

DOI: 10.5281/zenodo.1409802

TECHNOLOGICAL EXAMINATION OF IZNIK CERAMICS BY SEM-EDX, RAMAN, XRD, PLM: A CASE STUDY

Panagopoulou, A.^{1,2}, Lampakis, D.², Christophilos, D.³, Beltsios, K.⁴, Ganetsos, Th.⁵

¹Laboratory of Archaeometry, Institute of Materials Science, NCSR Demokritos,
15 310 Ag. Paraskevi, Attika, Greece.

²Department of Protection and Conservation of Cultural Heritage, University of Ionian Islands, School of
Technological Applications, Zante Island, 29 100, Greece.

³School of Engineering, Aristotle University, Thessaloniki 54124, Greece

⁴Department of Materials Science and Engineering, University of Ioannina, 45 110, Ioannina, Greece.

⁵Piraeus University of Applied Science, Laboratory of Non-destructive techniques, 250 Thivon & P. Ralli
Str., 12244, Egaleo, Attica, Greece

Received: 20/06/2018

Accepted: 07/08/2018

Corresponding author: Panagopoulou, A. (mpanagopoulou@hotmail.com)

ABSTRACT

A group of Iznik ceramics of the Islamic Museum, Benaki Museum in Athens was studied in this work. The ceramics originate from Nicaea in Asia Minor and date between 15th and early 18th century AD. A structural and chemical characterization of the sherds is pursued through the use of Raman Spectroscopy. In addition, technological properties such as the porous, mineral phases and glassy, texture and the orientation of grains and aggregates were given and important information concerning the aspects of construction and decoration of Iznik pottery were obtained through the use of Optical Microscopy, Scanning Electron Microscopy, Raman Spectroscopy and X-Ray Diffraction. The results confirm the presence of three layers: the body, the slip and the glaze that contains cassiterite (SnO_2). Also, the purple hues in addition to iron oxides contain manganese ones as well. Greens are characterized by enhanced presence of iron and copper. Finally, black contour lines are based on the Cr_2O_4 - MnO - Fe_2O_3 combination and are used for the definition of borders of colored area.

KEYWORDS: Iznik ceramics, Optical Microscopy, Scanning Electron Microscopy, Raman Spectroscopy, X Ray Diffraction

1. INTRODUCTION

Islamic ceramic art reached the pinnacle with the production of pottery and tiles in Iznik (Nicaea) between the 15th and early 18th centuries. The main characteristic of Iznik ceramics for both types of ceramics is the use of lead-rich fritted body mainly in the 16th century. The aim of using frit was to prevent the formation of bubbles on the glaze surface. The frit not only acts as flux but also promotes brightness and glossiness. The potters had first tried this new technological method with the production of vessels and it came into prominence during the 15th century (Watson, 2006; Colomban, 2004).

The best period of Iznik ceramics was during the 15th until the early 18th century AD and their main characteristic is the lead rich glaze; lead oxide not only acts as flux but also promotes brightness and gloss. In addition to lead oxide, tin oxide is also present as regards the glazes of the sherds under consideration. In Iznik pottery tin oxide often acts as an opacifier (Simsek *et al.*, 2009). During the peak period, Iznik pottery products exhibit decoration with rich coloration; blue, turquoise, green, black, purple, red and grey are the standard decoration colors of that period (Carswell, 1998; Atasoy and Raby, 1989).

With this study it is demonstrated the potential of Raman spectroscopy as a technique for the characterization of ceramics and glasses (Colomban, 2003;

Liem, 2002; Tite, 1989). A lot of information about the process remains written in the sample and the Raman analysis of the micro-structure) and nano-structure (for glasses and enamels) offers a way to identify it. Sometimes, is a helpful way to date ancient artefacts. Main characteristics 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 are demonstrating the potential of on-site Raman spectroscopy for the identification of precious artefacts and better understanding of past technologies. A one site analysis performed in the secure area of museums collection rooms appears as the only way to go further in identification/classification of these precious ceramics artefacts (Colomban, 2001).

