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Determination of platinum metals in carbonaceous mineral raw materials by stripping voltammetry

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Abstract

The paper considers the possibility of determining platinum metals in mineral raw materials by stripping voltammetry on a graphite electrode modified by metals. Stripping voltammetry method is characterized by low determination limit, wide intervals of determined content and high sensitivity. As a result of the research the conditions for the determination of gold, platinum and palladium by stripping voltammetry have been selected. The comparison of the results of gold, palladium and platinum determination by stripping voltammetry and atomic absorption is presented.

Keywords: stripping voltammetry method (SVM), graphite electrode, modification of the electrode

1. Introduction

In the folded structures of many regions of Russia, Kazakhstan, Kyrgyzstan and Uzbekistan large deposits of gold have been found in black-shale ores[1,2]. These deposits consist mainly of gold-sulfide quartz minerals with a high content of carbon (1-1.5% of organic carbon content) and a substantial content of silver and arsenic. The platinum potential of these deposits is rather poorly studied[3]. The processing of such ores by the conventional method of a cupelling test leads to the complete loss of platinum group metals at the opening stage[4]. Therefore, the analysis techniques that worked well on the copper-nickel sulfide ores of the Norilsk group of deposits, turned out to be inapplicable for the analysis of platinum group metals.

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Stripping voltammetry method (SVM) has been chosen for the research. It is suitable for determination of platinum metals in mineral raw materials, because it is characterized by low determination limit, wide intervals of determined content and high sensitivity[5]. An important component of the samples analysis by SVM is the choice of the indicator electrode. For the determination of platinum metals the graphite electrode (GE), modified by electronegative metals is used[5]. Modification of the electrode by metals not only increases the sensitivity of their determination, but also allows determining platinum and rhodium, which do not have electro oxidation peaks in the workspace of GE potential. Therefore, the determination of platinum by SVM is carried out by peaks of selective electro oxidation of electronegative component from a binary alloy with a metal-activator. Various electronegative metals which form intermetallic compounds with platinum are used as metal-activators and the selective dissolution of electronegative metal generates the analytical signal for determining platinum. The literature provides data on the possibility of using lead, copper, mercury, indium etc. to detect platinum[6-10]. These data do not answer the question of which of these metals is more sensitive and why.

The aim of this work is to select the conditions for the determination of gold, platinum and palladium by SVM and to develop the method for the determination of these elements in carbonaceous mineral raw materials.

2. Materials and Methods

All measurements were carried out on the voltammetric analyzer TA-4 produced by RPE "Tomanalyt" (Tomsk) with IBM as a set. For the current measurement a three-electrode cell was used in which the working electrode was GE impregnated by polyethylene. A silver-chloride electrode was used as a reference electrode and a platinum electrode was used as an auxiliary electrode. The stirring of the solution was carried out by the vibration of an indicator electrode. The oscillation frequency of the electrode was 40 Hz, the amplitude of vibration of the working surface of the electrode (electrode tip) was ± 3 mm. The electrochemical cleaning of a GE surface was carried out within a minute at a potential of +1.2 V in the background electrolyte or mechanically by polishing the electrode against the filter paper "blue ribbon", and then the GE surface was rinsed with double-distilled water. The electrode surface was polished after each measurement.

The determination of palladium ions (II) was carried out by the electro oxidation peak of palladium deposited on the surface of the GE electrode. An analytical signal of the electro oxidation of palladium precipitate on a background of 1 M HCl was observed in the potential range of + 0.4 V. The determination of gold was carried out by the peak of its electro oxidation using a bismuth-graphite electrode (BGE). The determination of platinum was carried out by the peak of selective electro oxidation of the metal-activator from the binary alloy. The selection of the metal-activator is described in the text.

The electrodeposition of the components of the binary alloys Hg-Pt and Hg-Rh was carried out from the solutions with different ratios of ion concentrations of complex platinum chloride (IV), indium (III), mercury (II), lead (II) in the "in situ" mode at the potential of electrolysis (E_e=-0.8 V). HCl solutions with concentration 1M were used as a background electrolyte. The standard solution of mercury (II) was prepared from the salts of $Hg(NO_3)_2 \cdot H_2O$, indium (III) and lead (II). Solutions of the chloride platinum complexes (IV) were prepared from standard samples by dissolving in 1M HCl. Anodic dissolution of binary precipitate was carried out at a linearly varying potential from -0.4V to 0.8 V with simultaneous recording of the current-voltage curve. Deaeration of the solutions was not carried out.

