

TECHNICAL PAPER

TOWARDS THE ESTABLISHMENT OF A RAMAN DATABASE OF EARLY EUROPEAN PORCELAIN

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This paper is based on a presentation at the 8th international conference of the Infrared and Raman Users' Group (IRUG) in Vienna, Austria, 26-29 March 2008.

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This work presents an update on the research work that is being carried out towards the establishment of a database and of an experimental protocol for the Raman analysis of porcelain. Several studies published since 2001 have in fact demonstrated how the Raman spectra of a porcelain object can be obtained in a non-invasive way to determine body and glaze composition, making it possible to determine the type and often the provenance of the porcelain. Many early European porcelain productions have been characterized by Raman spectroscopy so far, and a large corpus of spectroscopic data exists, which now needs systematization, in order to identify “reference” Raman signatures for each manufacture and possibly to standardize the experimental procedure for this kind of analyses. Up to now a similar need has been fulfilled mainly for the Raman spectra of single minerals, pigments and binders. This paper reports spectroscopic data acquired on 18th century porcelain objects from Capodimonte (Italy) and Buen Retiro (Spain), using them as examples of possible database entries.

1 Introduction

The non-destructive characterization by means of Raman spectroscopy of some 18th century porcelains issued from the Bourbon manufactures of Capodimonte (Italy) and Buen Retiro (Spain) has recently been the occasion for some investigation and considerations about the opportunity of establishing a Raman database for early European porcelain productions.¹ At present, available Raman databases deal in fact mostly with the spectra of single minerals and pigments.²⁻⁵ They are extremely useful in the field of porcelain analysis, e.g. in order to identify single mineral phases within a porcelain paste, but they do not completely fulfill the needs of those wanting to use them for the identification of a porcelain production.

Raman studies on porcelain artifacts were first published in 2001 thanks to the collaboration between the LADIR and the National Ceramics Museum and Manufacture of Sèvres, which allowed charac-

received: 27/06/2008
accepted: 17/10/2008

key words:

Raman spectroscopy, porcelain, database, experimental protocol, paste, glaze

terizing a large number of porcelain pigments on standard color “palettes”, as well as some 18th to 20th century French porcelain types, based on the spectroscopic analysis of both body and glaze.⁶⁻⁸ Some more studies followed, published by other groups, on the possibility to distinguish English porcelains issued from different manufactures,^{9,10} and on some Chinese shards from the Ming period.^{11,12} A few essays have also been made of the use of a portable spectrometer for the on-site characterization of extremely precious artifacts.¹³⁻¹⁴

These studies have well demonstrated how the Raman spectra of a porcelain fragment or whole object can be obtained in a completely non-destructive way to determine characteristic body and glaze signatures, making it possible to determine the type of porcelain (hard-paste, soft-paste, bone ash etc.). Being such a technologically advanced material, porcelain has had since its beginning very specific recipes, whose secrets were also carefully guarded and therefore represent a real “factory mark” from the point of view of manufacturing technology. In this sense, a technique such as Raman spectroscopy, which shows its efficacy in distinguishing technological parameters in a completely non-destructive way, is of unquestionable importance. There have in fact been cases in which a comparison between an (unmarked) porcelain artifact and a marked piece have been made, providing analytical support for an attribution to the same factory.¹⁰

1.1 Research Aims

During the 18th century the number of porcelain factories in Europe increased continuously, up to a maximum of over 50 manufactures working contemporaneously in 1780 (Figure 1). As already stated, the production of a few of these manufactures has already been analyzed by means of Raman spectroscopy, with the aim of a non-invasive characterization and the identification of specific Raman signatures. This article presents recent spectroscopic data on the manufactures of Capodimonte and Buen Retiro, which allow establishing reference signatures for these productions. Much work is however still needed for the establishment of a comprehensive database which would serve many scopes. For example, it would help with the identification of copies and forgeries, whose production was not uncommon, and give the possibility to distinguish among visually similar productions, e.g. factories which may have had different production technologies, but exchanged workers or had the same owner. It must be noted that aiding the historian/curator in differentiating

