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Determination of Au(III) and Ag(I) in Carbonaceous Shales and Pyrites by Stripping Voltammetry

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Abstract:

Techniques of stripping voltammetry (SV) determination of silver and gold in pyrites and carbonaceous matter were developed. The problem of quantitative transfer of the sample into the solution was solved. For this purpose, the ore matrix of carbonaceous shales was decomposed by mineral acids in autoclaves at high pressures. The element to be determined from the sample matrix was separated by extraction. Ag(I) ions from the solutions were extracted in the form of dithizonate complex in CCl₄. Au(III) ions were extracted by diethyl ether. The extracts were decomposed thermally. The dry residue was dissolved in the background electrolyte, and the element was determined by the SV method. The graphite electrode (GE) impregnated with polyethylene was used as a working electrode in SV-determination of silver. SV-determination of gold was carried out using GE modified by bismuth.

The limits of detection (LOD) of Ag(I) and Au(III) contents were equal to 0.016 mg L⁻¹ and 0.0086 mg L⁻¹, respectively. The results of SV-determination of gold and silver in standard samples, pyrites and carbonaceous shales were presented. The silver content in the pyrite was 13.6 g t⁻¹, in carbon shale—0.34 g t⁻¹. The concentration of gold in the pyrite ore zone "Kirovsko-Kryklinskaya" was 1.15 g t⁻¹; in carbonaceous shales—2.66 g t⁻¹. The obtained data were consistent with the data of atomic emission spectroscopy (AES) and inductively coupled plasma mass spectrometry (ICP—MS).

The error of determination of elements by stripping voltammetry was calculated when determining the silver content of 10...6 g t⁻¹ in pyrite and carbonaceous material, which was less than 12%, and when determining the gold content of 1...3 g t⁻¹ in pyrite and carbonaceous matter, which was less than 23%.

Keywords: gold; silver; mineral raw materials; carbonaceous shales; stripping voltammetry; graphite electrode modifiers

1. Introduction

In recent years, complex noble metal deposits have been discovered in carbon-containing strata. They are considered as a new promising source of silver, gold and platinum metals. Carbonaceous shales are of genuine interest due to the fact that in the fine-grained carbon fraction, the concentrations of precious metals exceed manifold (15-16 times) the contents of gold in the source (ore-hosting) rocks [1]. In the literature there is information [2-4] on the discrepancy between the results of interlaboratory analyses of carbonaceous rocks by 1-2 or even more orders.

The complexity of the analysis of carbon-bearing raw materials is associated with the peculiarity of the forms of existence of metals – both in mineral (in the form of nuggets, sulfides, arsenides, etc.) and in carboniferous parts of the rock (from metalorganic competent complex

compounds to graphitized formations), where platinum group metals (PGMs) may be located in the interplanar spacings of graphite and are directly bound with several carbon atoms [2–8].

Presence of carbon and oxygen fundamentally distinguishes these microinclusions from traditional (native) forms of extracting gold and platinoids, causing their exceptional resistance to external affects (annealing, oxidation, acid decomposition), which creates difficulties [9]. A distinctive feature of carbon-containing ores is uneven distribution of elements throughout the tested samples.

To average the results of the analysis, large samples are usually used, as is done in the assay method. For the analysis of carbonaceous shale, it is impossible to use methods of assay concentration. Silver, gold and platinum group metals form carbon compounds that volatilize at high-temperature opening of the sample [3].

Conducting exploration and prospecting of gold and silver in carbonaceous shales provides for the use of analytical techniques that have limits of detection at the level of the clarke or below it in these metals (10^{-4} ... $10^{-7}\%$ wt.). According to the literature data, when determining gold and silver by any highly sensitive methods of analysis, the tested sample must be averaged. Averaging of the sample occurs at the expense of its dissolution and separation of the determined elements from the sample matrix. Various methods are used for this purpose: sorption [10, 11], extraction [12, 13] and others.

SV has long been used to determine the concentrations of gold and silver in ores [14–16]. It is characterised by high sensitivity, uses cheap equipment, and allows determining the elements in a wide range of defined contents. When determining the gold content in mineral raw materials containing gold, silver, and platinum metals, a necessary stage in the analytical process is their separation from the sample matrix [17–19].

Electrochemical methods of analysis do not allow determining the elements directly in an extract or on a sorbent. It is necessary to re-extract the determined admixture, as is done, for example, in [11, 12], or to thermally decompose the extractant [13].

Silver(I) [16] and gold(III) [20–24] ions were determined by SV using GE. The electrodeposition of silver on the surface of carbon-bearing electrodes was carried out with potentials between minus 0.4 and minus 0.7 V from the solutions of nitric, perchloric acids, potassium nitrates, ammonium nitrates and other electrolytes [25, 26]. According to the literature data, nitrate, chloride and bromide media were recommended for SV-determination of gold(III) ions [20, 21]. Depending on the composition of the medium, electrooxidation of gold deposits was observed with potentials from plus 0.6 to plus 0.9 V.

Currently, the graphite electrodes are modified to reduce the LOD and the systematic error of SV-determination of the elements [27]. Various metals [28, 29] and organic compounds [30–33] are used as modifiers.

The purpose of this study was to develop the technique of determining gold and silver in carbon ores and their technological redistribution using both unmodified graphite electrodes and modified graphite electrodes by stripping voltammetry.

