

Micro-Raman spectroscopy of ancient ceramics: a study of French *sigillata* wares

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Micro-Raman spectroscopy was applied to the study of some French *sigillata* wares dating back to the end of the 1st century AD and coming from two important Roman ceramic production centres at La Graufesenque (Aveyron) and Glanum in Saint Rémi de Provence. The differentiation between the mineralogical composition of the reddish bright slip and the porous ceramic body underneath was accomplished, confirming the previous hypothesis by the CNRS research group at Toulouse that a different and finer clay material was used for the coating. This was primarily suggested by the highly heterogeneous body matrix mineralogy due to the presence of a large variety of minerals such as haematite, quartz, rutile and feldspar species, while the slip coating was basically made of haematite alone. The phase analysis results also gave an indication of the firing for insight into the production technology: an oxidizing atmosphere and a firing range between 850 and 1000 °C could be suggested, in good accordance with the acknowledged Roman *sigillata* pottery production procedure. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: micro-Raman spectroscopy; pottery; *sigillata*; firing

INTRODUCTION

It has been shown^{1,2} that technological and provenance studies of ancient ceramics can be carried out by the analysis of their mineralogical phases, by means of which it is possible to estimate the composition of the raw material and the transformations experienced by some minerals, which are indicative of the conditions of the firing process, i.e. atmosphere and temperature. The useful results obtained so far by means of micro-Raman spectroscopy in the field of cultural heritage have prompted its application also to the study of ancient pottery. The choice of using micro-Raman spectroscopy is due to the many advantages that this technique offers, such as the easy differentiation through vibrational Raman spectra of the minerals composing the mineralogical phases of a ceramic material³ and especially the lack of a requirement for special sample preparation: even whole objects, provided that they can suitably be put under a microscope, can be analysed without further manipulation, thus avoiding, at least at the beginning, the destruction of the sampled material, to obtain either a powder or a thin section, which are, for example,

the required forms for traditional investigative techniques on ceramics such as x-ray diffraction, optical microscopy and electron microprobe analysis. This is a valuable characteristic when the least destructive analysis has to be performed.

In the micro-Raman mode, the laser beam is focused on to the sample by means of a microscope objective, which also works as a backscattered light collector,⁴ leading to much reduced volume of the focal cylinder, which makes the technique highly sensitive and suitable for local analysis. The measurements being of the punctual type, it is necessary to repeat the analysis for a very large number of different points in order to obtain representative compositional results for the structural item.

The peculiar high spatial resolution feature allows the study of micro-structured samples, as these can be spatially discriminated from the surrounding matrix. This aspect assumes particular importance in the investigation of samples exhibiting a stratified structure, and there are many publications showing the high ability of micro-Raman spectroscopy to probe the composition of layered stripes in a transversal cut sample, in particular in the case of paintings and frescoes.⁵

This appears to be a considerable advantage for the investigation of the mineralogical composition of pottery, in particular when efforts are addressed to the distinction between the thin coat (varnish) and the thick ceramic body

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underneath, as for *terra sigillata* pottery, which is the case of the present study.

Relevant mineral structures in ceramics are well individualized by their Raman spectra so that the mineralogical composition may be readily elucidated. Furthermore, the technique is also suitable for verifying the correlation between the composition of the pottery sample and the mineralogical changes that had taken place during its lifetime, due to the production process, usage, burial, etc.

As far as the study of technological skill is concerned, a very significant aspect is the firing process. This can be investigated by means of the thermally induced chemical and mineralogical transformations, leading to the crystallization of new minerals or conversion into more stable polymorphs, that characterize the final mineralogy of the fired item. The evaluation of the pot composition can help in obtaining information on the firing conditions, i.e. atmosphere and temperature, because mineralogical transformations are practically irreversible and therefore indicative of a precise thermal situation reached during the firing process. This is an interesting archaeological aspect as it can help to unravel the technological skills of ancient potters.

