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PII: S1386-1425(17)30811-9  
DOI: doi:[10.1016/j.saa.2017.10.010](https://doi.org/10.1016/j.saa.2017.10.010)  
Reference: SAA 15516

To appear in: *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*

Received date: 9 March 2017  
Revised date: 28 September 2017  
Accepted date: 3 October 2017

Please cite this article as: Silvia Bruni, Vittoria Guglielmi, Elena Della Foglia, Marina Castoldi, Giovanna Bagnasco Gianni, A non-destructive spectroscopic study of the decoration of archaeological pottery: From matt-painted bichrome ceramic sherds (southern Italy, VIII-VII B.C.) to an intact Etruscan cinerary urn. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Saa(2017), doi:[10.1016/j.saa.2017.10.010](https://doi.org/10.1016/j.saa.2017.10.010)

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## **A non-destructive spectroscopic study of the decoration of archaeological pottery: from matt-painted bichrome ceramic sherds (southern Italy, VIII-VII B.C.) to an intact Etruscan cinerary urn**

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### **ABSTRACT**

A study is presented based on the use of entirely non-destructive spectroscopic techniques to analyze the chemical composition of the painted surface layer of archaeological pottery. This study aims to define both the raw materials and the working technology of ancient potters. Energy-dispersive X-ray analysis, micro-Raman spectroscopy, visible and near infrared (NIR) diffuse reflection spectroscopy and external reflection Fourier-transform infrared (FTIR) spectroscopy were applied to matt-painted bichrome pottery sherds (VIII-VII century B.C.) from the site of Incoronata near Metaponto in southern Italy. Two different raw materials, ochre and iron-rich clay, were recognized for the red decoration, while the dark areas resulted to have been obtained by the so-called manganese black technique. In any case, it was demonstrated that the decoration was applied before firing, in spite of its sometimes grainy aspect that could suggest a post-firing application. For the samples with a more sophisticated decorative pattern a red/black/white polychromy was recognized, as the lighter areas correspond to an “intentional white” obtained by the firing of a calcium-rich clay. Reflection spectroscopy in the visible-NIR and mid-IR as well as micro-Raman spectroscopy were then employed to characterize the decoration of an intact ceramic urn from the Etruscan town of Chiusi, evidencing a post-firing painting based on the use of red ochre, carbon black and lime, possibly imitating the “fresco” technique used in wall paintings.

**Keywords:** ancient pottery decoration, energy-dispersive X-ray analysis, micro-Raman spectroscopy, reflection visible-NIR spectroscopy, reflection Fourier-transform infrared spectroscopy

## 1. Introduction

When ancient painted pottery objects are under investigation, the archaeologist's demand for the chemical characterization involves not only the ceramic paste but also the decorated surface of the objects themselves. Regarding the latter, the main questions to which the scientist should answer concern on one side the raw materials and on the other one the firing technique used for the decoration. The responses to such questions can throw light on the level of technological evolution of a human settlement as well as on the possible diffusion of know-how and even raw materials among different sites.

As regards the Mediterranean area, abundant investigations have been reported on some well-known examples of painting on archaeological pottery such as black (and also red) gloss especially on Attic but also southern-Italian, Etruscan and Roman ceramics [1-9], while for other forms of decoration a site-by-site investigation is still needed. Numerous studies on the subject have been devoted in the past to the Greek civilization, as reviewed by Jones [10], while for a lot of fundamental work we are indebted to Noll [11,12]. It was thus clarified that, if the choice of colours was rather limited for ancient potters, comprising mainly red, black and sometimes white with really few examples of other hues, raw materials and firing conditions could be quite varied. So the red colour, almost always due to iron(III) oxide, could be obtained using ochre or ferruginous clay. For the black or brown colours, at least three basic compositions can be distinguished, namely iron(II) oxides, manganese or manganese/iron oxides and carbon in different forms. Kaolinite, talc and calcite have been instead recognized as white pigments. It should be finally emphasized that a rather limited number of studies has been devoted to decorations different from black gloss on pre-medieval pottery from the Italian peninsula [13-16].

From a methodological point of view, since the beginning morphological observation by scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDXA) and X-ray diffraction (XRD) have been mainly used in the above-mentioned studies. More recently, the use of other spectroscopic techniques has been developed, among others micro-Raman spectroscopy [8, 17-21], X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR) [15-17, 21], X-ray absorption (XAS and XANES) [5,22], particle-induced X-ray emission (PIXE) [23] and laser-induced breakdown spectroscopy (LIBS) [24]. On the methodological side the interest in applying such spectroscopic techniques is mainly related to the possibility of a non-destructive and/or compound-specific analysis.

The importance of non-destructivity stems from two main causes. The first one relates to the archaeological relevance of the decorative pattern even in the case of a sherd, that should be preserved in order to provide documentary evidence of the style of the decoration itself. The second one

concerns the risk that the painted layer is contaminated by the underlying ceramic paste when the surface is scraped off, thus leading to altered analytical results.

Finally, it should be emphasized that a multi-technique approach is usually mandatory, as each spectroscopy shows limits in recognizing one or the other pigment. For example, if micro-Raman analysis is ideal and almost unique in identifying black carbon, it is less efficient as regards iron(II) or manganese-containing oxides [25,26], while XPS cannot distinguish among the different oxidation states of manganese [16].

In this context, the present work aimed on the archaeological side to investigate two particular examples of pottery decoration from the Italian peninsula. First of all it was intended to give information on the painting of ancient pottery in the indigenous settlement of Incoronata. This settlement existed in the region of Metaponto (southern Italy) till the end of VII century B.C., when it was destroyed because of the arrival of Greeks and the foundation of their well-known colony [27]. A contribute could thus be given to the knowledge of the technological competence in southern Italy before the contact with the Greek civilization. Afterwards, the decoration of an intact Etruscan ceramic urn dating to the Hellenistic period was examined, to verify if the similarity of the decorative pattern with those found in wall paintings inside Etruscan tombs was maintained also in the execution technique.

On the analytical side, a procedure allowing to avoid any form of sampling was developed. In detail, the sherds were examined by energy-dispersive X-ray analysis (EDXA), micro-Raman spectroscopy, diffuse reflection visible and near infrared (NIR) spectroscopy, external reflection FTIR spectroscopy and, only for some sherds of proper thickness and planarity, XRD. For the intact artefact, due to its size, exclusively reflection visible-NIR and FTIR spectroscopy and micro-Raman spectroscopy were used. To the best of the authors' knowledge, reflection spectroscopic techniques both in the visible-NIR and in the mid-IR regions are here applied for the first time to investigate the decoration of archaeological pottery.

## **2. Materials and methods**

### *2.1 Instrumental methods*

EDX analyses were performed on the surface of the sherds as such by the Quantum Kevex Instrument attachment of a Hitachi S-2400 scanning electron microscope.

Micro-Raman spectra on the sherds were obtained by a Jasco TRS-300 Raman spectrometer equipped with an Olympus microscope and a diode-array detector. All measurements were performed using a

50× objective. The 676.5 nm line of a Kr ion laser and the 488 nm line of an Ar ion laser were chosen for excitation. The nominal laser power was about 40 mW.

Raman measurements on the urn were performed by a Jasco RMP 100 microprobe equipped with a 50x objective and connected by fiber optics to a Lot Oriel MS25 spectrometer with a CCD detector and to a frequency-doubled Nd-YAG laser emitting at 532 nm or to a diode laser emitting at 785 nm. The microprobe was mounted on a tripod and XYZ stage to ensure proper positioning.

Diffuse reflection visible-NIR spectra were recorded in the wavelength range from 350 to 2500 nm by a Jasco V-570 spectrophotometer with a BaSO<sub>4</sub>-coated integrating sphere as attachment. Black paper masks were used to isolate the coloured region of interest in each decorated surface. For the intact vessel, the radiation beam was deflected outside the sample compartment by means of a flat mirror, providing an incidence angle on the sample of 10°. Another flat mirror was placed symmetrically to deviate the reflected beam towards the detector. An area of the sample surface having a diameter of approximately 1.5 cm could thus be measured.

External reflection FTIR spectra were measured from 4000 to 400 cm<sup>-1</sup> by a Digilab FTS40 spectrometer using a Specac attachment with a 11° incidence angle. Reflectance spectra were converted to absorbance spectra by the Kramers-Kronig transform. A mirror system similar to that described for visible-NIR measurements was employed, together with a mercury cadmium telluride (MCT) detector, to obtain reflection FTIR spectra from the urn.

XRD analyses were performed using a PHILIPS PW 1820 vertical scan powder diffractometer, with Cu-K $\alpha$  incident radiation. Step-scanned data ( $\Delta 2\theta = 0.02^\circ$ ) were collected in the 5° - 65° ( $2\theta$ ) range, in the  $\theta - 2\theta$  mode, with time per step 1 s. Diffractograms were corrected for peak displacements due to the thickness and curvature of sherds using the proper function of EVA software (Bruker) and assuming as reference the pattern of quartz, always observed for the examined materials.

## 2.2 Description of samples

Nine pottery sherds were examined, dating to the VIII-VII century B.C. and found in the excavation of the site of Incononata near Metaponto in southern Italy. The site was a settlement of the indigenous population of Enotrii and decayed after the foundation of the Greek colony of Metaponto on the seaside.

All nine sherds are examples of the so-called matt-painted pottery and exhibit a bichrome red/black painting, usually on a creamy or pinkish white background [27]. The decoration is in all cases of the so-called geometric type but with very different patterns (Figure 1). It should be remarked that

different hues both of red and black (or dark brown) are observed. Sample **5** shows a peculiar bichromy, unique in this series and based on dark and light purple stripes.

The samples are quite variable in shape, size and also conservation state of the painted surface. Due to its large dimension and high curvature, for sample **9** only the visible-NIR spectra could be measured.

