UDC 544.1-026.87:930.85
DOI: 10.15587/1729-4061.2022.268175

DETERMINING DANGEROUS CHEMICALS ON THE SURFACE OF METALLIC HISTORICAL ARTEFACTS

Yuliia Vovk
Corresponding author
Postgraduate Student*
E-mail: y.vovk@knute.edu.ua
Nina Merezhko
Doctor of Technical Sciences, Professor, Head of Department*
Volodymyr Indutnyi
Doctor of Geological and Mineralogical Sciences, Associate Professor*
Kateryna Pirkovich
PhD, Associate Professor*
Yurii Lytvynenko
Junior Researcher
M. P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation of the National Academy of Sciences of Ukraine
Akad. Palladina ave., 34, Kyiv, Ukraine, 03142
*Department of Commodity Science and Customs Affairs
State University of Trade and Economics
Kyoto str., 19, Kyiv, Ukraine, 02156

The problem is to determine the threat of chemical damage to a person upon his contact with historical artifacts from metals. For this purpose, experimental studies of the process of accumulation of chemicals on the surface of historical metal products were carried out. The objects of this study were 3 samples of historical cold weapons selected from the museum fund, as well as samples from modern sheet steel.

The blades of museum objects were rubbed with a special ash-free swab, which was burned, and the chemical composition of the residue was determined. This makes it possible to obtain data on compounds from a significant surface area. A list of chemical elements that accumulate on the surface of metallic historical artifacts over time has been established. Theoretically, the possibility of the appearance on the surface of historical artifacts made of iron of such chemical elements as Mercury, Barium, Stibium, Phosphorus, Plumbum (Lead), Thallium, Chromium, Selenium, Cadmium has been theoretically proven. This can pose a threat to the health of museum workers and collectors who are in daily contact with such items.

The results of the experiment are provided with samples of modern steel, which, in order to accelerate the process of elimination of impurity elements, warmed up for 3 hours in a muffle furnace at a temperature of 700 °C. The surface of these samples was studied using an electron microscope, and local emission analysis of the chemical composition was carried out. The obtained results confirm the process of elimination of ions of individual chemical elements from the metal in the process of its heating. We can observe the release of Al, Si, S, K, Ca, Cu ions to the surface. Based on the results obtained, plots are built that describe the change in the chemical composition of the metal surface throughout the history of existence.

The use of the author's method of testing makes it possible to study the problem of safety of handling historical monuments in general. The results of the study are important for establishing the authenticity of metallic historical artifacts and assessing possible risks in contact with them

Keywords: metallic historical artifacts, hazardous chemicals, chemical composition, X-ray fluorescence analysis

Received date 19.09.2022
Accepted date 24.11.2022
Published date 30.12.2022

How to Cite: *Vovk, Y., Merezhko, N., Indutnyi, V., Pirkovich, K., Lytvynenko, Y. (2022). Determining dangerous chemicals on the surface of metallic historical artefacts. Eastern-European Journal of Enterprise Technologies, 6 (12 (120)), 6–12. doi: https://doi.org/10.15587/1729-4061.2022.268175*

1. Introduction

The museum fund, as well as private collections, now house hundreds of thousands of cultural monuments made of metals – cold weapons, military equipment, dishes, household items, coins, cult items, personal jewelry, and more. Many of these things are over a thousand years old; some are more than two thousand years old. The chemical composition and aggregate structure of the metals from which they were made in the historical past, which are primarily gold, copper, silver, and iron, have changed significantly as a result of the long-term natural processes of recrystallization. The surface of metals and their alloys gradually acquired new physical properties, such as hardness and brittleness [1]. In addition, the surface is freed from chemical elements that contrast in chemical properties. This is confirmed by the results of experimental studies using an X-ray fluorescent analyzer, as well as an emission analyzer of an electron microscope [2, 3].

Our studies are relevant because they can accurately indicate the surface composition of impurity elements. And this, in turn, will make it possible to establish quite accurately the age of metal samples and, therefore, their authenticity.

2. Literature review and problem statement

Experimental confirmation of the hypothesis of the concentration of impurity chemical elements on the surface of metallic historical artifacts became possible only with the introduction of the author's method of testing. The technique involves the study of the chemical composition of only those substances that are collected from a large surface area of the sample under study when it is rubbed with a special ash-free swab [4]. Next, the swab is burned, and the chemical composition of the material residue is studied. This makes it possible to move away from the practice of studying the chemical composition directly on the surface of the object using an X-ray fluorescent analyzer with a localization of the study area of 1.5 square millimeters. Thus, it is possible to obtain data on compounds present on the surface, the area of which ranges from 100 to 200 square centimeters (the testing area in this case is 100000–200000 times larger).

