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PORTABLE SPECTROSCOPIC INSTRUMENTATION AT THE SERVICE OF ARCHAEOLOGISTS AND CONSERVATORS FOR NON-INVASIVE IN SITU ANALYSIS: THE CASE OF POMPEII

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Introduction

Archaeological sites are parts of the cultural heritage and attract millions of people that want to learn the past and from the past. Archaeologists and historians primarily are shouldered with the duty of revealing the secrets of the ancient times. Furthermore, a plethora of scientists, such as chemists, biologists, engineers and more are responsible to answer questions concerning the physical and chemical nature of the materials, the manufacturing method of objects like ceramics and alloys, etc.

This identification of the materials from which the archaeological objects were made from is usually complicated, since the objects have suffered alterations during their burial and after their exposure to the atmospheric factors and pollutants. In the first case, the result can be the formation of a patina on the surface of the object, the transformation of the original material to another compound (like happens with the shell of an oyster) or the transfer on the surface of new elements present in the soil, wall, etc., in contact with the object coming from infiltration.

By atmospheric factors are meant the physical phenomena, like rain and other sources of water, heat, humidity, salt crystallization, etc. For example, water infiltrations from the rain, stagnant waters or ground and underground natural water sources, as well as humidity could influence a wall by changing its aesthetic appearance. In cases that the building materials are porous, the continuous cycle of reception of water and then the drying/evaporating can lead to salt crystallization on the surface or inside the pores that fatigue the material and can cause cracks. Furthermore, when water is present, it can provide the adequate conditions for the formation of biological attack (microorganisms). Nevertheless, the presence of water without the contribution of pollutants is not the main responsible for the loss of material and the subsequent collapse of it.

Moreover, the ultraviolet radiation of the sun can fade possible colors that are present. This process is called photodegradation and is explained by the ability of radiation of certain wavelength to break the chemical bonds from which a pigment is composed. Nevertheless, in the case of wall paintings from the antiquity and the Roman times, the pigments are inorganic and therefore stable against photodegradation.

The most prejudicial factor for the archaeological sites and their constituents is atmospheric pollution the that causes deterioration. In the majority of the cases, the burial environment has protected the remains archaeological for ages. Their exposure to the atmosphere has begun a continuous deterioration process that has formed new materials on the surface of the objects and their identification is essential in order to reveal the mechanisms of their formation. In this way, these mechanisms could be stopped, slowed down or even reversed.

In order to identify the different kinds of materials, various analytical techniques are used. In each case, the proper analytical technique is applied, depending if molecular or elemental analysis is required, how low detection limits are proper, which will be the precision and accuracy, etc. But especially in the case of the cultural heritage objects there is an extra requirement: the minimum intervention. Due to the high value of the archaeological objects, in the majority of the cases, archaeologists prohibit sampling and there is strict legislation concerning the



intervention on the objects or their transfer to an analytical laboratory. But, sampling is essential in the majority of the analytical techniques and therefore these techniques are discarded. Nevertheless, there are some techniques that not only do not require sampling but even can be incorporated in portable instruments. In this way big-scale archaeological remains, like archaeological sites, can be analyzed in situ. Furthermore, precious time is saved when conservation treatments have to be immediately applied, since sampling and sample preparation require much more time than the direct measurement on the sample. For these reasons, in the last decades it has increased the demand of the use of non-destructive portable analytical techniques in the field of art and archaeology. Raman spectroscopy, Infrared spectroscopy (IR) and X-Ray fluorescence (XRF) are the most widely used analytical techniques in this field.

The authors of the present work have experience since 2010 in the use of portable instrumentation in the archaeological site of Pompeii with the expedition APUV-2010 (Analytica Pompeiana Universitatis Vasconicae, funded by MICINN through the Complementary Action CTQ2010-10820-E) and more recently with the expedition APUV-2011 (funded by the University of the Basque Country through the Special Action AE11-27). During the past two years the group has been working in the identification of the wall painting materials in the House of Marcus Lucretius (Insula XI 3, Houses 5/24) by using a portable Raman spectrometer and a portable XRF instrument among others.

