

Analytical Methods

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Characterization of glue *sizing* under calcium carbonate ground layers in flemish and luso-flemish painting -analysis by SEM-EDS , μ -XRD and μ -Raman

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Abstract

This work regards the study of painting techniques in Portuguese workshops of the 15th and earlier 16th centuries, specifically addressing the methodology used on the preparation of ground layers. The influence of Flemish painting in Portugal is evident in stylistic and iconographic themes of that period. As regards the painting materials, we confirmed this influence also extended to the ground layer technique. The use of a *sizing* layer with calcium sulphate or garlic to isolate the support from the calcium carbonate layer was verified by SEM-EDS but not confirmed by μ -XRD or μ -Raman. This work is part of a larger project, “The invisible ground layer and its influence in Portuguese paintings from the 15th and 16th centuries: a question to be settled”.

Key words: Ground layer; *sizing* layer; calcium carbonate; garlic; calcium sulphate; SEM-EDS; X-ray Diffraction; X ray Fluorescence; Raman

Introduction

D. Manuel I, king of Portugal and the Algarves (1495-1521), has his name associated to major achievements both in political connections and the arts. The king’s ambition was to be recognized as one of Europe’s great sovereigns, and his power over the overseas Portuguese empire conquered by that time acknowledged. The territorial expansion abroad and the trade around Europe, especially Flanders, originated a great and wealthy empire which made possible the arrival in Portugal of the most famous painters, architects and scientists. As a totalitarian king in a universal path, he could then associate himself and his work to an aesthetic message. The *Manueline* style was thus characterized by the presence of the armillary sphere, the symbol he adopted to express

the realm's universal supremacy (e.g. in one of the paintings studied, *Santo Franciscano*, this symbol is present in the architectural representation).

The artistic renovation promoted by king D. Manuel I of Portugal also strengthened the connection with Flanders. Flemish paintings were imported, probably like in the case of *Évora's flemish altarpiece* and Flemish painters also came to Portugal, working with national artists or starting new painting workshops.

Besides the elements common to Flemish and Portuguese painting workshops during the 15th and earlier 16th centuries, overall addressing formal and iconographic issues (Flemish aesthetic influence can also be recognized in all the paintings comprised in this study), ground layers have proved to be a useful feature for identification of the painting technique..

The principal aim of this study is therefore to address the particular case of ground layers, specifically focusing on the characterization of glue *sizing* under calcium carbonate. To that purpose, complementary techniques of elemental and molecular characterization, such as Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS), μ - X-Ray Diffraction and μ -Confocal Raman analysis were utilized.

In a first multianalytical study of *Évora's flemish altarpiece*, published in 2009 by *Instituto Português de Conservação e Restauro* (IPCR) ¹, microchemical and μ -FTIR analysis identified traces of calcium sulphate in calcium carbonate ground layers. In cross-sections from the same paintings, however, μ -XRD and SEM-EDS did not detect gypsum or sulphur, respectively. In this work, the altarpiece and other paintings with calcium carbonate ground layers were analysed with a new methodology, to confirm and compare the results.

Materials and methods

Pictorial Corpus under study

In this study, two groups of paintings from Évora's Cathedral, of the early 16th century, and assigned to a Bruges Flemish painting workshop, are analyzed - Both groups were ordered by D. Afonso of Portugal, bishop of the city of Évora between 1485 and 1522, for the renovation of the main chapel of the city's Cathedral, started in 1495. A series of thirteen paintings is dedicated to the Life and Glorification of the Virgin Mary (**A**) and the other series of six paintings is dedicated to the Passion of Christ (**B**).

Another set of luso-flemish paintings with calcium carbonate ground layers (IPCR internal reports, at the time of restoration) are also analyzed:

- A large painting by the circle of followers of the royal painter Nuno Gonçalves, dated from the second half of the 15th century: *Adoração dos Magos e Santos Franciscanos (S. Francisco e Sto. António)* (**C**) ²⁻⁴, from *Santa Helena do Monte Calvário* monastery. Totally overpainted in the 17th century, it was uncovered during the 20th century restoration and is nowadays in Évora's Cathedral Museum;

- *Santo Franciscano (D)*, from Funchal Cathedral ⁴⁻⁸, from the second half of the 15th century, also partially repainted and uncovered in the 21st century.

- *Nossa Senhora da Rosa (E)*, also from the second half of the 15th century, kept several years at Coimbra's College of *S. Jerónimo* and presently in the Museu Nacional de Machado de Castro, Coimbra, and usually related to Coimbra's workshop. Attributed to *Mestre Delirante de Guimarães* ⁹, this painting is also a remarkable case study in the history of conservation and restoration in Portugal. The total 16th century overpainting was removed in the 20th century¹⁰.

- *Incredulidade de S. Tomé (F)*, from the last quarter of the 16th century, presently in Museu Nacional de Arte Antiga, assigned to Anthonis Blocklandt, dutch painter and master of the Spanish painter Fernão Gomes between 1570 and 1572¹¹.

Experimental

Paint samples for the study of the ground layer technique were carefully selected to contain all paint layers, from the surface down to the *sizing* layer. From the seven studied paints two samples of each one have been analysed. Some were prepared as cross-sections, mounted in epoxy polymeric resin and polished with silicon carbide. Others were kept unmounted, with no further treatment, to enable analysis of the *sizing* layer facing upwards¹².

Optical microscopy

Optical microscopy was carried out with a Leitz Wetzlar microscope coupled to a Leica DC500 digital camera, to prepare samples as described above. Images were recorded for the project database and also to help interpretation of the results.

Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS)

SEM imaging (SE and BSE modes) and SEM-EDS analysis was performed with a Hitachi 3700N scanning electron microscope coupled to a Bruker XFlash 5010 SDD detector characterization on both cross-sections and unmounted samples. The unmounted samples, positioned, as mentioned above, with the bottom preparatory layer facing upwards, were coated with a conductive film of carbon, allowing refined measurement of the relevant parameters for calcium carbonate and the *sizing*.

SEM-EDS was used to identify the elemental composition of cross-sections and unmounted samples. The unmounted samples, positioned, as mentioned above, with the bottom preparatory layer facing upwards, were coated with a conductive film of carbon, allowing refined measurement of the relevant parameters for calcium carbonate and the *sizing*.

μ - X-ray diffraction

Micro-X-ray diffraction (μ -XRD) was performed with a Bruker general area detection diffraction system (GADDS) microdiffractometer (Bruker AXS, D8 Discover), equipped with a two-dimensional HiStar gas filled area detector, a Goebel mirror, a

laser-video sample alignment system and a motorized XYZ stage. Diffraction data were recorded using Cu K α radiation, tube running at 40 kV, 40 mA, and incident beam collimated to 1 mm diameter. XRD patterns were measured in the range 8° to 70° 2 θ , 0.02° step size and 1800 s recording time for each step.

Phase identification was performed with the PDF-ICDD Powder Diffraction Database (International Centre for Diffraction Data) and the Bruker EVA software (Version 5).

μ -Confocal Raman analysis

Raman spectra of the unmounted micro-samples were obtained with a Horiba-Jobin Yvon XploRA Confocal Micro-Raman spectrometer, with a laser diode source operating at a 785 nm wavelength. A 0.5 mW incident power was applied to the sample, to achieve the best scattered intensity without any risk of damaging it. Spectrum acquisition conditions were 15 s of exposition time, 90 scans, 1200 lines/mm diffraction grating and more or less 4 cm⁻¹ resolution. Before acquisition a standby of 20mn under laser illumination was applied for photobleaching in order to diminish the fluorescence background. Scattered light collected by the objective was dispersed onto the air cooled CCD array of an Andor iDus detector. Pictures were taken with a BX41 microscope (Olympus), using x100 magnification and a Ueye 1640 camera. The LabSpec software was used for spectra deconvolution and corrections. Ground layer filler identification was performed with the Crystal Sleuth and Spectral ID databases, complemented by our own reference spectra.

Portable Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF)

A laboratory-made portable XRF spectrometer was used, consisting of an Eclipse IV Oxford Instruments X-Ray tube (45 kV, 50 μ A, 2.25 W max.) with a Rh anode, specifically selected to analyze the silver present in the samples. Radiation is collimated by a tantalum collimator yielding a 5 mm diameter incident beam. The detector is an Amptek XR-100SDD with a 25 mm² detection area collimated down to 17.12 mm² and 500 μ m thick fully depleted, and a 12.5 μ m Be window. Energy resolution is 140 eV at 5.9 keV and the acquisition system is an Amptek DppPMCA. The angle between the incident and emitted beam is 90°, this geometry minimizing the background due to Compton scattering¹³. Samples are placed at 55 mm distance from the tube and 10 mm from the detector, and positioned at the focal point of two laser beams. The X-ray generator was operated at 35 kV and 40 μ A, and an acquisition time of 200 s.

RESULTS AND DISCUSSION

Sample examination by SEM focused in particular on the identification of the *sizing* layers. With this technique, their exact location, between the support and the ground layer, was confirmed as seen in Fig. 1a.

SEM-EDS ground layer results layers (Figs.1a, 1b, 1c) identified Ca as the major element. Carbon was also detected indicating the presence of calcite (calcium carbonate), considering that S was not visible. This result was confirmed by μ -XRD (Fig. 2) and μ -Raman (Fig. 3). Figure 2 XRD sample analysis also included lead white ($2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$, hydrocerussite). This fact is due to the presence of a priming layer above the ground layer, because of the contribution to the desired visual effect of its opaque quality and smooth texture.

As seen on table 1, calcium sulphate was not detected with μ -XRD or μ -Raman, differently to the results reported in the first study mentioned above¹, where traces of calcium sulphate were detected in the calcium carbonate ground layers by microchemical and μ -FTIR analysis. However, S was identified at trace level in the unmounted samples **A/J-8**, **B/C-1** and **D-2** (figs.4a, 4b, 5a, 5b, 6a, 6b respectively) by SEM-EDS, although that was not the case with the painting cross-sections, where SEM-EDS did not detect S (as in fig. 1c). These results might suggest, in the second case, either the absence of calcium sulphate altogether or the unintentional elimination of the bottom layers during the mounting process, or even that the quantity present was below the detection limits of the techniques. In the first case, the entire sample's *sizing* layers faced upwards during analysis, indicating that S most probably is originated from that bottom layer.