There are many fundamental studies that consider metallurgical processes. Thus, work [5] analyzes the development of refining technologies in the steel production process over the past 60 years and the future prospects of the industry, aiming to reduce processing costs and improve the quality of steel. Nevertheless, it is important to consider the features of the technological process of manufacturing iron objects of an earlier period.

Work [6] considers the characteristics and properties of cast, cut, and forged jewelry made of metals, including precious ones, which can be dangerous if there are impurities in their composition. Several methods have been developed to determine the authenticity of cultural values in the Samaria region. These methods clearly show the features of the products of this particular region and can be adapted to any region of the world.

In [7], the authors cite the properties of cast and forged steel products, which can be dangerous if they contain impurity elements. The described impurities significantly reduce the quality of the final product. In order to reduce the content of impurity elements that can affect the properties of the product, several methods of refining molten metal have been developed. However, historical and cultural items from metals differ from objects made over the past decades in the peculiarities of production technology, which causes the release of various chemical elements on their surface over time, and the influence of the environment.

In [8], the process of vacuum casting of steel products was investigated, in which a crown (patina) is formed through the contact of steel with the spray limiter. It is a powerful source of impurity inclusions that can affect the quality of finished products. However, that paper does not mention the importance of impurity inclusions in determining the authenticity of metallic historical artifacts and their age.

In [9], the authors propose to use an X-ray fluorescent analyzer (XFA) to study the gold jewelry of ancient Egypt. Gold jewelry and weapons have been researched and divided into two fundamentally new types. This became possible thanks to X-ray fluorescent study of the composition of the metal and can be used in further studies of jewelry and weapons made of ferrous metals.

Studies of the chemical composition and microstructure of cultural values made from various metals were carried out. In particular, it is important to study the natural patina on the surface of bronze artifacts [10], and the classification and characteristics of patina structures for a deeper understanding of the mechanism of their formation.

Compositional and microstructural study of joining methods in archaeological gold objects of the pre-Roman era was investigated in [11] by analytical methods. The main purpose of the study was to examine their characteristics at both the compositional and microstructural levels (SEM–EDS, metallography, μ–XRF and μ–PIXE). Nevertheless, historical items of cold weapons made of iron are distinguished by the peculiarities of the crystal-chemical transformation, and therefore require in-depth study.

The problem is to determine the threat of chemical damage to a person upon contact with historical cold weapons. The application of the author's method of testing makes it possible to study the problem of safety in handling historical monuments in general. Dangerous chemical elements are concentrated on the surface of metal products, which, in contact with air and moisture, form easily soluble chemical compounds. These compounds can pose a threat to the health of museum workers and collectors who come into daily contact with such items.

3. The aim and objectives of the study

The aim of this work is to identify hazardous chemicals on the surface of metallic historical artifacts. This will make it possible to assess the level of threat of chemical damage to museum workers and collectors with harmful substances that form on the surface of samples naturally over a long period of life.

To accomplish the aim, the following tasks have been set:

– to prepare samples and conduct experimental studies of the chemical composition of historical objects made of iron;

– to describe the results of the experiment with sheet steel samples, which make it possible to describe the process of elimination of chemical elements on the surface of the alloy and assess the level of safety of handling products manufactured in the late XX - early XXI century.

4. The study materials and methods

The objects of our study were three samples of historical cold weapons selected from the museum fund, as well as samples of sheet steel, the age of which does not exceed 50 years.

Rubbing from the surface of historical cold weapons was studied using the Expert Mobile X-ray fluorescent analyzer (manufacturer INAM LLC, Kyiv). The device is equipped with an X-ray tube with direction/current parameters – 50 kV/0.1 mA, the anode is titanium. Photon energy detector for fluorescent (secondary) extraction from the image – SDD. In the air, it makes it possible to analyze the range elements from the 12th element of the periodic table of magnesium to the 92nd element of uranium. Small in size (1×1 cm) paired steel samples, which do not exceed 50 years old, with a cleaned and polished surface, were studied using the Jeol JSM–6700F Field Emission Scanning Electron Microscope (Japan) with the possibilities of chemical analysis by emission method.

At the first stage, the objects of our study were three examples of historical cold weapons. Preference was given to objects of the XVIII-XIX centuries, which were not subject to restoration work (according to museum documentation), and their surface was not treated with special substances and was not subjected to mechanical cleaning.

The steel blades of these objects were rubbed with a special ash-free swab to collect the substance that had accumulated on their surface. The swab was burned, and the residue was used to study the chemical composition.

