

RAMAN SPECTROSCOPY FOR THE NON DESTRUCTIVE CHARACTERIZATION OF ANCIENT POTTERY, PORCELAINS AND MOSAIC GLASSES

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INTRODUCTION

This thesis is in the first place an “adventure” in three domains of application of Raman spectroscopy as a diagnostic tool for the non-destructive study of cultural heritage materials, namely ancient pottery, porcelains and mosaic glasses. While the use of this technique is well established for the analysis of historic pigments and precious stones, its application to these three types of materials is more recent, and still an expanding field. The experimental work for this thesis was carried out at the CNR-ISTEC, Istituto di Scienza e Tecnologia dei Materiali Ceramici in Faenza (Ravenna, Italy) and at the LADIR, Laboratoire Dynamique Interactions et Réactivité (CNRS and Univ. Paris 06) in Thiais (France). The work benefitted also from collaborations with the Universities of Padova and Bologna, with the CSIC-ICV in Madrid, the Musée National de Céramique in Sèvres, and the Institute “G. Caselli” in Naples.

THE SCIENTIFIC ANALYSIS OF ANCIENT POTTERY, PORCELAIN AND GLASS

Chapter 1 illustrates the main objectives of the use of scientific techniques for the analysis of these kinds of materials. It also contains a synthetic review of how Raman spectroscopy has so far been applied to archaeometric studies on cultural heritage materials, and specifically on ancient pottery, porcelains and glasses. One remark in particular could be made, regarding the geographic provenance of these works; as it is evident from the schematic representation of Fig. 1, the main sources of the existing Raman data on



Fig. 1 – Schematic representation of the geographic provenance of published works dealing with the application of Raman spectroscopy to ancient pottery, porcelain and glasses (larger dots indicate a higher number of articles).

pottery, porcelain and ancient glasses can be identified in a limited number of labs in the United Kingdom (London, Edinburgh), France (Thiais) and Italy (Florence). In the past few years, this knowledge has gradually spread to labs in other European and extra-European countries, which have also started producing interesting although numerically still limited researches in this field, often thanks to collaborations with the above mentioned “pioneer” institutions. The research strategy and the organization of the thesis have been based on this review.

RAMAN SPECTROSCOPY: THEORY AND PRACTICE

Chapter 2 provides a brief introduction to Raman spectroscopy, with its advantages and limitations, as well as a description of the instrumentations and experimental conditions used during this work. The structure and Raman spectra of silicate glasses are also detailed, along with the methods employed to process these data.

I want to quickly point out here how there are many characteristics that make Raman spectroscopy such a well qualified technique for the analysis of cultural heritage materials, among which its molecular specificity, non-destructiveness, non invasivity, high spatial and spectral resolution, *in situ* analysis, portability, applicability to samples of large or non-uniform shape, and relative immunity to interference. Also, it can be applied to a wide range of materials, including organic and inorganic solids, and it can probe heterogeneous media or mixtures on a micrometric scale. Moreover, Raman spectroscopy is capable of differentiating between the polymorphic forms of a mineral species, and it gives at the same time some information on the physical structure and the qualitative elemental composition of the analyzed material. There are of course also some limitations, such as the high fluorescence signal arising in some materials, especially those who have been long buried, such as archaeological ceramics. It is not totally clear, up to now, what are the exact sources of this intense background. There are also difficulties in making this technique quantitative, due *e.g.* to the small surface it probes, and to the fact that its sensitivity strongly depends on the polarizability of the analyzed molecules. This yields, for example, an extremely good capacity to detect minimal amounts of anatase and rutile (TiO₂), and on the other hand a very low sensitivity towards cristobalite and tridymite (SiO₂). It is also not a suitable technique for the analysis of every single kind of cultural heritage material; for example nearly all pure metals are Raman silent, and some pigments are quite unstable under the local heating due to the impingement of the laser light.

RAMAN STUDIES ON ANCIENT POTTERY

Chapter 3 includes three different experiences regarding the application of Raman spectroscopy to ceramic materials, both in the form of ancient artifacts and of modern test samples. In all cases this technique was combined with other analytical methods (such as XRD, Mössbauer spectroscopy and SEM-EDS analysis), in order to provide information on the raw materials and/or on the production processes of ancient pottery.

