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Method for Qualitative and Quantitative Analysis of Ancient Lead Enamel Using Laser Inducted Breakdown Spectroscopy

The method of laser induced breakdown spectroscopy (LIBS) was used in analysis of the archaeological enamel samples from the ancient settlement of Jochi Khan (XIV century). During the qualitative analysis, it was found that the elements of the enamel matrix are Si, Pb, K, Na, Mg, Ca, Al. The glaze color is due to the presence of copper and iron. Clustering by the k-means method revealed two groups of samples similar in composition of enamel, but differing in place of origin within the settlement. For the studied samples the semi-quantitative composition of glazes was established from the spectra of LIBS using a method based on the hypothesis of local thermodynamic equilibrium (LTE) and a chemometric approach (Projection to Latent Structures, PLS). Probabilistic deterministic design of experiment was used to search for pairs of element lines that are not subject to changes when the conditions for spectra registration vary, and to determine the coefficients in the equations based on LTR. Calculations using the PLC method were carried out in the "R" programming environment. The following content of the matrix elements was obtained in terms of the most stable oxides, %: SiO_2 — 49–61, PbO — 23–31, MgO — 1.7–2.3, CaO — 4.6–6.9, Na_2O — 4.1–5.3, K_2O — 5.1–6.4, Al_2O_3 — 0.8–1.7, CuO — 0.32–0.4, Fe_2O_3 — 0.09–0.16. The results of both methods are generally consistent with each other. The inaccuracy between 4 parallel determinations were 15-24 % for LTE, and 9–14 % for PLS. Taking into account the data of semi-quantitative analysis, it was concluded that the division into two groups is based on a different ratio of copper and iron in enamel.

Keywords: LIBS, chemometrics, cluster analysis, PLS, low-melting lead enamels, probabilistic deterministic design of experiment, archeology, settlement of Jochi Khan.

Introduction

Method of laser induced breakdown spectroscopy (LIBS) in elemental analysis of a wide variety of materials is continuously becoming more demand, despite the problems with calibration. LIBS is characterized by relatively low values of accuracy and reproducibility of the analysis that are associated with the basic impossibility of reproducing the recording conditions accurately from spectrum to spectrum. This problem can hardly be eliminated by improving the method's hardware [1]. Therefore, there is a constant search for mathematical methods for LIBS signals processing, which makes it possible to improve the analytical characteristics of this analysis method [2]. Currently, in order to achieve acceptable metrological characteristics, both theoretical approaches based on the concept of local thermodynamic equilibrium (LTE) and empirical approaches based on chemometric methods, as well as various combinations of these two approaches are being developed [3–6].

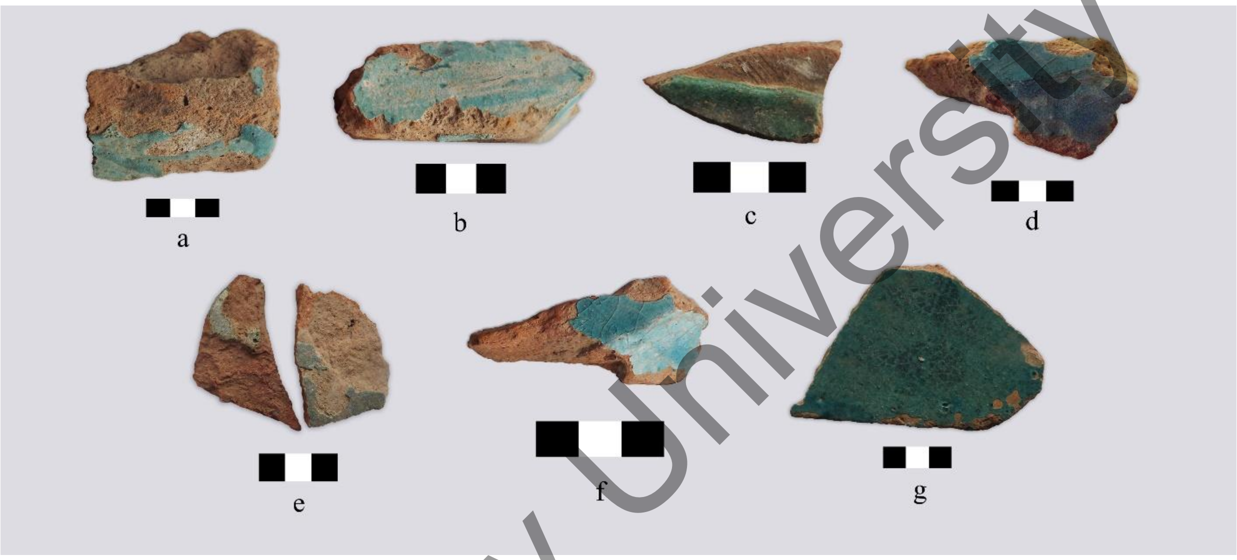
The LIBS method has a number of advantages along with limitations. First of all, the insignificance of damage to the object of analysis and the lack of sample preparation should be noted. A laser pulse carries information not only about the surface layer, but also about the bulk of the sample, since it evaporates the sample from a certain depth. This feature makes it possible to overcome the problems associated with the analysis of archaeological artifacts [7,8], which are characterized by differences in the chemical composition of the surface material and the bulk.

The mausoleum, located in the Ulytau region of Kazakhstan, 45 km from the city of Zhezkazgan, on the left bank of the Karakengir River, is associated by Kazakh folk tradition with the name of Jochi Khan as the eldest son of Genghis Khan. The upper dome of the mausoleum, lined with glazed turquoise tiles, was built over the lower early dome without cladding. According to radiocarbon analysis, there are two stages in the construction of the mausoleum in the XIV century [9]. In order to obtain additional historical information about the construction of the mausoleum and the settlement of Jochi Khan, it was useful to conduct a comparative study of the glaze of tile fragments from different points of the mausoleum and the settlement by the LIBS method.