Pompeii is one of the most famous cities of antiquity that stands out for the its architecture and all its decorative elements, such as wall paintings. Pompeii was destroyed from the eruption of the volcano of Vesuvius in 79 A.D. and as a consequence the whole city was buried under a stratum of ash and pumice. When the first scholarly excavations of Pompeii started at the beginning of the 19th century, it was surprisingly observed that the city with all its elements, like the famous Pompeian wall paintings, was well preserved. The most probable explanation is that the layer of ash and pumices, covering the walls to a height up to 6 m, acted as a protective layer and preserved the integrity of the underlying objects. Nevertheless, the exposure

of these wall paintings to the atmospheric factors has led to a considerable decay.

Pathologies identified in the House of Marcus Lucretius

The House of Marcus Lucretius is the largest home of the Insula IX (IX 3,5/24) and is situated in the Via Stabiana, Pompeii's main north-south street. The house consists of a combination of two houses - at some point in time the houses 5 and 24 have been connected- and it covers almost one fourth of the Insula (Figure 1). It represents fairly well a rich Roman's house in size, shape and luxury of decorations. It features over 30 rooms in the ground floor and several in the first floor. The majority of the walls are covered with Roman wall paintings of the first, second and fourth styles, some of them of great artistic value. The most valuable wall paintings have been transferred to the Archaeological Museum of Naples (MANN).



Figure 1. Plan of the Insula IX. The numbers of the doorways correspond to the numbers of the houses.

The walls and wall paintings of Pompeii suffer mainly from the chemical attack of the atmospheric pollutants that are abundant in the area of Naples and surroundings and as a consequence many wall collapses have been reported the last years (Reuters press release 2011). Carbon dioxide (CO₂) and monoxide (CO) are some of the dangerous gases present in the air of Pompeii. Carbon monoxide is oxidized by oxygen/ozone to carbon dioxide and this dissolves in water (H₂O) to form carbonic acid (H₂CO₃). Also, nitrogen dioxide (NO_2) and monoxide (NO) are the gases responsible for the formation of nitric acid (HNO_3) . Furthermore, sulfur dioxide (SO_2) by oxidation (and by the presence of catalysts like NO_2) is transformed into sulfuric acid (H_2SO_4) , which in turn contributes to the formation of acid rain.

Thus, if the above mentioned acids find a wall that contains calcite (CaCO₃), a major component of building materials such as stones (limestone, marble, etc.), lime mortars and plasters, several chemical transformations can take place.

First, the so-called *decarbonation* process must be taken into account due to the formation of soluble bicarbonate (Ca(HCO₃)₂) as a consequence of the reaction between calcite and carbonic acid, two non-compatible chemical forms of the carbonate system:

 $CaCO_3 + H_2CO_3 + 2H_2O \rightarrow Ca(HCO_3)_2$

Calcium bicarbonate, the new product formed by this reaction, is a highly soluble salt, easily washed away by the rain.

The presence of sulphuric acid along with water is responsible for the *sulphation* of calcite that means the transformation of calcite to calcium sulfate dihydrate (CaSO₄·2H₂O), commonly named as gypsum, through the following chemical reaction:

Gypsum is partially soluble in water and thus, it can be washed away in part by the rain.

Furthermore, the attack of nitric acid on the carbonated materials leads to the less known process of *nitrate formation*. For example, the attack of nitric acid on calcite provokes the formation of calcium nitrate (nitrocalcite, Ca(NO₃)₂·4H₂O) that is even more soluble than gypsum. The formation of nitrocalcite follows the next chemical reaction:

Consequently, when a wall having a calcite mortar with (or without) a fresco painting is permanently attacked by the atmospheric acid gases, calcium bicarbonate, gypsum and nitrocalcite will be formed. If this wall then is exposed to the rain, part of it will be dissolved. The bicarbonate and nitrate salts are the first to be dissolved as the most soluble salts. Also part of the sulphate salts will dissolve, but some part will remain on the wall due to its lower solubility comparing to that of bicarbonates and nitrates.