The oxidising or reducing atmosphere implies the formation and therefore the presence of characteristic minerals, especially haematite ($\alpha\text{-Fe}_2\text{O}_3$), which is responsible for the reddish colour, and magnetite (Fe_3O_4), which confers a dark shade on the ceramic material. *Sigillata* wares used to be fired under oxidizing conditions, leading to typical reddish tone of the ceramic paste. Furthermore, there are some types of minerals which crystallize at certain high temperatures, whose presence may allow a hypothetical maximum firing temperature to be guessed, while low-temperature components should be absent in order to confirm such extreme firing conditions. These minerals comprise the typical high-temperature mineralogical phases whose presence is also strongly related to the mineralogical composition of the raw clay material; common high firing phases are diopside for calcareous and mullite for non-calcareous clays.^{6,7}

For an accurate estimate of the mineralogical transformations, it is advantageous to consider also the effect of burial and post-burial steps.

TERRA SIGILLATA SAMPLES

The term *terra sigillata* strictly refers to classical fine wares of the early Roman period, characterized by a very fine slip, usually red, brown or ochre, with a rather waxy shine. The production of glossy red-slipped wares originated at Arezzo in Italy in the mid-1st century BC, where potters began to apply this new technique in place of the pre-existing black-slip method typical of Greek production, until it became definitely consolidated around 30 BC. Subsequently the production of Italian-type *sigillata* improved and new factories were founded at other centres, such as Pozzuoli and in northern Italy. Branch factories were also built

at the extreme boundaries of the Empire, reaching the Roman provinces, in particular South Gaul. The spread of competitive Gallic *sigillata* production centres to all provinces drove the Italian production into a slow decline, until the end of the second century AD when the growth of important workshops in the Eastern and African provinces made the situation even worse. This was accompanied by a decrease in Italic factories, as revealed by a reduction in the number of the seals (*sigillum*) that were applied on pots, together with general decline of Italian production quality.

Sigillata pottery could be decorated with figures or symbols in relief, applied by means of barbotine or previously impressed in the stamp, or be painted or not decorated at all, the common feature for all these varieties being the typical reddish coat. This varnish was obtained by using a water suspension of very fine and purified clay, probably enriched in flux components, but the debate is still open among researchers as to whether it was the same as for the ceramic body or whether potters used a different clay material prepared just for the slip.

The study presented here deals with the investigation of pottery samples belonging to three different specimens of *terra sigillata* dating from the end of the 1st century AD: two of them belong to La Graufesenque (Aveyron, France), a very important Roman ceramic production centre (samples TSG100 A/B and TSG50 A/A), and the third is from Glanum, in Saint Rémi de Provence (sample TSG100 GL5) although it was found in La Graufesenque. All these have a slip of good quality, especially the first two.

An on-going project, carried out in collaboration with a research group at Toulouse, concerns the accurate analysis of the mineralogical composition of French *terra sigillata* wares, with a view to studying provenance, the local workshops involved in the manufacturing process and the different technological solutions.

The group at Toulouse, consisting of an archaeologist, a conservator, a chemist and a physicist, has developed a coupled approach by combining x-ray diffraction and transmission electron microscopy in order to determine the chemical composition of both the crystallites and vitreous fraction, their crystallographic structure, disorder and defects and the quantitative mineral composition of the ceramic. The previous results obtained have shown that a slip of good quality was made with clay of different origin compared with that used for the body, while the same clay does not seem to have been systematically used for later productions. The electron microscopy study of the ceramic body seems to indicate anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), a high-temperature feldspar mineral, as the main phase, although it was very difficult to verify this point by x-ray diffraction analysis. Anorthite grains contain potassium in significant quantity, thus confirming their lamellar crystallites cluster structure.⁸

According to these previous results, a deeper investigation appeared to be essential for the definitive

characterization of the mineralogical composition of both the slip and the body. The micro-Raman measurements were therefore aimed at checking mainly the presence in the slip of anorthite and the presence of K-feldspar species in the body, since these phases had not been definitely identified.

EXPERIMENTAL

The samples had the right dimensions to be analysed without any preliminary preparation, hence they were observed under the microprobe 'as received', and measurements were carried out on both the coating and the inner body. For an overall view of the sample area to be analysed, a 20× magnification objective was used, and measurements were also with a 50× magnification objective, providing a global magnification of about 1650-fold and a spatial resolution, measured by the laser spot, of about 2 μm.