For comparison in the analysis of black or dark brown decorations, sherds of different provenance from the Italian peninsula were also examined. In particular, two groups of samples were analyzed (Figure S1). The first one included some samples of the so-called Etruscan-geometric pottery from Tarquinia, dating to the VIII-VII century and therefore representing, like those of the Incoronata site, an earlier production with respect to the cultural exchanges with the Greek civilization. Instead, the second group contains some examples of typical black gloss pottery, two from Tarquinia and a third one from the Magna Graecia site of Velia, all dating to the VI century B.C..

The intact bell-shaped ash urn (Civiche Raccolte Archeologiche e Numismatiche, Milano) examined in the present work dates to the Hellenistic period and for shape and decoration it belongs to a production typical of the Etruscan town of Chiusi. The decorative pattern is composed of red ribbons fixed with black nails and grey-black festoons on a white background. An inscription with red letters can be seen around the upper rim of the urn (Figure 2). Interestingly, a very similar decorative pattern can be found in some wall paintings of Etruscan tombs, particularly in the necropolis of Tarquinia (Figure 2).

### 3. Results and discussion

#### 3.1 The matt-painted bichrome pottery from the Incoronata of Metaponto

##### 3.1.1 EDXA

EDX elemental analysis was performed both on the painted surface and the ceramic body (internal surface) of the sherds. Results are detailed below and illustrated in Figure 3 for samples **1** and **8**. Table 1 reports the relative values for the detected elements obtained from the peak areas and referred to the Si peak, being silicon the most abundant and ubiquitous element both in the ceramic paste and generally also in the surface decoration.

For the *ceramic paste* of all samples, the identified elements are Si, Al, Ca, Fe and K with minor amounts of Cl and Ti, in agreement with what expected for ancient pottery and pointing to the use of an illitic calcareous clay [12]. The relative intensities for the characteristic peaks of these elements

are substantially the same for all the examined sherds, suggesting the use of a similar clay for all of them, which is reasonable for an indigenous production.

The *red* areas of the painted surfaces are all characterized by an increase in the iron content if compared with the corresponding ceramic bodies. For samples **2**, **3**, **4** and especially **8**, an increase of the relative amounts of potassium and, to a lesser extent, titanium is also observed (Figure 3).

All the *black* or *dark brown* areas contain relevant quantities of iron and manganese, with variable ratios of the two elements from point to point. In contrast with what observed for the red painting, all other elements maintain approximately the same relative amounts detected for the ceramic paste. The increase of the Ca content observed for sample 8 can be ascribed to the underlying white layer (see below).

Sample **5**, the sherd with alternated dark and light purple stripes (Munsell colours 6,0R 1/8 and 6,0R 3/4 respectively), shows an increase of the iron content (peak areas relative to Si peak are respectively 2.1 and 0.62) and a small amount of manganese (peak areas relative to the Si peak are 0.11 and 0.03 respectively), both proportional to the colour intensity.

The more or less brilliant *white* areas of the decorated surfaces show an elemental composition very similar to that of the ceramic body for samples **1**, **3**, **4** and **6**, while an increase in calcium content is evident for sherds **2**, **7** and **8** (Figure 3).

### 3.1.2 Micro-Raman spectroscopy

Micro-Raman spectroscopy allowed to identify iron oxide  $\alpha\text{-Fe}_2\text{O}_3$  as the compound to which the *red* colour of samples **1**, **6** and **7** is due. The observed bands at 218, 288, 407, 496 and 609  $\text{cm}^{-1}$  correspond with those reported in the literature [28,29] and with those measured for commercial iron(III) oxide (Figure 4).

It should be evidenced now that the Raman spectrum of iron(III) oxide could not be obtained, or only very weak signals were observed, for the *red* areas of the remaining samples (**2**, **3**, **4** and **8**), even if the presence of this compound was obviously expected based on the elemental analysis described in the previous section.

For *black* or *brown* decorations, a rather broad signal was obtained around 650  $\text{cm}^{-1}$ , a wavenumber that is characteristic of species with a spinel-like structure [30] (Figure 4). It is worth remembering that under the laser beam all manganese oxides tend to form  $\text{Mn}_3\text{O}_4$  [26], one of the phases that could give a band around that frequency, and therefore this spectrum should be considered rather uninformative.

For the light purple stripes of sherd **5** a Raman spectrum was obtained similar to that of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, but with small shifts to higher wavenumbers of the first three peaks, observed at 223, 291 and 413 cm<sup>-1</sup> (Figure 4). It is worth noting that Bikiaris *et al.* [28] report analogous even if smaller shifts for the spectrum of iron(III) oxide in burnt Sienna, derived from the calcination of the homonymous ochre that contains a small amount of manganese besides iron.

The dark purple stripes of the same sample **5** show again a peculiar Raman spectrum (Figure 4), where a broad signal around 630 cm<sup>-1</sup> appears besides the bands of iron(III) oxide and can be assigned to manganese oxides. Such spectrum exhibits a remarkable similarity to that reported in reference 23 for burnt umber, a dark earth like Sienna but containing larger amounts of Mn(III,IV) oxides [31]. Therefore, the hypothesis of the use of natural earths for the decoration of sample **5** can be put forward based on EDX and Raman analyses.

### 3.1.3 Visible-NIR diffuse reflection spectroscopy

First, it was considered the spectral response obtained in the NIR for both the painted and the internal surfaces of the sherds, in order to estimate the amount of absorbed water that is related to the firing temperature of the materials [32]. A possible dependence of such amount from burial conditions could be ruled out by heating some archaeological sherds at 300 °C for 2 hours and then exposing them to water vapour saturated air in a close chamber for 1 week. The examined sherds had different firing temperatures as demonstrated by the mineralogical phases of the ceramic paste (results not shown). As reported in Figure S2, bands due to absorbed water did not change significantly their intensity, thus demonstrating that it is mainly related to the capability of the different phases of the pottery material to bind water itself.

For this reason, the NIR spectra were examined with the aim of ruling out the possibility of a post-firing decoration, that could have been suggested by the friable or grainy aspect of some of the painted layers [10]. Indeed, while the intensities of the characteristic overtone and combination bands of H<sub>2</sub>O at about 1400, 1900 and 2200 nm vary considerably from one sample to another, no relevant differences were detected between the decorated surface and the ceramic paste of the same sherd, suggesting that the objects were painted before and not after firing. Figure S3 shows as examples the diffuse reflection NIR spectra obtained for samples **7** and **9**. Significantly, a remarkable difference was observed between the external and internal surface only for sample **6**, that is characterized by a very ruined painted surface showing a patina possibly formed during burial.

Moreover, in the visible-NIR spectral region bands are expected that should correlate with the oxidation state and coordination environment of those ions that are responsible for the observed colorations.

Therefore, for the *red* decorations of all sherds the reflection spectral pattern (Figure 5 shows the spectrum of sample **9**) resembles the one reported for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, with an edge around 545 nm, a shoulder at about 640 nm and a minimum at about 860 nm [33]. Nevertheless, variations in the relative intensities and, above all, in the exact wavelength values take place from one sample to another. Such variations, especially those involving the band at 545 nm, are directly linked to the observed colour differences, that can be expressed by the Munsell code. Table 2 lists the exact wavelength of the band, determined from the second derivatives of the spectra, and the Munsell colour for the red painting of all the examined sherds.

As expected, Munsell hue varies from smaller to greater values (from 7,0R to 1,0YR) as the absorption wavelength decreases from about 560 nm to about 545 nm. In the literature a correlation is reported between such wavelength and the specific surface area for several samples of hematite (the mineral form of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) [34]. More precisely, the band shifts to higher wavelengths when the surface area diminishes and as a consequence the particle size increases.

On the basis of this correlation we should assign greater dimensions to the iron oxide particles in samples **1**, **6**, **7** and **9** and smaller for iron oxide in the red painting of the remaining sherds **2**, **3**, **4** and **8**. But the latter are indeed those for which the Raman spectrum of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> could not be observed (as explained above, sample **9** should not be considered as it was not examined by that technique). Now it is worth reminding that when the particle size of a material becomes comparable with the exciting wavelength (676 nm in this work) a broadening of the Raman bands can take place [35]. As in the case of ancient pottery the Raman spectra of the pigments are usually superimposed on a fluorescence background, such enlargement could lead to the disappearance or considerable weakening of the spectrum itself, in agreement with our experimental finding.

In fact, different particle dimensions for iron oxide in the red painting of ancient pottery were already reported by Noll in a study based on the morphological observation of the painted layers by SEM [11]. In that study some samples showed characteristic and well-distinguishable rounded particles with a diameter of about one micrometer, while for other sherds the particles, being smaller in size, could not be distinguished at all. On this basis, the author hypothesized that in the first case the raw material used to obtain red was ochre, containing already well-formed iron oxide crystallites, while in the second case it was an iron-rich clay, developing upon firing a more finely divided form of the same compound.

The same hypothesis can be put forward for the two cases of red painting in the sherds from Incoronata. It is reinforced by the fact that those samples having smaller particles of iron oxide, namely **2**, **3**, **4** and **8**, also showed a peculiar elemental composition, with an increase in potassium and titanium in the red area compared with the ceramic paste (see section 3.1.1). Therefore the red colour of these sherds should have been obtained using an iron-rich clay, probably previously decanted to separate the finest fraction where more clay minerals, among which the potassium-containing illite, are found. This refinement procedure is well documented for example for the so-called “intentional red” in the later Roman-Samian pottery [2]. Instead, for red of sherds **1**, **6**, **7** and **9**, ochre should have been the raw material, probably mixed with the same clay of the ceramic body, as again the elemental analysis suggests.

It is interesting to note that in our investigation spectroscopic methods allowed to obtain, in a non-destructive manner, results corresponding to those derived in ref. 11 from morphological observation. However, requiring a fracture, the latter would alter the integrity of the samples.