If the in-situ analysis is performed on the attacked walls after a long time-period without rainfalls, the instruments will detect at least the sulphate and nitrate salts (the bicarbonate ones is not so easily detected because they transform to the carbonate ones after a dry period, reversing the decarbonation reaction). But, if the analysis is performed after a prolonged rain wash, only the sulphate compounds will be detected because all the nitrates and bicarbonates will have been dissolved.

The transformation of calcite to soluble salts starts usually from the exterior parts of the wall. As the external parts are dissolved, the more internal parts will be exposed to the atmosphere and, if calcite is also present, with a new chemical attack, it will be again transformed to one or more forms of soluble salts. This decaying process can be repeated many times and for many years till a big part of the wall has been consumed.

The final situation leads to the visible loss of material in both walls and wall paintings and in the worst case, to a possible collapse of the walls. For fresco paintings, this process dissolves the binder (calcium carbonate) and causes the fall of the pigment grains and even their transfer through the wind. For carbonate mortars, it dissolves first the *intonaco* and then the *arriccio* (its carbonate part), as it can be observed in most of the walls of the Pompeian houses without roof.

Also, the presence at the archaeological site of animals, like pigeons or dogs, is a source of another environmental stressor; their excrements transform into ammonium nitrate, a highly aggressive salt. Ammonium (NH4⁺) is an acid that can react with carbonate materials, forming ammonia gas (NH₃) and the soluble bicarbonate salt. Then the nitrate accompanying the ammonium and the calcium accompanying the carbonate interact forming calcium nitrate. As we have pointed out before, this is a highly soluble salt. Thus, the attack of ammonium nitrate gives rise to the formation of soluble salts that are dissolved by the rain, resulting in a net loss of the original calcite.

Other facts that jeopardize the walls of Pompeii and, in particular of the House of Marcus Lucretius, are previous unsuccessful conservation treatments. The presence of Portland cement in many parts of the walls testifies this kind of treatments. Unfortunately, Portland cement is a source of sulfate salts that are present in many surfaces in the walls of Pompeii. This is not only an aesthetic problem but also damages the wall. Furthermore, the lack of documentation is not helping scientists to know the exact places and extent of the application of Portland cement and consequently the magnitude of this problem.

Another important pathology of a wall is the appearance of efflorescence on its surface. The new salts formed after the precipitation of partially soluble compounds from the ions present in the water inside the pores of mortars and stones are called efflorescence. These salts are formed when the internal water evaporates enough in order that the ions that will compose the salts have enough concentration to reach the saturation index. Due to their high solubility, efflorescence crystals are easily dissolved by rain. In Figure 2 efflorescence from the Marcus Lucretius House is clearly visible as white "snow" over the red pigment.



Figure 2. Efflorescence on a wall painting.

Last but not least is the influence from biological factors, which is not only altering its aesthetic appearance but also can damage its surface. The growth of plants on the surface of the walls can result quite damaging. The colonization can affect with various ways a wall or wall painting (Gorbushina et al. 2004, Perez-Alonso et al. 2006). An example is the penetration of the lichen hyphae through the pigment that damages the mortar and can lead even to its detachment (Sterflinger 2010). Furthermore, algae, lichens, cyano-bacteria, etc. form green, black, brown or yellow stains or patches on frescoes exposed to the sunlight and the original color/tonality of the pigments is altered (Ciferri 1999). Additionally, carotenoids, biogenic pigments that occur naturally in photosynthetic microorganisms, like algae, some species of fungi, bacteria, lichens, bryophytes, etc., can also change the appearance of a wall.

Materials and Techniques

For the characterization of the walls and wall paintings of the House of Marcus Lucretius various portable systems were used. For the molecular characterization a portable innoRam spectrometer was used (B&WTEK, Inc., Newark, USA) with a 785 nm excitation laser (Figure 3a). For the control of the focal point, the Raman microprobe was mounted on a tripod (MICROBEAM S.A, Barcelona, Spain), with motorized the x-y-z axes and a spatial resolution of 1 µm per electrical pulse (Figure 3b). The tripod was equipped with a microvideo camera in order to localize the point of analysis and focus on the specific pigment or plaster grain. For the focusing of the laser and the collection of the Raman signal an objective lens with a magnification of 20x was used. The laser power was controlled low levels in order to avoid the in photodecomposition of the pigments.



