

Analysis of Silver and Gold Samples from the Borodino Treasure by Inductively Coupled Plasma Mass Spectrometry and Inductively Coupled Plasma Atomic Emission Spectrometry

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Abstract—One of the main requirements for the methods of elemental analysis of unique archaeological samples is to minimize the damage they cause. Two new procedures for analyzing silver and gold samples, weighing several milligrams, obtained by drilling from the inner surface of silver and gold artifacts of the Borodino treasure, stored in the State Historical Museum, are described. The procedures are based on the autoclave decomposition of samples and subsequent analysis of the obtained solutions by inductively coupled plasma mass spectrometry (ICP–MS) and inductively coupled plasma atomic emission spectrometry (ICP–AES). They enable the determination of more than 60 impurity elements in each sample with a determination limits from 1×10^{-2} to $n \times 10^{-3}$ wt % for common elements (Na, Mg, Al, K, Ca, Ti, and Fe) and to $n \times 10^{-7}$ wt % for REEs, Ir, Tl, and U. The correctness of the developed procedures is confirmed by the analysis of standard samples and by comparison with the ICP–MS results obtained with laser sampling, which allows direct analysis of samples without their dissolution.

Keywords: silver and gold of the Borodino treasure, inductively coupled plasma mass spectrometry, inductively coupled plasma atomic emission spectrometry, autoclave decomposition of samples

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Inductively coupled plasma mass spectrometry is widely used to solve various problems of elemental analysis, including in archeology, due to its high sensitivity, wide dynamic range, and the possibility of simultaneous determination of almost all elements of the Periodic Table. In 1987, just 4 years after the appearance of the first mass spectrometers, the first work was issued on the ICP–MS determination of 12 elements (Co, Ni, Cu, Zn, As, Sn, Sb, Te, W, Pb, Bi, and Hg) in archaeological silver specimens weighing from 3.5 to 15.6 mg [1]. Over the next 30 years, several dozens of papers have appeared, in which ICP–MS analysis of various historical artifacts made of silver and gold are discussed.

In analyzing archaeological samples, a combination of ICP–MS with laser ablation (LA–ICP–MS) has become widespread, because it can minimize damage to unique samples of both silver [2–6] and gold [2, 5, 7–11] during the analysis. However, LA–ICP–MS, along with undoubted advantages, has several serious disadvantages, for example, the effects of the fractionation of elements, matrix effects associated

with different degrees of absorption of laser radiation by different materials, and the lack of adequate standard samples. For these reasons, the number of elements to be determined in LA–ICP–MS is often smaller compared to the conventional ICP–MS method involving the preliminary dissolution of the test samples, and the error in determining impurity elements is usually higher. In the case of sample dissolution, the problem associated with the inhomogeneity of the sample is solved, and the high precision of the results of measurements is ensured. The ease of preparation of calibration samples and rapid measurements are also significant advantages of the conventional ICP–MS method, which involves the analysis of solutions.

Since silver and gold are widely used in the present-day industry, methods for their analysis are well developed, including ICP–AES [12–15]. The conditions for transferring samples to a solution in ICP–AES could also be used for the ICP–MS analysis of archaeological silver and gold samples, but there are two severe limitations. First, the sample weight in these