Reverting now to *black* or *dark brown* colours, the typical reflection spectrum obtained for all sherds is reported in Figure 6, with minima around 500, 700 and 1000 nm. The considerable amount of manganese determined for the black painting suggests that the raw material was a manganese mineral, probably pyrolusite  $\text{MnO}_2$ , admixed with clay, as clay alone cannot contain comparable amounts of that element [12]. The observed spectral pattern is markedly different from that of pure pyrolusite, shown as well in Figure 6, such ruling out once more the possibility of a post-firing decoration. Upon heating all manganese oxides transform into  $\text{Mn}_3\text{O}_4$ , hausmannite, [12,26], one of the possible species with spinel structure suggested by the Raman spectrum (see above), but this phase should be excluded on the basis of the reflection spectrum, as shown again in Figure 6. Indeed, considering the significant amount of iron besides manganese detected by EDXA in the black-painted areas, the  $\text{Fe}_2\text{O}_3\text{-Mn}_2\text{O}_3$  phase diagram as a function of temperature should be taken into account [12,13]. On the basis of that diagram the formation of a spinel  $(\text{Fe,Mn})_3\text{O}_4$ , jacobsite, is most probable and indeed a corresponding phase was observed for various examples of black-painted Greek pottery by Noll [12] and for Etruscan terracotta by Schweizer and Rinuy [13]. The spectral pattern observed for the samples from Incoronata can be well explained referring to this spinel, as the absorptions (reflectance minima) at 490-500 nm and 670-710 nm can be assigned to  $\text{Mn}^{3+}$  in an octahedral co-ordination environment, while around 1000-1100 nm we find the absorption due to  $\text{Fe}^{2+}$  again octahedrally co-ordinated [36]. In fact, for manganoferrites  $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$  the distribution of cations can be represented as  $\text{Mn}^{\text{II}}_{x-y}\text{Fe}^{\text{III}}_{1-x+y}(\text{Mn}_y\text{Fe}_{2-y})\text{O}_4$ , where the ions in parentheses occupy octahedral sites while the others lie in tetrahedral sites [37]. The ions in octahedral sites can be both bi- and trivalent, but the absorptions of  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  are usually rather weak [38].

Thus, the ancient potters of Incoronata used the manganese black technique, that was alternative to the so-called iron black technique and had the advantage, when a bichrome red/black decoration had to be obtained, to allow a single firing in air (oxidising atmosphere). Instead, in the case of iron black, the black part of the decoration had to be fired in a reducing atmosphere and, even better, at a temperature high enough to ensure sintering, in order to avoid re-oxidation during the subsequent firing cycle in air required to obtain the red part of the decoration [10,11,12]. Therefore, manganese black technique was in a sense more simple, but of course it implied the use of a less common raw material, i.e. manganese-containing minerals.

We wished to test if diffuse reflection visible-NIR spectroscopy is effective in distinguishing between the two techniques, even without the support of elemental analysis. To this aim, we examined various black-painted sherds, always from the Italian peninsula (Etruria and Campania) and dating to a period from VIII to VI century B.C., for which the use of an iron-rich clay as painting was demonstrated [39]. It is known that the phases to which the black colour has to be ascribed are in this case magnetite  $\text{Fe}_3\text{O}_4$  and hercynite  $\text{FeAl}_2\text{O}_4$  [4,39]. The reflection spectra, some examples of which are shown in Figure 7, show usually one or two broad minima between 950 and 1150  $\text{cm}^{-1}$  corresponding to  $\text{Fe}^{2+}$  in a more or less distorted octahedral co-ordination geometry (as in magnetite) and one less evident minimum at about 1800  $\text{cm}^{-1}$  assigned always to  $\text{Fe}^{2+}$  but tetrahedrally co-ordinated [38]. Therefore we can conclude that the visible-NIR reflection spectral pattern indicates quite clearly if the black painting of an ancient ceramic artefact is a manganese- or an iron-based one.

Diffuse reflection spectra allowed also an interesting observation concerning the *white* portions of the decorated surfaces. Indeed, the ceramic paste of the examined sherds is enough light-coloured to offer a sufficiently contrasting background for the red and black decorative pattern. Therefore the “white” part, even if rather pinkish, of the decoration could be obtained simply by leaving uncovered the ceramic body itself (the so-called “a risparmio” technique). In fact, for sherds **1**, **3** and **4** the elemental composition is similar for the ceramic paste and for the “white” areas (see section 3.1.1), and also alike are the diffuse reflection spectra, showing just some weak features due to iron(III) oxide always present in the fired clay (Figure 8). On the contrary, a different spectral pattern is observed for the white portions of the surfaces for sherds **2** and **8**, that also presented an increase in calcium content with respect to the ceramic body as detected by EDXA. In the reflection spectra of both samples (one of which is reported in Figure 8) a not very intense but evident minimum appears around 450 nm. The most probable hypothesis is that a clay with a higher content of calcium carbonate was used to decorate the white areas of those samples. In fact, it is known that such clays develop upon firing a light colour due to the formation of calcium silicates, such as diopside and anorthite, that can incorporate  $\text{Fe}^{3+}$  ions in their lattices thus preventing the growth of iron oxide particles

[40,41]. The absorption at 450 nm can therefore be assigned [42] to  $\text{Fe}^{3+}$  ions in the octahedral sites of diopside where they are preferentially allocated [41,43]. As a consequence we can speak in this case of an “intentional” white, i.e. a third colour added on purpose to the red/black combination. For samples **6** and **7**, that show only very thin white stripes, it was not easy to obtain spectral evidences corresponding to those of elemental analysis, due to the small size of the white-coloured area.

#### 3.1.4 External reflection FTIR spectroscopy

In order to identify the phases responsible for the *black* colour in the examined decorations, also external reflection FTIR spectra were acquired (Figure 9). According to the literature, the possible phases show typical absorption bands between 700 and 400  $\text{cm}^{-1}$ , as listed in Table 3 together with bands due to quartz, always present in the ceramic materials.

After conversion by means of the Kramers-Kronig transform, all reflection FTIR spectra obtained on black or dark brown areas of the sherd surface showed bands at about 1080 and 470  $\text{cm}^{-1}$ , similarly to the ceramic body of the same sherds and thus attributable both to the amorphous silicate material and to quartz.

In the range from 700 to 400  $\text{cm}^{-1}$ , bands lying above 500  $\text{cm}^{-1}$  resulted to be more informative about the species responsible for black or brown colours, in particular for samples from **1** to **4**, whose spectra are reported in Figure 9 for sample **1** and in Figure S4 for the remaining sherds. For samples **1** and **2** a broad signal around 550-545  $\text{cm}^{-1}$  was observed, suggesting that the black colour is due in this case to a phase of composition  $\text{Mn}_{3-x}\text{Fe}_x\text{O}_4$ , with  $x$  around 2. A shoulder at a similar wavenumber was present next to a band at 537  $\text{cm}^{-1}$  in the spectrum of sample **3**, leading to hypothesize the coexistence of hematite and iron-manganese spinel in the black decoration of this sample. For sample **4**, bands at 630, 580 and 540  $\text{cm}^{-1}$  are observed, possibly indicating also the presence of both  $\alpha$ - and  $\gamma$ - $\text{Mn}_2\text{O}_3$ . The possibility of distinguishing manganese black from iron black was verified also for this technique, again by examining the sherds from Tarquinia. Figure 9 reports the transformed FTIR spectra obtained in reflection mode from the black decoration of a sherd of Etruscan-geometric pottery and of a sherd of black gloss pottery. Indeed in the interval 700 - 400  $\text{cm}^{-1}$  they show a different spectral pattern, with two bands at 680 – 650  $\text{cm}^{-1}$  and, respectively, 560 – 545  $\text{cm}^{-1}$  that suggest the presence of hercynite according to Table 3.

#### 3.1.5 XRD

Thanks to their almost flat surface, the black decoration of samples **1** and **3** from Incoronata could be analysed also by XRD (Figure S5) and the presence of jacobsite was thus definitely assessed for these sherds.

### 3.2 Etruscan cinerary urn from Chiusi

The analytical results obtained by means of non destructive techniques for the decoration on pottery sherds from Incoronata prompted us to use, among such techniques, those that were not affected by the size of the artefact to characterize the painted surface of the Etruscan pottery ash urn.

#### 3.2.1 Micro-Raman spectroscopy

Micro-Raman spectra acquired on the *red* details of the urn, namely the inscription and the ribbons, showed a good correspondence with that of hematite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Figure S6).

*Black* nails and *grey* festoons yielded the typical Raman pattern of amorphous carbon with bands at 1580 and 1350 cm<sup>-1</sup> [48] (Figure 10).

#### 3.2.2 Visible-NIR reflection spectroscopy

The expected pattern for iron(III) oxide could be observed for the *red* painting of the urn surface (Figure S7), in agreement with the corresponding Raman spectrum.

#### 3.2.3 External reflection FTIR spectroscopy

The *white* colour of the background of the urn surface is due to calcite, as clearly demonstrated by the FTIR spectrum showing the characteristic broad band at about 1430 cm<sup>-1</sup> and sharp bands at 875 and 713 cm<sup>-1</sup>. (Figure 11). The spectral pattern of calcium carbonate as calcite was obtained on the entire decoration of the urn, also on *red* and *black* details, with no significant loss of intensity.

The presence of calcite “per se” could be an indication of post-firing painting, but it could also be possibly of secondary origin, due to hydration and re-carbonation of calcium oxide deriving from thermal decomposition of a calcareous material. However, post-firing painting is definitely demonstrated by the coexistence of iron(III) oxide and carbon. Indeed, traditionally these two raw

materials were not used together to decorate pottery before firing, as amorphous carbon cannot be maintained upon heating in oxidising atmosphere [11].

#### 4 Conclusions

The present work succeeded in answering specific archaeological questions on the decoration of ancient pottery with a totally non-invasive approach towards the examined artefacts.

