On-site, non-destructive studies at Iznik Tile Kilns Excavation

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Abstract: The research ethic in the world limits sampling and destructive analyses as much as possible and accepts only the use of non-destructive techniques to maintain the integrity of the excavation finds. Up to now, the research on Iznik tiles was carried out on a limited number of artifacts with which the researchers were not able to perform any statistical assessment to define different workshops that existed in the excavation area of Iznik Tile Kilns. Moreover, most of the previous studies were concerned with artistic and morphological investigations rather than the analyses of glaze and coloring agents. Since 2018, non-destructive analyses with pXRF and stereo microscope started on the excavation materials to define the glaze, coloring agents, and body composition. Some ceramics and tile sherds were also characterized with a confocal Raman spectrometer in the laboratory to complement the chemical data obtained with pXRF.

Keywords: Iznik Tile Kilns, portable XRF, Raman, stereo microscope, non-destructive

Resumen: Los principios éticos de la investigación en el mundo limitan al máximo el muestreo y los análisis destructivos y acepta únicamente el uso de técnicas no destructivas para mantener la integridad de los hallazgos de las excavaciones. Hasta ahora, la investigación sobre los azulejos de Iznik se llevó a cabo sobre un número limitado de artefactos con los que los investigadores no pudieron realizar ninguna evaluación estadística para definir los diferentes talleres que existían en el área de excavación de los Hornos de Azulejos de Iznik. Además, la mayoría de los estudios anteriores se centraron en investigaciones artísticas y morfológicas más que en análisis de vidriados y agentes colorantes. Desde 2018 se iniciaron una batería de análisis no destructivos con pXRF y estereomicroscopio sobre los materiales de excavación para definir los esmaltes, los colorantes y la composición de la pasta. También se caracterizaron algunas piezas de cerámica y azulejos con un espectrómetro Raman en el laboratorio para complementar los datos químicos obtenidos con pXRF.

Palabras clave: Hornos de tejas de Iznik, XRF portátil, Raman, Microscopio estereoscópico no destructivo

INTRODUCTION

Since the 1980s, mostly laboratory studies with large-scale, destructive/invasive instruments and few on-site measurements with some portable, non-invasive techniques were conducted about the characterization of Ottoman period ceramics, where the research on Iznik and Kütahya productions lead by international (Henderson, 1989: 115-132; Tite, 1989: 115-132; Panagopoulou, 2018: 27-33; Burlot et al., 2020:1-11) and national researchers (Kapur *et al.,* 1998: 181-189; Tulun *et al.,* 2002: 34-44; Geçkinli, 2011: 1-151). Due to the destructive character of the techniques, ethical rules of cultural heritage studies now limit these types of analyses as much as possible. Moreover, the sherds from Iznik kilns are rare and the research ethic, especially in Turkey, covers the use of non-destructive techniques to maintain the integrity of the samples. Most laboratory-scale studies comprise artistic and morphological examinations rather than the elemental and molecular analyses of the glaze and colouring agents. These non-invasive, on-site analyses enabled us to study many more samples than studied before at Iznik Tile Kilns Excavation (Simsek *et al.,* 2019: 2199-2209; Demirsar Arli *et al.,* 2020: 1302-1329).

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Figure 1. pXRF analysis in the excavation house

Figure 2. Representative examples of on-site studied sherds from Iznik Tile Kilns Excavation

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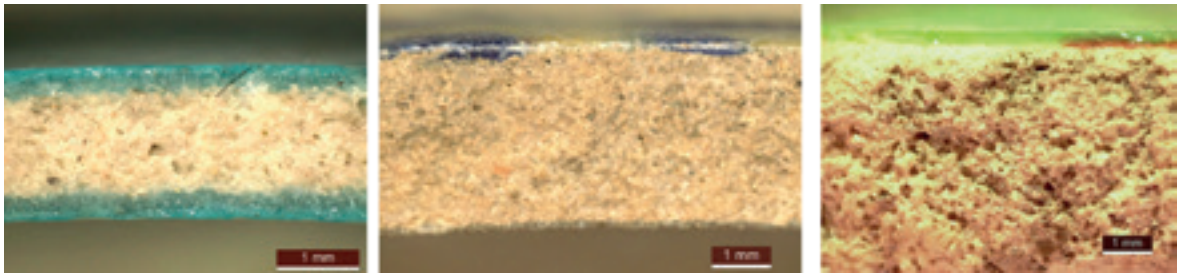

Figure 3. Representative cross-sections of the sherds examined with the stereo microscope

Each year since 2018, we performed one-to-four days campaigns on-site with handheld X-ray fluorescence (pXRF) instrument (Fig. 1) for the elemental analysis of the body, glaze, and colouring agents, and a stereo microscope for the morphological investigation of the cross-sections. At the laboratory, we used a non-invasive, confocal Raman spectrometer to define the glaze signature and pigments found in the decors.

