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A non-invasive spectroscopic study to evaluate both technological features and conservation state of two types of ancient Roman coloured bricks

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ABSTRACT

The study of both original and decaying compounds is relevant in understanding the chemistry behind the deterioration processes, above all in open museum contexts where environmental stressors affect the artefacts. In this sense, a combination of non-invasive spectroscopy techniques (Raman spectroscopy, μ -X-ray fluorescence and X-ray diffraction) was applied on an ancient Roman building (130 CE), the "Casa di Diana" *Mithraeum* at Ostia Antica archaeological site. The aim is to study the raw materials, manufacturing and decaying products of the two observed types of Roman fired bricks (red and yellow) that compose the building.

The present study estimates an illite raw material of carbonate-bearing marine clay likely referring to the common deposits of central/southern Italy, which contain calcite as accessory phase and a-plastic fraction constituted by quartz, feldspar and opaques. This clay material was added with volcanic temper characterised by abundant clinopyroxene and analcime (from analcimization of leucite) that are typical of the Roman Province volcanism. The firing would be probably the result of oxidizing conditions, as proved by the hematite presence. Thanks to the existence of specific neoformed mineral phases during firing it was possible to assess different temperatures ranges. In detail, the red/orange bricks, for the existence of gehlenite (formed from calcite and its reaction with silicates), were fired at 800–900 °C range; whereas, the yellow ones are characterised by the lack of gehlenite and the disappearance of illite/muscovite, which indicates firing temperature at over 900 °C.

Regarding the decaying products, the gypsum covers most of the surface of most bricks, both red and the yellow ones, but these latter are more susceptible to environmental stressors (sulphates and carbonates).

Therefore, this work points out how by integrated non-invasive approaches it is possible trace back to original firing temperature, technology of manufacture, interpreting ceramic data.

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1. Introduction

Nowadays, a broad range of analytical techniques is available and applied in the preservation of Cultural Heritage [1–3]. In this context, destructive and/or invasive techniques should be avoided, whenever possible, to preserve the integrity of the studied artefacts [4, 5]. Therefore, the development of non-destructive and non-invasive and in-situ analysis is extremely important [6–10] substituting invasive methods and minimizing the risk of damage.

In recent years, several reviews can be found in the literature summarizing the most important applications of XRF and Raman spectroscopy to the service of artwork studies, proving the suitability of these techniques for non-destructive analysis [1, 4, 10–12].

These techniques allow the study of both original and decaying compounds that is crucial to understand the chemical behaviour of the artefacts [13–17] above all when they are set in harsh environment conditions. The archaeological sites represent one of those cases in which the buildings materials suffer accelerate weathering and ageing processes.

Two different coloured bricks (red/orange and yellow) that compose the Roman masonry, "Casa di Diana" *Mithraeum* at Ostia Antica, were studied to understand the differences between them by non-invasive

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techniques (μ -EDXRF, Raman spectroscopy and XRD), maximizing the information with a minimum amount of sample (so without destroy it).

1.1. Firing Processes on Ceramic Materials

Bricks, which are ceramic materials widely used in the manmade building material history [18] are obtained by firing clay added with coarse grains as temper or whatever at temperatures ranging between 650 and 1100 °C [19, 20], producing series of mineralogical, textural and physical changes [21, 22]. Colour, composition and mechanical properties are dependent on the nature of the clay (kaolinite, illite, and smectite), kiln environment (oxidative or reductive), kiln operator, temperature of the firing process, nature and amount of temper (quartz, carbonates, grounded fired clays) [23, 24].

In the case of clays with carbonate fraction two main thermic processes are involved: clay dehydroxylation (ca. 400–600 °C) and decarbonation of the calcareous materials (750–850 °C). Higher firing temperatures lead the calcite decomposition products to react with fired clays to form new calcium silicate phases such as gehlenite, plagioclase feldspar and/or pyroxenes (diopside, wollastonite, fassaite) [25, 26].

In the archaeological artefacts, it is possible to distinguish and classify the *primary minerals*, that are those that were present in the raw material, like quartz and that does not undergo reactions in a wide range of temperature, from the *firing minerals*, which are the products of thermally induced reactions (i.e. they are formed during firing). Whereas, the *secondary minerals* are those formed after the production: during their use and mainly their burial because of either transformation of metastable firing minerals or infiltration of any solution [27].

Different methods to analyse the mineralogical changes occurring during firing in ceramics with different raw materials were widely addressed in the literature. But, it is mostly via invasive and destructive methods [22, 28], enough to used ceramic replicas [24], or by subjecting the original materials at rigging [29] and/or forced firing processes (fired and re-fired) [30–32].