In the case of the bichrome ceramic sherds from the southern-Italy indigenous settlement of the Incoronata di Metaponto, the hypothesis of a post-firing painting suggested by the friable and grainy aspect of the decoration could be ruled out on the basis of: (i) the mineralogical phases detected in the coating, whose formation took place most probably at high temperature, as summarised below; (ii) the similar water content of both painting and ceramic paste, as detected by NIR reflection spectroscopy, indicating that they underwent firing in analogous conditions. As regards raw materials, the red colours are due to iron(III) oxide and were obtained by using red ochre for those samples that show particles of greater size or iron-rich clay for those samples where smaller particles of hematite were present. The black colours were instead obtained from a manganese-rich raw material, most probably clay to which manganese oxides were added and then fired to about 950 – 1000 °C to form the spinel phase jacobite that is more frequently encountered in the examined decorations. The identification of the corresponding mineralogical phases, particularly by means of reflection visible-NIR and FTIR spectroscopy, allowed to distinguish effectively the use of the manganese black technique from the iron black one, responsible for colour in both geometric and black gloss pottery from the Etruscan town of Tarquinia. The pinkish-white areas of the various decorative patterns were in many cases obtained “a risparmio”, i.e. by leaving unpainted a part of the underlying ceramic body. However, at least for two sherds the intentional use of a calcareous clay to develop a creamy colour was detected by reflection visible spectroscopy, demonstrating the presence of iron(III) ions incorporated in the lattices of calcium silicates formed upon firing the clay over 900 °C. It was probably not casual that such “intentional white”, giving rise together with red and black to a real polychromatic decoration, was observed for those sherds that exhibited more elaborated patterns.

The decoration of the Hellenistic pottery urn from Chiusi resulted to be, on the contrary, an example of post-firing painting. Red ochre and carbon, recognised by Raman spectroscopy, were used respectively as red and black pigments and were spread on a thin layer of lime, as demonstrated by reflection FTIR spectroscopy. This procedure corresponds to the “fresco” technique in mural paintings, where pigments were mixed with water and then deposited with a brush on a plaster or lime layer, thus being fixed by the carbonation of lime itself. Therefore, the results obtained in the

present work on the Etruscan urn demonstrate that it shares not only the decorative pattern but also the pictorial technique documented for the coeval wall paintings in the necropolises [49].

### **Acknowledgements**

The authors wish to thank Salvatore Lombardo for preliminary analyses on the sherds from Incoronata di Metaponto.

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**References**

- [1] M. Maggetti, G. Galetti, H. Schwander, M. Picon, R. Wessicken, *Archaeometry* 23 (1981) 199–207.
- [2] M.S. Tite, M. Bimson, I.C. Freestone, *Archaeometry*, 24 (1982) 117–126.
- [3] W.D. Kingery, *Archeomaterials* 5 (1991) 47-54.
- [4] Y. Maniatis, E. Aloupi, A.D. Stalios, *Archaeometry* 35 (1993) 23–34.
- [5] E. Gliozzo, I.W. Kirkman, E. Pantos, I. Memmi Turbanti, *Archaeometry* 46 (2004) 227– 246.
- [6] G. Giorgetti, E. Gliozzo, I. Memmi, *European journal of Mineralogy* 16 (2004) 493-503.
- [7] P. Mirti, M. Gulmini, A. Perardi, P. Davit, D. Elia, *Analytical and Bioanalytical Chemistry*, 380 (2004) 712-718.
- [8] F. Ospitali, T. Sabetta, F. Tullini, M.C. Nannetti, G. Di Lonardo, *Journal of Raman Spectroscopy* 36 (2005) 18–23.
- [9] A. Mangone, L.C. Giannossa, A. Ciancio, R. Laviano, A. Traini, *Journal of Archaeological Science* 35 (2008) 1533–1541.
- [10] R. E. Jones, *Greek and Cypriot Pottery*, The British School at Athens, 1986.
- [11] W. Noll, *Fortschr. Miner.* 57 (1979) 203-263.
- [12] W. Noll, R. Holm, L. Born, *Angew. Chem. Int. Ed.* 14 (1975) 602-613 .
- [13] F. Schweizer, A. Rinuy, *Studies in Conservation*, 27 (1982) 118-123.
- [14] A. Mangone, L.C. Giannossa, G. Colafemmina, R. Laviano, A. Traini, *Microchemical Journal* 92 (2009) 97–102.
- [15] G. E. De Benedetto, F. Catalano, L. Sabbatini, P.G. Zamboni,, *Fresenius Journal of Analytical Chemistry* 362 (1998) 170–175.
- [16] L. Sabbatini, M. G. Tarantino, P. G. Zambonin, G. E. De Benedetto, *Fresenius Journal of Analytical Chemistry* 366 (2000) 116-124.
- [17] J. van der Weerd, G. D. Smith, S. Firth, R. J.H. Clark, *Journal of Archaeological Science* 31 (2004) 1429-1437.
- [18] D. Parras, P. Vandenabeele, A. Sánchez, M. Montejo, L. Moens, N. Ramos, *Journal of Raman Spectroscopy*, 41 (2010) 68–73.
- [19] Ali İssi, Aleksandra Raškovska, Alpagut Kara, Orhideja Grupce, Biljana Minčeva-Šukarova, Fisun Okyar, *Ceramics International* 37 (2011) 1879–1887.
- [20] P. Ballirano, C. DeVito, L. Medeghini, S. Mignardi, V. Ferrini, P. Matthiae, D. Bersani, P. P. Lottici, *Ceramics International* 40 (2014) 16409–16419.

- [21] S. Akyuz, T. Akyuz, S. Basaran, C. Bolcal, A. Gulec, *Journal of Molecular Structure* 834–836 (2007) 150–153.
- [22] L. Lühl, B. Hesse, I. Mantouvalou, M. Wilke, S. Mahlkow, E. Aloupi-Siotis, B. Kanngiesser, *Anal. Chem.* 86 (2014) 6924–6930.
- [23] C.P. Swann, S. Ferrence, P.P. Betancourt, *Nuclear Instruments and Methods in Physics Research Section B* 161–163 (2000) 714–717.
- [24] K. Melessanaki, M. Mateo, S.C. Ferrence, P.P. Betancourt, D. Anglos, *Applied Surface Science* 197–198 (2002) 156–163.
- [25] S. Bruni, F. Cariati, V. Guglielmi, in: H. G. M. Edwards, J. M. Chalmers (Eds.), *Raman Spectroscopy in Archaeology and Art History*, Royal Society of Chemistry, Cambridge, 2005, pp. 142–150.
- [26] F. Buciuman, F. Patcas, R. Craciun, D. R. T. Zahn, *Phys. Chem. Chem. Phys.* 1 (1999) 185–190.
- [27] M. Castoldi, *La Ceramica Geometrica Bicroma Dell'Incoronata Di Metaponto (scavi 1974-1995)*, British Archaeological Reports International Series, John and Erica Hedges Ltd., Oxford, 2006.
- [28] D. Bikiaris, Sister Daniilia, S. Sotiropolou, O. Katsimbiri, E. Pavlidou, A.P. Moutsatsou, Y. Chrysoulakis, *Spectrochim. Acta A* 56 (1999) 3–18.
- [29] D.L.A. de Faria, S. Venancio Silva, M.T. de Oliveira, *J. Raman Spectrosc.* 28 (1997) 873–878.
- [30] A. Zoppi, C. Lofrumento, E.M. Castellucci, M.G. Migliorini, *Spectroscopy Europe* 14 (2002) 16–21.
- [31] D. Hradil, T. Grygar, J. Hradilavá, P. Bezdička, *Applied Clay Science* 22 (2003) 223–236.
- [32] S. Bruni, F. Cariati, G. Bagnasco Gianni, M. Bonghi Jovino, G. Artioli, U. Russo, in: I.C. Druc (ed.), *Archaeology and Clays*, British Archaeological Reports, John and Erica Hedges Ltd., Oxford, 2001, pp. 27–38.
- [33] R.V. Morris, H. V. Lauer, C.A. Lawson, E.K. Gibson, G.A. Nace, C. Stewart, *J. Geophys. Res.* 90 (1985) 3126–3144.
- [34] J. Torrent, V. Barrón, *Clays Clay Miner.* 51 (2003) 309–318.
- [35] G. Turrel, J. Corset (Eds.), *Raman microscopy, Developments and Applications*, Academic Press, 1996.
- [36] M.B. Volf, *Chemical Approach to Glass*, Elsevier, Amsterdam, 1984, p. 341 and p. 348.
- [37] V.A.M. Brabers, *Phys. Stat. Sol.* 33 (1969) 563–572.
- [38] A.B.P. Lever, *Inorganic Electronic Spectroscopy* (2<sup>nd</sup> edition), Elsevier, Amsterdam, 1984.

- [39] S. Bruni, in: D. Frère (ed.), *Ceramiche fini a decoro subgeometrico del 6. secolo a. C. in Etruria meridionale e in Campania* (Collection de l'École française de Rome; 389), École française de Rome, Roma, 2007, pp. 165-173.
- [40] R. B. Heimann, *Archeomaterials* 3 (1989) 123-148.
- [41] J. Molera, T. Pradell, M. Vendrell-Saz, *Applied Clay Science* 13 (1998) 187–202.
- [42] S. W. Karickhoff, G. W. Bailey, *Clays and Clay Minerals* 21 (1973) 59-70.
- [43] R. G. Burns, *Chem. Geol.* 5 (1970) 275-283 .
- [44] G. Gattow, O. Glemser, *Z. Anorg. Allg. Chemie*, 309 (1961) 1-19.
- [45] W. B. White, V. G. Keramidas, *Spectrochim. Acta A* 28 (1972) 501-509.
- [46] G. Agiortis, *Tschermaks Miner. Petrogr. Mitt.* 13 (1969) 273-283.
- [47] J. A. Gadsden, *Infrared Spectra of Minerals and Related Inorganic Compounds*, Butterworths, London, 1975.
- [48] I. M. Bell, R. J. H. Clark, P. J. Gibbs, *Spectrochim. Acta A* 53 (1997) 2159-2179.
- [49] A. Cecchini, *Le tombe dipinte di Tarquinia*, Nardini Editore, Firenze, 2012

**Figure captions**

Figure 1 – Sherds of matt-painted bichrome pottery from Incoronata di Metaponto (southern Italy, VIII – VII century B.C.)

