USING XRF ANALYSIS TO DETERMINE THE ELEMENTAL COMPOSITION OF PIGMENTS IN THE PAINTING OF MEDIEVAL ORIENTAL FAIENCES

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An X-ray fluorescence analysis (XRF) of the glaze of a glazed medieval Oriental ceramics batch was carried out in the NAA group of the IREN research facility of the Frank Laboratory of Neutron Physics, JINR, to determine the marker elements characteristic of various types of raw glaze materials used to manufacture of pigments. As a result, it was found that the blue color in the studied samples is due to the addition of cobalt, green one is due to copper or chromium, brown – manganese or iron, and turquoise – copper.

Sampling

13 samples of glazed medieval eastern ceramics were obtained from the Institute of Archeology, RAS to the NAA group of the IREN research facility of the Frank Laboratory of Neutron Physics, JINR. Each sample was examined from the glazed sides. This type of artifact is not only very numerous but also the most informative object. Studies of the composition of glazes of oriental faience have already been carried out in the past [1, 2], but the number of analyzed samples remains insufficient. This article presents the results of a study of 13 glaze samples obtained from fragments of imported ceramics discovered during excavations of the city of Bulgar (X–XV centuries, in the territory of Tatarstan, Russian Federation). Of these, 6 samples belonged to the products of the urban centers of the Golden Horde in the Lower Volga region (No. 1, 3, 4, 6, 7, 13), Persia (No. 2, 5, 9–12) and the not yet established center in Persia or Syria (No. 8). All of them came from layers and buildings dated by the middle – the second half of the 14th century.

The remarkable thing is that this study of archaeological ceramics in the NAA group is not carried out for the first time [3].

Equipment

A portable Bruker Tracer 5^{i} device (Fig. 1) was used for carrying out the X-ray fluorescence analysis [4]. The device is equipped with a 40 mm^2 SDD detector with resolution <140 eV on the Mn-K$_a$ line (250,000 pulses/s). The features of the device are the ability to install interchangeable collimators and the availability of a built-in video camera (Fig.2, Fig.3Fig.). The collimator with a diameter of 3 mm was used for the study. The built-in video camera made it possible to position the sample under investigation relative to the place of the X-ray beam penetration. These features of the device allowed to study the elemental composition of not only the glaze itself, but also to carry out a non-destructive research of various decorative elements with dimensions of more than three millimeters.

Experiment

Spectra of glazes, glaze decoration elements with different colors and sizes greater than 3 mm, and background ceramics spectra were collected for each sample.

For the analysis of the spectrogram, only those peaks were selected that were present in one color and were absent in the others ones. If such peaks were found, it was concluded that the corresponding chemical element was the main component of the coloring pigment to obtain this color. To exclude the possibility of influence the spectrum of the ceramic substrate on the glaze spectrum, the spectrum of ceramic substrate was also added to the final spectrogram. For example, in Fig. 7, we see that the peaks of copper (Cu) is present only in the glaze spectra and is completely absent in ceramic substrate.

Fig. 1. Bruker Tracer 5[i] XRF device.

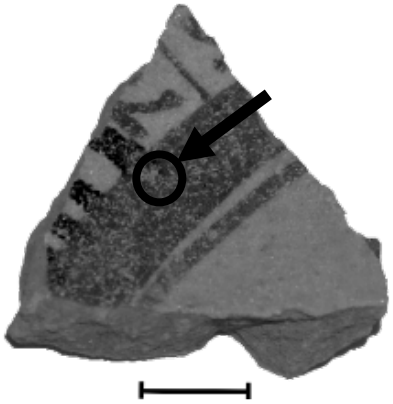


Fig. 2. Sample with marked test point.

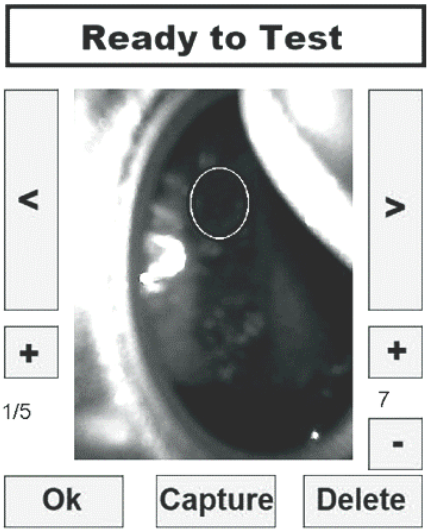


Fig. 3. Test point on built-in video camera.