Firing temperature determination

Raman spectroscopy proved a unique tool to investigate the anatase to rutile transition within ceramics. This study also allowed reasserting how careful the researcher should be when attempting to use this transition as a temperature marker for pottery firing. Experimental data in fact confirmed that this transition has a strong dependence on the composition of the clay, and that it can hardly be used as a

mineralogical thermometer in the archaeometric study of pottery. Some applications could perhaps be found in studies on ceramic typologies fired at temperatures above 1000°C. It still seems interesting to deeply investigate in a systematic manner the dependence of this transition on the composition of the raw material. Mössbauer spectroscopy also proved once more to be a useful tool to follow the evolution of iron oxides during firing, in a temperature range interesting for ancient pottery studies. Data collected at 298 K suggested that a deeper understanding of the evolution of iron compounds, particularly the formation and size increase of iron oxide crystals, is needed. These results were published in the proceedings of the EMAC'05 conference (Nodari *et al.*, 2007).

Slips and decorations of Neolithic pottery

The study of slips and decorations of ancient pottery showed how Raman spectroscopy in this case could not completely replace other techniques, but it could be useful for preliminary screening, *e.g.* to identify which seemed to be the most significant samples on which a more comprehensive analytical study should be carried out. The combination with XRF and XRD data allowed to characterize these materials and to reconstruct the production stages of some ceramic fragments recovered during archaeological excavations in a few Neolithic sites in Romania. The slip was obtained probably with a fine-grained carbonate clay with high contents of illite, which was applied on the unfired body, smoothed and/or polished, and painted using iron-rich materials before being fired at a temperature comprised between about 600 and 900°C. One comment could also be made, regarding the suitability of Raman spectroscopy for the study of archaeological materials such as these Neolithic potteries: in many cases, obtaining a “good” spectrum was a difficult task, due to a high fluorescence background which could mask the Raman peaks completely, and often saturated the detector. This research on Neolithic pottery was partly carried out within the framework of the EU Commission-funded “SEE PAST” project; some of these results were presented during national and international conferences (Ricciardi *et al.*, 2008a).

Engobes and glazes of “sgraffito” Renaissance ceramics

As for the engobes of “sgraffito” pottery, interesting results came from the combination of the Raman and chemical characterization. Raman spectroscopy therefore proved once again to be a good complementary technique for the analysis of ceramics, with the advantage of being non-destructive. Engobes from Tuscany could be distinguished from those from Udine, due to their high Mg content and to the presence of feldspars in their Raman spectra. A larger set of data might allow putting on more sound ground some of the hypotheses which have been made regarding the raw materials used and the possibility to differentiate among production sites. Further distinction among Tuscan engobes might in fact be possible based on the identification of enstatite and/or forsterite only in some of them. Analytical results on glazes did not allow distinguishing among production sites, indicating in all cases the use of a typical “recipe” for transparent glazes, based on Pb-oxide (minium) and a quartz-rich sand, seemingly used in different proportions. A good correlation could be established between the total amount of fluxes in each glaze and the value of the polymerization index, calculated on representative spectra on the basis of non-destructive Raman analyses. These results were presented during the EMAC'07 conference, and are being published in its proceedings (Ricciardi *et al.*, 2008b).

RAMAN CHARACTERIZATION OF 18TH CENTURY PORCELAIN

Chapter 4 constitutes the most voluminous part of this thesis. It deals in general with the potentials of a Raman study of porcelain, and more specifically with the characterization of the 18th Century productions of the Bourbon manufactures of Capodimonte and Buen Retiro. These factories have had a very peculiar history; this makes it interesting *per se* to characterize their production, which can however also be of use as a “case study” for a methodological objective. Some results of my work, focused on the analysis of a single porcelain typology, could in fact be extended to the whole variety of artifacts made with such an aesthetically perfect and technologically advanced material.

