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External milli-beam PIXE analysis of the mineral pigments of glazed Iznik (Turkey) ceramics

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Abstract

25 Iznik glazed ceramics fragments - shards of vessels, plates for wall decorations found in Moldova's capital Suceava, in Prince Vasile Lupu (1600-1640) palace and shards excavated from a Danube ford - Piua Pietrii, a renowned commercial centre during 17th Century were studied. We used external milli-beam PIXE (Particle Induced X-ray Emission) spectroscopy to investigate the capabilities of this method to identify the metals from ceramics mineral pigments. Cobalt, Lead-Antimony, Copper, Chromium, Iron and Manganese minerals used to obtain blue, yellow, green, red and brown colours were identified. Our PIXE results were compared with data from literature obtained on Iznik tiles samples using Raman spectroscopy proving a good compatibility.

Key words: external milli-beam PIXE; Iznik ceramics; pigments; Cobalt sources.

Introduction

Following the establishment of the Ottoman Empire, the name of Iznik became famous throughout the world due to the development of a ceramics industry in the 16th and 17th centuries (Paynter et al., 2004). Combining the Ottoman style with external influences from China, Asia, the Balkans and even Europe, Iznik vessels and tiles reached the peak of Ottoman ceramic art. Iznik fritware was the result of a search by the Ottoman court in Istanbul for a recipe to make porcelain with the goal of imitating the much-admired and pricey Chinese Yuan and Ming Dynasty blue-and-white porcelain. The initial copies of the Chinese designs gradually gave way to a uniquely Turkish style which included a broader color palette. The mineral pigments used for the famous Turkish Iznik ceramics are very important for the understanding of commercial routes of late Middle-Age period. The most interesting problem related to the Iznik mineral pigments is the use of Cobalt to obtain the blue color, because Cobalt minerals deposits in Europe and Middle-East are only in Saxony ("Erzgebirge") and in Persia (Kashan region), both deposits involving special trade, political and military relations (Figure 1). A detailed presentation of Iznik ceramics can be found in (Tite, 1989). The technology used for the pottery in the 17th century is described in (Okyar, 1995); its main characteristics was the Lead-rich faience-bodied ware (white-ware) - 20 wt% frit - with 80 wt% quartz within the body. The glaze contained 2-12 wt% Tin oxide (SnO_2), mostly soluble. The under-glaze decoration were multicolored, including turquoise derived from Cu-oxide, blue for Co-oxide, black line mainly from chromite and red from hematite.

The analyzed ceramic pieces come from recent excavations (2010-2011) in two archaeological sites: some of them in the ruins of Prince Vasile Lupu's palace located in Suceava - the historical capital of Moldavia (1600-1640) and others in an excavation site from a Danube settlement - Piua Petrii - a renowned commercial center

Figure 1. Illustrative map - Cobalt mineral deposits (Saxony, Kashan); Iznik - pottery production centre; Sites - Piua Petrii (Commercial settlement) and Suceava (Historical Capital of Moldavia).

during the Late Middle Age - 16th and 17th Centuries (Figure 1). The curators from the National Museum of Romania's History, Bucharest, from which the ceramics fragments were obtained decided on visual grounds that these ceramics shards are made in Iznik style, being manufactured during the 17th Century (Figure 2). Some similar shards excavated in 2001-2005 in the same archaeological sites were analyzed using ED-XRF (Energy-Dispersive X-Ray Fluorescence) at the National Institute of Nuclear Physics and Engineering "Horia Hulubei", Bucharest and at Istituto Nazionale di Fisica Nucleare (INFN), Sezioni di Genova, Italy (see Bugoi et al., 2007).

Background

External beam PIXE (Particle Induced X-ray Emission) spectroscopy is a widely applied method for non-destructive elemental analysis of archaeological objects (Gyódi et al., 1999). Surface spots on the object are bombarded by energetic protons and the characteristic X-rays produced are used for quantitative analysis. Due to the slowing down of the bombarding protons in the sample and the absorption of the out-coming X-rays, the method is sensitive for the surface region of thicknesses up to some tens of micrometer. Similar studies of mineral pigments using PIXE method are in (Pappalardo et al.,

Figure 2. Examples of analyzed Iznik shards.