Investigated samples were grouped as follows:

a) turquoise transparent glazes without additional decor,
b) white and greenish covered with tin glazes, including luster painting,
c) transparent colored glazes with over-glaze colorful and luster decor, and
d) colorless glazes of vessels decorated with polychrome underglaze painting.

Each of groups is considered in detail below.

a) Figs. 4 and 5 illustrate the turquoise transparent glazes without additional decor.

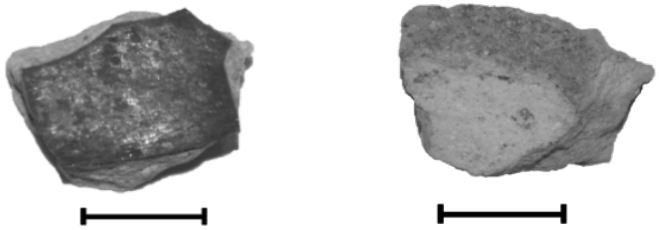


Fig. 4. Sample C-3.

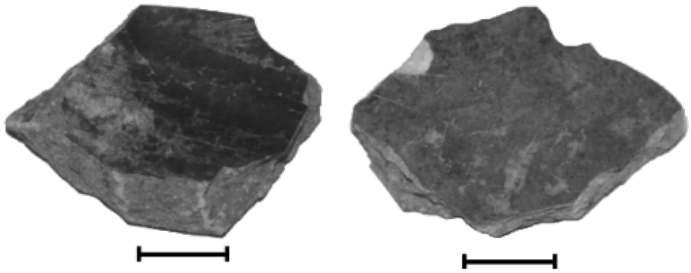


Fig. 5. Sample C-7.

The turquoise color in the group of turquoise transparent glazes without additional decor is caused by a high content of copper oxide in the mixture (Figs. 6 and 7). An opalescent view was obtained by iridescence.