The programmable high temperature laboratory furnace "TOMA 3" (RPE "Tomanalyt" Tomsk) with a range of operating temperatures (100-999C°) was used for sample decomposition. The decomposition of the samples was carried out by the sintering of the sample with the fivefold excess of potassium tetrafluorobromate in the glass-carbon or corundum 50 ml crucibles at low temperatures (350-400°C) within 1.5-2 hours. Then, melting was leached with 6M HCl. To prevent the loss the conversion of the fluoride forms of precious metals in chloride ones was carried out in the same crucible, in which the opening of samples was carried out during the material overload.

3. Results and Discussion

In [13] it is shown that the determination of gold by SVM in 1 M HCl is possible by the peak of gold electro oxidation from the surface of the graphite electrode (GE) (E_s=0.8V), by the peak of gold electro oxidation from the surface of the bismuth-graphite electrode (BGE) (E_s=0.8V), and by the peak of selective bismuth electro oxidation from the intermetallic compound $BiAu_2$ from the surface of BGE (E_s=0.15V). Figure 1 shows the current-voltage

curves of gold precipitate electro oxidation from the surface of the bismuth-graphite electrode (BGE).

Figure 2 represents calibration curves showing the possibility of the gold determination with GE and BGE. As we can see from these data, the most sensitive method is the gold determination by the gold electro oxidation peaks from the surface of BGE (sensitivity coefficient is 140).

The compound BiAu2 contains two times less bismuth than gold, so the sensitivity of gold determination by the peak of bismuth selective electro oxidation is two times less than by the peak of gold electro oxidation. Therefore, it is advisable to detect the gold by the peak of its electro oxidation (Ep=0.8 V) using BGE.
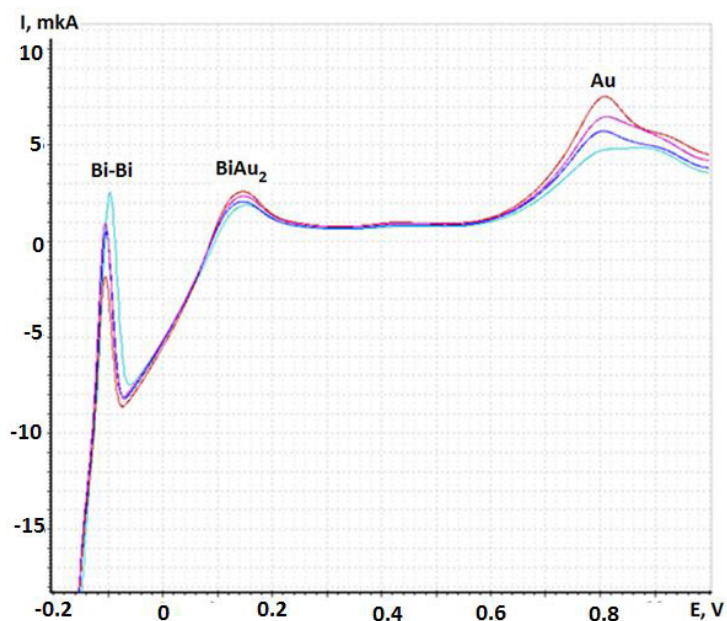

Fig.1. Current-voltage curves of bismuth-gold precipitate electro oxidation from GE surface. The experimental conditions: background - 1M HCl; E_e=-1.0V; τ_e=100 s; υ=30mV/s; C_{Bi}=100 mg/l; C_{Au}= 0.02 mg/l; 0.04 mg/l; 0.06 mg/l; 0.08 mg/l.
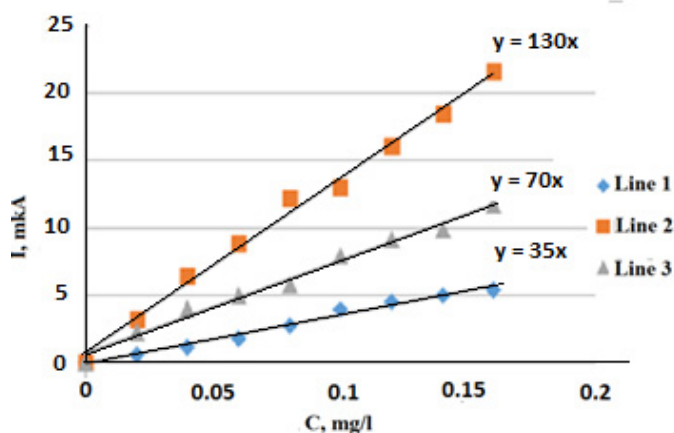

