Analytical Diagnosis Protocol to Assess the Impacts of Environmental Stressors on Historical Mortars Acting as the Support of Wall Paintings

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Abstract This work describes a new analytical diagnosis protocol to assess the environmental impacts on historical mortars acting as supports of wall paintings. The adequate assessment of such impacts requires not only the identification of the original and decaying products but also clarify the mechanisms (chemical reactions between original materials and environmental stressors) that promote the decaying. The proposed protocol is divided in four steps: (1) Analytical (both elemental and molecular) characterization by means of portable non-destructive spectroscopic and micro-destructive analytical techniques to identify the original and decaying compounds of the mortars, (2) Chemometric analysis on quantitative data of soluble salts, (3) Chemical simulations (MEDUSA, RUNSALT…) to explain the reactions between mortar components and environmental stressors and (4) Validation of the decaying reaction taking into account the agreement between the spectroscopic information and the chemometric calculation + chemical simulation results. The possibilities offered by this diagnosis protocol are described on two case studies: (a) mortars from medieval wall painting affected by ammonium nitrate rich infiltration waters and (b) Pompeian mortars of wall paintings exposed outdoors from the last 150 years after its excavations.

1 Introduction

A mural or wall painting is the general term for a painting applied directly to a wall. The mortar of a wall painting is composed of two layers, the arriccio layer
(the inner one composed mainly of slaked lime, sand, and/or brick dust and organic matter) and the intonaco layer (a much finer layer intended for painting). Mortars and pigments included in wall paintings can be affected by different factors (i.e., humidity, light, etc.). Some of these are the environmental stressors, such as infiltration waters, the impact of atmospheric pollutants, and the biodeterioration processes [1-5], which promote decay (different kind of efflorescence, black crusts, loses of binding strength, etc.). These affect the integrity of the wall painting, impacting first the painting layer; this layer can act as a protection for the plaster underneath, but sometimes the pigmented layer is not enough to prevent the external aggressions inside the mortars. In fact, deterioration in plasters of wall paintings is a well-known topic.

Many efforts have been carried out in recent years to investigate the nature of those decay products and the formation process of these salts, both of which promote the decay, including the enhancement effects between several stressors. Research also has been focussed on the development of innovative methods to remove these salt crusts [6]. The complexity of the problem requires a sound analytical protocol to assess the nature of the decaying salts (in the mortar of the wall painting, but sometimes also in the pigment layer) promoted by the effect of environmental stressors.

In this work, such a new analytical methodology is presented and discussed. The protocol is composed of a combination of spectroscopic techniques to identify the molecular composition of the products, including infrared spectroscopy, Raman spectroscopy, and μ-x-ray fluorescence, in addition to quantitative analysis (ionic chromatography) on the solubilised ions coming from those salts. The structural and quantitative data are treated by chemometric tools (correlation analysis and principal component analysis) and by chemical simulation (thermodynamic models to predict the formation of salts under specific conditions) to ascertain the possible decay reactions resulting from environmental stressors on the original materials.

To exemplify how to apply this methodology, two case studies are presented: (a) mortars from a medieval wall painting affected by infiltration waters and (b) mortars from wall paintings from a Pompeian house excavated 150 years ago and exposed since then outdoors.

2 Experimental

2.1 Samples

Mortar samples (intonaco or plaster and arriccio layer) were taken from two locations with different environmental conditions. Nine mortar fragments (with remains of red pigment) were taken from a 12 m² medieval wall painting of a
church (Bay of Biscay coast, north of Spain) affected by ammonium nitrate rich infiltration waters. Three mortar fragments were taken from the upper part (left-middle-right part of the painting, A1-B1-C1), three from the middle part (left-middle-right, A2-B2-C2), and three more from the lower part (left-middle-right, A3-B3-C3) [see sample distribution in Fig. 3]. A wall crack is observed down A2 till C1. Additionally, two mortar fragments with red pigment remains (hematite) from a wall, as well as six mortar samples with pigment layer remains coming from wall paintings, were collected from the House of Marcus Lucretius in Pompeii (Insula IX 3,5/24) for analysis. This house was first excavated more or less 150 years ago, and since that time it has been exposed to the open air. These last samples were collected during the excavation works performed by the Finnish EPHU project (Expeditio Pompeiana Univeristatis Helsingiensis) from 2002 to 2007.