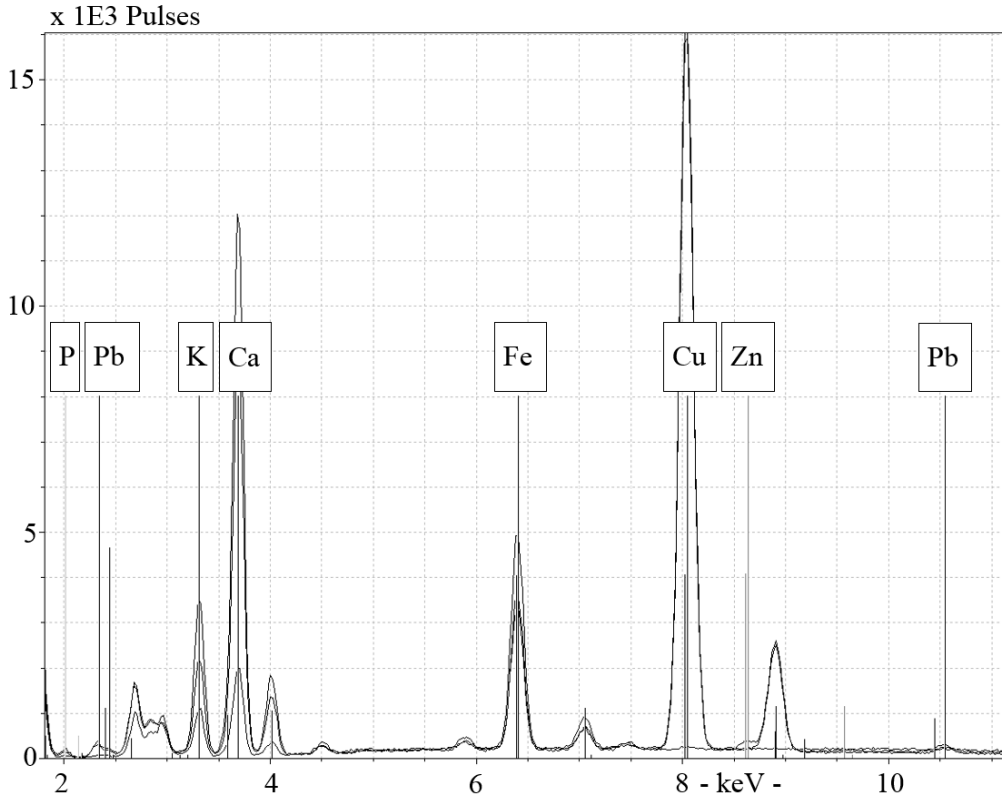


Fig.6. Full spectra of glaze and ceramic base of C-7 sample.

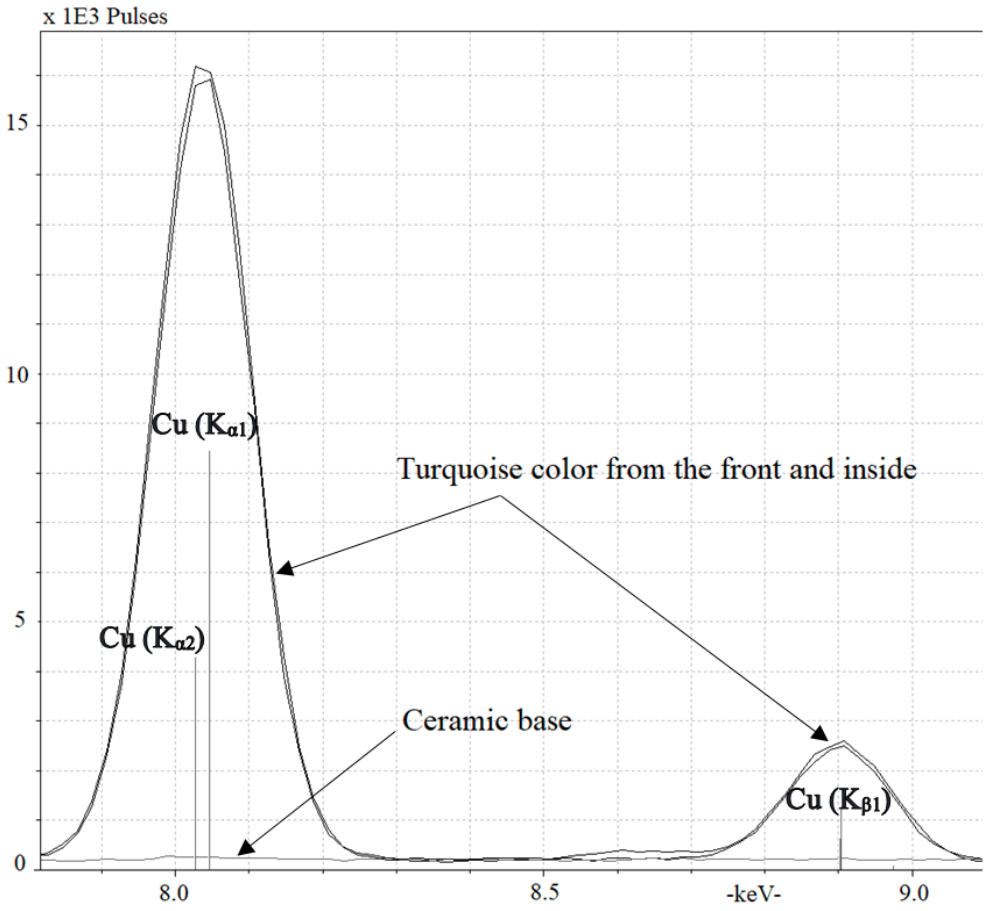


Fig.7. Peaks of Cu in spectrum of C-7 sample.

b) White and greenish samples covered with tin glazes, including luster painting, are shown in Figs. 8, 9 and 10.