Fig.2. Calibration curves of gold determination at the electro oxidation of precipitate from the surface of GE and BGE. The experimental conditions: background - 1M HCl, Ee = - 1.0 V; τe = 100 s, υ = 30 mV/s; C_{Bi} = 100 mg/l; 1 - electro oxidation of gold from the surface of GE; 2 - selective electro oxidation of bismuth from IMC BiAu$_2$; 3 – electro oxidation of gold from the surface of BGE.

The determination of palladium (II) ions was carried out by the palladium electro oxidation peak deposited on the surface of GE electrode. The analytical signal of the electro oxidation of palladium precipitate in the background of 1M HCl was observed in the potential range of + 0.4V [14]. The disturbing influence of gold was eliminated by irradiating the analyzed sample solution by UV within 60 seconds.

It is known from the literature [5] that the process of the platinum precipitate electro oxidation from the GE surface is covered by the process of water decomposition and cannot be fixed on the current-voltage curve. Therefore, the determination of platinum by SV method is possible only after electro concentration of platinum with an electronegative element (metal-activator). A few additional anodic peaks of the selective metal-activator electro oxidation from IMC with platinum at potentials of 0.15–0.25V, which are more positive than electro oxidation peak potential of electronegative metal[6-11], appear in all cases on the volt-ampere-grams of electro oxidation of binary alloys of platinum with cadmium, lead, copper, mercury and indium from the surface of GE. The number of peaks in the anodic volt-ampere curves is affected both by the possibility of forming platinum-metal of different composition on the IMC electrode and potential of electro concentration of the binary alloy. For example, two anodic peaks of selective mercury electro oxidation from different IMC with platinum are observed on the volt-ampere curve of precipitate electro oxidation at mercury-platinum binary alloy electro concentration at a potential -1B [6].

At electro oxidation of precipitate of bismuth-platinum there are three additional peaks[7], and there are seven observed peaks (possible number of IMC in the platinum-indium system) at electro oxidation of indium-platinum precipitate which depend on the concentration of platinum in the precipitate. The picture changes if we carry out electrodeposition of the binary alloy at the potential of minus 0.4V. One peak in each case of selective electro oxidation of mercury or indium from a binary alloy is observed on the volt-ampere curve of the precipitate electro oxidation of mercury-platinum and platinum-indium (Figure 3, Figure 4)[8,9]. Comparing the sensitivity of platinum determination by the selective electro oxidation peaks of mercury from IMC $PtHg_4$ and by the selective electro oxidation peaks of indium from IMC $PtIn_2$, we can see that the sensitivity of platinum determination is twice bigger at electrodeposition of platinum into the alloy with mercury (Figure 5). Therefore, further determination of platinum ions (IV) was conducted by the peaks of selective electro oxidation of mercury from IMC with platinum (E = 0.3 V).
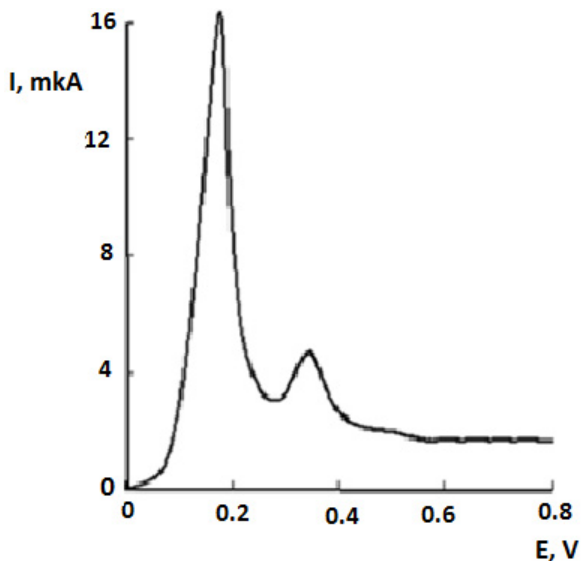

