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Composition of glaze layer of the 18th century tiles

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Abstract. There were studied glaze layers of fragments of painted tiles estimated by art historians basing on external signs as fabricated in the Netherlands in the 18th century. The paper presents results of glaze surface composition measurements by X-ray fluorescence (XRF) and X-ray photoelectron spectroscopy (XPS), time-of-flight mass-spectroscopy (TOF-SIMS) methods in comparison with literature data. Information on composition of glaze layers including pigments will be used obtained in this research will be used in further conservation efforts.

1. Introduction

Now we can state the growing interest of specialists in the art of Dutch faience tiles of the 17th and 18th centuries. It is stimulated in particular by discovering newly found items of such kind in archaeological and architecture archaeology studies, and its results are exposed in new thematic exhibitions and specialized researches. Among recent researches in this direction we can select the report [1] proposing the set of instrumental methods and criteria allowing to distinguish locations of the tiles fabrication.

In 2017, the ceramic restoration workshop of the Department of Restoration and Examination of Cultural Heritage Objects of the St. Petersburg State Institute of Culture received 22 faience tiles from a private collection. The tiles dimensions were 13x13 cm. The tiles are made of ceramic dough of light yellow color with a fine texture, covered with a white glaze (enamel) and painted in an underglaze technique. Five of them have an ornamental painting in brown pigment, eight ones have an ornamental painting in blue, the ornament in both cases is floral. Nine tiles painted with blue pigment are decorated with a plot painting in a circle with corner ornamental filling, three of them contain image of a ship, six ones have a landscape painting including images of buildings and people. Visually identifiable technical-technological and stylistic features and the presence of analogs [2] are providing basis to identify these tiles as Dutch products of the 18th century. In addition to the features of forming and painting, one can observe technological imperfections such as small bubbles in the glaze bulk and other minor defects. On the edges and the back of the tiles there are remnants of a mortar with which they were attached to vertical surface.



For restoration work, it is extremely important to obtain reliable information about the chemical composition of the glaze layer and pigments, so it was the key aim of this study.

2. Materials and methods

To study features of glaze chemical composition with blue painting there were selected two fragments with dimensions suitable for sample holders of instruments. Figure 1 presents the layout of the selected samples.

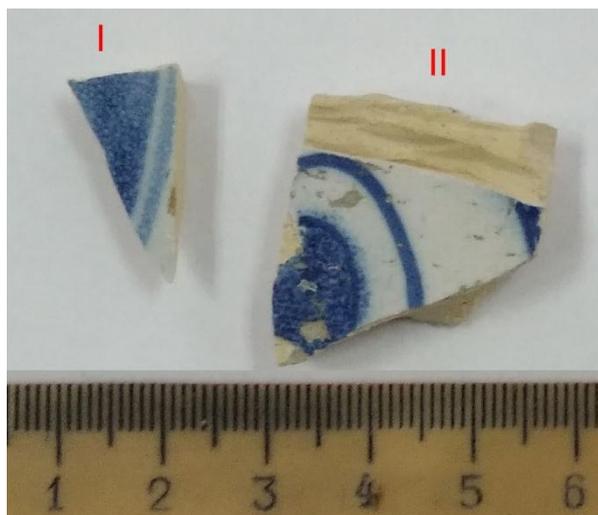


Figure 1. Layout of the selected fragments of glaze tiles.

The analysis of generalized elemental composition of glaze layer was carried out by X-ray fluorescence spectroscopy (XRF) using AXIOSmax Advanced (PANalytical, Netherlands) spectrometer.

Surface composition measurements with high depth and spatial locality were performed by secondary ions mass-spectroscopy (SIMS) on the time-of-flight mass-spectrometer TOF.SIMS5-100 (IONTOF GmbH, Germany) equipped by Bi ions source with spatial resolution 25 nm, Cs and O ion sources for depth profiling, and by X-ray photoelectron spectroscopy on electron spectrometer ESCALAB Mk2 (VG, Великобритания) using Al K α radiation of the twin anode Al-Mg source ($h\nu = 1486.6$ eV, Au 4f $_{3/2}$ –5/2 full width at half maximum (FWHM, half-width) = 0.9 eV). Sample charge was suppressed by low energy electron beam ($E_0 = 70$ eV) from EMU-50 source. The spectrometer control and spectra acquisition was performed by Spectrum2 [3] software, spectra processing was carried out using UNIFIT2007 [4] software. Binding energies values were corrected basing on C 1s peak position.

3. Results and discussion

The average composition of the samples from the glaze side determined by the XRF method is presented in table 1. It should be taken into account that the XRF has an analytical depth up to 3 mm on ceramic materials [5], and the presented composition partially refers to the ceramic base.

Table 1. Tiles composition from the glaze side measured by XRF, %mass.

Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	Co ₃ O ₄	NiO
1.80	1.58	3.15	54.1	4.77	4.75	0.12	0.05	1.20	0.25	0.11
CuO	SnO ₂	PbO	P ₂ O ₅	S	Bi ₂ O ₃	HgO	Cr ₂ O ₃	ZnO	SrO	
0.03	7.53	19.3	0.43	0.46	0.25	0.02	0.01	0.01	0.06	

Figure 2 shows the XPS spectra from the glaze surface in the region of the characteristic lines of the main elements according to the XRF data and literature [1]. Content of some elements in the glaze is listed in table 2.