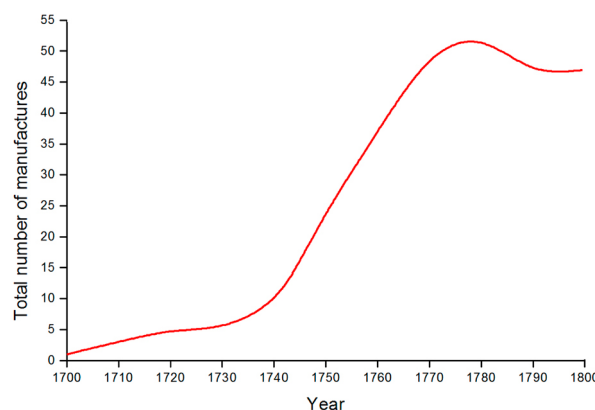


Figure 1: Number of porcelain manufactures in Europe during the 18th century.

between productions which look alike is essentially the only way in which porcelain “identification” via a spectral database can be intended. That is to say that “absolute” identification is today virtually impossible, both because very few productions have been characterized, and because of the undeniable technological similarities which exist within each main porcelain type.

This paper therefore aims at reviewing which seem to be the key issues which should be kept in mind when performing Raman analyses on porcelain samples, which have been addressed in a previous publication.¹⁵ It also aims at further specifying the possible structure of a database for the Raman analysis of porcelain.

2 Materials and Methods

Raman analyses were conducted on a series of excavation fragments and museum objects attributed to the porcelain manufactures of Capodimonte (Naples, Italy) and Buen Retiro (Madrid, Spain), some of which are presented in Figure 2. These two factories have much in common; the Spanish one can be seen as a continuation of the other, as both were founded by Charles of Bourbon, when he was king of Naples (1743) and king of Spain (1759), respectively. Previous papers have reported the results of the characterization of Capodimonte porcelain¹⁶ and of the late Buen Retiro production¹⁷ by means of traditional techniques. Raman data on these productions have been partly published^{1,15} and are complemented here by the results of most recent experiments.

Raman analyses were performed at the lab with three different spectrometers using green or violet lasers. Some analyses were also performed at the National Ceramics Museum of Sèvres, with a fiber optics portable instrument (Figure 2, center). The



Figure 2: Some of the analyzed excavation fragments and museum objects attributed to the manufactures of Capodimonte (P140, P180, P185 and MNC28202) and Buen Retiro (BR6 and MNC3091-1). Images are not to scale.

availability of several Raman spectrometers gave, among other things, the possibility to test the suitability of each of them (in terms of laser power and color, experimental setup etc.) for the analysis of each kind of material. Different instruments bear in fact different optics, which affect the characteristics of the acquired spectra. Finally, different colors of the laser produce varying spectral backgrounds. All these parameters, together with the availability of different configurations (macro- vs. microscopic), have to be taken into account when choosing the spectrometer for the analysis of a specific material, e.g. a porcelain paste, glaze, or pigment.

3 Results

3.1 Characterization of Pastes

The nature and relative abundance of mineral phases in the paste partially characterize a porcelain production. As an example, Table 1 lists the phases found in the paste spectra of samples from Capodimonte (CdM) and Buen Retiro (BR). Note

Sample attribution	Raman signature (mineral phases)		
	Necessary	Complementary	Accessory
CdM (excavation fragments)	quartz, cristobalite	β -wollastonite	trydimite, glassy phase
CdM (museum objects)	quartz, cristobalite		trydimite, glassy phase
BR1	quartz, cristobalite	β -wollastonite	trydimite, clinoenstatite
BR2	quartz, cristobalite, α -wollastonite, scapolite		trydimite
BR3	quartz, cristobalite, protoenstatite		trydimite

Quartz, cristobalite and trydimite: SiO_2 ; α - and β -wollastonite: CaSiO_3 ; clinoenstatite and protoenstatite: MgSiO_3 ; scapolites: $\text{Na}_4(\text{Al}, \text{Si})_{12}\text{O}_{24}\text{Cl}$ or $\text{Ca}_4(\text{Si}, \text{Al})_{12}\text{O}_{24}(\text{CO}_3, \text{SO}_4)$
CdM: Capodimonte, BR: Buen Retiro