Much of the European porcelain production since the 18th century has been classified into the two main typologies of “soft” and “hard” paste, and yet quite a few “hybrid” or peculiar productions exist, which do not fit in either of these categories (*e.g.* English bone-ash porcelain). Due to their quite special composition, Capodimonte products can also hardly be defined as belonging to either of the two main types of porcelain, and this fact makes them quite an interesting object for archaeometric analyses. This research conducted by means of Raman spectroscopy aimed at completing the characterization of the Capodimonte production and, most of all, at laying the basis for a correspondence between the results of destructive and non-destructive analyses on porcelains. In addition to some excavation samples provided by the Caselli Institute of Naples and by the Spanish CSIC-ICV of Madrid, I in fact analyzed a few porcelain artefacts, belonging to the Sèvres Museum, which could not have been sampled for destructive analyses (Fig. 2). Raman analyses confirmed the uniqueness of the Capodimonte production, and specific Raman signatures were identified for pastes and glazes, which might serve as a “reference” group for the

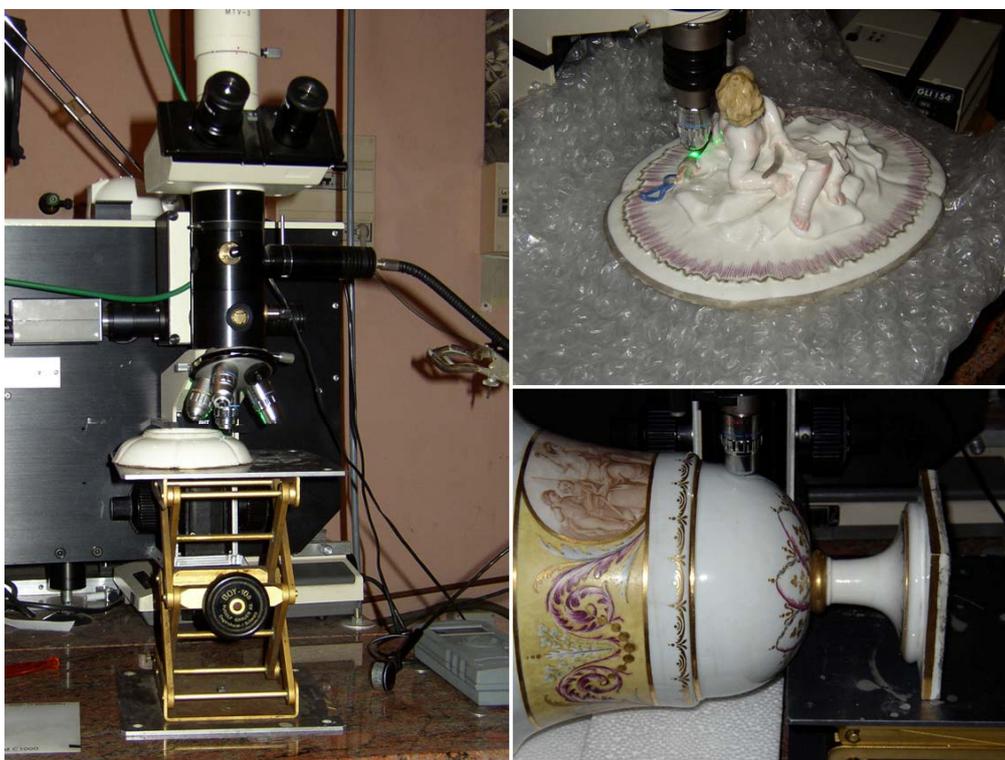


Fig. 2 – Typical experimental configuration used while acquiring micro-Raman spectra on the Sèvres Museum porcelain objects (images are not to scale).

identification of products issued from this manufacture. High similarities were found with the Raman signatures of some Buen Retiro samples, which would assign them to the early stage of the Spanish production. On the other hand, other Spanish samples belonging to later periods of the same factory display peculiar signatures both in the paste and in the glaze (Fig. 3). A part of these results was presented at the Raman in Art and Archaeology 2007 conference and published (Ricciardi *et al.*, 2008c).

