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# RECENT CASE STUDIES IN THE RAMAN ANALYSIS OF ANCIENT CERAMICS : Glaze Opacification in Abbasid Pottery, Medici and 18th century French Porcelains, Iznik and Kûtayha Ottoman Fritwares and an Unexpected Lapis Lazuli Pigment in Lajvardina Wares

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## ABSTRACT

We demonstrate the potential of Raman spectroscopy as an on-site technique for the characterization of ancient ceramics. This non-destructive analysis offers a way to get information on the process and even sometimes on the date of ancient artifacts. Much information remains written in the microstructure of ceramics bodies and in the nanostructure of glasses, glaze and enamels. Raman signatures are specific to the technology that was applied to a given starting batch and to the process of manufacture. Recent studies that demonstrate : i) the use of cassiterite for opacification and its role in Islamic three-color wares and polychrome lustred pottery from the Abbasid to Fatimid period, ii) the invention of the "hybrid-paste porcelain" by the Duke of Medici, known as Medici porcelain and of the "soft-paste" porcelain by the French Manufactures in the eighteen century (Chantilly, Mennecy, Saint-Cloud), iii) the development of the underglaze pigment technology by Iznik and then Kütayha Ottoman potters; iii) the use of lapis lazuli gem as an unexpected pigment in the Iran *Lajvardina* wares. Finally we explore the relationship between glass makers and potters.

## INTRODUCTION

Leading experts generally base their certification of ancient artifacts on stylistic analysis and on a personal feeling involving the five senses. More objective proof is mandatory for authentication and dating purposes. We demonstrate the potential of Raman spectroscopy as a non-destructive on-site technique [1-7]. Salient features thus can be extracted from bodies, glazes and pigments from different types of production covering the history of ceramic industry. In this review we will demonstrate the potential of on-site Raman spectroscopy for the identification of precious artifacts and better understanding of past technologies.

Tin oxide (cassiterite) is a very good Raman scatterer and its detection is straightforward from its 635-775 $cm^{-1}$ doublet, for example see the Chantilly glaze in Figure 1. Thus, the recognition of its use is one of the very useful applications of Raman scattering. We review here some of our recent examinations. First, Abbasid copies of three-color Tang Dynasty pottery and eighth to fourteenth lustre pottery. We demonstrate the un-expected use of cassiterite to opacify some early Iznik fritwares as well the use of cassiterite to lighten some pigments [8]. The data processing of the Raman signature of Iznik and Kütahya pottery glaze is used to discriminate between early and late productions [9]. Particular attention is paid to Iznik and Kütayha pigment, the role of black line drawing in Iznik wares to prevent color diffusion is pointed out. Finally we will address the use of calcium phosphate ("bone ash") as opacifier for Medici porcelain glaze [10] and of lapis lazuli as blue pigment [11].