2004) - combined use of PIXE and XRF to study the famous Della Robbia sculptures from Florence museums, in (Pappalardo et al., 2010) - studies on Minoan pottery pigments from Phaistos, in (Crider, 2013) - identification of Mexican pottery paint recipes, in (Bajnoczi et al., 2014) - characterization of tin-glazed Hungarian Anabaptist faience, in (Zucchiatti et al., 2006) - an exhaustive study on Cobalt pigments used by Della Robbia artists. As concerning Budapest milli-PIXE facility, it was recently used together with PGAA and ToF-ND methods, to analyse a Bronze Age defensive armour - (Mödlinger et al., 2013) and (Mödlinger et al., 2014).

Materials and methods

The aim of our study was to investigate the capabilities of in-air Milli-PIXE method (Figure 3) to identify the metals from ceramics mineral pigments.

25 Iznik glazed ceramics fragments - shards of vessels and plates for wall decorations - were studied. Milli-PIXE measurements were performed at the 5 MV Van de Graaff accelerator of the Institute of Particle and Nuclear Physics, Wigner Research Centre of the Hungarian Academy of Sciences. The properly collimated proton beam of 3MeV energy was extracted from the evacuated beam line to air through a 7.5 μm thick Kapton foil. A target-window distance of 10 mm was chosen where the beam diameter was found to be about 1 mm. For the analyses the external beam intensity was varied from 1 to 10 nA depending on the actual total X-ray count rate. The ceramics were fixed to a micro-manipulator allowing for an accurate three-dimensional positioning. The final target positioning was achieved using a mechanical "aiming pin pointer". X-ray spectra were collected by using a computer controlled Amptek X-123 spectrometer with an SDD type detector of 25mm^2 x 500 μm active volume and 8 μm thick Be window. The detector with an energy resolution of 130 eV for the Mn Kα line was positioned at 135° with respect to the beam direction. The target-detector distance was 25 mm. The net X-ray peak intensities and concentrations were calculated subsequently with the GUPIXv.2.1 program package (Campbell et al., 2000). In order to arrive at some conclusions our PIXE results were compared to data from the literature obtained on samples from the same geological sources using different analytical techniques (Simsek et al., 2009).

Results and discussion

As concerning blue pigment, two types of Cobalt minerals were found:

- for the shards from Suceava palace - minerals having Nickel, Iron, Copper and Arsenic as minor elements and traces of Arsenic (see Figure 4)

- for the shards from Piua Petrii - minerals also having Nickel, Iron and Copper as minor elements and a sensitively lower amount of Arsenic (see Figure 5); a similar amount of Arsenic is present on the same shard in green area (see Table 1), so, most probably, Arsenic is not related to Cobalt minerals.

In a similar study on Iznik tiles using Raman spectroscopy (Simsek et al., 2009), the authors