EXPERIMENTAL

Objects

In the first year of the campaign (2018), the scientific studies started with monochrome and polychrome glazed and unglazed tiles dated from the 14th- to the 17th-centuries. In 2019, unglazed bricks, impressed/molded ceramics, and molding materials were examined with pXRF, in addition to the studies of tiles. Three glazed blue-and-white sherds among the studied samples were chosen for a statistical study to estimate the uncertainty of the instrument for the (semi-quantitative) analyses of tiles with underglaze decoration. The third year continued with the analysis of Sgraffito productions, blue-and-white ceramics, Rhodes, and Damascus-type objects (Fig. 2).

Techniques

The cross-sections of the sherds were examined macroscopically with a Leica s9i stereo microscope at different magnifications that vary from 6.1x to 55x, to define the structure of the glaze, colored decors, and body (Fig. 3).

For pXRF measurements, Hitachi X-MET 8000 Expert Geo (Oxford Instruments) was positioned in contact with the samples. The instrument, which was equipped with a rhodium (Rh) target X-ray tube (4 W, 50 kV max) and a silicon drift detector (SDD), was operated by using the Mining Light Elements (LE) method, in which two shots were performed, one at the lower energy (10 keV) for determining low Z elements (e.g., Al, Si, Ca, K, P) and the second at the high energy (40 keV) to identify heavier elements (e.g., Fe, Co, Cu, Ni, Rb, Sr, Zr, Sn, Pb). Due to the variation of the minerals found in the body and the glaze thickness, the measurements were carried out on at least three different areas of the body and colored areas of the glaze, with the 30s of radiation time. Before the analyses, the radiation time between 10 and 360 s was tested, hence 30s was found reliable.

Raman measurements were performed to identify the glaze signature and pigments found in the colored decors (either in-glaze or underglaze) in addition to the mineral phases found in the slip and body layers. Therefore, a completely automated Renishaw in Via confocal Raman microscope was used with a 532 nm (green) laser excitation (Fig.4).

HIGHLIGHTS ABOUT THE ON-SITE AND NON-INVASIVE STUDIES IN IZNIK

Use of different recipes for the paste composition

Until the beginning of the studies at Iznik Tile Kiln Excavations in 2018, it was assumed that only two types of recipes for the body were used in the productions of Iznik tiles. The early productions (14th-15th-centuries) were made with a mixture of a high amount of alumina (12-16 wt% Al_2O_3) and a low amount of quartz (around 50 wt% SiO_2) which was named as redware. However, the productions of 16th and 17th