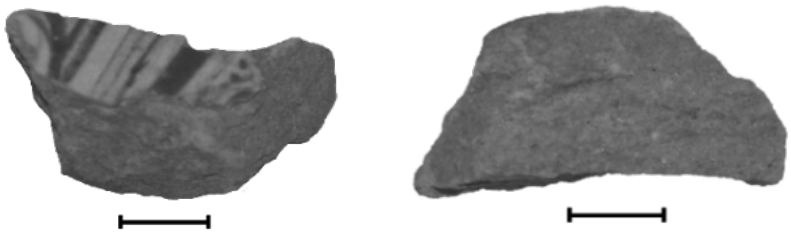


Fig. 8. Sample C-5.

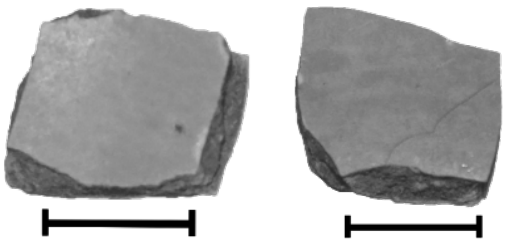


Fig. 9. Sample C-13.

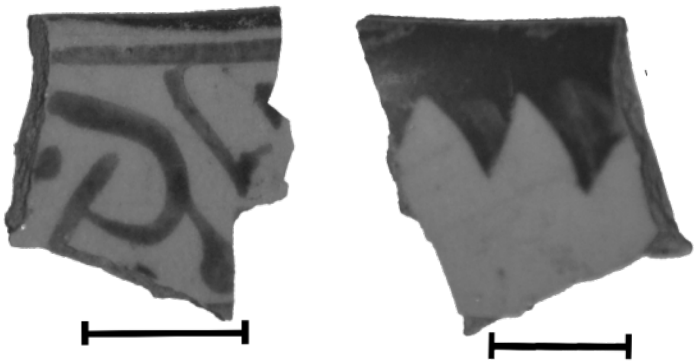
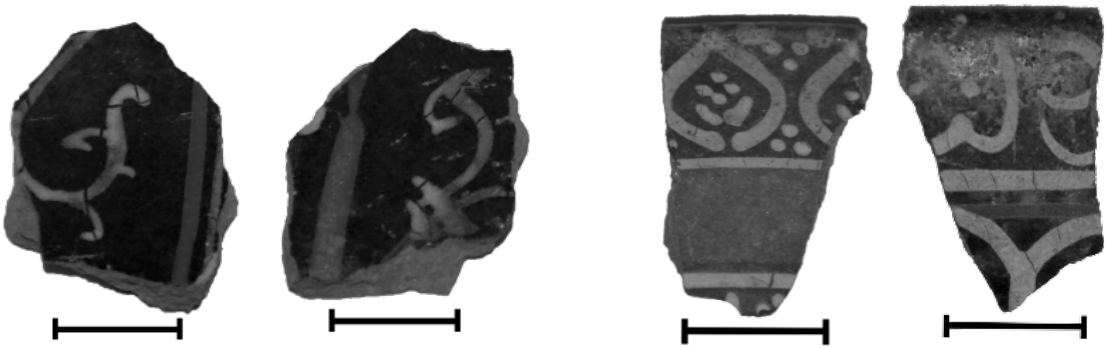


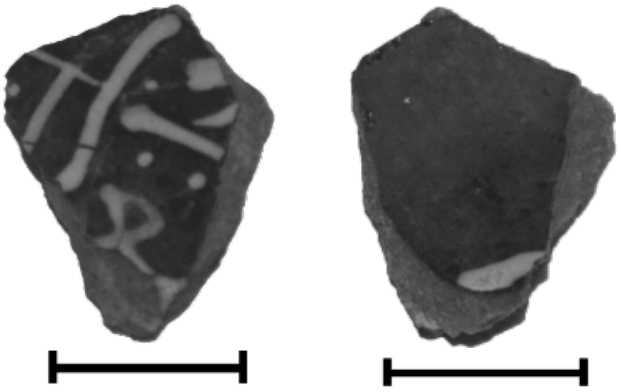
Fig. 10. Sample C-9.

Tin is present in large quantities in white glazes muffled by tin, as well as lead – an impurity to tin. A small amount of arsenic is possible. There is an interesting sample in this group (Fig. 8). A gold pigments (luster) is applied on this sample. This color is based on the addition of silver to the mixture.

c) Transparent colored glazes with over-glaze colorful and luster are shown in Figs. 11–13. Two samples belong to vessels of the "lajvardina" type – with transparent deep-blue (C-2) and turquoise (C-10) glazes, last one (C-8) were parts of bowl covered by deep-blue glaze, decorated by lustre painting.