Figure 2 – (a) Etruscan pottery ash urn from Chiusi (central Italy, Hellenistic period); (b) wall painting from a tomb of the Etruscan necropolis of Tarquinia (central Italy).

Figure 3 – EDX spectra of samples 1 and 8: (a) ceramic paste; (b) white painting; (c) black painting; (d) red painting.

Figure 4 – Micro-Raman spectra ( $\lambda_{\text{exc}} = 676.5$  nm) of: (a) red painting of sample 1; (b) hematite; (d) dark purple stripes and (e) light purple stripes of the decoration of sample 5; (c) micro-Raman spectrum ( $\lambda_{\text{exc}} = 514$  nm) of the black painting of sample 6.

Figure 5 – Visible-NIR diffuse reflection spectrum of red painting of sample 9.

Figure 6 – Visible-NIR diffuse reflection spectrum of: (a) black painting of sample 4; (b) hausmannite; (c) pyrolusite.

Figure 7 - Visible-NIR diffuse reflection spectra of black painting on sherds of: (a) black-gloss pottery from Velia; (b) black-gloss pottery from Tarquinia; (c) Etruscan-geometric pottery from Tarquinia.

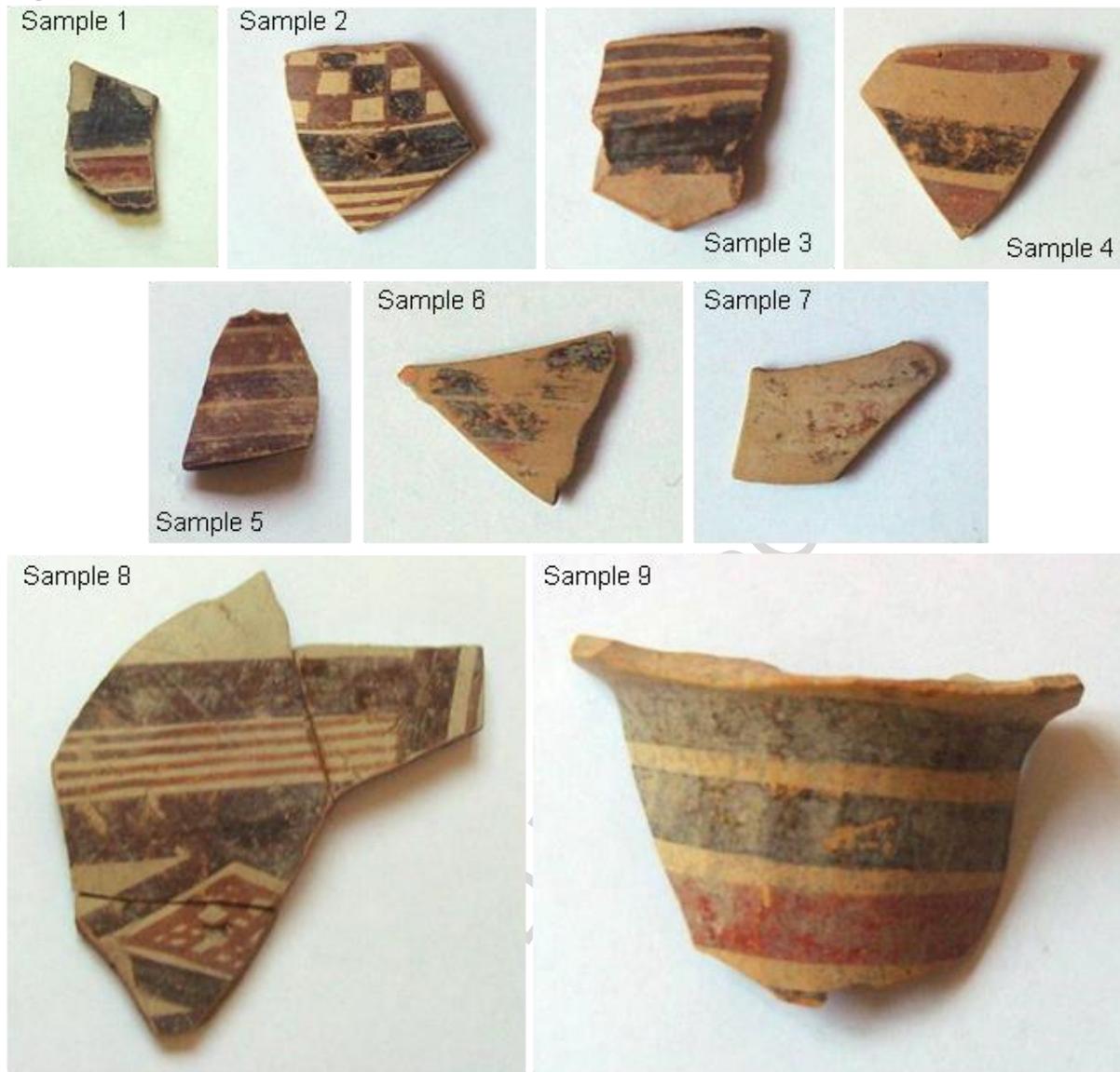
Figure 8 – Visible-NIR reflection spectra of: (a) white area of sample 1; (b) ceramic body of sample 1; (c) white area of sample 2; and (d) ceramic body of sample 2.

Figure 9 – FTIR spectra obtained in external reflection mode from the black decoration of: (a) sample 1 from Incoronata; (b) Etruscan-geometric sherd from Tarquinia; (c) black gloss sherd from Tarquinia. The asterisk indicates a spurious band.

Figure 10 – Micro-Raman spectrum ( $\lambda_{\text{exc}} = 785$  nm) obtained on a black nail in the decoration of the Etruscan urn.

Figure 11 - FTIR spectra obtained in external reflection mode from the decoration of the Etruscan urn: (a) white background; (b) grey-black festoon; (c) red ribbon.