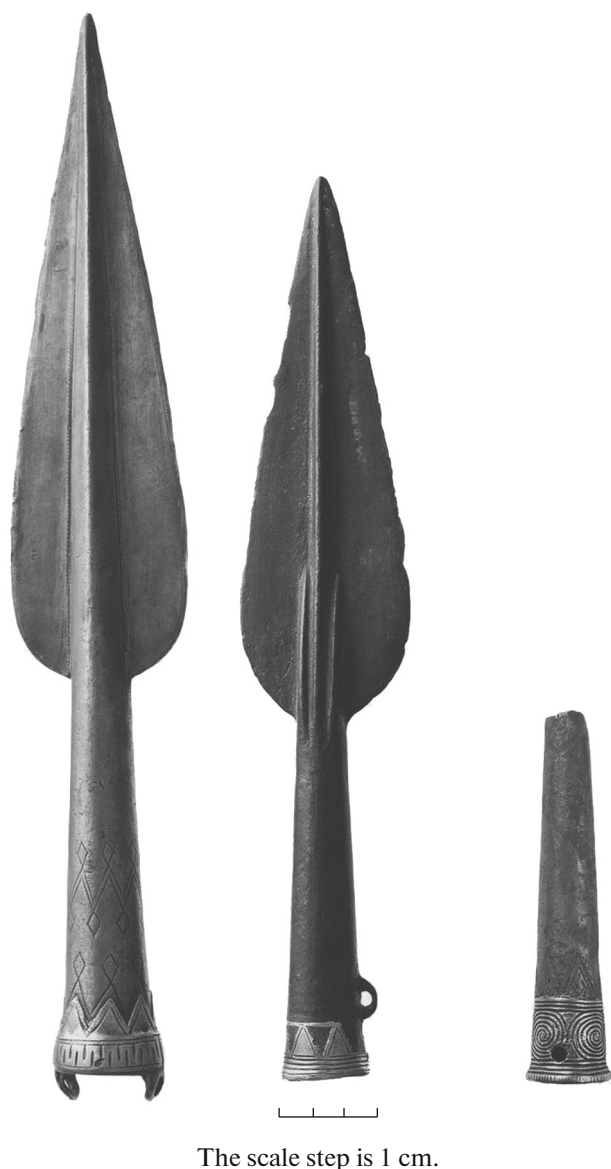


Fig. 1. Spears of the Borodino treasure (silver, gold).

methods, as a rule, ranges from 200 mg for silver [15] and 500 mg for gold [14], up to 20 g in the case of silver [16], which is often utterly unacceptable from the point of view of the preservation of historical artifacts made of precious metals. Second, the ICP–AES methods are focused on the analysis of relatively pure samples of silver and gold with the concentration of impurity elements less than 0.01–0.05 wt %, while archaeological samples of silver and gold may contain a large number of alloying elements or be alloys. In this case, the use of conventional dissolution procedures can lead to errors in the results of analysis. For example, in ICP–MS analysis of gold samples with high silver content, the dissolution of samples only in a mixture of HCl and HNO₃ leads to the formation of insol-

uble silver chloride [17]. Silver chloride can also capture other elements [15], which leads to significant errors in determining the composition of the gold sample. Similar problems of incomplete dissolution can occur in the analysis of silver products containing gold or platinum elements, if one uses only nitric acid to dissolve them.

For these reasons, we developed two new procedures for analyzing silver and gold samples weighing a few milligrams, based on the autoclave dissolution of the samples and the subsequent analysis of the resulting solutions by ICP–AES and ICP–MS. These procedures are used to analyze samples obtained by drilling from the inner surface of silver and gold artifacts of the Borodino treasure stored in the State Historical Museum (Fig. 1), as well as other silver and gold archaeological samples.

EXPERIMENTAL

Reagents and glassware. We used the following concentrated acids: HNO₃ (nitric acid 65%; max 0.0000005% of Hg; GR, ISO) and H₂SO₄ (sulfuric acid 95–97% for analysis EMSURE) manufactured by Merck (Germany), HCl (hydrochloric acid 37%; max 0.0000005% of Hg; PA-ACS-ISO) manufactured by Panreac (Spain). Deionized water with a specific resistance of 18.2 MΩ cm was used to prepare solutions.

For the storage of solutions, glass measuring flasks with ground-glass stoppers according to *GOST 1770-74* and 15- and 50-mL disposable polyethylene test tubes from Labcon (United States) and Deltalab (Spain) were used. The glassware was presoaked for 4–5 days in 5% HNO₃ and washed with deionized water prior to use. The samples were dissolved in an open system using quartz 20-mL glasses with “watch glass” covers.

Reference samples. For the preparation of calibration solutions for ICP–AES and ICP–MS measurements, we used solutions of the following multielement and single-element standards from High-Purity Standards (United States):

—An ICP-AM-6A ICP Analytical Mixture multielement standard solution with a weight concentration of 100 mg/L of Li, Be, B, Na, Mg, Al, Si, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Cd, Sb, Ba, Tl, and Pb.

—An ICP-MS-68-A multielement standard solution with a weight concentration of 10 mg/L of Al, As, Ba, Be, Bi, B, Cd, Ca, Ce, Cs, Cr, Co, Cu, Dy, Er, Eu, Gd, Ga, Ho, In, Fe, La, Pb, Li, Lu, Mg, Mn, Nd, Ni, P, K, Pr, Re, Rb, Sm, Sc, Se, Na, Sr, Tb, Tl, Th, Tm, U, V, Yb, Y, and Zn.

—An ICE-MS-68-B multielement standard solution with a weight concentration of 10 mg/L of Sb, Ge, Hf, Mo, Nb, Si, Ag, Ta, Te, Sn, Ti, W, and Zr.

—An ICP-MS-68-C multielement standard solution with a weight concentration of 10 mg/L of Au, Ir, Os, Pd, Pt, Rh, and Ru.

—Standard single-element solutions of B, Al, P, S, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Rh, Ag, Ba, Pt, Au, and Hg with a weight concentration of 1000 mg/L.

The accuracy of the analysis of silver and gold samples was controlled using a set of standard samples of silver SN2/GSO 10738-2015 and standard samples of gold Z14aK1/GSO 10589-2015, Z14aK2/GSO 10590-2015, and Z14a-6/SOP 0279-2015, produced by Yekaterinburg Non-Ferrous Metals Processing Plant, Russia.