Figure 3: Analyzing a deteriorated wall in Marcus Lucretius House with the portable Raman spectrometer with the microprobe: a) on hand and b) on the tripod.

The processing of the Raman spectra was done via the GRAMS 8.0 software

(ThermoFisher Scientific Inc., Waltham, USA) and the interpretation of the spectra was performed by comparing the obtained Raman spectra with the spectra of standard materials contained in the e-VISARCH and e-VISART Raman spectral database.

For the in situ elemental analysis a hand-held energy-dispersive X-ray fluorescence spectrometer (EDXRF) was used from OXFORD Instruments (X-MET5100, UK) (Figure 4). The instrument uses an X-ray tube as excitation source, being Rhodium the standard target material that works at a maximum voltage of 45 kV. The analyzer has a high resolution Silicon Drift Detector (SDD). The semi-quantitative analyses were performed using a short integration time (50 s).



Figure 4. Analyzing the pigments of a wall painting with the portable EDXRF system

Analytical results

For the rescue of the wall paintings the first step is to characterize all the materials that constitute them, including building materials and colored layers, as well as materials that were formed due to the environmental factors. In this way, the mechanisms that accelerate the deterioration could be revealed and, thus, slowed down or stopped. Furthermore, conservators could use the most compatible materials for the restoration of the walls and wall paintings.

In order to better understand the results, the construction typology of a typical Pompeian wall painting should be mentioned. A Roman wall painting (fresco) is consisted of three basic layers: the support (commonly a brick or stone wall); the *arriccio* (the preliminary layer of lime plaster with sand spread on the masonry); and the *intonaco* (top layer lime plaster). For the protection of the fresco it

was applied Punic wax, according to Pliny the Elder. Pigments are painted on this outer layer of lime still wet. Pigments used in the Pompeian frescoes are inorganic substances that are mainly coming from minerals, such as the various ochres or azurite. In some cases mixtures of pigments can be used in order to achieve the desired color. From chemical studies made in Pompeii some typical pigments that were used were identified. Thus, for white colors calcite was widely used. For yellow tones, yellow ochre or goethite (Fe₂O₃·H₂O and FeO(OH) respectively) and massicot (PbO) were used. For the green tonalities malachite (CuCO₃·Cu(OH)₂) or green earth (celadonite), were applied, while for the blue colors Egyptian blue (CaO·CuO·4SiO₂) or azurite (2CuCO₃· Cu(OH)₂) were employed (Aliatis et al. 2009, Piovesan et al. 2011).

Typical red pigments were red iron oxide (Fe_2O_3) coming from the mineral hematite (Vahur, 2009), cinnabar (HgS) and realgar (As_4S_4) (Aliatis et al. 2009). Some of these pigments have suffered alterations that unfortunately have modified the aesthetic appearance of the wall paintings. From all the red pigments, cinnabar was the most expensive. Therefore, it was used selectively in the richest houses of Pompeii and in the most important rooms of these houses. For example, in the House of Marcus Lucretius, cinnabar was found only in the *triclinium* (Maguregui et al. 2010).

With the years and for unspecified reasons, the red color of cinnabar has been transformed into a grey-silver color. This phenomenon is known as blackening of cinnabar (McCormack 2000). The reason for this is not yet completely understood. Some researchers support the hypothesis of the transformation of the structure of the cinnabar from the red hexagonal cinnabar into a black cubic metacinnabar by the action of light (Zafiropulos et al. 2003). This hypothesis though is lately being abandoned and new hypotheses appear, attributing the blackening to other factors, like chlorine (Cotte et al. 2006).