2. Materials and Methods

2.1. Reagents and solutions.

According to the purity level and the purpose, all reagents used in sample preparation had the grade of LR (laboratory reagents) and CP (chemically pure). The diluted solutions used in the work were prepared on the day of the tests.

Standard solutions of Au(III) ($c = 10.0$ and 1.0 mg L^{-1}) were prepared by sequential dilution of a certified solution of gold(III) in flasks with a capacity of 25.0 mL with a solution of 1 mol L^{-1} HCl.

Standard solutions of Ag(I) ($c = 10.0$ and 1.0 mg L^{-1}) were prepared by sequential dilution of a certified solution of silver(I) in flasks with a capacity of 25.0 mL with a solution of 1 mol L^{-1} HNO₃.

The standard solution of Bi(III) ($c = 10.0 \text{ mg L}^{-1}$) was prepared by sequential dilution of a certified solution of bismuth(III) in flasks with a capacity of 25.0 mL with a solution of 1 mol L^{-1} HNO_3 .

Solutions of 1% (w/v) tosylate diazonium, 1% (w/v) ϵ -Caprolactam (azepan-2-one), ethylenediaminetetraacetic acid (EDTA) ($c = 0.25 \text{ mol L}^{-1}$), NH_3 (aq) ($c = 3 \text{ mol L}^{-1}$, 25% purity), HCl ($c = 1 \text{ mol L}^{-1}$; 6 mol L^{-1} , 38% purity), HNO_3 ($c = 6 \text{ mol L}^{-1}$; 70% purity), HClO_4 ($c = 6 \text{ mol L}^{-1}$; 70% purity), HF ($c = 1 \text{ mol L}^{-1}$, 6 mol L^{-1} ; 70% purity) were prepared by dilution with bidistilled water.

The 0.001% (w/v) dithizone solution was obtained by dilution with CCl_4 (99.8% purity).

2.2. Devices and electrolysis procedure

The studies were undertaken by means of voltammetry analyzer TA-4 ("TomAnalit" LLC, Tomsk) completed with a personal computer. The device was registered in the State Register of Measuring Instruments and approved for use in the Russian Federation (No.25353-03). The pattern approval certificate of measuring instruments, RU.C.34.007.A No.15550, is available. Electrolysis was conducted in quartz glasses with a capacity of 20 mL.

The working cell contained three electrodes. The graphite electrode (GE) impregnated with polyethylene served as a working electrode [16]. Auxiliary and reference electrodes were saturated silver/silver chloride electrodes (plus 0.22 relatively the N hydrogen electrode) filled with the 1 M KCl solution.

Electrooxidation of deposits was carried out at linear changes in the potential ($v = 0.06 \text{ V s}^{-1}$) window from minus 0.6 V to plus 1.0 V. The electrodeposition of deposit components on the surface of a GE was carried out *in situ*.

Electrochemical cleaning of the electrode surface was carried out for a minute with a potential of plus 1.0 V in the medium electrolyte, or mechanically by grinding the electrode against the sandpaper and then against the filter paper. Mixing of the solution during electrolysis was carried out automatically by vibration of the working electrode, which is provided by the analyzers used.

To study the composition of rock-forming minerals in the sample by X-ray structural analysis, powder diffractometer D2 PHASER produced by the "Bruker" company was used, which allowed detecting the presence of the mineral phase in the mixture under study at a level of 0.5%.

The elemental chemical composition of the rock was determined using the method of scanning the sample surface by means of the "Hitachi S-3400N" electron microscope, which was equipped with an energy-dispersive attachment made by "Bruker".

Dissolution of the sample was carried out in hermetic autoclaves using a microwave system "Mars-5" per one loading sequence according to the following temperature-time modes: 1) 90°C (30 min); 2) 120°C (45 min). Two-stage heating was chosen to avoid the rapid formation of an excessive volume of gaseous products during the sample decomposition because it could lead to depressurization of the system.

In order to determine the total chemical composition of the initial sample, taking into account microinclusions, an ICP-analysis was carried out by means of mass spectrometer Agilent, ICP MS7700x.

3. Results and Discussion

3.1. Objects of analysis.

The research objects were mixed gold-bearing carbonaceous shales, pyrites of the "Kirovsko-Kryklinskaya" ore zone.

When analyzing the composition of rock-forming minerals in the ore by X-ray structural analysis using powder diffractometer D2 PHASER ("Bruker"), it was established that clay minerals of the following types: illite 2M1 (46.0%), illite 2M2 (11.5%), muscovite 2M1 hydrated to varying degrees (11.5%), muscovite 1M (4.5%), (sericite, hydrosericite), quartz (11.4%), kaolinite 1A (7.6%), muscovite 1M (4.5%), prevail in the sample composition. Zeolite is present in trace amounts. By its chemical composition, this is aluminosilicate rock with a high content of potassium (3.2%), iron

gross (3.1%), as well as sodium and sulfur gross (1.2%). The content of the carbonaceous matter is about 7%.

The microelement composition of the sample was investigated by electrothermal vaporization inductively coupled plasma mass spectrometry (ICP-MS). According to the analysis, the samples contain a high content of iron (30134 g t^{-1}), arsenic (948 g t^{-1}), selenium (1 g t^{-1}), antimony (58.9 g t^{-1}), tellurium (0.34 g t^{-1}). As is well known, the mentioned elements are potential fixers of gold in the ore matrix [34]. The copper content is 160 g t^{-1} .

