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On-Site Raman Analysis of Rare Ancient Ceramics : Medici Porcelain and Iznik Pottery

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Abstract

On site Raman analyses were performed at the Musée national de Céramique, Sèvres, France, on rare Iznik Ottoman pottery produced between ~1480 and ~1620 and Florentine Medici porcelain produced between 1575 and ~1587. Comparison is made with similar Sefavid (Persia, ~1500-1730) and Kütahya (from 1550 or more probably from 1680) pottery. In most Iznik/Kütahya fritwares; the white colour arises from an α-quartz slip, cassiterite (SnO_2) opacifier being present only in some early blue-and-white Iznik fritwares (Master of the Knots and Baba Nakkas style, ca. 1510-1530). We do not have other evidence of tin oxyde intentional use as an opacifier. Intentional addition of tin oxide is likely for colour lightening in some red, blue and in clear green boles. At least two types of red glazes and two types of Cr-containing dark-green to black pigments are evidenced. Analysis of Medici Porcelain shows the material was prepared using feldspar, sand and calcium-rich glass, i.e. associating hard- and soft-paste technologies. The presence of calcium phosphate in the Medici enamel indicates that calcined bone was used to opacify the glaze, like in Islamic glasses.

Introduction

Leading experts generally base their certification of ancient artefacts on stylistic analysis and on a personal feeling involving the five senses. More objective proofs are mandatory for identification and dating purpose. We demonstrate the potential of Raman spectroscopy as a non-destructive on-site technique for the characterization of ceramics and glasses [1-4]. Different technologies will often give products of very similar outward appearances (from the visual and sensory points of view), but completely different in their micro/nanostructure. Much information about the process remains written in the sample and the non-destructive Raman analysis of the micro-structure (for ceramics) and nano-structure (for glasses and enamels) offers a way to identify it and, sometimes, to date ancient artefacts. Salient features can be extracted from bodies, glazes and pigments from different productions covering the history of ceramic industry. Different Raman signatures are obtained if different technologies were applied to the same starting batch or if a given technology was applied to raw materials processed differently. In this review we will demonstrate the potential of on-site Raman spectroscopy for the identification of precious artefacts and better understanding of past technologies.

The exact origin of "Iznik" product (Iznik, Damascus ?, Istanbul ?, Kütahya ? or elsewhere) still is an open question. As for Medici porcelains, wares being very rare and shards even rarer, they are not well documented. A non-destructive analysis performed in the secure area of museums collection rooms appears as the only way to go further in identification/classification of these precious artefacts.

Experimental Procedure

Raman spectroscopy is an optical technique and can therefore be performed through different optical devices: camera lenses, microscope, remote fibre optic probe, etc. The size of the laser spot determines the surface analysed in one shot. 5000 μm^2 are illuminated, typically, in a macro configuration, while the laser spot is reduced to ~ 1 μm^2 for measurements with high magnification microscope objectives. Specific analysis of overpainting décor, glaze, underglaze décor and glaze/body interface can be made from the top (Fig. 1), using long focus microscope objectives. Body analysis can be performed on glazed or unglazed regions (rim, bottom or support spurs). The choice of the exciting radiation must be optimised as a function of the colour of the analysed pigment. Last generation prototype instruments are portable, ready to use in 10 minutes and only require an electric plug to operate. Experimental details on laboratory and on-site procedures (Fig. 1) and on the reliability of the technique have been provided in refs. [5-6].

Figure 2 shows some of the studied Iznik artefacts: a typical polychrome Iznik dish with flowers and Saz leaf and a Chinese style wave-and-rock pattern border (ca. 1575), a polychrome Iznik tile showing a brilliant white glaze, a chromite-based drawing and a red overglaze (ca. 1580-1600) and a blue-and-white dish Master of the Knots style (ca. 1510-1520). A two orifice Medici bottle and a dish with the famous S. Maria del Fiore & F letter mark as well as a typical Kütahya tile from the S. Sepulcre Church in Jerusalem are also shown.