![Fig. 1 Details of the location of the nine mortar fragments taken from the medieval wall painting from a church place in the Bay of Biscay coast (north of Spain).](image)

### 2.2 Analytical diagnosis protocol

The analytical diagnosis protocol is divided into four steps. First, several non-destructive spectroscopic and micro-destructive analytical techniques are used to perform the mineralogical characterization (molecular and elemental) of the bulk sample. The elemental analysis is conducted with a portable $\mu$-ED-XRF
equipment provided with a molybdenum X-ray tube of 50 KeV and 800 mA intensity. The molecular analysis is done with a combination of Raman spectroscopy and FT-infrared spectroscopy [Diffuse Reflectance Infrared Transmission (DRIFT) mode]; Raman measurements were performed using a Renishaw RA100 portable Raman microprobe (785 nm diode laser) and a Renishaw inVia Raman microspectrometer mounted on a DMLM Leica microscope (785 and 514 lasers). Long-range objectives of 20x and 40x (for the first one) and 50x and 100x (for the second one) were used to analyse the samples without damage. The FTIR (DRIFT mode) analysis was performed using a SensIR (Smiths Detections) IlluminatIR FT-infrared spectrometer with nitrogen cooled MCT detector and mounted on an Olympus BX51 microscope. The interpretation of the spectra was carried out by comparison with the collected Infrared and Raman spectra of pure standard compounds in two databases [7, 8].

Then, a micro-destructive analysis is carried out to quantify the soluble anions and cations in the mortar samples (the soluble salts are extracted using an ultrasonic method developed as an alternative to the NORMAL method [9]) using a Dionex ICS 2500 suppressed ion chromatograph with a ED50 conductivity detector. The quantification of soluble salts is performed for both external and internal areas.

In a second step, chemometric tools are applied to treat the quantitative results. For this purpose, the Unscrambler ® 7.6 software is used. First, correlation analysis between the anions and cations (concentrations in milliequivalents Kg\(^{-1}\) units, balancing the charge of the different ions) is carried out, followed by Principal Component Analysis (PCA) to observe different groupings among data (according to sample type, external-internal areas, sample position, etc.).

In a third step, thermodynamic chemical simulation calculations are performed. These calculations are intended to explain the reactivity (the decaying mechanisms) between the original porous compounds and the environmental stressors (SO\(_x\), NO\(_x\), excretions of biological nature, etc.). Software packages such as MEDUSA and RUNSALT were used.

Finally in the fourth step, the analytical results (mineralogical and quantitative results) are compared with the predictions from the chemometric calculations and thermodynamic simulations, in an attempt to diagnose the possible decaying pathways to explain the experimentally observed decay compounds.
3 Results and discussion

3.1 Mortars from a medieval wall painting located in a Romanic church (13th century) in the North of Spain

The spectroscopic analysis of the unexposed areas of the mortars to the inner infiltration waters showed calcite (CaCO₃), quartz (SiO₂), and iron oxide (hematite type, Fe₂O₃) as the original components in the intonaco layer. These results were obtained with both Raman and infrared spectroscopy. Also carbon black (C) was detected and could be attributed to the soot promoted after the firing of the candles of the church. The elemental analysis performed with μ-X-ray-fluorescence revealed K, Ca, Sr, Fe, and Mn as major components of the mortars; traces of Ba, Mg, Zn, and Cu also were identified in some samples. No additional elements that could be attributable to impacts of environmental stressors were detected.

The most surprising finding in the mortar fragments was the presence of a wide variety of nitrates [i.e., Mg(NO₃)₂·6H₂O, KNO₃], with Ca(NO₃)₂·4H₂O or nitrocalcite and NH₄NO₃ the nitrate salts appearing most frequently (see Figure 3 A). The presence of both nitrates in a higher percentage could be explained if we consider the impact of infiltration waters, rich in ammonium nitrate [10], which react with calcite to produce the corresponding nitrocalcite and the other nitrate compounds.

Apart from the presence of nitrate salts, signs of biodeterioration were also identified. For example, traces of calcium oxalate dihydrate (wedellite) were identified with Raman spectroscopy (see Fig. 3B). These compounds are formed in the mortar as a consequence of a reaction between the oxalic acid excreted by the microorganisms with the calcium carbonate of the mortar.

The quantification of soluble cations and anions present in the intonaco and arriccio layers revealed nitrate and chlorides as the highest concentration among anions. The highest values for nitrate (till 16.2 mg/g sample) in the intonaco layers belong to samples labelled with A and B. These samples are closer to the crack from which the infiltration water could enter. The concentrations in the arriccio layers were a little higher than those found in the intonaco ones, which means waters should come from outside the walls to the inner parts of the church.

