

TECHNICAL PAPER

PAINTING AND MORTARS FROM VILLA ADRIANA, TIVOLI (ROME, ITALY)

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Villa Adriana is a Roman building dating back to 117-138 AD. The emperor Hadrian built this construction which is characterised by numerous buildings of different uses: pavilions, gardens and *nymphaeums*. In our work we aimed to identify the materials used both in pigments and in mortars (binders and aggregates). Attenuated Total Reflection (ATR) infrared spectroscopy and Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS) have been used to study the pigments, which have been classified as inorganic. Expensive pigments, such as Egyptian blue and cinnabar have been used. X-Ray Diffraction (XRD), observations by polarizing microscopy and ATR-FTIR analyses have been used to study mortars, which have been divided in two fractions: binder and aggregate, after an acidic digestion. The material used to prepare the fresco preparation layers is a local aggregate of volcanic origin coming from the Alban Hills, while the carbonatic binders come from a different area in Abruzzese.

1 Introduction

Villa Adriana (Figure 1) has been built between 117 and 138 AD by the Roman emperor Hadrian. It was built in an idyllic position, from where Rome could be seen and was considered as the “private city” of the emperor. It consists of 28 buildings (770 rooms have been identified) in which some of the rooms - whose names came from Historia Augusta – remind of famous places and cities visited by the emperor. Villa Adriana includes a previous republican building, probably owned by the family of emperor's wife Sabina.¹ There is great archaeological interest in this Villa, as it has not been subject to big alterations apart from natural ageing and environmental impact, therefore, all the decorations and paintings are from Hadrian's period.

For the first time, a complete scientific investigation, aimed to clarify the nature of the materials and the techniques employed for wall paintings, has been carried out. This study could provide explanation about the provenance of the materials used to prepare the paintings

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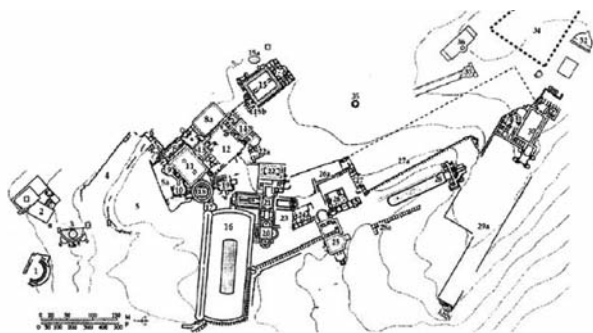


Figure 1: Map of the archaeological site of Villa Adriana (2nd century AD).¹

(pigments, binders and aggregates). The synergic use of different analytical techniques was mandatory for this purpose.

2 Materials and Methods

2.1 Samples

Approximately a hundred samples were analysed, pigments and mortars, from 8 rooms of the Villa: *Palazzo Imperiale* (Emperor building), *Ninfei* (nymphaeums), *Hospitalia*, *Terrazza di Tempe* (terrace), *Accademia*, *Palestra* (gymnasium) and *Pecile* (big colonnade bounding a garden with a big pool in the centre). Mortar samples came only from the *Palestra* and its surrounding and they have been classified as building mortars.

Fragments collected directly from the painted walls were analysed with scanning electron microscopy in combination with energy dispersive x-ray spectroscopy (SEM-EDS). The pigments were analysed after scraping them from the outermost layer of the pigmented samples in order to carry out infrared analyses.

In the first approach to the study of mortars, infrared, elemental and x-ray analyses of the samples were carried out, following an approach suggested in the literature.²⁻⁴ Subsequently, the aggregate fraction was separated from the binder, so that a more detailed identification of the material was possible. The separation was carried out on 1 g of the powdered mortar in a solution of diluted 1 M HCl, using a magnetic stirrer for 1 h.⁵ After filtration, two fractions were obtained: the aggregate as the insoluble part deposited on the filter and the binder as the soluble portion.⁶ Thin sections were prepared on the mortar, in order to study the minerals present using a polarizing microscope.⁷

2.2 Infrared Spectroscopy (FTIR)

IR analyses were carried out using a Thermo-Nicolet 380 infrared spectrometer equipped with

the Smart Orbit accessory and a diamond cell, in order to be able to work in the attenuated total reflection (ATR) mode; 32 scans per sample were collected in the range of 500-4000 cm⁻¹.

2.3 Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy (SEM-EDS)

The images and elemental analyses (by backscattered electrons and x-ray fluorescence analysis) were acquired with a Scanning Electron Microscopy, coupled with Energy Dispersive Spectroscopy (SEM-EDS) Stereoscan 420 from Leica (Cambridge, UK) at different magnifications. The images were taken under high vacuum conditions; in order to avoid charging effects, the samples were coated with a thin layer of graphite (approx. 70 nm).