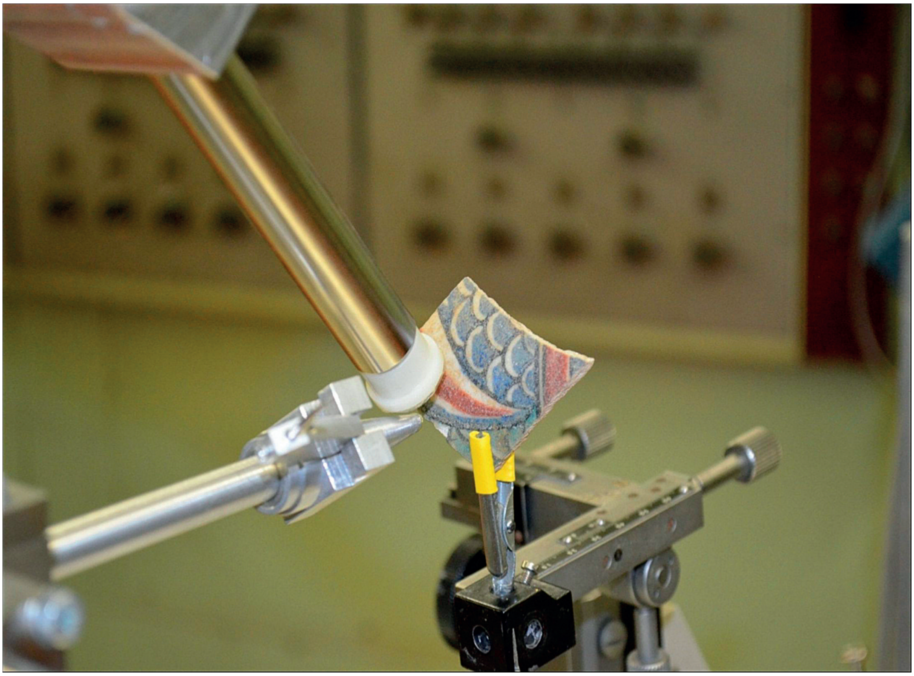

Figure 3. Experimental set-up.

identified for blue a Cobalt pigment dissolved in the alkaline silicate glaze and a Copper pigment for turquoise also dissolved.

For the red pigment, a relevant Iron (ochre?) presence was put in evidence (see Figure 6). In (Simsek et al., 2009) the red color was identified as produced by a natural mixture of hematite (ochre main component) and quartz.

As concerning the green color, a Copper based pigment was detected (see Figure 7). In (Simsek et al., 2009), for green color chromite-based compounds are identified ($FeCr_2O_4$).

A special case is the black lines separating the under-glaze decoration, where we detected Chromium and some Iron and Copper. In the same case, using Raman spectroscopy, (Simsek et al., 2009) identified spinel ($MgAl_2O_4$) and chromite ($FeCr_2O_4$).

For the yellow color pigment, Antimony yellow (lead-antimonate) $Pb(SbO_3)_2/Pb_3(Sb_3O_4)_2$ was used. Tin could suggests a possible reduced presence of Lead-Tin-Antimony yellow ($Pb_2SnSbO_{6,5}$) (see Figure 8).

For the brown-black color, Manganese is a strong presence - most probably from an oxide.

Lead and Tin were found practically in all the analyzed shards, due to the known technology (see Introduction) to produce Iznik ceramics.

In the case of blue color (the most relevant for Iznik style), a difficult problem is to interpret the results in relation with the technical evolution of pigments production (see Zucchiatti et al., 2006).

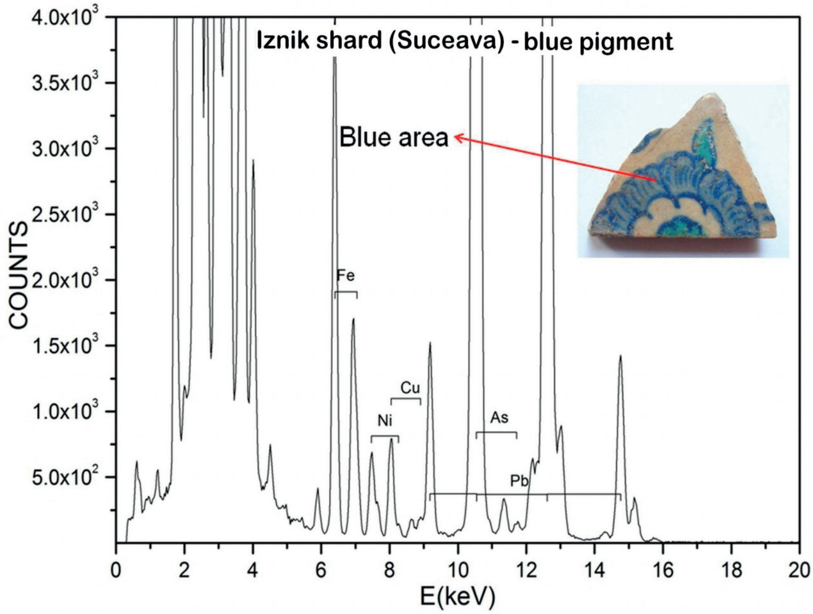

Figure 4. Iznik shard (Suceava) - blue pigment.

