A NEW METHOD OF STUDYING THE CHEMICAL COMPOSITION OF THE SURFACE OF HISTORICAL MELEE WEAPONS IN THE CONTEXT OF THE QUESTION OF ITS AUTHENTICITY

Abstract. The results of the study of the chemical composition of the surface of 4 items of melee weapons made of iron — bayonets and sabers — are given. This allows us to establish the authenticity of samples of cold steel of one chronological period.

The author's method of the research of chemical composition of a surface of historical objects of
One of the methods for studying the cold weapon by rubbing of samples with tampons from cotton wool and their further research was offered. This makes it possible to examine objects of cold steel, large in size, without damaging the surface, as well as to simplify the procedure of research of objects of historical and cultural value.

**Keywords:** cold steel, metal refining, metal crystallization, impurity chemical elements, X-ray fluorescence analysis.

**Introduction.** The results of the study of historical objects made of iron with the X-ray fluorescence analyzer (hereinafter – X-ray diffraction) often surprise experts with high purity of metal (100% iron) and almost complete absence (less than 0.1%) of traditional chemical impurities present in primary ores – Mn, Cr, Ni, etc. An example is ancient swords, which are more than a thousand years old [1]. The reason for this is the process of gradual and long-term natural elimination of chemical impurities from the surface of the metal during its gradual recrystallization and as a result of the processes of "aging" [2]. With this in mind, we make assumptions about the possibility of using the results of studying the chemical composition of the surface of historical melee weapons in the context of solving practical problems related to establishing its authenticity, which currently has a high level of relevance in modern expertise. At the same time, studies of the chemical composition of such objects by X-ray diffraction do not allow to study in detail the composition of chemical elements that are in very small concentrations on the surface of objects, because in this case the device registers only iron and those elements whose concentration reaches more than 0.1%.

**The aim of the work** is to demonstrate the practical application of a fundamentally new method of obtaining information about the chemical composition of the surface of historical artifacts made of iron, which allows studying the chemical composition of chemical elements eliminated on the metal surface in ultra-low concentrations.

**The way to solve the problem.** The traditional method of using X-ray diffraction to study the surface of cold steel [3] does not allow to detection of chemical impurities that are in very small concentrations, because the spectral lines of iron fluorescence completely overlap the lines of other chemical elements.
To overcome this problem, the author's method of testing the surface by rubbing was proposed.

The research method proposed by the authors is that the metal surface of the test sample was rubbed with a cotton swab at any point in the sample (for example, it can be a blade, guard, handle, sheath or metal trim (if available)). Rubbing the surfaces was carried out by several point frictions (usually two or three) with a diameter of up to 1 cm.

As a result of rubbing on cotton swabs, some chemical compounds remain, which were once eliminated from the primary alloy and could not be introduced from the environment. Up to 20 consecutive rubs were performed on the surface of each object to increase the reliability of the experiment.

In the next stage of the study, the tampons were burned to obtain ash. The resulting ash was subjected to research by X-ray diffraction.

Indicators determined during the study indicate the use of certain technologies of metal processing and certain features of the manufacture of objects in the past. In addition, the indicators determined in the study of object surfaces are indicators of chemical and physicochemical changes in the structure of samples that occurred with objects due to, for example, long-term interaction of the sample with the environment, destructive acidity of soil or oxygen and restoration work during the restoration and storage of specimens in museums, funds or private collections.

The results of the research indicate the possibility of detecting traces of diffusion or mass transfer processes – gradual adaptive changes in the chemical composition and structure of the metal [1]. The diffusion process occurs through the mutual penetration of metal molecules or atoms between molecules or atoms of the iron alloy during the long existence of iron objects, in particular, cold steel objects.

Examples and results of the study. To confirm the scientific hypotheses described above, four samples of cold steel, made in about one historical period, were selected. Spot samples for the study were taken from both the blade and the metal components of the finish, such as the guard, the metal tip of the sheath and the handle.
Fluorescence spectra were obtained on an X-ray fluorescence spectrometer Expert Mobile (manufactured by INAM LLC, Kyiv). The device is equipped with an X-ray tube with direction / current parameters – 50 kV / 0.1 mA, anode – titanium. The photon energy detector of fluorescent (secondary) extraction from the image – SDD, which in the air allows you to analyze the range elements from element 12 of magnesium to element 92 of uranium [1].