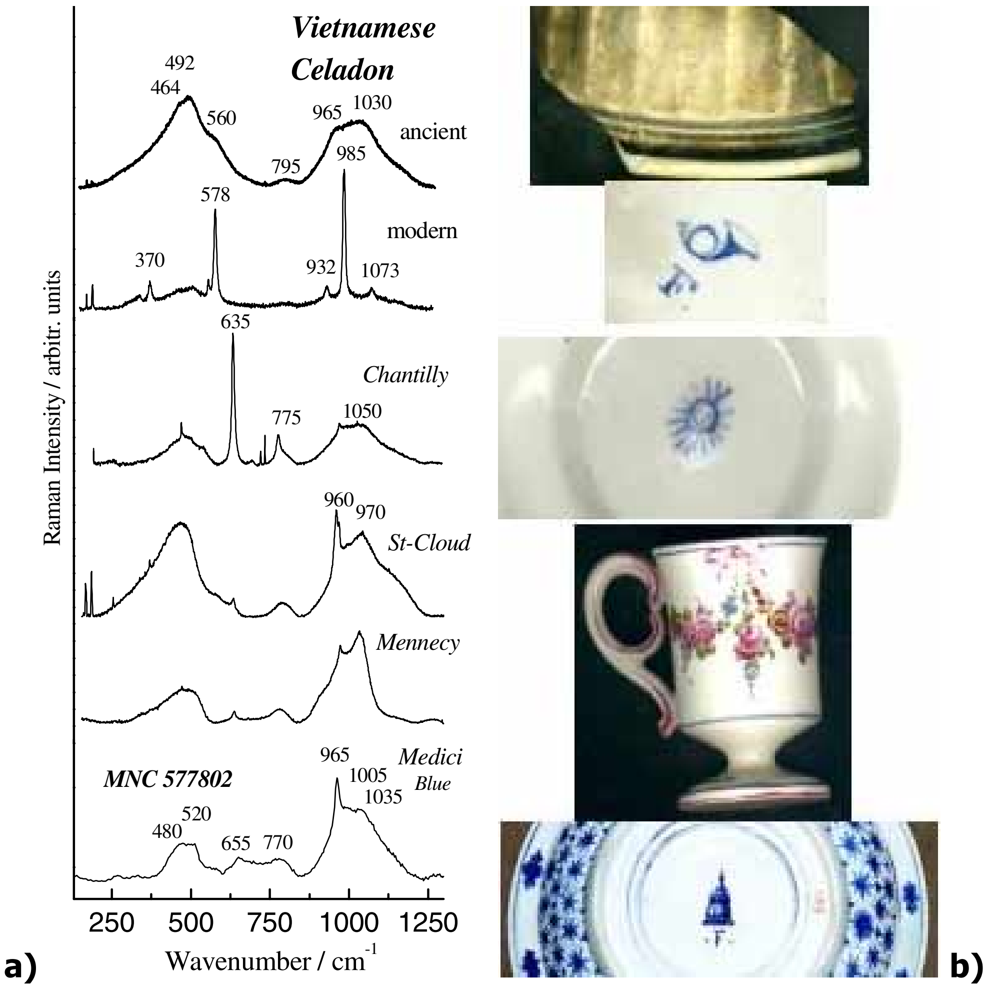


**Figure 1** : Representative Raman spectra recorded on different glazes : from the top, a Vietnamese original 15th century and a modern celadon, French 18th century Chantilly, Saint-Cloud and Mennecy factory soft-paste porcelains and hybrid 16th century Medici porcelain from the Musée National de Céramique (Sèvres, France) ; note the narrow peaks arise from nano- and microcrystals within the glaze: quartz ~465 $cm^{-1}$, feldspar ~510 $cm^{-1}$, wollastonite ~575-985 $cm^{-1}$, cassiterite 635-775 $cm^{-1}$ and calcium phosphate ~965 $cm^{-1}$. Corresponding samples are shown on the right : celadon, Chantilly, Saint-Cloud, Mennecy and Medici wares (photographs © Ph. Colomban).

Details about the Raman procedure can be found in previous publications [1,3-11] and in a companion paper in this volume [2].

## GLAZE WITH DISSOLVED TIN AND CASSITERITE ($SnO_2$) OPACIFICATION

Cassiterite has a high refractive index and precipitates from a tin-saturated silicate glass containing more than 6-8 wt% Sn. Abbasids potters are considered by many researchers to be the first to use tin oxide as an opacifier [12,13]. Three-color Tang Dynasty copies are considered to be representative of this same new technology [12]. These conclusions are based on chemical/elemental analysis, which cannot distinguish between dissolved tin atoms in solution and those belonging to cassiterite micro/nanocrystals [13]. Effectively, EDS analysis of the cream, blue and green glazes of the three-color sample presented on Figure 2 [7] shows that cream, blue and green glazes contain tin element, at very different contents (Table 1). Some points of the cream glaze have up to Sn 50 at. %.

**Table 1**: Tin and Lead content in a early three-color Tang Dynasty Abbasid copy

| Color | Cream | Green | Blue |
|---|---|---|---|
| EDS of Sn / at. % | 6-20 | 2-3 | 4-5 |
| EDS of Pb / at. % | ~1-5 | ~5 | ~11 |

However, as shown in Figure 3, the Raman signature of cassiterite is only observed in the Ca-rich green glaze and especially at the border with the lead-poor cream glaze [7]. Note that cream, blue and green glazes contain respectively ~1 (rare points contain up to 5), ~11 and ~5 Pb % at.