The second stage of experimental research was to clearly confirm the process of elimination of chemical elements from steel to its surface and describe it meaningfully. For this, 4 small paired samples were made. Their surface was polished. Two samples were heated in a muffle furnace at a temperature of 700 degrees Celsius for 3 hours, after which the surface of the samples was studied using an electron microscope with the possibility of conducting local emission analysis of the chemical composition, for which the Jeol JSM–6700F Field Emission Scanning Electron Microscope was used.

5. Results of the study of the process of accumulation of hazardous chemicals on the surface of metallic historical artifacts

5. 1. Results of the study of the chemical composition of historical objects made of iron

Heat treatment of metal samples leads to energy activation of processes in its crystal lattices. Iron, having a cubic volume-centered structure of the crystal lattice, in which the ions are in a state of covalent chemical bond [12], under the action of temperature activates its own oscillations of the crystal lattice. Increasing their amplitude contributes to the ejection of ions of foreign chemical elements. The rate of extraction of foreign ions depends on the degree of their chemical affinity for iron ions – by the mass and structure of the outer electron shells.

It is clear that the most actively and, accordingly, first of all, chemical elements with large ion sizes – K, Ca, Na – will be extracted from the iron alloy [13]. Elements with close and much smaller ion sizes will be extracted more slowly – Al, Si, Mn, Cr, Ni, Zn, Mg, Pb, Ag, Sn, P, Cu, Ti, Si, S. This is due to the fact that metals have the ability to push out impurity chemical elements, the size of the ions of which is much larger than the size of the ion of iron itself.

Among the named chemical elements, theoretically, only the Mn^{+3} ion can isomorphically replace iron in the crystal lattice, forming a disintegration-resistant dislocation. Consequently, its elimination is the slowest and can be considered an indicator of the age of the artifact. Si will also slowly release but because the size of its ions is abnormally small. Thus, to study the process of recrystallization of an iron alloy, the named chemical elements are the most informative. In addition, they are always present in iron ores in large quantities and, regardless of the method of smelting metal, remain in it in sufficient concentration for analytical study [14].

It should also be borne in mind that the real iron alloy contains a certain amount of mineral inclusions of heat-resistant chemical compounds accepted from ores – carbides and oxides of silicon, iron, aluminum, and others [15]. These compounds can also decompose over time, and the corresponding substances accumulate on the surface of historical artifacts. Therefore, the interpretation of the results of experimental observations is difficult for mathematical modeling due to the variety of physicochemical processes that take place. In addition, the method of metal processing, for example, forging, can lead to the introduction of certain substances on its surface.

Table 1 gives the results of the study of the chemical composition of substances on the surface of three samples of historical cold weapons.

It can be clearly seen that harmful substances are present in unacceptable concentrations in accordance with the requirements of current sanitary standards. In addition, it is clear that if there are other impurity chemical elements in the primary metal, for example, such as Mercury, Barium, Stibium, Phosphorus, Plumbum (Lead), Thallium, Chromium, Selenium, Cadmium, and others, they will also appear on the surface within a short time of existence. This means that in the process of working with these samples, which involves constant contact with the skin of the hands, there is chemical damage to their surface, which leads to a negative impact on health. Especially dangerous is the long and daily work of museum workers.

5. 2. Results of an experiment with sheet steel samples

It is advisable to assume that the process of extraction of ions can be significantly accelerated by warming up prototypes. So, there is an experimental opportunity to prove that the harmful substances present on the surface are not introduced from the environment in the process of the existence of weapons, their cleaning with special substances, but are the result of the gradual natural recrystallization of the metal. For a more meaningful study of this process, small samples of sheet iron were made. Their surface was polished. Half of the samples were heated in a muffle furnace at 700 degrees Celsius for 3 hours. The subject of our study was thermally treated and thermally untreated surfaces of iron samples.

Fig. 1 shows images of the surfaces of iron samples under an electron microscope. The surface image was magnified from 45 to 160 times. The points where the chemical composition was investigated are indicated by blue numbers. Table 2 gives the results of determining the content of chemical elements on the metal surface by emission method.

Photos show that the release of chemical elements is uneven – in the form of separate islands, represented by crusts and formed in places where there are micro-dislocations and micro-seals. The chemical composition of these new formations is significantly different from the chemical composition of the metal surface. This proves the presence of activation of the process of self-cleaning of the metal and the possibility of concentration of harmful substances on its surface.

Among the chemical elements harmful to humans that pose a danger to humans (mainly hydroxides, hydro silicates, sulfates, and chlorides), copper, zinc, titanium should be distinguished.