X-ray spectra of photon energies, which are obtained as a result of measuring samples, are processed using the same software as the spectrometer. Pre-calibration of the energy scale along the X-axis of the X-ray spectra allows for mutual comparison by normalizing the background intensity (scattered radiation). In this way, the elemental composition of the material is revealed, excluding the elemental composition of the "pure sample" (cotton swab).

To obtain a sample of "pure sample" of the method of X-ray fluorescence analysis, a study of a cotton swab, which did not rub the surface. This sample will be considered "pure" from chemical impurities.

The results of spot tests and detected elements are presented in the table 1. "Pure sample" is made separately for comparison.

<table>
<thead>
<tr>
<th>Description of the subject</th>
<th>Sample</th>
<th>Cl</th>
<th>P</th>
<th>Ca</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>K</th>
<th>Ti</th>
<th>Mn</th>
<th>Pb</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bayonet-knife German, 1883/98 of a new type (1933-1945) to the 98K carbine</td>
<td>blade</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>sheath</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Spanish bayonet knife 1913 to the Mauser rifle 1893/1916 in leather sheaths</td>
<td>blade</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>blade</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td></td>
<td>blade</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Russian officer’s cavalry saber, 1827/1909 (without sheath)</td>
<td>blade</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>blade</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>handles</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
In the results of the study of the chemical composition of the metal surface of the selected items of cold steel, given in table 1, you can see the high level of variability of the detected chemical elements. It is important to note that certain chemical elements occur more often than others.

The "pure sample" of a cotton swab did not show the presence of impurity elements, so all samples of rubbing were compared with this sample.

The chemical element phosphorus can be observed in three of the four samples (except for the saber of the Russian officer cavalry), but only in one spot sample. The elements calcium, iron, zinc, and copper are also found in almost every sample.

Chlorine is observed only on the surfaces of two specimens of bayonets, namely sample № 1 (bayonet-knife German, 1883/98 new type (1933-1945) to carbine 98K) and № 2 (bayonet-knife Spanish, 1913 to the Mauser rifle 1893/1916 in leather sheaths).

The element nickel was found only once in the sample saber of the Russian officer cavalry, 1827/1909, and in the Polish sword with the image of the emblem "Gonytva", -a copy of the twentieth century. And lead was detected in sample № 2 (Spanish bayonet knife, 1913 to the Mauser rifle 1893/1916 in leather sheaths) and № 4 (Polish sword with the image of the emblem "Gonytva", a copy of the twentieth century).

Manganese was also found in only two specimens of bayonet knives dating back to the early twentieth century.

The chemical element titanium, as well as calcium, iron, zinc, copper, is found in every test sample and in almost every spot sample of both the blade and the finishing elements.
This heterogeneity of chemical elements is a direct indication of the processes of elimination of impurity chemical elements on the metal surface with the formation of areas covered with ultra-thin films of hydroxides.

On the surface of metal objects that have been made over the past 50 years, such high differences in chemical composition will not be observed, so this feature may be the main criterion for the authenticity of antique and museum samples of cold steel [4].

In addition, indicator chemical elements that are isomorphic in the crystal lattice and can indicate the approximate age of the artifacts should be identified. Such elements in the studied subjects are manganese, nickel.

The new method practically demonstrates that during storage of metal objects there are gradual adaptive changes in their chemical composition and structure.

Chemical elements also have the ability to accumulate and concentrate on the surface [5].

In table 2 we can observe the quantitative characteristics of the composition of the surface of the saber of the Russian officer cavalry, sp. 1827/1909 (without sheath). Such changes may occur over a long period of time during the display and storage of artifacts, in particular, cold steel weapons, in the museum’s funds.