Table 1: Principal mineral phases identified in the Raman spectra of pastes of the analyzed samples, subdivided depending on their abundance and representativeness.

that the presence of a glassy phase can also be considered as a “signature”, although its quantification is especially difficult, due to the usually high background signal. Crystalline phases can more easily be “quantified” by carrying out a Raman mapping on a surface.⁸ The relative abundance and representativeness of the identified phases allow subdividing them into three groups: necessary, complementary and accessory phases, whose definition can be illustrated with the example of the Capodimonte reference group (see Table 1). The Raman signatures of both quartz and cristobalite (*necessary phases*) must be identified in a paste in order to hypothesize its ascription to the CdM production, while the possible presence in the paste of β -wollastonite (*complementary phase*), linked to the unavoidable variability of paste composition, is not mandatory for an attribution. Trydimite and glassy phase (*accessory phases*), while often present in CdM pastes, cannot be used for classification purposes, due either to the very low Raman cross section or to difficult quantification. Italian excavation fragments and museum objects have compatible Raman signatures, as do the samples belonging to the first period of the Spanish production (BR1: 1760-1783). This is expected, because of the historical background. On the other hand, very specific features (e.g. α -wollastonite, scapolite, protoenstatite) can be identified for the second (BR2: 1783-1803) and third period (BR3: 1803-1808) of the Buen Retiro production. All the recognized phases are well in agreement with the results of the comprehensive characterization of the two productions.^{16,17}

3.2 Characterization of Glazes

The shape of the Raman spectrum and the so-called “Raman parameters”^{18,19} are good indicators of similarities and differences among glazes. Figure 3 shows representative glaze spectra for Capodimonte and Buen Retiro artifacts.

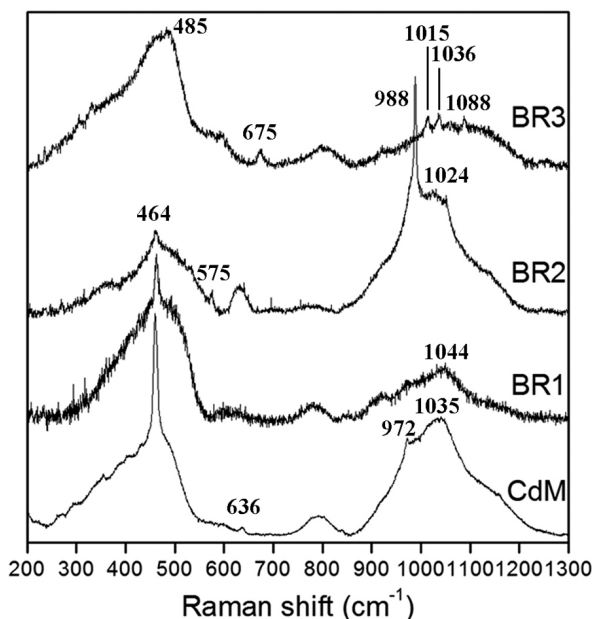


Figure 3: Representative Raman spectra of Capodimonte (CdM) and Buen Retiro (BR1, BR2, BR3) glazes. Some crystalline phases can be identified: quartz (464 cm^{-1}), β -wollastonite (636 and 972 cm^{-1}), α -wollastonite (575 and 988 cm^{-1}), enstatite (675, 1015, 1036 and 1088 cm^{-1}).

Capodimonte glazes are very homogeneous; instead, in the case of Buen Retiro, these data help identifying the three periods in which the manufacture's life is divided. All the analyzed glazes have Raman signatures similar to those observed in samples from other 18th century soft-paste manufactures,⁸ with the exception of BR3 samples, which resemble hard-paste glazes.¹⁴

3.3 Proposals for the Database

As already stated, thanks to the availability of several instruments, different experimental setups were tested, in order to optimize the data acquisition process. An in-depth discussion on this topic is beyond the scope of this paper, and details can be found elsewhere.¹⁵ It must be underlined, however, that information relative to the experimental configuration adopted should be included in all Raman database entries.