3.2. Determination of silver(I) ions by SV

The technique, developed by the authors of [16], with some additions, was used for SV-determination of silver in gold-bearing carbonaceous shales of the "Kirovsko-Kryklinskaya" ore zone.

In this paper, silver was deposited on the GE surface from the solutions of $1 \text{ mol L}^{-1} \text{ HCl}$ (with addition of NH_4OH and bringing the solution to $\text{pH}=6.5$) with a potential of minus 0.7 V , which corresponded to the current limit of silver electroconcentration. A peak of silver electrooxidation was observed with a potential of plus 0.1 V . In this work, a linear potential sweep was applied.

Figure 1 shows the current-voltage curves of the anodic electrooxidation of silver from the GE surface.

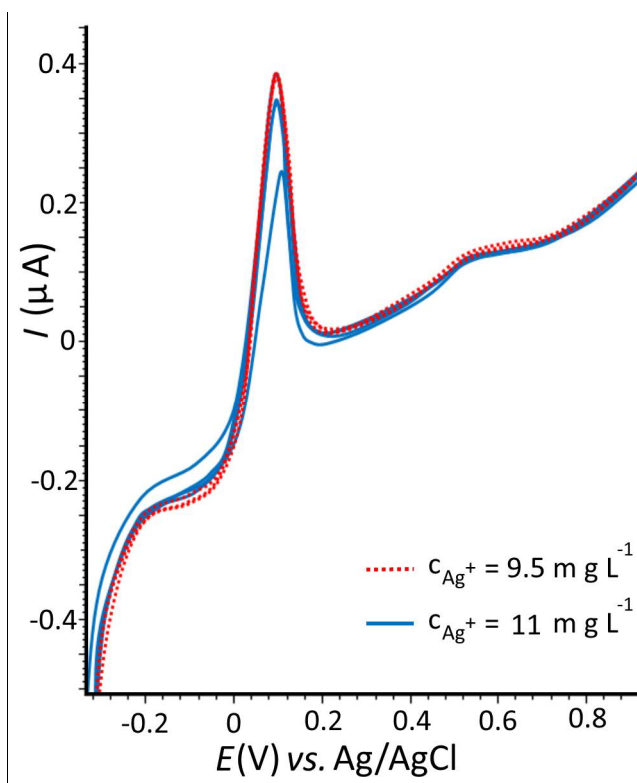


Figure 1. Current-voltage curves of Ag(I). Conditions of experiments: medium $1 \text{ mol L}^{-1} \text{ HCl} + \text{NH}_4\text{OH}$, $E_e = -0.7 \text{ V}$; $\tau_e = 120 \text{ s}$; $v = 0.06 \text{ V s}^{-1}$

Since the analyzed samples contained increased quantities of copper(II) ions (160 g t^{-1}), after the extraction of silver, the analyzed solutions could contain residual quantity of Cu(II) ions. The increased quantity of copper(II) ions exerts a harmful influence on SV-determination of silver(I) ions by distorting the electrooxidation peaks of silver up to their complete overlapping.

Figure 2 (a,b) shows the current-voltage curves and electrooxidation currents of deposits containing silver and copper.

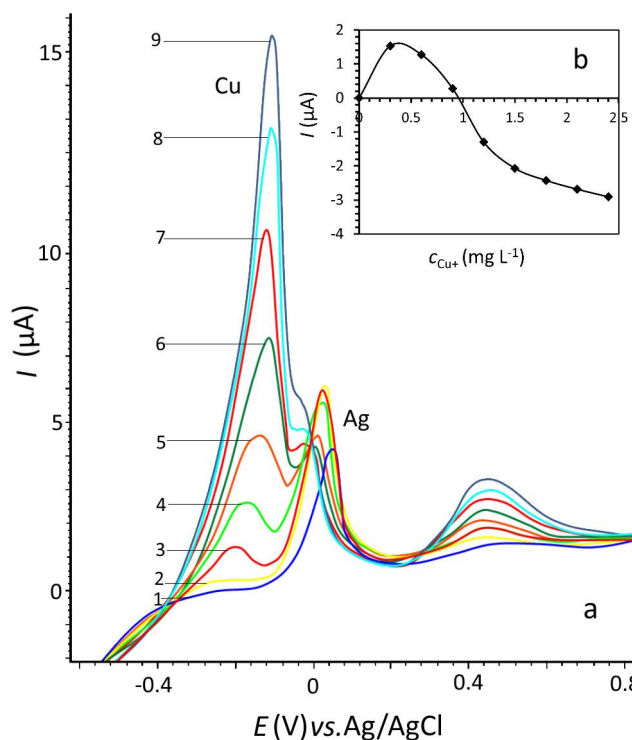


Figure 2. Current–voltage curves (a) and electrooxidation currents (b) of deposits containing silver and copper. Experimental conditions: medium 1 mol L⁻¹ HCl + NH₄OH, $E_e = -0.7$ V; $\tau_e = 120$ s; $v = 0.06$ V s⁻¹; $c_{Ag^+} = 2$ mg L⁻¹; $c_{Cu^{2+}}$, mg L⁻¹: 1) 0; 2) 0.3; 3) 0.6; 4) 0.9; 5) 1.2; 6) 1.5; 7) 1.8; 8) 2.1; 9) 2.4.