Apparatus. The autoclave decomposition of the samples was carried out in the autoclave sample opening system developed in the Institute of Microelectronics Technology Problems and High-Purity Materials, Russian Academy of Sciences, which is a modification of the well-proven MKP-05 system (ANKON-AT-2, Russia). The system enables heating of 30-mL Teflon reaction chambers to a maximum temperature of 240°C at a pressure of 20 MPa (200 bar). The thermostat unit for six autoclaves is equipped with two independent thermocouples and an automatic control unit based on a TRM-251 programmable PID temperature controller (OVEN-K, Russia). The control unit implements a five-stage program for heating the thermostat; the temperature, the duration of heating and maintaining the selected temperature are set at each stage. RP-1 electric plates with a variable output (Tom'analit, Russia) were used for heating and evaporation of solutions. A CE224-C analytical balance (Sartogsm, Russia) was used for weighing.

For the AES analysis of the obtained solutions, an iCAP-6500 Duo spectrometer (Thermo Scientific, United States) was used at the following operating parameters: generator output power, 1250 W; VeeSpray nebulizer; cyclone glass spray chamber; argon plasma forming gas flow rate, 12 L/min; argon auxiliary gas flow rate, 0.5 L/min; argon flow rate in the nebulizer, 0.57 L/min; and sample flow rate, 1.8 mL/min. The list of elements under determination, the lines used, and the method of observation of the plasma are given in Table 1.

For the mass spectrometric determination of the elements, an X-7 quadrupole mass spectrometer (Thermo Scientific, United States) was used at the following parameters of operation: generator output power, 1300 W; set of standard nickel cones; concentric atomizer PolyCon; quartz conical spray chamber cooled to 3°C; plasma-forming argon flow rate, 13 L/min; auxiliary argon flow rate, 0.9 L/min; flow rate of argon in the atomizer, 0.95 L/min; and sample flow rate, 0.8 mL/min. The detected elements and isotopes used are listed in Table 2.

For laser sampling, a UP266 MACRO unit (New Wave Research, United States) was used at the follow-

Table 1. List of elements determined by ICP–AES, used spectral lines and their types, and measurement conditions

Element	Wavelength, nm	Type of line	Measurement conditions
Li	670.784	I	A, R
B	249.678; 249.773	I	A
Na	588.995; 818.326	I	A, R
Mg	279.553; 285.213	II; I	R
Al	396.152	I	A, R
Si	251.611	I	A, R
P	178.284; 185.942	I	A, R
S	182.034	I	A, R
K	766.490; 769.896	I	A, R
Ca	393.366; 422.673	II; I	A, R
Ti	334.941; 336.121	II	A, R
V	292.402	II	A, R
Cr	267.716	II	A, R
Mn	257.610	II	A, R
Fe	233.280; 259.940	II	A, R
Co	228.616	II	A
Ni	221.647; 231.604	II	A
Cu	204.379; 324.754	II	A
Zn	206.200; 213.856	II; I	A, R
Sr	404.771; 421.552	II	A, R
Ba	455.403	II	A, R

A, the axial observation of plasma; R, the radial observation of plasma.

ing operating parameters: wavelength, 266 nm; pulse duration, 4 ns; pulse repetition frequency, 10 Hz; pulse energy, 5 mJ; and crater diameter, 100 μm. The sampling was carried out by purging the chamber with a helium flow at 0.6 L/min, which was mixed with an argon flow at 0.6 L/min before being fed into the mass spectrometer. The resulting aerosol was analyzed using an X-2 quadrupole mass spectrometer (Thermo Scientific, United States). The $^{197}\text{Au}^{16}\text{O}^+$ polyatomic ion was used as an internal standard.

Autoclave decomposition of samples. *Silver.* Before decomposition, silver samples were kept for 5–10 min in 10–15% HCl to remove surface contaminants, washed 2–3 times with deionized water, and dried. The autoclave decomposition of the samples was carried out in batches of 4–5 samples, the weight of which was 10 mg. A control (blank) experiment was performed in each batch, and a standard reference sample of composition was decomposed together with the test samples in each second batch. The samples were placed in the reaction chambers of the autoclaves; 1 mL of HNO_3 was added to the samples. The reaction chambers were heated on the hot plate until the solution boiled and the samples were completely or par-

