Identification of pigments of Russian icons by means of X-ray fluorescence spectroscopy

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Abstract. In this work the analysis of paint layers of Russian icons of the 16th-19th centuries was carried out by means of X-ray fluorescence spectroscopy. The data obtained on the elemental composition of pigments made it possible to identify them. Main problems of identification were described in this paper. The results of the research will be used to create a database of XRF-spectra of pigments, which were used by Russian icon painters of certain schools and time periods.

1. Introduction
This work is devoted to use of the method of X-ray fluorescence analysis (XRF) in the field of conservation and restoration. Before starting the restoration process of an art object, it is necessary to conduct studies, which mainly rely on experience of restorers and art historians, according to the current practice in Russia, where instrumental methods of artwork analysis started to be used in recent years only. Meanwhile, non-destructive optoelectronic diagnostic methods are actively developed and widely used in museum work all over the world, due to the fact that they are non-invasive and do not require sampling [1]. Currently, one of the most frequently used methods for studying Cultural Heritage objects is the XRF method. It is based on the detection of X-ray fluorescence emission from inorganic substance atoms, which occurs when X-ray radiation interacts with a substance. As a result, obtained XRF-spectra give information about the elemental composition of analyzed substances. XRF analysis of artworks provides information about the time of its origin, modifications that could occur to it, and about the authenticity of objects [2–4]. Furthermore, this technique may be used for quantitative analysis of effectiveness of restoration of artworks [5].

In Russia, icon painting was the main type of fine art from the end of the 10th century to the beginning of the 18th century. Such a long period of development singled out Russian icon painting as a separate branch in fine art, and as a result, many ancient icons have been saved nowadays in the depositories of museums and cathedrals. Most of them are in critical condition and require essential restoration. That is why problems of preservation of icons are very actual for our country. The use of XRF method in studying pigment layers of ancient icons makes it possible to develop a reliable restoration methodology based on evidential proof prerequisites. Exactly for that reason this approach is important for further development of scientific restoration in our country. However, one of most actual tasks of practical use of XRF is creating the database of XRF-spectra of pigments, which were used by Russian icon painters of certain schools and time periods. This is the main goal of researches conducting by our research group, and in this paper we report the preliminary results of our work.
2. Investigation of the paint layer from Russian icons

NitonXL3tGold+ spectrometer (Thermo Fisher Scientific, USA) was used in the experiments. Operating voltage on X-ray tube - 6 ... 50 kV, operating current - up to 200 μA. Icons for investigation were provided by the Department of Easel Painting Restoration of the St.Petersburg State Academic Institute of Painting, Sculpture and Architecture named after I.E. Repin.

2.1. Method

Figure 1 shows a methodology of XRF-spectrum registration and analysis at the example of icon “Five-figure half-length Deisus” (Vologda State Historical-Architectural and Art Museum-Reserve, 18th century).

![Figure 1](image_url)

**Figure 1.** Measurement of XRF-spectra: general view of the icon (a), the same photo with set of reference points (b), example of XRF-spectrum (c).

Measurements were carried out according to a set of reference points (RP), which correspond to the main colors of paints and were chosen by restorers.

2.2 Results

XRF - spectra were obtained at each reference point. The main elements identified from each XRF-spectrum are presented in table 1.
Table 1. Main elements from XRF-spectra in reference points (RP).

| № of RP | 1       | 2       | 3       | 4       | 5       |
|---------|---------|---------|---------|---------|---------|
| Main elements | Pb, Ca, Cu | Ca, Fe, Cu, Pb, Ag | Cu, Pb, Ca | Hg, Ca, Pb | Fe, Ca, Pb |
| Color on icon | Dark - green | Gold | Dark - green | Red | Ocher |

There is a calcium peak in the spectrum of each RP. This is due to the fact that the ground layer of icons – gesso ground, was usually made from a mixture of chalk, which contains calcium, and animal or fish glue. Therefore, calcium peaks will not be taken into account during the pigment identification.

2.2.1 Reference point 1 and 3

The spectra at these points contain the same basic elements and their general view is similar (Figure 2).

![Figure 2](image_url)

Figure 2. General view of XRF – spectra: RP 1 (a), RP 3 (b).

It is assumed that at both points there is the pigment verdigris (Cu(CH₃COO) ∙ 2Cu(OH)₂), mixed with lead white (2PbCO₃ ∙ Pb(OH)₂) at different concentrations. Verdigris mixed with white lead was widely used in Russian icon painting of the 18th century to paint backgrounds and clothing. As it is seen from Figure 1, RP 1 is laid in the area of background, while RP 3 is in the area of sleeve. Difference in the intensities of Cu peaks may be explained by the change in the concentration of verdigris in these areas. It is possible to obtain different shades of color by changing concentration one of the mixture components.

2.2.2 Reference point 4

The most intensive peak in this point is Hg, the color in the area of RP 4 is red. There is an explicit peak of Pb also (Figure 3).

In the 18th century, a pigment such as cinnabar was often used to highlight something on an icon, for example, an element of the background or clothing. Its color is bright – red, sometimes blood – red. The cinnabar mineral is mercury (II) sulfide (HgS). Because of the fact, that the spectrum contains
a slightly less intensive lead peak, this may mean that the cinnabar was mixed with white lead and applied to the icon.

Another assumption is that the red tint was obtained by mixing the pigments of cinnabar and red lead (Pb₃O₄). Such mixtures have been used since the Roman Empire period to reduce the price of the cinnabar pigment, because its extraction was under the strict control.

2.2.3 Problems of pigment identification
The spectrum at RP 2 showed the absence of explicit peaks of metallic components, and at RP 5 (Figure 4) intensive peak of iron and color in that area indicate that ocher was used in that point - a natural pigment consisting of iron oxide hydrates in combination with clay.
The RP 2 is on the golden halo. Since no gold was found in the spectrum, the use of gold leaf when writing this icon is excluded. Also, no explicit peaks of other metals were found in the spectrum. This could mean that the golden pigment is made from either organic components or non-metals that are difficult to detect with XRF.

The most common group of pigments containing ferrous components (RP 5) is ocher. There are a lot of ocher shades, which makes it difficult to analyze this pigment. However, such pigments as mustard ocher and limonite were often used to mark the frame of the icon. RP 5 is also situated in the frame area. Though the XRF - data is not enough to determine unequivocally which pigment was used at point 5.

In the experiment, 7 icons were investigated with XRF – method. All icons had gilding or ocher areas. Based on XRF method identification of such pigments was not reliable for all investigated icons.

3. Conclusion

Our studies allowed to identify most typical red and green pigments consisting Cu, Hg and Pb, which were used in Russian icon art created by artists of Russian cities Pskov and Novgorod. Obtained XRF-spectra will be used for systematization of information about specific pigments of different time periods and icon painting schools. It allows creating a database of XRF-spectra of Russian icons of that period, which will become an important information resource for restorers and art historians.

It should be noted that in the experiments it was revealed that some groups of pigments could not be identified with XRF analysis, for example, pigments imitating gilding, or ocher. These pigments require additional study by means of alternative analytical methods to identify impurities in them, including organic ones, which may provide more complete information about their origin and properties.

Acknowledgments

Authors are grateful to the Department of Easel Painting Restoration of the St.Petersburg State Academic Institute of Painting, Sculpture and Architecture named after I. E. Repin for providing access to spectrometer NitonXL3tGold+, as well as Professor F. Bobrov for valuable advice.

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