In Fig. 2 (b) it is evident that with an increase of the copper content in the silver deposit, the current of the silver anodic peak first increases and then goes down. With the concentration of copper(II) ions in the analyzed solution equal to 1.5 mg L⁻¹, there is overlapping of the silver peak with the constant concentration of silver(I) ions equal to 2 mg L⁻¹. The increase in the peak height and a shift of the silver dissolution potential by 0.03 V to a less positive region are due to the formation of Ag–Cu solid solutions of variable composition on the electrode surface [35].

The harmful influence of copper(II) ions at the stage of silver(I) ions extraction was corrected by adding a higher concentration of EDTA (0.25 mol L⁻¹) and by reducing the time of the solution extraction by dithizone (from 120 to 60 s).

The technique of the ore matrix decomposition for the extraction of silver (I) ions consisted in dissolving the sample. To do this, a sample weighing 1 g was preliminary ashed, gradually increasing the temperature to 650°C, and cooled to room temperature. Next, the sample was decomposed in a corundum crucible with a mixture containing 10 mL of HNO₃ ($\rho = 1.40$) and 10 mL of 10% HF. The solution was evaporated almost to dryness at a temperature of 100°C. Then, 10 mL of HClO₄ ($\rho = 1.68$) and 10 mL of 40% HF were added to decompose silicates and carbon-bearing substances. The residue, after cooling, was dissolved in hot water, cooled and filtered through the filter “blue tape”. Then, 5 mL of a 0.25 mol L⁻¹ solution of EDTA was added to the sample solution; the pH of the solution was adjusted to 6.8 by ammonia. The obtained solution was transferred to a separating funnel; there a 0.001% dithizone solution was added and the silver(I) dithizonate was extracted by the CCl₄ solution. After separation of the phases, silver was re-extracted in two portions (10 mL and 10 mL each) by the 1 mol L⁻¹ HCl+NH₄OH (pH=6.5) solution. Before SV-determination of silver, drops of dithizone in CCl₄ were removed from the aqueous phase by evaporation; the sample was calcinated at a temperature of 220°C; the media (1 mol L⁻¹ HCl+ NH₄OH) was added and the content of silver(I) ions in the samples was determined.

Fig. 3 shows the dependence of the silver electrooxidation current on the concentration of silver(I) ions in the solution.

The limit of detection (LOD) of the silver contents determined by SV was estimated according to the 3σ -criterion with the help of the equation given below [36]:

$$\text{LOD} = \frac{3 \times S_{\text{bl}}}{\text{tg } \theta} = \frac{3 \times 0.020}{3.6} = 0.016 \text{ mg L}^{-1} \tag{1}$$

where $\text{tg } \theta$ is the slope of the calibration line taken from the graph (Fig. 3); S_{bl} is the standard deviation of the blank test. With a sample weight of 1 g, this will correspond to 0.016 g t^{-1} . The limit of quantitation (LOQ) is 0.055 g t^{-1} .

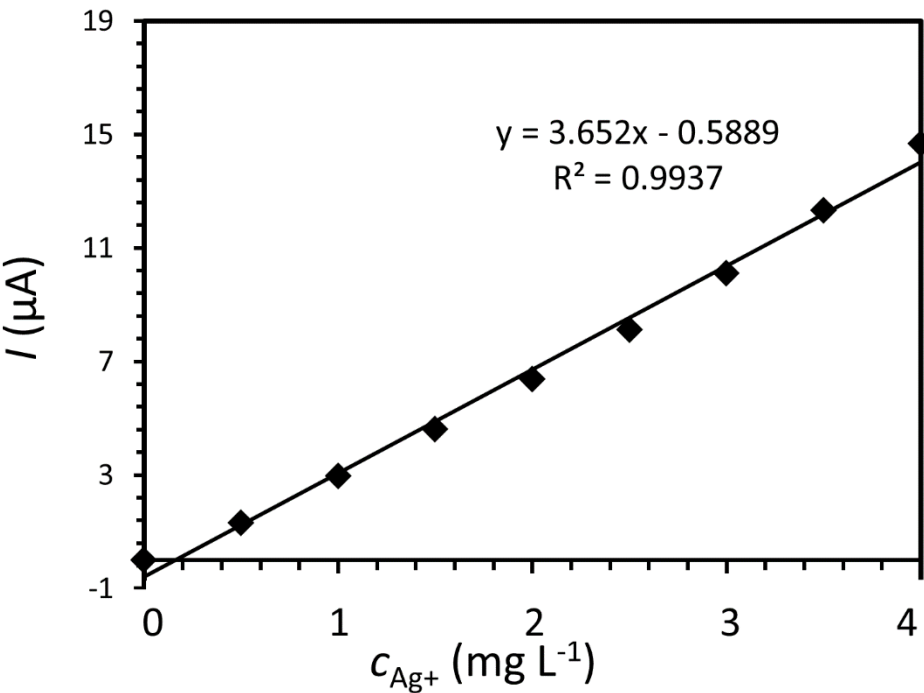


Figure 3. The dependence of peak current of silver electrooxidation on the concentration of silver(I) ions in the solution. Experimental conditions: medium $1 \text{ mol L}^{-1} \text{ HCl} + \text{NH}_4\text{OH}$ up to $\text{pH}=6.5$, $E_e=-0.7 \text{ V}$; $\tau_e=120 \text{ s}$; $v=0.06 \text{ V s}^{-1}$; $c_{\text{Ag}^+}=0.5\text{--}4 \text{ mg L}^{-1}$.

