

Archaeometric analysis of ancient pottery

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Leading experts generally base their certification of ancient artifacts on stylistic analysis and on personal sensory perceptions. However, greater objectivity is mandatory for identification and dating purposes. Different manufacturing technologies often result in products of very similar external appearance (from the visual and sensory points of view), but which differ completely in their micro/nanostructure. A lot of information about the production process remains written in the sample and non-destructive Raman analysis of the micro-structure (for ceramics) and nano-structure (for glasses and enamels) offers a way to retrieve the information, which assists in the identification and sometimes dating of ancient artifacts (Figure 1).



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Figure 1: Iznik dishes during analysis with a HE532 & Superhead instrument, Musée National de la Céramique, Sèvres, France

As an optical method, Raman (micro)-spectroscopy offers a great advantage over most other techniques in that it can be performed without any contact with the studied artifact, both in the laboratory using high-resolution, large spectral window instruments, as well as on-site using medium resolution, portable instruments.

All applications in the science, art and technology of glass, glazes and enamels consist in a controlled modification of the 3D Si-O network by replacement of Si⁴⁺ covalent bonded atoms by non-covalent bonded atoms, hence decreasing the number of Si-O bridges and the connectivity of the network. Consequently, the melting temperature, the viscosity at a given temperature, i.e. any physical/chemical properties related to the density and network connectivity (thermal expansion, ion diffusion, reactivity, etc.) are modified accordingly.

Direct relationships between the silica content, or more precisely the ratio between the glass-former (chiefly Si and Al -oxides) and the flux content (Na, K, Ca, Pb oxides) and the properties of glassy silicates have been established for a long time (Seeger's rules). Because strong covalent bonded structures have Raman signatures orders of magnitude larger than those of ionic ones, the Raman spectrum of a silicate consists, as a first approximation, solely of the signature of the Si-O network (Si-O stretching, bending and librational/collective modes).

Because a SiO₄ tetrahedron is a solid chemical and vibrational entity (molten silicates retain a strong polymeric character), it is well established that the different tetrahedral arrangements have characteristic Raman signatures (Figure 2). These arrangements include an isolated tetrahedron referred to as Q₀, tetrahedra linked by a common oxygen atom (Si₂O₇ or Q₁), tetrahedra linked by sharing 2 oxygen atoms (three (Si₃O₉) and n tetrahedral-cycles: Q₂), tetrahedra linked by sharing 3 oxygen atoms (Q₃, e.g. in some chains, ribbons and layers) and Q₄ (as in pure SiO₂).

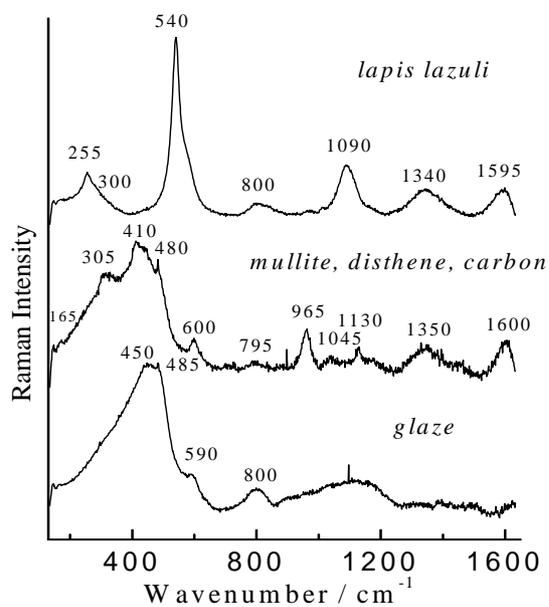


Figure 2: Representative Raman spectra recorded at the laboratory on the glaze-body interface fracture of a Böttger ewer stopper from ~1725 (MNC 7152); note the lapis lazuli signature (Meissen, Saxony)



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Figure 3: Della Robbia pot, Musée National de la Céramique, Sèvres, France

Six years of experience on various materials has enabled us to propose a tentative guide to identify different types of glassy silicates and to classify them as a function of their composition [1-7] using two main tools:

i) the spectral decomposition of the Si-O stretching peak into its components associated to the different types of SiO₄ tetrahedra of the silicate polymerized network area and

ii) a new concept, the polymerization index Ip calculated as the ratio (A₅₀₀/A₁₀₀₀) of the Si-O bending (~500 cm⁻¹) and stretching (i.e. ~1000 cm⁻¹) [3,4]. However, many properties of a glass depend on its chemical composition, which is a result of the kind and ratio of the raw materials used in the batch (mixture of raw materials).