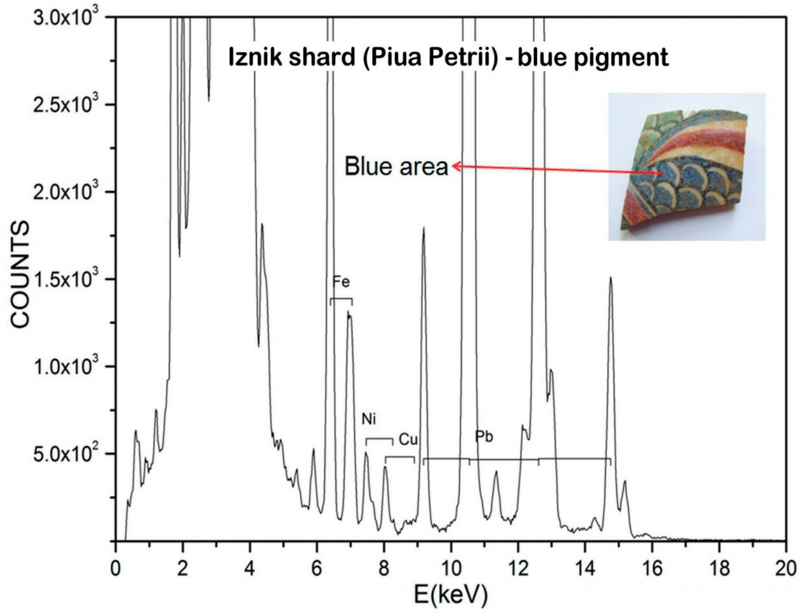

Figure 5. Iznik shard (Piua Petrii) - blue pigment.

Table 1. Elemental concentrations for the analyzed shards.

Samples	Iznik Suceava - blue area	Iznik Piua Petri - blue area	Iznik Piua Petrii - red area	Iznik Piua Petrii - green area	Iznik Piua Petrii - black line*	Iznik Piua Petrii - yellow area**	Iznik Piua Petrii - brown area
SiO_2%	31.92	47.12	44.21	44.64	33.72	42.59	42.29
P_2O_5%	1.39	2.64	1.98	2.74	0.59	0.11	0.43
K_2O%	1.28	2.98	2.32	2.98	0.89	13.51	3.11
CaO%	3.76	4.97	4.30	4.85	2.27	2.43	5.15
TiO_2 ppm	1069	691	393	550	0	1369	3542
MnO ppm	617	369	293	300	822	414	153662
FeO ppm	8522	7168	6334	7771	9668	59205	14362
CoO ppm	3579	1211	0	0	144	0	794
NiO ppm	1532	553	37	31	186	53	493
Cu_2O ppm	1979	533	867	19435	14049	779	3885
ZnO ppm	363	82	94	144	177	1340	407
As_2O_5 ppm	7055	2369	0	2624	0	0	3606
Rb_2O ppm	0	77	0	0	0	0	0
SrO ppm	207	32	222	58	334	206	1062
Y_2O_3 ppm	892	1576	1808	1418	1237	1261	3757
ZrO_2 ppm	575	0	0	347	0	0	0
PbO%	46.70	29.70	36.32	30.38	40.74	23.09	19.21
SnO%	0	1.65	2.24	2.46	4.06	2.40	0

* Cr_2O_3 16598 ppm
**Sb_2O_5 18842 ppm

Initially, cobalt was thought to be of no value and to be a disturbance for the metallurgy. In the 15th century, its value for coloring was discovered, and cobalt blue gained in importance. This circumstance led to the establishment of the so-called blue-colors mills. A rapid change in the composition of the blue glazes was observed just before 1520 from the correlation amongst elements constituents of the Co minerals. The change from 1520 is marked essentially by the presence of As and Bi and by reduced amounts of Fe and Ni, as compared to the blue cobalt pigments composition before 1500 (see Zucchiatti et al., 2006). One can speculate that this was due to procedures introduced to industrialize the blue pigments production more than to exploitation of different families of Co minerals (Zucchiatti et al., 2006).