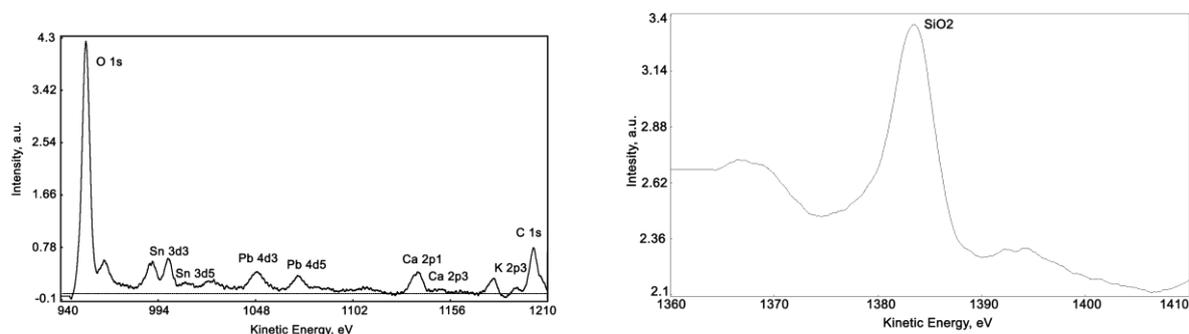


Figure 2. XPS spectra in regions of characteristic lines of Sn, Pb, Ca, K (a) and Si (b).

Table 2. The content of chemical elements on the glaze surface, %at.

Sn 3d3	Pb 4d3	Ca 2p1	K 2p3	Si 2p
0.46	0.43	1.53	0.7	96.87

Figure 3 shows the spatial distribution of some secondary ions corresponding to the white and blue areas of the glaze.

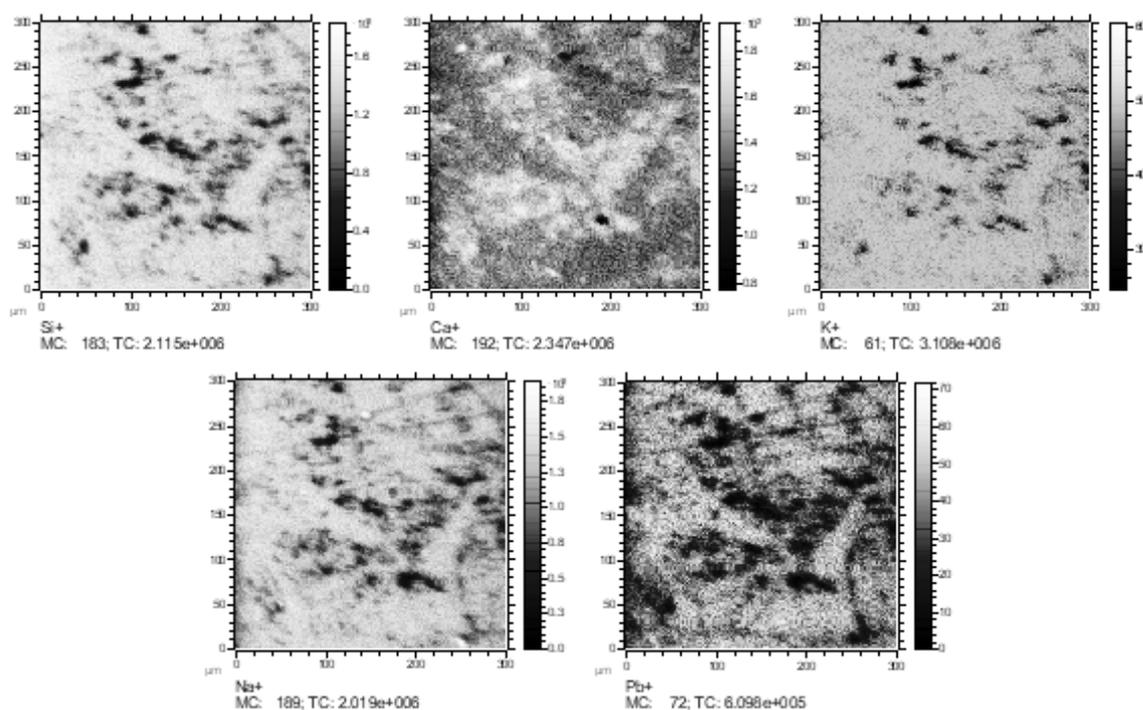


Figure 3. Spatial distribution of secondary ions of Si, Ca, K, Na, Pb on the glaze surface.

One can see that elements at different sites are forming associations characterizing the compositions of pigments used. According to the literature, these spatial correlations of elements are characteristic for certain centers of ceramic production. A comparison of the results obtained with the geometric data given in [1] allowed us to evaluate the studied samples as produced in Holland in the early-mid-18th century.

4. Conclusions

The comprehensive application of surface analysis methods for the examination of historical ceramics allows us to obtain information about their elemental and phase composition including the content of small impurities, which together with the available archaeometric information gives the possibility to accurately link the samples under study with the place and time of their production.

Acknowledgements

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