Qualitative analysis by the LIBS method was carried out in the traditional way. The aim of this study was to develop methods of analysis for classification and quantification that provide satisfactory accuracy with limited possibilities for sample preparation and registration of spectra.

Experimental

Samples of ceramic tiles containing enamel coating of various shades of blue and green were received from historians and returned to the National Historical, Cultural and Natural Reserve-Museum “Ulytau” (Ulytau village, Karaganda region, Kazakhstan) immediately after registration of the spectra (Figure 1).



a — the mausoleum of Jochi Khan. A fragment of a tile. Sample 3 (Obr3.1);
b — the mausoleum of Jochi Khan. A fragment of a tile. Sample 4 (Obr4);
c — the mausoleum of Jochi Khan. Fragment of the mausoleum crown 2 (preliminary definition). Sample 5 (Obr5);
d — the settlement of Jochi Khan. A fragment of a tile. Sample 2 (Obr2);
e — the settlement of Jochi Khan. Small house. A fragment of ceramics. Sample 6 (Obr6);
f — the settlement of Jochi Khan. House 2. Tile fragment. Sample 1 (Obr1);
g — the settlement of Bytygai. Workshop. A fragment of a tile. Sample 7 (Obr2007)

Figure 1. Samples of tiles from different points of the mausoleum and the settlement

Samples were analyzed on a two-pulse spectrometer “LAES Matrix Continuum” (SJSC Spectroscopic Systems, 2016, Russia) with a double Paschen-Runge optical scheme with an optical path length of 250 mm and 125 mm, with diffraction gratings of 2400 groove/mm and 1200 groove/mm and 7 CCD detectors from Toshiba and a wavelength range of 190 up to 800 nm. The emission spectrum of all samples was recorded at the same instrument settings to facilitate subsequent comparison and interpretation of the spectra. The energy of the pump lamp was 18 Joules. The remaining settings were chosen based on previous experience [10, 11], namely: the laser frequency was 10 Hz, the delay time of the first Q–switch was 100 μs, the second was 110 μs, the exposure start delay was 2 μs and the total exposure time was 5 ms. The number of pulses was limited to 15, including 2 firing pulses. Spectra were recorded at four randomly selected points without scanning by area to minimize damage and provide some smoothing of random effects. The samples were returned to storage after the spectra recording. The obtained spectra were used for qualitative analysis of samples. Both the standard spectrometer software and the NIST [12] database were used to assign lines in the spectrum.

Since each sample was examined at four points, the total number of spectra seemed sufficient for cluster analysis using the “teaching without a teacher” approach. The spectra were normalized by the intensity of the MgI_{280} line, then cluster analysis was performed in the “R” programming environment [13]. Taking into account the similarity of the qualitative composition of the samples, the reasons for the cluster separation could only be established by quantitative analysis in the absence of the possibility of re-registration of the spectra. Variants using thermodynamic [14] and chemometric [15, 16] approaches were applied to consider the possibility of quantitative analysis of samples. A set of artificially obtained samples with a qualitative composition close to the enamel on the archaeological samples was used for training in both variants. The range of variation in the ratios of elements in the composition of the furnace-charge was selected according to the data [17]. The furace-charge, composed of oxides of silicon, lead, magnesium, iron and copper, sodium, potassium and calcium carbonates, and aluminum hydroxide, was mixed by abrasion in a mechanical mortar for 20 minutes and fused in alund crucibles for 1 hour at 1000 °C, with periodic rocking of the crucible (Table 1).

Table 1

Composition of calibration and control enamel samples

№	PbO	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	CuO	Fe_2O_3
1	0.202	0.503	0.008	0.121	0.05	0.05	0.05	0.005	0.01
2	0.287	0.43	0.019	0.076	0.076	0.067	0.029	0.008	0.008
3	0.329	0.376	0.028	0.15	0.009	0.084	0.009	0.009	0.006
4	0.371	0.325	0.037	0.046	0.112	0.009	0.084	0.011	0.005
5	0.431	0.239	0.048	0.01	0.153	0.029	0.067	0.019	0.004

The appearance of the calibration samples is shown in Figure 2.

Figure 2. Calibration samples of enamel

A number of methods for calibration of atomic emission spectrometers are based on the fact that the intensity of the analytical lines of different elements, which are low in excitation energy, almost equally depends on random factors and conditions of spectrum registration. This means that the ratio of intensities depends only on the concentration of elements. The possibility of the method of probabilistically deterministic design of the experiment (PDDoE) was used [18, 19] to search for such pairs of lines, and to identify factors on which the variable in question does not depend. PDDoE method has proven itself well for optimizing the conditions of the LIBS [20, 21] as well as for other physicochemical methods of analysis [22]. When compiling a six-factor experiment plan with five levels of variation (Table 2), the possibility of using the sample composition as a single factor was used [23]. The excitation energy of the lines was retrieved from the Atomic Spectra Database [12].

Table 2

Factors and levels of their variation in the experimental plan

№	Factor	Symb.	Level 1	Level 2	Level 3	Level 4	Level 5
1	C_n/C_m	X_1	1	2	3	4	5
2	E_{lamp}, J	X_2	12	14	16	17	18
3	QSW_1, mks	X_3	100	120	140	160	180
4	ΔQSW, mks	X_4	1	3	5	10	20
5	Delay, mks	X_5	1	2	3	5	10
6	Expos, ms	X_6	1	2	3	4	5

The ratios of element concentrations for each sample (levels of the first factor) were calculated according to Table 1.

The spectra of the calibration samples were recorded in five repetitions, and averaged as described in [11].