In the famous book "De re metallica" of Georgius Agricola (Georg Bauer) from 1556, cobalt-blue is described as a by-product of silver melting. Agricola describes after the silver extraction of the smelting furnace the presence of solidified juices or "fluores" that "they can make colours that the artists use". In the book "Ars vitralia experimentalis" of Johannes Kunckel (1689), a Co-reverberatory oven is described from which "fumi" (coloured gaseous

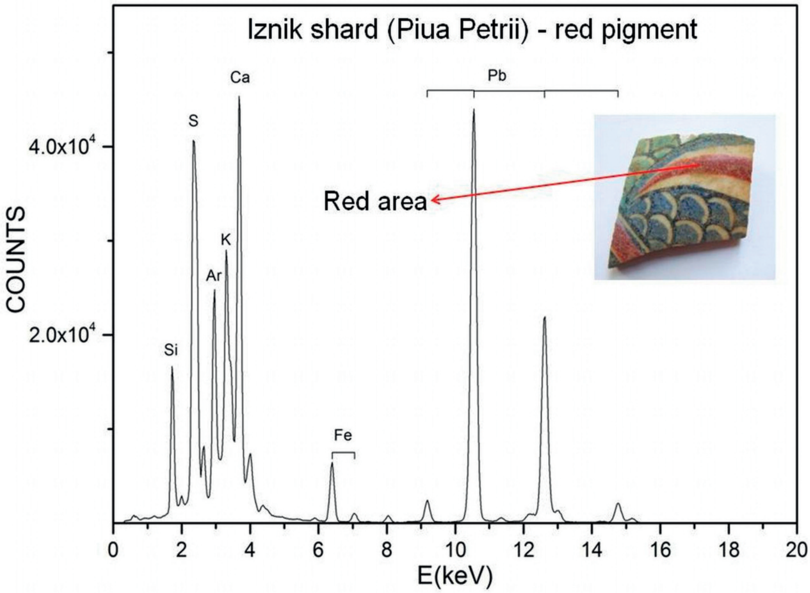

Figure 6. Iznik shard (Piua Petrii) - red pigment.

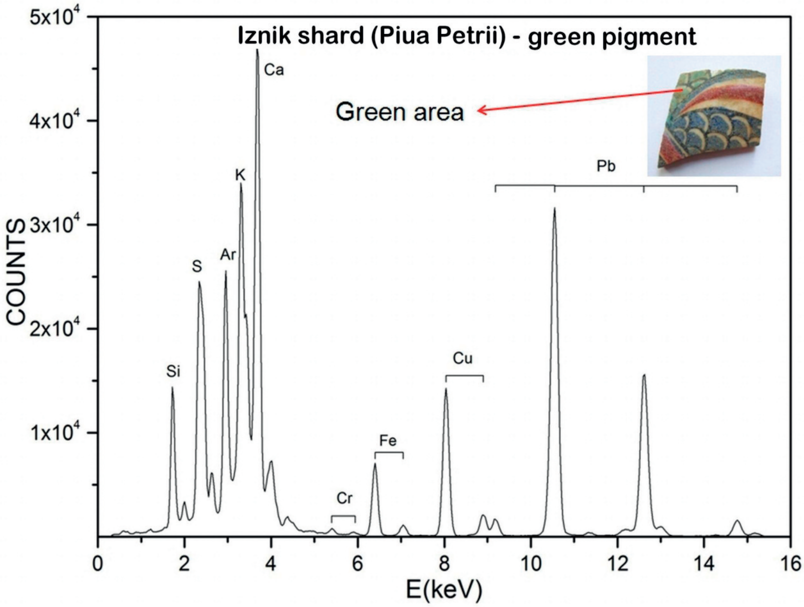

Figure 7. Iznik shard (Piua Petrii) - green pigment.