**Figure 1**



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Figure 2

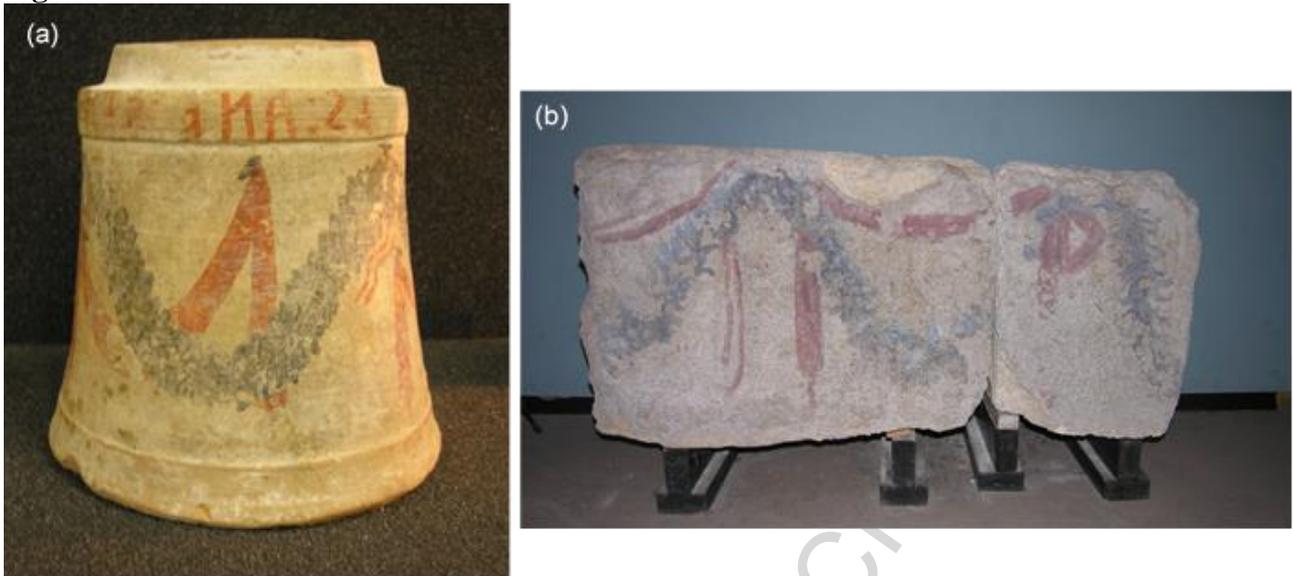


Figure 3

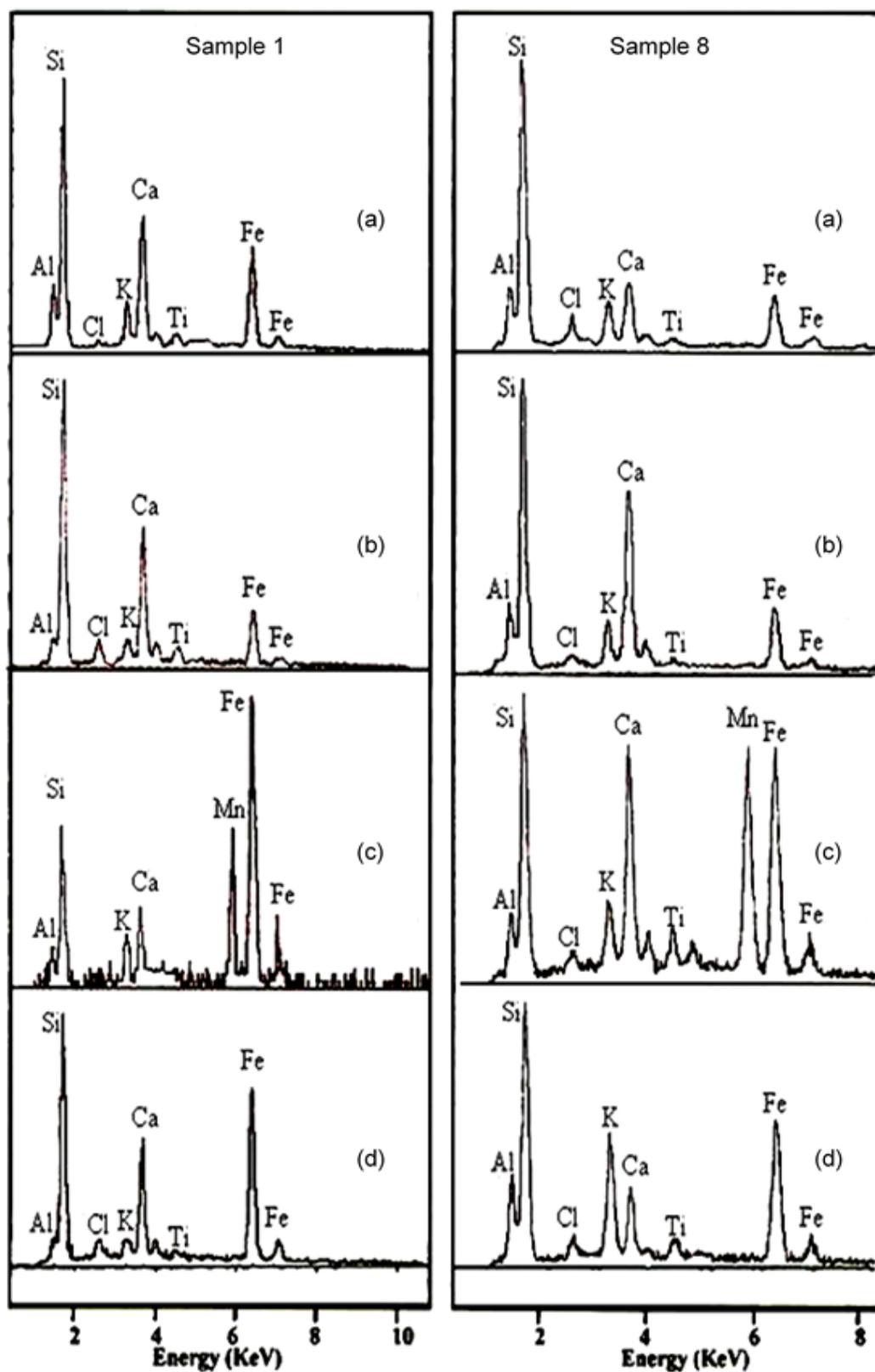


Figure 4

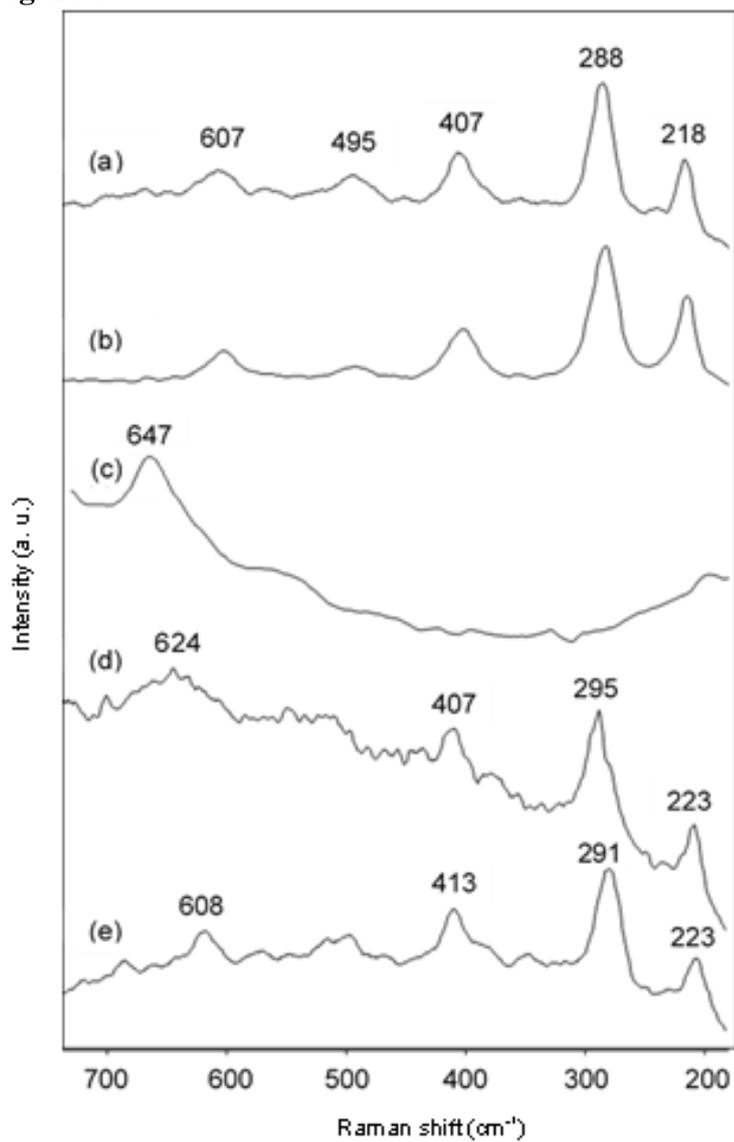
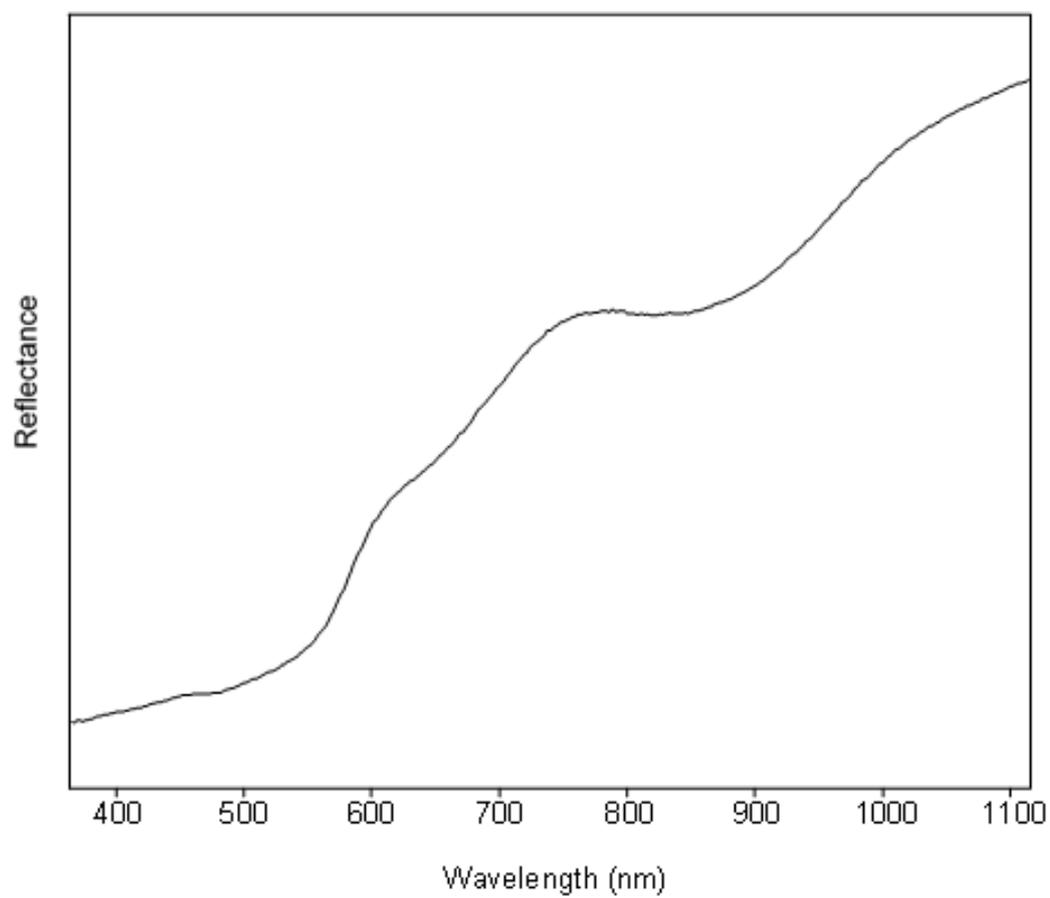


Figure 5



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Figure 6

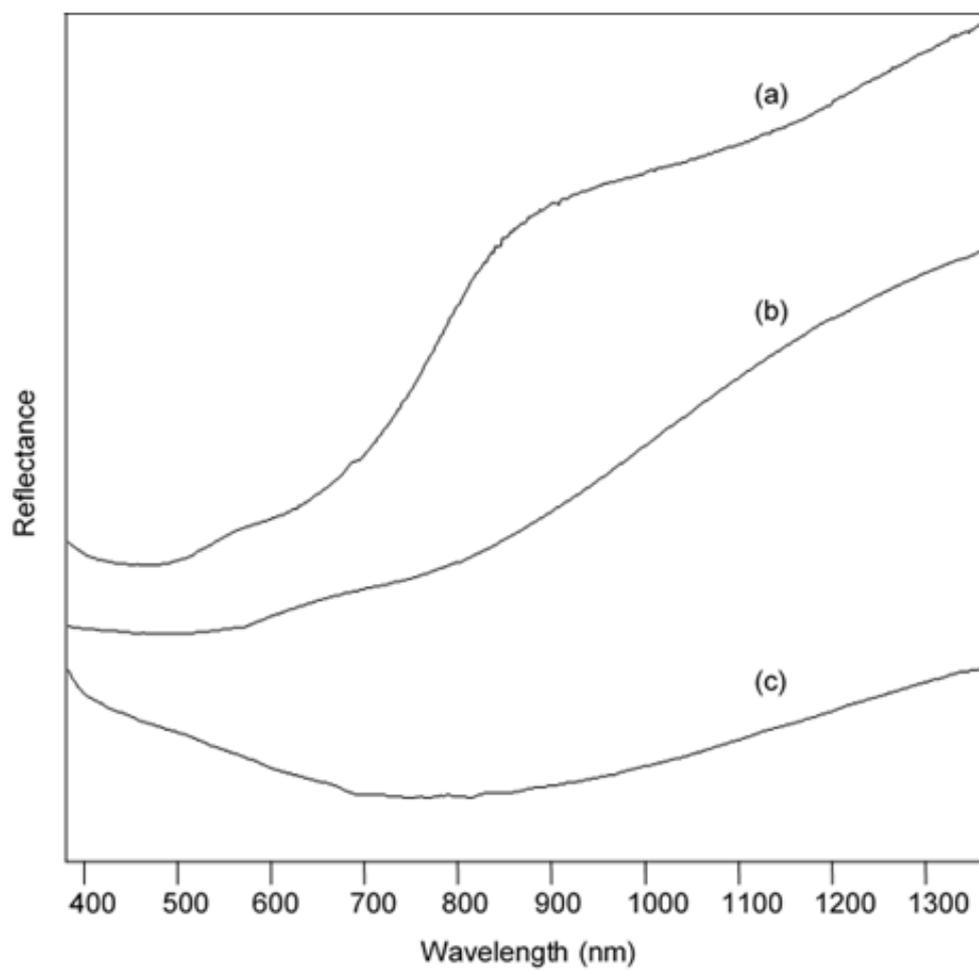
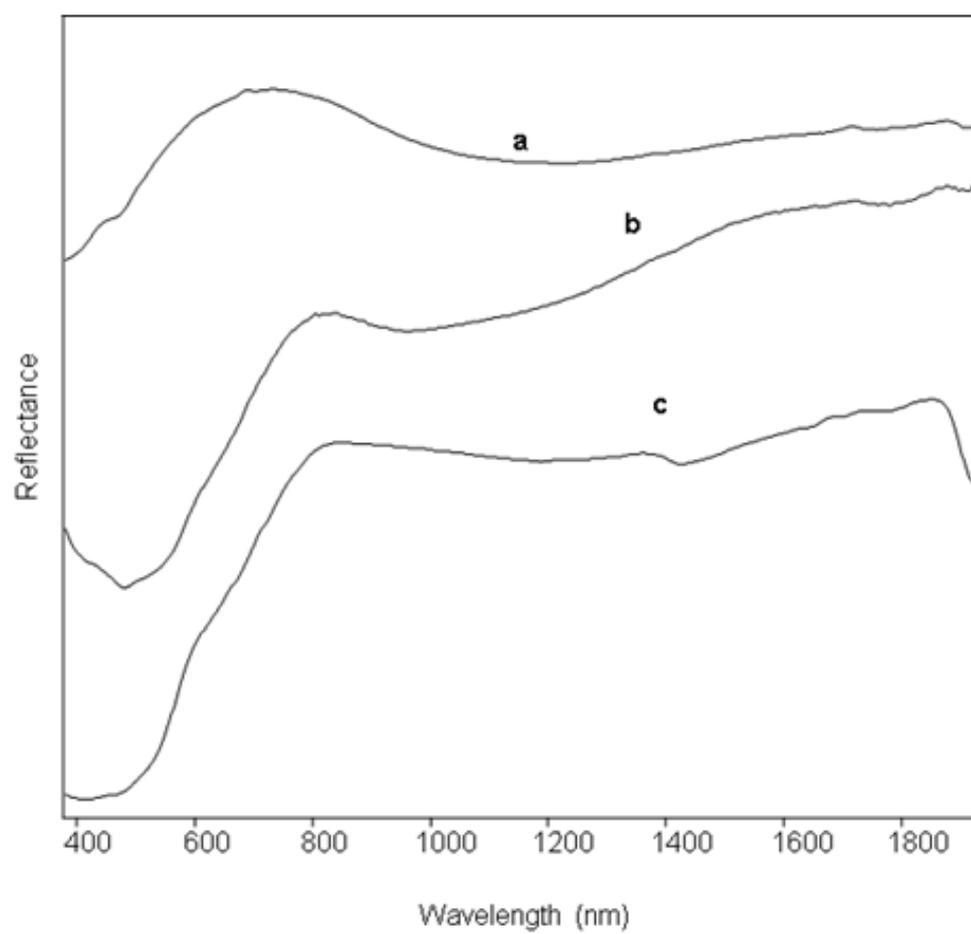