The element S identified in the unmounted samples of the *Évora's flemish altarpiece (A,B)* and *Santo Franciscano (D)* paintings with the SEM-EDS technique may be due to several hypotheses:

- The typology "gesso beneath and chalk above" as independent layers¹⁴, usually related to northern Europe techniques^{14, 15}, and already identified in Portuguese paintings of the early and late 16th century^{16, 17}.
- Application of a *gesso aguada* (thin layer of glue and vestigial gypsum) as a first layer before grounding, similar to the technique referred in several treatise recipes of southern Europe for calcium sulphate ground layers¹⁸⁻²⁰.
- A chemical reaction due to the acidic degradation of the wood support (Baltic oak) and of the bottom of the CaCO_3 ground layer. The accumulation of elemental sulphur on oak wood surfaces exposed to high humidity, by internal formation of sulphuric acid (H_2SO_4), has been studied²¹. The chemical alteration of calcium carbonate to calcium sulphate, carbon dioxide and water in a atmosphere of sulphuric acid is also well known²². We tested this hypothesis, and the resulting compound was analyzed by μ -Raman. We mixed CaCO_3 commercial powder with water and a few drops of sulphuric acid, once the release of CO_2 was finished the liquid mixture was dried and the obtained powder was analyzed by μ -Raman. Spectrum (exposition 3s, 60 scans, without photobleaching) shows the presence of CaCO_3 (which was initially in excess) and CaSO_4 (product of the reaction). The main difference we can notice here with the CaCO_3 detected in samples of work of art and the one we detect after the reaction, is the pics at 707 or 713cm^{-1} , this just shows two forms of the same compound CaCO_3 which are respectively aragonite and calcite²³ (fig.7).
- The use of garlic in the paintings preparation for degreasing the wood or as an antibacterial and antifungal agent. In fact, of all the preparation prototypes prepared for this Project, those where the ground layer included a garlic *sizing* layer did not show any alteration after a few months, as opposed to the non-garlic containing ones,

presenting a very evident fungus colonization after the same time. The use of *ajicola* (garlic and glue) for panel painting is described in several treatises¹⁸⁻²⁰ and the presence of S in garlic extract has been reported by SEM-EDS analysis^{24, 25}. We further analyzed fresh garlic and a prototype of a calcium carbonate ground layer with a garlic-containing *sizing* layer by EDXRF. On both instances (fig.8), the presence of S was very evident, confirming the possibility of identifying the presence of garlic by this method.

CONCLUSION

The ground layers of all the paintings analyzed in this study were of calcium carbonate /calcite), as expected and reported in a previous study for part of them. However, calcium sulphate was not identified by any of the techniques used.

Sulphur was detected at trace level by SEM-EDS analysis, but only in the unmounted samples, where *sizing* layers faced upwards. This might suggest that the element S detected is present in the bottom preparation layers, and not in the calcium carbonate top layers, where it could indicate the presence of very small amounts of calcium sulphate, as reported in the first study referred (were the results of the analyses referred to the sample as a whole, with no layer differentiation), and not confirmed by the present methodology.

Accepting the possibility of S coming from the bottom/*sizing* layers of preparation, which certainly contributed mainly to the analyses results of the unmounted samples, and the results of our experiments, the presence of garlic in the *sizing* layer seems the most likely conclusion, also because it was a well known and common painting technique reported in the major treatises of that period.

The microanalytical approach followed in this study was able to improve the knowledge on the technical options of Flemish and Luso-Flemish painters from the late 15th and 16th centuries. Critical analysis of the results obtained for the inorganic materials of the *sizing* layers, brought new conclusions relative to their characterization, thus providing a deeper understanding of the materials included in the *sizing* of calcium carbonate ground layers. The presence of sulphur as an indicator of the presence of a garlic-containing *sizing* layer (or even from calcium sulphate in the *sizing* layers), needs further investigation using analytical methods with better detection limits. Being an important issue to further clarify the technique of Portuguese painting in the 15th and 16th centuries, it will be explored in our following research. Table I summarizes the results for the presence of S in the *sizing* layer of Calcite rich (calcium carbonate) ground layers in the several analyzed samples, by the different techniques.

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PTDC/EAT-HAT/100868/2008 - “The invisible ground layer and its influence in Portuguese paintings of the 15th and 16th centuries: a question to be settled” (through the program Ciência e Inovação POCI2010 and QREN-POPH –typology 4.1 (co-participated by the European Social Fund (ESF) and national funds MCTES), as well as LJF-DGPC.

Table 1. Analytical results for the presence of trace S in the *sizing* layer of Calcite rich (calcium carbonate) of ground layers in sample J-8 of one painting of group A, sample C-1 of group B and samples 5,2,4,7 from paintings C, D, E, F respectively.

Painting or group of paintings/sample	SEM-EDS	μ -XRD	μ -Raman
A/J-8	Ca,S	Calcite	Calcite
B/ C-1	Ca,S	Calcite	Calcite
C/5	Ca	Calcite	Calcite
D/2	Ca, S	Calcite	Calcite
E/4	Ca	Calcite	Calcite
F/7	Ca	Calcite	Calcite