On-site analysis in Museum-secured areas has been performed on different productions: Della Robbia sculptures and pots (Figure 3), Bernard Palissy rocaille shards excavated from Louvre site, Medici Firenze [5] and Böttger Meissen first European porcelains (Figure 4), as well as Ottoman ceramics. [7-10]



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Figure 4: Medici Porcelain, Musée National de la Céramique, Sèvres, France

In order to draw conclusions about artifacts whose origins are in debate, it is necessary to study systematically and in a non-destructive manner artifacts with good pedigree in order to go further in identification/classification of these precious items. Using the protocols described in the previous paragraphs, classification of such artifacts was performed by plotting the polymerization index as a function of ν_{max} , the main Si-O stretching component wavenumber (Figure 5). Classification in 7 distinct families is evident: from top to bottom as a function of the melting/processing temperature (at the top porcelain and then stoneware glazes, below,

faience and terra-cotta glazes and glasses, all types of low temperature processed silicates), and from left to right as function of the main flux.

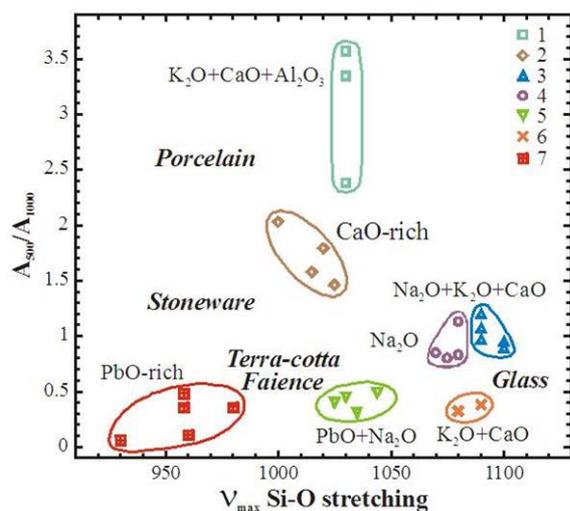


Figure 5: Plots of the polymerization index as a function of the main Si-O stretching component wavenumber

However, Iznik and Kütahya wares and the history of their production remain a source of debate among scholars. The exact origin of “Iznik” products (Iznik, Damascus, Istanbul, Kütahya or elsewhere) is still an open question. As for Medici porcelains, wares (and shards) being very rare, they are not well documented and some fakes have been made for centuries. Some of the earlier fritwares are generally assigned to Iznik productions (blue and white wares sometimes classified as Touran, Roumi or Abraham of Kütahya style), but their production by Kütahya kilns was questioned. The real development of the production of Kütahya wares dates back to the end of the 17th century, following the emancipation of Byzantine and Armenian Christian communities. Furthermore, copies or fakes were made since the 19th century in different places.

The same analysis and classification was thus performed on Iznik and Kütahya wares (Figure 6). Some of the Kütahya glazes can be associated to family 7 (PbO-rich glass) but some of them are also located in the Iznik group (e.g. sample 7460). On the other hand, Iznik glazes are all located in between family 5 (Na₂O + PbO) and family 4 (Na₂O-rich silicates)

except for two types of glazes located in family 7 (PbO-rich) and in family 2 (CaO-rich).

The Raman signature of the Iznik production thus appears to be fairly homogeneous. This is due to the fact that Iznik manufacturers were controlled by the *nakkashane*, the Ottoman office for décor and drawing. By contrast, the significant variation in the Raman signature of the Kütahya glazes reflects the autonomy of different production centers working according to the Kütahya style. Furthermore, the procedure was also efficient to discriminate between early and late Iznik production, based on a small compositional shift of the silicate glaze at the decline of the production (17th century) [8].