A Raman database for porcelain productions requires a different approach from the one usually adopted in spectroscopic archives. The first and main difference lies in the fact that a single spectrum cannot by any means be considered as sufficient in order to provide a typical "Raman signature" for a porcelain manufacture. Due to the material structure of a porcelain artifact, each production should be identified by coupling the information deriving from at least two spectra: one for the paste and one for the glaze. Furthermore, it is

clear that a certain degree of variability can be expected within each artifact and each production. Each object should therefore be analyzed in several spots, and several objects with the same attribution must necessarily be analyzed in order to establish a representative "reference group", as it has been the case for Capodimonte.

Figure 4 shows a general scheme which illustrates what could be the overall structure for a database entry. Historical and technological information about each manufacture should not be overlooked but rather coupled to the spectral data. The same can be said about the details pertaining to the typology, dating, visual appearance etc. of each of the objects which have been analyzed and consti-

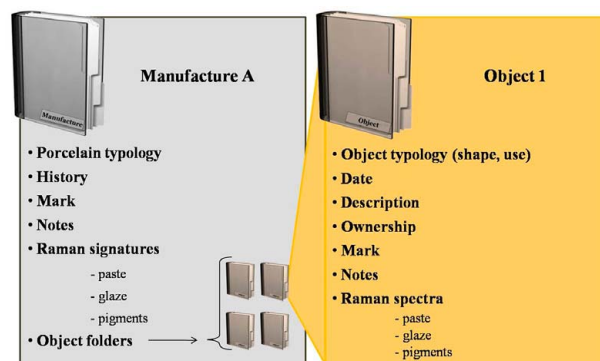


Figure 4: General scheme for an entry of the proposed Raman database for porcelains including information on a single manufacture (left) and on each of the objects attributed to it (right).

tute the "reference group" for the manufacture. Within each manufacture's folder, the "Raman signatures" field should contain information regarding the "typical" signatures of the paste, glaze and pigments of products issued from that manufacture. Specifically: - for pastes: two or three representative spectra are shown, and mineral phases are listed, which can be divided into three categories depending on their abundance and representativeness: necessary, complementary and accessory phases; - for glazes: besides the image of a representative spectrum, a number of Raman parameters should be listed, which characterize a glassy material, along with details about the methodology used for the baseline subtraction and the deconvolution of the spectra. The identification of typical values for these parameters,²⁰ as well as their classification by means of statistical methods such as principal components and cluster analysis,²¹ can be of great importance towards the identification of different productions.

Within each object's folder, the "Raman spectra" field should be linked to the single spectral files relating to the analysis of the paste, glaze (both raw and baseline-subtracted) and pigments for each analyzed object.

4 Conclusions

The Raman analyses of some Capodimonte and Buen Retiro porcelain samples allowed identifying specific signatures for pastes and glazes, leading to the establishment of “reference groups” which could serve as the base for database entries relative to each of these two manufactures. For this purpose, an experimental protocol had been previously suggested for the Raman analysis of ancient pottery and porcelain, which must be prior to the establishment of a database, in order to allow more reliable comparisons among data obtained in different labs. Of course, further Raman analyses are needed on a certain number of manufactures for validating the utility of the database. In fact, only the availability of a large number of case studies can tell us, if there exist sufficient parameters to characterize a single production. In any case, the database should be “open” so that further “identity cards” could be included in the future, as soon as analytical data become available. Finally, the combination of several non-invasive analyses, e.g. by means of portable Raman and XRF equipments, could lead to the establishment of an integrated database which would characterize each porcelain production in a more comprehensive and completely non-destructive way.

5 Acknowledgements

The authors wish to thank all the individuals and institutions which provided samples for the Raman analyses, particularly Ms. Antoinette Fay-Hallé, director of the Sèvres Museum, for allowing access to the museum’s repository and exhibition areas. Dr. Janet Ambers of the British Museum is also gratefully acknowledged for her collaboration and for fruitful discussions.

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