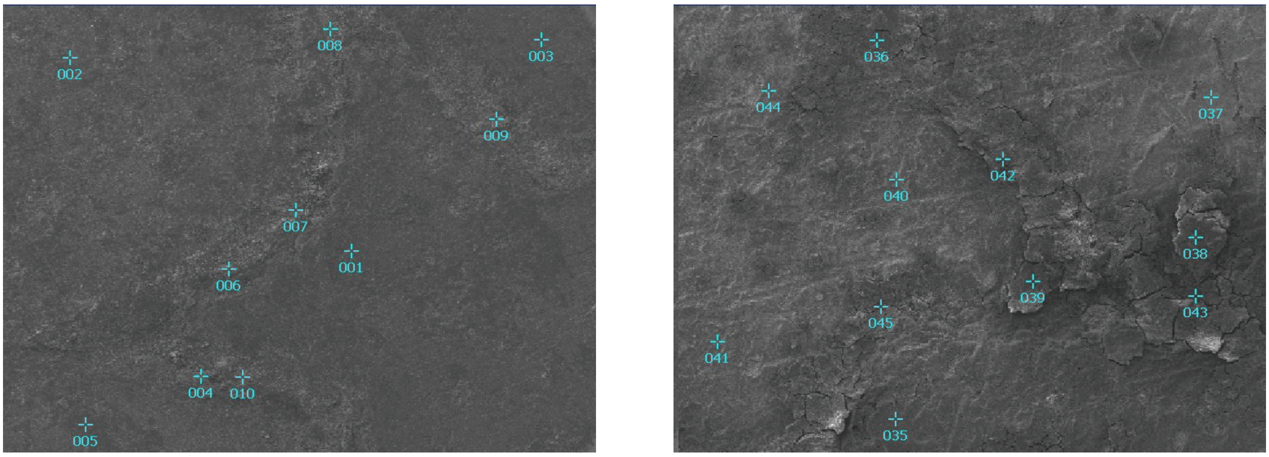
As can be seen from Table 2, in thermally untreated metal samples, two chemical elements are mainly observed on the surface – O and Fe.

Table 1

Chemical composition of substances from the surface of historical cold weapons collected with a swab

No.	Photo and brief description (name) of historical cold weapons	Fe	Mn	Al	Si	S	Ti	Zn	Pb	Ag	Sn	Sr	P	Cu	K
1	Eagle's Saber 	87.61	–	–	–	–	–	–	–	–	10.36	2.03	–	–	–
2	Machete Austrian sapper soldier 	76.33	–	–	–	–	1.01	–	–	6.27	11.51	4.88	–	–	–
3	Bayonet-knife Spanish 1913 to Mauser rifle 1893/1916 	65.79	1.35	0.69	4.92	7.44	–	2.24	5.17	–	–	–	3.11	7.43	1.86

Note: the table is compiled by the authors. Photos are taken by the authors.



a *b*

Fig. 1. Surface image: *a* — thermally untreated metal; *b* — thermally treated metal

Note: photos were *taken by the authors. The image* was *taken from Jeol JSM—6700F Field Emission Scanning Electron Microscope*

Table 2

Chemical composition of the substance on the surface of thermally untreated and treated metal according to the results of emission analysis

No.	Sample	O	Fe	Al	Mn	Si	S	K	Ca	Cu	Zn	Ti	Mg	Sum without iron	Total
1	Thermally untreated metal samples	22.27	77.73	–	–	–	–	–	–	–	–	–	–	22.27	100
2		22.27	77.73	–	–	–	–	–	–	–	–	–	–	22.27	100
3		22.27	77.73	–	–	–	–	–	–	–	–	–	–	22.27	100
4		–	65.31	4.55	–	26.44	–	–	3.7	–	–	–	–	34.69	100
5		–	98.68	–	–	1.32	–	–	–	–	–	–	–	1.32	100
6		–	98.99	–	–	1.01	–	–	–	–	–	–	–	1.01	100
7	Thermally treated metal samples	32.83	30.78	3.78	–	10.59	2.28	4.12	2.69	12.93	–	–	–	69.2	100
8		–	93.27	–	–	2.27	–	–	1.92	–	2.55	–	–	6.73	100
9		3.76	88.95	–	–	–	3.84	–	–	–	–	–	2.12	11.95	100
10		21.84	62.32	–	–	–	–	–	–	15.84	–	–	–	37.68	100
11		–	60.43	3.73	–	–	1.95	2.34	3.17	–	–	1.66	–	39.6	100
12		–	64.72	3.58	0.01	30.05	–	–	–	–	1.64	–	–	35.28	100

Note: the table is compiled by the authors

Thermally processed metal samples, after exposure to a temperature of 700 degrees Celsius for 3 hours, show a high variety of chemical elements on the surface. Thus, it is possible to observe elements such as Ca and K, whose radii are quite large and equal to 0.104 pm and 0.133 pm, respectively. The release of such elements is the fastest.