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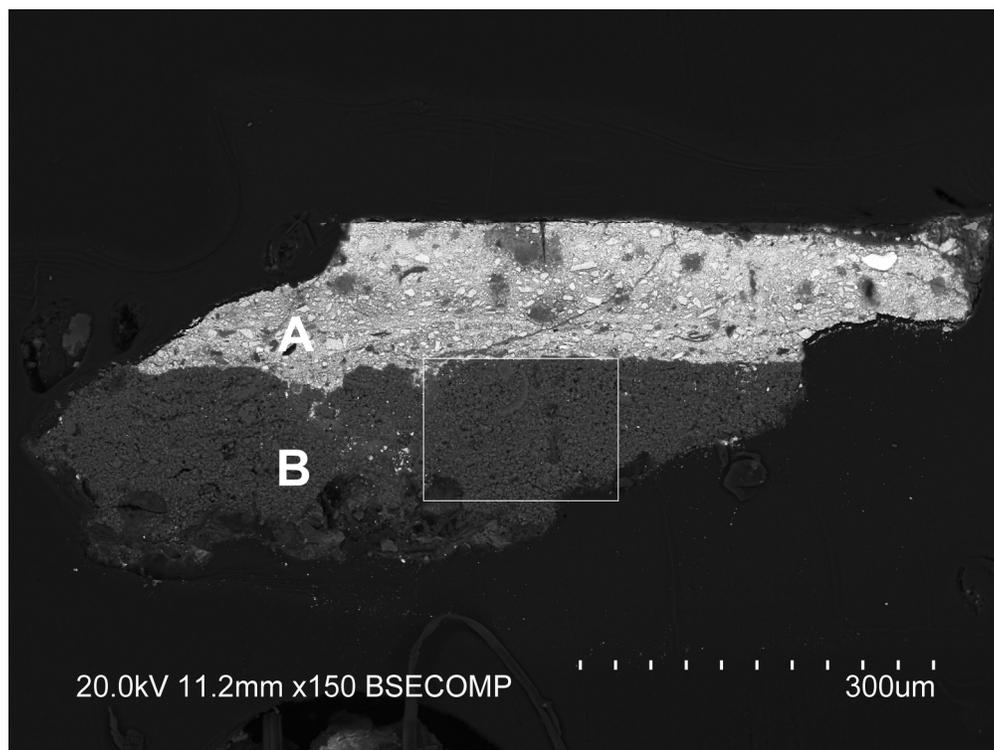


Fig. 1a. SEM-EDS (BSE mode) of one sample of the painting *Glorificação da Virgem*, Life and Glorification of the Virgin Mary altarpiece (sample (A)A-19, Carnation of Virgin's neck). A- chromatic layers; B-ground layer; the white square, indicates the localization of elemental analysis map by SEM-EDS.
95x71mm (600 x 600 DPI)

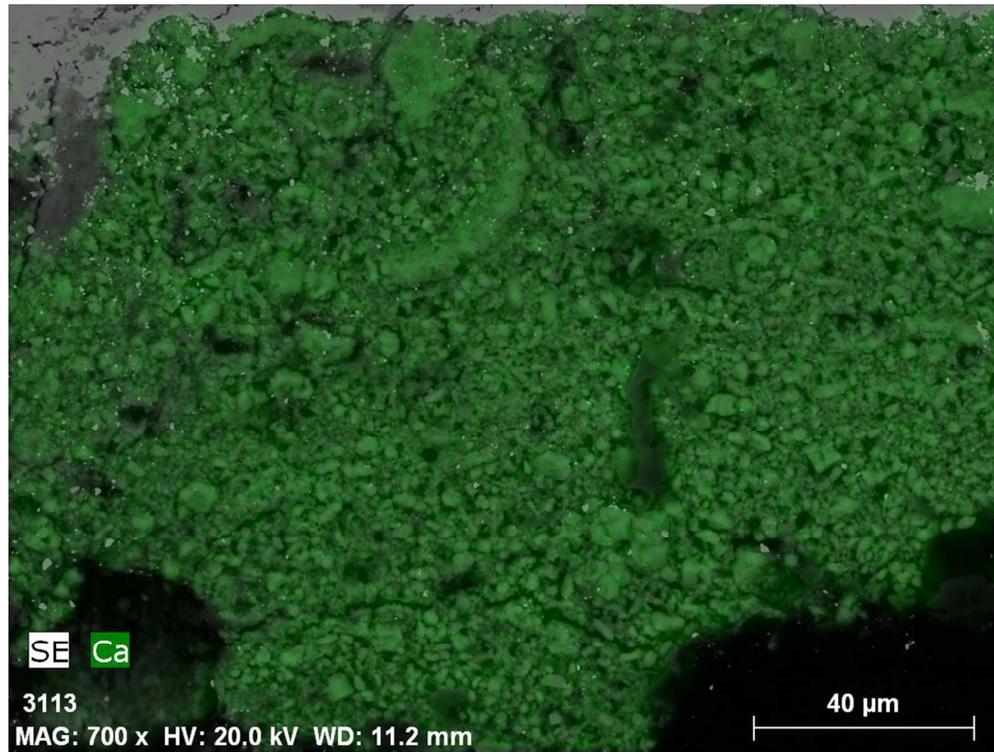


Fig. 1b. Elemental analysis map by SEM-EDS of painting Glorificação da Virgem, Life and Glorification of the Virgin Mary altarpiece (sample (A) A-19, ground layer).
388x291mm (72 x 72 DPI)