The correctness of the determination of silver by the developed technique was verified by comparing the results of the silver content in standard samples (SS) of copper and nickel sludge, determined by different methods (Table 1).

Table 1. Results of SV-determination of silver(I) in standard samples (SS) of copper and nickel sludge analyzed by different methods ($n=5$, $P=0.95$).

SS	Certified value, g t ⁻¹	Ag content, g t ⁻¹			Relative error, %
		AES	ICP-MS	SV	
copper sludge	6.38	5.8	5.5	5.6 ± 0.2	11.6
nickel sludge	0.19	0.2	0.19	0.2 ± 0.02	9.9

*AES – atomic emission spectroscopy. ICP-MS –inductively coupled plasma mass spectrometry.

As can be seen from the above-mentioned data, the relative error of SV-determination of silver does not exceed 12%.

Table 2 presents the results of determining silver in the pyrite samples of the “Kirovsko-Kryklinskaya” ore zone. The silver content determined by electrothermal vaporization inductively coupled plasma mass spectrometry was 13.6 g t^{-1} .

Table 2. Results of SV–determination of silver in the pyrite of the “Kirovsko–Kryklinskaya” ore zone (n=5, P=0.95).

No. of experiment	Ag content, g t ^{−1}			C, g t ^{−1}	Relative error, %
1	13.8	11.7	11.0	12.2±1.6	10.3
2	9.5	17.9	9.09	12.2±3.8	10.3
3	6.1	16.3	13.7	12.0±3.2	11.8

3.3. Determination of gold(III) ions by SV

Electroconcentration of gold(III) ions on the surface of carbon–bearing electrodes is carried out with potentials between minus 0.6 and minus 0.8 V [22]. A current limit can be observed with potentials that are more negative. To increase the selectivity of gold determination, after electroconcentration of deposit, Monieen H. [23] recommends conducting post–electrolysis with a positive potential. In this case, foreign base metals dissolve, and gold remains on the electrode surface and can be determined by the peak of its electrooxidation.

The author of [28] shows that gold is determined on GE, impregnated by polyethylene in the presence of the following elements: Ag⁺(1:10), Tl³⁺(1:10), Zn²⁺(1:10³), Cu²⁺(1:10²), Pb²⁺(1:10³), Sb³⁺(1:10), Co²⁺(1:10²), Ni²⁺(1:10³), Bi³⁺(1:10), As⁵⁺(1:10²), Cd²⁺(1:10²). Maximum ratios of Au³⁺:M are given in brackets.

Figure 4 shows the current–voltage curves for the electrooxidation of gold deposits from the GE surface.

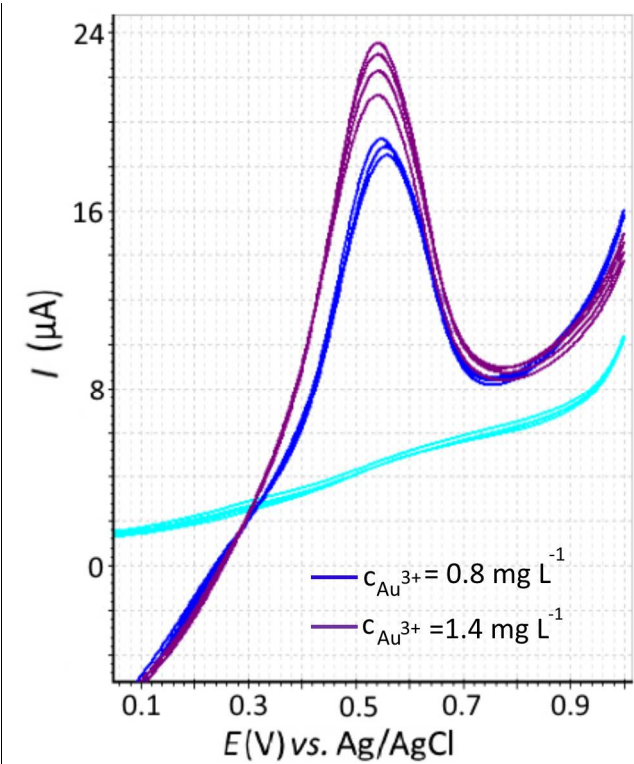


Figure 4. Current–voltage curves of gold deposits electrooxidation from the GE surface. Experimental conditions: medium 1 mol L^{−1} HCl, E_e = −0.7 V; τ_e = 120 s; v = 0.06 V s^{−1}

The sensitivity of gold determination by the SV method can be significantly increased when modifying the GE surface by organic or inorganic modifiers: bismuth(III) [29], tosylate salts of aryldiazonium [30], polyethylene polyimine [31] and acrylic polyelectrolyte [32], ε-Caprolactam [33].

Modification of the GE surface is usually carried out *in situ*.

Fig. 5 (a,b) show the current–voltage curves and the calibration dependences of the electrooxidation currents of gold deposits taken from the surface of the unmodified GE .

Fig. 6, 7 (a,b) show the current–voltage curves and the calibration dependences of the electrooxidation currents of gold deposits taken from the surface of GE modified by salts of 1% diazonium tosylate (Fig. 6a,b); by 1% (w/v) ε-Caprolactam (Fig. 7a,b).