Table 2. List of elements determined by ICP–MS and the isotopes used

Element	Isotopes	Element	Isotopes	Element	Isotopes
Li	6, 7	Rh	103	Ho	165
Be	9	Pd	105, 108	Er	167, 168
Sc	45	Ag	107, 109	Tm	169
V	51	Cd	111, 114	Yb	171, 174
Cr	52, 53*	In	113, 115	Lu	175
Co	59	Sn	118, 120	Hf	178, 180
Ni	60, 62	Sb	121, 123	Ta	181
Zn	66, 68	Te	125, 126	W	184, 186
Ga	71	Cs	133	Re	185, 187
As	75	Ba	135, 138	Os	189, 192
Se	77*, 78, 82	La	139	Ir	191, 193
Rb	85	Ce	140, 142	Pt	195, 196
Sr	86, 88	Pr	141	Au	197
Y	89	Nd	143, 146	Tl	203, 205
Zr	90, 91	Sm	147, 149	Pb	206, 207, 208
Nb	93	Eu	151, 153	Bi	209
Mo	95, 98	Gd	157, 160	Th	232
Ru	99, 101	Tb	159	U	238
Rh	103	Dy	161, 163		

* Required for the calculation method of accounting for interferences.

tially (depending on their composition) dissolved. After cooling, portions of HCl (0.5 mL) and HNO₃ (0.5 mL) were added to the reaction chambers, and the chambers were closed with lids and sealed in titanium enclosures of the autoclaves. The autoclaves were placed in an electric heater and heated at 160°C for 1 h. After cooling, the autoclaves were opened, and the resulting solutions were transferred to plastic test tubes. The silver chloride precipitates were washed with 2–3 mL of deionized water, and this water was combined with the previous solutions from autoclaves. The volume of the resulting solutions was adjusted to 10 mL (solutions with index a). Portions of H₂SO₄ (2 mL) were added to the reaction chambers, and the chambers were closed with lids and sealed in titanium enclosures of the autoclaves. The autoclaves were placed in an electric heater and heated at 160°C (1 h), 180°C (1 h), 200°C (1 h), and 220°C (1 h). After cooling, the autoclaves were opened, the solutions from the reaction chambers were transferred to plastic test tubes, and the volume of the solutions was adjusted to 10 mL (solutions with index b). The remains of silver chloride at the bottom of the reaction chambers were discarded. The solutions obtained from the reaction chambers, underwent the above procedures and those containing no sample were used as blank samples. Before starting the measurements, solutions with indices a and b were diluted tenfold, and an internal standard (cesium) was introduced. The concentrations of

elements in both diluted and initial solutions were determined by ICP–AES, and ICP–MS was used for only diluted solutions.

Gold. Before decomposition, gold samples were kept for 5–10 min in 10–15% HCl to remove surface contaminants, washed 2–3 times with deionized water, and dried. The autoclave decomposition of the samples was carried out in batches of 4–5 samples, the weight of which was 10 mg. A control (blank) experiment was performed in each batch, and a standard reference sample of composition was decomposed together with the test samples in each second batch. The samples were placed in reaction chambers of the autoclaves; portions of HCl (0.5 mL) and HNO₃ (1 mL) were added, and the chambers were closed with lids and sealed in titanium enclosures of the autoclaves. The autoclaves were placed in an electric heater and heated at 160°C for 1 h. After cooling, the autoclaves were opened, and the resulting solutions were transferred to plastic test tubes. If precipitates (silver chloride) formed during the dissolution, they were washed with 2–3 mL of deionized water, and this water portions were combined with the previous solutions. The volume of the resulting solutions was adjusted to 10 mL (solutions with index a). Portions of H₂SO₄ (2 mL) were added to the reaction chambers, and the chambers were closed with lids and sealed in titanium enclosures of the autoclaves. The autoclaves were placed in an electric heater and heated at 160°C

Table 3. Results ($\mu\text{g/g}$) of analysis of standard reference samples of refined silver GSO 10738–2015 (CH2-4 and CH2-7)