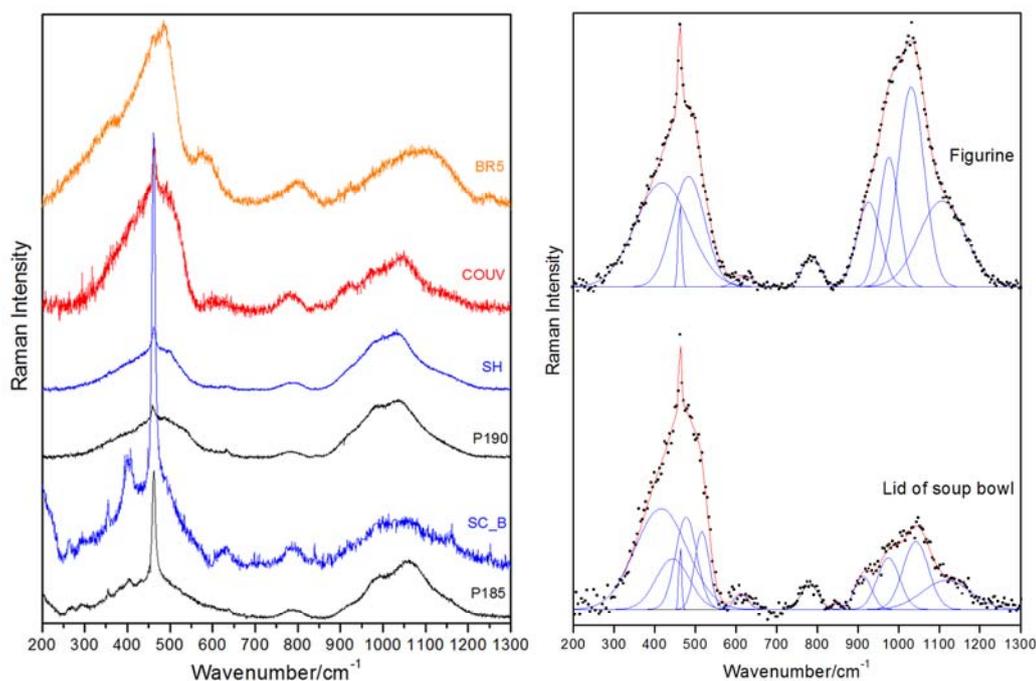


Fig. 3 – Representative spectra (left) and sample decomposition (right) of Capodimonte and Buen Retiro porcelain glazes.

Furthermore, the Raman analysis of pastes and glazes of a few porcelain samples of different origin allowed pointing out the similarities and the differences existing with the Capodimonte production. Medici porcelain, for example, turned out to be easily recognizable from its Raman spectra, even though the chemical composition of its paste is very similar to that of Capodimonte. The analysis of a figurine showed how the production of the Real Fabbrica Ferdinanda did not bear much difference from that of the earlier Neapolitan factory. The paste signature of biscuit samples from Vicenza could not be distinguished from that of Capodimonte. This result underlined the importance of the combined characterization of both paste and glaze for a correct identification of the products; many pastes in fact yield signatures characterized only by the peaks of the polymorphs of crystalline silica (quartz, cristobalite, tridymite). This is for example the case of the objects from Doccia, whose paste is totally similar to that of Capodimonte, but which show a peculiar glaze signature. Finally, the Vögt soft paste showed Raman signatures completely comparable to those of Capodimonte in both paste and glaze.

Finally, a Jobin Yvon Horiba HE532 portable spectrometer, recently acquired by the LADIR, was used in the very last period of this thesis, in order to test its performances and to compare the obtained spectra with those acquired with the other, non-portable, instruments. The HE532 is equipped with a

green Nd:YAG laser at 532 nm, a grating with 1800 lines/mm and Notch filter, a CCD detector cooled to 200 K and optical fibers for conveying both the laser light and the Raman signal (Fig. 4). It is also coupled to a 50x long focus objective. The spectrometer was first tested at the lab on some of the same museum objects which had been previously characterized using the other instruments, and then transported to the Sèvres Museum for on-site analyses. It was soon clear that this portable spectrometer benefits of a high luminosity, which yields very intense and sharp spectra even with a very short acquisition time.

