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Case study

Spectroscopic analyses of Hellenistic painted plasters from 2nd century B.C., Sicily (South Italy)

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ABSTRACT

In the present work, an analytical characterization of painted plaster samples coming from ancient buildings dated back to 2nd cent. B.C., located in Licata (Sicily, Southern Italy), has been carried out. The investigation has been performed through different spectroscopic techniques: X-ray fluorescence (XRF) using an handheld energy-dispersive XRF analyzer, scanning electron microscopy equipped with an Energy Dispersive Spectrometry microanalysis detector (SEM-EDS) and Fourier transform infrared absorbance spectroscopy (FT-IR). The main goal is to identify the plaster and pigments material. In particular, the XRF investigation of surfaces is the first step for a preliminary elemental characterization. Then, through SEM-EDS measurements, a quantitative analysis of the chemical composition of the plaster and the pigmenting agents along with eventual components related to deterioration processes has been obtained. Finally, FT-IR absorbance spectra have proven to be a useful tool to investigate the molecular nature of the used materials.

1. Research aims

In a broadly vague and poorly defined scenario as is that of the origin and development of Hellenistic art in Sicily, whose findings are still unknown, and especially difficult to fit chronologically, an important contribution in defining the historic-social and economic production contexts and use of findings, can be represented by the integrated approach between Archaeology and Archaeometry of materials. In this scenario, the physico-chemical analysis applied on samples of painted plaster, duly selected by the archaeologists, can provide information on production. Actually, there is a lack of systematic analyses of the Hellenistic wall paintings in the Southern and Western Sicily.

In principle, as is well known, a comparison of the pigmenting agents and the particular techniques used in different geographical areas, could help in tracing the possible routes of their origin and diffusion. In the last decade, many analytical techniques, such as Raman spectroscopy [1–3], X-ray fluorescence (XRF) [4–6], X-ray powder diffraction (XRD) [7,8], Laser Induced Breakdown Spectroscopy (LIBS) [9,10], were applied to determine the nature of "archaeological" pigments. In particular, some recent authoritative papers by Brysbert et al. [11,12], concerning a detailed spectroscopic investigation on Bronze Age painted plasters from Aegean and Eastern Mediterranean area, have characterized the painted surface showing that the mainly used technique was "al fresco" painting.

Here, we propose a spectroscopic study performed on Hellenistic plasters coming from Licata (Sicily, Southern Italy) excavations, through complementary techniques, focusing our interest on the characterization of the pigments. In particular, we carried out non-destructive XRF measurements, followed by micro-destructive analyses through SEM-EDS technique and FT-IR absorbance spectroscopy.

It is worth noting that this work is part of a wider project, aiming to study and identify the pigments and the pictorial techniques used in various Sicilian cities (Gela, Heraclea, Morgantina) in different periods.

2. Materials and methods

2.1. Sampling

We analysed samples of plasters (labelled as LIC#), coming from excavations at Licata (Sicily, Southern Italy). The findings, dated back to 2nd cent. B.C., belong to ancient buildings located in Via S. Maria and on Monte Sant'Angelo. The selected specimens are representative of the variety and differences of colour present in each site. The size of the fragments ranged from 4 to 20 cm^2. Some examples are shown in Fig. 1.

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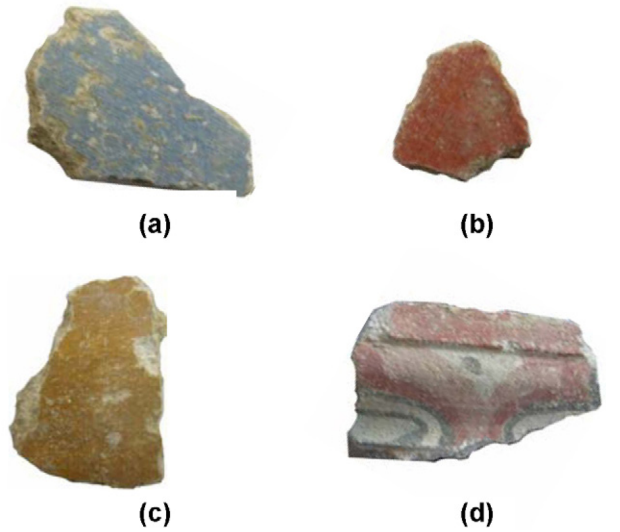

Fig. 1. Pictures of some fragments under study: a: LIC2; b: LIC4; c: LIC6 and d: LIC15.

2.2. XRF measurements

XRF measurements were carried out through an handheld XRF analyzer (Innov-X Systems Alpha 4000), equipped with an X-ray tube with Ta anode and a high resolution Si PiN diode detector (FWHM < 220 eV at 5.95 keV for Mn k_α line). A 2-mm Al filter was coupled to the tube to suppress the characteristic Ta peaks of the anode. The spot size for analyzer is approximately 170 mm^2. The calibration was performed on international standards using the software "Soil LEAP II (Light Element Analysis Program)". The characterized elements were carried out through two consecutive runs: the first one with X-ray tube operation conditions of 40 kV and 7 μA, the second one with the X-ray tube operating at 15 kV and 5 μA range. The LEAP suite works by changing the operation condition in order to optimize the detection of elements lighter than iron.

2.3. SEM-EDS measurements

SEM-EDS measurements were carried out using the Tescan Vega LMU scanning electron microscope equipped with an EDAX Neptune XM4-60 micro-analyzer characterized by an ultra-thin Be window. The experiments were performed at 20 kV accelerating voltage and 0.2 nA beam current. Precision of collected data is of the order of 5%. EDS microanalysis was carried out in order to obtain quantitative information on the elemental composition of the sample.

Small chips were drawn from the coloured surfaces of the shards. Then, each sample was attached to an aluminium stub with double-sided tape and coated in carbon. Each spectrum was recorded for 100 s and the measurements were performed on various points of the specimen.

2.4. FT-IR measurements

FT-IR measurements were collected on the coloured surface of the samples by means of the Thermo NICOLET 380 spectrometer in Attenuated Total Reflectance geometry (ATR), with a Smart Orbit accessory used in the following arrangement: a KBr beamsplitter, an HP-DTGS-KBr detector and an Ever-Glo lamp used as source. Experimental spectra were directly performed on few milligrams of fine powders and/or on small chips.

Table 1
Elemental composition obtained by XRF analysis. The minor or trace elements are presented between brackets. The main key-element for pigment identification is marked in bold.

Sample	Colour	Detected elements
LIC2	Blue	K, Ca, Fe, **Cu**, Sr, Pb (S, Cr, Mn, As, Ag, Sn, Ba, Hg)
LIC8	Blue	S, K, Ca, Fe, **Cu**, Sr (Mn, As, Hg)
LIC9	Blue	K, Ca, Fe, **Cu,** Sr, I (Mn, Ba, Hg, Pb)
LIC12	Blue	P, K, Ca, Fe, **Cu**, Sr, Pb (Ti, Mn, Sn, Ba, Hg)
LIC14	Blue	K, Ca, Fe, **Cu**, Sr, Pb (Ti, Mn, As, Hg)
LIC3	Red	K, Ca, **Fe**, Sr (Mn, Zn, As, Hg, Pb)
LIC4	Red	K, Ca, **Fe**, Sr (Ti, Mn, Zn, Zr, Pb)
LIC5	Red	**S**, K, Ca, **Fe**, Sr, **Hg** (Mn, Zn, As, Se, Rb, Ba, Pb)
LIC6	Yellow	K, Ca, **Fe**, Sr (Ti, Mn, Ni, Zn, As, Ba, Hg, Pb)
LIC15	Red	S, K, Ca, **Fe**, Sr (Mn, Zn, I)
LIC15	Pink	S, K, Ca, **Fe**, Sr (Mn, Pb)
LIC15	Black	S, K, Ca, **Fe**, Sr (Mn)

3. Results and discussion

Firstly, we carried out an extensive preliminary surface investigation through XRF measurements. In principle, XRF results act as a valuable guideline for subsequent targeted sampling actions, thus minimizing the sampling damage. After that, we used SEM-EDS technique to obtain quantitative analysis on the chemical composition of pigments and preparation layers, including also the oxides of light elements (such as Na, Mg, Al, Si), not revealed by the used XRF apparatus. Finally, the analysis of FT-IR spectral features, performed by comparing the experimental spectra with those of an IR spectra database (Sadtler database "Mineral and Clays" [13]) permitted us to unambiguously determine the mineral composition of the findings and the molecular nature of pigments.

The whole spectroscopic results will be presented in the following accordingly to the different analysed colours.

3.1. Blue pigments

XRF elemental results performed on blue samples, namely LIC2, LIC8, LIC9, LIC12 and LIC14, are summarized in Table 1. As an example, the fluorescence spectra in the two analysed energy regions, together with the peaks identification on sample labelled LIC2 are reported in Fig. 2 (a) and (b). From an inspection of the table, it is evident that Cu is the key element characterizing the blue pigment. The other major elements, such as Ca and Sr are due to the binder of the plaster. Traces of As revealed in some fragments (LIC2, LIC8 and LIC14) can indicate impurities in the Cu ores. Finally, the presence of Pb revealed in all XRF spectra of blue-coloured samples could be due to cerussite ($PbCO_3$) usually used in the preparation layer and/or to lighten a colour, or to plattnerite (PbO_2) that is an alteration of cerussite.

The presence of S, revealed in LIC2 and LIC8, can be ascribed to gypsum ($CaSO_4{\cdot}2H_2O$) in the original preparation or can be related to the phenomenon of sulphating. Indeed, this mineral is a product of alteration due to the chemical reaction, in the presence of water, between SO_2, coming from the atmosphere, and the carbonate matrix of the original materials. This occurrence leads to a serious deterioration process because the replacement of calcium carbonate ($CaCO_3$) by gypsum causes cracks in the pictorial layer along with pulverization phenomena.

On the blue portions of the fragments, further information is furnished by SEM-EDS measurements. The resulting average chemical composition of the analysed samples, expressed as weight percentage (wt%), is reported in Table 2.

In particular, the quantitative SEM-EDS analysis on three blue-coloured samples (LIC2, LIC8, LIC12) has mainly shown the presence of CaO and SiO_2 in significant amounts together with variable contents of Na_2O, MgO, Al_2O_3, SO_3, K_2O, FeO and SrO. These oxides can