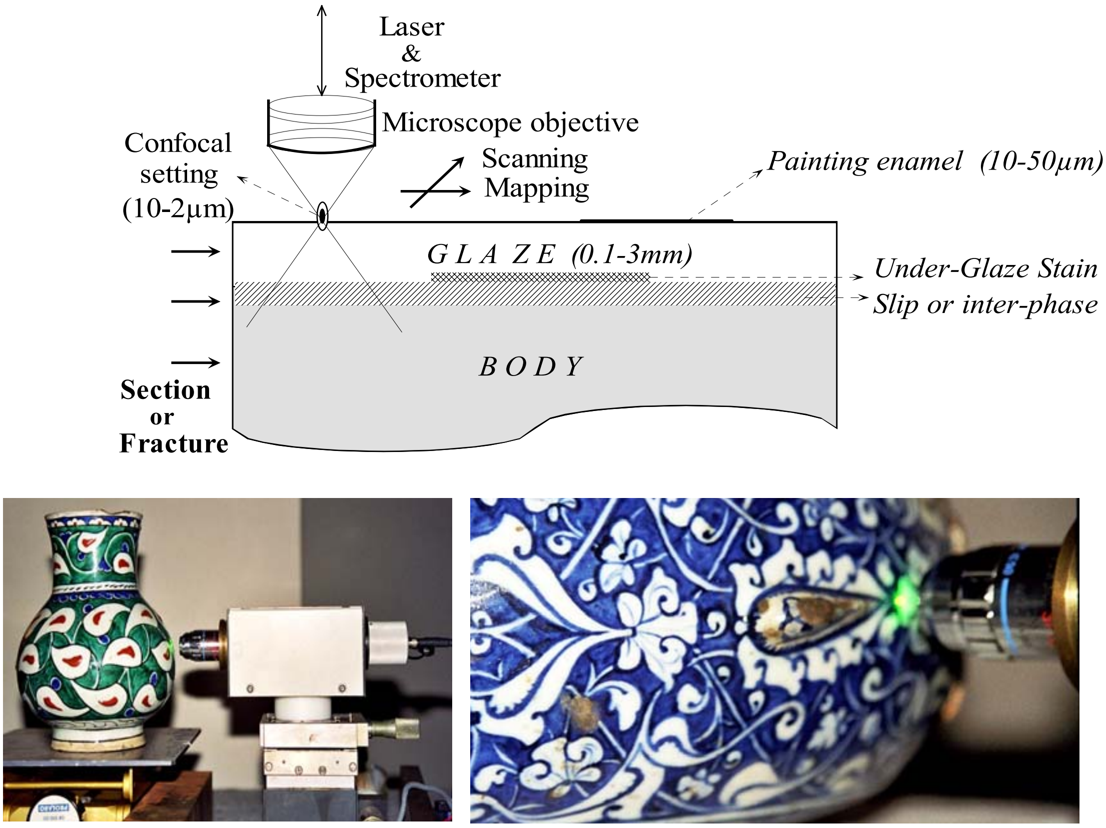

Figure 1: *The Raman analysis of a glazed ceramic. The choice of the right microscope objective enables selective examination of the over- and underglaze décor as well as the slip or glaze-body interphase. The photographs show on-site analysis of Iznik artefacts performed at the Musée national de Céramique, Sèvres, using a remote fibre optic probing through laser/spectrograph coupled microscope objectives (magnification x800); note the 3D micrometer support below the optical head. Also, the effective laser spot is much smaller than its visible halo. (Photographs © Ph. Colomban)*

Identification procedures

Raman spectra allow for:

- i) the identification of crystalline phases within the body. It is easily obtained by comparison with spectra databases ([3,4,7] and refs therein). The procedure is very similar to that employed for X-ray diffraction but Raman spectrometry is non-destructive and can be performed on-site [5,6]. For instance Raman signatures of quartz and felspar in Medici body are characteristic of an hard-paste porcelain [4], but the observation of calcium silicate signature, typical of soft-paste porcelain [4,8] indicates an hybrid technology. Furthermore small size precipitates can be detected within the glaze whereas they are hardly detected by X-ray diffraction. Figure 3 shows a typical spectrum recorded on Medici glazes. The narrow peak is the main signature of calcium phosphate [8].