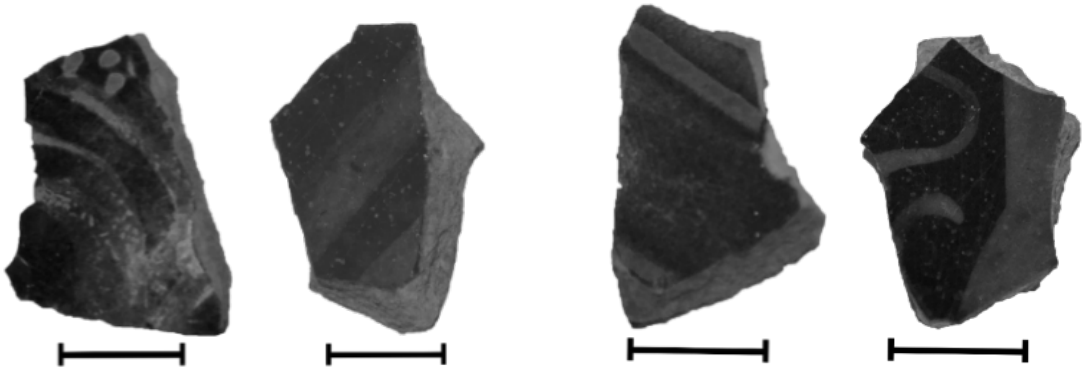


I. The first fragment. II. The second fragment.



III. The third fragment.

Fig. 11. Sample C-2 (three fragments).



I. The first fragment. II. The second fragment.

Fig. 12. Sample C-8 (two fragments).

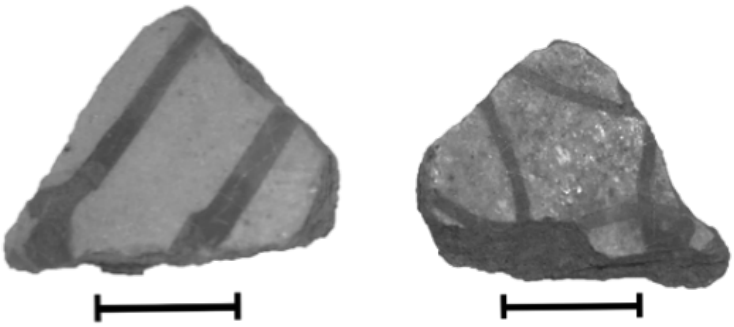


Fig. 13. Sample C-10.

The group of transparent glazes colorful cobalt-blue (Fig. 11 (I) and (III), 12) and copper-blue or turquoise (Fig. 11 (II), 13) is represented by samples with multi-colored (white, brown-red) overglazed patterns (Fig. 11, 13) and luster decor (Fig. 12). The blue color everywhere in the group is due to the presence of cobalt in the pigment, which has a strong coloring effect. Turquoise color, as in group 1, was obtained by adding copper to the pigment. Green one in luster (Fig.12) is also due to the presence of copper. Brown one is formed by iron. Tin, lead and arsenic are noted in some samples.

d) Colorless glazes of vessels decorated with polychrome underglaze painting are shown in Figs. 14–18.

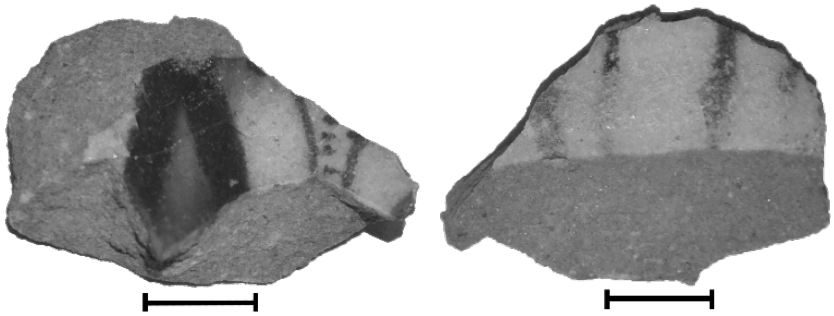


Fig. 14. Sample C-1.