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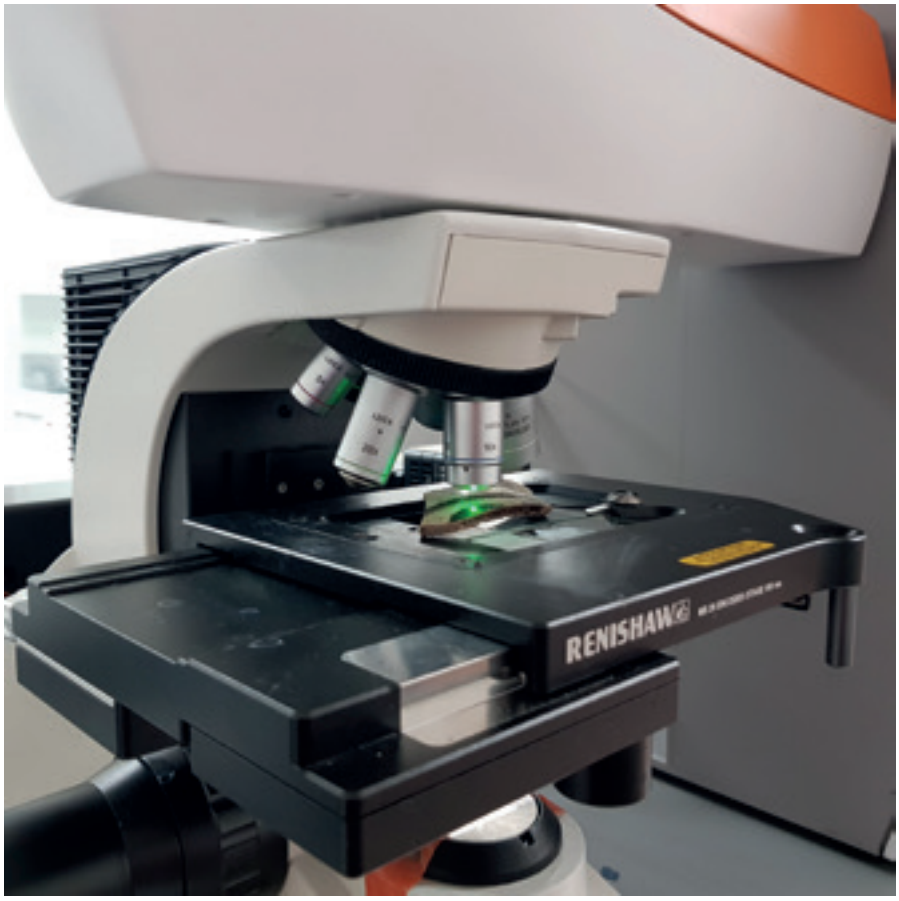

Figure 4. Raman analysis in the laboratory

centuries were containing a high amount of quartz (65-85 wt % SiO_2) and low alumina (3-6 wt% Al_2O_3) which were referred to "stonepaste" (known also as fritware) group. The on-site analyses with pXRF evidenced a new group that has a medium level of SiO_2 (39-62 wt%), a low amount of Al_2O_3 (3.6-6.3 w%) and an additional amount of calcium (11-37 wt% CaO). This composition represents the presence of a calcareous paste rather than a siliceous – clayey body. A systemic investigation of the paste composition with a pXRF and determination of the minerals found in the body with a Raman spectrometer will allow identifying different groups of productions, probably made at different workshops and/or by different artists.

Differences in the composition and thickness of the slip layers

Ceramic artists in Iznik were applying a slip layer to provide a white base for the colored decorations. Therefore, firstly biscuit firing was applied, and the second firing was applied for glazing. The white colored-slip layer reflects better the hues of different colors. However, the thickness of the slip layer may differ regarding the desire of the artists who work in different workshops. The composition of the slip layer is also an important factor for the distinction of the productions. The raw materials used for the slip layer may be quartz-rich (rich in SiO_2) or clayey (rich in Al_2O_3).

Differences of the glaze composition and evaluation of tin content relating to the production periods

The previous on-site studies carried out with pXRF at the Iznik Tile Kilns Excavation showed that the glazes of the tiles contain 23-46 wt% lead oxide. However, the amount of tin oxide found in the colorless glaze and decor for the opacification and stabilization of the color decreases by centuries. Because tin (Sn) mining places are rare, making the cost of tin high. Thus, the potters limited Sn content. Sn can be also associated with Pb (lead), in particular, if

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bronze waste is used. Tin oxide is detectable on-site with two techniques, pXRF and portable Raman. It also enables a distinction of the technology used in Iznik and Kütahya produced in the same period. Moreover, the calculation of the ratio of the fluxes (Pb, K, Bi and possibly Na) to the network formers (Si+Al) is necessary to estimate the firing temperature. In addition to pXRF measurements, the glaze parameters which are calculated from the Raman spectra of the glaze allow calculating the index of polymerization (Ip: the ratio of the Si-O bending area divided by that of the stretching area) related to the firing temperature.

CONCLUSION

The monochrome and polychrome Iznik tiles and different types of potteries are the masterpieces of the Ottoman period which were produced from the 15th to 17th centuries. On-site methodologies of scientific research in Iznik will lead to a statistical assessment of Iznik productions indicating different workshops, kilns, production periods. For this assessment study, binary and ternary scattering plots and hierarchical clustering analyses will be used.

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