

Research Article

Spectrophotometric Determination of Palladium(II) Ions Using a New Reagent: 4-(*N*'-(4-Imino-2-oxo-thiazolidine-5-ylidene)-hydrazino)-benzoic Acid (*p*-ITYBA)

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The simple, rapid spectrophotometric method for palladium(II) ions determination using a new analytical reagent is described. The interaction of Pd(II) ions with a reagent, of the class of azolidones, 4-(*N*'-(4-imino-2-oxo-thiazolidine-5-ylidene)-hydrazino)-benzoic acid, in water medium results in the formation of a complex. The Pd(II)-*p*-ITYBA complex shows maximum absorbance at a wavelength of 450 nm. The molar absorptivity is $4.30 \times 10^3 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. The optimal pH for complex formation is 7.0. The developed method has a wide linearity range of $0.64\text{--}10.64 \mu\text{g}\cdot\text{mL}^{-1}$ for Pd(II). The detection limit is $0.23 \mu\text{g}\cdot\text{mL}^{-1}$. It was found that Co(II), Ni(II), Zn(II), Fe(III), Cu(II), Al(III), and many anions do not interfere with the Pd(II) determination. The proposed method was tested in the analysis of model solutions and successfully applied for the determination of palladium in catalyst. The obtained results show that this method can be used for serial determinations of palladium in various objects.

1. Introduction

Among the all platinum metals, the palladium has the widest practical application in various branches of industries. Palladium is used in the production of autocatalysts and jewelry, as well as in the orthopedic stomatology for the manufacture of dental prostheses. Due to its high stability and good conductivity, Pd is used in many electrical devices, which makes it an alternative to gold in galvanic elements. Palladium is also used to create drugs for cancer treatment [1–4].

In the chemical industry, palladium is a component of the scheme for the manufacture of nitric acid and petroleum. It is widely used in the production of synthetic polymers, in particular rubber and nylon. Alloys that contain palladium are used during fuel cells creation [4–6].

Significant use of palladium in the chemical industry and automotive catalysts has led to an increase in the

concentration of this metal in the objects of the environment. Due to the significant growth of palladium objects, there is a need for the development and improvement of methods for its determination. The control of the content of palladium in mineral raw materials, industrial products, and waste production is an important task of analytical chemistry [4, 6].

The spectrophotometric methods are widely used to determine the palladium. Palladium provides intense-colored complexes with hydrazones, oximes, thiosemicarbazones, dithiocarbonates, thiazolilazo, nitroso dyes, and others [2, 7, 8].

However, existing methods have a number of limitations, such as temperature control, a narrow range of pH, and low selectivity. Therefore, it is necessary to find new selective, sensitive, available reagents that would allow the determination of the content of palladium in complex objects. In analytical chemistry, organic reagents containing

the functional-analytical group $\text{NH}\dots\text{X}$ ($\text{X}=\text{S}, \text{N}, \text{O}$) are successfully used for element determination. These reagents are azolidones [9]. This class of compounds can be used not only as reagents for spectrophotometric determination of elements, but they can also be considered as analytes, since there is a problem of their determination in biological substrates because of their biological activity.

Rhodanine is used for noble and heavy metals identification since it belongs to the class of azolidones and its derivatives. We can achieve a very high sensitivity determination ($\epsilon = 10^6 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) of platinumoids [10–12] using azorhodanine, azothioproprorhodanine, and their derivatives as a reagent for the platinum metals determination in a form other than chloride. These azoheterocycles play an important role in organic chemistry [13–16].

In our previous studies, we investigated the analytical properties of several new reagents of the class of azolidones proposed for the spectrophotometric determination of a number of elements: Pd(II), Pt(IV), Ir(IV), Rh(III), Ru(IV), Co(II), Ni(II), Cu(II), Hg(II), Cd(II), and Zn(II) [17–29]. The obtained results were characterized by good metrological characteristics; therefore, we continue to synthesize new reagents of the class of azolidones and investigate them as analytical reagents. This work is devoted to the research of palladium ion interaction with reagent 4-(N' -(4-imino-2-oxo-thiazolidine-5-ylidene)-hydrazino)-benzoic acid (*p*-ITYBA), which is a representative of the azolidones and was synthesized for the first time by our research group [30].