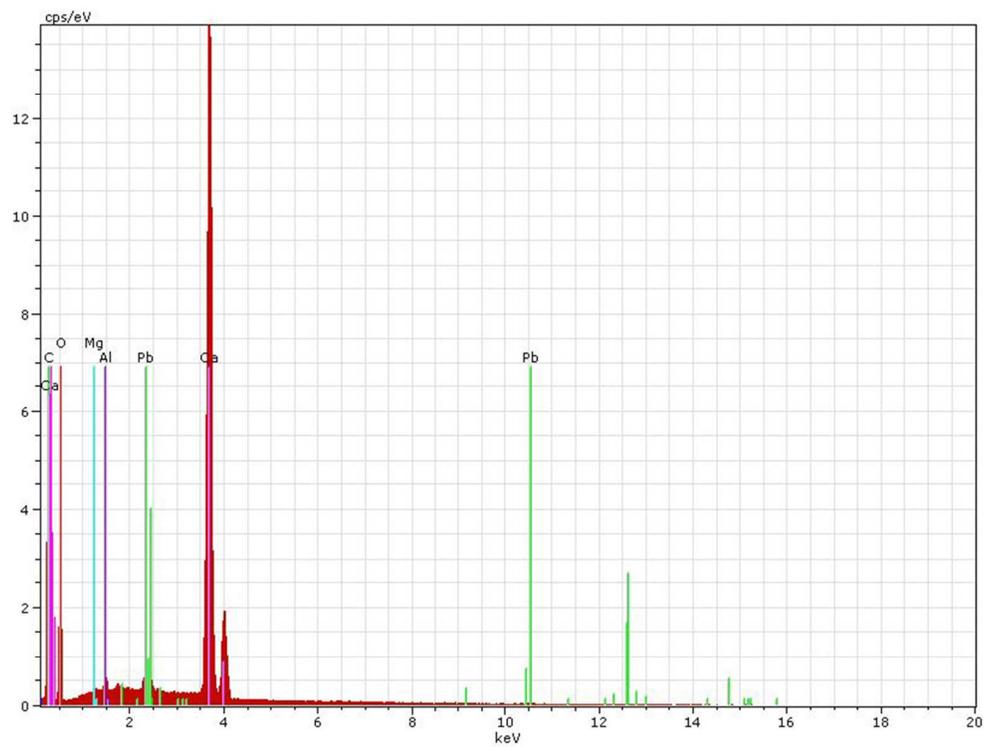


Fig. 1c. EDS spectrum of elemental analysis of painting Glorificação da Virgem, Life and Glorification of the Virgin Mary altarpiece (sample (A)A-19,ground layer), showing the presence of the elements.
293x221mm (72 x 72 DPI)

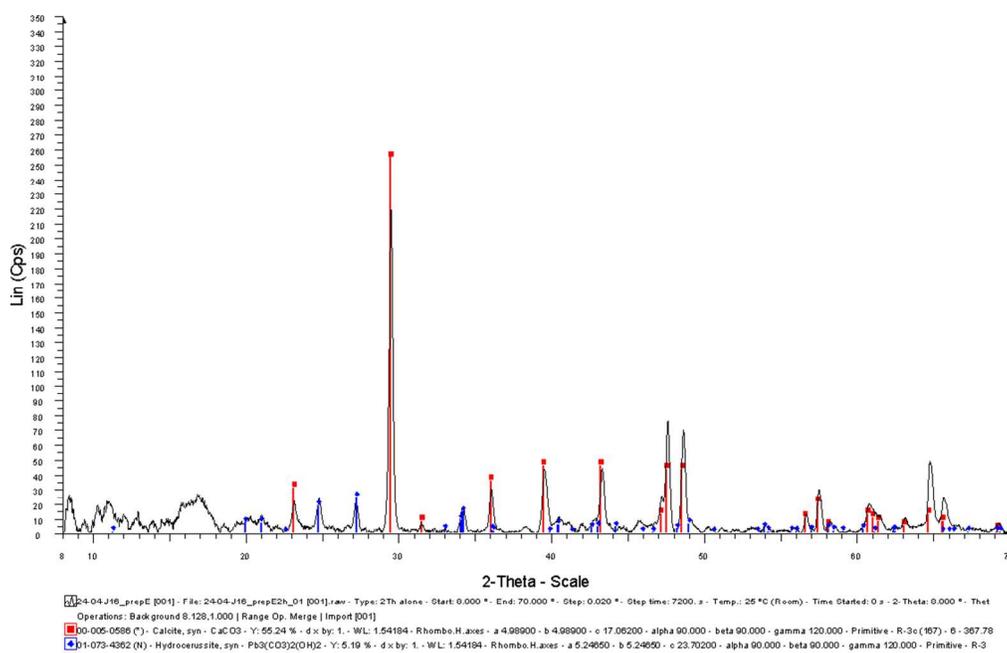


Fig. 2. Diffractogram of principal component of calcite CaCO_3 rich ground layer and hydrocerussite ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) from priming layer of the painting Adoração dos Magos (sample J-16) of group A.

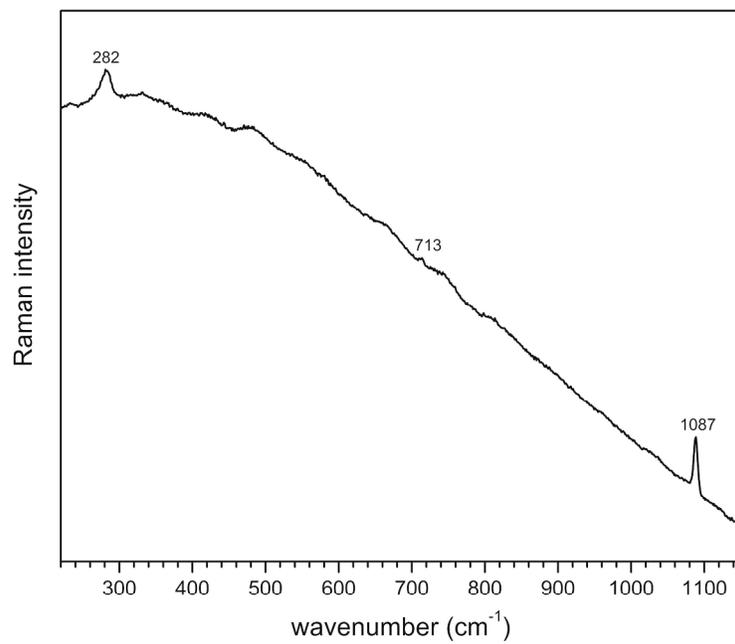


Fig 3. Raman spectrum of the painting Adoração dos Magos (sample J-8) of group A. Pic 713cm-1 indicates the presence of calcite.
558x431mm (150 x 150 DPI)