Element	DL, $\mu\text{g/g}$	CH2-4		CH2-7	
		found	certified	found	certified
Li	0.7	<DL	–	<DL	–
Be	0.1	<DL	–	<DL	–
B	6	<DL	–	<DL	–
Na	86	<DL	–	<DL	–
Mg	25	<DL	1.5 ± 0.3	<DL	15 ± 1.6
Al	19	<DL	7.3 ± 0.7	46.2 ± 8	44 ± 3
K	43	<DL	–	<DL	–
Ca	168	<DL	–	<DL	–
Sc	2	<DL	–	<DL	–
Ti	13	<DL	–	<DL	–
V	1	<DL	–	<DL	–
Cr	9	59.6 ± 9.0	69 ± 4	<DL	2.9 ± 0.3
Mn	2	4.1 ± 0.8	4.4 ± 0.5	79.9 ± 6	84 ± 7
Fe	82	212 ± 24	204 ± 6	<DL	39 ± 3
Co	2	<DL	–	<DL	–
Ni	9	<DL	2.1 ± 0.2	80.2 ± 10	86 ± 3
Cu	11	50.0 ± 10.3	52.2 ± 1.3	826 ± 42	870 ± 40
Zn	6	<DL	5.2 ± 0.3	<DL	7 ± 0.3
Ga	1	<DL	–	<DL	–
As	3	<DL	3.0 ± 0.3	<DL	3.4 ± 0.6
Se	8	<DL	3.7 ± 0.3	<DL	–
Rb	0.3	<DL	–	<DL	–
Sr	0.9	<DL	–	<DL	–
Y	0.4	<DL	–	<DL	–
Zr	1	<DL	–	<DL	–
Nb	1	<DL	–	<DL	–
Mo	0.4	<DL	–	<DL	–
Rh	0.6	5.9 ± 0.5	7.0 ± 1.0	11.4 ± 1	15.1 ± 1.5
Pd	0.5	5.5 ± 0.8	6.0 ± 0.4	319 ± 29	314 ± 10.0
Ag		Matrix	–	Matrix	–
Cd	0.4	3.1 ± 0.3	3.2 ± 0.3	<DL	–
In	0.8	<DL	–	<DL	–
Sn	1	4.7 ± 1.2	4.5 ± 0.6	1.3 ± 0.3	1 ± 0.2
Sb	0.3	4.5 ± 0.7	4.5 ± 0.5	36.1 ± 4	30 ± 3
Te	0.9	5.4 ± 0.4	5.3 ± 0.6	23.2 ± 2	23.0 ± 2.0
Ba	0.7	<DL	–	<DL	–
La	0.1	<DL	–	<DL	–
Ce	0.1	<DL	–	<DL	–
Pr	0.1	<DL	–	<DL	–
Nd	0.1	<DL	–	<DL	–
Sm	0.1	<DL	–	<DL	–
Eu	0.08	<DL	–	<DL	–
Gd	0.05	<DL	–	<DL	–

Table 3. (Contd.)

Element	DL, $\mu\text{g/g}$	CH2-4		CH2-7	
		found	certified	found	certified
Tb	0.09	<DL	—	<DL	—
Dy	0.09	<DL	—	<DL	—
Ho	0.04	<DL	—	<DL	—
Er	0.06	<DL	—	<DL	—
Tm	0.04	<DL	—	<DL	—
Yb	0.05	<DL	—	<DL	—
Lu	0.04	<DL	—	<DL	—
Hf	0.3	<DL	—	<DL	—
Ta	0.4	<DL	—	<DL	—
W	0.2	<DL	—	<DL	—
Re	0.1	<DL	—	<DL	—
Ir	0.05	<DL	—	<DL	—
Pt	0.1	8.5 ± 0.6	8.0 ± 1.0	0.59 ± 0.2	—
Au	1	8.2 ± 0.9	7.8 ± 0.8	17.9 ± 1	18.1 ± 1.2
Hg	0.3	<DL	—	<DL	—
Tl	0.05	<DL	—	<DL	—
Pb	1	2.9 ± 0.6	3.4 ± 0.4	3.8 ± 0.3	4.3 ± 0.6
Bi	0.1	2.7 ± 0.4	3.0 ± 0.2	<DL	—
Th	0.09	<DL	—	<DL	—
U	0.05	<DL	—	<DL	—

* DL, the limits of determination, calculated as tripled standard deviations of the blank experiments.

(1 h), 180°C (1 h), 200°C (1 h), and 220°C (1 h). After cooling, the autoclaves were opened; the reaction chambers were placed on the hot plate. The solutions were boiled for 15–20 min, cooled, and transferred to plastic test tubes; and the volume of the solutions was adjusted to 10 mL (solutions with index b). The solutions obtained from the reaction chambers, underwent the above procedures and those containing no sample were used as blank samples. Before starting the measurements, solutions with indices a and b were diluted tenfold, and an internal standard (cesium) was introduced. The concentrations of elements in both diluted and initial solutions were determined by ICP–AES, and ICP–MS was used for only diluted solutions.

RESULTS AND DISCUSSION

In developing methods for analyzing silver and gold, the decomposition procedures described earlier [12–15] were taken as the basis. In contrast to the known procedures, the weight of the test samples was no more than 10 mg; therefore, it was necessary to ensure a low level of uncontrolled contamination from the laboratory glassware, air, reagents, etc. We also should eliminate or minimize the uncontrolled loss of the analytes through incomplete dissolution, spatter-

ing, volatility, adsorption, incomplete transfer of solutions, and other reasons. Therefore, the dissolution of the samples was carried out in autoclaves at elevated pressure and temperature up to 220°C, which ensured, on the one hand, low values of the blank experiment, and, on the other hand, the most severe dissolution conditions. Finally, to expand the range of elements to be determined and increase the reliability of their determination, the resulting solutions were analyzed by two methods: ICP–AES and ICP–MS.

The above-described ICP–AES and ICP–MS procedures were tested in analyzing a set of standard samples of silver SN2/GSO 10738-2015 and standard samples of gold Z14aK1/GSO 10589-2015, Z14aK2/GSO 10590-2015, and Z14a-6/SOP 0279-2015. We used the conventional measurement procedures of ICP–AES and ICP–MS; they were described in previous works (for example, [18]) and are not given in this paper.