Results and Discussion

Qualitative analysis of the samples was conducted by identification of all analytical lines of the obtained spectra. The matrix in all cases is silicon, lead, potassium, sodium, calcium, magnesium (Figure 3). Enamel coloring is due to the presence of a small amount of iron and copper. Lines of aluminum are also present.

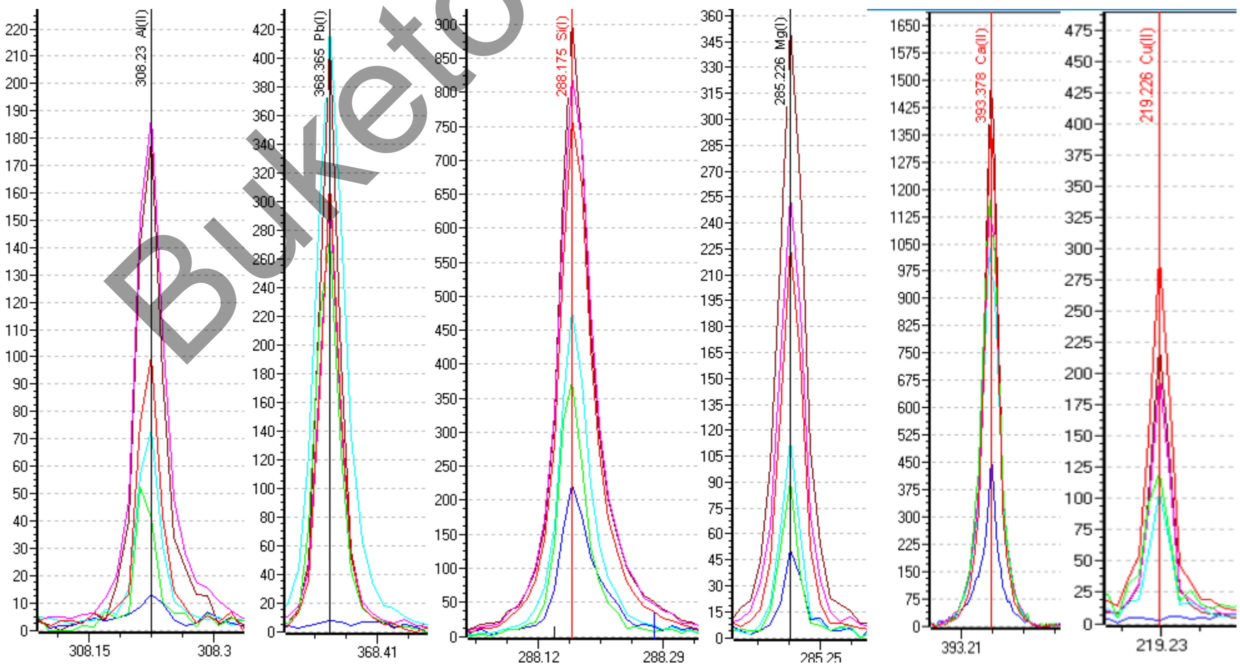


Figure 3. Some analytical lines of elements of the enamel matrix

There are analytical lines of tin in the enamel samples of modern tiles used in the restoration of the mausoleum. Tin compounds were used to reduce transparency. There is no tin in historical samples, so the restored materials were not considered in further study.

A dendrogram was obtained as a result of the classification analysis of the samples (Figure 4). The dendrogram makes it possible to distinguish 4 groups of enamel spectra.

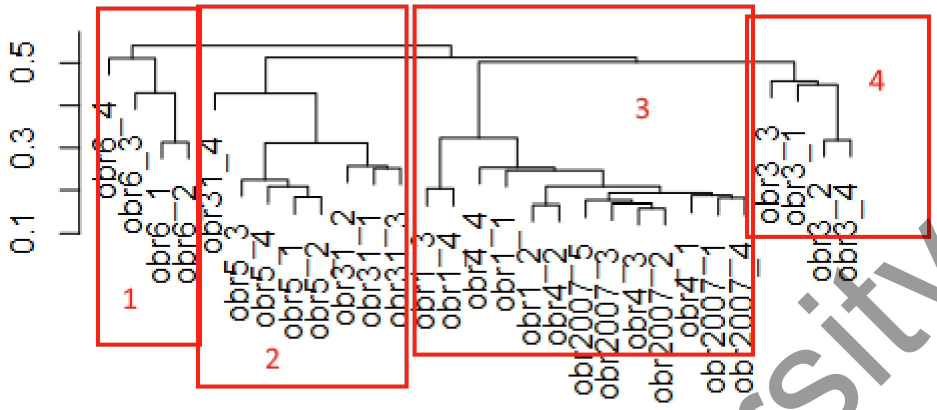
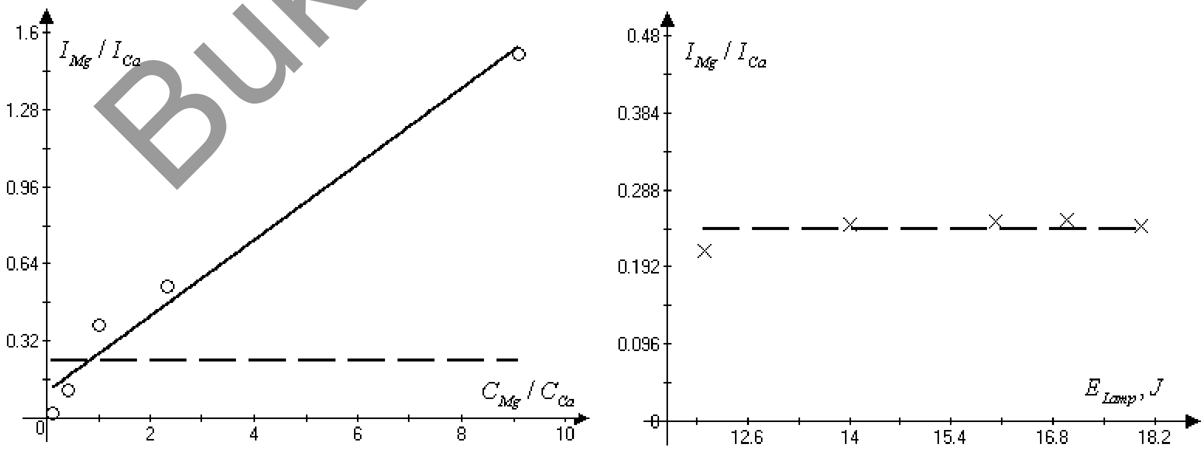