Fig.3. Voltampere curves of mercury electro oxidation (E = 0.1 V) and selective mercury electro oxidation from IMC PtHg4 (E = 0.3 V) from the surface of graphite electrode.
Experimental conditions: background - 1M HCl, $C_{Hg(II)}$=1.34mg/l; $C_{Pt\,(IV)}$=0.03 mg/l; Ee =- 0.4V; τe = 80 s, v = 80mV/s .
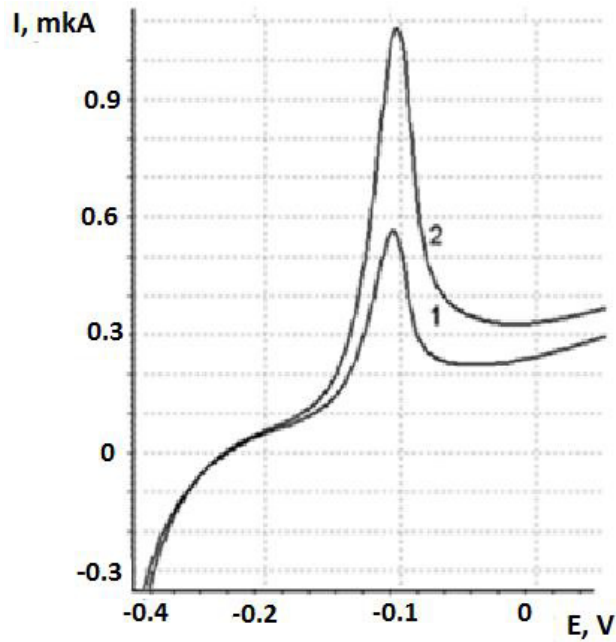
Fig.4 Current-voltage curves of selective electro oxidation of indium from IMC PtIn$_2$ from the surface of graphite electrode.
Experimental conditions: background - 1M HCl; τe=100 s, v=120 mV/s; Ee =-0.4V; C$_{In(III)}$=0.5g/dm^3; C$_{Pt(IV)}$=0.05mg/dm^3.
1 – sample; 2 - sample with the addition of standard solution C$_{Pt (IV)}$=0.05 mg/dm^3.
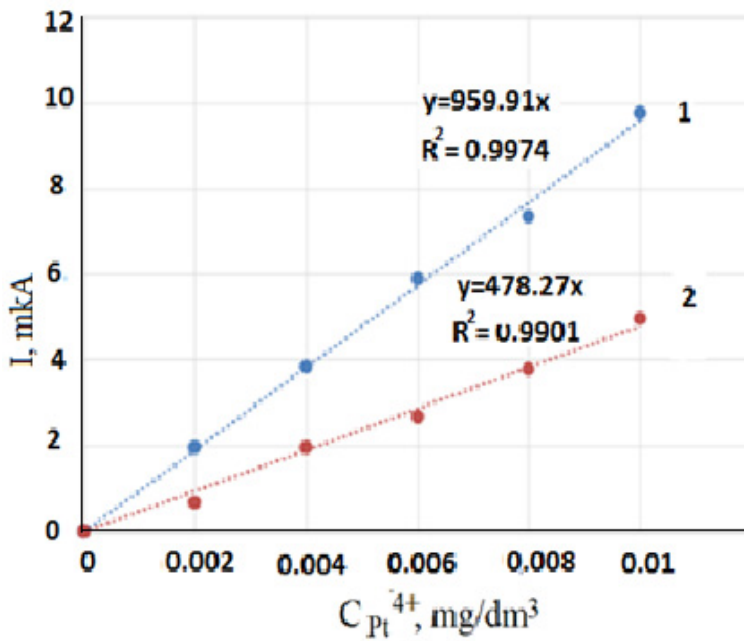

Fig.5. Calibration dependence for determination of platinum ions (IV) by selective electro oxidation peaks of mercury (1) and selective electro oxidation of indium (2) from IMC with platinum.
Experimental conditions: background - 1 M HCl; τe=80s; C$_{In(III)}$ = 5g /dm^3; C$_{Hg}$=100 mg/dm^3.