Upon the decomposition of standard silver samples, it was found that most of the impurity elements were entirely transferred to the solution at the first stage of autoclave decomposition (solution a). The second solution (solution b), obtained after the treatment of the silver chloride precipitate with 2 mL of sulfuric acid, contained the total amount of rhodium

Table 4. Results ($\mu\text{g/g}$) of analysis of a standard sample of gold Z14aK2/GSO 10590–2015

Element	DL, $\mu\text{g/g}$	Found	Certified	Element	DL, $\mu\text{g/g}$	Found	Certified
Li	0.4	<DL	–	Sn	1	9.1 ± 0.2	9.8 ± 0.8
Be	0.1	<DL	–	Sb	0.6	9.1 ± 0.3	9.2 ± 0.7
B	7	<DL	–	Te	1	10.3 ± 0.4	9.9 ± 1.0
Na	50	<DL	–	Ba	1	<DL	–
Mg	51	<DL	7.6 ± 0.8	La	0.1	<DL	–
Al	57	<DL	9.5 ± 0.9	Ce	0.3	<DL	–
K	59	<DL	–	Pr	0.06	<DL	–
Ca	135	<DL	–	Nd	0.09	<DL	–
Sc	1	<DL	–	Sm	0.03	<DL	–
Ti	22	<DL	8.8 ± 1.0	Eu	0.06	<DL	–
V	2	<DL	–	Gd	0.03	<DL	–
Cr	6	9.6 ± 2	10.1 ± 1.2	Tb	0.06	<DL	–
Mn	2	8.4 ± 1.2	9.5 ± 0.8	Dy	0.03	<DL	–
Fe	88	<DL	9.5 ± 1.2	Ho	0.05	<DL	–
Co	1	<DL	–	Er	0.03	<DL	–
Ni	2	9.0 ± 1.0	9.6 ± 0.6	Tm	0.02	<DL	–
Cu	6	54.0 ± 1.4	50.0 ± 4.0	Yb	0.02	<DL	–
Zn	9	<DL	5.4 ± 0.6	Lu	0.02	<DL	–
Ga	1	<DL	–	Hf	0.1	<DL	–
As	1	7.6 ± 0.4	10.4 ± 1.0	Ta	0.3	<DL	–
Se	11	<DL	8.7 ± 1.2	W	0.3	<DL	–
Rb	1	<DL	–	Re	0.1	<DL	–
Sr	2	<DL	–	Os	0.2	<DL	–
Y	0.4	<DL	–	Ir	0.06	0.074 ± 0.01	–
Zr	1	<DL	–	Pt	0.1	9.6 ± 0.2	9.7 ± 1.1
Nb	1	<DL	–	Au		Matrix	–
Mo	1	<DL	–	Hg	1	<DL	–
Ru	0.6	<DL	–	Tl	0.05	<DL	–
Rh	0.6	24.2 ± 0.8	27.2 ± 1.7	Pb	1	9.9 ± 0.2	10.9 ± 0.6
Pd	0.4	10.4 ± 0.5	10.1 ± 0.7	Bi	0.1	9.5 ± 0.6	9.1 ± 1.0
Ag	2	89.2 ± 2.0	97.0 ± 8.0	Th	0.2	<DL	–
Cd	1	<DL	–	U	0.06	<DL	–
In	1	<DL	–				

* DL, the limits of determination, calculated as tripled standard deviations of the blank experiments.

and up to 20% of lead and bismuth relative to their total concentration in the sample. This procedure could be modified to quantify silver. To do this, the obtained solutions b must be boiled for 15–20 min after the second heating of autoclaves with sulfuric acid, until the complete destruction of silver chloride. In this case, silver completely passed to the solution and can be determined, for example, by ICP–AES. The results of the ICP–AES and ICP–MS analysis of two standard silver samples (Table 3) confirm the excellent reproducibility and accuracy of the determination.

In decomposing standard gold samples containing up to 0.03% of silver (Z14a-6/SOP 0279-2015), all impurity elements, including silver, were completely dissolved in the solution at the first stage of autoclave decomposition (solution a). However, in analyzing real gold samples containing appreciable amounts of silver (>1%), a precipitate of silver chloride formed, and the second stage of autoclave decomposition was required to dissolve it. In addition to silver, we observed lead and bismuth in solution b in the amount of up to 10% of their total concentration in the sample. As for rhodium, most of it was in solution a, unlike sil-

Table 5. Comparison of the results of the ICP–AES/ICP–MS (the developed procedure) and LA–ICP–MS analysis of a gold sample