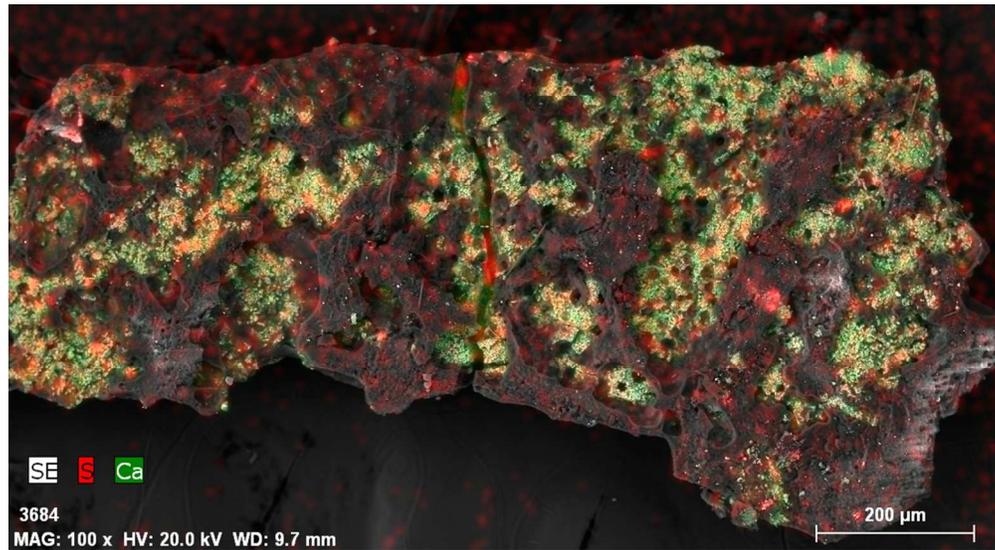


Fig. 4a. Elemental analysis map by SEM-EDS detecting S and Ca in glue sizing of the painting Adoração dos Magos (sample J-8) of group A.
100x54mm (279 x 279 DPI)

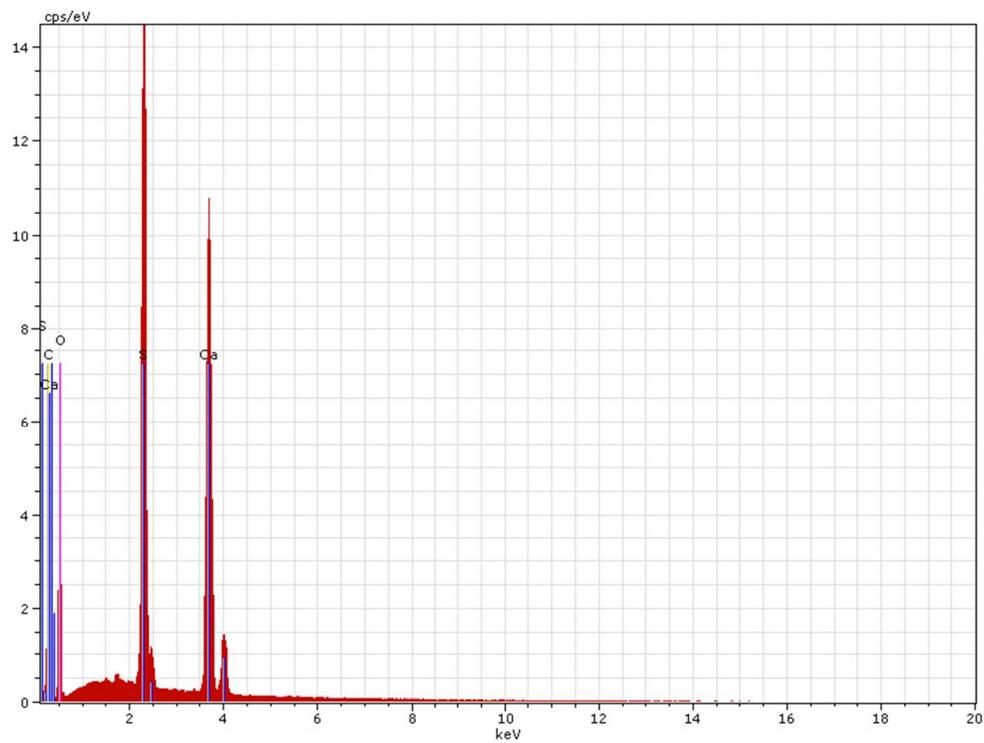


Fig. 4b. EDS spectrum of elemental analysis detecting S and Ca in glue sizing of the painting Adoração dos Magos (sample J-8) of group A.
99x75mm (213 x 213 DPI)



Fig 5a. Elemental analysis map by SEM-EDS detecting S and Ca in glue sizing of the painting Cristo e Pilatos (sample C-1) of group B.
100x75mm (279 x 279 DPI)

