Оптика и спектроскопия

$\mathbf{O}_{\text{PTICS}}$ and spectroscopy

УДК 533.9.082, 533.922, 533.924, 621.373.8

АНАЛИЗ СОСТАВА ПОКРЫТИЙ СТАРИННЫХ ХРУПКИХ МЕТАЛЛИЧЕСКИХ ОБРАЗЦОВ С ПОМОЩЬЮ ДВУХИМПУЛЬСНОГО ЛАЗЕРНОГО СПЕКТРОМЕТРА

К. Ф. ЕРМАЛИЦКАЯ¹⁾, П. А. ИВАНОВА¹⁾, Я. И. МАТЮШ¹⁾

¹⁾Белорусский государственный университет, пр. Независимости, 4, 220030, г. Минск, Беларусь

Исследованы возможности использования лазерной атомно-эмиссионной спектроскопии для элементного анализа многокомпонентных металлических артефактов железного века. Большое внимание уделено влиянию грязи, патины, ржавчины, окалины на процесс лазерной абляции и, как следствие, на относительную интенсивность спектральных линий. Предложен метод оценки толщины молекулярных соединений на поверхности металлических изделий для последующего исключения соответствующих спектральных данных из результатов элементного анализа. Установлено, что относительная интенсивность спектральных линий для современного образца будет значительно (до 30 %) выше, чем для артефакта, который длительное время находился под землей. Таким образом, количественный анализ с использованием градуировочных кривых, построенных на основе данных для современных стандартных образцов, даст неверные результаты. При этом переход от одноимпульсной лазерной абляции к двухимпульсной, приводящий к многократному увеличению относительной интенсивности спектральных линий слектральных линий, очень важен, так как позволяет значительно повысить чувствительность анализа и снизить ошибку.

Ключевые слова: лазерная атомно-эмиссионная спектроскопия; элементный анализ артефактов; сдвоенные лазерные импульсы; лазерная абляция.

Образец цитирования:

Ермалицкая КФ, Иванова ПА, Матюш ЯИ. Анализ состава покрытий старинных хрупких металлических образцов с помощью двухимпульсного лазерного спектрометра. *Журнал Белорусского государственного университета.* Физика. 2023;1:78–84 (на англ.). https://doi.org/10.33581/2520-2243-2023-1-78-84

Авторы:

Ксения Федоровна Ермалицкая – кандидат физико-математических наук, доцент; доцент кафедры лазерной физики и спектроскопии физического факультета. Полина Александровна Иванова – студентка физического

факультета. Научный руководитель – К. Ф. Ермалицкая.

Научный руководитель – К. Ф. Ермалицкая.

Яна Игоревна Матюш – студентка физического факультета.

For citation: Ermalitskaia KF, Ivanova PA, Matyush YaI. Elemental analysis

of obsolete brittle metal samples using a two-pulse laser spectrometer. *Journal of the Belarusian State University. Physics.* 2023; 1:78–84.

https://doi.org/10.33581/2520-2243-2023-1-78-84

Authors:

Ksenia F. Ermalitskaia, PhD (physics and mathematics), docent; associate professor at the department of laser physics and spectroscopy, faculty of physics. *ermalitskaia@gmail.com https://orcid.org/0000-0002-2134-6938*

Polina A. Ivanova, student at the faculty of physics. *Yana I. Matyush*, student at the faculty of physics.

ELEMENTAL ANALYSIS OF OBSOLETE BRITTLE METAL SAMPLES USING A TWO-PULSE LASER SPECTROMETER

K. F. ERMALITSKAIA^a, P. A. IVANOVA^a, Ya. I. MATYUSH^a

^aBelarusian State University, 4 Niezaliežnasci Avenue, Minsk 220030, Belarus Corresponding author: K. F. Ermalitskaia (ermalitskaia@gmail.com)

The possibilities of using laser induced breakdown spectroscopy for elemental analysis of multicomponent metal iron age artefacts are studied. Much attention is paid to the influence of dirt, patina, rust, scale on the process of laser ablation, and, as a result, on the relative intensity of spectral lines. A method is proposed to estimate the thickness of molecular compounds on the surface of metal artifacts to subsequently exclude the corresponding spectral data from the analysis results. It has been found that during laser ablation of pure metal samples at fixed radiation parameters, the relative intensity of spectral lines during ablation of a modern sample can significantly (up to 30 %) exceed the intensity for an old sample that has been underground for a long time. Thus, a quantitative analysis using calibration curves, built on the basis of modern standard samples, will lead to incorrect results. In this case, the transition from single-pulse to double-pulse laser ablation, which leads to a multiple increase in the relative intensity of spectral lines, is very important, since it allows one to significantly increase the sensitivity of the analysis and reduce the error.