2. MATERIALS AND EXPERIMENTAL TECHNIQUES

The study includes 20 Iznik sherds, which originate from Nicaea in Asia Minor and now are belonging to the collection of the Benaki Museum, Athens (Fig.1). The sherds date from the 15th to the early 18th century AD.

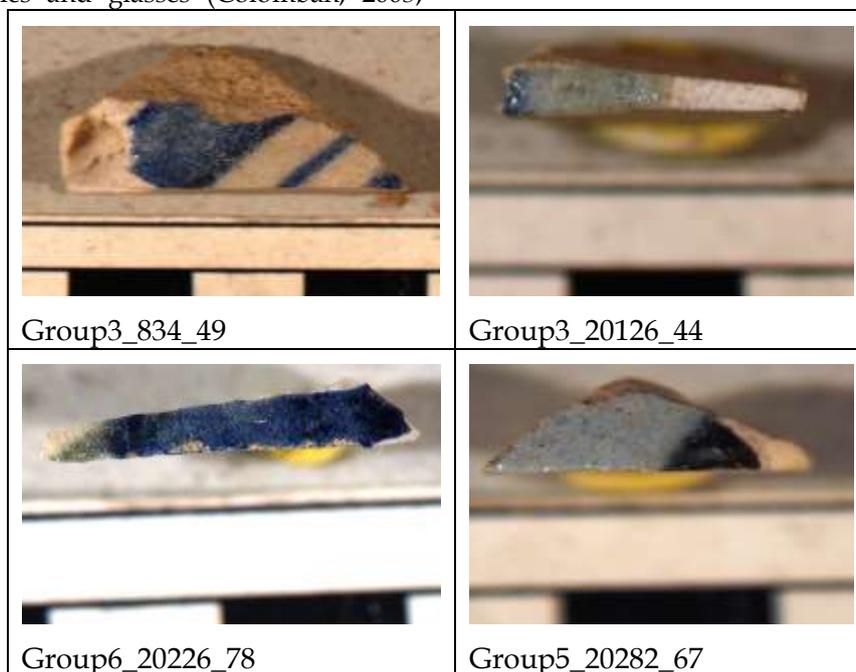


Figure 1: Samples of the Iznik wares.

The initial visual examination and photography of the samples cross sections was conducted using a LEICA DM 2500 M polarizing microscope, equipped with a quartz halogen lamp and an UV excitation light source (100 W).

Scanning Electron Microscope images and EDAX measurements were obtained by using the SEM-EDX: FEI SEM-EDX-EDAX system.

The X-Ray Diffraction patterns were collected at room temperature using a Siemens XRD 500 with anticathode Cu-K α setup.

Raman measurements were performed on a Lab Ram (Jobin Yvon) spectrometer equipped with a confocal aperture. The samples were investigated in the backscattering geometry under the microscope (objective 100 \times). The green beam ($\lambda=514$ nm) of an Ar⁺ laser was focused to a spot of diameter 1-3 μ m. The instrument was calibrated just before and right after each measurement, by using the spectrum of a silicon wafer as a reference.

3. RESULTS AND DISCUSSION

Figure 2 presents the stratigraphy of an Iznik sample (G3_49) based on microphotographs in reflected light and the SEM images of the cross-section.

