Determination of platinum in mineral raw materials by switching chronoamperometry

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Abstract. The technique of platinum (IV) determination in mineral raw materials with the application of switching chronoamperometry has been offered. The graphite electrode impregnated with polyethylene was used as the working electrode. The hydrolytic precipitation method with 3% NaOH solution has been developed to separate platinum from the sample matrix. The use of switching chronoamperometry applied to the assessment of the platinum content in geological objects has been demonstrated.

1. Introduction
Nowadays the majority of conventional precious metal deposits have been exhausted. Therefore, it is necessary to search for alternative composite sources with poor ores. However, the interest to such deposits in recent years has revealed serious difficulties in the analytical base in the process of the platinum group metals content assessment in this type of mineral raw materials. It is connected, first of all, with the deficiency of high sensitivity and good reproducibility techniques of analyses. Besides, large scattering and low content of precious metals in minerals and rocks are also concerned [1].

Several ways of platinum determination have been suggested by means of using a highly sensitive method of stripping voltammetry [2, 3, 4]. However, this method is complex and multistage, because the determination of platinum (II or IV) in solutions with anodic stripping voltammetry is feasible only after the platinum electrodeposition in an alloy with a metal-activator on the surface of the graphite electrode with the following selective electrooxidation from the electronegative component alloy.

Until recently the application of the simplest express way of platinum determination obtained in chloride complexes by switching chronoamperometry has been complicated by its low sensitivity.

The purpose of the study is to develop the platinum determination technique in mineral raw materials with the application of switching chronoamperometry by means of the limiting impulse current testing for platinum (IV) in the solution.

2. Experimental part
Reagents and chemicals
All the chemicals used were of analytical or pharmaceutical grade and the solutions were prepared with deionized water. The standard platinum solutions were supplied by Merck. The hydrochloric, hydrofluoric and nitric acids were provided by Sigma. The control was carried out by Pt content measuring in the following reference standards (RS) from «SIBTZVETMETNIIPROEKT», Krasnoyarsk: RS 8770-2006 (SOP 107.1 RMK-4), RS 8771-2006 (SOP RMO-5 107.2), RS 519-88P (ST-2), RS 927-76 (VP-2), RS 8772-2006 (SOP 108.1).
Electrochemical measurements
Chronoamperometrical measurements were carried out with the universal research analyzer “MultiLab” (Tomsk). A three-electrode system and special quartz beakers of V=20 ml were used. A polyethylene-impregnated graphite electrode produced according to [5] was used as the working electrode. The determination of platinum was carried out by means of using 0.1 M HCl as the supporting electrolyte. Saturated silver chloride electrodes served as the reference and the auxiliary electrodes. Deaeration of solutions was not conducted.

3. Results and discussion
The principle of switching chronoamperometry or pulsed potentiostatic method of the platinum determination in mineral raw materials is the following: the potential of the working electrode being set and constant, the current contour of the electrochemical cell with the determined solution is periodically commuted [6]. Thus there occurs the determined ion recharging: the transition of platinum (IV) in platinum (II) in the solution near the electrode surface. The recorded maximum impulse current is proportional to the concentration of the input element.

The determination of platinum ions (IV) in the study was carried out close to the surface of the graphite electrode in the solution being stirred in real time with the controlled potential electrolysis - 0.24 V. Selecting of the working electrode and the electrolysis potential value was due to the reproducibility and the maximum value of the analytical signal under these conditions. As the platinum was introduced in the form of chloride complexes [PtCl₆]²⁻, the measurements were carried out using 0.1 M HCl supporting electrolyte with the following chronoamperometrical curves registration. Platinum (IV) ions concentration was determined with the signal response in relation to the saturated silver/silver chloride electrode (figure 1).

**Figure 1.** Chronoamperogramm of the platinum (IV) determination on the surface of the graphite electrode in the solution. The experimental conditions: supporting electrolyte - 0.1 M HCl; Eₑₑ = -0.24 V. Response 1 (ΔI = 34 mA) – the sample containing 0.1 Pt (IV) and Response 2 (ΔI = 33.5 mA) – the additive containing 0.1 mg L⁻¹ standard solution of Pt (IV).