All samples appeared very similar in colour and consistency, exhibiting a bright and compact slip without decorations but with sporadic scratches letting the lighter shade of the body underneath appear. A transverse, in-plane, high-magnification inspection reveals a thin red varnish ~20 μm thick, highly compacted, and on moving far from the surface the ceramic becomes light in shade: the body appears as a reddish matrix with isolated small black bright grains and a large quantity of white–yellow crystals (see Plate 1).

Micro-Raman spectra were acquired by means of a Renishaw RM2000 single-grating spectrograph apparatus, coupled to two external low-power laser sources for sample irradiation: a near-infrared diode laser (785 nm) and an argon ion laser source (514 nm). Sample irradiation was kept at low power values, about 2 mW or less, to avoid any thermal damage, and typical acquisition times were of the order of a few hundred seconds. The backscattered light collected by the microscope objective was filtered by a notch holographic filter, dispersed by a single grating (1200 lines mm⁻¹), and then gathered by a CCD detector cooled to -20 °C by the Peltier effect. The spectral resolution was about 7 cm⁻¹. For a better comparison, all spectra were subjected to baseline subtraction.

Subsequently, the same apparatus was used to carry out some global imaging via the angle-tuned bandpass filter optics, with a resolution of about 20 cm⁻¹. Preliminary Raman images were obtained using the 50× objective, defocusing the laser beam to half its value, with an area to be irradiated up to about 22 μm of diameter, with exposure times of 100–300 s.

RESULTS AND DISCUSSION

Spectral results

The results obtained for the three *terra sigillata* samples are summarised in Table 1; each sample is discussed separately below, to show better any particular characteristic composition and correlation between the slip and the body.

Table 1. Mineralogical composition obtained for the ceramic body and the slip of the investigated French *sigillata* wares

Sample	Body	Slip
TSG50 A/A	Haematite, α-quartz, calcite, anorthite, rutile, goethite, maghaemite, diopside	Haematite, α-quartz, anorthite
TSG100 A/B	Haematite, feldspars	Haematite, feldspars
TSG100 GL5	Haematite, anorthite	Haematite, α-quartz, anorthite

TSG50 A/A

All the Raman spectra acquired on the body material indicate the presence of a mineral which typically forms under oxidizing conditions, i.e. haematite (α-Fe₂O₃). Haematite was found in the red matrix and also in the corresponding small, dark grains, for which the spectra acquired had a better signal-to-noise ratio due to sharper Raman bands (Fig. 1). This could be related to a higher degree of crystallization of the iron oxide inside the dark agglomerates. Other iron minerals were identified in the body such as goethite (α-FeOOH), maghaemite (γ-Fe₂O₃) and magnetite (Fe₃O₄). Goethite is the hydrated form of iron(III) oxide and was probably formed during burial, whereas maghaemite and magnetite may be indicative of an incomplete phase transformation⁹ according to the following scheme:



Magnetite exhibits a characteristic feature near 665 cm⁻¹, small shifted values also being reported in the literature.¹⁰ A rather strong but broad feature at 670–680 cm⁻¹ was frequently observed in the haematite spectrum (Fig. 2) and this was attributed to a residual magnetite content. Otherwise

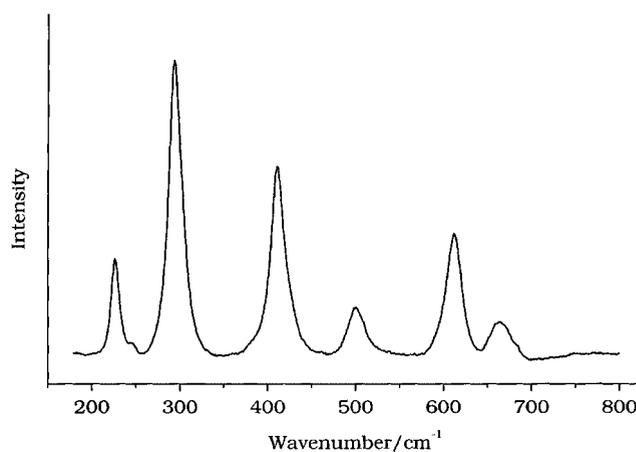


Figure 1. Raman spectrum of haematite acquired on a black grain in the inner body of sample TSG50 A/A (laser source, 785 nm; laser power, ~2 mW; accumulation time, 200 s; number of accumulations, 1; objective magnification, 50×).

