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A NEW METHOD OF CONTROL OVER THE CONTENT OF PALLADIUM IN INTERMETALLIC ALLOYS

O. S. Tymoshuk,[1,2] O. S. Fedyshyn,[1] L. V. Oleksiv,[1] P. V. Rydchuk,[1] and I. O. Patsai[1]

We study the interaction of 4-methoxy-1-(5-benzylthiazol-2-yl)azo-naphthalene-2-ol with palladium (II) ions. The conditions required for the formation of a complex and for getting the optimal fractions of its components are established. We propose a new extraction-photometric method for the analytic control over complex palladium-containing compounds with the use of 4-methoxy-1-(5-benzylthiazol-2-yl)azo-naphthalene-2-ol and verify it for $Yb_{40}Pd_{40}Ga_{20}$ and $Yb_{40}Pd_{38}Sn_{22}$ alloys.

Keywords: palladium(II), azodyes, spectrophotometry, extraction, alloys.

Introduction

Palladium-containing materials have valuable chemical and physical properties. Hence, they are extensively used in various branches of industry (chemical industry, jewelry, electro-engineering, electronics, medicine, pharmaceutics, etc.) [1, 2]. In particular, the materials are used as catalysts for the creation of fuel elements (Pd–Ni, Pd–Ag, Pd–Au, Pd–Fe) [3, 4] and in the production of hydrogen sensors (Pd–Y, Pd–Ag) [5, 6]. In addition, the intermetallic compounds of palladium are good superconductors (Pd_2ZrAl, Pd_2HfAl, $YbPd_2Sn$, etc.) [7, 8]. Therefore, it is necessary to develop new sensitive selective methods for the analytical control over the palladium content of alloys.

Materials, Equipment, and Experimental Procedure

The source solution of Pd(II) was prepared by the dissolution of metallic palladium (99.999%) in a mixture of reagent-grade concentrated acids HNO_3 and HCl (1:3). Its working solutions were obtained as a result of the dilution of the source solution in a 1.0 M HCl. The solution of 4-methoxy-1-(5-benzylthiazol-2-yl)azo-naphthalene-2-ol was prepared by the dissolution of exact weighed portions of the recrystallized reagent in 96% ethanol of the “pharm” grade, while the solution of HCl was obtained as a result of the dilution of concentrated reagent-grade hydrochloric acid. In our spectrophotometric measurements, we used a ULAB 108-UV spectrophotometer, quartz cuvettes ($l = 1.0$ cm), and a KFK-3 photocolorimeter ($l = 5.0$ cm). The acidity of solutions was measured by a pH-150 M device with combined glass electrode.

Results and Discussion

Most frequently, the content of palladium is found photometrically, by using organic reagents containing functional groups with electrodonor atoms, such as S, N, and O [1, 2]. The aim of the present work is to study

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[1] Ivan Franko Lviv National University, Lviv, Ukraine.

[2] Corresponding author; e-mail: otymoshuk@ukr.net.

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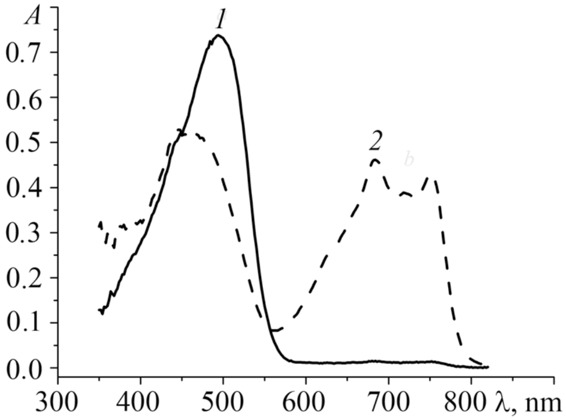

Fig. 1. Absorption spectra of the toluene extract of MetOBnTAN in the absence (curve 1) and in the presence (curve 2) of Pd(II) ions ($C_{\mathrm{MetOBnTAN}} = 4.24 \cdot 10^{-5}$ M; $C_{\mathrm{Pd(II)}} = 1.88 \cdot 10^{-4}$ M; l = 1.0 cm).

the interaction of a new reagent, i.e., of

4-methoxy-1-(5-benzylthiazol-2-yl)azo-naphthalene-2-ol (MetOBnTAN)

with Pd(II) ions in a broad interval of acidities of the medium and to develop a procedure of extraction-photometric control of palladium-containing complex objects. These studies were stimulated by the detected interaction of Pd(II) ions with new reagents from the class of azolydones, in particular, with an 1,3-thiazole derivative [9–11] and by the possibility of application of 1-(5-benzylthiazole-2-yl)azonaphthalene-2-ol and 1-[(5-(4-sulfoneamidebenzyl-4-methyl-1,3-thiazole-2-yl)diazenyl]naphthalene-2-ol as analytic reagents for the evaluation of the contents of Pd(II), Co(II), Ni(II), Cu(II), Zn(II), Pb(II), Cd(II), and Hg(II) [12–17].