2.4 X-Ray Diffraction (XRD)

The crystalline phases have been identified through a Philips PW 1830 powder XRD (X-ray diffraction) with a Cu-K α source, a monochromator on the diffracted beam and a proportional counter. Measurements have been taken in the range of 10°-80° (2 θ) at 0.02 scan/s.

2.5 Polarizing Microscopy

Thin sections (30 μ m) were analysed with a petrographic microscope. Using polarized light, the identification of rock(s) and mineral(s) could be carried out. The extinction angle was observed using cross polarization: at this angle most light transmission is blocked by the polarized filters and birefracting samples are observed, together with changes of colouration due to pleochroism, which is an important parameter in discrimination of minerals.⁷

3 Results and Discussion

3.1 The Pigments

The pigments identified on the wall paintings were mainly red and yellow ochre, Egyptian blue and green earth.

Ochres⁸ were determined using SEM-EDS thanks to the identification of iron which indicates the presence of haematite (Fe₂O₃) for red and goethite (FeO(OH)) for yellow.

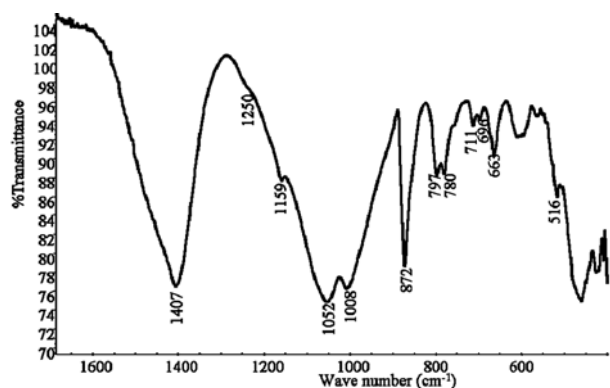


Figure 2: ATR spectrum of the pigment Egyptian blue of a sample from the Nimphaeus.

Green earths⁹ could also be identified by SEM-EDS due to the simultaneous presence of Al, Si, Fe, K and Mg. Egyptian blue was determined by SEM-EDS, due to the characteristic ratio of Si, Ca and Cu. Further confirmation came from infrared spectra, where the Si-O-Si bond in Egyptian blue¹⁰ gives rise to a typical triplet at 1004, 1049 and 1162 cm^{-1} (here 1008, 1052 and 1159) and a shoulder at about 1250 cm^{-1} (Figure 2). This pigment is always accompanied by calcium carbonate, usually calcite, derived from the underlying plasters. In one occasion it has been found in mixture with aragonite, calcium carbonate of marine origin, usually used for dilution of the blue pigment in order to provide a particular hue.¹¹ Another precious pigment found in the Villa was red cinnabar, i.e. mercury sulphate (HgS), recognised using SEM-EDS.

In the majority of samples traces of calcite have been found, but in a very distinct set of samples it was possible to distinguish two different layers: the upper one made of an inorganic pigmented material and the lowest one made of either calcite or gypsum. The separation of these two layers made it possible to propose that different techniques were probably used: false fresco or pigmented stucco. As a matter of fact, their positions support this hypothesis: they have been found on ceiling and vaults, where the application of decorations was more difficult. Possibly, the stuccoes have been applied on rounded surfaces and a layer of gypsum was needed in order to give the desired shape to the wall on which a layer of pigment has been applied.

3.2 The Mortars

Mortars are composite materials whose structure is characterised by a mixture of silica sand with a binder fraction. The integral samples (binder and aggregate) were readily analysed using infrared

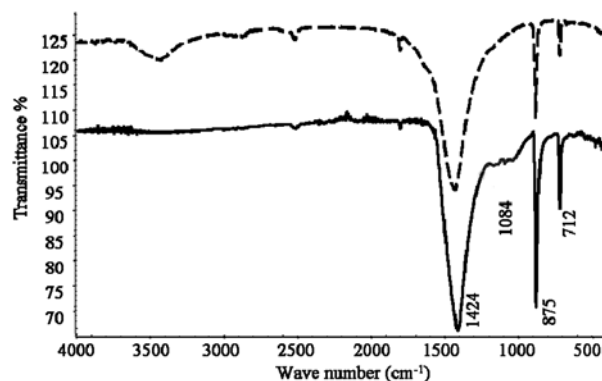


Figure 3: ATR spectrum of a mortar (below) and of the calcite standard (top).