The presence of such elements may indicate a rather young age of the metal, not exceeding 50–60 years. Samples of metal objects, whose age exceeds hundreds and thousands of years, in the course of their existence have a long-term influence of various natural environmental factors. In this regard, the period of recrystallization in the metal is accelerated. Therefore, during the study of such subjects today it is possible to observe an almost 100 % presence of one main chemical element in the composition.

In addition, there are elements whose ion radii are much smaller, their release occurs more slowly.

However, many impurity elements that actively form new chemical compounds, and in particular organometallic ones, can be dangerous when interacting with human skin in particular.

An example of such an interaction of metals, which are considered dangerous, can be considered amalgam. Amalgam is a solution of metal in mercury, usually silver or gold. The use of amalgam is quite wide: in equipment – for metallization of the surface of the material (gilding, silvering), in dentistry – for filling teeth [15].

If mercury is part of the metal, it is very quickly eliminated, and it is almost impossible to detect it in the metal. At the same time, it can concentrate on the surface.

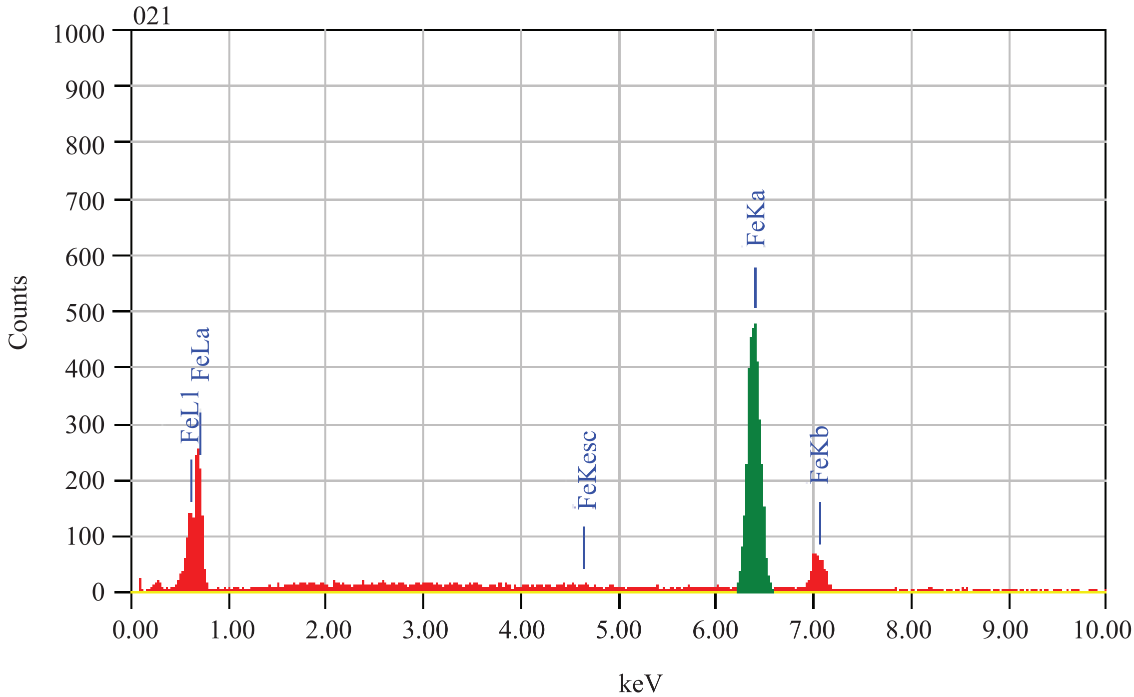
Elements that can be dangerous when interacting with the environment and humans include Zn. Zinc is vital for humans; however, an excess of this element can lead to general intoxication and DNA mutations.

Si was also found on the surface of cold weapons. Silicon is classified as highly hazardous chemical element. An overdose of silicon can be expressed in the development of diseases such as pulmonary fibrosis.