The maximum absorption of light by the complex compound of Pd(II) with reagent in a medium of toluene was recorded at a wavelength λ = 684 nm, whereas the maximum absorption for the reagent under the same conditions was observed at λ = 485 nm (Fig. 1). The location of the maximum of absorption for the complex is independent of the acidity of the source aqueous solutions of Pd(II) at pH 1–12. The highest values of the optical density of the extract were obtained for the solutions with pH 1.0. As this parameter decreases, the analytic signal becomes weaker. This is explained by the formation of hydroxocomplexes of Pd(II) whose interaction with the reagent is more complicated.

The ratios of components in the complex compound were found by the methods of saturation and isomolar series (Fig. 2).

It was discovered that one ion of the platinoid is associated with two molecules of the reagent. Therefore, in order to ensure the quantitative yield of the colored compound, the subsequent studies were carried out for its threefold excess. The optimal conditions of extraction-spectrophotometric determination of the content of palladium in the Pd(II)–MetOBnTAN system in a medium of toluene were as follows: pH 1.0; λ = 684 nm; $C_{\mathrm{MetOBnTAN}} : C_{\mathrm{Pd(II)}} = 3$; the limits of linearity were 0.5–19 μg, and the correlation coefficient $R = 0.9993$.

The negative influence of foreign ions was determined by introducing them up to the deviation of the analytic signal by more than 5% from the midpoint (10.0 μg) of the calibration plot ($A = 0.008 + 0.041\, m_{\mathrm{Pd(II)}}$). It was discovered that a twofold excess of Ir(IV), a fivefold excess of Rh(III), a tenfold excess of Pt(IV), Fe(III), Mn(II), Co(II), and Ni(II), a 50-ford excess of Ga(III) and Yb(III), and more than 100-fold excesses of Fe(II), Zn(II), Cu(II), Sn(II), Sn(IV), Cd(II), and Ti(III) should be regarded as admissible. Since the indicate foreign ions exert no harmful effect in the indicated concentrations, we did not make attempts separate or hide them.

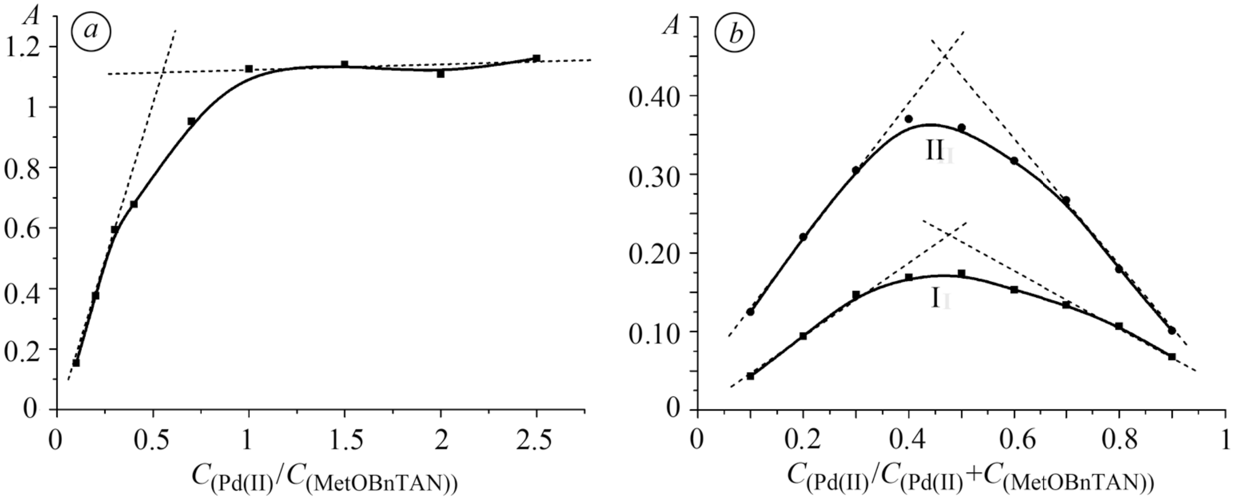

Fig. 2. Determination of the composition of Pd(II)–MetOBnTAN complex (λ = 684 nm; pH 1.0; l = 1.0 cm; (a): $C_{\mathrm{MetOBnTAN}} = 9.2 \cdot 10^{-5}$ M; $C_{\mathrm{Pd(II)}} = 9.2 \cdot 10^{-6}$–$2.3 \cdot 10^{-4}$ M; (b): (I) $C_{\mathrm{tot}} = 2.0 \cdot 10^{-5}$ M; (II) $C_{\mathrm{tot}} = 4.0 \cdot 10^{-5}$ M) by the mole-ratio (a) and continuous variations (b) methods.