2. Materials and Methods

2.1. Apparatus. All spectrophotometric measurements were performed using a computerized spectrophotometer ULAB 108-UV with 1.0 cm quartz cuvettes. Acidity of the solution was measured by using a pH-meter model pH-150M equipped with a combination glass electrode. A CLA-03 oscillogpolarograph and computerized polarographic setup equipped with linear potential scan in three-electrode cell (dropping mercury electrode: indicator electrode; saturated calomel electrode: reference electrode; and platinum: auxiliary electrode) were used for voltammetric measurements. ^1H NMR spectra were obtained using a spectrometer Varian Mercury VX-400 (400 MHz) in $\text{DMSO}-d_6$ with tetramethylsilane as reference.

2.2. Reagents. All reagents used were of analytical grade.

A stock solution of palladium(II) was prepared by dissolving this metal (99.999% purity) in a mixture of concentrated nitric and hydrochloric acids (1 : 3, v/v) by heating on a sand bath. A standard working solution of Pd(II) was prepared by diluting the stock solution with $1.0 \text{ mol}\cdot\text{L}^{-1}$ HCl.

A stock solution of 4-(N' -(4-imino-2-oxo-thiazolidine-5-ylidene)-hydrazino)-benzoic acid was prepared by dissolving the purified reagent in pure dimethyl sulfoxide (DMSO). The working solution was prepared by diluting the stock solution in DMSO.

Solutions of NaOH ($4.0 \text{ mol}\cdot\text{L}^{-1}$) and NaCl ($2.0 \text{ mol}\cdot\text{L}^{-1}$) were prepared by dissolving 39.997 g and 29.22 g,

respectively, in distilled water in a 250.0 mL volumetric flask. The solution of HCl was prepared by dilution of concentrated acid. The universal buffer solution (UBS) was made by mixing solutions of acetic, boric, and phosphoric acids. Standard solutions of metals ($M = \text{Yb(III)}, \text{Ga(III)}, \text{Au(III)}, \text{Fe(III)}, \text{Ni(II)}, \text{Co(II)}, \text{Mn(II)}, \text{Cd(II)}, \text{Pb(II)}, \text{Zn(II)}, \text{Pt(IV)}, \text{Rh(III)}, \text{Ir(IV)}, \text{Ru(IV)}, \text{Cu(II)}, \text{Cr(III)}, \text{Ca(II)}, \text{Mg(II)}, \text{Ba(II)}, \text{and Al(III)}$) were prepared by dissolving their salts in distilled water or dilute acids (HCl or HNO_3). Solutions of anions ($\text{EDTA}, \text{F}^-, \text{NO}_3^-, \text{SiO}_3^{2-}, \text{Cit}^{3-}, \text{Tart}^{2-}, \text{C}_2\text{O}_4^{2-}, \text{and Sal}^-$) were prepared by dissolving the appropriate sodium salts in distilled water.

2.3. General Procedure for Determination of Pd(II) Ions. To sample solutions containing $0.64\text{--}10.64 \mu\text{g}\cdot\text{mL}^{-1}$ of Pd(II) in a 25.0 mL volumetric flask, 0.75 mL of $2.5 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ *p*-ITYBA, 1.25 mL of $2.0 \text{ mol}\cdot\text{L}^{-1}$ NaCl, 1.0 mL of $0.5 \text{ mol}\cdot\text{L}^{-1}$ UBS, and distilled water (~ 20 mL) were added. Then pH was adjusted by NaOH to $\text{pH} = 7.0$, and distilled water was added to complete volume. The absorbance of the Pd(II)-*p*-ITYBA complex at 450 nm against a reagent blank was measured.

