. Archaeological sites studied in Campania region (Southern Italy): a) the funerary slab at Paestum (modified from [7]); b) the funerary chamber in Cumae (modified from [8]); c) the domus of M. Vipsanius Primigenius at Abellinum (modified from [9]); d) the domus of Octavius Quartio at Pompeii (modified from [10]).
yellow, 1 blue, and 1 grey originating from the upper parts of the walls.

Five samples from the *Abellinum domus* (1 red, 1 yellow, 2 blue, 2 pink, 2 red, 1 orange, and 1 yellow) came from the collapse layer, making it unfeasible to pinpoint their specific locations on the wall.

2.2. Methods

The multi-analytical approach used to characterize ancient paintings consists of a first observation via Digital Microscopy (DM, Dino-Lite Digital Microscope 400–470× served by Dino-Capture2.0 software) and spectroscopic analyses.

X-ray Fluorescence (XRF) spectroscopic analysis was carried out using different portable X-ray fluorescence spectrometers: a SKYRAY LTD Genius 9000 in Pompeii; a Mini-X-Amptek in Paestum; a Bruker Tracer 5G in the other contexts. Bruker ARTAX Spectra 8.0 software was used for processing the spectra from all the contexts.

Fourier Transform Infrared (FTIR) spectroscopy was carried out using a Bruker Alpha instrument equipped with External Reflectance mode for the acquisitions *in situ* (Paestum and Pompeii) and with Attenuated Total Reflectance module for the analyses of pigment powders (Cumae and *Abellinum*). Raman spectroscopic analyses were carried out by a Bruker BRAVO Handheld Raman spectrometer. Both FTIR and Raman spectra were processed by Bruker Opus 7.2 software.

Measurements of colour and reflectance spectra were performed via Fiber Optics Reflectance Spectroscopy (FORS) in a visible spectral range using a tungsten lamp as source and the grating Ocean Optics (model HR2000) as detector for the analyses of slabs from Paestum, whereas the grating Qmini Broadcom was used for the analyses of samples from *Abellinum* and Cumae. FORS spectroscopy was not carried out in Pompeii. Waves open-source software was used for the data acquisition and processing. For more details of the instrumentation and acquisition parameters used in each context, please refer to the respective individual studies [7], [8], [9], [10].

3. RESULTS

The results of the microscopic and spectroscopic analyses carried out in the contexts, which allowed the identification of the pigments used to decorate the Campanian environments, are illustrated. Chemical characterisation becomes complementary to the molecular analyses to verify the materials that the ancient painters have chosen to use.

A. White

Under the digital microscope the white colour appears constituted of a white matrix in which small dark (brown – grey) grains are dispersed (Figure 2a). Chemical analyses of white decorations showed the ubiquitous presence of calcium (Table 1), as well as the infrared and Raman bands of calcium carbonate (Table 2 and Table 3), which suggested the diachronic use of calcite as white pigment. Occasionally, aragonite was also observed, another calcium carbonate associated to precious coloured pigments (e.g., in the compound with the Egyptian blue in the samples from *Abellinum*) [9], [15].

![Figure 2](image-url)

**Figure 2.** Representative images (scale 0.1 mm) of pictorial layers obtained by Digital Microscopy performed on fragments from Cumae and *Abellinum*: a) white paint from *Abellinum*; b) red paint from Cumae; c) yellow paint from Cumae; d) orange paint from *Abellinum*; e) violet paint from Cumae; f) blue paint from *Abellinum*; g) pink paint from Cumae; h) grey paint from Cumae; i) brown paint from Cumae.
the peculiar Raman shifts at 344 cm\(^{-1}\) in the relevant Pompeian style paintings during the Roman period, as proved by the additional presence of Hg (Table 1) and the peculiar Raman shifts at 344 cm\(^{-1}\) (Table 3). Moreover, in the

tombs of Paestum the presence of lead (Table 1) suggested the addition of a lead oxide (Pb\(_2\)O\(_4\)) as pigment.