The platinum concentration was determined at the limited current of the standard additive according to the following equation:

\[ C = \frac{I_{sp}C_{ad}V_{ad}}{(I_{ad} - I_{sp})W_{sp}}. \]

C – the concentration of platinum in the solution, mg L⁻¹;
I_{sp}, I_{ad} – the current limit of the sample and the additive of platinum standard solution respectively, uA;
$V_{ad}$, $V_{sp}$ – the volume of the sample and additive, L;

$C_{ad}$ – the concentration of the platinum standard solution additive, mg L$^{-1}$.

The platinum (IV) determination results in the supporting electrolyte indicate that the maximum error in the measurements in the experiment is equal to 20% (table 1). The calculation of the detectable platinum concentrations was carried out according to the standard addition method.

| Added of Pt, g t$^{-1}$ | Found of Pt, g t$^{-1}$ | Relative accuracy ± δ, % |
|------------------------|-------------------------|--------------------------|
| 0.025                  | 0.020                   | 20                       |
| 0.050                  | 0.058                   | 16                       |
| 0.100                  | 0.087                   | 13                       |
| 0.500                  | 0.438                   | 12                       |
| 0.900                  | 1.000                   | 11                       |

The linear dependence of the platinum (IV) current electroreduction on its concentration in the solution is observed (figure 2).

![Figure 2: The dependence of the platinum (IV) limited current on its concentration in solution.](image)

Figure 2. The dependence of the platinum (IV) limited current on its concentration in solution. Straight line equation: $Y = 138.13 \cdot X + 0.08$. The experimental conditions: supporting electrolyte - 0.1 M HCl; $E_e = -0.24$ V.

The detection limit was calculated to determine the platinum content by means of measurement limiting pulse-current with the application of switching chronoamperometry.

The detection limit was calculated on the 3-δ criterion with the help of the equation below:

$$C_{min}, p = \frac{3\delta}{tg\alpha} = \frac{3 \cdot 0.01}{138.13} = 0.00022 \text{gt}^{-1}.$$  

Where δ is the minimum signal of Pt (IV) in the supporting electrolyte; $tg\alpha$ is the angle of inclination from the calibration curve (figure 2).

Sample pretreatment for platinum determination in geological objects

Preconcentration of metals is required for reliability improvement of their low content determination with the simultaneous separation of metals from the bulk of macro components.

At the beginning of the sample preparation, dry ashing of the sample was carried out in the furnace at $t = 500$ °C for 45 minutes. Then the sample was cooled down. $H_2O$, $S$, $CO_2$, $As$, $Sb$, $Hg$, etc.
volatilize under these conditions. The matrix sample was treated with concentrated HF for the decomposition of silicates. The obtained mixture was heated at \( t = 170 \degree C \) until white fumes associated with the formation of volatile \( \text{SiF}_4 \). The solution was evaporated to dryness on the hotplate. The residue in the crucible was treated with aqua regia by means of heating (\( t = 170 \degree C \)). There Pt and Pd dissolved and formed \( \text{H}_2[\text{PtCl}_6] \) and \( \text{H}_2[\text{PdCl}_6] \). Then, after the concentrated HCl with heating (\( t = 170 \degree C \)) being added, the complex \( (\text{NO}_2)_2[\text{PtCl}_6] \) was decomposed and it was converted into \( \text{H}_2[\text{PtCl}_6] \) \[10\].

The mixture was filtered, and then was washed with the double amount of distilled water. The filtrate was evaporated to wet salts and then diluted with a small amount of distilled water. The use of hydrolytic precipitation method with 3% NaOH solution makes the platinum transform into another complex – hexachloroplatinate sodium \( \text{Na}_2[\text{PtCl}_6] \) and remains in the solution. The flasks with the filtrate were evaporated to dryness. Further HCl was added to neutralize the excess of NaOH, and to transit chloride complexes of platinum: \( [\text{PtCl}_6]^{2-} \). The obtained mixture was evaporated on the plate to a dry residue. The platinum content was then determined by means of switching chronoamperometry (table 2).