Keywords: laser induced breakdown spectroscopy; elemental analysis of artifacts; double laser pulses; laser ablation.

Introduction

Laser induced breakdown spectroscopy (LIBS) is one of the most common methods of low-destructive elemental analysis. It is widely used in industry, research of biological objects, minerals, medicines, explosives, artifacts, etc. [1; 2]. The popularity of this method is associated with a number of advantages: small amounts of substance required for analysis, lack of preliminary chemical and mechanical surface preparation, low sample destruction (crater diameter 100 μ m, layer thickness 3–5 μ m), the possibility of studying in the air, simultaneous determination of the concentration of all elements, including those that are difficult to detect by other methods, the possibility of remote analysis of samples, including those under water. Despite the ability to analyse almost any sample using the LIBS method, this method is most often used to study metals and multicomponent alloys. In addition to modern industrial products and raw materials for them, LIBS has been used for several decades to analyse ancient objects and artifacts, where it successfully competes with such a popular approach as X-ray fluorescence analysis [3–5]. Despite the fact that the latter is completely non-destructive, it does not make it possible to study the change in concentration with depth.

During the LIBS of objects from archaeological excavations, the authors of publications practically do not pay attention to preparing the surface for analysis. Indeed, practically in all software of LIBS spectrometers it is possible to set a certain number of laser prepulses that will evaporate the substance, while the spectra will not be recorded. After such cleaning of the sample from contamination, patina, rust, the object is analysed, in the same way as in the case of modern industrial samples. However, the question remains how to accurately determine the number of prepulses needed to completely remove all contamination from the surface and get to the material of the original sample. If there are not enough prepulses, the resulting spectrum used to determine the concentration may contain data related to contamination or compounds on the surface.

Too large (about 100) number of pulses leads to the fact that the ablation plasma will spread inside a rather deep cylindrical crater, settling on its walls. As a result, the intensity of the recorded signal will decrease, and hence the sensitivity of the analysis.

Another important issue is often left out of the number of articles on LIBS artifacts. Metal multicomponent products made several centuries, and sometimes millennia ago, can differ significantly in properties and structure from modern products. So, in the times of the bronze and iron ages, the masters could not control the quality of the raw materials used, the required parameters of the technological process, such as, for example, temperature, speed and uniformity of crystallisation. As a result, even in an outwardly homogeneous ancient sample, the concentration of elements at different points can differ significantly. The further fate of the artifact also has a significant effect on the concentration of elements in the sample (especially in its surface layers with a depth of less than 100 μ m). So, for example, jewelry during the iron age was often made from Roman or Arabic coins, which could either be heated or subjected to strong mechanical stress to change the image on the surface. Further, there was a possibility that jewelry, coins or weapons would be sent with the owner after his death to the funeral pyre, which was not uncommon in the first millennium of our era. Thus, the initially inhomogeneous product for several hours, and sometimes days, was exposed to high temperatures, sufficient to melt lead and tin, but insufficient for iron. In our time, ancient artifacts fall into the hands of spectroscopists, not only covered with scale, but also having a significant gradient in the concentrations of elements in depth. Another circumstance that leads to a change in the concentration of elements in alloys is their long-term (several centuries) residence in various types of soil or in water. Additional factor influencing the change in the concentration of elements is the aggressive impact of agricultural chemistry in the 20th century. A significant number of artifacts were found in the fields used at a depth of a couple of tens of centimeters.