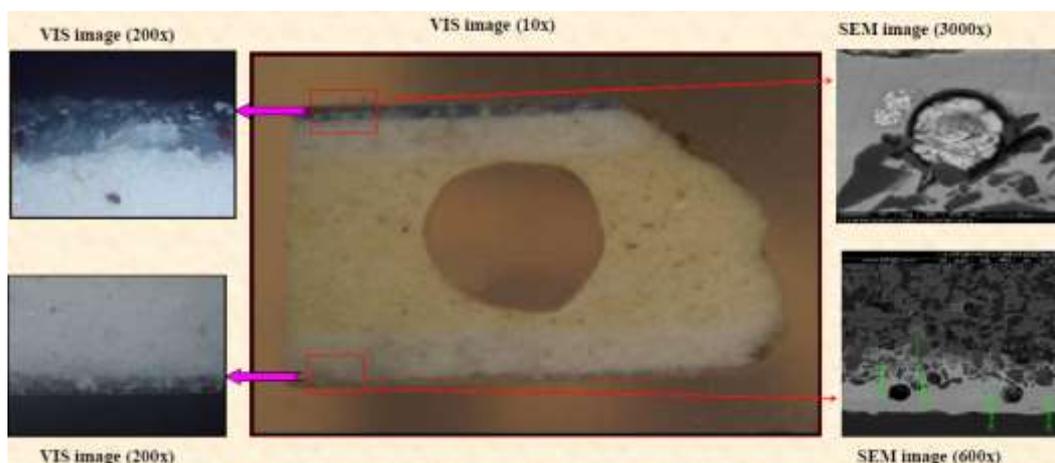


Figure 2: The stratigraphy of the Iznik wares based on VIS and SEM images. The presence of blue glaze is confirmed at the VIS image (200x up) and SEM image (3000x). The presence of slip is confirmed at the VIS image (200x down) and SEM image (600x).

	Glaze	Glaze (colorless)	slip	Body
Oxides	Wt%	Wt%	Wt%	Wt%
Na ₂ O	8.36	7.96	1.15	1.77
SiO ₂	51.31	53.59	89.82	85.70
SnO ₂	4.74	5.05	-----	-----
PbO	32.23	30.67	2.60	2.78

The μ Raman spectrum obtained from the glaze layer of the sample with code-name G3_49 is shown in Fig. 4 and demonstrates the presence of an amorphous material (glass). Similar spectra obtained for the glaze layers of all samples studied in this work.

Similar images were obtained for all the other samples. The results confirm the presence of three layers: the glaze, the slip and the body.

EDAX measurements showed that the above mentioned layers consist of the SiO₂, PbO, Na₂O and SnO₂ primary oxides. As an example, Table 1 shows the composition results of a typical (G3_49) sample as emerged from the elemental analysis.

Structural measurements confirm in a large extent the EDAX analysis outcomes, since compounds like *a*-quartz, cristobalite, and diopside (MgCaSi₂O₆ or FeCaSi₂O₆) were clearly detected. Figure 3 shows a typical XRD pattern of the G3_49, which demonstrates the presence of *a*-quartz (Q), diopside and cristobalite (C).

However, a weak peak that appears around 549 cm⁻¹ probably indicates the presence Lazurite for the G3_49 sherd. This characteristic peak is assigned to the totally symmetric stretch of the S₃⁻ ion (Clark and Franks, 1975; Colomban, 2003).