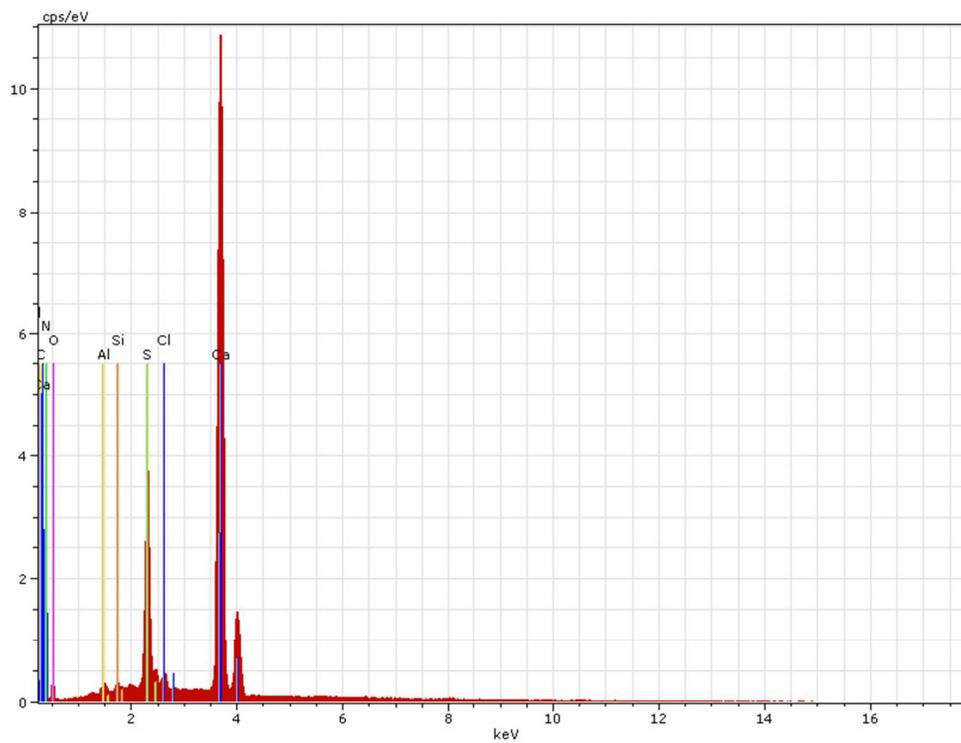


Fig 5b. EDS spectrum of elemental analysis detecting S and Ca in glue sizing of the painting Cristo e Pilatos (sample C1) of group B .
99x75mm (213 x 213 DPI)

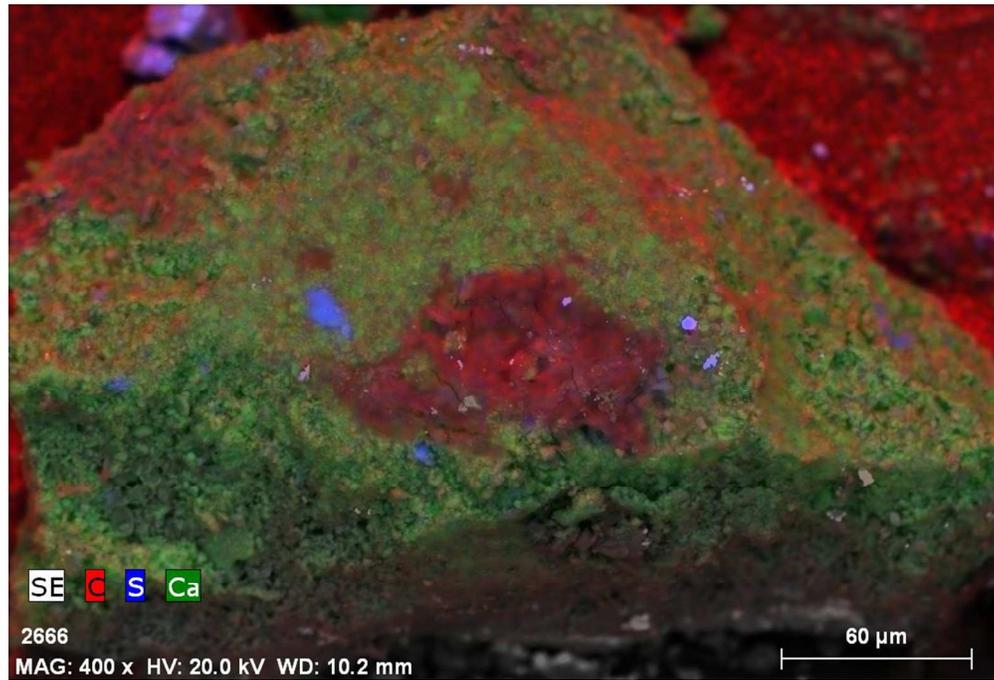


Fig. 6a. Elemental analysis map by SEM-EDS detecting S and Ca in glue sizing of the painting D Santo Franciscano (sample 2).
383x260mm (72 x 72 DPI)