The scientific team of the present work, by the first year of the analytical campaign, analyzed the main pigments in order to evaluate the efficiency of the portable analytical techniques. Furthermore, the degradation state of the walls was estimated by analyzing efflorescence and soluble salts. A published research result from this first year campaign was that hematite is also suffering blackening. The most probable reason is its transformation into magnetite, a black iron oxide (Fe₃O₄) at the presence of sulfur dioxide (Maguregui et al. 2011a).

Besides, various wall painting and wall fragments were analyzed at the laboratory (Maguregui et al. 2011b). The pigments as well as the decaying compounds of these fragments were identified by a laboratory Raman spectrometer. In this way, the information obtained *in situ* was complemented with laboratory work.

The colonization of microorganisms on the walls and wall paintings was also measured (Maguregui et al. 2011b) by both portable and laboratory instrumentation. The research was focused on the characterization of the nature and distribution of carotenoids, biogenic pigments, on brown patinas.

As far as the identification of the soluble salts is concerned it should be pointed out that if the analysis is performed after a rainy period, only gypsum will be detected and not the nitrate salts. This happens because after a wet period the highly soluble nitrate salts will be washed out. Therefore, for the detection of the nitrate salts, it was necessary to wait for a dry period (like September in the case of Pompeii) in order to let the atmospheric attack take place and form enough nitrate salts as to be detectable by the instruments.

In the second year, the main goal was to answer questions that were created during the first year campaign. Therefore, concerning the pigments, the reason of blackening of cinnabar was intended to be found. In this sense the west wall of the triclinium was scanned by the portable XRF system and the content of mercury (Hg) was monitored (this wall was suffering from blackening of cinnabar). It was found that its concentration was changing from positions far from the door to positions near the door. More specifically, it was found a considerable drop-down of mercury, while approaching the door. This could be attributed to a possible transformation of cinnabar (HgS) to elemental mercury (Hg), which has a black color, and then the volatilization of Hg at very high temperatures like those that were occurring during the eruption of the volcano.

Also, various pigments that did not give Raman signal in the first year of the campaign were again analyzed.

One of the main reasons for the absence of Raman signal for the portable Raman instrument was the fluorescence interference. The origin of fluorescence was probably due to the application on the surface of the wall paintings of an organic layer. This layer could be either the original Punic wax referred by Pliny or a new protective layer, applied later by conservators. Therefore, in many cases the fluorescence signal made difficult the acquiring of a clear Raman spectrum. Still, it was encouraging that many pigments could be identified despite the fluorescence interference. In Figure 5 a Raman spectrum of red iron oxide (hematite) is displayed with the Raman bands at 226, 295 and 411 cm⁻¹. This is very important for the applicability of the portable Raman system, because it proves its utility.



Figure 5. Raman spectrum of hematite found in room 8 of the House of Marcus Lucretius.

As far as the environmental impact is various walls with different concerned, orientation as well as covered with roof or exposed to the open air were analyzed by Raman in order to create the profile of the sulphate content and the atmospheric conditions that may favor their formation. Also, the detection of nitrate salts was pursued, especially because the analysis period was dry and it would be easier to detect the nitrates. Indeed, nitrate salts were found in some parts of the House of Marcus Lucretius, like the scriptorium. The characteristic Raman band of nitrocalcite appears at 1048 cm⁻¹. Signal from the underlying calcite was also recorded - Raman band at 1085 cm⁻¹ (Figure 6).



Figure 6. Raman spectrum of an efflorescence, where nitrocalcite and calcite bands are visible

Conclusions

The experience of the use of portable spectroscopic instrumentation for the analysis of materials in the field of art and archaeology is encouraging. Still, there is a lot of work to be done and more issues to be clarified in order to understand what processes occurred during the burial and what new decaying procedures started after the excavation of the archaeological remains. This will be one of the important tasks for further future field work. More specifically, from the analytical experience with portable instrumentation from the previous two years, the forthcoming research will be focused on many open issues, like the causes of the blackening of cinnabar or the role played by the organic wax applied in past or recent times to the wall painting remains.

This forthcoming research will be undertaken using three portable instruments, the two shown in this work (Raman and EDXRF) and a portable FT-IR device, working in the Diffuse Reflectance Mode (DRIFT).

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