Investigation of Microstructure and Composition of 18th Century Dutch Tiles in the Context of Conservation

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INTRODUCTION

A series of heavily damaged and previously treated (figs. 1, 2) «blue-and-white» tiles from a private collection (clay, underglaze painting) was consigned for conservation. Though technological and stylistic features and existing analogs [1] (fig. 4) provided attribution of the tiles as Dutch production of the 18th century, due to the lack of historical context it was considered necessary to conduct a study of ceramic materials composition and microstructure. When planning re-treatment, it was taken into consideration that conservation in progress provides extended opportunities for thorough study of the objects. Two samples (fig. 3) were selected for instrumental studies: sample II for XRF measurements and sample I for XPS and SIMS.

Fig. 1

Fig. 2

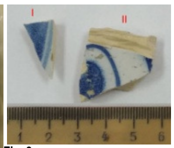


Fig. 3

Fig. 4

INVESTIGATION: METHODS AND MATERIALS

The averaged elemental composition of glaze layers and ceramics was carried out by X-ray fluorescence spectroscopy (XRF) using AXIOSmax Advanced (PANalytical, Netherlands) spectrometer. Microstructure of the samples' fractured surface was studied by scanning electron microscopy (SEM) on JSM-6400LV (JEOL, Japan) microscope. 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 Ar, O ion sources for depth profiling, and by X-ray photoelectron spectroscopy (XPS) on electron spectrometer ESCALAB Mk2 (VG, Great Britain) using Al Kα radiation of the twin anode Al-Mg source (hν = 1486.6 eV, full width at half maximum (FWHM, half-width) $\Delta E_{Au\ 4f7/2-5/2}$ = 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 [2] software. Spectra processing was carried out using UNIFIT2007 [3] software. Binding energies values were corrected basing on C 1s peak position. A sample of the adhesive composition was studied by infrared spectroscopy.

Table 1.

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	S	Cl	K_2O	CaO	TiO_2	Cr_2O_3	MnO
1.26	9.06	6.78	59.1	0.18	0.16	0.69	2.47	16.2	0.30	0.02	0.05
Fe_2O_3	NiO	CuO	ZnO	Rb_2O	SrO	ZrO_2	Nb_2O_5	SnO_2	BaO	PbO	Bi_2O_3
2.53	0.004	0.014	0.005	0.013	0.03	0.03	0.004	0.12	0.03	0.94	0.005

Table 2.

Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Co_3O_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_2O_5	S	Bi_2O_3	HgO	Cr_2O_3	ZnO	SrO	
0.03	7.53	19.3	0.43	0.46	0.25	0.02	0.01	0.01	0.06	

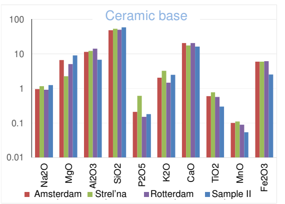


Fig.5 Composition of the ceramic base in comparison with published data on Dutch tiles (XRF)

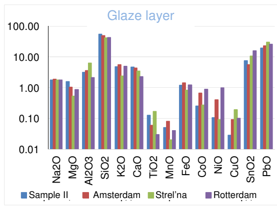
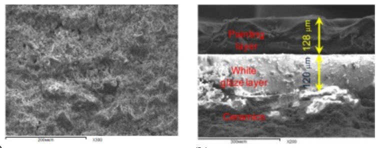


Fig.6 Composition of the glaze layer in comparison with published data on Dutch tiles (XRF)



(a) (b)

Fig. 8 Microstructure of ceramic base (a) and glaze layers (b) fracture surfaces (SEM, secondary electrons images)

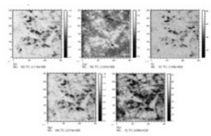


Fig. 9 Spatial distribution of secondary ions of Si, Ca, K, Na, Pb on the glaze surface (SIMS).