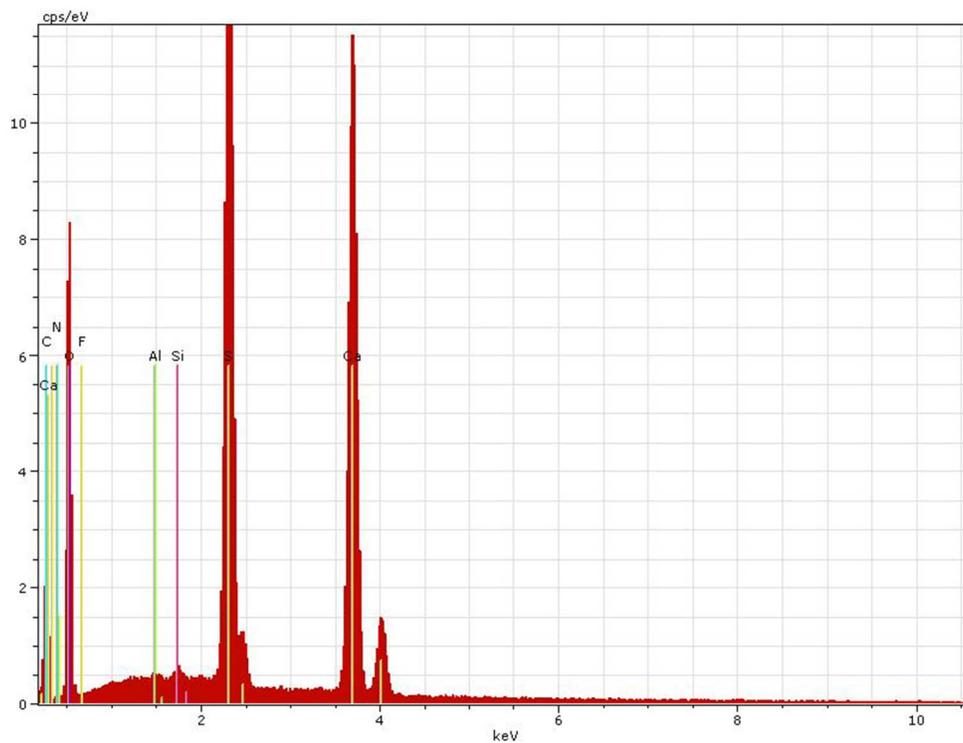


Fig.6b.EDS spectrum of elemental analysis detecting S and Ca in glue sizing of the painting D Santo Franciscano.
295x222mm (72 x 72 DPI)

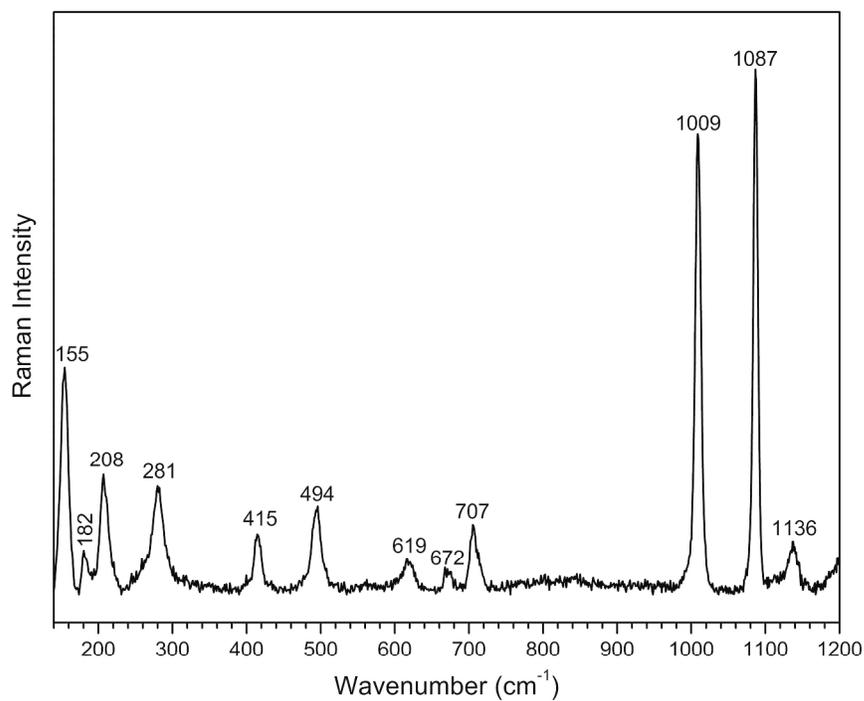


Fig.7. Raman spectrum of the solid dried product coming from the reaction between CaCO_3 (in excess) in water with H_2SO_4 . Pic 707 cm^{-1} indicates the presence of aragonite and pic 713 cm^{-1} indicates the presence of calcite.

715x552mm (150 x 150 DPI)

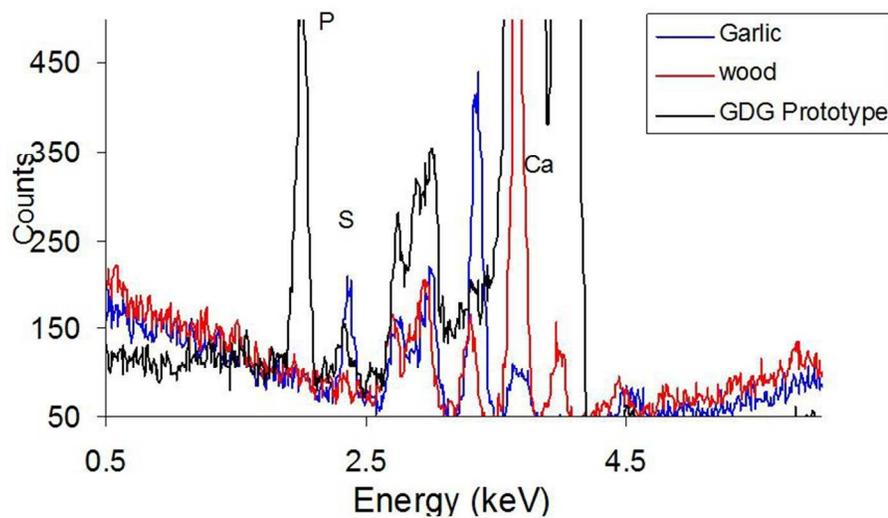


Fig.8. EDXRF spectra of sliced fresh garlic, wooden support and garlic-containing sizing of calcium carbonate ground layer prototype.
254x190mm (96 x 96 DPI)