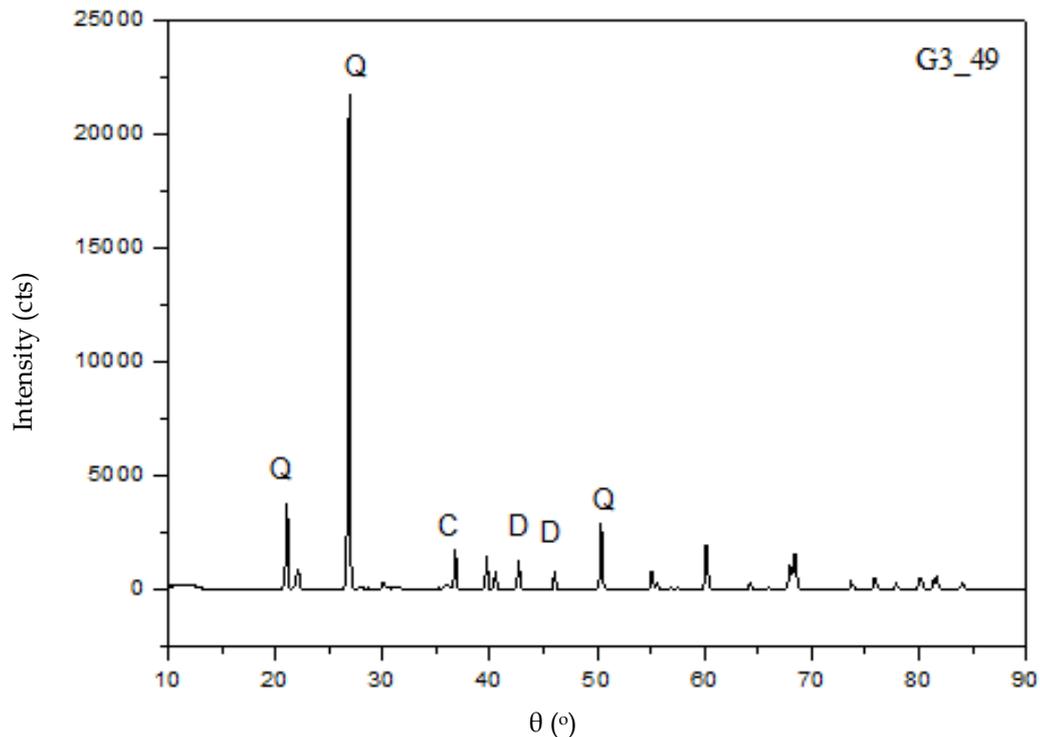


Figure 3: A typical XRD pattern of the G3_49 sherd showing the presence of α -quartz (Q), diopside and cristobalite (C).

Fig. 5 presents a typical μ Raman spectrum of the body layer of the G3_49 sample, which indicates that body consists mainly of α -quartz, since the most intense Raman line at 465 cm^{-1} , which can be described as the resultant of two opposed Si - O stretching vibrations within the SiOSi linkage, can be clearly observed, while, in the low frequency region of the spectrum, a characteristic weak mode appears at 206 cm^{-1} , which is due to motion of Si and O around a 3-fold screw axis (related to the α - β displacive transition in quartz) (McMillan, 1984; McMillan et al., 1990; Sato et al., 1987). It should be noted that similar results obtained for the body layers of all samples studied in this work.