All the data acquired on porcelain objects during this thesis could be further treated, in order also to investigate more deeply the correlations existing between the results of Raman analysis and those obtained from other (destructive) techniques. They will also hopefully integrate those relative to a number of other early European productions of porcelain which have so far been published. Such a large corpus of spectroscopic data needs now to be systematized, in order to identify “reference” Raman signatures for each manufacture and possibly to standardize the experimental procedure for Raman analyses on ancient porcelains. Up to now a similar need has been fulfilled for the Raman spectra of pigments, which have been the object not only of many publications, but also of some systematization and implementation over the internet. Hopefully the establishment of such a database and experimental protocol will be the object of more research in the near future.

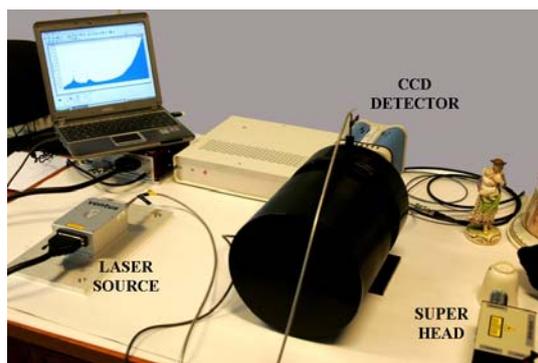


Fig. 4 – The Jobin Yvon Horiba HE532 portable spectrometer during tests at the LADIR.

RAMAN CHARACTERIZATION OF MOSAIC GLASSES

Chapter 5 details the results of a preliminary Raman study carried out on Roman age mosaic glass *tesserae*, which allowed a good characterization of both the glass matrix and the crystalline inclusions. It also led to the identification in some blue, turquoise and green *tesserae* of calcium antimoniate, whose Raman signature does not seem to have been recognized so far in the scientific literature on mosaic glasses. Moreover, the extreme homogeneity of the Raman spectra of all the ancient samples well reflected the limited variability of their chemical composition, and gave yet another proof of the high level of standardization of glass production in the Roman Age, through a completely non-destructive analytical approach.

GENERAL CONCLUSIONS

These were then the reasons of interest and the main results obtained in the three chosen domains of application of Raman spectroscopy; while dealing with different materials, they are far from being “stranger” to each other. In fact, we deal with colouring agents used as pigments in the decoration layers of ancient pottery and porcelain, as well as in bulk glasses. Also, pottery and porcelain glazes have the same material structure as mosaic glasses, and therefore the treatment of their Raman spectra is exactly

the same, and similar kinds of information can be extracted for glazes and glasses. Needless to say, these three types of materials are often found together in historical and archaeological contexts, or even in the same work of art (such as ancient mosaics, often realized using both ceramic and glass *tesserae*), and may therefore suffer similar pollution and degradation conditions, or need to be jointly analyzed and restored.

Studying such different types of materials allowed making comments on the importance of choosing the “best” Raman instrument for the analysis of each of them. Different spectrometers were used, allowing testing different laser colours, instrumental optics and filters. Macroscopic and microscopic approaches were compared, and a last generation portable Raman spectrometer was used for the on-site analysis of some museum objects, demonstrating its high-standard performances, fully comparable with those of lab instruments. This work follows a path designed in the past few years, towards the classification of Raman signatures of cultural heritage materials. Much of it rests upon the work of Colomban and co-workers, who first sorted the Raman spectra of historic glasses into well-defined categories, providing numerical tools for such grouping. All the Raman data acquired during this work were therefore added to some published graphs, to support the proposed classifications and to validate in a way the reliability of both the analytical technique and the data treatment methods. Fig. 5 shows the plot of I_p values vs. ν_{MAX} Si-O wavenumbers for all the glazes and glasses analyzed in this thesis (closed symbols). Open symbols refer to previously published data and represent all seven “families” identified among all the glassy samples which were analyzed during previous studies. The data relative to the mosaic glasses and the glazes of the “sgraffito” pottery fall exactly within the categories of alkali-silicate and lead-silicate glasses, respectively. Data relative to porcelain glazes contribute to enlarge and better define the variation range of the Raman parameters of Na-Pb silicate glasses.