Figure 4. Cluster dendrogram of the archeological enamel samples

Samples 3, 1 and 5 have similar spectra. Samples 1, 4 and 7 can also be classified as parts of the same specimen. The spectra of samples 6 and 3 did not enter into clusters, forming separate groups. It should be noted that there is a possibility of random separation of closely related samples, while the probability of random cluster unification in the analysis by the emission spectrum is very small.

According to the results of qualitative and cluster analysis, it is possible to make conclusions of an archaeological nature that are beyond the scope of this work. At the same time, clustering can only be explained using quantitative analysis, which is difficult in this case due to limited access to the samples. In this regard, only methods of mathematical processing of obtained spectral data were used further in qualitative analysis. The first approach to quantitative analysis of samples tested in the study was based on the fact that the intensities of the analytical lines with similar excitation energies almost equally depend on the conditions of spectrum registration according to the hypothesis of local thermodynamic equilibrium (LTE). Consequently, the ratio of the intensities of such lines will depend only on the ratio of concentrations, but not on the conditions of the spectra registration and/or random factors. Figure 5 shows graphs of the dependence of the ratio of the intensities of the $Mg(I)_{293.67}$ and $Ca(II)_{315.9}$ lines on the ratio of the concentrations of elements and the energy of the laser pump lamp.



a *b*

Figure 5. Dependence of the ratio of the intensities of the $Mg(I)_{293.67}$ and $Ca(II)_{315.9}$ lines on the:
a) ratio of the concentrations of elements; *b*) the energy of the laser pump lamp

As can be seen from Figure 5, even without calculations, the pump lamp energy in the selected range has almost no effect on the ratio of the intensities of the analytical lines under consideration. The influence of other factors on this pair of lines is even less significant.

The intensity ratio of a pair of lines of different elements selected by the excitation energy and the actual presence in all 25 spectra of artificial and archaeological samples (Table 2) was used for calculation by the PDDoE method. In this case, regardless of the usual practice of the method, those lines were selected for which only the partial dependence of the intensity ratio on the concentration was significant, and the remaining partial dependencies were insignificant. Preference was given to those alternatives in which insignificant functions were most accurately described by the equation $Y = \bar{Y}$ (Fig. 5). The relationship between the concentration and the intensity ratio was approximated by linear functions:

$$a\left(C_1/C_2\right)+b=I_1/I_2 \ . \tag{1}$$

The coefficients a and b of these functions were used in further calculations.

Table 3

Analytical lines used for calculations

Element	λ	E
Mg I	293.67	55891
Mg II	279.08	71490
Mg I	383.23	47957
Pb I	261.42	46060
Al II	263.126	123470
Cu II	223.01	117928
Si I	252.41	39683
Si II	385.6	81251
Fe II	259.84	38858
Ca II	373.71	52166
Na I	588.96	16973
K I	769.83	12985

There are an infinite number of solutions for the equation with the formula of a function 1, as well as for systems composed of such equations. Based on this, one of the equations of the system should be normalizing, traditionally represented as the sum of the concentrations of all considered elements or elements oxides. The resulting system of equations with formula (2) was solved using the wxMaxima computer algebra system [23]:

$$\left\{\begin{array}{l} a_1\left(C_1/C_2\right)+b_1=I_1/I_2 \\ a_2\left(C_2/C_3\right)+b_2=I_2/I_3 \\ a_3\left(C_3/C_4\right)+b_3=I_3/I_4 \\ a_4\left(C_4/C_5\right)+b_4=I_4/I_5 \\ a_5\left(C_5/C_6\right)+b_5=I_5/I_6 \\ a_6\left(C_6/C_7\right)+b_6=I_6/I_7 \\ a_7\left(C_7/C_8\right)+b_7=I_7/I_8 \\ a_8\left(C_8/C_9\right)+b_8=I_8/I_9 \\ C_1+...+C_9=1 \end{array}\right\} \tag{2}$$

For nine elements of the considered matrix, the set includes eight equations with ratios and one normalizing equation.

The solution of such equation set in the course of checking the operability of the method for enamel samples of known composition obtained in the laboratory allows us to calculate the concentrations of the matrix elements with an accuracy of ± 6–8 %. In the case of archaeological samples, the composition was calculated for each point of spectrum registration in order to determine the uncertainty of the result. The obtained values of the concentrations of the matrix elements are presented in Table 4.