### B. Red

The red paint (Figure 2b) is the most common colour in the analysed wall paintings, observed in different shades corresponding to some compositional differences. Dark red shades are featured by the presence of iron and calcium (Table 1), the latter attributed to the underlying plaster and/or the medium in which the pigment was dispersed. Infrared bands (Table 2) between 600–400 cm\(^{-1}\), along with the bands of silicates between 1200 and 900 cm\(^{-1}\) allowed us to associate this pigment to red ochre, a natural red earth containing iron oxides, identified by Raman spectra as hematite (Fe\(_2\)O\(_3\)) (Table 3). This oscillation is due to the difference in the size and especially in the shape of the hematite particles such as to the crystallinity degree [15], [16]. Even the different shades of colour may depend on the size of the grains: finer grains made a lighter paint, while coarser ones made it darker, as seen later in the violet pigment. In Figure 2b a finer red earth seems to be mixed to black and more frequent white grain. Red ochre was used in almost all contexts and the FORS data confirmed the use of an earth-based pigment.

A mercury sulphide (HgS), i.e., cinnabar, was used as pigment in the relevant Pompeian style paintings during the Roman period, as proved by the additional presence of Hg (Table 1) and the peculiar Raman shifts at 344 cm\(^{-1}\) (Table 3). Moreover, in the

### C. Yellow

DM images showed a yellow matrix with many white particles sometimes related to the alteration of paintings but above all to the binder. Chemical analyses of yellow paints (Figure 2c) revealed high concentrations of iron (Table 1) as well as the infrared bands of silicates and iron oxides/hydroxides (Table 2). Raman bands defined the presence of goethite (Fe\(_2\)O(OH)), an iron hydroxide showed characteristic peaks at 385 and 568 cm\(^{-1}\) (Table 3). This mineralogical phase represents the main constituent of yellow ochre, used in each archaeological context analysed.

### D. Orange

The orange colour was found only on the decorations on the walls of the Abellinum donus (Figure 2d). The XRF analysis revealed the presence of iron and calcium (Table 1) and consistently the ATR analysis showed the presence of iron oxides, in association with calcite (Table 2). The paint applied in this context was obtained by mixing red and yellow pigments, as it seems evident from the Digital Microscopy images (Figure 2d). Therefore, the mixture is obtained by combining two types of iron-based ochre namely yellow and red ochre.
Table 3. Raman results (cm\(^{-1}\)) on painted fragments from the studied archaeological sites. Raman spectroscopy was not carried out on the Abellinium fragments and the restored surfaces did not allow for the pigment identification at Paestum. Raman spectra for the blue and green pigments are not available, as the high fluorescence obscured their diagnostic bands. The slash indicates the total measurements performed on two different shades of the same colour. Abbreviation: n, total number of measurements.

<table>
<thead>
<tr>
<th>Colour</th>
<th>n</th>
<th>Paestum</th>
<th>Cumae</th>
<th>Pompeii</th>
</tr>
</thead>
<tbody>
<tr>
<td>White</td>
<td>23</td>
<td>1086, 712</td>
<td>1086, 710, 280</td>
<td>1086, 713</td>
</tr>
<tr>
<td>Red</td>
<td>23/5</td>
<td>612, 498, 410</td>
<td>614, 498, 410, 291, 224</td>
<td>610, 410, 496 / 344</td>
</tr>
<tr>
<td>Yellow</td>
<td>23</td>
<td>388</td>
<td>553, 386, 298</td>
<td>547, 488, 388</td>
</tr>
<tr>
<td>Violet</td>
<td>3</td>
<td>—</td>
<td>611, 495, 408, 291, 223</td>
<td>—</td>
</tr>
<tr>
<td>Black</td>
<td>14</td>
<td>1596, 1320</td>
<td>—</td>
<td>2880, 2846, 1598, 1325</td>
</tr>
<tr>
<td>Pink</td>
<td>5</td>
<td>—</td>
<td>—</td>
<td>1086, 608, 412</td>
</tr>
<tr>
<td>Grey</td>
<td>3</td>
<td>—</td>
<td>1086, 711, 281, 209</td>
<td>—</td>
</tr>
<tr>
<td>Brown</td>
<td>3</td>
<td>—</td>
<td>1625, 1310, 1085, 705, 553, 386, 298, 282, 207</td>
<td>—</td>
</tr>
</tbody>
</table>

E. Violet

Violet pigment was identified in a funerary context from Cumae tomb (Figure 2c).