The chemometric analysis on the concentrations of soluble salts gave a high correlation between nitrates and both ammonium (0.712 as the correlation coefficient) and calcium (0.810 as the correlation coefficient). Both correlations agree with the spectroscopic results, since calcium and ammonium nitrates were found by means of Raman spectroscopy.

After Correlation Analysis, Principal Component Analysis (PCA) was applied to the data from samples of intonaco and arriccio layers. With this mathematical procedure it is possible to obtain associations of samples according to specific variables. Taking into account the score representation of the PCA, samples A1,
A2, A3, B1, and B2 are highly clustered, and the rest of the samples are clustered apart. Moreover, the first group (A1-A2-A3-B1-B2) is closer to the nitrates if the scores are compared with the loadings representation (see Fig. 2). Quantitatively, these samples have higher nitrate salt concentrations.

These chemometric results (Correlation Analysis and PCA) agree with the spectroscopic and quantitative results, and they reveal that the samples taken near the crack (A1, A2, B1 and B2) have a greater abundance of salts (especially nitrates). Therefore, it appears that the crack is favouring the entrance of the dissolved salts.

![Fig. 2 PCA representation (scores and loadings) of the arriccio layers of medieval mortars (71% of the total variance explained).](image)

### 3.2 Mortars from wall and wall paintings from the House of Marcus Lucretius (Pompeii, Italy)

The mortar samples were taken from areas with clear aesthetic damage such as cracks, fissures, etc., exposed to the open air for the 150 years since its first excavation. The typical infrared and Raman features of calcite and also small amounts of quartz were observed as the original composition of the mortars. A micro-spectroscopic FT-IR and Raman screening on the surface of the plaster showed a high variety of sulphate salts such as gypsum, mirabilite (Na₂SO₄·10H₂O) [see Fig. 3 D], and epsomite (MgSO₄·7H₂O). These sulphate salts were only detected in the first 40-50 μm with a decreasing profile when moving inwards, thus it was possible to rule out the intentional application of a layer of gypsum over the calcite mortar previous to the application of pigments. Therefore, the most logical explanation for the presence of sulphate salts is the
impact of atmospheric SO₂ (probably wet deposition of H₂SO₃ or H₂SO₄) on the carbonate mortar, giving as a result the correspondent sulphate. Apart from sulphate salts, nitrate traces also were detected [i.e., Ca(NO₃)₂·4H₂O], thus a probable impact of atmospheric NOₓ has taken place only on the surface of the mortars, as nitrates were not identified in the inner parts.

The soluble salt test (water extraction assisted by ultrasound energy) on these mortar samples was essential to attribute the sulphate and nitrate presence to environmental impacts. The quantitative analysis by ionic chromatography clearly agreed with the spectroscopic evidences, since the concentration of sulphates was the highest one (see Table 1). Also, important concentrations of nitrates were quantified (see Table 1). Chlorides and fluorides were present in the samples, but these last were almost always near the detection limit (see Table 1). Moreover, the highest value of soluble cations belongs to calcium (see Table 2).

Table 1 Concentrations of anions in milligrams/kilograms of extracted mortar sample

<table>
<thead>
<tr>
<th>ANIONS (mg/g)</th>
<th>F⁻</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>C₂O₄²⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-1- intonaco</td>
<td>0.8 ± 0.1</td>
<td>3.2 ± 0.4</td>
<td>5.9 ± 0.5</td>
<td>*&lt; D.L</td>
<td>107 ± 1.2</td>
</tr>
<tr>
<td>W-1- arriccio</td>
<td>0.1 ± 0.1</td>
<td>2.2 ± 0.3</td>
<td>2.8 ± 0.3</td>
<td>No peak</td>
<td>10 ± 0.3</td>
</tr>
<tr>
<td>W-2- intonaco</td>
<td>0.6 ± 0.1</td>
<td>4.7 ± 0.4</td>
<td>8.9 ± 0.4</td>
<td>*&lt; D.L</td>
<td>178.4 ± 1.8</td>
</tr>
<tr>
<td>W-2- arriccio</td>
<td>0.3 ± 0.1</td>
<td>4.3 ± 0.3</td>
<td>6.2 ± 0.3</td>
<td>No peak</td>
<td>7.4 ± 0.6</td>
</tr>
<tr>
<td>W-2- arriccio-sand</td>
<td>0.3 ± 0.1</td>
<td>4.5 ± 0.7</td>
<td>7.5 ± 0.8</td>
<td>No peak</td>
<td>15.8 ± 0.4</td>
</tr>
</tbody>
</table>

According to these results, the soluble salts (mainly sulphates and nitrates) are distributed in the outer parts of the mortar. This evidence reinforced the hypothesis that the superficial impact of atmospheric acid aerosols (SO₂ and NOₓ) is the source of the decaying in the calcite.