Here, a combined non-invasive spectroscopic method and mineralogical analysis achieving the use of distinct types of clayey raw materials and predicting the firing dynamics, is presented. In detail, the first two techniques addressed information on the main and the accessory minerals with micrometric size, thanks also to an appropriate descriptive statistical technique applied to μ -EDXRF data by distribution analysis. The XRD helped to estimate the original firing temperature via the growth or disappearance of different mineral phases, as “fingerprints” of the stable and also the metastable solid phases formed during firing.

2. Materials and Methodology

2.1. Site Description

The ancient city of Ostia, sited at the mouth of the Tiber River, 15 km downstream from Rome, is built mainly of brick-faced conglomeratic concrete structures that remained largely intact for nearly 2000 years. The “Casa di Diana” *Mithraeum* is a *domus* that dates back to 130 CE, remaining partly in use until the early fourth century, while the completely archaeological site was inhabited until the 9th century CE [33]. Ostia Antica, and in particular the *Mithraeum* (ritual place at north-east of the “Casa di Diana” house), represents a particularly complicated scenario due to the numerous conservative problems that it is affected [17, 34–39].

The entire house is mainly composed of bricks and pozzolanic mortar aligned with the “opus caementicium” technique. Efflorescences, displayed throughout the entire year, both on internal and external walls, producing a mattifying veil on the bricks that completely affected the building. A recent study ongoing has determined that acid gases, probably the main source of salt weathering (sulphates attack), come from the nearby Leonardo da Vinci airport (also known as Fiumicino)

and that the mechanism of the acid attack involves the dry deposition of the atmospheric acid gases [17]. The wall building under study results mainly affected by rising damp, biological proliferation (cyanobacteria, green algae, and lichens) [36, 38] that both occurred mainly from the pavement up to 0.75 m and cracking phenomena. Interesting geo-electrical investigations [15, 16, 37] detected a freshwater aquifer at a depth of 2.5 m (0 m a.s.l.), within the sand deposits, whereas salt water was found at a depth of 8 m (–5.5 m a.s.l.). Focusing on bricks, two main typologies it is possible to identify red and yellow coloured bricks, with a predominance of the first one. In both, a wide range of hues is present; varying from dark red, light red or orange to light yellow. The red bricks appear more compact and in a better state of conservation than the yellow bricks [17, 35].

Moreover, a pre-screening study on the colour of these bricks, revealed some differences in the composition of the bricks and their interaction with the *hypogeum* environment [34] via in-situ analysis [17].

However, this way did not produce enough data to solve completely the reason for these differences [17]. The need to a deeper analysis on the raw materials, processes and decaying products, justifying a sampling step and minimizing it as much than possible, is emerged [17]. This new work arises from this effort.

2.2. Sampling Design

Taking into consideration the results obtained by the previously in-situ analysis [17], 16 micro-samples (red/orange and yellow bricks) were collected from the wall building. A micro sampling based on rooms, orientation and colour was carried out (Fig. 1a, Table 1).

The latter was obtained via colorimetric measurements (Fig. 1b, Table 1) to collect significant samples per class of colour, optimizing, in this way, the micro sampling. Although the size of sample was so “micro” (maximum of 16 mm per brick), the differentiations between the mattifying veil, the formed salts (damage products) and the supposed raw materials were possible thanks to the selected analyses (μ -EDXRF in particular) able to deal with them (Fig. 2).

2.3. Spectroscopic Techniques

Firstly, the micro-samples were investigated with non-destructive μ -EDXRF by a TORNADO M4 X-ray spectrometer [<https://www.bruker.com/products/x-ray-diffraction-and-elemental-analysis/micro-xrf-and-txrf/m4-tornado/technical-details.html>] to differentiate the elemental composition of the coloured bricks, as well as the mattifying veil and efflorescences present in the types of bricks. The system was equipped with an X-ray tube working at a voltage of 50 kV and an anode current of 599 μ A. Tungsten was used as the anode material. The emitted X-ray photons were detected with a silicon drift detector (SDD). To increase the sensitivity for the Ag L-line, an Al filter (12.5 μ m) was used. The sample chamber operated under vacuum conditions (20 mbar), to avoid signal overlap of the Ag line and argon from the surrounding air. The samples were mapped with a spot size of 15 μ m and an acquisition time of 20 ms for each spot. In this way, multi-point analyses were carried out, obtaining both different mapping areas per sample and separated elements linked to the alteration or belonged to the bulk (Fig. 2). The control of the measurements has been possible thanks a fish eye camera and two optical video microscopes. For each area investigated an average quantitative result were carried out (from a minimum of three up to seven points) with an error in wt% (1 σ). A complete and speedy mapping was obtained, investigating each part of sample (frontal, lateral and the back part).

The spectra were acquired and analysed using ESPRIT 2 software [<https://www.bruker.com/products/x-ray-diffraction-and-elemental-analysis/eds-wds-ebds-sem-micro-xrf-and-sem-micro-ct/esprit-2.html>].

The molecular composition of the samples was performed using two different spectrometers, with the purpose of analysing the original

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