It is clear that Sn was not used as opacifier, and its precipitation at the green to cream border results from the reaction between the green and cream glazes. For each type of glaze the Pb/Sn ratio is almost constant indicating that Sn is an impurity in the Pb source.

**Figure 2** : Representative pottery from the top, left then right : on-site examination of a late Iznik polychrome dish (ca. 1625-1650, MNC19577), polychrome Kütahya bowl (MNC4630-3), blue and white Baba Nakkas style Iznik tile (ca. 1510-1530) and three-color pottery from Bagdad or Basra, 9th century (private coll.) ; 13-14th century Iran *Lâjvardina* ewer (private coll.) ; details of the interface between the body and the glaze are shown for two cuts, one // to the interface, the other perpendicular. Detail of the green to cream border is shown for the three-color Abbasid copy of a Tang Dynasty ware. (photographs © Ph. Colomban).

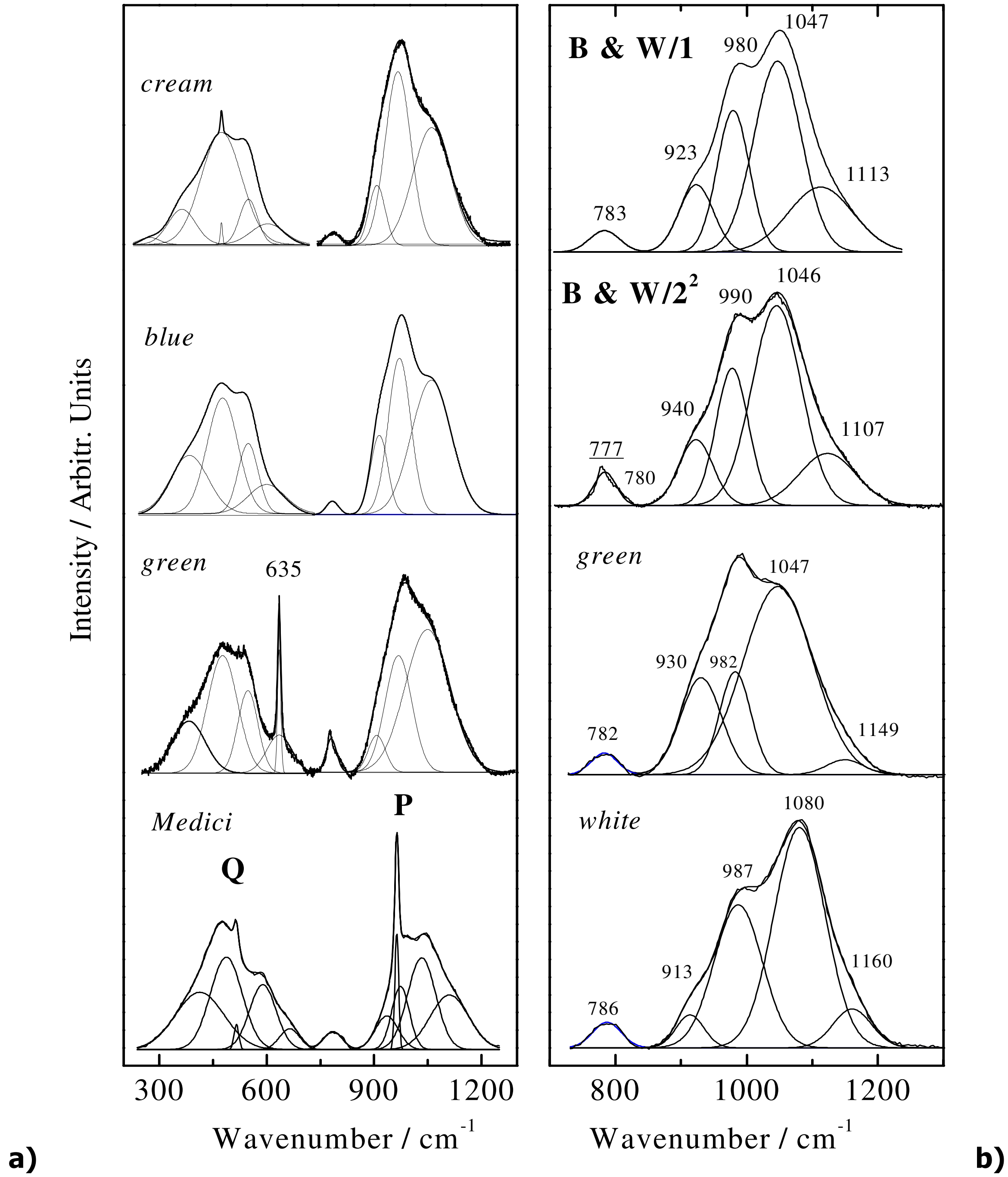


**Figure 3** : (a) Comparison of the representative Raman signatures of cream, blue and green (border) glazes of the three-color Abbasid Tang's copy and of Medici porcelain glaze ; (b) details of the Raman signature for different location of the blue and white Iznik ware shown ; type 1 (green) and type 2 (white) Kütahya glaze signatures are shown.

In most Iznik/Kütahya fritwares, the white color arises from an α-quartz slip (sharp peak at 465 $cm^{-1}$), 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, Figure 2) [8,10]. We do not have other evidence of the intentional use tin oxide as a white opacifier. On the contrary, intentional addition of tin oxide is clear for color lightening in some red, blue and light-green glazes.

## THE ROLE OF TIN OXIDE IN LUSTRE FORMATION

To date, all lustre glazes studied by Raman scattering contain elemental tin and also a clear cassiterite Raman signature in the region below the lustre-containing film [7]. Thus, the use of cassiterite as an opacifier to create a white background for the decoration drawing is straight forward. Another important characteristic of tin protoxide is its ability to electroreduce $Ag^+$ and $Cu^+$ (or $Cu^{++}$) ions into the corresponding Ag° and Cu° metal particles [14,15], which is consistent with this analysis.