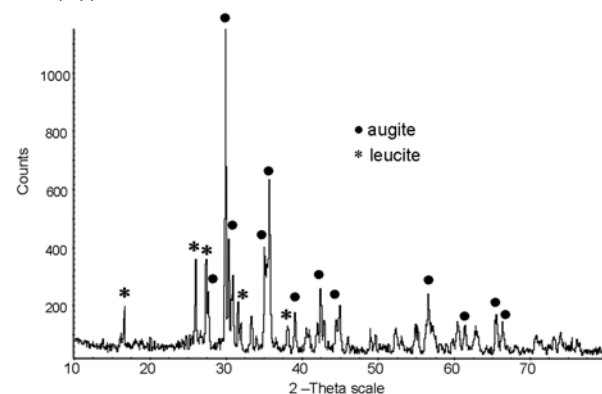


Figure 4: XRD analysis of a typical aggregate obtained after the mortar separation: the two phases augite, $\text{Ca}(\text{Mg,Fe,Al})(\text{Si,Al})_2\text{O}_6$ and leucite, $\text{K}(\text{AlSi}_2\text{O}_6)$ are observable.

spectroscopy: it is possible to identify the carbonate binder or gypsum, due to the characteristic absorptions of calcite¹² (1406, 872 and 711 cm^{-1} due to the carbonate group), calcium sulphate¹³ (1150-1142, 1124-1111, 673-661, 605-595 cm^{-1} due to the sulphate group and bands at 3540-3410 and 1617 cm^{-1} , related to O-H).

An example of the IR spectrum acquired on a mortar is shown in Figure 3, where calcite is present together with a peak centered at 1084 cm^{-1} , which indicates the presence of a silicate, not clearly identified.

XRD analyses of the separated aggregates showed two minerals:

augite, $\text{Ca}(\text{Mg,Fe,Al})(\text{Si,Al})_2\text{O}_6$, and leucite, $\text{K}(\text{AlSi}_2\text{O}_6)$ in most of the samples, as it can be seen in the diffractogram in Figure 4.

Identification of these two minerals has been attempted also by ATR-FTIR spectroscopy. The infrared spectra were first acquired on two reference samples of augite and leucite (Figure 5); the vibration of Si-O-Si and of Si-O-Al in the range 1100-900 cm^{-1} are evident in the Figure, as well as bending¹⁴ at lower wavenumbers. Because of the partial superposition of the signal due to the two

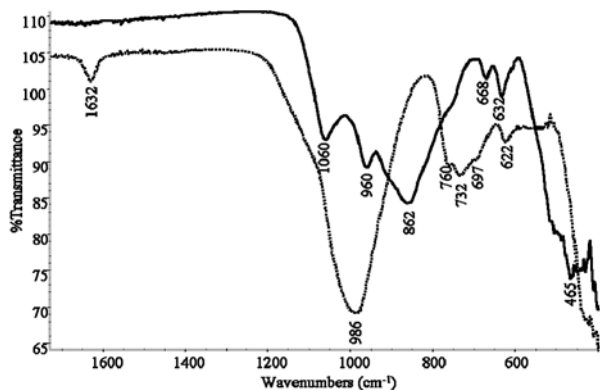


Figure 5: ATR spectra acquired using two standards: augite (top) and leucite (below).

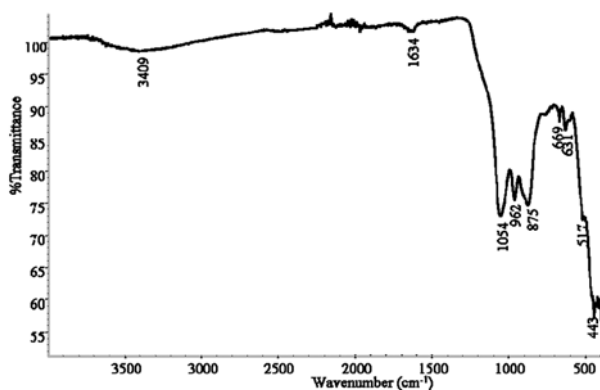


Figure 6: A typical ATR spectrum acquired on an aggregate after mortar separation in the two phases; augite spectrum is easily identifiable (signals at 1054, 962 and 875 cm^{-1}).

species, only augite can be clearly identified using FTIR even if the presence of leucite cannot be excluded.

