

THE STUDY OF THE CAPODIMONTE PRODUCTION: AN OCCASION FOR THE PROPOSAL OF A RAMAN DATABASE FOR ANCIENT PORCELAINS

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ABSTRACT

In the past few years a comprehensive interdisciplinary study has been undertaken on some excavation fragments of 18th century porcelain from Capodimonte (Naples, Italy). The Capodimonte manufacture has had a very peculiar history; this makes it interesting per se to characterize its products, which can also be of use as a “case study” for a methodological objective. Analyses have been carried out on pastes, glazes and decorations in order to assess compositional and technological aspects of this production. Several analytical techniques were used, which included Raman macro- and micro-spectroscopy and WD-XRF. We wanted in fact to test the suitability of Raman spectroscopy for a non-destructive and non-invasive analysis, possibly coupled with portable ED-XRF, in order to establish a significant “reference group” of Raman spectra for the Capodimonte production. The following step would be to enlarge this kind of study to other porcelain factories, in order to assess the possibility of an attribution of a porcelain object to a certain production on the basis of the Raman signatures of its paste and glaze. Several studies have in fact been published, demonstrating how the Raman spectra of a porcelain fragment or whole object can be obtained in a completely non-invasive way to determine body and glaze composition, making it possible to identify the type of porcelain, its manufacturing technology and often its provenance. There seems now to be a great need for the systematization of such a large corpus of spectroscopic data. Moreover, only a limited number of porcelain manufactures have been investigated so far; the study of other productions would be of great use for the establishment of a complete and reliable spectroscopic database on these materials. In order to assure as much as possible reliability, this will also require the standardization of the experimental procedure, for which some general criteria are presented.

INTRODUCTION

Historical Background

In 1739 Charles of Bourbon, king of Naples, following the example of Royal Courts all over Europe, promoted the establishment of a porcelain manufacture, at first housed in the Royal Palace. After a few years devoted to the search for suitable raw materials and to experimentations of different recipes for the porcelain paste, in 1743 the porcelain manufacture officially started its work, and was relocated in the Royal woods of Capodimonte. During the following sixteen years, the factory produced high quality porcelain, often in the form of decorative objects, which served as gifts from the king to Italian and foreign noblemen, and were commercialized since 1745. The factory mark used all along the manufacture's activity was a fleur-de-lis painted in underglaze blue, or sometimes impressed under the bottom of the artefact, mostly in the case of figurines. It is clear from the rare historical sources that during the short life of the manufacture the quest for raw materials and the experimentations never ceased. In 1759, when he rose to the Spanish throne becoming Charles III of Spain, the king decided to move the porcelain production to Madrid, completely dismantling the Neapolitan factory.

The Archaeometric Research Project

The short-lived production of Capodimonte has not so far been the object of extensive archaeometric studies. Prof. Orazio Rebuffat was the first, in 1905, to provide chemical data regarding Capodimonte pastes and glazes. Only in 1995 more data were published regarding the chemistry, mineralogy, density and microstructure of some porcelain fragments found during excavations in the 1950s in the area formerly occupied by the manufacture. In the past

few years a more comprehensive interdisciplinary study has been undertaken on some of the mentioned excavation samples, which has included their characterization by means of SEM-EDS, XRD, optical microscopy on thin sections, porosimetry, and the determination of their apparent and real density. Such study has been carried out within the framework of a bilateral project between the Italian CNR and the Spanish CSIC on “the Bourbon porcelain from Capodimonte to Buen Retiro: continuity or innovation”, whose results have been presented in some occasions and are being partly published.

Most recently, Raman spectroscopy has been used to characterize non-destructively a number of the mentioned excavation samples, in addition to a series of objects produced at Capodimonte and belonging to the collections of the Musée Nationale de Céramique de Sèvres, near Paris. This characterization has included both pastes and glazes.

Aim of this Work

The aim of the present work is to lay the basis for the establishment of a Raman database of early European porcelain productions, starting from the work which has so far been carried out on the Capodimonte production.

RESULTS OF THE ARCHAEOMETRIC INVESTIGATIONS

Traditional Analyses

Even after many archaeometric analyses, Capodimonte porcelain can still neither be exactly defined as a “soft-paste” nor as a “hard-paste”. The high silica content ($\geq 79\%$ SiO₂) and the low values of alumina (4-8% Al₂O₃) and calcium oxide (<2% CaO) make its composition anomalous with respect to the standards of late 18th century European manufactures, and more similar from the chemical point of view to the early production of “Medici porcelain” (end of the 16th century). So far, the Capodimonte paste has usually been identified as a “mixed” or hybrid porcelain, having a melting point of about 1200°C.