## BONE ASH OPACIFICATION OF MEDICI GLAZE

Analysis of Medici porcelain body shows that the body was prepared using feldspar, sand and a calcium-rich glass, i.e. associating hard- and soft-paste technologies [9]. The presence of calcium phosphate signature in the Medici glaze (characteristic peak at ~965 $cm^{-1}$, see Figure 1) indicates that a bone ash or a calcium phosphate-containing raw material was used. A similar signature is observed for Saint-Cloud glaze. The addition of calcined bone is well documented for the eighteenth and nineteenth century pottery. This composition technique also is reported for some Islamic enamels [16,17].

## THE PIGMENT TECHNOLOGY

Examination of Iznik fritware shows that the Raman signature of the silicate glaze, boths its composition and nanostructure, does not change very much from the beginning to the decline of the production. On the contrary, different ways were used to achieve the decoration. A quartz slip was used almost continuously in order to mask the yellow color of the body except in the 1510-1530 period. However, different green, blue and red pigments were used. Spinel (main peak at ~700 $cm^{-1}$) or garnet/chromite (main peak at ~845 $cm^{-1}$) are simultaneously used for Iznik and Kütahya green and black productions (Figure 4) [10,18]. The non-stoichiometry of these two compounds allows trapping of any ions ($Cu^+$, $Co^{2+}$, etc.) diffusing from a colored region to a color-less one. Thus, the black line has two functions, the drawing and the sharpening of the decoration.

Raman analysis of an ancient ewer (Iran, 13$^{th}$ century) belonging to the *Lâjvardina* blue glazed ceramic tradition shows that the ultramarine color results from the unexpected deposit of a lazurite- and diopside-rich slip at the interface between the body and a cobalt-containing lime-rich glaze (~0.9 Co, ~15 Ca %at.). This confirms the use of *Lâjvard* or lapis lazuli as a pigment, as reported in the old alchemical treatise of Abû'l Qâsim Kâshâni (14$^{th}$ century). Until now, the mention of *Lâjvard* was interpreted as a way of imitating the lapis lazuli color. Raman spectra recorded on the glaze and on the blue dispersion are given in Figure 5. The 1$^{st}$ order Raman signature of the blue *lapis lazuli* grains has peaks at 260 and 548 $cm^{-1}$. The Raman spectrum also shows multiple bands (548 x 2 = 1096, 548 x 3 = 1644 $cm^{-1}$, x4, x5, x6…) or combinations (260 + 548 = 808 $cm^{-1}$; 260 + (2 x 548) = 1358 $cm^{-1}$ …), which are characteristic of the resonance Raman spectrum of $S_3^-$ ions [11].