In the decorated tomb, the pictorial layer revealed only the presence of iron and calcium (Table 1) and Raman spectra identified the hematite (Table 3). Therefore, the violet colour was obtained by heat—treating red iron oxide in an oxidizing environment, using a technique equally common in the Romanizing world. In this pigment typology, the darker colour hue is due to the α—Fe\(_2\)O\(_3\) particle size effect, bigger than the hematite constituting the red pigment [17]. In Figure 2c it is possible to see the higher size of hematite grains, mixed to small white particles, in contrast with the grains in Figure 2b.

F. Black

Raman bands at ca. 1600 and 1320 cm\(^{-1}\) (Table 3) carried out on the painted wall surfaces of the domus in Pompeii as well as on the painted tombs from Paestum revealed that black decorations were obtained by using the black carbon, a pigment derived from the burning or pyrolysis of organic material (coal, wood, oil) to give heavily carbonized products [18], [19]. These are forms of elementary carbon of widely differing degrees of purity [20].

G. Blue

Chemical analysis on blue paints identified the ubiquitous use of a copper—based pigment (Table 1). Infrared spectroscopy and reflectance curves related to electronic transitions attributable to Cu\(^{2+}\) ions confirmed the use of Egyptian blue (Table 2), a synthetic pigment prepared by mixing a sand containing quartz, feldspar, and carbonates with copper colouring compounds and alkaline flux to form a synthetic frit containing cuprorivaite (CaCuSi\(_4\)O\(_9\)O\(_2\)) [21]. The latter is visible in DM images in the blue crystals dispersed in white background (Figure 2f). Due to the high florescence of the pigment, no Raman spectra were acquired on the blue paintings [10].

H. Green

Two contexts (Paestum, Pompeii) offered the possibility of analysing green pigments directly in situ. The results revealed the use of two different typologies of pigment used for the green decorations. Chemical composition (Table 1) of these colours, in fact, showed the presence of aluminium, silicon, iron, calcium and potassium referred to the use of green earths. This hypothesis was confirmed by FTIR analyses, which revealed diagnostic bands at 3700—3500 cm\(^{-1}\) characteristic of the stretching of hydroxyl groups [22].

Chemical analyses, however, also highlighted the presence of copper in lighted shades, confirmed by FTIR spectra that recorded the infrared bands of Egyptian blue (Table 2), suggesting the use of a mixture, made by the addition of Egyptian blue pigment to the green earths, a recipe widely used in the ancient world [23]. As the blue pigment, also for the green one the high florescence did not allow us to acquire Raman spectra.

I. Pink

Chemical and mineralogical analyses revealed that pink colour was obtained using two different “recipes”. Skin tones come from the depiction of domus in Pompeii were obtained by mixing inorganic red pigment (red ochre) with calcium carbonate, to lighten the red colour [10]. The same recipe seems to be used in the domus of Abellinium.

On the bright pink decorations found at Cumae (Figure 2g), on the other hand, ATR—FTIR highlighted the presence of a phyllosilicate mineral namely kaolinite (Al\(_2\)Si\(_4\)O\(_{10}\)(OH))\(_4\) (Table 2). The strong hydroxyl bands at 3700 cm\(^{-1}\) and 3620 cm\(^{-1}\) are characteristic of kaolin—group clays. Because few other minerals absorb in this region, infrared spectroscopy is a sensitive technique for kaolin-based compound identification. It suggests the use of a white kaolinite—bearing clay as an extender, in which other materials were mixed. In fact, the presence of copper and iron (Table 1) suggests the addition of hematite and Egyptian blue, likely to give more brilliance to the colour shade, as observed also in the painted tombs from Paestum.