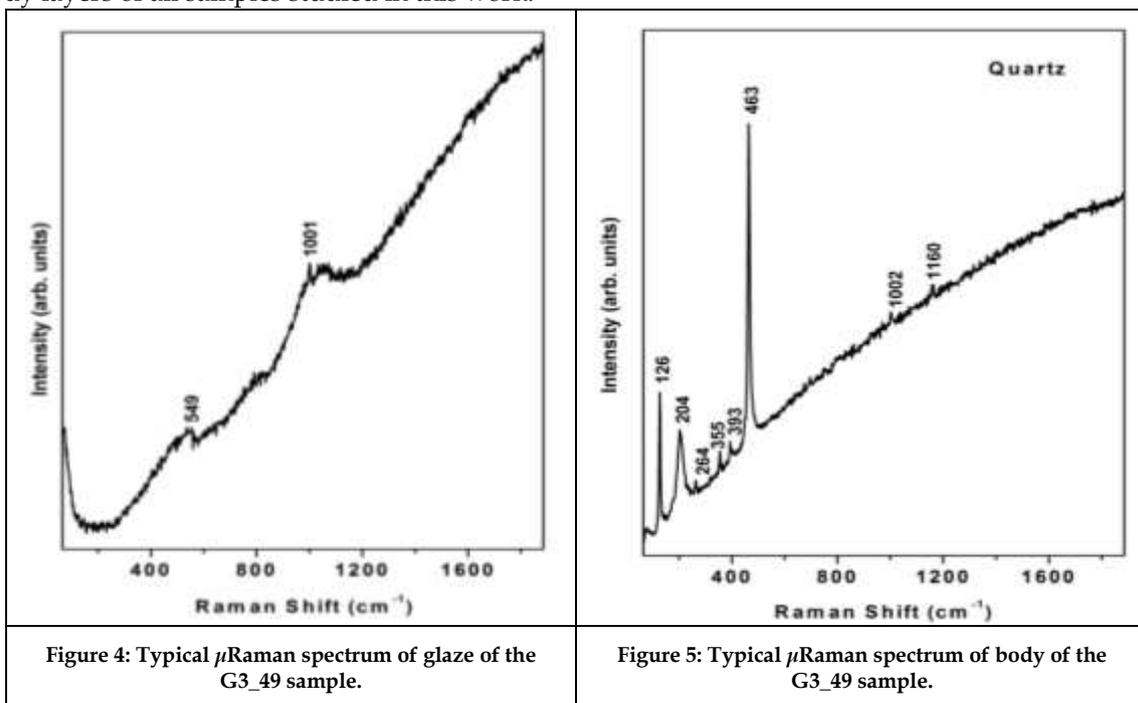
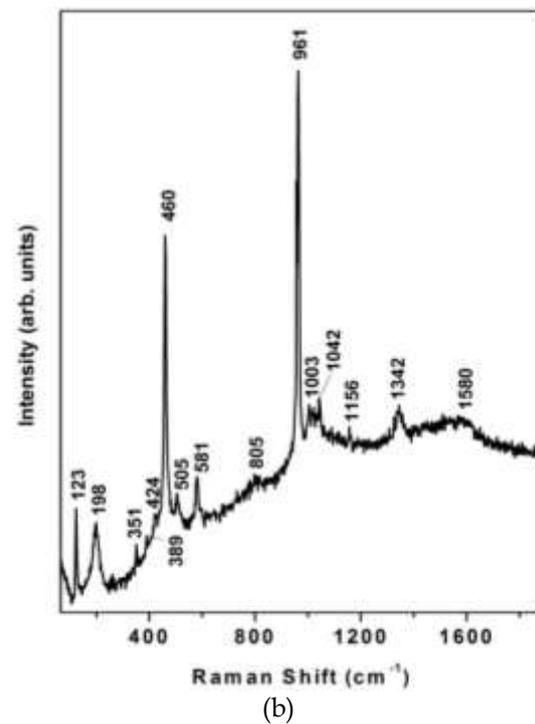
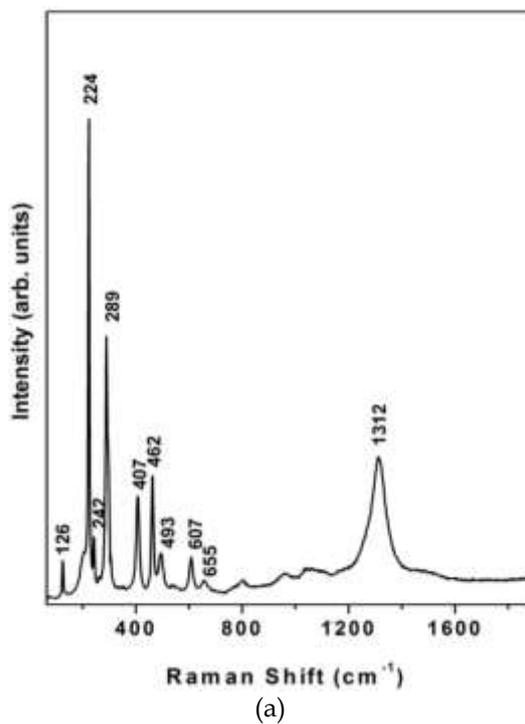