The Correlation Analysis on the quantitative data gave the highest correlation coefficient between calcium and sulphates (0.949) among all the ions considered. This high correlation means that both ions must necessarily come from the same soluble compound, i.e. gypsum. Moreover, the application of Principal Component Analysis (PCA) showed a clustering of the intonaco samples (outer area) in the Scores representation; these samples are close to sulphate and calcium, which are also near in the Loading representation of the PCA (64% of the total
variance was explained). Once again, the chemometric results (Correlation and PCA analysis) agreed with the spectroscopic data.

Apart from the impact of atmospheric pollutants, clear evidence of biodeterioration was observed in the mortar samples. As in the medieval mortars from the North of Spain, traces of calcium oxalate dihydrate (wedellite) were identified with Raman spectroscopy. Moreover, brown-orange patina was identified in some samples and analyzed. Spectroscopic analysis revealed that they belonged to deposits of carotenoids. Given the Raman results, it could be concluded that the carotenoids present are those composed of 9 C=C bonds linearly conjugated. Considering the Raman bands at 1521, 1180, 1156, 1004, and 963 cm⁻¹, it could be attributable to zeaxanthin carotenoid [11], but other carotenoids such as β-carotene or lutein cannot be ruled out (see Fig. 3C). The presence of carotenoids in the mortars could be attributable to excretion products of some microorganisms such as lichens, cyanobacteria, moss, etc. These biodeterioration signs should be studied further, thus new sampling and additional analysis will be carried out, focused on the investigation of the biodeterioration of Pompeian mortars from walls and wall paintings in the House of Marcus Lucretius.

![Raman spectra of intonaco of medieval mortars (A, B) and brown-orange patina (C) and intonaco (D) of Pompeian mortars.](image)

4 Conclusions

The proposed analytical diagnosis protocol was used to analyse two kinds of mortars exposed to different environments: a rural non-polluted area with infiltration water processes (medieval mortars) and a moderately polluted
atmosphere impacting mortars for roughly 150 years (Pompeian mortars). In both cases the analytical protocol was successfully applied, since not only the original and decaying compounds were identified, but it was also possible to identify the probable causes of the decay and the most probable decaying mechanisms:

The chemical simulations gave this reaction

\[
\text{CaCO}_3 + 2\text{NH}_4\text{NO}_3 + 4\text{H}_2\text{O} \rightarrow \text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{HCO}_3^- + \text{NH}_4^+ + \text{NH}_3
\] (1)

as the most probable explanation of the decay in the Mediaeval wall painting.

However, the reactivity for the Pompeian mortars can be expressed by:

\[
\text{SO}_2 \rightarrow \text{SO}_3 \ [\text{Oxidation}] \rightarrow \text{H}_2\text{SO}_4 \ [\text{Inclusion in the rain water}] \quad (2)
\]

\[
\text{NO} \rightarrow \text{N}_2\text{O}_5 \ [\text{Oxidation}] \rightarrow \text{HNO}_3 \ [\text{Inclusion in the rain water}] \quad (3)
\]

\[
\text{CaCO}_3 + 2\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CO}_2 \quad (4)
\]

\[
\text{CaCO}_3 + 2\text{HNO}_3 + 4\text{H}_2\text{O} \rightarrow \text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{CO}_2 + \text{H}_2\text{O} \quad (5)
\]

It must be taken into account that Pompeii is near Naples, a city with a middle-high polluted atmosphere due to the traffic and the industrial harbour.

Both case studies illustrate how it is possible to use this procedure to identify decay processes promoted by the effect of different environmental stressors like infiltration waters, atmospheric acid pollutants, and even biodeterioration.

5 References

spectroscopy as a tool to diagnose the impacts of combustion and greenhouse acid gases on properties of Built Heritage. J. Raman Spectrosc. 39:1042-1049