Most of the aggregates have the fingerprint of the sample shown in Figure 6, where augite can be easily distinguished. The signals due to leucite are partially hidden by those of augite. In particular, the main peak of leucite can be hidden by augite signals at 1060 and 960 cm^{-1} . Other minor peaks related to leucite, are the absorptions at 1634, 760 and 732 cm^{-1} , and the slight shoulder at 1124 cm^{-1} , which overlaps with the augite absorption, again. The signal at 1634 cm^{-1} is clearly visible also in the aggregate samples (Figure 6) so we could identify leucite presence on the base of this signal alone. Furthermore, it has been observed that the presence of leucite together with augite in the mortar samples gives rise to a shift of the main peaks from 1068 cm^{-1} to lower wavenumbers, at about 1054 cm^{-1} .

In conclusion, from both XRD and ATR analyses we can confirm that the composition of mortar aggregates of the Villa is very homogeneous, indicating that all of them were made with a material of the same provenance.

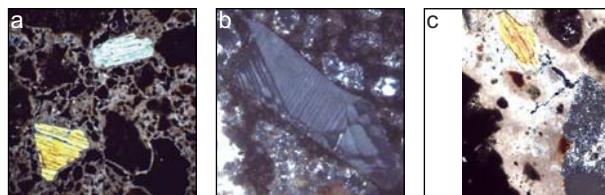


Figure 7: Augite (a) and leucite (b) under polarizing light microscope. Augite (c) (yellow at the top) and flint (below on the right) under polarizing light microscope for sample: amb13 int1.

From the observation of thin sections by means of the polarizing microscopy, leucite seems to be the main mineral, even though in each mortar, augite and leucite are always present (Figure 7a and b). Only one sample (identified as *amb13 int1*) is different (Figure 7c) in view of the aggregate composition. It is more heterogeneous and quartz and flint could be identified, being typical of an orogenic sedimentation transported along a river. Augite and leucite are of ultrapotassic volcanic origin. These minerals can be found in a few locations in Italy. One of these areas is Vulcano Laziale, in the Alban Hills¹⁵ (South-West of Tivoli, zone 1 in Figure 8). As concerns the binder materials¹⁶ they could come from the carbonate Abruzzese platform¹⁷ (South-East from Tivoli, zone 2 in Figure 8). For the aggregate reported in Figure 7c we can assume that it is of river origin from an area nearby Villa Adriana, North-East of Tivoli (zone 3 in Figure 8).

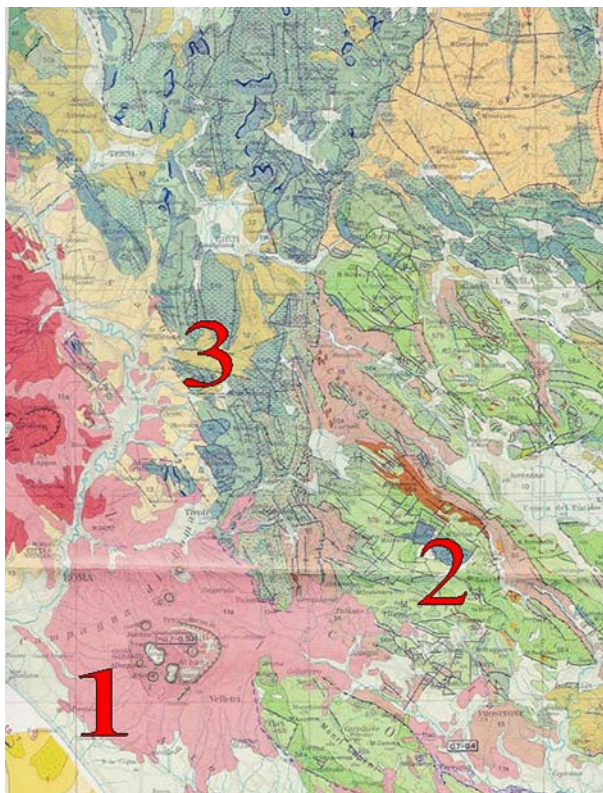


Figure 8: Geological map next to Tivoli. Zone 1, 2 and 3 are the areas of provenance of the material used for mortars.

4 Conclusions

The analytical techniques applied for the characterization of both pigments and mortars allowed us to understand the materials employed in production of the wall paintings decorating the Villa Adriana. In particular, ATR-FTIR provide to be very useful since the measurements are fast, no sample preparation required, and the analyses are accurate, even on small samples. Pigments are all inorganic (mainly ochres, earths and silicates). Stuccoes were also made with valuable blue pigments. They have been employed on vaults and ceilings, which are more difficult to decorate.

With regard to the mortars, they represent composite materials, whose structural properties are due to a mixture of silica with a binder fraction. The separation of the binder and the aggregate fractions turned out to be essential. All the binders of Villa Adriana are calcite-based and the aggregate is of local volcanic origin.

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