Fig.6 shows typical μ Raman spectra of the slip layers of various sherds. The analysis showed that Haematite, $\text{Ca}_3(\text{PO}_4)_2$, Anatase and Carbon Black are probably the main pigments used. More specifically, the Raman spectrum shown in Fig. 6a indicates the presence of Haematite, since the fundamental "internal" modes at ~ 224 , 289, 407, 493, and 607 cm^{-1} were observed, which involve motion within a single Fe_2O_3 unit, as well as the high energy broad line at $\sim 1312\text{ cm}^{-1}$, which is assigned to an overtone associated with a Raman-forbidden longitudinal optical (LO) weak phonon near 655 cm^{-1} (McCarty, 1988; Bell et al., 1997). Several peaks appear in the Raman spectrum of Fig. 6b. However, the low frequency strong peak (at $\sim 461\text{ cm}^{-1}$) is related with quartz, while the second intensive band (at $\sim 961\text{ cm}^{-1}$) emerges in a frequency region where the symmetric P-O stretching vibrations of the phosphate ion occur. Thus, the presence of a Calcium Phosphate Compound (probably Tricalcium Phosphate) may be deduced (de Aza et al., 1997). Anatase has been detected by the emergence in the spectra of the characteristic Raman bands at ~ 138 , 193 and 392 cm^{-1} , which are

attributed to the O-Ti-O bending type vibrations, and the peaks at ~ 511 and 635 cm^{-1} , which are due to the stretching vibrations of the Ti-O bond (Fig. 6c) (Ohsaka et al., 1978; Clark et al., 2007). Finally, the black areas which were revealed in the cross sections of the samples seem to consist of carbon black as observed by the appearance of a characteristic strong and broad band at $\sim 1566\text{ cm}^{-1}$ that is assigned to a doubly degenerate deformation vibration of the hexagonal ring and a weaker one at $\sim 1343\text{ cm}^{-1}$, which is attributed to a crystalline size effect (Fig. 6d) (Tuinstra and Koenig, 1970; Nakamizo et al., 1974).

Finally, Fig. 7 shows a μ Raman spectrum obtained on the of the slip layers of few sherds. The appearance of the band at $\sim 630\text{ cm}^{-1}$ is probably related with Laser-induced degradations of Mn oxides, which may generate a species of unknown composition (Bernard et al., 1993; Smith and Clark, 2004). However, the presence of second peak at $\sim 775\text{ cm}^{-1}$ may denotes the presence of cassiterite (SnO_2), which was used in plating processes of ceramic objects or used as an opacifier in decoration works (Barilaro et al., 2005).