	Paste	Colourless glaze
SiO ₂	79.7 – 85.5	50.5 – 57.6
Al ₂ O ₃	3.5 – 7.8	1.4 – 3.7
TiO ₂	< 0.3	< 0.4
Fe ₂ O ₃	< 0.6	< 0.4
MgO	< 0.5	< 0.4
CaO	< 2.0	< 3.0
Na ₂ O	1.3 – 4.8	4.4 – 7.8
K ₂ O	2.3 – 5.2	1.6 – 3.5
PbO	< 1.2*	21.7 – 36.8
SnO ₂	< 1.5*	< 5.5
P ₂ O ₅	< 0.4	n.d.
SO ₃	< 0.4	n.d.

*with the exception of sample P185, which contains 2.8% PbO and 3.5% SnO₂

Table 1 – Compositional range of Capodimonte pastes and glazes (weight % oxides; n.d. = not determined)



Figure 1 - Some of the analyzed excavation samples (P173, P182, P192) and museum objects (MNC4423, MNC13534, MNC25343). Images are not to scale

The chemical composition of Capodimonte porcelain is quite homogeneous, as shown in Table 1. On the contrary, phase composition and density are very variable, due to the different development of the microstructure during firing, because temperatures can vary greatly from a firing to another, or also in different positions inside the kiln. Quartz is in fact always present, together with variable quantities of cristobalite and tridymite. The amount of glassy phase and the closed porosity are also variable, which causes the density to vary as well.

Raman Spectroscopy

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 traditional and non-destructive analyses on porcelains. In addition to some excavation samples, we in fact analyzed a few porcelain artefacts, belonging to the Sèvres Museum, which could not have been sampled for traditional and generally destructive analyses (fig. 1). Among them, notably, the tabletop of a precious pedestal table (MNC 4423, acquired in London in 1853), which was undergoing restoration in the occasion of an exhibition at the Musée Cernuschi in Paris (“Pagodes et dragons: exotisme et fantaisie dans l’Europe Rococo 1720-1770”, february 23rd to june 24th, 2007).

Paste analysis showed that all the Capodimonte objects have Raman signatures which are compatible with those of the excavation fragments. The presence of crystalline α -quartz (peaks at 200, 262, 353, 464, 1080, and 1160 cm^{-1}), cristobalite (225 and 415 cm^{-1}), tridymite (290, 350, and 430 cm^{-1}) and occasionally of β -wollastonite (637 and 971 cm^{-1}) is in agreement with the average chemical composition of Capodimonte pastes (table 1 and fig. 2). This allows considering the obtained spectra as a good reference for future analysis of porcelains possibly attributed to this manufacture. It is also true, though, that the polymorphs of silica are often observed in several types of both soft and hard porcelain pastes; glaze analysis is therefore necessary in order to fully characterize the Capodimonte production. The presence of slightly different paste signatures, obtained from the analysis of samples of the same provenance and relative to such a short time interval (the sixteen years of activity of the manufacture), well agrees with documentary evidence of the fact that testing for suitable raw materials and production technologies, started in 1740, went on at least until 1752. The glaze spectra of the Capodimonte fragments (fig. 2) show a general homogeneity which does not allow subdividing them into groups, let alone reproducing the same grouping made for the corresponding pastes. Some spectral features can however be highlighted:

- on the basis of their spectral shape and calculated parameters, all the colourless glazes can be attributed to the family of Na-Pb silicate glasses;
- all glazes contain undissolved quartz crystals, as shown by the peak at 462 cm^{-1} which also corresponds to the position of the maximum of the first massif;
- the glazes of museum artefacts are evidently comparable with those of the excavation samples;
- all the analyzed glazes have Raman signatures and parameters which are similar to those observed in samples from other 18th century soft-paste manufactures.