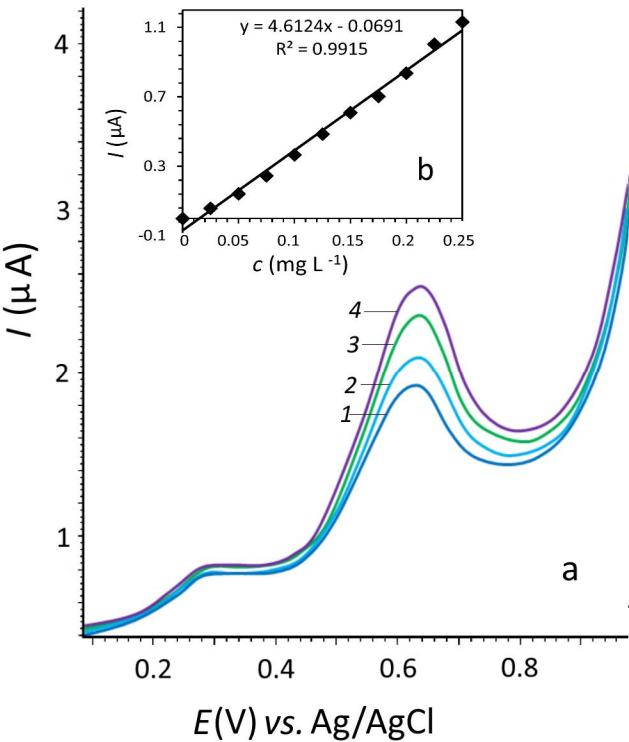


Figure 5. Anodic current–voltage curves (a) and calibration dependences (b) of gold determination from the unmodified GE surface by SV. Experimental conditions: medium 1 mol L^{−1} HCl, E_e = −0.7 V, t_e = 120 s, v = 0.06 V s^{−1}, c_{Au³⁺}, mg L^{−1}: 1) 0.15; 2) 0.175; 3) 0.2; 4) 0.225

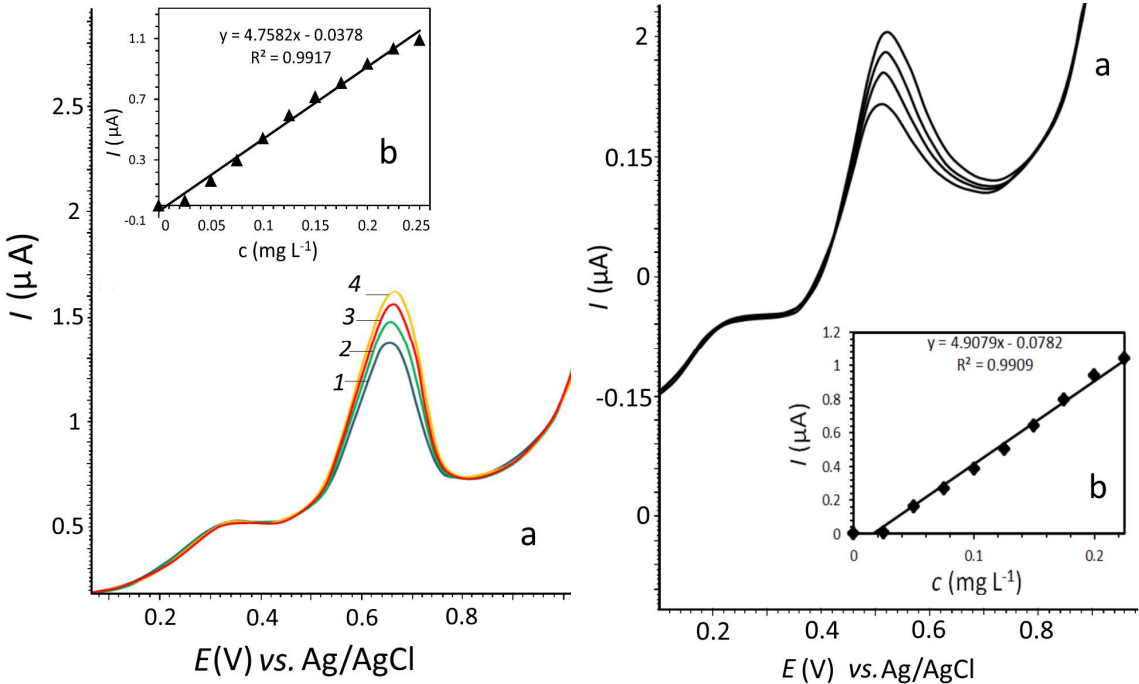


Figure 6. Anodic current–voltage curves (a) and calibration dependences (b) of gold determination

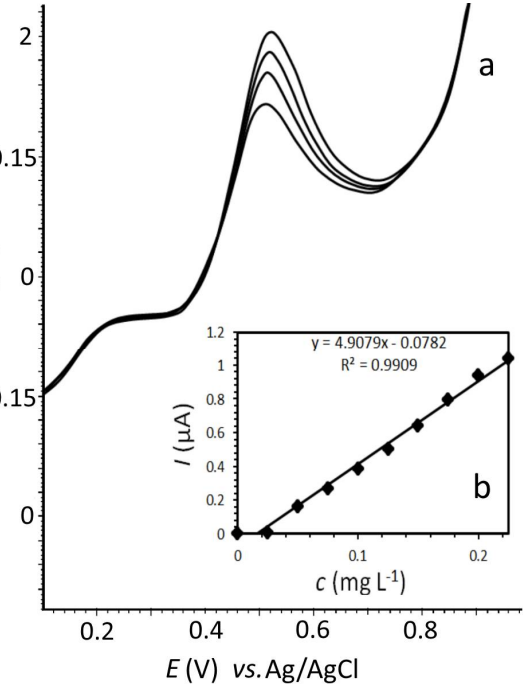


Figure 7. Anodic current–voltage curves (a) and calibration dependences (b) of gold determination