Modern instrumental methods of analysis do not provide the required determination limits of the platinum metals directly in the solid phase. Therefore, a necessary step of the analytical process is the opening of the sample by sintering, melting or acid decomposition and separating of the sample from macro-components using such techniques as co-precipitation, extraction or adsorption from the final solutions[15]. The decomposition of the samples was carried out by sintering with fivefold excess of potassium tetrafluorobromate in glass-carbon or corundum 50 ml crucibles at low temperatures (350-400°C) within 1.5-2 hours[12]. SV method eliminates disturbing influences of many "base components" which can be found in the sample by choosing such a potential of platinum-group elements electrodeposition at which electro concentration of "base" components does not occur. Therefore, the overall salt pattern of the system and the presence of such elements as sodium, potassium, chromium, lead, manganese and many others does not interfere with the determination of platinum metals and gold.

In order to extract gold from the complex matrix obtained after the dissolution of the sample, the method of extraction of chloride complexes with diethyl ether was offered. The organic phase was evaporated after extraction to the dry salt and was dissolved in 1M HCl and polarographized as described in[13]. The isolation of palladium (II) from the sample matrix was conducted by the extraction of dimethylglyoximate palladium complex with chloroform, decomposition of the organic phase and palladium determination by SV method. The technique is described in[14]. The removal of the disturbing influence of gold on the anode pick of palladium was carried out by irradiating of the solution with UV within 10 minutes before electrodeposition of palladium.

To isolate platinum (IV) the method of hydrolytic sample matrix deposition, known in the literature[16], was used. Using the concentrated solution of NaOH pH of the analyzed solution was brought to 10-11, the resulting suspension of hydroxides was heated within 20 minutes (or left for a few hours) for the "aging" of the precipitate. The suspension was then filtered through a "blue ribbon" in a conical flask. The filtrate was evaporated to a moist salt, treated with 6M HCl and again evaporated to moist salts. If necessary (e.g., when the solution has a yellowish coloration) the processing is repeated. The precipitate was dissolved in 10 ml of the supporting electrolyte 1M HCl and platinum was detected (IV) as described in[17]. The correctness of conducted determinations was monitored by the results of the analysis of certified reference standards (CRS), by the comparing of the data obtained by atomic absorption spectroscopy. The results are shown in Table 1.

Table 1. Comparison of the data obtained by atomic absorption spectroscopy with the data obtained by stripping voltammetry

Standard sample	Content, g/t, n=5		
	Au	Pd	Pt
Atomic absorption spectroscopy,			
SLg-1	2.4±0.3	0.55±0.04	0.22±0.04
SChS-1	0.12±0/05	0.05±0.005	1.2±0.08
Stripping voltammetry			
SLg-1	2.6±0.3	0.52±0.04	0.24±0.03
SChS-1	0.14±0.05	0.05±0.01	1.2±0.06

As we can see from the results of the analysis, the discrepancy of the experimental data obtained by different methods is insignificant. Table 2 shows the analysis data of some ores of black-shale formations obtained by SV.

Table 2. Results of the determination of gold, palladium and platinum in carbonaceous shale by stripping voltammetry

Deposit, type of ore	Content, g/t, n=5		
	Au	Pd	Pt
Sukhoy Log, disseminated gold-sulfide ores in listvenites	2.7±0.3	0.14±0.07	1.4±0.2
Olympiadinskoe, disseminated sulphide ores in beresites-argilisites	10.8±0.5	4.6±0.4	2.4±0.6
Zun-Kholba, veined quartz-sulfide ores in beresites	11.3±0.8	0.2±0.06	2.7±0.4
Irokindinskoe, veined quartz-sulfide ores in beresites	4.7±0.3	0.02±0.008	2.3±0.5
Nezhdanenskoe, veined disseminated quartz-sulfide ores in beresites	16.1±0.6	0.12±0.06	14.5±0.3
Nezhdanenskoe, sulfidized carbon-bearing alevroits	18.7±0.7	0.013±0.008	3.2±0.5

4. Conclusion

As a result of the research the conditions for the determination of gold, platinum and palladium by stripping

voltammetry have been selected. It has been proposed to carry out the decomposition of the ore by low-temperature sintering of the samples with fivefold excess of potassium tetraflourobromate.

The methods of sample preparation for determination of gold, palladium and platinum by the method of stripping voltammetry have been developed.

Acknowledgement

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