2.4. Effect of Reagent Concentration. Various volume ($0.125\text{--}12.5$ mL) of $1.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ *p*-ITYBA was added to the solution containing 0.5 mL of $2.5 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ Pd(II). Then, 1.25 mL of $2.0 \text{ mol}\cdot\text{L}^{-1}$ NaCl, 1.0 mL of $0.5 \text{ mol}\cdot\text{L}^{-1}$ UBS, and distilled water ~ 20 mL were added. The pH was adjusted to $\text{pH} = 7.0$ by NaOH and diluted to a volume of 25.0 mL with water. The absorbance was measured in a 1.0 cm cell at 450 nm.

2.5. Determination of the Composition of the Pd(II)-*p*-ITYBA Complex. The mole-ratio method was performed in the following way: into a series of 25.0 mL volumetric flasks, an aliquot ($0.125\text{--}6.25$ mL) of $1.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ Pd(II) solution, *p*-ITYBA solution with fixed concentration (0.5 mL of $2.5 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$), 1.25 mL of $2.0 \text{ mol}\cdot\text{L}^{-1}$ NaCl, 1.0 mL of $0.5 \text{ mol}\cdot\text{L}^{-1}$ UBS, and distilled water ~ 20 mL were added. The pH was adjusted to $\text{pH} = 7.0$ by adding NaOH and diluted up to the mark with water. Then, the absorbance at 450 nm was measured.

In Job's method of continuous variation, the equimolar solutions of Pd(II) and *p*-ITYBA ($1.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) were used. Then, 1.25 mL of $2.0 \text{ mol}\cdot\text{L}^{-1}$ NaCl, 1.0 mL of $0.5 \text{ mol}\cdot\text{L}^{-1}$ UBS, and distilled water (~ 20 mL) were added, and the pH was adjusted to 7.0 by NaOH. The absorbance values were recorded at 450 nm.

2.6. Procedure of Catalyst Preparation for Pd(II) Determination. The sample of catalyst was dissolved in a mixture of concentrated nitric and hydrochloric acid (1 : 3, v/v) by heating on a sand bath with further decantation. Pd(II) ions were converted to the chloride form by evaporation of the resulting solution to wet salts and the addition of 10.0 mL of concentrated hydrochloric acid until the nitrogen oxides were lost [31]. After that, the resulting solution was

transferred quantitatively into a volumetric flask of 50.0 mL and brought to the mark with distilled water. The working solution was prepared by dilution of the stock 100 times. Suitable aliquots of this solution were used for the determination of palladium according to the recommended procedure.

3. Results and Discussion

In this work, a new reagent from the class of azotiazolidones 4-(*N'*-(4-imino-2-oxo-thiazolidine-5-ylidene)-hydrazino)-benzoic acid was used for analytical researches. ^1H NMR (400 MHz, $\text{DMSO-}d_6$; δ , ppm): 7.99 (d, $J = 8.5$ Hz, 2H, C_6H_4), 8.12 (d, $J = 8.5$ Hz, 2H, C_6H_4), 9.21 (s, 1H, NH), 9.39 (s, 1H, NH), 11.15 (s, 1H, NH), 13.61 (s, 1H, COOH). Structural formula of *p*-ITYBA is shown in Figure 1.

This reagent is a crystalline powder of yellow-sand color. The melting point is 543 K. It is poorly soluble in water and ethanol, but is well soluble in dimethylformamide and dimethyl sulfoxide.

The maximum absorption of a reagent does not depend on the acidity of the medium and corresponds to a wavelength of 390 nm. The imino group is hydrolyzed in a highly alkaline medium ($\text{pH} > 11.0$). Our previous work [30] provides more details about the spectral characteristics of this reagent.

3.1. Investigation of the Formation of the Pd(II)-*p*-ITYBA Complex. It was found that Pd(II) ions form a yellow-orange complex compound with *p*-ITYBA. The electronic absorption spectra of dye solutions and the complex compound Pd(II)-*p*-ITYBA are shown in Figure 2. At a pH 1.0–10.0, there is a decrease in the maximum of absorption of the reagent when palladium(II) was added to *p*-ITYBA. This indicates that there is an interaction between palladium(II) ions and *p*-ITYBA. At higher values of pH, this effect is not observed. We can also see the formation of the shoulder of absorption in the range of wavelengths 430–480 nm. All further studies of complex formation were carried out at a wavelength of 450 nm, where the maximum difference between the absorption of the complex and the reagent is observed.