Table 2

Quantitative results of testing the saber of the Russian officer cavalry, 1827/1909 (without sheath)

<table>
<thead>
<tr>
<th>Chemical element</th>
<th>Spot test from the blade</th>
<th>Spot test from the blade</th>
<th>Spot test from the handle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>45,239</td>
<td>69,24</td>
<td>32,637</td>
</tr>
<tr>
<td>Fe</td>
<td>11,304</td>
<td>6,097</td>
<td>2,87</td>
</tr>
<tr>
<td>Cu</td>
<td>0,518</td>
<td>-</td>
<td>31,08</td>
</tr>
<tr>
<td>Zn</td>
<td>0,984</td>
<td>-</td>
<td>6,118</td>
</tr>
<tr>
<td>K</td>
<td>22,475</td>
<td>-</td>
<td>22,309</td>
</tr>
<tr>
<td>Ti</td>
<td>12,6</td>
<td>24,663</td>
<td>5,081</td>
</tr>
<tr>
<td>Ni</td>
<td>6,919</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

As can be seen from the table 2, the composition of both samples rubbed from the blade of the saber of the Russian officer cavalry, 1827/1909 (without sheath),
includes such elements as iron, calcium, titanium. Spot test, which was taken near the handle, as well as on the handle itself, also contains copper, potassium and zinc.

In addition, a considerable amount of nickel is present in the spot test from the blade.

Impurity elements found on the surface of the sample can be identified as confirmation of the process of mass metabolism on the surface and serve as confirmation of the fact that the metals undergo complex processes of differentiation of substances and their recrystallization [1].

It is the process of recrystallization of metals that leads to the expulsion of impurity chemical elements from the balanced structures of the crystal lattice of the metal. Such elements accumulate in the intercrystalline space and also have the ability to interact with the environment and form various chemical compounds. Accumulation of chemical impurities on the surface of metal artifacts usually occurs in the form of patina minerals (a thin layer of corrosion products with a clear, sharply different color formed on the metal surface, in particular, the surface of cold steel objects affected by air or water).

On the surface of metals are concentrated ions of those chemical elements that are much larger or smaller than the size of iron ions that are in the crystal lattice. Ions of chemical elements that are smaller than the size of iron have a lower intensity of removal from the metal.

Another important fact is the results of analytical studies, which recorded the absence of iron.

This fact can be explained as follows:
– the presence of ultra-thin hydroxide films on the surface, which concentrates freshly eliminated from the alloy chemical elements from ultra-small mineral impurities (such as calcium, potassium, chlorine, phosphorus, copper, zinc). According to this hypothesis, iron is a newly formed and well-crystallized substance;
– surface treatment with preservatives to remove iron hydroxides and preserve the appearance and condition of the sample.

Thus, observing the peculiarities of the diversity and content of chemicals on the
surface of samples of cold steel, we can obtain a new method for determining the authenticity of samples and the presence of traces of restoration intervention.

Also in the future, it will be expedient to conduct refinement experiments that will theoretically substantiate the observed features of the chemical composition of the surface and form a base of isomorphic indicator elements characteristic of certain historical periods [1].

Research conducted by the new method confirms the hypothesis that the main features for constructing claims about the authenticity of historical artifacts may be X-ray fluorescence analysis of samples taken by a method that does not destroy or damage the surface.

Thus, monuments of history and culture of metals have a special property – to be constantly covered with new mineral layers with slight changes in temperature and humidity in their places of storage [1].

**Conclusions.** The proposed method of research allows studying museum exhibits and samples of private collections without damaging their surface. This method was confirmed by the author's method of studying the chemical composition of the surface of historical melee weapons by rubbing samples with cotton swabs and their subsequent study and allows to study the surface layer of melee weapons, which usually have a wide range of sizes (usually artifacts are larger, than the working chamber of the X-ray fluorescence analyzer) [2].

In addition, this technique simplifies the procedure of sample examination, as it is not necessary to deliver items of historical and cultural value to a specialized laboratory, and accordingly there will be no depreciation of samples due to damage during transportation.

As for the results of studies of cold steel samples, they may be evidence of heterogeneity in the composition of patina formations on their surface. These results confirm the authenticity of ancient objects of history and culture.

In addition, elements that are found in almost every sample were identified. Such elements are calcium, iron, zinc, copper.

Studies of the surface of the samples showed a difference in the chemical composition of the surface layers of different parts of individual samples of antique
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melee weapons, which may indicate different times or different technology of their manufacture.

The described method makes it possible to more accurately determine the chemical composition of the patina of historical melee weapons and to exclude from the composition of impurity chemical elements those elements that may remain in cotton wool after the process of its manufacture and packaging.

Thus, research confirms the possibility of using X-ray fluorescence analysis to draw conclusions about the authenticity of historical and cultural objects made of iron and other metals (such as bronze, silver or copper), as well as additional research to create mathematical models for predicting their age.

References: