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VOLTAMMETRIC DETERMINATION OF RHODIUM BY MEANS OF FURAN-OXIME DERIVATIVES IN INDUSTRIAL SAMPLES WITH CONSIDERABLE CONTENT OF PALLADIUM

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Received: January 03, 2011 / Revised: April 03, 2011 / Accepted: May 26, 2011

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Abstract. The selectivity of rhodium(III) voltammetric determination by means of furan-oxime derivatives has been investigated. The proposed methods have been approved on model solutions and during the determination of rhodium(III) in the presence of palladium(II) in complex industrial samples.

Keywords: palladium, rhodium, voltammetric determination, oxime derivatives.

1. Introduction

Rhodium due to its unique physico-chemical and operational properties is the necessary component for the development of many modern fields of industry: from fine organic synthesis and precise instrument engineering to large-tonnage manufacturing. A high efficiency of different units exploitation is often achieved by means of the combination of few platinum group elements, and the industrial utilization of rhodium is not an exception. However, even the insignificant change of platinoid content can result in substantial changes of object's properties, which makes the problem of precise control of rhodium content in various samples still actual. Taking into account the complications, caused by the similarity of chemical and analytical properties of platinum group metals, their determination at the simultaneous presence is one of the important tasks of analytical chemistry. Usually the methods of atomic absorption analysis and spectrophotometry are used for solving this task, though the first one is expensive and the last one – low selective in most cases [1, 2]. On the other hand, the methods for rhodium voltammetric determination are more available and compete with other mentioned above methods in other chemical and analytical characteristics [1-5]. Besides, only voltammetric techniques provide the

possibility of the simultaneous determination of few platinum group elements [6, 7].

2. Experimental

2.1. Reagents

All aqueous solutions, utilized in the research, have been prepared using distilled water.

The stock solution of Rh(III) ($[\text{RhCl}_6]^{3-}$) has been prepared by sintering the exact mass of metallic rhodium with the oxidizing mixture of $\text{NaNO}_3 + \text{NaOH}$ (3:1) with the further dissolving of the obtained fusion in 3 M HCl [1, 8]. The existence form of Rh(III) in the obtained stock solution has been confirmed by comparing its electronic absorbance spectra with the literary data [9-11]. Since some losses of rhodium may occur during sintering with the oxidizing mixture, so the obtained solutions of Rh(III) were additionally standardized according to the titrimetric techniques of V. Syrokmskiy and N. Proshenkova [12, 13]. The standard working solutions were prepared by dissolving an exact aliquot of stock solution with 3 M hydrochloric acid.

The solutions of 5-(2-chlorophenyl)-furan-2-carbaldehydeoxime (FOD-o) and 5-(4-chlorophenyl)-furan-2-carbaldehydeoxime (FOD-p) have been prepared by dissolving an exact mass of the reagent in 80 % v/v ethanol.

HCl, HNO_3 , NaOH, $\text{CH}_3\text{COOH}_{\text{glacial}}$, CH_3COONa , NH_4OH , NH_4Cl , used in the research for preparation of solutions, were of analytical grade.

2.2. Apparatus

Voltammetric measurements were performed using an oscillopolarograph CLA-03 (Russia) with a digital setup equipped with a computer and a three-electrode cell

using linear potential sweep. A dropping mercury electrode (d.m.e.), a platinum electrode and a saturated calomel electrode served as indicator, auxiliary and reference electrodes, respectively. The pH measurements were carried out with pH-meter model pH-150 M equipped with glass electrode (Gomelsky Plant of Measuring Devices, Belarus). Proper pH value were adjusted using dissolved solutions of CH_3COOH and CH_3COONa .

2.3. Procedure of Rhodium(III) with 5-(2-Chlorophenyl)-Furan-2-Carbaldehydeoxime Determination

2.0 ml of 2.0 M acetate buffer solution (pH 3.5) and an aliquot of Rh(III) solution containing $1.5 \cdot 10^{-7}$ – $5.0 \cdot 10^{-6}$ M of rhodium is added into a 25.0 ml volumetric flask. Then 5.0 ml of $\text{C}_2\text{H}_5\text{OH}$, 1.0 ml of newly prepared $1.25 \cdot 10^{-3}$ M solution of 5-(2-chlorophenyl)-furan-2-carbaldehydeoxime is added to the obtained solution and distilled water is added to the total volume of ~ 20 ml. The acidity of the media is controlled with a pH-meter and, if necessary, adjusted to pH 3.5 by means of CH_3COOH and CH_3COONa (do not get into an alkaline pH region!). Then distilled water is added to the mark. The investigated solution is transferred into the electrolytic cell and dissolved oxygen is removed by a barbotage of purified argon through the cell for 15 min, and then the voltammetric curves are obtained using a polarizing range of 0 to -1.5 V and the potential sweep rate of $0.5 \text{ V} \cdot \text{s}^{-1}$. The approximate rhodium(III) content is estimated using the method of calibration curve. The exact value of

rhodium(III) concentration in the investigated solution is established with the method of standard additions.