Table 4

Composition of archaeological samples according to LTE-based data

Sample	SiO_2	PbO	CaO	MgO	K_2O	Na_2O	Al_2O_3	CuO	Fe_2O_3
Sample 1 (Obr1)	56.43 ±6.21	28.84 ±4.04	5.89 ±1.18	1.92 ±0.33	3.84 ±0.69	6.06 ±1.21	1.18 ±0.30	0.34 ±0.05	0.10 ±0.02
Sample 3 (Obr3.1)	55.29 ±6.08	28.00 ±3.92	5.72 ±1.14	1.90 ±0.32	4.40 ±0.79	6.48 ±1.30	1.26 ±0.32	0.34 ±0.05	0.15 ±0.02
Sample 4 (Obr4)	55.29 ±6.08	27.16 ±3.80	5.78 ±1.16	1.90 ±0.32	3.76 ±0.68	6.54 ±1.31	1.43 ±0.36	0.36 ±0.06	0.10 ±0.02
Sample 5 (Obr5)	58.71 ±6.46	29.12 ±4.08	5.67 ±1.13	2.00 ±0.34	3.92 ±0.71	6.60 ±1.32	1.34 ±0.33	0.36 ±0.06	0.16 ±0.02
Sample 6 (Obr6)	55.29 ±6.08	30.80 ±4.31	6.05 ±1.21	2.00 ±0.34	4.16 ±0.75	6.42 ±1.28	1.38 ±0.34	0.29 ±0.06	0.19 ±0.02
Sample 7 (Obr2007)	60.42 ±6.65	26.88 ±3.76	5.67 ±1.13	2.06 ±0.35	3.96 ±0.71	5.94 ±1.19	1.31 ±0.33	0.37 ±0.06	0.11 ±0.02

Calculated error of the results for the mass fractions of oxides is 15–24 % that can be considered a good result for the LIBS in the absence of sample preparation. At the same time, it seemed possible to improve the accuracy of spectrum analysis using a chemometric data processing method. Based on the literature data, the projection onto latent structures (PLS) method was chosen as giving good results in most spectrometric studies [24]. The calculations were carried out in the "R" programming environment.

Table 5

Composition of archaeological samples according to PLS data

Sample	SiO_2	PbO	CaO	MgO	K_2O	Na_2O	Al_2O_3	CuO	Fe_2O_3
Sample 1 (Obr1)	54.72 ±5.47	26.73 ±2.94	5.62 ±0.79	2.08 ±0.27	5.70 ±0.74	4.70 ±0.66	1.44 ±0.36	0.35 ±0.03	0.01 ±0.01
Sample 3 (Obr3.1)	55.29 ±5.53	28.08 ±3.09	5.57 ±0.78	2.04 ±0.26	5.82 ±0.76	4.95 ±0.69	1.74 ±0.44	0.35 ±0.03	0.02 ±0.01
Sample 4 (Obr4)	57.57 ±5.76	27.00 ±2.97	5.25 ±0.73	2.14 ±0.28	5.94 ±0.77	5.45 ±0.76	1.66 ±0.42	0.36 ±0.03	0.01 ±0.01
Sample 5 (Obr5)	59.28 ±5.93	26.46 ±2.91	5.19 ±0.73	2.12 ±0.28	6.54 ±0.85	5.10 ±0.71	1.76 ±0.44	0.36 ±0.03	0.02 ±0.01
Sample 6 (Obr6)	59.85 ±5.99	26.19 ±2.88	5.04 ±0.70	2.21 ±0.29	6.06 ±0.79	5.15 ±0.72	1.50 ±0.38	0.35 ±0.03	0.01 ±0.01
Sample 7 (Obr2007)	56.43 ±5.64	27.54 ±3.03	5.04 ±0.70	2.04 ±0.26	5.40 ±0.70	5.10 ±0.71	1.65 ±0.41	0.37 ±0.03	0.01 ±0.01

As can be seen from Table 5, the error in the results of 4 parallel determinations was 9–14 %. It should be noted that when testing the PLS model on samples of known composition prepared artificially, the accuracy was much higher, and the error did not exceed 4 %. Therefore, the greatest contribution to the inaccuracy of the quantitative composition determination was made not by calculations, but by the lack of the possibility of sample preparation and registration of the spectrum with significant destruction of the sample.

Conclusions

In this work, LTE thermodynamic and PLS chemometric approaches have been proposed and tested for quantitative analysis of samples using their obtained spectra. The error for each element was 15–24 % when using the LTE hypothesis approach. The chemometric approach with the use of PLS has improved the accuracy. In this case, the error for the results of 4 parallel experiments was 9–14 %. As a result of the studies carried out by the LIBS method using calculation methods based on the LTE hypothesis and the chemometric approach, the qualitative and semi-quantitative composition of the enamel of tiles from the ancient settlement of Jochi Khan was determined. It was shown that the archaeological samples are lead-silicate glass with a high potassium content, which can only be explained by its purposeful introduction into the charge. Presumably, potassium could have been introduced by using the ashes of local plants.

Classification analysis identified two groups of samples that are similar in chemical composition, therefore, made from the same raw materials. This may provide additional information on the chronology of the settlement's construction. The study also revealed that contemporary restorers used a similar enamel composition, but used tin compounds for opacification.

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References

1 Cremers D.A. Handbook of Laser-Induced Breakdown Spectroscopy. (2nd ed.) / D.A. Cremers, L.J. Radziemski. — Hoboken, NJ: John Wiley & Sons, 2013. — 432 p.

2 Basic Chemometric Techniques in Atomic Spectroscopy / Eds. J.M. Andrade-Garda. — London: RSC Publishing, 2009. — 300 p.

3 Zhang T.L. Progress of Chemometrics in Laser-induced Breakdown Spectroscopy / T.L. Zhang, S. Wu, H.S. Tang, K. Wang, Y.X. Duan, H. Li // Chinese Journal of Analytical Chemistry. — 2015. — Vol. 43. — P. 939–948.