from the surface of GE modified by tosylate ions. Experimental conditions: medium 1 mol L⁻¹ HCl + 20 µl of 1% tosylate diazonium. $E_e = -0.7$ V, $t_e = 120$ s, $v = 0.06$ V s⁻¹, $c_{Au^{3+}}$, mg L⁻¹: 1) 0.15; 2) 0.175; 3) 0.2; 4) 0.225

from the surface of GE modified by ε-Caprolactam. Experimental conditions: medium 1 mol L⁻¹ HCl + 20 µl of 1% ε-Caprolactam, $E_e = -0.7$ V, $t_e = 120$ s, $v = 0.06$ V s⁻¹, $c_{Au^{3+}}$, mg L⁻¹: 1) 0.15; 2) 0.175; 3) 0.2; 4) 0.225

The data show that the sensitivity of gold determination on GE modified by tosylate ions and ε-Caprolactam has increased insignificantly.

Figure 8 shows the current–voltage curves and the calibration dependences for SV–determination of gold on GE modified by bismuth.

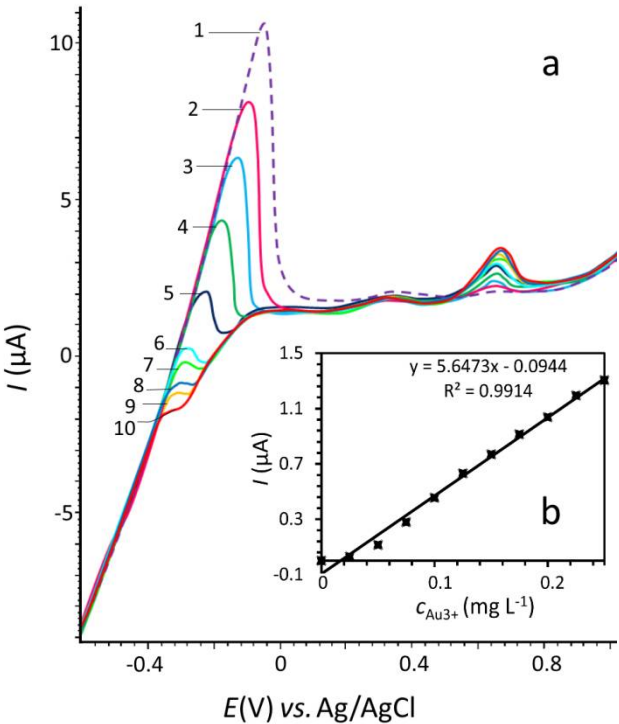


Figure 8. Anodic current–voltage curves (a) and calibration dependences during electrooxidation of gold deposits from the surface of GE modified by bismuth (b). Experimental conditions: medium 1 mol L⁻¹ HCl, $E_e = -0.7$ V, $t_e = 120$ s, $v = 0.06$ V s⁻¹, $c_{Bi^{3+}} = 10$ mg L⁻¹; $c_{Au^{3+}}$, mg L⁻¹: 1) 0; 2) 0.025; 3) 0.05; 4) 0.075; 5) 0.1; 6) 0.125; 7) 0.15; 8) 0.175; 9) 0.2; 10) 0.225

As can be seen in Figures 5–8, the most sensitive method for determination of gold(III) ions in chloride electrolytes is with the use of the polyethylene-impregnated GE modified by bismuth.

During SV–determination of gold in mineral raw materials, gold dithizonate extraction in CCl₄ is often used, followed by re–extraction of gold(III) ions with 20% KBr, removal of CCl₄ from the re–extract by heating, and determination of gold(III) ions by SV in the bromide solution [24, 37].

When determining gold by the SV method in mineral raw materials, the simplest method is extraction of gold(III) ions by diethyl ether from muriatic solutions [29]. Diethyl ether volatilizes easily from the extract during heating. The solid deposit dissolves in the background electrolyte, and the gold is determined by SV.

To dissolve the ore with the view of determining the concentration of gold(III) ions, the technique developed by the authors was used [38]. The scheme of sample preparation for determining the content of gold(III) ions is given in Figure 9.