**Table 2.** The results of switching chronoamperometry determination of the platinum (IV) content in the reference standards of copper-nickel ore \( (n = 9; P = 0.95) \).

| Ref. standard | Content of Pt in ref. sample, g t\(^{-1}\) | Result of determination of Pt, g t\(^{-1}\) | Relative accuracy ±δ, % |
|--------------|-------------------------------------------|-----------------------------------------|------------------------|
| SOP 107.1    | 4.10                                      | 3.00                                    | 34                     |
| VP-2         | 2.64                                      | 3.18                                    | 36                     |
| SOP 108.1    | 2.50                                      | 1.87                                    | 38                     |
| SOP 107.2    | 2.10                                      | 2.51                                    | 39                     |
| ST-2         | 2.50·10\(^{-2}\)                         | 1.98·10\(^{-2}\)                       | 40                     |

As table 2 shows, the systematic error is not significant in the chronoamperometrical method of the platinum determination, after the separation of interfering impurities by the 3% NaOH solution hydrolytic precipitation.

The suggested technique for the platinum (IV) determination was tested on real objects of mineral raw materials. The research objects were ores of different formation types from Siberia, the Urals, Tuva, Yakutia and Kazakhstan. The choice of these objects is due to the fact that the Innovative Scientific and Educational Center "Gold and Platinum" of Tomsk Polytechnic University revealed low concentrations of platinum by means of methods of the stripping voltammetry and atomic absorption spectroscopy in these deposits (table 3).

**Table 3.** The comparative analyses of platinum determination in the mineral raw materials by switching chronoamperometry (SCA) and atomic absorption spectroscopy (AAS), \( (n = 9; P = 0.95) \).

| Type and name of deposits         | Sample no | Content of Pt, g t\(^{-1}\)       |
|----------------------------------|-----------|-----------------------------------|
|                                  |           | SCA                               | AAS                               |
| Maisko-Lebedskoe gold-skarn      | PR-3      | 0.003±0.00061                      | 0.0009±0.00018                     |
|                                  | PR-10     | 0.004±0.0008                       | 0.0035±0.0006                     |
|                                  | ML-4 EPG  | 0.007±0.0020                       | 0.0063±0.0015                     |
|                                  | CAF-1 EPG | 0.004±0.0007                       | 0.003±0.00065                     |
| Bakchar iron ore                 | PR-3      | 0.003±0.00061                      | 0.0009±0.00018                     |
|                                  | PR-10     | 0.004±0.0008                       | 0.0035±0.0006                     |
|                                  | ML-4 EPG  | 0.007±0.0020                       | 0.0063±0.0015                     |
|                                  | CAF-1 EPG | 0.004±0.0007                       | 0.003±0.00065                     |
| Aksu copper-molybdenum           | K-79      | 0.004±0.0010                       | 0.0035±0.0009                     |
|                                  | K-90 D    | 0.006±0.0013                       | 0.0067±0.0013                     |
|                                  | K-92 G    | 0.007±0.0016                       | 0.003±0.0006                      |
|                                  | K-97 ZH   | 0.005±0.0011                       | 0.0017±0.00034                    |
As table 3 shows, the results of the comparative analysis of the methods of switching chronoaamperometry with AAS demonstrate a good data convergence of platinum content determination in the ore material.

Thus, the discussed method for the platinum determination in mineral raw materials with SCA application by means of measurement of limited pulse current can be used to control the platinum content in geological objects.

4. Conclusion
1. The technique of the platinum determination in mineral raw materials with the application of switching chronoaamperometry by means of the limited impulse current of platinum (IV) in the solution has been proposed.
2. The platinum detection limit in the solution has been calculated with the 3σ-criterion application and is equal to 0.22 mg t⁻¹.
3. The data convergence obtained by means of the atomic absorption spectroscopy and switching chronoaamperometry in the process of the platinum content determination in ore materials has shown the reliability of the developed technique.

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