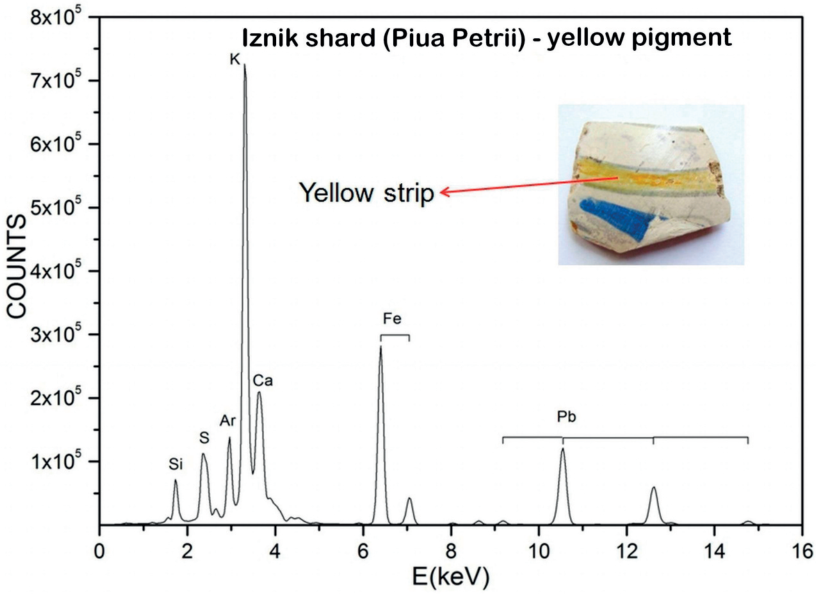

Figure 8. Iznik shard (Piua Petrii) - yellow pigment.

emissions) were obtained (arsenic and sulphur?). With this procedure "saffre" (cobalt oxide mixed with silica) should have been made by P. Weidenhammer in Schneeberg starting from 1520. In 1540, C. Schurer mixed the cobalt oxide with sand and potash to produce a blue, finely ground glass: the "smalt". However, it is not possible to estimate how much from the As component of the Co mineral was lost as gas - "fumo". It is quite probable that a fraction of As remained attached to the pigment. As concerning our results, at the present stage of investigation, we can only suppose for the shards from Suceava palace the most probably provenance of minerals is Saxony ("Erzgebirge") deposits and for Piua Petrii shards there are two possibilities: also Saxony but using a new procedure to industrialized blue pigment production involving Arsenic evaporation (Zucchiatti et al., 2006) or, less probable, minerals from Kashan - Central Iran (Porter, 2000). To verify Kashan hypothesis it is necessary to measure Boron concentration (high content is a fingerprint from this Iranian region (see Wen and Pollard, 2014); because PIXE is not suitable to detect very low Z elements, we intend to use PGAA (Prompt Gamma Activation Analysis) based on neutrons from Budapest Reactor. The use of Saxony Cobalt sources could demonstrate the active commercial routes of Turks with Germany space. The commercial route with Central Europe passed through Moldavia (e.g. Leipzig-Breslau-Krakow-Lemberg (Lvov)-Suceava-Danube Dobroudja-Istanbul-Iznik).

Concluding remarks

Milli-PIXE method proved to be an adequate tool to determine chemical elements, especially metals, from ceramics pigments composition. Our results are compatible with the Raman spectroscopy investigation on Iznik tiles from (Simsek et al., 2009). However, for our samples, an extended study using other techniques as Raman spectroscopy and SEM-EDAX (Scanning Electron Microscopy coupled to X-rays analysis) is obviously necessary. To also investigate the minerals used for other component of Iznik ceramics (glaze, frit, clay) XRD (X-Ray Diffraction) is an adequate analytical method. Consequently, a complete study in the case of Iznik artifacts must include at least four analytical tools: XRD, SEM-EDAX, Raman spectroscopy, PIXE - the last one having the advantage it can be used for in-air experiment directly on the ceramic objects (no sampling is necessary).

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