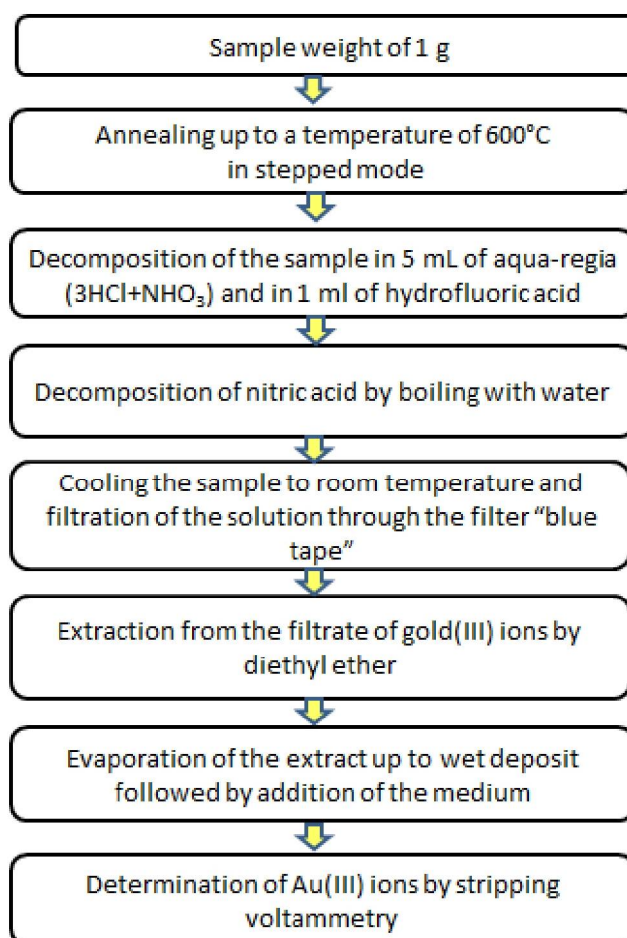


Figure 9. A scheme of sample preparation to determine gold(III) ions.

The sample weight of the ore weighing 1 g was preliminary ashed by stepped mode up to the temperature of 600°C and cooled to room temperature. To dissolve the sample it was placed into the autoclave with addition of 5 mL of aqua-regia and 1 mL of hydrofluoric acid. Decomposition of nitric acid was carried out by boiling with water. After completing the decomposition procedure, the sample was cooled to room temperature and filtered through the filter "blue tape". The gold(III) ions were extracted by 10 mL of diethyl ether from the obtained solution. The upper ether layer, rinsed with water, was evaporated up to minimal deposit, whereupon 1 mL of 6 mol L⁻¹ HCl was added to the sample, and the solution was boiled dry. The background electrolyte (1 mol L⁻¹ HCl) was added, and gold(III) ions were determined in the presence of 10 mg L⁻¹ of bismuth(III) ions (modifier) by SV.

LOD of the contents of gold(III) ions, determined by SV, was estimated by the 3 σ -criterion according to equation (1):

$$\text{LOD} = \frac{3 \times S_{\text{bl}}}{\text{tg } \theta} = \frac{3 \times 0.016}{5.6} = 0.0086 \text{ mg L}^{-1} \quad (2)$$

where $\text{tg } \theta$ – slope of the calibration line taken from the graph (Fig. 8 (b)); S_{bl} – standard deviation of the blank test. With a sample weight of 1 g, it will correspond to 0.0086 mg L⁻¹. LOQ is 0.028 g t⁻¹.

In Table 3, there are results of determination of gold by the method of AES, SV, ICP-MS in the standard samples (SS) of copper and nickel sludge.

Table 3. Results of determination of gold in standard samples (SS) of copper and nickel sludge analyzed by different methods.

SS	Certified value, g t ⁻¹	Content of Au, g t ⁻¹			Relative error, %
		AES	ICP-MS	SV (n=5)	

Copper sludge	0.21	0.25	0.26	0.25 ± 0.02	19.05
Nickel sludge	0.059	0.060	0.058	0.060 ± 0.02	16.9

*AES—atomic emission spectroscopy. ICP—MS—inductively coupled plasma mass spectrometry.

Table 3 shows that the relative error of determination does not exceed 20%. In Table 4, the results of determination of gold(III) in gold-bearing carbonaceous shales are given. The gold concentration in these samples, according to the data obtained by mass spectrometry analysis, was 2.66 g t⁻¹.

Table 4. Results of SV-determination of gold in different samples of carbonaceous shales in the “Kirovsko–Kryklinskaya” ore zone (n=3, P=0.95).

No.	Value of gold contents, g t ⁻¹			Average content of Au, g t ⁻¹	Relative error, %
1	1.6	2.2	2.9	2.2±0.6	17.2
2	1.8	1.9	2.6	2.6 ±0.7	22.5
3	2.0	1.8	2.7	2.2±0.3	17.2

Table 5 shows the results of determination of gold in gold-bearing samples. The average content of gold in such samples determined by inductively coupled plasma mass spectrometry was 1.15 g t⁻¹.

Table 5. Results of determining the gold in solutions after precipitation of gold(III) ions from pyrite of the “Kirovsko–Kryklinskaya” ore zone (n=3, P=0.95).

No.	Value of gold contents, g t ⁻¹			Average content of Au, g t ⁻¹	Relative error, %
1	1.4	0.8	0.9	1.0±0.2	13.0
2	1.2	0.7	0.8	0.9±0.2	21.7
3	1.0	0.9	0.8	0.9±0.1	21.7

As the obtained data show, it becomes possible to precipitate gold from carbonaceous shales. This is connected with the presence of carbon and oxygen in samples.

4. Conclusions

The techniques utilized in determining gold and silver in the extract are unified and allow precipitating precious metals from the solution with their subsequent determination by stripping voltammetry. The process was conducted on real-world samples – pyrites and carbon-bearing ores. Carbon-bearing samples, such as gold- and silver-bearing objects of analysis, differ by quite a wide range of concentrations of the determined elements, by a great variety of accompanying components.

Acknowledgments: The results were obtained within the framework of the state task of the Ministry of Education and Science of Russia, project No. 10.3031.2017/4.6, and with the support of the TSU Competitiveness Program.

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