2.4. Procedure of Rhodium(III) with 5-(4-Chlorophenyl)-Furan-2-Carbaldehydeoxime Determination

2.0 ml of 2.0 M acetate buffer solution (pH 5.5) and an aliquot of Rh(III) solution containing $2.0 \cdot 10^{-7}$ – $4.5 \cdot 10^{-6}$ M of rhodium is added into a 25.0 ml volumetric flask. Then 5.0 ml of $\text{C}_2\text{H}_5\text{OH}$, 1.0 ml of newly prepared $1.25 \cdot 10^{-3}$ M solution of 5-(4-chlorophenyl)-furan-2-carbaldehydeoxime is added to the obtained solution and distilled water is added to the total volume of ~ 20 ml. The acidity of the media is controlled with a pH-meter and, if necessary, adjusted to pH 5.5 by means of CH_3COOH and CH_3COONa (do not get into an alkaline pH region!). The rest of the procedure is the same as described in Subsection 2.3.

3. Results and Discussion

3.1. Validation Results of the Voltammetric Determination of Rhodium(III) by Means of Furan-Oxime Derivatives

Previous researches of the voltammetric behaviour of furan-oxime derivatives [14, 15] have shown, that their reduction on d.m.e. is followed by the appearance of somewhat bifurcated peak, which shifts linearly to the

Table 1

The validation parameters of the voltammetric determination of rhodium(III) by means of 5-(2-chlorophenyl)-furan-2-carbaldehydeoxime ($C(\text{FOD-}o) = 1.25 \cdot 10^{-3} \text{ M}$; $C(\text{CH}_3\text{COONa}) = 0.16 \text{ M}$; $\text{pH} = 3.5$; $V = 0.5 \text{ V} \cdot \text{s}^{-1}$) and 5-(4-chlorophenyl)-furan-2-carbaldehydeoxime ($C(\text{FOD-}p) = 1.25 \cdot 10^{-3} \text{ M}$; $C(\text{CH}_3\text{COONa}) = 0.16 \text{ M}$; $\text{pH} = 5.5$; $V = 0.5 \text{ V} \cdot \text{s}^{-1}$)

Method	Linearity range, $I_p^c, \mu\text{A}$ vs. $C_{\text{Rh(III)}}, \text{M}$	Calibration equation	Correlation coefficient R	Limit of quantification, M
Rh(III)+FOD- <i>o</i>	$5.0 \cdot 10^{-6}$ – $1.5 \cdot 10^{-7}$	$I_p^c = 0.98 + 1.616 \cdot 10^6 C_{\text{Rh(III)}}$	0.9964	$1.5 \cdot 10^{-7}$
Rh(III)+FOD- <i>p</i>	$4.5 \cdot 10^{-6}$ – $4.0 \cdot 10^{-7}$	$I_p^c = 0.02 + 0.059 \cdot 10^6 C_{\text{Rh(III)}}$	0.9934	$4.06 \cdot 10^{-7}$

Table 2

Tolerance ratios of interfering ions during the voltammetric determination of rhodium(III) in the presence of 5-(2-chlorophenyl)-furan-2-carbaldehydeoxime ($C(\text{FOD-}o) = 5.0 \cdot 10^{-5} \text{ M}$; $C(\text{Rh(III)}) = 4 \cdot 10^{-6} \text{ M}$; $V = 0.5 \text{ V} \cdot \text{s}^{-1}$; $\mu = 0.16 \text{ M}$; $\text{pH} = 3.5$)

Extraneous ion	$C(\text{M}^{n+}) : C(\text{Rh(III)})$	Extraneous ion	$C(\text{M}^{n+}) : C(\text{Rh(III)})$
Ca(II)	100	Cr(III)	100
Ba(II)	100	Co(II)	50
Cd(II)	50	Pb(II)	50
Sn(IV)	50	Pd(II)	0.5
Cu(II)	50	Pt(IV)	10
Ni(II)	100	Ru(IV)	10
Fe(III)	100	Ir(IV)	0.1

Table 3

Tolerance ratios of interfering ions during the voltammetric determination of rhodium(III) in the presence of 5-(4-chlorophenyl)-furan-2-carbaldehydeoxime
 ($C(\text{FOD-}p) = 5.0 \times 10^{-5} \text{ M}$; $C(\text{Rh(III)}) = 4 \times 10^{-6} \text{ M}$; $V = 0.5 \text{ V s}^{-1}$; $\mu = 0.16 \text{ M}$; $\text{pH} = 5.5$)