3.2. Effect of pH. Figure 3 shows the results of studies of the pH effect on the maximum yield of colored complex compound Pd(II)-*p*-ITYBA against sodium chloride background. The formation of complex Pd(II) with *p*-ITYBA is observed in a wide range of pH. The maximum absorbance of the compound Pd(II)-*p*-ITYBA is achieved at $\text{pH} = 7.0$.

3.3. Effect of Heating Time. The results of studies have shown that the complexation of palladium(II) ions with *p*-ITYBA occurs at room temperature (~ 291 – 296 K) immediately after establishing the acidity of the medium. The heating of solutions in a boiling water bath (~ 371 K) causes a decrease in the absorption of solutions, but the complex compound Pd(II)-*p*-ITYBA is not completely

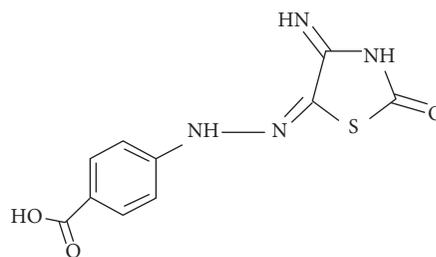


FIGURE 1: Structure of the 4-(*N'*-(4-imino-2-oxo-thiazolidine-5-ylidene)-hydrazino)-benzoic acid.

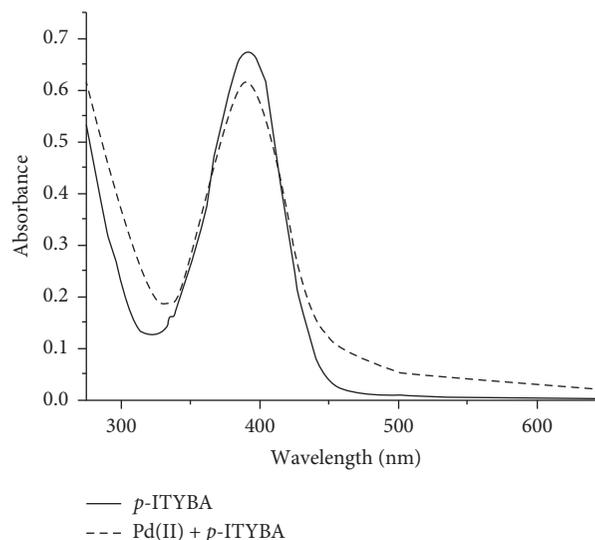


FIGURE 2: Absorbance spectra of the *p*-ITYBA and Pd(II)-*p*-ITYBA complex ($C_{p\text{-ITYBA}} = 5.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{Pd(II)}} = 2.50 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{NaCl}} = 0.10 \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{UBS}} = 0.020 \text{ mol}\cdot\text{L}^{-1}$; $\text{pH} = 7.0$; $l = 1.0 \text{ cm}$).

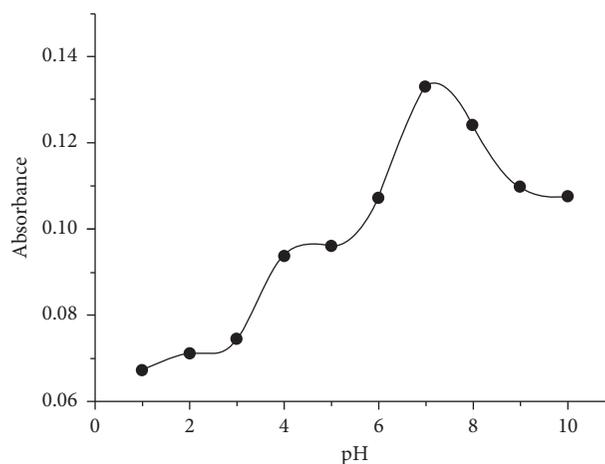


FIGURE 3: Effect of pH on the absorbance of the Pd(II)-*p*-ITYBA complex at a wavelength of 450 nm ($C_{p\text{-ITYBA}} = 5.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{Pd(II)}} = 2.50 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{NaCl}} = 0.10 \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{UBS}} = 0.020 \text{ mol}\cdot\text{L}^{-1}$; $l = 1.0 \text{ cm}$).