Element	ICP–AES/ICP–MS		LA–ICP–MS		Element	ICP–AES/ICP–MS		LA–ICP–MS	
	DL, µg/g	c, µg/g	DL, µg/g	c, µg/g		DL, µg/g	c, µg/g	DL, µg/g	c, µg/g
Li	0.5	<DL	0.2	<DL	Sn	0.4	52.6	0.2	60.5
Be	0.1	<DL	0.02	<DL	Sb	1	3.0	0.01	3.1
B	7	<DL	1	<DL	Te	0.3	<DL	0.2	<DL
Na	80	<DL	30	<DL	Ba	2	<DL	0.1	<DL
Mg	23	<DL	40	<DL	La	0.3	<DL	0.03	<DL
Al	24	69.8	80	<DL	Ce	0.4	<DL	0.1	<DL
K	28	<DL	20	<DL	Pr	0.1	<DL	0.02	<DL
Ca	170	<DL	300	<DL	Nd	0.2	<DL	0.05	<DL
Sc	1	<DL	1	<DL	Sm	0.03	<DL	0.01	<DL
Ti	6	<DL	2	<DL	Eu	0.03	<DL	0.01	<DL
V	2	<DL	0.3	<DL	Gd	0.02	<DL	0.01	<DL
Cr	3	<DL	3	<DL	Tb	0.02	<DL	0.01	<DL
Mn	4	<DL	0.1	3.8	Dy	0.02	<DL	0.01	<DL
Fe	45	379	2	360	Ho	0.02	<DL	0.01	<DL
Co	0.6	<DL	0.01	0.41	Er	0.02	<DL	0.01	<DL
Ni	2	4.7	0.1	8.2	Tm	0.02	<DL	0.01	<DL
Cu	8	31700	0.1	35700	Yb	0.03	<DL	0.01	<DL
Zn	5	25.1	1	34.3	Lu	0.02	<DL	0.01	<DL
Ga	0.3	<DL	0.2	<DL	Hf	0.09	<DL	0.01	<DL
As	1	20.7	0.1	17.2	Ta	0.02	<DL	0.02	<DL
Se	7	<DL	1	<DL	W	0.07	<DL	0.04	<DL
Rb	0.4	<DL	0.06	<DL	Re	0.04	<DL	0.005	<DL
Sr	2	<4	0.01	5.8	Os	0.03	1.6	0.01	1.5
Y	0.1	<DL	0.1	<DL	Ir	0.1	1.9	0.01	2.0
Zr	0.3	<DL	0.3	<DL	Pt	0.2	351	0.01	330
Nb	0.6	<DL	0.1	<DL	Au		Matrix		Matrix
Mo	0.6	<DL	0.05	<DL	Hg	0.4	11.5	0.1	11.3
Ru	0.3	<DL		–	Tl	0.04	<DL	0.01	<DL
Rh	0.4	4.2	0.001	3.5	Pb	0.7	30.0	0.01	35.1
Pd	0.2	14.2	0.007	14.4	Bi	0.04	2.3	0.01	4.7
Ag	1	132000	0.01	133000	Th	0.08	<DL	0.01	<DL
Cd	0.3	<DL	0.01	<0.4	U	0.02	<DL	0.01	<DL
In	0.3	<DL	0.2	<DL					

ver samples. The procedure of the autoclave decomposition of gold samples was checked by the standard addition method using reference solutions of standard samples containing all platinum elements (an ICP–MS–68–C standard solution). It was found that the loss of impurity elements during the autoclave decomposition described above did not occur. Moreover, the yield for osmium was $620 \pm 10\%$. The reason for this, apparently, was the difference in the forms of osmium in the initial standard solution used for calibration,

and in the solution obtained after autoclave decomposition. The results of the ICP–AES and ICP–MS analysis of the standard gold samples (Table 4) confirmed the excellent reproducibility and accuracy of the determination.

The real and standard samples of gold and silver were also analyzed by LA–ICP–MS. In most cases, there was a good agreement between the results obtained by two independent methods. For some elements, substantial differences seem to be associated

Table 6. Concentration ranges (wt %) of elements in the silver and gold samples of the Borodino treasure

Element	Silver	Gold
Mn	0.0002–0.0015	0.00002–0.0013
Fe	0.01–0.10	0.002–0.17
Co	<0.0002	0.0001–0.00010
Ni	0.0001–0.014	0.00006–0.0074
Cu	0.1–68.2	0.1–12.4
Zn	0.002–0.095	0.0002–0.0080
As	0.0001–0.97	0.00001–0.012
Se	0.002–0.0087	<0.0001
Mo	<0.00001	0.00002–0.000042
Ru	<0.000001	<0.00003
Rh	<0.00003	0.00003–0.00042
Pd	0.00001–0.00022	0.00002–0.0021
Ag	31.6–99.8	0.52–31.0
Cd	<0.00002	0.00008–0.00036
Sn	0.0005–1.6	0.00005–0.028
Sb	0.00006–0.0087	0.00008–0.0043
Te	0.0003–0.0014	0.0001–0.00015
Os	<0.000003	0.000002–0.00027
Ir	0.000003–0.000020	0.000002–0.00037
Pt	0.00003–0.0027	0.000005–0.041
Au	0.002–5.2	59.7–99.3
Hg	0.00008–0.044	0.0002–0.0088
Pb	0.0009–0.15	0.0002–0.0080
Bi	0.0006–0.12	0.00001–0.0049

with the possible nonuniform distribution of impurity elements in the samples. As an example, typical results of analysis of one of the archaeological samples of gold are presented in Table 5.