- ii) the identification of the structure and composition of glassy silicates. Silicates structure consists of more or less connected (polymerised) SiO_4 tetrahedra. The Raman intensity of Si-O bending and stretching massifs vary with composition. The different components inform on the connectivity of the SiO_4 polymeric units and, thus, on the glass composition, nanostructure and processing temperature [1,2].

First, a clear differentiation is possible through the relative intensities of the components of the Si-O stretching and bending modes at ca. 1000 and 500 cm^{-1} respectively (Fig. 3). Because the SiO_4 tetrahedron is a very well defined vibrational and structural entity, its different configurations have specific vibrational fingerprints. From the literature [e.g. 1,2 and refs therein] the different spectral components of the stretching envelope were assigned to the silica vibrations with zero (Q_0 or isolated SiO_4 at ca. 800-850 cm^{-1}), one (Q_1 or dumbbell $-SiO_3$ at ca. 900-950 cm^{-1}), two (Q_2 or $=SiO_2$ at ca. 950-1000 cm^{-1}), and three (Q_3 or $\equiv SiO$ at ca. 1030-1100 cm^{-1}) bridging oxygens per tetrahedral group. Q_4 corresponds to fully polymerised tetrahedra (ca. > 1050 cm^{-1}), as in pure silica. The fitting of the bending and stretching massifs is illustrated in Fig. 3 for typical Medici (Si-O bending and stretching envelopes) and Iznik (Si-O stretching envelope) glazes.

Figure 2: *Example of Iznik fritwares (top) and blue-and-white Medici porcelains (bottom). The tile is from the S. Sepulcre church in Jerusalem and assigned to Kütahya. (Photographs © Ph. Colomban)*