EDS measurements confirm that calcium is the chief fluxing element. A rather large amount of magnesium is observed as well as some cobalt (0.9 %at), iron (4.3 %at) and titanium (1.1 %at). Raman analysis of the white grains in between the blue ones yields the spectrum of diopside, a mixed magnesium calcium silicate. Traces of Ni, Cr and Zn are observed, which is consistent with a previous analysis on Co-colored glasses and glazes from Iran [16]. We conclude that a dispersion of lapis lazuli (lazurite and diopside) has been deposited at the body/glaze interface in order to get a true ultramarine shade and not a light-blue, as obtained by dissolving cobalt in the glass network. The glaze appears to be made of many layers. This phenomenon arises either from the deposition of each layer, successively, or from the cracking of the deposit in many layers due to the thermal expansion mismatch of different glaze layers or to the slip. Careful observation of the coating shows blacker regions in between successive layers, and these regions exhibit the characteristic Raman spectrum of carbon-containing material (doublet at 1360 and 1580 $cm^{-1}$). This observation is consistent with a multi-layer deposition. The presence of rather large amounts of magnesium and iron in

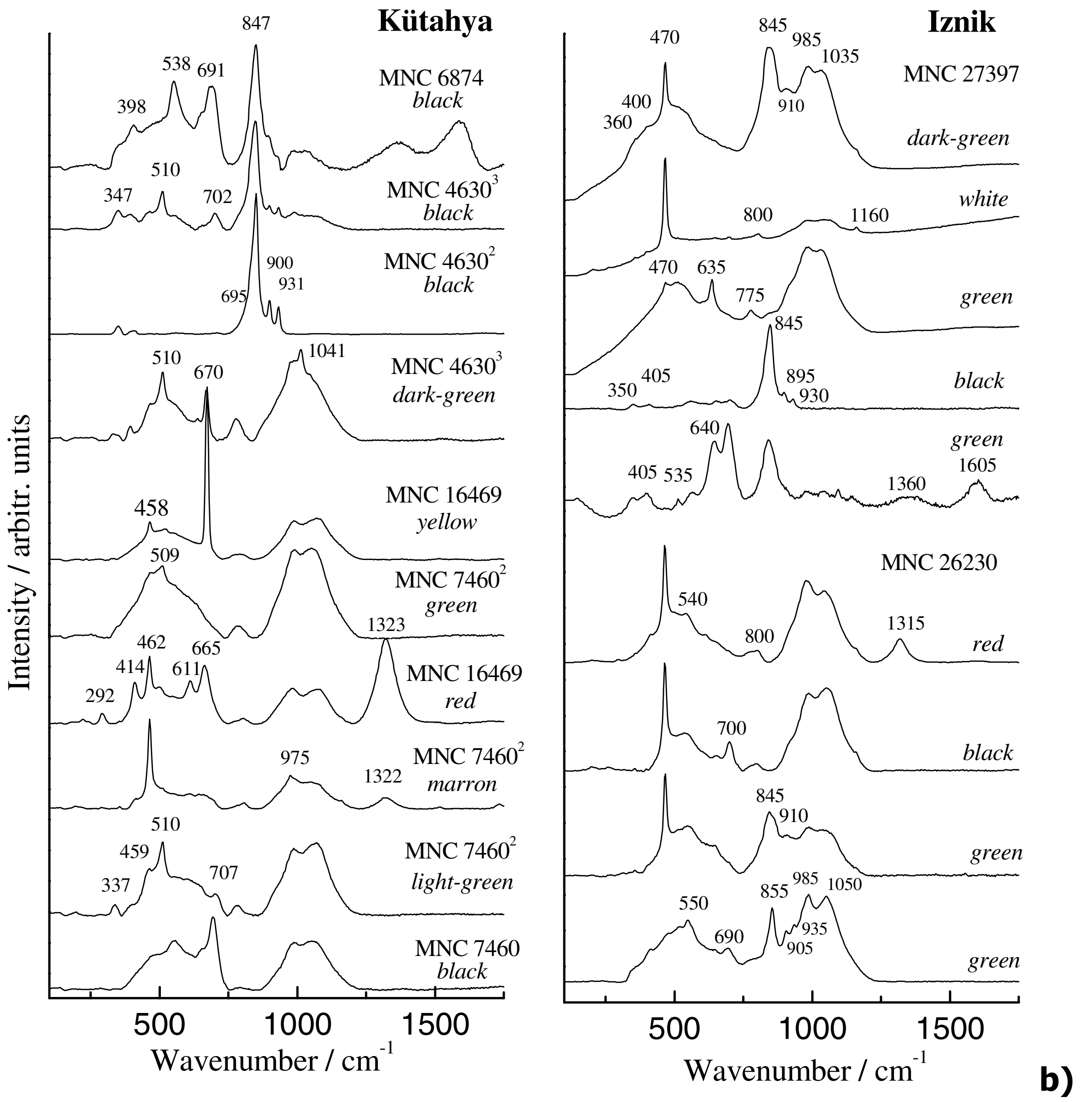


**Figure 4** : Typical on-site recorded Raman signatures for green and black pigments of Kütahya and Iznik wares. Note that similar colors show different Raman signatures.

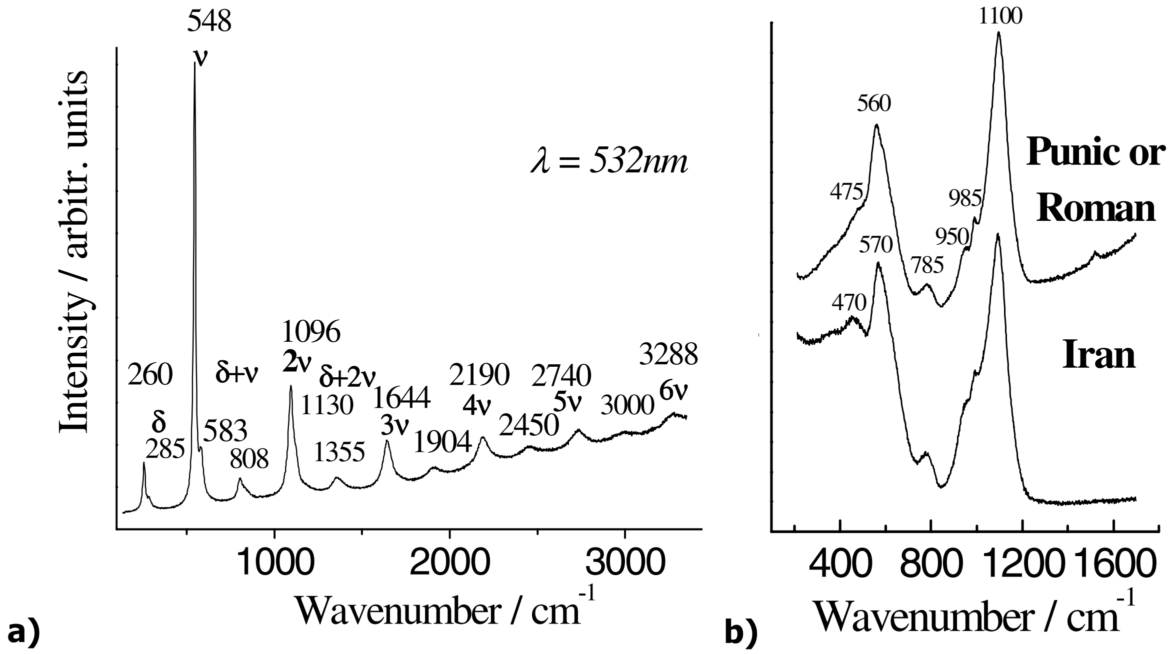


**Figure 5** : (a) Resonance Raman signature of lapis lazuli grains in a Lâjvardina ewer ; note the similarity between the signature of the Iranian *Lâjvardina* glaze and (b) that of a typical Punic or Roman glass (second B.C. to second A.D. century).