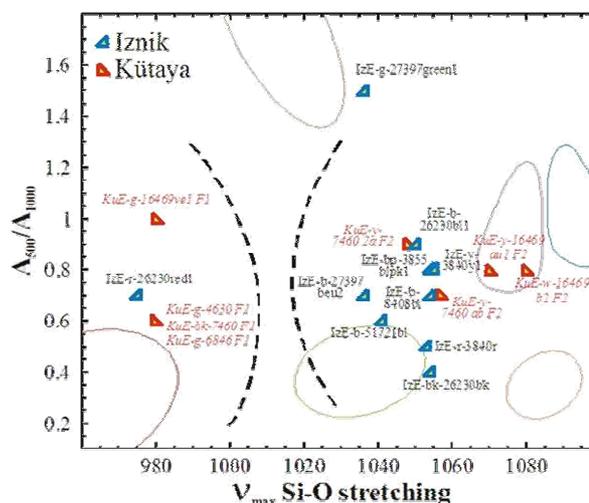


Figure 6: Bi-plot of the polymerization index (I_p) as a function of the Si-O stretching wavenumber maximum for the series of Iznik and Kütahya fritware glazes. Sample label: Curator' assignment (Iz, Iznik; Ku, Kütahya), color (b: blue, r: red, ...), artifact record number.

The two parameters I_p and v_{max} , thus appear to be good tools for classification, and differentiation between Kütahya and Iznik Ottoman pottery is relatively straightforward from the Raman fingerprint [7,8].

Analysis of the colorless/white regions of the samples always reveals the more or less strong Raman signature of α -quartz (Figure 7). By modifying the focal point of the laser with the XYZ plate it is possible to confirm that the white color is obtained by an α -quartz-rich slip

deposited below the glaze. This quartz layer is at the origin of the high gloss and very powerful colored décor. Note that the technique of a white α -quartz slip to mask the red color of the body was already used for Vietnamese porcelain and stoneware.

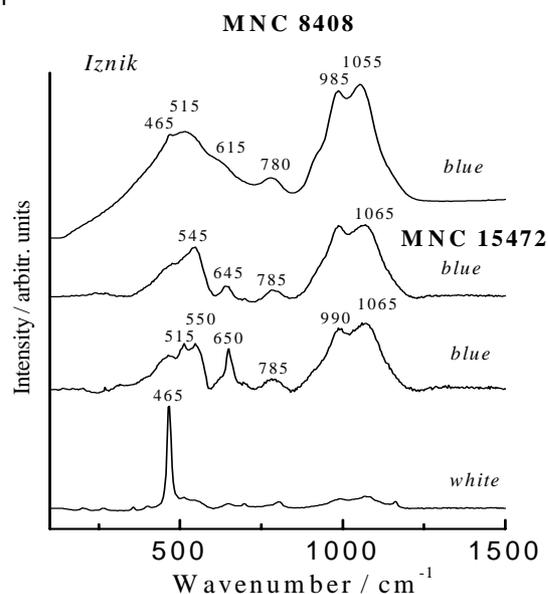


Figure 7: As-recorded spectra for Iznik glazes. Note the very strong quartz fingerprint for white glaze due to the characteristic quartz slip deposited on the body, below the glaze layer.

Strongly colored regions give a strong Raman signature, nearly free of any background (Figure 7). The ways to obtain a blue glaze are rather limited: copper in alkaline silicate (turquoise), cobalt (blue) and lapis lazuli (ultramarine blue), whatever the fluxing agent [7]. The last pigment has a very typical resonance Raman signature when excited with the 532nm laser. If small amounts of cobalt (copper) dissolve in the glaze, no specific Raman signature is expected. Saturation leads to cobalt mixed silicates or to cobalt aluminate. Cobalt-containing Mn-rich ores (spinel) can also be used as blue pigments, if the firing is conducted in a reducing atmosphere. The observed color excludes the use of lapis lazuli and Cu. In most blue regions analyzed, we only observed the Raman signature of the glaze,

which indicates that cobalt is dissolved within the glaze network.

In conclusion, this work has shown that Raman microanalysis is invaluable in assisting in the characterization of all types of ceramic artifacts. The information obtained on the composition of the glaze and pigments can yield important information on the fabrication and processing of these ancient artifacts and may even help putting to rest many controversies about the provenance of certain pieces.

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