4 Li L.N. A review of artificial neural network based chemometrics applied in laser-induced breakdown spectroscopy analysis. / Li L.N., Liu, X.-F., Yang, F., Xu, W.-M., Wang, J.-Y., Shu, R. // Spectrochim, Acta Part B: Atomic Spectroscopy. — 2021. — Vol. 180, article id. 106183. https://doi.org/10.1016/j.sab.2021.106183

5 Zhang T.L. Chemometrics in laser-induced breakdown spectroscopy / T.L. Zhang, Tang, H. Li // Journal of Chemometrics. — 2018. — Vol. 32, Issue 11. — e2983. https://doi.org/10.1002/ H.S.cem.2983

6 Hahn D.W. Laser-Induced Breakdown Spectroscopy (LIBS), Part I: Review of Basic Diagnostics and Plasma-Particle Interactions: Still-Challenging Issues Within the Analytical Plasma Community / D.W. Hahn, N. Omenetto // Appl Spectrosc. — 2010. — Vol. 64(12). — P. 335A–366A. https://doi:10.1366/000370210793561691

7 Tate, J. Some problems in analysing museum material by nondestructive surface sensitive techniques // Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms. — 1986. — Vol. 14(1). — P. 20–23. https://doi.org/10.1016/0168-583x(86)90417-9

8 Anglos D. Laser-Induced Breakdown Spectroscopy in Art and Archaeology // Applied Spectroscopy. — 2001. — Vol. 55(6). — P. 186A–205A. https://doi.org/10.1366/0003702011952398

9 Panyushkina I.P. Chronology of the Golden Horde in Kazakhstan: ^{14}C Dating of Jochi Khan Mausoleum / I.P. Panyushkina, E.R. Usmanova, K.Z. Uskenbay, M.B. Kozha, D.A. Dzhumabekov, G.A. Akhatov, A.T. Jull // Radiocarbon. — 2022. — Vol. 10, No. 24. — P. 1–9. https://doi.org/10.1017/RDC.2022.24

10 Fomin V.N. Chemical-technological analysis of slags from the “Altynshoky” complex / V.N. Fomin, E.R. Usmanova, R.M. Zhumashev, A.V. Pokussayev, G. Motuza, Kh.B. Omarov, et al. // Bulletin of the University of Karaganda Chemistry. — 2018. — № 3 (91). — C. 64–73. https://doi.org/10.31489/2018Ch3/64-73

11 Фомин В.Н. Оптимизация параметров лазерно-искрового эмиссионного спектрометра с применением вероятностно-детерминированного планирования эксперимента / В.Н. Фомин, С.К. Алдабергенова, К.Т. Рустембеков, Х.Б. Омаров, И.Е. Рожковой, А.В. Дик, Д.М. Саулебеков // Заводская лаборатория. Диагностика материалов. — 2021. — № 87(5). — С. 14–19. https://doi.org/10.26896/1028-6861-2021-87-5-14-19

12 Kramida A. NIST Atomic Spectra Database (version 5.9) [Online]. Available: https://physics.nist.gov/asd [Tue Feb 22 2022]. / A. Kramida, Yu. Ralchenko, J. Reader and NIST ASD Team. — Gaithersburg, MD: National Institute of Standards and Technology, 2021. https://doi.org/10.18434/T4W30F

13 R Core Team. R: A language and environment for statistical computing. R Foundation for Statistical Computing. — 2021. Vienna, Austria. https://www.R-project.org/

14 Korneev V.A. Method of standardless quantitative emission spectral analysis in criminalistic, expert legal, and forensic medical practice / V.A. Korneev, V.K. Ivanov, A.M. Pcheiintsev, T.F. Odinochkina, A.V. Agrafenin // Journal of Applied Spectroscopy. — 1990. — Vol. 52. — P. 4.

15 Wold, S. PLS-regression: a basic tool of chemometrics / S. Wold, M. Sjöström, L. Eriksson // Chemometrics and Intelligent Laboratory Systems. — 2001. — Vol. 58, No. 2. — P.109–130, https://doi.org/10.1016/S0169-7439(01)00155-1

16 Mevik B.H. The pls package: Principal component and partial least squares regression in R / B.H. Mevik, R. Wehrens // Journal of Statistical Software. — 2007. — Vol.18, No. 2. — P. 1–24.

17 Абдуразаков А.А. Химические составы керамики и глазурей архитектурных памятников Узбекистана / Абдуразаков А.А. // История материальной культуры Узбекистана. — 1987. — Вып. 21. — С. 176–189.

18 Малышев В.П. Вероятностно-детерминированное планирование эксперимента. — Алматы: Наука. — 1981. — 115 с.

19 Беляев С.В., Малышев В.П. Пути развития вероятностно-детерминированного планирования эксперимента // Комплексная переработка минерального сырья Казахстана. Состояние, проблемы, решения: В 10 т. — Т. 9. Информационные технологии в минерально-сырьевом комплексе. Гл. 8. — Алматы, 2008. — С. 599–633.

20 Fomin V.N. Method for increasing the accuracy of quantitative determination of iron by LIBS / V.N. Fomin, S.K. Aldabergenova, K.T. Rustembekov, A.V. Dik, Yu.Yu. Kim, I.E. Rozhkovoy // Bulletin of the University of Karaganda Chemistry. — 2018. — No. 3(91). — P. 74–83. https://doi.org/10.31489/2018Ch3/74-83

21 Fomin, V.N., Aynabaev, A.A., Kaykenov, D.A., Sadyrbekov, D.T., Aldabergenova, S.K., Turovets, M.A., Kelesbek, N.K. Optimization of coal tar gas chromatography conditions using probabilistic-deterministic design of experiment // Bulletin of the University of Karaganda Chemistry. — 2021. — No. 4(104). — P. 39–46. https://doi.org/10.31489/2021Ch4/39-46

22 Фомин В.Н., Ковалева А.А., Алдабергенова С.К. Использование многофакторных переменных в вероятностно-детерминированном планировании эксперимента // Вестник Карагандинского университета. Сер. Химия. — 2017. — № 3(87). — С. 91–100

23 Maxima, a Computer Algebra System. Version 5.46.0 (2022). https://maxima.sourceforge.io/

24 Kucheryavskiy S. Mdatools — R package for chemometrics, Chemometrics and Intelligent Laboratory Systems. — Vol. 198. — 2020. https://doi.org/10.1016/j.chemolab.2020.103937.