the glass is also consistent with the deposition of lapis lazuli powder in between each glassy layer. The thermal stability of sodalite is rather limited and bleaching of lazurite is observed above 1000-1100°C. The vivid ultramarine color is thus not easy to obtain because the glaze is processed at a temperature very close to that at which lazurite-bleaching occurs. Could the potter have used a "*raku*" or fast-fire technique in introducing the ceramic just after the deposition of the layers of lapis lazuli and glaze in a hot furnace ? What is the proportion of *Lâjvardina* ceramics produced with this advanced technique? Note that the use of lapis lazuli in place of cobalt to color glass enamels has been recently established in many thirteenth and fourteenth century Islamic enamelled glasses [15,17].

## CONCLUSION

Combination of on-site and laboratory Raman microspectrometry appears as a very powerful non-destructive technique to investigate the ancient technology. 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…). A cautionary note is that the Raman intensities of chromophores are strongly modified as a function of the laser energy [6]. The cases studies presented here show that the determination of elemental composition is not sufficient to understand pottery micro/nanostructure and its technology. The results also demonstrate the similarity between the processing of glasses and glazes.

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## REFERENCES


1. Ph. Colomban, “Glasses, glazes and ceramics – Recognition of the ancient technology”, *Raman Spectroscopy in Archaeology and Art History*, ed. H.G.M. Edwards and J.M. Chalmers (Royal Society of Chemistry, Cambridge, 2005), 192-206.
2. Ph. Colomban, this volume.
3. Ph. Colomban, J. Non-Crystalline Solids, **323**, 180 (2003).
4. N.Q. Liem, N.T. Thanh and Ph. Colomban, *J. Raman Spectr*. **33**, 287 (2002).
5. Ph. Colomban and F. Treppoz, *J. Raman Spectr*. **32**, 93 (2001).
6. Ph. Colomban, G. Sagon and X. Faurel, *J. Raman Spectr*. **32**, 351 (2001).
7. Ph. Colomban and C. Truong, *J. Raman Spectr*. **35**,195 (2004).
8. Ph. Colomban and V. Milande, Proc. 1st Worshop on Science, Technology and Cultural Heritage”, 29 June-2nd July 2004, Venice, AIV.
9. Ph. Colomban, Milande V. and H. Lucas, *J. Raman Spectr*. **35**, 68 (2004) ; see also W.D. Kingery and P. Vandiver, Ceramic Masterpieces, 1986.
10. Ph. Colomban, V. Milande V. and L. Le Bihan, *J. Raman Spectr*. **35**, 68 (2004).
11. Ph. Colomban, *J. Raman Spectr*. **34**, 420 (2003).
12. J. Allan, *Islamic Ceramics*, Christie’s handbooks, Ashmolean Museum, Oxford (1991).
13. M.S. Tite, I. Freestone, R. Mason, J. Molera, M. Vendrell-Saz, and N. Wood, *Archaeometry* **40**, 241 (1998).
14. M.W. Medlin, K.D. Sienerth and H.D. Schreiber, *J. Non-Crystalline Solids* **240**, 193 (1998).
15. Ph. Colomban and H.D. Schreiber, *J. Raman Spectr*. **36**, (2005).
16. I.C. Freestone and C.P. Stapleton, “Composition and technology of Islamic enamelled glass of the thirteenth and fourteenth centuries”, *Gilded and Enamelled Glass from the Middle East*, ed. R. Ward (BMP, London, 1998).
17. W.E.S. Turner and H.P. Rooksby, *Glastechnische Ber.*, Sonderband V, International Glaskongress, **32k-8**,17 (1959).
18. Ph. Colomban, R. de Laveaucoupet and V. Milande, *J. Raman Spectr*. **36**, (2005).
19. J. Henderson**,** “Blue and other colored translucent glass decorated with enamels : possible evidence for trade in cobalt-blue colorants “, *Gilded and Enamelled Glass from the Middle East*, Ed. R. Ward, (BMP, London, 1998).