The combined effect of all the above circumstances can lead to the fact that the metal artifact will have a porous (bread-like) texture, rather than a dense, characteristic for modern products. Such results were obtained by the author in the study of coins of the Gnivan treasure [6]. It was found that the weight of some samples (Lvov and Krakow coins of Jagiello, partly Prague pennies) is significantly lower than expected. At the same time, light coins are characterised by a dull, «cardboard» sound when they hit a hard surface, in contrast to their full-weight «counterparts», for which a metallic ringing is clearly audible. At the same time, light coins are characterised fragility, the edges of the breaks are white, which indicates the loss of plasticity by silver. Visual inspection showed that samples with cracks as a result of a strong impact of the stamp were more susceptible to corrosion, weight loss and increased brittleness. Two-pulse laser microanalysis made it possible to determine that lighter and more brittle samples under study a significant drop in the intensity of the spectral lines of silver is observed, and a drop in the intensity of the spectral lines of copper is absolutely synchronous with it.

However, laser ablation of porous samples differs from ablation of metals, and it is quite likely that the registered analytical signal in the analysis of a modern item and an ancient object similar in composition may differ. Then the generally accepted approaches to quantitative analysis (construction of calibration graphs based on the data of standard samples of alloys and a calibration-free method based on the assumption of local thermo-dynamic equilibrium) can lead to a significant distortion of the results.

The purpose of this study was to evaluate the possibilities of using LIBS to analyse artifacts covered with scale, patina, and rust, to develop a method for determining the thickness of these coatings on the surface of products, and to compare spectral data obtained by ablation of modern and old multicomponent alloys.

Materials and methods

The experiment was carried with the help of LAEMS (laser atomic emission multichannel spectrometer) developed and manufactured in the Belarusian State University at the department of laser physics and spectroscopy of the physics faculty and the spectroscopy laboratory of the A. N. Sevchenko Institute of Applied Physical Problems. A solid-state laser with semiconductor pumping is used as a source of excitation. The use of semiconductor pumping instead of pulse lamp pumping allows to increase the system resources and stability of output characteristics significantly [7].

The laser consists of two radiator and provides the generation of double pulses with the following characteristics: the duration of pulses is 15 ns, pulse energy variation range is 0-100 mJ, the range of variation of the delay duration between double laser pulses is 1-100 ns, pulse pair repetition rate is up to 10 Hz. The other analytical characteristics of the laser include spectral range (190–800 nm), spectral resolution (0.5 nm), the diameter of the laser beam on a sample surface (50 μ m), dimensions of the analysed samples (200 × 200 × 200 mm), positioning accuracy on a sample surface (100 μ m), the number of chemical elements to be determined (50). The sample is placed on a table moved along the beam using a linear low-profile positioned platform (manual movement), and in two directions perpendicular to the beam using linear motorised positioned platforms, which provides the possibility of computer-controlled scanning of the sample surface.

To register plasma spectra, spectrometers with registration on a CCD ruler are used: based on the SDH-1 polychromator (the spectral range is 190–800 nm, the resolution is 0.1 nm with a width of the simultaneously recorded spectral range of 130 nm) and a lattice spectrometer of the original design.

Main parameters of LAEMS:

• plasma excitation source – two-pulse diode-pumped Nd : YAG laser with pulse repetition frequency 10 Hz and wavelength 1064 nm;

- pulse duration 10 ns;
- interpulse interval (Δt) 0–100 µs (step 1 µs);
- range of analysed wavelengths 260-760 nm;
- laser pulse energy (E_{imp}) 10–100 mJ.

The specialised software of the LAEMS spectrometer allows you to set the following parameters:

• mode of single (time shift between pulses is $0 \ \mu$ s, i. e. both pulses act on the surface of the sample simultaneously) and dual laser pulses (the time interval between pulses can vary from 1 to 100 μ s with a step of 1 μ s).

It should be noted that when using LAEMS, the transition from single to double laser pulses occurs without changing the total energy and radiation power;

• number of pulses per point, while you can additionally set the number of pre-firing pulses – pulses that affect the surface before the main ones, but the spectrum from them is not recorded. The use of pre-firing pulses is necessary when examining samples whose surface is covered with visible impurities, oxides, rust, patina;

• energy of dual laser pulses and their repetition rate.

The software allows you to move the subject table with a fixed sample in two planes (up-down, left-right). Also the microscope mode in conjunction with LED illumination and an aiming laser allows you to accurately determine the method of laser radiation exposure to a sample, which is necessary when examining finished industrial products, art objects and artefacts, jewelry, samples whose dimensions are not exceed a few millimeters. The destruction of the sample surface was monitored using a Linnik MII-4 microinterferometer (*LOMO*, Russia).