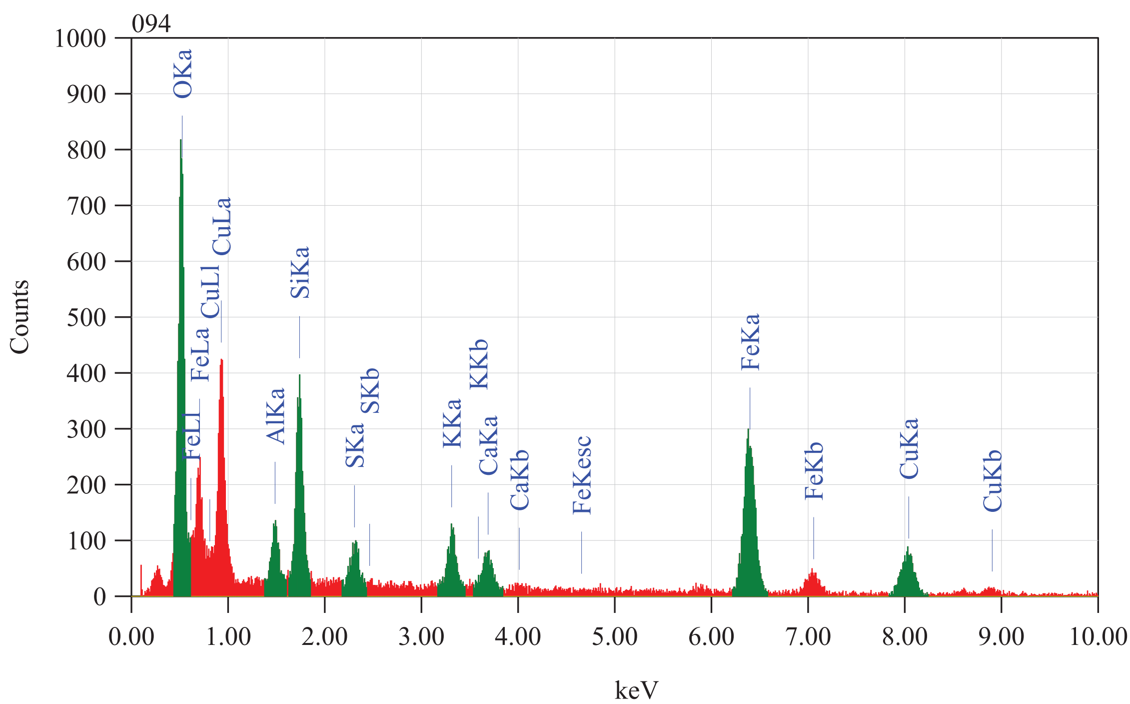
Another dangerous detected surface element is S. Sulfur, and in particular sulfur dust, irritates the respiratory system, mucous membranes.

It is possible to compare the number of chemical elements on the surfaces of thermally untreated metal samples and thermally treated metal samples using the emission spectrum of the chemical composition, where spectral lines corresponding to the elements present in the metal are observed.

Fig. 2, *b* shows the results of the study of the chemical composition of the surface in the sample exposed to temperature. It is possible to observe the appearance of at least six spectral lines that correspond to the following chemical elements eliminated to the surface: Fe, Si, Al, K, Cu, O. From Fig. 2, it can be concluded that under the influence of temperature, chemical elements are pushed to the surface. It is in the presence of these elements that we can conclude about the age of the object under study and the safety of interaction with historical cold weapons and other cultural items made of metals.



a



b

Fig. 2. Emission spectra of chemical composition: *a* – obtained as a result of the study of the surface of thermally untreated metal; *b* – obtained as a result of the study of the surface of thermally treated metal

If we assume that over time the metal is self-cleaning from impurities, then we can appropriately fragment the time of the process at regular intervals – i=1, 2, 3 ... and so on. Reducing the total concentration of impurities can be modeled using a function that describes gradual changes in concentrations as "fraction of a particle", and described by the expression:

$$C = e^{(1-i)}, \quad (1)$$

where C is the concentration of impurity elements in the metal at the i-th period of time; i – the value described in the relative unity-normalized dimensionless scale, which is functionally related to the time of existence and the heating temperature.

The concentration of iron in the surface layers of the sample will increase accordingly and will be described by the expression:

$$C = 1 - e^{(1-i)}. \quad (2)$$

Fig. 3 shows theoretically simulated plots of changes in the chemical composition of the metal surface throughout the history of existence (series 1) and changes in the concentration of impurity chemical elements in it (series 2), which is described discretely by the scale of relative time "*i*" during the process of its heating. Thus, the abscissa axis describes the relative value of time "*i*", which is proportionally dependent on real time:

$$T = \alpha i, \quad (3)$$

where T is real time; α is the coefficient responsible for the ratio of real and relative time.

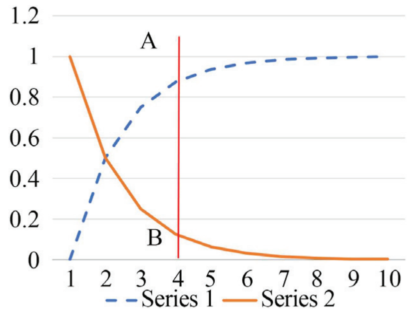


Fig. 3. Theoretical plots describing the change in the chemical composition of the metal surface over a long history of existence or when heated; ordinate axis – the total concentration of iron on the surface of the alloy (series 1) and the concentration of impurity chemical elements that are released to the surface (row 2) during the time described by the abscissa axis (*i*)

Line AB in Fig. 3 indicates the initial composition of the metal alloy, in which the concentration of iron is 88 %, and the total concentration of impurity chemical elements is 12 %.