Extraneous ion	$C(\text{M}^{n+}) : C(\text{Rh(III)})$	Extraneous ion	$C(\text{M}^{n+}) : C(\text{Rh(III)})$
Ca(II)	100	Cr(III)	50
Ba(II)	100	Co(II)	50
Cd(II)	50	Pb(II)	50
Sn(IV)	30	Pd(II)	0.5
Cu(II)	50	Pt(IV)	10
Ni(II)	100	Ru(IV)	10
Fe(III)	–	Ir(IV)	0.2

range of negative potentials when decreasing the acidity of a media. The observed effect denotes the two-stage mechanism of the electrochemical transformation and the participation of hydrogen ions. The reduction of furan-oxime derivatives is an irreversible process, which is confirmed by the absence of anodic peaks on the voltammograms of organic reagents solutions

We have established that in the presence of rhodium(III) ions the increase of furan-oximes derivatives cathodic peaks, proportional to the concentration of Rh(III) in the solution, is observed [16, 17]. It has been investigated that the maximum increase of furan-oximes derivatives cathodic peaks is observed in acetate buffer media at pH 3.5 for 5-(2-chlorophenyl)-furan-2-carbaldehydeoxime and at pH 5.5 for 5-(4-chlorophenyl)-furan-2-carbaldehydeoxime. Based on the effects observed, the methods for the voltammetric determination of rhodium(III) have been elaborated, and their validation results are presented in Table 1.

The investigations of the selectivity of rhodium(III) voltammetric determination with furan-oxime derivatives have shown that ions of base metals (Tables 2 and 3) and ten-fold excesses of platinum(IV) and ruthenium(IV) practically do not interfere. However, the elaborated methods possess low selectivity towards Pd(II) and Ir(IV) ions.

The study of the selectivity of rhodium(III) voltammetric determination with furan-oxime derivatives has been carried out by the gradual increase of the concentration of extraneous ion until the analytical signal deviation were 5 %.

3.2. Methods Approbation

The accuracy of rhodium(III) voltammetric determination using furan-oxime derivatives has been tested on model solutions. As it is shown in Table 4, both methods possess good reproducibility and the accuracy of the determination.

In addition, the developed techniques of rhodium voltammetric determination have been applied for rhodium assay in the palladium-rhodium catalyst and the resistor SP-5-35B.

In order to extract rhodium from the catalyst, based on a ceramic material, an exact mass of the sample was transferred into a thermostable beaker and treated three times with a mixture of concentrated HCl and HNO₃ (3:1) on heating on a sand bath during 1 h with further decantation [18]. Obtained palladium(II) and rhodium(III) were transferred into chloride forms by means of evaporation of solution to wet salts and adding 10.0 ml of concentrated HCl until nitrogen oxides stopped to be liberated.

During rhodium(III) determination in the resistor SP-5-35B, all details, containing platinum group elements, have been transferred into a beaker and dissolved in a mixture of concentrated HCl and HNO₃ (3:1). The transformation of platinum group metals ions into chloride complexes has been carried out in the same way as for the catalyst, *viz.* by means of adding 10.0 ml of concentrated HCl and evaporation of solution to wet salts until nitrogen oxides stopped to be liberated.

Taking into account the considerable interfering influence of palladium(II) on rhodium(III) voltammetric determination by means of furan-oxime derivatives and the information concerning its prevailing content over rhodium in the examined samples [19], it was necessary to establish an exact palladium content in the samples. The amount of palladium(II) in the analyzed specimens has been determined by polarography according to the cathodic peaks of its ammonium complexes [1, 2], using the method of standard additions.

Since a direct rhodium(III) determination with the elaborated techniques was not possible because of a considerable palladium content in the investigated samples, so we have suggested the following mathematical device using the method of standard additions: at two different pH of a solution the coefficients of the increase (in the case of rhodium(III)) and the decrease (in the case of palladium(II)) of furan-oxime derivatives cathodic peaks have been ascertained. The obtained results have been combined into the system of equations, from which the formula for the calculation of rhodium content has been deduced:

$$\Delta I^{pH3.5} = K_{Rh(III)}^{pH3.5} C_{Rh(III)} + K_{Pd(II)}^{pH3.5} C_{Pd(II)} \quad (1)$$

$$\Delta I^{pH8.5} = K_{Rh(III)}^{pH8.5} C_{Rh(III)} + K_{Pd(II)}^{pH8.5} C_{Pd(II)} \quad (2)$$