The objects of the study were 200 specimens of artifacts (from the collections of the Museum of Historical Faculty of the Belarusian State University, the collections of the Institute of History of the National Academy of Sciences of Belarus, the National Historical Museum of the Republic of Belarus, and private collections) found on the territory of Belarus during archaeological excavations dating back to the 5th century BC – 15th century AD. The objects under study belonged to different time periods, but they were united by the fact that they had been underground for a long time and were covered with a significant layer of patina, scale, rust and other compounds and impurities, which made it impossible to visually determine the colour of the original compound (white, yellow metal, copper-based alloys). Photos of some of the studied old samples covered with patina, rust, scale are shown in fig. 1.



Fig. 1. Photos of some of the studied old samples covered with patina, rust, scale

Results and discussion

At the first stage of the study, a qualitative analysis of the samples was carried out: elements were determined, analytical lines were selected (two for each element). It was found that some of the artifacts consist of pure metals – copper, lead, tin. These samples were combined into a separate group in order to compare laser ablation of modern and ancient products that have been exposed to long-term exposure to natural conditions and soils. A complete list of elements found in the studied samples includes silver, copper, zinc, tin, lead, iron. Modern standard samples corresponding to the composition of artifacts were selected.

The optimal parameters of laser radiation, providing maximum spectral line intensity, were determined during laser ablation of modern samples (the energy of laser pulses was 100 mJ, the time interval between double laser pulses was from 7 to 12 μ s (depending on the metal)). It should be noted that the transition from the single-pulse mode ($\Delta t = 0 \,\mu$ s; two laser pulses simultaneously act on the surface) to the double-pulse mode leads to a multiple increase in the analytical signal (up to 10 times). Similar measurements were carried out for

artifacts, in the absence of samples of pure metals, ablation of alloys was carried out, where the content of the element under study was maximum close to 100 % (80-98 %). The values of the optimal interpulse interval for two-pulse laser ablation of metals, as well as the magnitude of the increase in the analytical signal are given in table 1.

Table 1

Sample	Chemical element							
	Silver	Copper	Iron	Tin	Lead	Zinc		
Optimal interpulse interval, providing maximum analytical signal, μs								
Ancient	8	10	10	6	6	9		
Modern	9	11	12	8	7	10		
The magnitude of the increase in the analytical signal								
Ancient	6–7	6–7	5-6	6-7	7-8	6–7		
Modern	7–8	7–8	6–7	9–10	9–10	8–9		

The optimal interpulse interval, providing maximum spectral line intensity, for two-pulse laser ablation of metals and the magnitude of the increase in the analytical signal

It can be seen from the table 1 that the transition from single-pulse to double-pulse excitation leads to a smaller increase in the analytical signal for ancient samples. In addition, for all alloy components, the optimal value of the interpulse interval is lower in the case of artifacts, which may indicate a porous structure of the products, as a result of which less substance enters the plasma, the plasma is less dense, and therefore it is more efficient to additionally excite it at earlier stages of expansion. In favour of the hypothesis of the porous structure of ancient samples, the fact that in most cases the intensity of the spectral lines of artifacts is significantly lower (sometimes by almost 50 %) compared to modern samples can also testify. In this regard, when carrying out a quantitative analysis of ancient samples that have been under the influence of moisture and soil for a long time, it is fundamental to use two-pulse LIBS. Otherwise, the analysis error will increase, especially when determining third elements and impurities. The optimal time interval between dual laser pulses, which provides the maximum sensitivity of LIBS for the analysis of metal artifacts, is 8 μ s. In the case of modern samples, this interval is 10 μ s.

The next stage of the study consisted in the development of a method for determining the thickness of scale, patina, rust and other contaminant compounds on the surface of the sample, it makes possible to set the number of prepulses during which the spectrum is not recorded. At first, a layer-by-layer qualitative elemental analysis of the samples was carried out on a LAEMS spectrometer: the spectra from each double laser pulse were recorded and the intensity dynamics of the spectral lines was compared. The transition from scale, patina and rust to uncontaminated metal in all cases led to a significant increase in the relative intensity of the spectral lines, with further ablation the analytical signal remained practically unchanged. At the second stage of the study, two-pulse laser ablation of the samples was carried out, and the number of pulses per point in each case corresponded to the ablation of only patina (10 pulses), scale (14 pulses) and rust (22 pulses), and did not affect the uncontaminated metal. The dimensions of the craters formed as a result of ablation were measured using a Linnik MII-4 microinterferometer. Similarly, craters, which are formed on the previously cleaned surfaces of copper, iron and brass, were measured. The measurement results are shown in table 2.