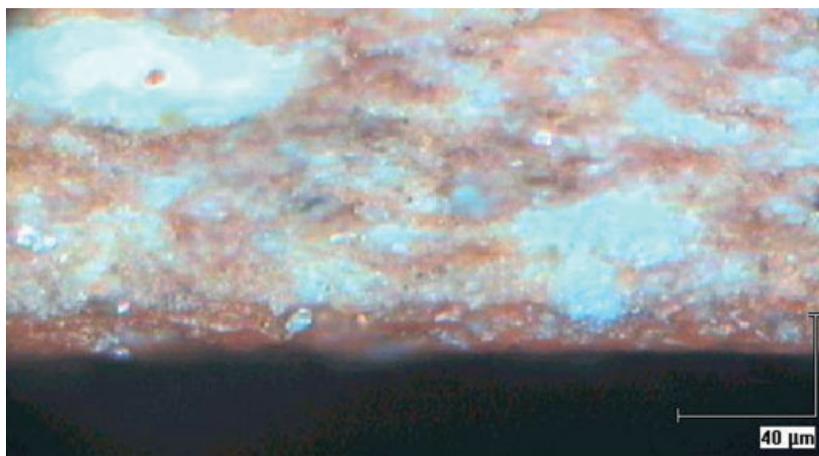


Plate 1. Enlarged view of the body-slip boundary in sample TSG100 GL5 ($\times 620$).

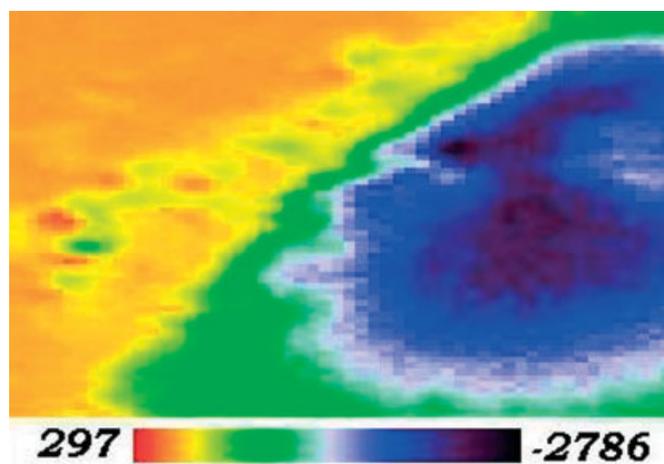


Plate 2. Intensity distribution of the 297 cm^{-1} haematite Raman band allows the scratch line to be visible at the slip (left)-body (right) boundary (sample TSG100 GL5).

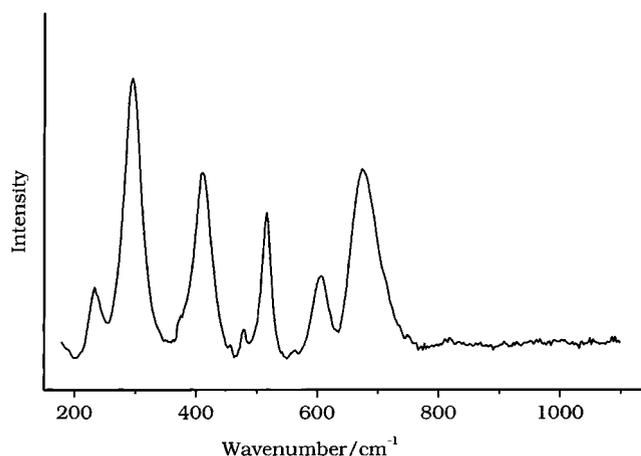


Figure 2. Raman spectrum acquired on a reddish area of the inner body of sample TSG50 A/A showing the characteristic peaks of haematite together with a prominent band at 674 cm^{-1} ; the feature at 516 cm^{-1} was attributed to plagioclases (anorthite) (laser source, 514.5 nm ; laser power, $\sim 3\text{ mW}$; accumulation time, 600 s ; number of accumulations, 1; objective magnification, $50\times$).

this feature could be related to a disordered, not perfectly stoichiometric structure of haematite itself,⁹ thus confirming for the haematite black grains a high degree of crystallization. At least this band could be attributed also to amphiboles as well, which are variously coloured iron-rich silicates that give rise to an intense band at 674 cm^{-1} .