destroyed even when heated for 60 min (Figure 4). Absorption of the obtained product remains constant for more than 48 h.

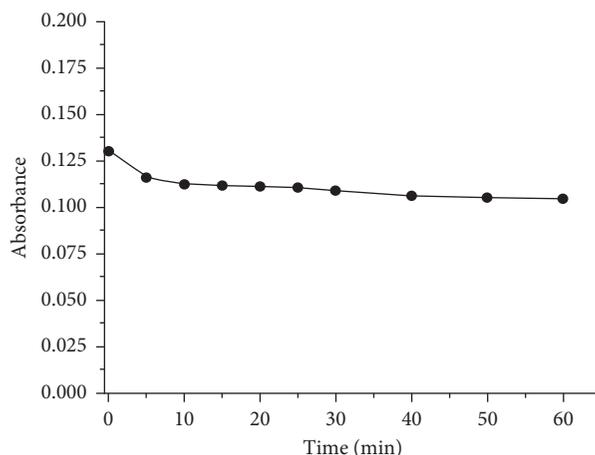


FIGURE 4: Effect of heating time on the absorbance of the Pd(II)-*p*-ITYBA complex at a wavelength of 450 nm ($C_{p\text{-ITYBA}} = 5.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{Pd(II)}} = 2.50 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{NaCl}} = 0.10 \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{UBS}} = 0.020 \text{ mol}\cdot\text{L}^{-1}$; $l = 1.0 \text{ cm}$; $t \sim 98^\circ\text{C}$).

TABLE 1: Selectivity of Pd(II) spectrophotometric determination using *p*-ITYBA ($C_{\text{Pd(II)}} = 2.50 \cdot 10^{-5} \text{ mol}\cdot\text{L}^{-1}$; $C_{p\text{-ITYBA}} = 7.50 \cdot 10^{-5} \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{NaCl}} = 0.10 \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{UBS}} = 0.020 \text{ mol}\cdot\text{L}^{-1}$; $\text{pH} = 7.0$; $l = 1 \text{ cm}$; $\lambda = 450 \text{ nm}$).

Foreign ion	Molar ratio ion: Pd(II)	Foreign ion	Molar ratio ion: Pd(II)
Pt(IV)	1	Cu(II)	>100
Rh(III)	1.25	Cr(III)	10
Ir(IV)	1	Ca(II)	>100
Ru(IV)	2	Mg(II)	>100
Yb(III)	5	Ba(II)	>100
Ga(III)	10	Al(III)	>100
Au(III)	15	EDTA	>100
Fe(III)	>100	F ⁻	>100
Ni(II)	75	NO ₃ ⁻	>100
Co(II)	>100	SiO ₃ ²⁻	>100
Mn(II)	10	Cit ³⁻	>100
Cd(II)	25	Tart ²⁻	>100
Pb(II)	10	C ₂ O ₄ ²⁻	>100
Zn(II)	50	Sal ⁻	>100

3.4. *Stoichiometric Ratio of Pd(II)-p-ITYBA.* The ratio of components in the system Pd(II)-*p*-ITYBA was determined by two methods: continuous variations (Job's method) and the mole-ratio method. These methods confirm the formation of a complex with the ratio of components Pd(II) : *p*-ITYBA = 1 : 1. It was calculated that the formal stability constant of the complex relative to the palladium aqua hydroxychloride complex is 1.96×10^5 . The 3-fold excess of the reagent is optimal for the maximum yield of the colored compound of Pd(II) with *p*-ITYBA.