Table 2

Results of laser ablation of metal surfaces by double laser pulses

Denorschart	Chemical element			
Parameters	Copper	Brass	Iron	
Thickness of the metal layer evaporated by 1 double laser pulse, µm	3	3	2	
Compound on the surface of the sample	Patina	Scale	Rust	
Number of laser pulses for which complete ablation was performed	10	14	22	
Thickness of the compound layer on the sample surface, µm	26	36	38	
The thickness of the evaporated layer of the compound for 1 double laser pulse, μm	2.4	2.6	1.9	

Undoubtedly, in each specific case, the thickness of the considered joints on the surface of the sample may differ. However, the data obtained will make it possible to approximately estimate the required number of pre-firing pulses. Of particular difficulty in the analysis are samples covered with scale as a result having spent a long time in a funeral pyre or fire. As the study showed, such samples do not have a sharp boundary between the connection on the surface and the original alloy of the product (fig. 2).



Fig. 2. Dependence of the relative intensity of the spectral lines of artifact components on the depth of laser ablation for a sample covered exclusively with patina (*a*) and scale (*b*)

The dependence of the relative intensity of the spectral lines of copper, lead and tin on the depth of laser ablation for a sample covered only with patina is shown in fig. 2, *a*. The coverage boundary in this case can be taken as 55 μ m: after reaching this depth, the fluctuations in the relative intensity of the spectral lines become much smaller for all elements. In the case of scale (see fig. 2, *b*), the coating boundary can also be determined (42 μ m). However, even after this depth, periodic changes in the analytical signal by almost 1.5 times are observed, which indicates the presence of pores and caverns 3–9 μ m in size in this artifact.

In this regard, a number of limitations on quantitative analysis should be highlighted. So, when examining a sample covered only with patina, it is necessary to determine the thickness of this coating (usually 25–55 μ m) in order to set the appropriate number of prepulses. However, the same number of prepulses must also be used in the ablation of standard samples when constructing calibration curves. Otherwise, the evaporation of the substance from the studied and standard samples will occur from different depths of the crater, which will affect the process of plasma propagation, and, as a result, the magnitude of the analytical signal. Unfortunately, the standard approach to analysis based on calibration curves is not suitable for scale-coated samples. Due to sharp jumps in intensity, and due to a lower analytical signal, a certain concentration of the components will be significantly lower than the real one, and the total concentration will be less than 100 %. In this case, non-calibration methods may turn out to be more effective, however the total analytical signal for several 10 pulses cannot be used, since averaging will lead to an increase in the analysis error.

It should be noted that the analysis of samples of fusible tin and lead that have been on fire is of difficulty. Even outwardly, these artifacts resemble a porous sponge, and not a metal product. The study of the dynamics of the intensity of the spectral lines of these elements in depth does not allow one to accurately determine the boundaries of the coverage. The dependence of the relative intensity of the spectral lines of tin and lead on the depth of laser ablation for a sample covered with a visible layer of scale is shown in fig. 3.

Separately, a group of artifacts made of iron-based alloys coated with a layer of rust was studied. This type of coating, unlike patina, is more heterogeneous even within the same sample, so it is necessary to create a technique that would allow to determine the approximate value of laser prepulses visually. For the study, three samples were selected with varying degrees of surface coverage with rust: sample 1 covered a visually thin layer of iron hydroxide with small gray spots, related to intact metal; sample 2 covered visually thick homogeneous layer of red-brown colour; sample 3 covered heterogeneous red-brown layer with a pronounced relief. The thickness of the rust for each sample was determined from the change in the relative intensity of the spectral lines of chromium, nickel, manganese, and iron during layer-by-layer two-pulse laser ablation. Upon reaching the intact alloy, the intensity of the spectral lines of all elements increased and became more stable (fluctuations did not exceed 3 %). The measurements carried out showed that the thickness of the iron hydroxide layer on the surface of the studied samples is $9-10 \mu m$ (sample 1), $22-23 \mu m$ (sample 2), $44-45 \mu m$ (sample 3). However, it should be noted that in

the sample 3, the thickness of rust, both visually and measured as a result of the experiment, differed significantly (from 40 to 61 μ m). With an increase in the thickness of rust, its heterogeneity also increases: cavities appear in size from 2 μ m with a rust thickness of 10 μ m, up to 5 μ m at a depth of 50 μ m.