The developed procedures for determining silver and gold samples were used to analyze archaeological silver and gold issues, including samples from the Borodino treasure. More than 60 samples of silver and gold were analyzed in total. Table 6 shows the found concentration ranges of the elements in these samples. The concentrations of elements not included in Table 6 in almost all samples of the Borodino treasure were below the limits of determination (see Tables 3 and 4). The results of analysis of silver and gold samples from the Borodino treasure are presented more fully in [19].

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REFERENCES

- Longerich, H.P., Fryer, B.J., and Strong, D.F., *Spectrochim. Acta, Part B*, 1987, vol. 42, nos. 1–2, p. 101.
- Kogan, V.V., Hinds, M.W., and Ramendik, G.I., *Spectrochim. Acta, Part B*, 1994, vol. 49, no. 4, p. 333.
- Devos, W., Moor, C., and Lienemann, P., *J. Anal. At. Spectrom.*, 1999, vol. 14, no. 4, p. 621.
- Sarah, G., Gratuze, B., and Barrandon, J.-N., *J. Anal. At. Spectrom.*, 2007, vol. 22, no. 9, p. 1163.
- Schlosser, S., Reinecke, A., Schwab, R., Pernicka, E., Sonetra, S., and Laychour, V., *J. Archaeol. Sci.*, 2012, vol. 39, no. 9, p. 2877.
- Gentelli, L., *J. Archaeol. Sci.: Rep.*, 2016, vol. 9, p. 536.
- Watling, R.J., Herbert, H.K., Delev, D., and Abell, I.D., *Spectrochim. Acta, Part B*, 1994, vol. 49, no. 2, p. 205.
- Dussubieux, L. and Van Zelst, L., *Appl. Phys. A*, 2004, vol. 79, no. 2, p. 353.
- Kovacs, R., Schlosser, S., Staub, S.P., Schmiderer, A., Pernicka, E., and Gunther, D., *J. Anal. At. Spectrom.*, 2009, vol. 24, no. 4, p. 476.
- Nocete, F., Sáez, R., Bayona, M.R., Nieto, J.M., Peramo, A., López, P., Gil-Ibarguchi, J.I., Inácio, N., García, S., and Rodríguez, J., *J. Archaeol. Sci.*, 2014, vol. 41, p. 691.
- Brostoff, L.B., Gonzalez, J.J., Jett, P., and Russo, R.E., *J. Archaeol. Sci.*, 2009, vol. 36, p. 461.
- GOST (State Standard) 28353.2-89: *Silver. Method of Atomic-Emission Analysis with Inductive Plasma*, Moscow: Izd. Standartov, 1990.
- GOST (State Standard) 27973.2-88: *Gold. Method of Atomic-Emission Analysis with Inductive Plasma*, Moscow: Izd. Standartov, 1989.
- GOST (State Standard) R 53372-2009. *Gold. Methods of Analysis*, Moscow: Standartinform, 2009.
- Zhitenko, L.P., Taldonov, Yu.V., Pakhomova, S.B., Knyaz'kin, G.S., and Ozerova, L.E., *Inorg. Mater.*, 2015, vol. 51, no. 14, p. 1404.
- Sun, Y.C., Mierzwa, J., Lin, C.F., Yeh, T.I., and Yang, M.H., *Analyst*, 1997, vol. 122, no. 5, p. 437.
- Zaikov, V.V., Filippova, K.A., Udachin, V.N., Zaikova, E.V., Rassomakhin, M.A., and Krainev, Yu.D., *Mineralogiya*, 2016, no. 2, p. 82.
- Karandashev, V.K., Leikin, A.Yu., Khvostikov, V.A., Kutseva, N.K., and Pirogova, S.V., *Inorg. Mater.*, 2016, vol. 52, no. 14, p. 1391.
- Khommel', P., Brai, P., Khvostikov, V.A., Karandashev, V.K., Loboda, A.Yu., Kolchina, A.S., and Shishlina, N.I., in *Borodinskii klad geroicheskoi epokhi bronzovogo veka. Estestvenno-nauchnyi i istoricheskii kontekst* (Borodino Treasure of the Heroic Era of the Bronze Age: Natural-Scientific and Historical Context), Shishlin, N.I., Ed., Moscow: Gos. Istorich. Muzei, 2019, p. 74.

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