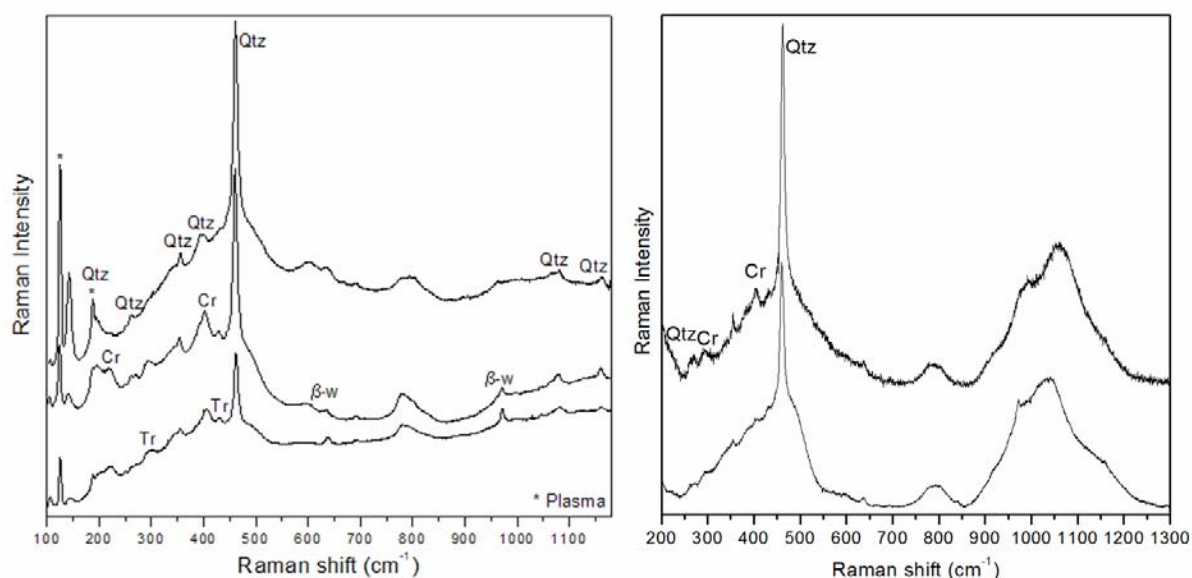


Figure 2 - Representative Raman spectra of Capodimonte pastes (left) and glazes (right)

ESTABLISHMENT OF A RAMAN DATABASE

Reasons for the Proposal

Besides the one presented in this work, a number of other early European productions of porcelain have so far been characterized by Raman spectroscopy, and numerous data have appeared, spread in articles published in several specialized journals. There seems now to be a great need for the systematization of such a large corpus of spectroscopic data, 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. A standard procedure for the Raman analysis of porcelain would be of great use, especially given the increasing availability of portable spectrometers (fig. 3), extremely compact and reliable, which will hopefully facilitate the on-site study of large numbers of porcelain artefacts in museum and art galleries.

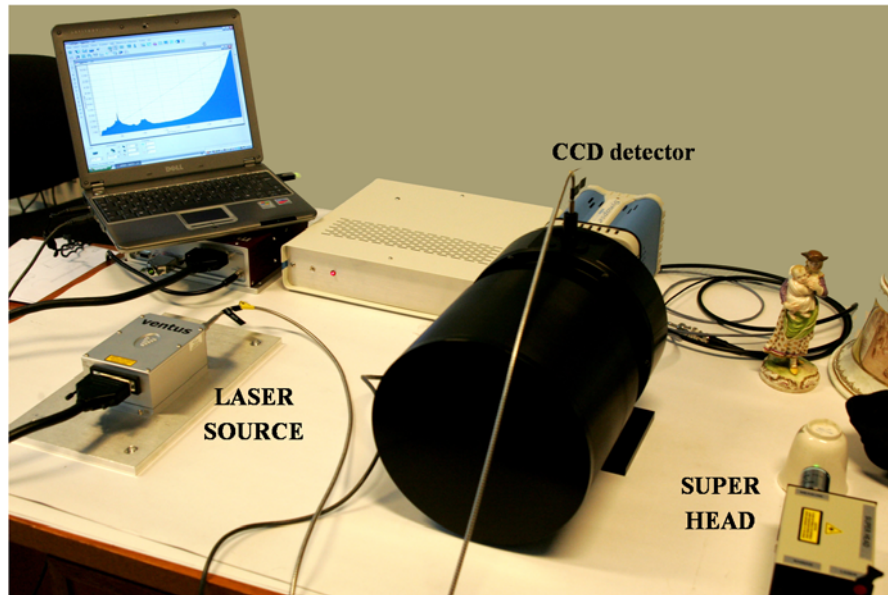


Figure 3 – A portable Raman spectrometer (Horiba-Jobin Yvon HE532), connected to a laptop.
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Needs for the Realization