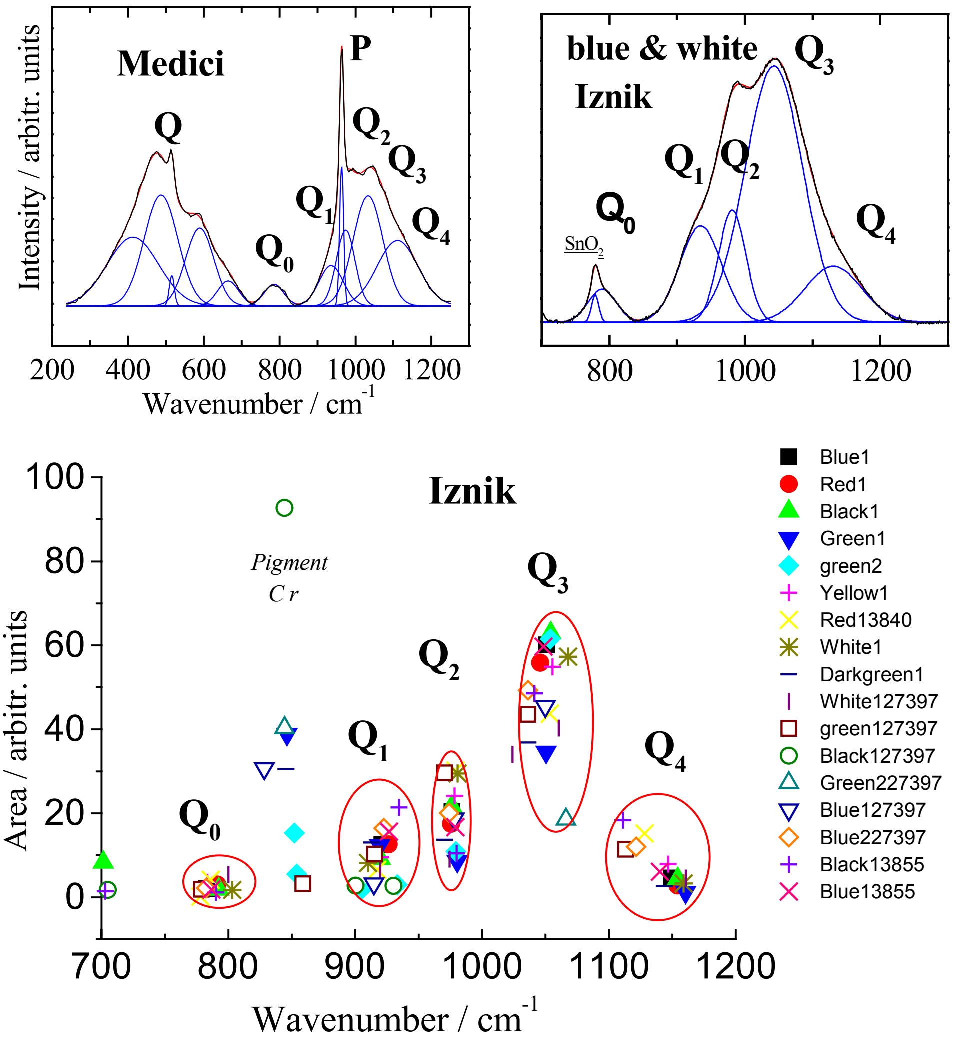

Figure 3 : Raman signatures of Medici (top left) and Iznik (top right, Master of the Knots style dish) white glazes; the baseline has been subtracted; the different Q_n components are drawn. Note the narrow peaks of calcium phosphate (P~963 cm^{-1}), quartz (Q~464 cm^{-1}) and cassiterite (SnO_2, 775 cm^{-1}). The peak area and centre of gravity of the Iznik Raman components for 12 artefacts examined in different places are shown at the bottom; circled data correspond to the Q_n components of Iznik glaze.
Other values correspond to pigments signature.

The plot of all components area as a function of their centre of gravity gives a representative view of the intrinsic homogeneity of the ceramic production (Fig. 3) and can be used to identify artefacts made with different processes. By comparison with other fritwares studied in our laboratory, the production of Iznik ware appears very homogeneous. Note the variability of Q_0 component is always very small. The variability of Q_4 component is not significant because of its strong sensibility to the baseline subtraction.

The polymerisation index I_P is calculated as the ratio of the Si-O bending envelope area divided by that of the stretching envelope ($I_P = A_{500}/A_{1000}$). The relationship between I_p, the glass composition and the processing temperature is well documented [1,8]: a first family ($I_p < 0.3$-0.5) mostly corresponds to Islamic lead-containing or lustre potteries and some Punic/Roman glasses. A second family ($0.5 < I_p < 0.8$) consists of lead-based soft-paste porcelain enamels, some Punic/Roman glasses and Iznik glazes. A third family ($0.8 < I_p < 1.1$) corresponds to most ancient glasses and 18th century soft-paste porcelain enamels. Family #4 ($1.1 < I_p < 1.3$) corresponds to celadon Ca-based enamels, family #5 ($1.3 < I_p < 2.5$) to Ca-based porcelain enamels and family #6 ($2.5 < I_p < 7$) corresponds to K-based hard-paste porcelain glazes. I_p is strongly correlated to the processing temperature (~1400°C for I_p ~7, 1000°C for I_p ~1 and ~600°C or less for I_p ~0.3).

The different Q_n components are directly related to the glass nanostructure. Considering the centre of gravity and the ratios of Q_n ($n = 1$, 2 and 3) components allows for the classification of the different productions, as shown in Table 1. Differentiation between Medici, Sefavide and Ottoman pottery glazes is straightforward from the centres of gravity but differentiation between Iznik and Kütahya production is subtler. It requires considering the area ratios. Note the procedure is also efficient to discriminate between early and late Iznik production. The scattering of the value for some types of glaze (red, green, etc.) seems to indicate that the glaze composition is a function of the glaze colour.