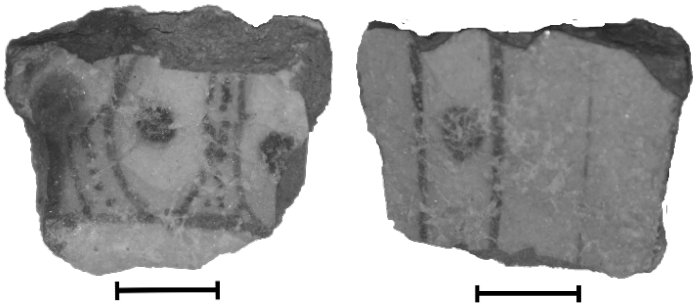


Fig. 15. Sample C-4.

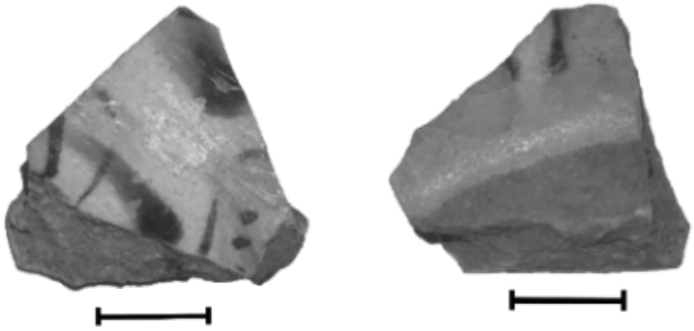


Fig. 16. Sample C-6.

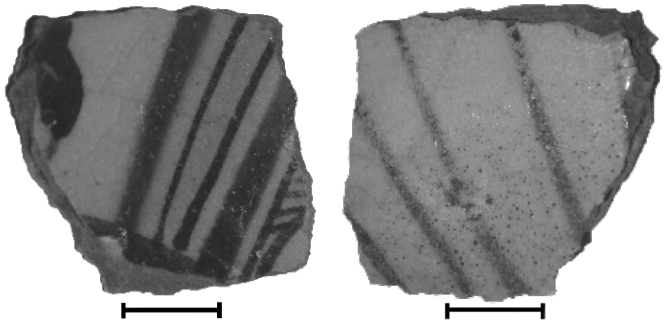


Fig. 17. Sample C-11.

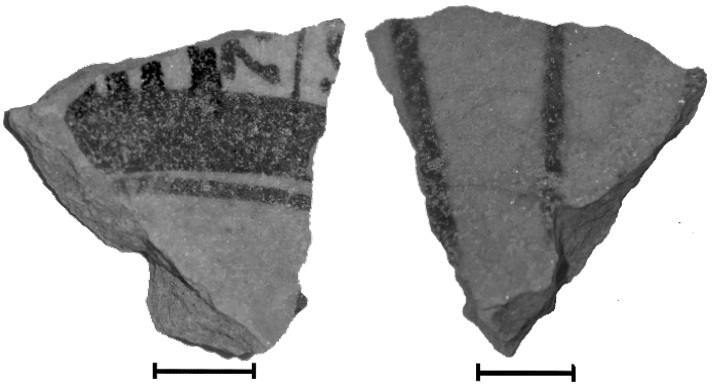


Fig. 18. Sample C-12.

The study of colorless glazes with underglaze painting was complicated by the fact that X-ray fluorescence analysis is a surface method. This fact limited the ability to fix the elements under the glaze. However, some elements of the pigments were found: manganese, causing brown color, cobalt – blue one, chromium (Fig. 14) and copper (Figs. 15–18) – green, copper – turquoise colors.

Conclusions

Portable XRF device Bruker Tracer 5^{i} was used for research of glazed medieval eastern ceramics. The elemental composition of not only the glaze was studied, but non-destructive studies of various decor elements with dimensions of more than three millimeters were also carried out. It was found that the blue color in the test samples was due to the addition of cobalt, the green due to copper or chromium, the brown due to manganese or iron, and the turquoise to copper.

References

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