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Лазерлік ұшқын эмиссиялық спектроскопия көмегімен құрамында қорғасыны бар археологиялық қорғасын эмальын сапалық және сандық талдау әдісі

Жошы хан қалашығының (XIV ғ.) эмаль археологиялық үлгілерін талдау үшін лазерлік ұшқын эмиссиялық спектроскопия (ЛҰЭС) әдісі қолданылды. Сапалық талдау барысында эмаль құрамының негізгі элементтері Si, Pb, K, Na, Mg, Ca, Al екені анықталды. Глазурьдің түсі мыс пен темірдің болуына байланысты. Орташалау әдісімен кластерлеу барысында эмальдің құрамына ұқсас, бірақ қалашық ішінде шыққан жері бойынша ерекшеленетін екі үлгі тобы анықталды. ЛҰЭС спектрлері бойынша жергілікті термодинамикалық тепе-теңдік (ЖТТ) гипотезасына негізделген әдісті және хемометриялық тәсілді (жасырын құрылымдарға проекция, ЖҚП) қолдана отырып, қарастырылған үлгілерде глазурьдің жартылай сандық құрамы анықталды. Спектрді тіркеу шарттары өзгерген кезде өзгеріске ұшырамайтын элементтер түзуінің жұптарын іздеу және ЖТТ негізіндегі теңдеулердегі коэффициенттерді анықтау үшін эксперименттің ықтималдық-детерминирленген жоспарлауы қолданылады. ЖҚП әдісі бойынша есептеулер “R” ортасында жүргізілді. Тұрақты оксидтерге қайта есептегенде негіз элементтердің құрамы келесідей болды, %: SiO_2 — 49–61, PbO — 23–31, MgO — 1.7–2.3, CaO — 4.6–6.9, Na_2O — 4.1–5.3, K_2O — 5.1–6.4, Al_2O_3 — 0.8–1.7, CuO — 0.32–0.4, Fe_2O_3 — 0.09–0.16. Екі әдістің де нәтижелері бір-біріне сәйкес келеді. ЖТТ үшін төрт параллель анықтама арасындағы айырмашылық 15–24 %, ЖҚП үшін 9–14 % құрады. Жартылай сандық талдау деректерін ескере отырып, екі топқа бөлінудің негізінде эмальдағы мыс пен темірдің әртүрлі қатынасы жатыр деген қорытындыға келді.

Кілт сөздер: ЛҰЭС, химометрика, кластерлік талдау, ЖҚП, жеңіл балқитын қорғасын эмальдары, эксперименттi ықтималды-детерминирленген жоспарлау, археология, Жошы хан қалашығы.

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Метод качественного и количественного анализа свинцовой археологической эмали с использованием лазерной искровой эмиссионной спектроскопии

Метод лазерно-искровой эмиссионной спектроскопии (ЛИЭС) применен для анализа археологических образцов эмали с городища Джучи-хана (XIVв.). В ходе качественного анализа показано, что элементами основы эмали являются Si, Pb, K, Na, Mg, Ca, Al. Окраска глазури обусловлена присутствием меди и железа. Кластеризацией методом *k* средних было выявлено две группы образцов, сходных по составу эмали, но отличающихся по месту происхождения внутри городища. С применением метода, основанного на гипотезе локального термодинамического равновесия (ЛТР), и хемометрического подхода (проекция на латентные структуры, ПЛС) по спектрам ЛИЭС установлен полуколичественный состав глазурей на рассмотренных образцах. Для поиска пар линий элементов, не подверженных изменениям при изменении условий регистрации спектра, и определения коэффициентов в уравнениях, основанных на ЛТР, использовано вероятностно-детерминированное планирование эксперимента. Расчеты по методу ПЛС проведены в среде “R”. Содержание элементов основы в пересчете на наиболее устойчивые оксиды сотавило, %: SiO_2 — 49–61, PbO — 23–31, MgO — 1.7–2.3, CaO — 4.6–

6.9, Na_2O — 4.1–5.3, K_2O — 5.1–6.4, Al_2O_3 — 0.8–1.7, CuO — 0.32–0.4, Fe_2O_3 — 0.09–0.16. Результаты обоих методов в целом согласуются между собой. Расхождения между 4мя параллельными определениями для ЛТР составили 15–24 %, для ПЛС 9–14 %. С учетом данных полуколичественного анализа сделан вывод о том, что в основе разделения на две группы лежит разное соотношение меди и железа в эмали.

Ключевые слова: ЛИЭС, хемометрика, кластерный анализ, ПЛС, легкоплавкие свинцовые эмали, вероятностно-детерминированное планирование эксперимента, археология, городище Джучи-хана.

References

1 Cremers, David & Radziemski, Leon. (2013). *Handbook of Laser-Induced Breakdown Spectroscopy*: Second Edition. Hoboken, NJ: John Wiley & Sons. https://doi.org/10.1002/9781118567371

2 Andrade-Garda, J.M. (Eds.) (2009). *Basic Chemometric Techniques in Atomic Spectroscopy*. London: RSC Publishing.

3 Zhang, T.-L., Wu, S., Tang, H.-S., Wang, K., Duan, Y.-X., Li, H. (2015). Progress of Chemometrics in Laser-induced Breakdown Spectroscopy. *Chinese Journal of Analytical Chemistry, 43*, 6, 939-948. https://doi.org/10.1016/S1872-2040(15)60832-5

4 Li, L.-N., Liu, X.-F., Yang, F., Xu, W.-M., Wang, J.-Y., Shu, R. (2021). A review of artificial neural network based chemometrics applied in laser-induced breakdown spectroscopy analysis. *Spectrochim, Acta Part B: Atomic Spectroscopy, 180*, article id. 106183. https://doi.org/10.1016/j.sab.2021.106183