It is impossible to calculate the coefficient for the real steel of a historical weapon since it depends on the chemical composition of impurity elements, the storage temperature of the weapon, the chemical composition of the environment and the content of chemically active elements in it, the structure of the metal and the form of entry of impurity elements into its composition.

The speed of the process, therefore, is described by the expression:

$$V = \frac{\Delta C}{\Delta i}. \quad (4)$$

As the temperature "t" rises, the process is accelerated.

The total content of harmful substances on the surface of the heated metal will be:

$$C = \sum_{i=a}^{i=10} C_i, \quad (5)$$

where a is the initial concentration of impurity chemical elements in the alloy.

If we describe the increase in the content of impurity chemical elements over the sample area, we conclude that the accumulation of harmful substances can be very intense:

$$C = \sum_{i=a}^{i=10} C_i \times S, \quad (6)$$

where S is the area of the object in contact with human hands.

6. Discussion of results of studying the process of accumulation of hazardous chemicals on the surface of metallic historical artifacts

The results of our experiment (Table 2, Fig. 2) fully confirm the process of elimination of ions of individual chemical elements from the metal in the process of its heating. In particular, we can observe the release of ions Al, Si, S, K, Ca, Cu. It is clear that the same process will occur with other chemical elements if they are present in the alloy. All chemical elements that can form harmful compounds have their own elimination rates and a tendency to accumulate on the surface of the metal.

Thus, the hypothesis is confirmed that the crusts of patina that forms on the surface are a source of information about impurities that were inherent in metals at the time of manufacturing the objects under study from them, from ferrous metals in particular.

The ratio of the concentrations of chemical elements on the surface of the samples under study is determined not only by their primary content in the metal alloy but also by the speed of the elimination process. In turn, the speed of the elimination process depends on the duration of storage of the metal and the degree of its mechanical stress created as a result of primary processing – different parameters and conditions of forging, rolling, or quenching.

Thus, the process of their accumulation in concentrations harmful to humans can occur at different speeds and lead to contrasting results when studying related objects. This indicates the need for mass research of museum exhibits.

The method described in the current article is non-destructive and safe for the surface of historical cultural items, unlike many other methods for studying the chemical composition. This will make it possible to obtain information about the authenticity and safety of interaction with samples without interfering with and destroying the samples themselves.

It is worth considering that this study has a certain limitation. Samples selected for study should not be processed. Restoration and renovation work, canning affect the possible results.

If the samples were conserved, then the study of the surface by rubbing and subsequent analysis with the help of XFA would not give results. And the study with an electron microscope will not be sufficient for conclusions about authenticity.

The described experiment suggests that the amount of harmful substances on the surface of iron artifacts can pose a threat to human health. However, it has not been considered exactly what concentration of different chemicals on the surface of metallic historical artifacts is harmful to humans, this requires further research in the medical field.

The disadvantage of this study can be determined by the fact that in the case of insufficient power of the XFA device itself, surface analysis will not show impurity elements. In this case, it is possible to analyze only the main composition of the metal. In-depth study of the processes of "natural recrystallization" of metals in historical artifacts and the construction of appropriate models to explain their nature is an important and relevant scientific and applied task in expert matter. This work is an attempt, on the basis of the results of analytical studies, to confirm the hypothesis of the process of gradual self-purification of metals, which is accompanied by the elimination of individual chemical elements, including harmful or those that are capable of forming harmful compounds, with their subsequent accumulation on the surface of historical objects. In the future, it is planned to deepen these studies with the involvement of modern instruments and a wider range of historical subjects. In particular, it is planned to conduct further studies of the chemical composition and microstructure of metallic historical artifacts.

7. Conclusions

1. Using the author's technique, a study of the chemical composition of the surface of 3 samples of historical cold weapons from the museum fund, made of iron, was carried out. The blades of the objects were rubbed with a special ash-free swab, which was then burned, and the residue was used to study the chemical composition. This made it possible to obtain data on compounds that are present on a large surface area. Harmful substances that accumulate on the surface of historical weapons made of iron are the product of the gradual recrystallization of the metal over a long history of existence and are not associated with their introduction from the environment. The process of recrystallization of the metal leads to the accumulation of harmful substances in large quantities and can affect the state of human health.

2. The results of the experiment with samples of sheet steel, which were heated in a muffle furnace, after which the surface of the samples was studied using an electron microscope, and local emission analysis of the chemical composition was carried out. The obtained results confirm the process of elimination of ions of individual chemical elements from the metal in the process of its heating. In particular, we can observe the release of Al, Si, S, K, Ca, Cu ions to the surface. The results of the study are important for establishing the authenticity of metallic historical artifacts and assessing possible risks in contact with them.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

Financing

The study was conducted without financial support.