→ Pb(I) (406 nm) → Sn(I) (380 nm)

Fig. 3. The dependence of the relative intensity of the spectral lines of tin and lead on the depth of laser ablation for a product covered with a visible layer of scale F(x)

Based on the studies carried out, methods were developed for the quantitative analysis of artifacts dating back to the $3^{rd}-4^{th}$ centuries AD, found during excavations on the territory of the settlement of Domatovo near Turov. A significant layer of patina is visually noticeable on the surface of the samples, and scales are noticeable on the samples from the funeral pyres. The developed technique made it possible to determine the thickness of the joints on all samples (35–50 µm) and scale (40–52 µm). Taking into account the layer of compounds on the surface, the number of pre-firing pulses during the quantitative analysis of artifacts was 25.

Accurate determination of the thickness of the patina using two-pulse laser atomic emission spectroscopy allows us to draw a conclusion about the environment in which the ancient coin was located for a long time (a dry place, peat bog soils, clays, etc.). The results of the concentrations of the main elements were subsequently used by the staff of the Institute of History of the National Academy of Sciences of Belarus, the National Historical Museum of the Republic of Belarus, the Museum of Historical Faculty of the Belarusian State University to clarify and establish time limits for the origin of artifacts.

Conclusions

Double-pulse LIBS is the preferred method for the analysis of metal samples covered with patina, scale, rust, because it allows not only to clean the surface directly during the study, but also to estimate the thickness of the layer of these compounds. It was found that during laser ablation of scale and patina, the thickness of the evaporated layer is much lower than when exposed to the cleaned surface of metals, which is caused by the infusibility of these compounds. The process of laser ablation of rust is more complex, hydrated iron oxide and iron metahydroxide are porous materials. In addition, it is necessary to take into account the fact that the thickness of the rust, even in localised nearby surface areas, may differ.

References

1. Musazzi S, Perini U. Laser-induced breakdown spectroscopy. Berlin: Springer; 2014. 565 p. DOI: 10.1007/978-3-642-45085-3.

2. Galbács G. Laser-induced breakdown spectroscopy in biological, forensic and materials sciences. Berlin: Springer; 2022. 313 p.

3. Alberghina MF, Barraco R, Brai M, Schillaci T, Tranchina L. Integrated analytical methodologies for the study of corrosion processes in archaeological bronzes. *Spectrochimica Acta. Part B: Atomic Spectroscopy.* 2011;66(2):129–137. DOI: 10.1016/j.sab. 2010.12.010.

4. Abdelhamid M, Grassini S, Angelini E, Ingo GM, Harith MA. Depth profiling of coated metallic artifacts adopting laser-induced breakdown spectrometry. *Spectrochimica Acta. Part B: Atomic Spectroscopy.* 2010;65(8):695–701. DOI: 10.1016/j.sab.2010.03.017.

5. Pitarch A, Queralt I, Álvarez-Perez A. Analysis of Catalonian silver coins from the Spanish war of independence period (1808–1814) by energy dispersive X-ray fluorescence. *Nuclear Instruments and Methods in Physics Research. Section B: Beam Interactions with Materials and Atoms.* 2011;269(3):308–312. DOI: 10.1016/j.nimb.2010.11.045.

6. Huletski DV, Ermalitskaia KF. Laser microanalysis of corroded ancient silver-copper coins. Vestnik BGU. Seriya 1. Fizika. Matematika. Informatika. 2016;2:21–25. Russian.

7. Voropay ES, Gulis IM, Tarasau DS, Ermalitskaia KF, Samtsov MP, Radko AE, et al. Laser atomic emission spectrometer with achromatic optical system. *Journal of Applied Spectroscopy*. 2021;88(3):603–609. DOI: 10.1007/s10812-021-01215-2.

Received 03.01.2023 / revised 20.01.2023 / accepted 20.01.2023.