Figure 7



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Figure 8

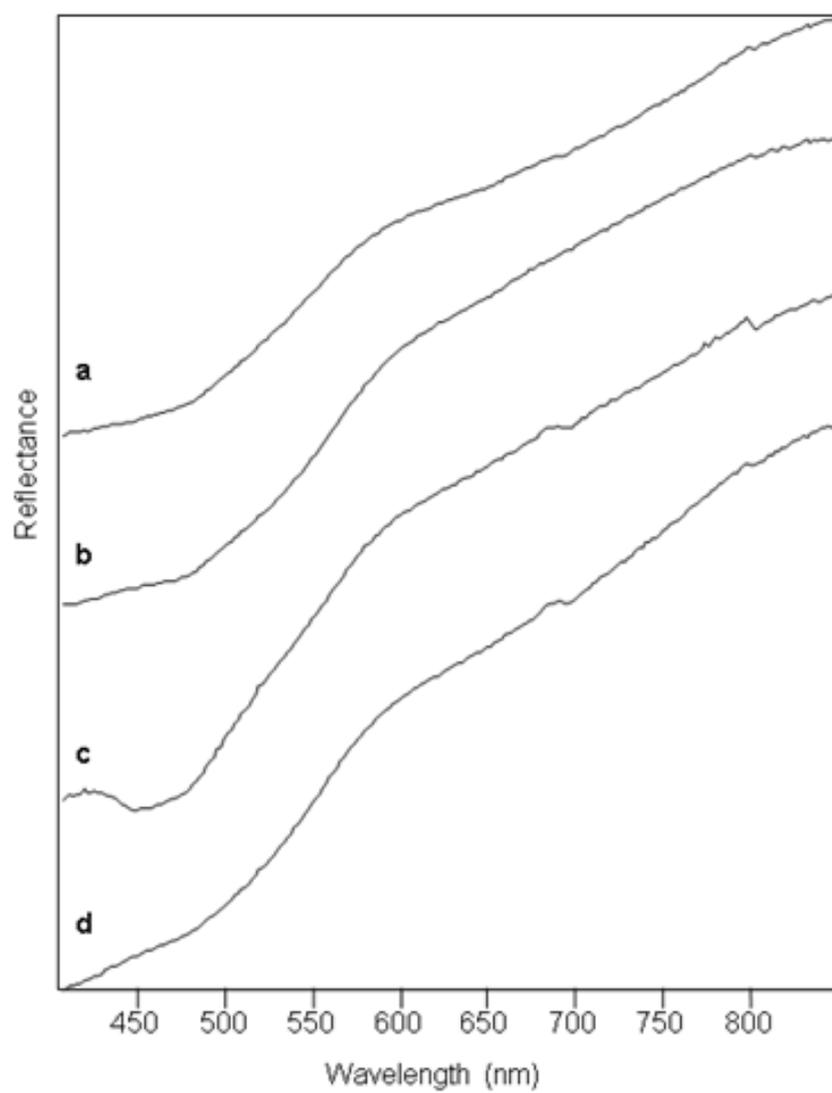


Figure 9

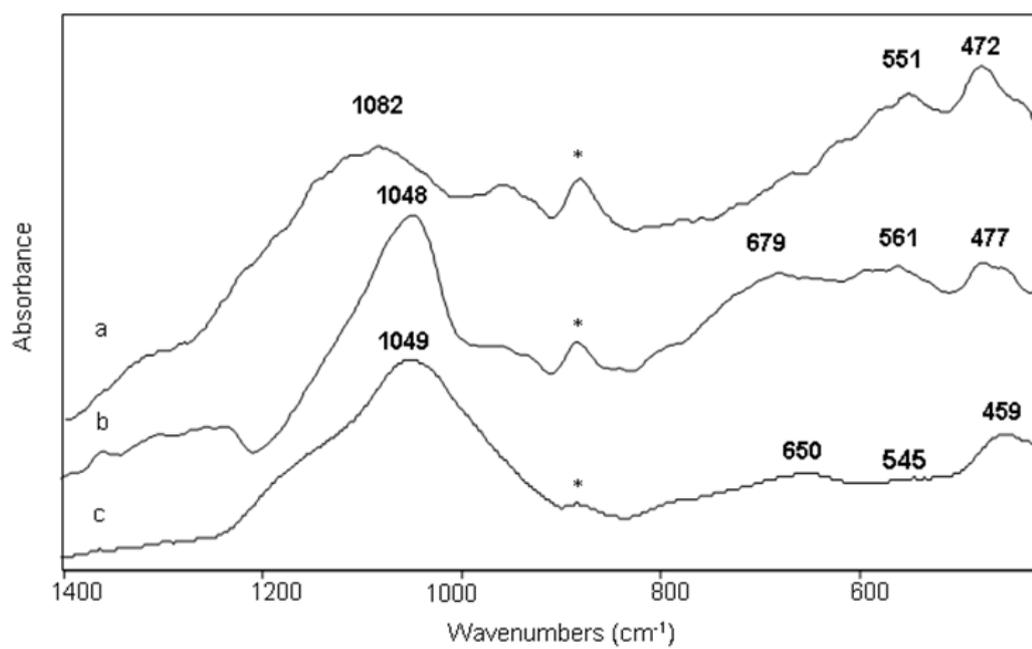


Figure 10

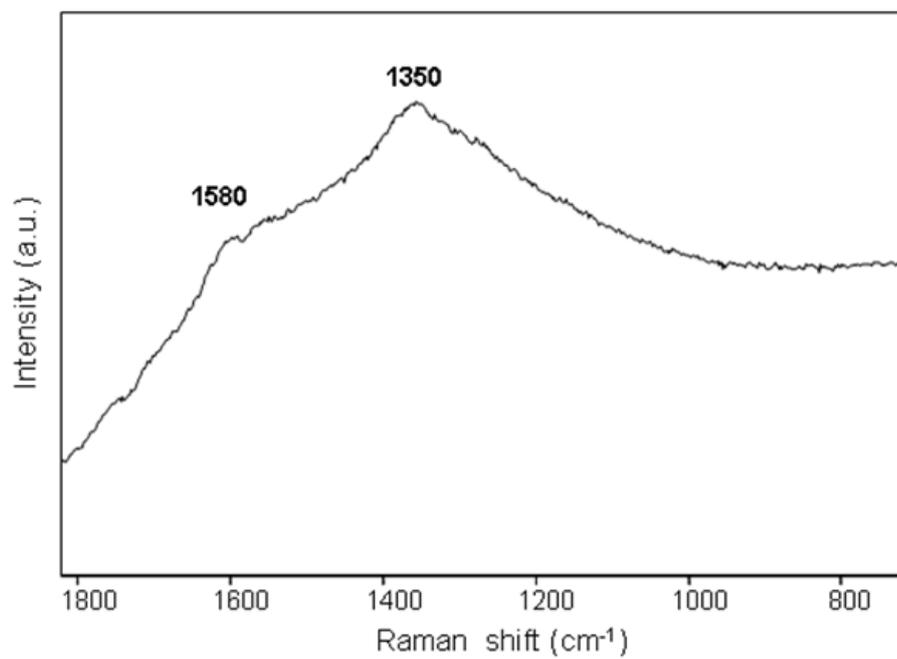


Figure 11

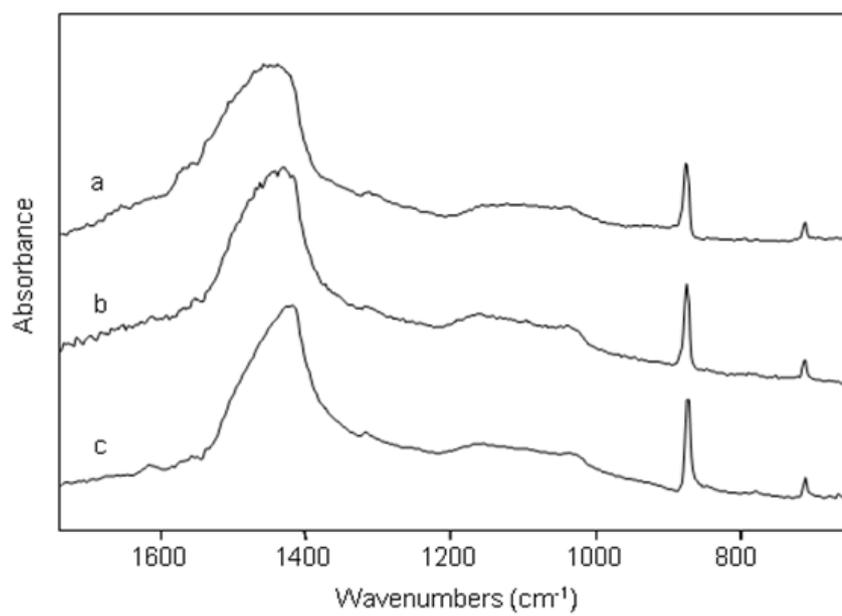


Table 1 – Relative values (referred to the Si peak) of peak areas for the elements detected in the EDX spectra of samples 1 and 8 (see Figure 3)

		Al	Cl	K	Ca	Ti	Mn	Fe
<b>Sample 1</b>	Ceramic paste	0,22	0,023	0,12	0,46	0,04	--	0,35
	White	0,087	0,1	0,072	0,35	0,072	--	0,19
	Black	0,32	--	0,33	0,5	0	0,8	2,2
	Red	0,2	0,11	0,11	0,48	0,03	--	0,83
<b>Sample 8</b>	Ceramic paste	0,19	0,07	0,15	0,26	0,04	--	0,22
	White	0,21	0,036	0,11	0,6	0,016	--	0,2
	Black	0,22	0,09	0,27	0,66	0,14	0,87	0,97
	Red	0,28	0,08	0,43	0,16	0,078	--	0,52

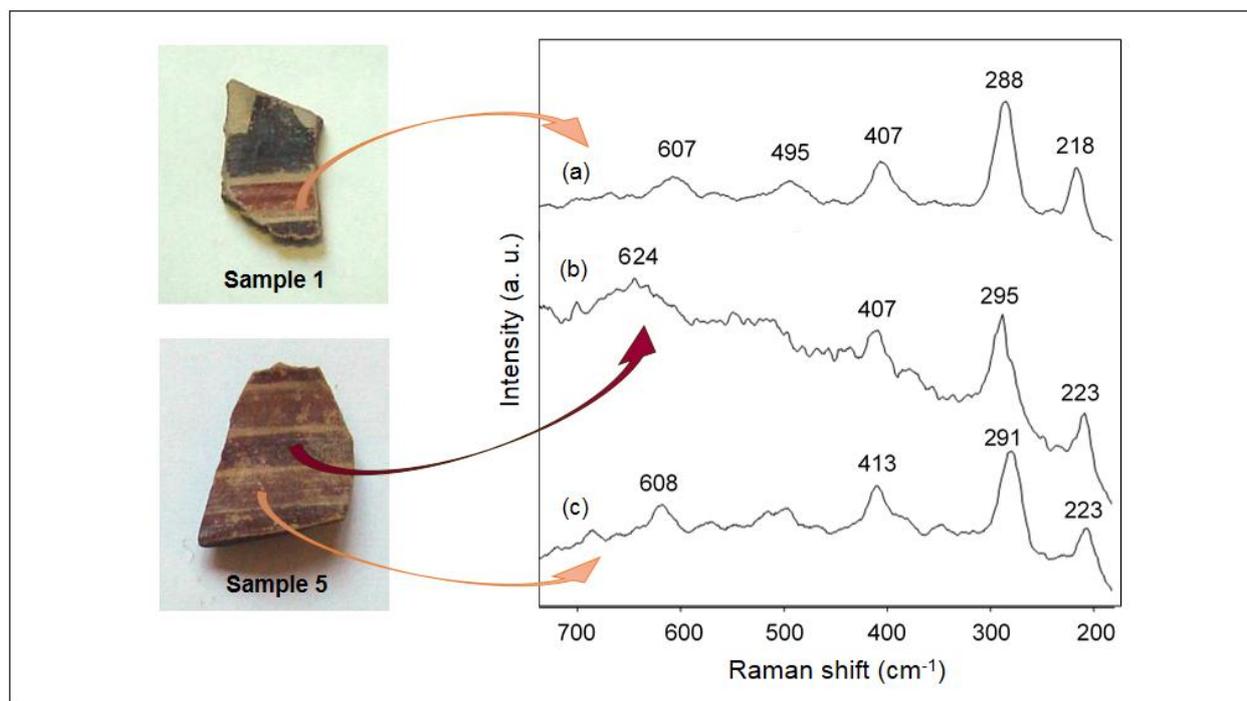
Table 2 - Munsell colours and exact position of the 545-nm band for the red areas of the sherds from Incoronata

<b>Sample</b>	<b>Munsell colour</b>	<b>Wavelength (nm)</b>
<b>1</b>	9,0R 4/12	566
<b>2</b>	1,0YR 3/7	548
<b>3</b>	1,0YR3/7	545
<b>4</b>	10,0R 3/7	550
<b>6</b>	9,0R 4/12	560
<b>7</b>	9,0R 4/12	566
<b>8</b>	1,0YR 3/7	545
<b>9</b>	7,0R 4/20	564

Table 3 – Main IR bands (700 – 400 cm<sup>-1</sup>) of some oxides possibly present in the surface decoration of the pottery sherds.

Oxide	Wavenumbers (cm <sup>-1</sup> )	References
$\beta$ -MnO <sub>2</sub> (pyrolusite)	520, 600, 650	[26,44]
Mn <sub>2</sub> O <sub>3</sub> (bixbyite)	490, 530, 580, 600, 670	[26,44,45]
Mn <sub>3</sub> O <sub>4</sub> (hausmannite)	520, 610	[37,46], this work
Mn Fe <sub>2</sub> O <sub>4</sub> (jacobsite)	540	[37]
Mn <sub>1.25</sub> Fe <sub>1.75</sub> O <sub>4</sub>	420, 550	[37]
Mn <sub>0.8</sub> Fe <sub>2.2</sub> O <sub>4</sub>	550	[37]
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	470, 536	[28]
Fe <sub>3</sub> O <sub>4</sub> (magnetite)	575	[26,47]
FeAl <sub>2</sub> O <sub>4</sub> (hercynite)	510, 562, 675	[47]
$\alpha$ -SiO <sub>2</sub> (quartz)	465	[47]

## Graphical Abstract



**Highlights**

- The decoration of archaeological pottery was analyzed by non-destructive techniques
- Visible-NIR and FTIR reflection techniques were applied in an innovative manner
- Different kinds of black paintings could be distinguished
- Pre- and post-firing decoration could be recognized

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