Among the lighter grains cemented in the ceramic body, the grey ones are essentially made of α -quartz, and in some cases calcite was also detected; yellow particles contain essentially titanium dioxide in the rutile form.¹¹

There are also present large white areas surrounding the red, black and yellow grains which contain some members of the plagioclase series of feldspars; in particular anorthite was detected. These minerals are easily recognised by a strong Raman signal occurring between 500 and 510 cm^{-1} which, according to its intensity and the crystal structure, can be assigned to a characteristic A_g vibrational mode, and a second intense band falls in the range 478 – 488 cm^{-1} (Fig. 2).¹² Some members of the alkali feldspars series were also identified; the spectra of these minerals also contain the A_g (Raman-active only) vibrational mode which gives rise to the most intense band at 513 – 514 cm^{-1} , whereas two additional peaks lie in the 450 – 500 cm^{-1} region, making this triplet a characteristic feature of alkali feldspar spectra.¹² Further, diopside was sporadically identified inside the white areas, whose presence is related to calcite transformation, which is very important for firing considerations.¹³

As far as the slip is concerned, the ceramic material exhibits a different morphology. It appears more compact and the aspect is like a red fine matrix which includes sporadic dark and white grains. The whole reddish area contains haematite, which exists as a well-crystallized form

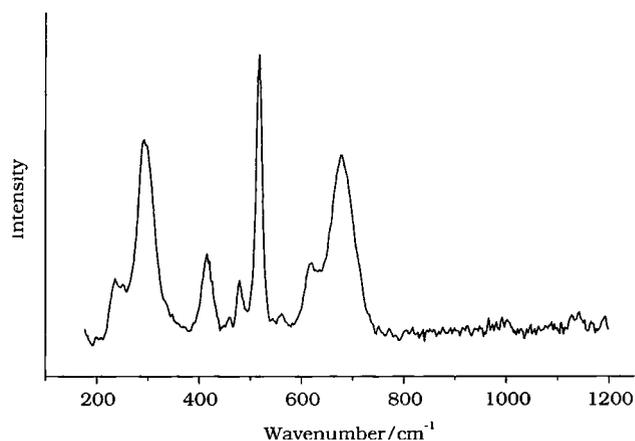


Figure 3. Raman spectrum of feldspars (plagioclases) and haematite acquired on light stripes in the slip of sample TSG100 A/B (laser source, 514.5 nm ; laser power, $\sim 3\text{ mW}$; accumulation time, 240 s ; number of accumulations, 1; objective magnification, $50\times$).

in the black grains, while the white particles are made of α -quartz. The slip also contains a small quantity of feldspars, among which anorthite was easily identified.

TSG100 A/B

The composition of the ceramic body is similar to that described above: haematite was found in the red regions and feldspars were detected in large amounts. In the corresponding slip, apart from haematite there was only a restricted area where feldspars could be well identified, making possible in some cases even a distinction between plagioclases and alkali feldspars (Fig. 3).

TSG100 GL5

The body and the slip of this sample were also studied separately. The spectra measured on the body are those of haematite and anorthite, whereas in the coating haematite was sporadically detected together with grey grains of α -quartz and with a scant amount of plagioclases (i.e. anorthite). The variation of the mineralogical composition moving further from the border is easily shown in Fig. 4, where the increasing signal at 510 cm^{-1} is attributed to feldspar components and the weak peak at 647 cm^{-1} to quartz.