### Table 4. Use of pigments and mixtures over time in the examined Campanian archaeological contexts.

<table>
<thead>
<tr>
<th>Colour</th>
<th>Paestum</th>
<th>Cumae</th>
<th>Abellinium</th>
<th>Pompeii</th>
</tr>
</thead>
<tbody>
<tr>
<td>White</td>
<td>6th-4th BCE</td>
<td>1st BCE</td>
<td>1st CE</td>
<td>1st CE</td>
</tr>
<tr>
<td>Red</td>
<td>+min</td>
<td>r.ochre</td>
<td>+e.b.</td>
<td>cin</td>
</tr>
<tr>
<td>Yellow</td>
<td>y.ochre</td>
<td>+r.ochre</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Orange</td>
<td>hem</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Violet</td>
<td>c.b.</td>
<td>e.b.</td>
<td>c.b.</td>
<td></td>
</tr>
<tr>
<td>Black</td>
<td>g.e.</td>
<td>mad+e.b.</td>
<td>r.ochre+cal</td>
<td></td>
</tr>
<tr>
<td>Green</td>
<td>e.g.</td>
<td>feO</td>
<td>e.g. + e.b.</td>
<td></td>
</tr>
<tr>
<td>Pink</td>
<td>kln+e.b.+FeO</td>
<td>gth+c.b.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brown</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Legend: cal, calcite; r.ochre, red ochre; min, minimum; cin, cinnabar; y.ochre, yellow ochre; hem, hematite; c.b., carbon black; e.b., Egyptian blue; g.e., green earths; mad, madder; kln, kaolinite; feO, iron oxides; gth, goethite.
4. DISCUSSIONS

The analysis of pigments discovered across different Campanian archaeological contexts reveals a remarkable continuity in their usage over time (Table 4). Spanning from the 6th century BCE to the 1st century CE, the pigments employed for adorning the walls of residential and funerary settings displayed consistency.

Calcium carbonate was the recurring choice for achieving white paint during this period, while carbon black was consistently used for black decorations. Yellow and red ochre remained unvaried throughout, offering a large available source of the yellow and red paintings. These colours have received extensive scrutiny within these contexts, owing to the substantial wall coverage found in Pompeian domus and Paestan tombstones. The large use can be attributed to the aesthetic choices and the pictorial style, but it may also be indicative of a cost-effective use of pigments, which facilitated the widespread application of resources such as earths, coal, and carbonates. Notably, the carbonate formations in the Campanian region [25], along with the availability of local earths, certainly provide a straightforward source for pigments [26]. However, the absence of geological material sampling in the surrounding areas, which might serve as a potential primary resource, does not allow us to go beyond the hypothesis.

It should be noted that red ochre was used for red decorations in all contexts, although some variations in the recipe are found in the oldest Campanian context. In fact, the addition of lead or minimum secondarium (using Pliny’s words [3]), detected in the painted slabs of Paestum was probably due to the desire of darkening the red decorations. Although we observed this particular formulation only in Paestum, literature offers evidence of its application in other Campanian contexts from the 1st century CE, showing the technological continuity in the use of this combination [27]. Moreover, to obtain violet shades, Egyptian blue was mixed to red ochre, as observed in the decorations of the domus of Abellinum (1st century CE) (Table 4), and as also observed in other Campanian contexts [28], [29]. Although there is evidence in the Roman world to attest the organic origin of the violet pigment [30], or the mixture of hematite and Egyptian blue, the violet pigment studied does not fall into these typologies. The larger grain size of hematite and its subsequent firing process finds comparisons in recent studies [17], [31].

In red decoration, an alternative recipe was used in the studied Pompeian domus (Table 4). In fact, in the contexts from the Vesuvian environment, more brilliant red shades were obtained by cinnabar, a mercury sulphide called minimum in the ancient world [3], [16] and for that term often cause of confusion [32].