Table 4

Accuracy of the voltammetric determination of rhodium(III) by means of 5-(2-chlorophenyl)-furan-2-carbaldehydeoxime ($C(\text{FOD-}o) = 1.25 \times 10^{-3} \text{ M}$; $C(\text{CH}_3\text{COONa}) = 0.16 \text{ M}$; $\text{pH} = 3.5$; $V = 0.5 \text{ V}\cdot\text{s}^{-1}$; $n = 5$; $P = 0.95$) and 5-(4-chlorophenyl)-furan-2-carbaldehydeoxime ($C(\text{FOD-}p) = 1.25 \times 10^{-3} \text{ M}$; $C(\text{CH}_3\text{COONa}) = 0.16 \text{ M}$; $\text{pH} = 5.5$; $V = 0.5 \text{ V}\cdot\text{s}^{-1}$; $n = 5$; $P = 0.95$)

Content of matrix solution	Added Rh(III), μg	Found with FOD-o		Found with FOD-p	
		$m(\text{Rh(III)}), \mu\text{g}$	S_r	$m(\text{Rh(III)}), \mu\text{g}$	S_r
420 μg Cd(II) 230 μg Cu(II) 10 μg Pt(II)	10	10.15	0.020	10.20	0.017
		10.27		9.96	
		9.85		10.15	
		9.95		10.30	
		10.30		9.88	
420 μg Cd(II) 420 μg Pb(II) 220 μg Co(II)	10	10.05	0.018	9.95	0.019
		9.80		9.85	
		10.25		10.28	
		9.90		10.25	
		9.90		10.15	
300 μg Ca(II) 220 μg Ni(II) 230 μg Cu(II)	10	9.85	0.014	10.15	0.023
		10.05		10.22	
		9.90		9.78	
		10.10		10.28	
		10.20		9.86	

We have expressed the concentration of palladium by the Eq. (1):

$$C_{\text{Pd(II)}} = \frac{\Delta I^{\text{pH}3.5} - K_{\text{Rh(III)}}^{\text{pH}3.5} C_{\text{Rh(III)}}}{K_{\text{Pd(II)}}^{\text{pH}3.5}} \quad (3)$$

and substituted the expression (3) into the Eq. (2). Then the formula for the estimation of rhodium concentration in the analyte's solution has been deduced:

$$C_{\text{Rh(III)}} = \frac{\Delta I^{\text{pH}8.5} K_{\text{Pd(II)}}^{\text{pH}3.5} - \Delta I^{\text{pH}3.5} K_{\text{Pd(II)}}^{\text{pH}8.5}}{K_{\text{Rh(III)}}^{\text{pH}8.5} K_{\text{Pd(II)}}^{\text{pH}3.5} - K_{\text{Pd(II)}}^{\text{pH}8.5} K_{\text{Rh(III)}}^{\text{pH}3.5}} \quad (4)$$

Before the analyses of the industrial samples we have verified this method of calculation on model solutions and obtained the correct results. The results of rhodium determination in complex industrial samples by means of furan-oxime derivatives and using the described mathematical device are presented in Table 5.

Table 5

The results of rhodium content in the palladium-rhodium catalyst and the resistor SP-5-35B by means of furan-oxime derivatives ($C(\text{FOD}) = 1.25 \times 10^{-3} \text{ M}$; $C(\text{CH}_3\text{COONa}) = 0.16 \text{ M}$; $\text{pH} = 3.5$ (FOD-*o*); $\text{pH} = 5.5$ (FOD-*p*); $V = 0.5 \text{ V}\cdot\text{s}^{-1}$; $n = 3$; $P = 0.95$)

Reagent	Sample			
	Resistor		Catalyst	
	$m(\text{Rh}), \text{mg}$	S_r	$\omega(\text{Rh}), \%$	S_r
FOD- <i>o</i>	1.10±0.10	0.05	0.10±0.03	0.11
FOD- <i>p</i>	1.00±0.14	0.06	0.10±0.02	0.08

4. Conclusions

The selectivity of the methods for rhodium(III) voltammetric determination by means of furan-oxime derivatives towards concomitant metals ions, including platinoids, has been investigated. The results of the accuracy testing for suggested methods on model solutions and their approbation during rhodium determination in complex industrial samples containing considerable molar excesses of palladium have been presented. The mathematical method for processing of experimental results at the additive influence of extraneous component has been proposed.

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**ВОЛЬТАМПЕРОМЕТРИЧНЕ ВИЗНАЧЕННЯ
РОДІЮ ЗА ДОПОМОГОЮ ФУРАН-ОКСИМОВИХ
ПОХІДНИХ В ПРОМИСЛОВИХ ОБ'ЄКТАХ ЗІ
ЗНАЧНИМ ВМІСТОМ ПАЛАДІЮ**

Анотація. Досліджено селективність вольтамперометричного визначення родію (III) за допомогою фуран-оксимових похідних. Проведено апробацію запропонованих методик на модельних розчинах та при визначенні родію (III) в присутності паладію (II) у складних промислових об'єктах.

Ключові слова: паладій, родій, вольтамперометричне визначення, оксимові похідні.