Fig. 10

Fig. 11

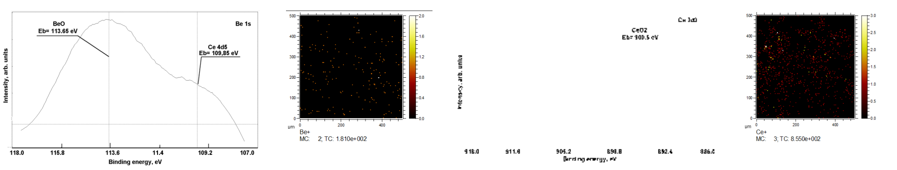
Fig. 12

INVESTIGATION: RESULTS AND DISCUSSION

Table 1 presents XRF data for ceramic base, and Table 2 gives composition of glaze layer of Sample II. It is necessary to take into consideration that XRF is characterized by a depth of analysis of ceramic materials up to 3 mm [4], and the composition presented is partly related to the ceramic base. It is obvious from the data on the composition of the ceramic base and the glaze layer presented in diagrams on figs. 5 and 6 that they correspond to the composition of the dough and glaze of Dutch tiles of the 18th century [5]. Fig. 9 shows the distribution of secondary ions over the area corresponding to the white and blue areas of the glaze. It can be seen that different elements in different areas form associations that characterize the compositions of the dyes. According to the literature data, these spatial correlations of elements are typical for certain centers of ceramic production. Comparison of the results obtained with the available archaeometric data [5] also makes it possible to evaluate the studied samples as being produced in Holland in the early to mid-eighteenth century. Figure 8 a,b shows the microstructure of ceramic base and coatings: the average thickness of the glaze was 128 µm, and that of the pigment was 120 µm. The use of XPS and SIMS methods made it possible to identify elements such as B, Be, Ce, Cs, V and Y in the ceramic base (Fig. 7). The presence of an epoxy group in the adhesive composition was detected.

CONSERVATION AND RECONSTRUCTION

The presence of epoxy group in the glue confirmed that previous treatment did not meet conservation requirements [6]. The tiles were disassembled via acetone poultices application (fig. 10). The joints were cleaned mechanically, remnants of glue softened locally by acetone. Chips were impregnated with 10% solution of Paraloid B-72 in acetone, fragments assembled with a 30% one. To get clean white joints, the adhesive was tinted with acetone-soluble paint "Vetro" by "Maimeri", edges previously isolated with a 10%solution of Paraloid B-72 in acetone. The losses were filled in with plaster (figs. 13,17), molds made of "Zeta Plus" compound. Chips and joints filled in with a putty of talc and tempera white in equal parts, the composition also used as a primer for tinting (fig. 11). Since the tiles are designed to be modular, the tinting is done with a high degree of imitation of the original painting (fig. 12,14). On one of the tiles, more than a half of the painted area was to be reconstructed. Since there is a similar landscape in the painting of another tile, a complete reconstruction of the image seems to be legitimate here (fig. 15,16,18,19).



(a) (b) (c) (d)

Fig.7: Sample I: (XPS spectrum of the Be 1s line (a) and distribution of secondary Be ions (b); XPS spectrum of the Ce 1s line (c) and distribution of secondary Ce ions (d).

Fig. 13

Fig. 15

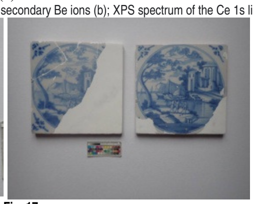


Fig. 17

Fig. 19

Fig. 14

Fig. 16

Fig. 18

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CONCLUSIONS

1. The complex application of surface analysis methods for the study of historical ceramics makes it possible to obtain information about their elemental and phase composition, including small impurities, which, together with available archaeometric information, provides a fairly accurate binding of the samples under study to the place and time of their production.

2. The study confirmed the attribution of the tiles as belonging to the Dutch production of the beginning - the first half of the 18th century.

3. The data revealed can be used in comparative analysis of composition and microstructure of materials of similar ceramic pieces so as to identify new significant features important for their attribution.

4. Studies of the kind can most fully be implemented in the process of conservation, so it seems prolific to carry out a complex conservation and study of items.

ACKNOWLEDGEMENTS

The research is supported by Russian Scientific Foundation grant No. 21-19-00412.