It is worth emphasizing that cinnabar pigment is predominantly present in the pictorial elements within the Pompeian-style frames, while an abundant application of red ochre is observed on the background areas of the walls beyond these frames. One plausible explanation for this disparity could be the preciousness of the pigment [33]. However, in other examples from Campania [34], [35], cinnabar is used on the entire wall decoration, leaving the question of use to the choice of the client and perhaps to its representative function [15].

Red ochre was also used for pink decorations in contexts dated to the 1st century CE (Abellinum); here it was used both to create large figurative representations and as a wall background. However, in the funerary context of Cumae (1st century BCE), a pink pigment of organic nature was used only in a small spot of the floral decoration of the upper parts of the walls (Table 4).

Green paints were identified on vegetal details and decorative geometries or Pompeian style frames and in chronologically distant contexts (6th–4th BCE and 1st CE), featuring different recipes. Although green earth pigment (i.e., creta viridis or appianium in ancient times) [36], was prevalent in both time periods, the later contexts exhibited the addition of blue pigment (Table 4). The different recipes could open new interesting research into the possibility of tracing specific uses of workshops over time.

The use of the Egyptian blue pigment in Campania region is not surprising in the archaeological contexts dated to the 1st century BCE and later, considering that between the 1st century BCE and the 2nd century CE factories of Egyptian blue were born in the Phlegrian territory with the Gaius Vestorius workshop, and for that also sometimes called Vestician blue, and then widely used in regional and extra–regional construction [14], [23]. Nevertheless, the specific use of Egyptian blue in all contexts analysed from the 6th century BCE to the 1st century CE (Table 4) raises new question to this topic. Although the use of locally produced Egyptian blue in the workshop of Gaius Vestorius is known and handed down from historical sources, the use of the same pigment in 6th–4th century BCE funerary contexts raises a question about the pigment production. In fact, if produced locally [37], it would greatly anticipate the well-known workshop in Campania region, from which Vestorius would later acquire the technological knowledge to produce the pigment used in Egypt and appreciated in Rome. Alternatively, the use of this pigment could suggest overseas importation [38], indicating clear trade connections between the Greek–Lucan world and Campania. The pigment was employed in all contexts,
likely associated with the elite individuals who resided in these spaces during their lives and after their passing.

In contrast to the paintings already discussed, some shades (purple, grey, brown) appear only in the large palette of 1st century BCE, whereas the orange colour was observed only in the domus of Atellium (Table 4). The analysis of the paintings was carried out on fragments derived from the collapsed portions of the structures, rendering it challenging to determine the full extent of their application on the wall surfaces. Frequently, paint mixtures exhibit visible variations, reflecting diverse ratios of constituent pigments, and such variations are often categorized with arbitrary colour names in the literature. This practice can complicate bibliographic comparisons across various contexts. Nevertheless, it is imperative to reevaluate the instances where positive correlations are identified within the Campania region.

5. CONCLUSIONS

The analysis and comparison of the pigments used in Campania region in both funerary and residential contexts emphasized the similarity in the technological choices made by the ancient master of the Roman world over time. The chemical–mineralogical analyses allowed the identification of natural and synthetic pigments useful to evaluate the technological skills of the ancient painters and the used recipes mixing various typologies of pigments to obtain different colour shades. The study leads us to reflect on the continuity of use of some pigments and mixtures in the Campania area. Therefore, this continuity can also be seen in the modus operandi of the local workshops, which produce synthetic pigments as well as use local raw materials. Nevertheless, the use of colour could respond to choices of a purely typological nature linked to the will of the client or the artist themselves, potentially bypassing intricate technological considerations.

The present research is a first overview carried out on important Campanian contexts of different chronological phases, but a more in-depth review integrating the wall paintings of the entire Campania landscape over time could hopefully shed light on the issues raised here. Analyses of Campanian geological material could represent an initial and foundational step in starting specific provenance studies.

ACKNOWLEDGEMENT


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