Parameter	**Iznik**	**Late Iznik**	**Kütahya 1**	**Kütahya 2'**	**Medici**	**Sefavide**
$\nu\ Q_1$ / cm^{-1}	920	925	929	924	943	944
$\nu\ Q_2$ / cm^{-1}	978	979	982	981	976	1016
$\nu\ Q_3$ / cm^{-1}	1052	1039	1053	1054	1035	1097
AQ_2/AQ_1	2.6	2.27	1.12	2	1.45	3.1
AQ_2/AQ_3	0.43	0.43	0.26	0.33	0.43	0.65

Table 1 *: Comparison of the Q_1 , Q_2 and Q_3 components centre of gravity (ν) and area ratio(AQ_i/AQ_j) for different glazes from the 16-17th century Ottoman productions, Medici porcelains and Sefavid fritwares. Late Iznik corresponds to artefacts assigned from stylistic analysis to production after year 1650. Differentiation between Kütahya 1 and 2' is made by considering the summit of the Si-O stretching envelope: K1~980 cm^{-1}, K2'~1050-1070 cm^{-1}.*

Pigment processing

Examination of Iznik fritware shows that the composition of the colourless glaze did not change from the beginning to the decline of the production. On the contrary, different ways were used to achieve the décor: although a quartz slip was used continuously, except in the 1510-1530 period, to mask the yellow colour of the body, different green, blue and red pigments were used. Some blue and green shades are enlightened with cassiterie addition; spinel (main peak at ~700 cm^{-1}) or garnet/chromite (main peak at ~845 cm^{-1}) are simultaneously used as for Kütahya productions (Fig. 4).

Conclusion

Combination of on-site and laboratory Raman microspectrometry appears as a very powerful non-destructive technique to go inside the ancient technology and to give an objective support to the classification (and sometime dating) of ceramics, glasses, gems, pigments used in parchments, paintings, frescoes, etc. This requires the determination of the Raman signature of the different amorphous, nanocrystalline and crystalline phases with the help of databases or using other laboratory techniques (X-ray diffraction, optical and electronic microscopy, chemical analysis, EDS, etc…). Note chromophores Raman intensities should be strongly modified as a function of the laser energy [9]. Data processing (baseline subtraction, component extraction) is the first step; the second step, which is familiar to scientists working in materials science, economy or in biology is the processing of the extracted parameters.

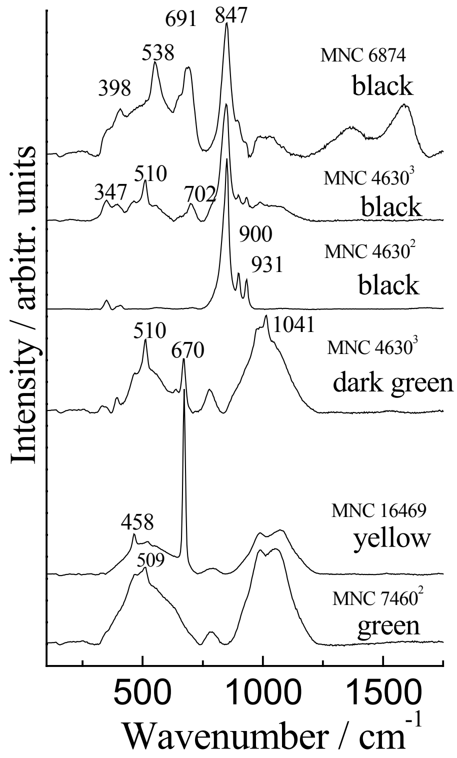

Figure 4 *: Examples of Kütahya pigments Raman signatures. Note the different signatures for dark-green and black pigments as a function of composition and concentration.*

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