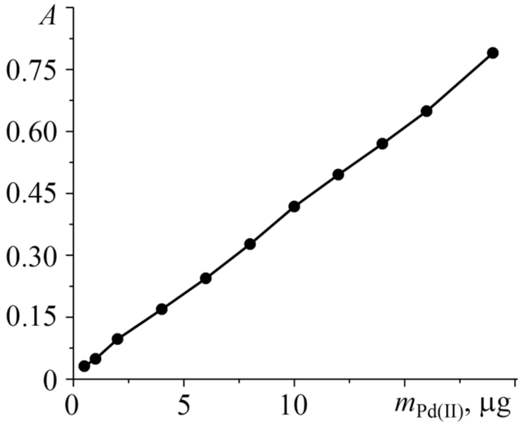

Fig. 3. Calibration plot for the determination of Pd(II) by using the MetOBnTAN reagent ($C_{\mathrm{MetOBnTAN}} = 1.08 \cdot 10^{-4}$ M; pH = 1.0; l = 5.0 cm; λ = 684 nm).

Method for the Determination of the Palladium Content

Into a separating funnel 25 mliter in volume, we add 5.0 mliter of a $5.4 \cdot 10^{-4}$ M solution of a reagent and the aliquot fraction of a solution of Pd(II) with a palladium content of 0.5–19 μg. Using solutions of HCl and NaOH, we established the necessary acidity of the medium (pH 1.0) with the help of a combined electrode and extracted twice with 5 ml of toluene. The extract was transferred into a graduated flask 25.0 mliter in volume and added toluene up to a mark. To prevent the scattering of a light flux by microresidues of water, we added anhydrous Na_2SO_4. The optical density was measured at λ = 684 nm in a cuvette with l = 5.0 cm. As a reference solution, we took toluene. By the measured values of optical density (A), we constructed a calibration plot in the $A - m_{\mathrm{Pd(II)}}$ coordinates (Fig. 3).

Table 1

Results of Extraction-Photometric Determination of Palladium with the Help of MetOBnTAN Compound in $Yb_{40}Pd_{40}Ga_{20}$ and $Yb_{40}Pd_{38}Sn_{22}$ Alloys

($n = 3$, $P = 0.95$, $\lambda = 684$ nm, pH 1.0, $l = 1.0$ cm)

Alloy	ω_{Pd}^{calc}, %	Spectrophotometric method	S_r	Voltammetric method	S_r
		$\bar{\omega}_{Pd}^{pr} \pm St_\alpha/\sqrt{n}$, %		$\bar{\omega}_{Pd}^{pr} \pm St_\alpha/\sqrt{n}$, %	
$Yb_{40}Pd_{40}Ga_{20}$	33.9	34.0 ± 1.2	0.014	34.3 ± 0.6	0.007
$Yb_{40}Pd_{38}Sn_{22}$	29.8	30.5 ± 0.9	0.012	30.2 ± 0.8	0.011

The alloys of palladium 0.1–0.2 g in mass were dissolved in a 20 mliter mixture of concentrated acids HCl and HNO_3 (3:1). In order to transform palladium ions quantitatively into the form of $[PdCl_4]^{2-}$, the mixture was boiled in a chemical pot on a sand bath for ~ 1 h (until the termination of the release of nitrogen oxides) and then evaporated up to dry salts. These salts were dissolved in a 2.5 M solution of hydrochloric acid and placed into a graduated flask 100.0 mliter in volume. The working solutions were obtained by the 10-fold dilution of the initial 1.0 M HCl solutions. To detect palladium, we selected the aliquots of working solutions under the assumption that its expected content varies within the range 0.5–19 μg. The extraction-photometric studies were carried out as described above and the concentration of Pd(II) was determined from the calibration plot. The obtained results are in good agreement with the results of evaluation of the content of palladium by the voltammetric method in a medium of ammonium [1] (see Table 1).

CONCLUSIONS

We study the interaction of ions Pd(II) with a new analytic reagent [4-methoxy-1-(5-benzylthiazol-2-yl)azonaphthalene-2-ol]. The following optimal conditions for the complex formation and extraction were determined: the ratio of the metal to the organic reagent in the complex compound should be equal to 1:2; the optimal value of $pH_{\text{p-ny Pd(II)–MetOBnTAN}}$ is 1.0; at least threefold excess of 4-methoxy-1-(5-benzylthiazol-2-yl)azonaphthalene-2-ol is required, and it is not necessary to heat the solutions. The extraction-photometric method of analytic control over complex palladium-containing objects is developed with the use of a new reagent. It is characterized by the minimum determined mass of palladium equal to 0.5 μg. The proposed method was checked for $Yb_{40}Pd_{40}Ga_{20}$ and $Yb_{40}Pd_{38}Sn_{22}$ alloys.

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