Data availability

All data are available in the main text of the manuscript.

Acknowledgments

The research was carried out thanks to the support from Director of the National Military History Museum of Ukraine, Andriy Ilyenko, and the chief custodian Valentyna Davydyuk, to whom the authors express their sincere gratitude.

References

1. Indutnyi, V. V., Pokhodiashcha, O. B. (2021). Ekspertyza pamiatok kultury. Kyiv: Litera LTD, 516.
2. Indutnyi, V., Merezhko, N., Pirkovich, K. (2019). Studying the authenticity of the golden element from a mongolian warrior's armor by physicalchemical methods. Eastern-European Journal of Enterprise Technologies, 1 (12 (97)), 34–40. doi: https://doi.org/10.15587/1729-4061.2019.157156
3. Indutnyi, V., Merezhko, N., Pirkovich, K., Andreiev, O. (2021). Identification of patterns of crystal-chemical transformations in historical artifacts made of metals. Eastern-European Journal of Enterprise Technologies, 1 (12 (109)), 44–51. doi: https://doi.org/10.15587/1729-4061.2021.225418
4. Merezhko, N., Vovk, Y., Indutnyi, V., Pirkovich, K., Davydiuk, V., Andreiev, O. (2021). Devising criteria for the authenticity of historical cold weapons based on X-ray fluorescence analysis of their surface. Eastern-European Journal of Enterprise Technologies, 6 (12 (114)), 6–11. doi: https://doi.org/10.15587/1729-4061.2021.247624
5. Kikuchi, N. (2020). Development and Prospects of Refining Techniques in Steelmaking Process. ISIJ International, 60 (12), 2731–2744. doi: https://doi.org/10.2355/isijinternational.isijint-2020-186
6. Ashkenazi, D., Gitler, H., Stern, A., Tal, O. (2017). Metallurgical investigation on fourth century BCE silver jewellery of two hoards from Samaria. Scientific Reports, 7 (1). doi: https://doi.org/10.1038/srep40659
7. Mincu, V., Constantin, N. (2013). Refining steels produced in electric arc furnace. U.P.B. Sci. Bull., Series B., 75 (2), 109–116. Available at: https://www.scientificbulletin.upb.ro/rev_docs_arhiva/full80c_761668.pdf
8. Mincu, V., Negru, M., Constantin, N. (2012). Increase the Ingots Quality Cast in Vacuum. Solid State Phenomena, 188, 339–345. doi: https://doi.org/10.4028/www.scientific.net/ssp.188.339
9. Guerra, M. F., Pagès-Camagna, S. (2019). On the way to the New Kingdom. Analytical study of Queen Ahhotep's gold jewellery (17th Dynasty of Egypt). Journal of Cultural Heritage, 36, 143–152. doi: https://doi.org/10.1016/j.culher.2018.09.004
10. Robbiola, L., Blengino, J.-M., Fiaud, C. (1998). Morphology and mechanisms of formation of natural patinas on archaeological Cu–Sn alloys. Corrosion Science, 40 (12), 2083–2111. doi: https://doi.org/10.1016/s0010-938x(98)00096-1
11. Scrivano, S., Gómez Tubío, B., Ortega-Feliu, I., Ager, F. J., Paul, A., Respaldiza, M. A. (2017). Compositional and microstructural study of joining methods in archaeological gold objects. X-Ray Spectrometry, 46 (2), 123–130. doi: https://doi.org/10.1002/xrs.2738
12. Uzlov, K. I. (2015). Krystalohrafiya, krystalokhimiya ta mineralohiya. Chastyna II: Konspekt lektsiy. Dnipropetrovsk: NMetAU, 52. Available at: https://nmetau.edu.ua/file/konspekt_lektsiy_kristalogr_ch_ii.pdf
13. Voroshilov, Yu. V., Pavlishin, V. I. (2011). Osnovy kristallografii i kristallokhimii. Rentgenografiya kristallov. Kyiv: KNT, 568.
14. Smyrnov, V. O., Biletskyi, V. S. (2022). Fizychni ta khimichni osnovy haluzevoho vyrobnytstva. Lviv: Novyi Svit-2000, 148. Available at: http://repository.kpi.kharkov.ua/bitstream/KhPI-Press/56004/1/Book_2022_Smyrnov_Fizychni.pdf
15. Biletskyi, V. S. et al.; Biletskyi, V. S. (Ed.) (2004). Mala hirnycha entsyklopediya. Vol. 1. Donetsk: Donbas, 640.