Establishing a Raman database for porcelain requires dealing with a series of issues which emerge during the spectroscopic analysis of this and other ceramic materials:

- the information deriving from a single spectrum is incomplete, because it represents either the paste or the glaze; this leads to the direct consequence that paste and glaze analysis must be coupled in order for the information on each porcelain production to be as complete as possible.
- the information deriving from a single spectrum of the paste is often incomplete;
- different objects produced by the same manufacture may show different Raman signatures (i.e. different phase compositions), due to changes in the technological production process, e.g. the paste recipe or the firing cycle;
- the baseline subtraction and the deconvolution method for glaze spectra are of the utmost importance;
- different experimental configurations, in terms of degree of magnification and laser colour, are most suitable for paste and glaze analysis, respectively;
- pigments are not fully significant for distinguishing among different productions, because of their large standardization. A few exceptions exist, such as the use of lapis lazuli at Meissen, and some yellow pigments. Opacifying techniques were also often typical of a certain manufacture.

Each “entry” of the proposed database should therefore be made up of at least two spectra, referring respectively to the typical paste and glaze produced by each manufacture. Still, the

needs of such a database cannot be completely fulfilled by linking each production to a number of spectra. Each entry should in fact also contain a list of mineral phases which must (*necessary phases*), should (*complementary phases*) or may (*accessory phases*) be found while analyzing an object attributed to a certain production. Another topic that should be the object of further discussion is the minimum number of samples which ought to be analyzed in order to establish a good “reference group” for a certain manufacture, and therefore a significant entry for the database. These will necessarily depend on how much standardized or on the contrary how much varied the production was during the manufacture’s lifetime.

PROPOSALS FOR AN EXPERIMENTAL PROTOCOL

As already stated, a series of issues emerge during the Raman analysis of porcelain samples, which need to be dealt with in order to design a suitable experimental protocol. Table 2 shows the typical experimental conditions used during the campaign of Raman analyses on Capodimonte porcelain. The most important issues that we’ve been faced with during this study are listed below, together with the general guidelines which we could derive from them:

- thanks to the real-time acquisition of the spectra, brief tests can be made on numerous spots for each sample. Only a few spectra, representative of phases which appear to be most present in the sample material, are usually recorded, allowing a longer acquisition time, and saved to file. Spectra should also be recorded when peculiar even though rare signatures are observed, which might be interesting in view of a differentiation between manufactures. It should be pointed out how the choice of “representative” spectra, considered as “significant” ones, is by no means straightforward. It is rather a most critical phase of the whole experimental process, whose standardization would be important in order to give Raman spectroscopy a less “qualitative” character;
- different approaches are needed for paste and glaze analysis (macroscopic vs. microscopic, respectively). This depends on the different “scale” at which inhomogeneities appear in these two materials. Crystals within the paste can be in the range of 10 to 100 μm , therefore a single macroscopic measure probes an area 9 to 900 times larger than each crystal. Five measures should then be necessary to give a complete view of the paste. In the glaze, on the other hand, crystal sizes remain below about 10 μm ; three measures with a 10x objective (or about 10 with a 50x objective) should therefore be enough to fully characterize the glaze;
- the choice of the laser power is usually not a problem when analyzing porcelains, with the exception of some low-fired pigments (reds, purples) which might be unstable and undergo structural modifications under the focused laser light. Powers as high as ~ 100 mW at sample can be used in all other cases. Due to the high stability of the material, any laser colour is suitable (see following subsections for details);
- a spectral “range of interest” needs to be defined. Experience shows that the vast majority of phases which are liable to be found within porcelain have Raman signatures in the range 100 to 1300 cm^{-1} , with the exception of amorphous carbon, occasionally used as a black pigment/darkener (large Raman bands at ~ 1350 and 1590 cm^{-1}). The Raman signature of the glassy phase also lies within the mentioned range, whose analysis is therefore usually sufficient to fully characterize the material.

Parameter	Paste	Glaze
Laser	violet (406.7 nm) and green (532 nm)	green (514.5 and 532 nm)
Objective	none (macroscopic)	10x and 50x
Number of measures	3 to 5	3 (10x) or 10 (50x)
Spectral range analyzed	$\sim 100 - 1200$ cm^{-1}	$200 - 1300$ cm^{-1}

Table 2 – Typical experimental conditions used for the Raman analysis of porcelains

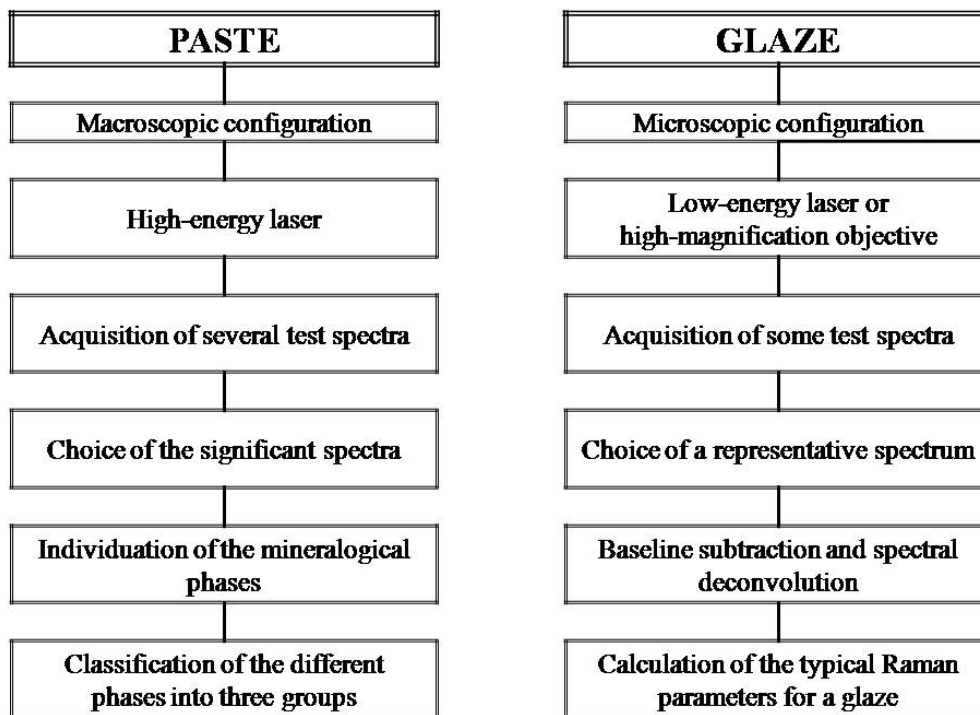


Figure 4 – Schematic representation of a possible experimental protocol for the Raman analysis of porcelain

Further comments can be made, which are specific to the analysis of either the paste or the glaze of porcelain artefacts, and which are detailed in the following subsections.

Figure 4 contains a schematic representation of all the guidelines presented for a possible experimental protocol for the Raman analysis of porcelain artefacts.

Paste Analysis

From the methodological point of view, the use of a macro- rather than a micro-Raman approach seems sufficient in order to obtain data as representative as possible of the overall composition of each paste. In addition, the use of a high-energy laser, such as the violet line of a Kr^+ laser, helps “cleaning” the sample’s surface and thus reducing to some extent the spectral background. Moreover, the intensity of Raman scattering is proportional to ν^4 , with ν the frequency of the exciting light; a violet laser therefore enhances the acquired signal. Microscopic measures can also become useful, for example when the visual inspection of a sample reveals the existence of marked inhomogeneities within the material.

Even in macroscopic configuration, it is important to acquire a certain number of spectra of each sample, because it is most probable that not all the mineral phases characterizing the paste will be identified in one spectrum. Figure 5 shows the example of a Capodimonte excavation fragment whose paste contains β -wollastonite, which is however not visible in all the recorded spectra. It is also clear how the quantities of cristobalite and glassy phase vary within the sample, so that several spectra are needed in order to get an analysis as adherent as possible to the actual composition of the paste.

Glaze Analysis

The thickness of the glaze layer of porcelain artefacts is of the order of about 100 microns. In this case the use of a low-energy laser or of a high magnification objective is appropriate, in order to avoid that signals coming from the paste interfere with the Raman spectrum of the

glaze. In both cases, in fact, the exciting light will have a small penetration depth into the glaze layer, and it will not excite the Raman bands of phases within the paste.

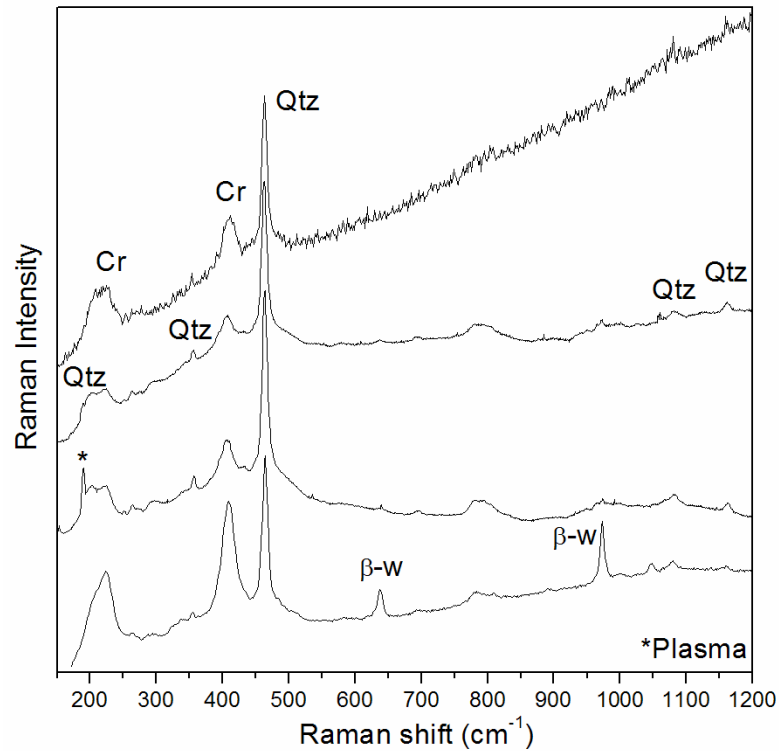


Figure 5 - Representative Raman spectra of the paste of sample P173 (see fig. 1)

Glaze spectra are further treated in order to extract relevant information. First, a linear baseline is subtracted in the region of interest. Such line is defined by connecting a minimum of four points (usually around 200, 700, 850 and 1300 cm^{-1}), where the intensity of the Raman signal is lowest, between two adjacent regions of a glassy spectrum. More points are added in between if the defined baseline crosses the spectrum.

Much care should be taken during baseline subtraction, in order to take into account the shape of the low-wavenumber portion of the spectrum, which is highly dependent on the type of filter present on the spectrometers (monochromator vs. Notch filter). Low-cutting filters in fact do not completely eliminate the signal due to the so-called “boson peak”, often present especially in lead-containing glazes.

An appropriate software (e.g. the Peak Fitting Module of Microcal Origin) is then used to decompose the two “massifs” which make up the spectrum into a certain number of bands, following a deconvolution model based on the description of silicate glasses as a network of five types of silicate tetrahedra (called Q_n , $n=0-4$). Such deconvolution of the glaze spectrum allows calculating a series of “Raman parameters”, which can be used effectively to compare different materials. Among the most useful are the wavenumber positions of the Q_n bands and of the maxima of the bending and stretching massifs (δ_{MAX} Si-O and ν_{MAX} Si-O, respectively). Also the so-called “polymerization index”, calculated as the ratio of the areas of the two massifs, has often been successfully related to the composition and structure of glazes and glasses.

Finally, it seems that a more accurate interpretation of glaze spectra acquired in macroscopic configuration, together with a thorough comparison with the corresponding microscopic spectra, would yield interesting information on the composition of the interface between paste and glaze. This would in turn give technological indications about the production process of the artefacts.

CONCLUSIONS

The characterization of the 18th century porcelain production of Capodimonte (Naples, Italy) has recently been the occasion for the reassessment of the usefulness of the Raman spectroscopy technique for the non-destructive analysis of porcelains. It has also allowed making some remarks about the growing need for the systematization of both the experimental protocol for the Raman analysis of this material, and of the existing amount of spectroscopic data. The establishment of a Raman database for porcelains will require a different approach from that typical of other spectral databases, mostly because a single spectrum cannot fully characterize one porcelain production. A well-structured experimental protocol should take into account a variety of factors, such as the different conditions needed for paste and glaze analysis, and the need to standardize data treatments such as baseline subtraction and spectral deconvolution. It is our hope that this work will lay the way for a constructive discussion on the presented subjects, with the final objective to establish a comprehensive Raman database of early European porcelain productions.

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