Generally speaking, this work showed once again the usefulness of Raman spectroscopy for the

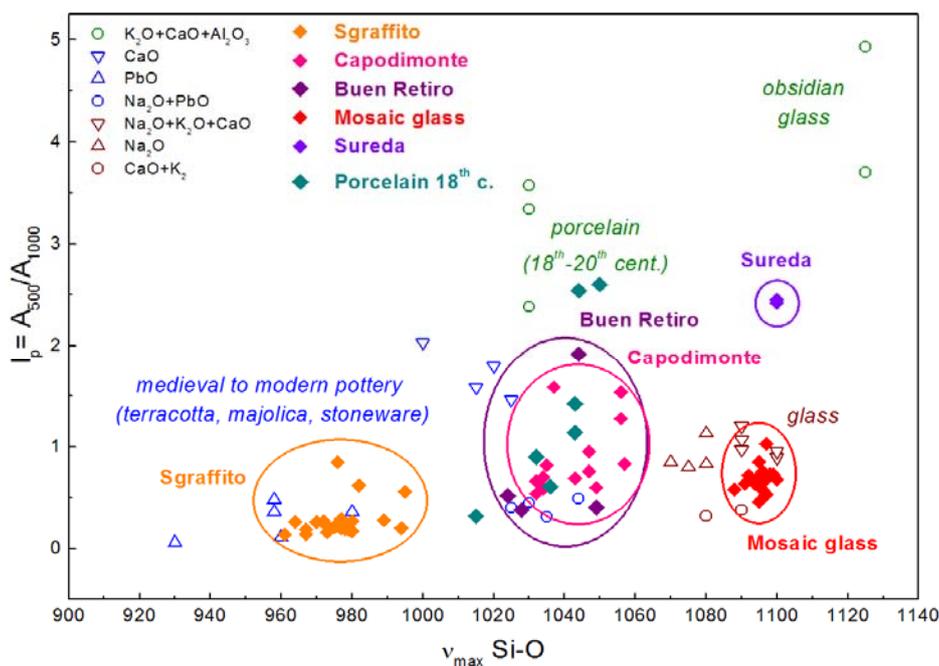


Fig. 5 – Plot of I_p vs. ν_{MAX} Si-O for all the analyzed glazes and glasses (closed symbols). Open symbols refer to published data (Colomban *et al.*, 2006, modified from Fig. 9a).

non-destructive analysis of cultural heritage materials. Further results could be obtained by enlarging the set of samples of which both the chemical composition and the Raman spectra are known. This may in fact improve the correlations established in previous works and in the present thesis between the results of chemical and spectroscopic analyses. This would in turn enhance the reliability of Raman spectroscopy and support its role as a routine technique, both fast and non-invasive, useful for preliminary screenings of large numbers of artefacts.

REFERENCES

- Colomban, Ph., Tournié, A., Bellot-Gurlet, L. (2006): Raman identification of glassy silicates used in ceramics, glass and jewellery: a tentative differentiation guide. *J. Raman Spectrosc.*, **37**, 841-852.
- Nodari, L., Ricciardi, P., Fabbri, B., Gualtieri, S., Russo, U. (2007): Contribution for a mineralogical thermometer to be applied to low-fired and/or non carbonatic clays. In "Archaeometric and archaeological approaches to ceramics", S.Y. Waksman, ed. Archaeopress, London, 13-18.
- Ricciardi, P., Varvara, S., Fabbri, B., Gualtieri, S., Gligor, M. (2008a): Analisi archeometriche su ceramica neolitica ingobbiata e dipinta (cultura di Lumea Noua, IV millennio a.C.) da siti in Transilvania (Romania). Atti della X Giornata di archeometria della Ceramica, Roma 2006, in press.
- Ricciardi, P., Amato, F., Colomban, Ph. (2008b): Raman spectroscopy as a tool for the non-destructive characterization of slips and glazes of a "sgraffito" Renaissance production. Proceedings of the EMAC'07 conference, in press.
- Ricciardi, P., Colomban, Ph., Milande, V. (2008c): Non-destructive characterization of Capodimonte and Buen Retiro porcelain. *J. Raman Spectrosc.*, **39**, D.O.I. 10.1002/jrs.1918.