5 Zhang, T.-L., Tang, H.-S., Li, H. (2018). Chemometrics in laser-induced breakdown spectroscopy. *Journal of Chemometrics, 32*, 11. https://doi.org/10.1002/cem.2983

6 Hahn, D.-W., Omenetto, N. (2010). Laser-Induced Breakdown Spectroscopy (LIBS), Part I: Review of Basic Diagnostics and Plasma-Particle Interactions: Still-Challenging Issues Within the Analytical Plasma Community. *Appl Spectrosc, 64*(12), 335A-366A. https://doi:10.1366/000370210793561691

7 Tate, J. (1986). Some problems in analysing museum material by nondestructive surface sensitive techniques. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 14*(1), 20–23. https://doi.org/10.1016/0168-583x(86)90417-9

8 Anglos, D. (2001). Laser-Induced Breakdown Spectroscopy in Art and Archaeology. *Applied Spectroscopy, 55*(6), 186A-205A. https://doi.org/10.1366/0003702011952398

9 Panyushkina, I.P., Usmanova, E.R., Uskenbay K.Z., Kozha M.B., Dzhumabekov D.A., Akhatov G.A., Jull, A.T. (2022) Chronology of the Golden Horde in Kazakhstan: ^{14}C Dating of Jochi Khan Mausoleum. *Radiocarbon, 10*, 24, 1–9. https://doi.org/10.1017/RDC.2022.24

10 Fomin, V.N., Usmanova, E.R., Zhumashev, R.M., Pokussayev, A.V., Motuza, G., Omarov, Kh.B., et al. (2018). Chemical-technological analysis of slags from the “Altynshoky” complex. *Bulletin of the University of Karaganda Chemistry*, *3*(91), 64–73. https://doi.org/10.31489/2018Ch3/64-73

11 Fomin, V.N., Aldabergenova, S.K., Rustembekov, K.T., Omarov, Kh.B., Rozhkovoy I.E., Dik A.V., Saulebekov D.M. (2021). Optimization of the parameters of a laser induced breakdown spectrometer (LIBS) using probabilistic-deterministic design of experiment. *Industrial laboratory. Diagnostics of materials*, *87*(5), 14–19. https://doi.org/10.26896/1028-6861-2021-87-5-14-19 [in Russian]

12 Kramida, A., Ralchenko, Yu., Reader, J. and NIST ASD Team (2021). NIST Atomic Spectra Database (version 5.9), [Online]. Available: https://physics.nist.gov/asd [Tue Feb 22 2022]. National Institute of Standards and Technology, Gaithersburg, MD. https://doi.org/10.18434/T4W30F

13 R Core Team (2021). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL https://www.R-project.org/

14 Korneev, V.A., Ivanov, V.K., Pcheiintsev, A.M., Odinochkina, T.F., Agrafenin, A.V. (1990) Method of standardless quantitative emission spectral analysis in criminalistic, expert legal, and forensic medical practice. *Journal of Applied Spectroscopy*, *52*, 4.

15 Wold, S., Sjöström, M., Eriksson L. (2001). PLS-regression: a basic tool of chemometrics. *Chemometrics and Intelligent Laboratory Systems, 58*, 2, 109–130, https://doi.org/10.1016/S0169-7439(01)00155-1

16 Mevik, B.-H. & Wehrens, R. (2007). The pls package: Principal component and partial least squares regression in R. *Journal of Statistical Software, 18*, 2, 1–24.

17 Abdurazakov, A.A. (1987). Himicheskie sostavy keramiki i glazurej arhitekturnyh pamyatnikov Uzbekistana [Chemical compositions of ceramics and glazes of architectural monuments of Uzbekistan]. *Istoriya material'noj kul'tury Uzbekistana — History of Material Culture of Uzbekistan, 22*, 176–189 [in Russian].

18 Malyshev, V.P. (1981). *Veroyatnostno-determinirovannoe-planirovanie-ehksperimenta [Probabilistic-deterministic mapping]*. Almaty: Nauka [in Russian]

19 Beliaev, S.V., Malyshev, V.P. (2008). Puti razvitiia veroiatnostno-determinirovannoho planirovaniia eksperimenta [Ways of stochastic-determinated design of experiments development]. (Vols. 1-10; Vol. 9): Informatsionnye tehnolohii v mineralno-syrievom komplekse. *Information technologies in the mineral-raw complex, 8*, Almaty [in Russian].

20 Fomin, V.N., Aldabergenova, S.K., Rustembekov, K.T., Dik, A.V., Kim, Yu.Yu., Rozhkovoy, I.E. (2018). Method for increasing the accuracy of quantitative determination of iron by LIBS. *Bulletin of the University of Karaganda Chemistry, 3*(91), 74–83. https://doi.org/10.31489/2018Ch3/74-83

21 Fomin, V.N., Aynabaev, A.A., Kaykenov, D.A., Sadyrbekov, D.T., Aldabergenova, S.K., Turovets, M.A., Kelesbek, N.K. (2021). Optimization of coal tar gas chromatography conditions using probabilistic-deterministic design of experiment. *Bulletin of the University of Karaganda Chemistry, 4*(104), 39–46. https://doi.org/10.31489/2021Ch4/39-46

22 Fomin, V.N., Kovaleva, A.A., Aldabergenova, S.K. (2017). Using multivariate variables in probabilistic-deterministic design of experiments. *Bulletin of the University of Karaganda Chemistry, 3*(87), 91–100.

23 *Maxima, a Computer Algebra System. Version 5.46.0* (2022). Retrieved from https://maxima.sourceforge.io/

24 Kucheryavskiy S. (2020). *Mdatools — R package for chemometrics. Chemometrics and Intelligent Laboratory Systems,* 198, https://doi.org/10.1016/j.chemolab.2020.103937

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