Imaging results

Micro-Raman results were employed to achieve preliminary Raman imaging of mineralogical components in restricted areas of the samples, with a particular consideration for the feldspar distribution along the coating–body boundary. Due to the difficulty of making a proper distinction between plagioclase and K-feldspar imaging, images were taken for feldspar species altogether, centring the filter bandpass at 510 cm^{-1} . The haematite contribution, coming from the weak

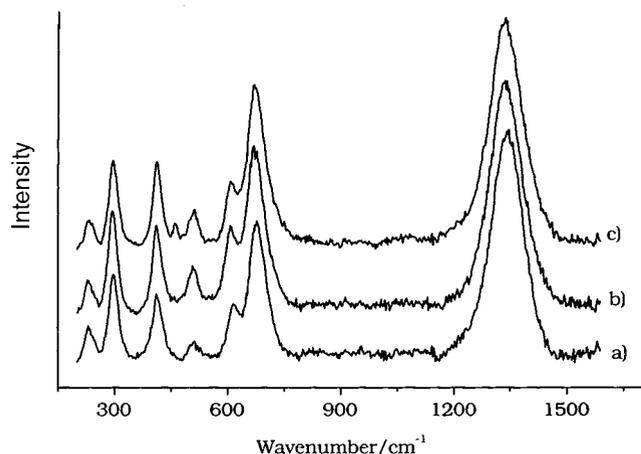


Figure 4. Raman spectra acquired at different depths from the external slip of sample TSG100 GL5 (laser source, 514.5 nm; laser power, ~ 3 mW; accumulation time, 200 s; number of accumulations, 1; objective magnification, 50 \times), after baseline subtraction and normalisation of data: (a) external slip; (b) 25 μm inside; (c) 40 μm inside.

signal at 500 cm^{-1} , was removed by recording on the same areas the intensity distribution of the 297 cm^{-1} peak, which is the most intense Raman signal of haematite.

Images captured on sample TSG50 A/A revealed a very scarce presence of feldspar species in all the coating, for which the most intense signal came from the haematite band. The measurement was repeated on sample TSG100 GL5, for which the feldspar/haematite distribution was checked along a scratch (Plate 2): the comparison of the relative images revealed a prominent contribution coming from the body side due to feldspars whereas the haematite intensity distribution was higher on the reddish slip side.

DISCUSSION

The results obtained by means of micro-Raman spectroscopy show a compositional conformity among the three samples analysed: the inner body has in general a much more heterogeneous composition than the external slip. This is partly confirmed by high magnification images that show for the ceramic body a much more coloured aspect than the slip, for which a compact fine-grain red matrix is observed with few black and grey grains sporadically cemented within the layer. The mineralogical composition revealed by micro-Raman analyses shows good agreement with that reported using x-ray diffraction results,⁸ which attribute haematite, quartz and anorthite to the principal crystalline phases present in this type of *sigillata* wares.

The clay used for the bulk seems to be different from the slip clay, in particular in the TSG50 A/A sample as rutile and a fairly large amount of feldspars were found in the body, whereas the prevalent slip phase is haematite.

The presence of the high-temperature mineral anorthite implies that certain high temperatures were reached during the firing process, as this mineral begins to form near 950 $^{\circ}\text{C}$.¹² On the other hand, the crystallization of diopside starts when temperature is higher than 850 $^{\circ}\text{C}$ and α -quartz is stable up to 1000 $^{\circ}\text{C}$, thus leading to the hypothesis that a firing between 850 and 1000 $^{\circ}\text{C}$ could have been applied.

The second aspect which involves the firing conditions is the kiln atmosphere. It is known that this kind of *terra sigillata* used to be fired under an oxidizing atmosphere, hence the abundance of haematite, which is the highest oxidized form among iron oxides.

CONCLUSIONS

The investigation of *sigillata* wares by micro-Raman spectroscopy proved a helpful tool for the characterization of the mineralogy of the ceramic body and the slip, confirming the hypothesis of a different compositional raw material used for the coating. Feldspars were mainly identified in the inner body, especially anorthite and the varnish was found to be a highly compacted layer of haematite. Also quartz and rutile were mostly detected in the inner body, together with some diopside, whose presence suggested that a calcareous clay was employed. On the other hand, the more homogeneous composition of the slip may be related to a finer clay material, that was applied to the item surface to give it the typical bright varnish characteristic of *terra sigillata*.

The 2D Raman imaging technique was tested for the spatial distribution of mineralogical phases, in particular feldspars. The results obtained were encouraging and the implementation of measurements in the imaging mode will be a promising technique for future applications of the Raman technique in checking the presence of given minerals finely distributed over specific areas of the sample.

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