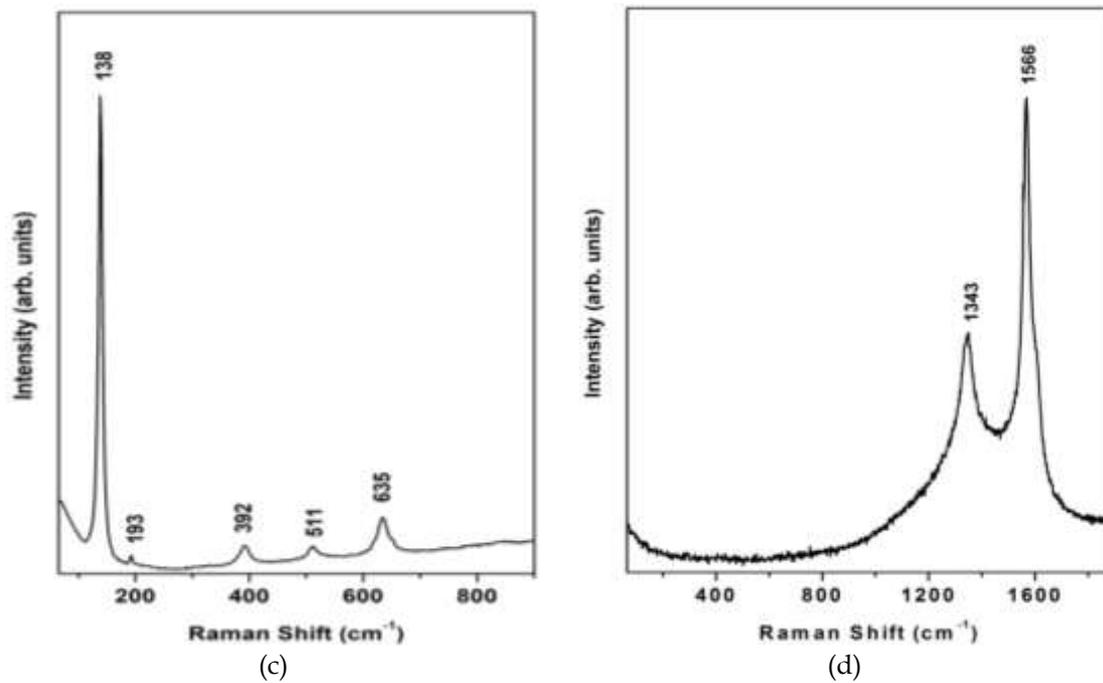


Figure 6: typical μ Raman spectra of the slip layers of various sherds showing the presence of (a) Haematite, (b) $\text{Ca}_3(\text{PO}_4)_2$, (c) Anatase and (d) Carbon Black.

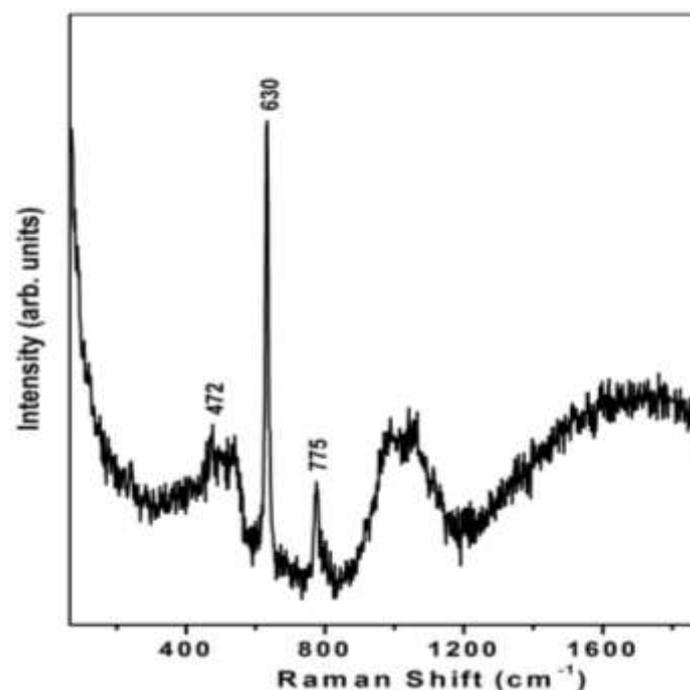


Figure 7: Slip μ Raman spectrum showing the presence of cassiterite at $\sim 775 \text{ cm}^{-1}$.

4. CONCLUSIONS

All the key Iznik pottery colors are represented in this collection while in most of the samples a diffuse interface between the glaze and slip layers was observed. Taking into account the results of the analytical techniques employed in this work, it may be concluded that the blue hues are achieved by a com-

bination of cobalt and copper oxides, while the reds are largely based on iron oxides. Also, the purple hues in addition to iron oxides contain manganese ones as well. Greens are characterized by enhanced presence of iron and copper. Finally, black contour lines are based on the Cr_2O_3 - MnO - Fe_2O_3 combination and are used for the definition of borders of colored areas.

ACKNOWLEDGEMENTS

We thank the anonymous reviewers for their constructive comments. This work was supported by the Division of Conservation of Antiquities and Works of Art, Technological Educational Institute of Ionian Islands, School of Technological Applications in Zakynthos Island, Greece. We are grateful to the Islamic Museum, Benaki Museum in Athens, especially to Mrs Mina Moraitou for her trust and support for granting us permission to study the collection.

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