3.5. *Calibration Curve.* The analytical signal of palladium(II) determination using *p*-ITYBA linearly depends on the concentration of metal in the solution and is described by the equation $\Delta A = (0.009 \pm 0.001) + (0.0416 \pm 0.0004) \times C$, where C is the concentration of Pd(II) in $\mu\text{g}\cdot\text{mL}^{-1}$ (the correlation coefficient is 0.9997). From the calibration curve, it was found that Beer's law is obeyed over the Pd(II) concentration range of 0.64 to 10.64 $\mu\text{g}\cdot\text{mL}^{-1}$. The detection

limit is 0.23 $\mu\text{g}\cdot\text{mL}^{-1}$. The molar absorptivity is $4.30 \times 10^3 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.

3.6. *Effect of Foreign Ions.* As shown in the literature [7, 8, 20, 32–37], most spectrophotometric methods of palladium determination are characterized by not very high selectivity towards such cations as Ni(II), Co(II), Cu(II), Fe(III), Fe(II), Ag(I), REE (rare earth elements), platinum metals, and others. We investigated the effect of platinum metals and heavy and alkaline earth metal ions that can be present in the studied samples or can be introduced during dissolution. Also typical masking anions (fluoride, citrate, tartrate, and salicylate ions) were investigated for the possibility of palladium(II) determination using *p*-ITYBA (see Table 1).

It was found that cations Ca(II), Mg(II), Ba(II), Pb(II), Cd(II), Ni(II), Co(II), Zn(II), Al(III), Fe(III), and Cu(II) do not interfere in 25-100-fold excess. But, small amounts of Rh(III), Pt(IV), Ir(IV), and Yb(III) ions affect Pd(II)

TABLE 2: Comparison of the present method with other spectrophotometric methods for Pd(II) determination.

Reagent [references]	Conditions	λ_{\max} , nm	ϵ_{\max} , L·mol ⁻¹ ·cm ⁻¹	M : L	Linear range, $\mu\text{g}\cdot\text{mL}^{-1}$	Interfering ions
3,4-Dihydroxy-benzaldehydeisonicotinoylhydrazone [3]	pH = 3.0, acetate buffer	380	5.3×10^3	1 : 1	0.5–20.0	Cu ²⁺
Dimethylglyoxime [7]	2 mol·L ⁻¹ HCl or H ₂ SO ₄ , CHCl ₃ ; 0.8 mol·L ⁻¹ HNO ₃ , pH = 1.0, CHCl ₃	270; 370	9.0×10^3 ; 1.9×10^3	1 : 2	25–125; 100–800	Pt ²⁺ , Fe ²⁺ , Ir ³⁺ , Au ³⁺
A-Furildioxim [7]	0.1–1.4 mol·L ⁻¹ HCl, CHCl ₃	380	2.2×10^4	1 : 2	1–3	–
Arsenazo III [7]	pH 3.4–5.9	630	4.2×10^4	1 : 1, 2 : 1	1.16–3.0	Cu ²⁺ , Ni ²⁺ , Co ²⁺
Nitroso-R-salt [7]	pH = 5.6 to 0.1 mol·L ⁻¹ HCl; 0.05 mol·L ⁻¹ HNO ₃ , 2.6 mol·L ⁻¹ CH ₃ COOH	510; 520–560	1.2×10^4 ; 9.7×10^4	1 : 2	1.3–4.3; 0.1–2.6	Co ²⁺ , Cl ⁻
B-Nitroso- α -naphthol [7]	pH = 1.0–2.0, CHCl ₃ , toluene	308; 385; 370	2.2×10^4	1 : 2	1–5; 0.1–10	Cu ²⁺ , Co ²⁺ , Ni ²⁺ , Cr ³⁺ , Fe ³⁺ , CN ⁻ , Pb ²⁺ , Bi ³⁺ , Cl ⁻ REE
Palladiazol [7]	pH = 3.5, <i>n</i> -butanol	640, 675	5.7×10^4	1 : 1, 2 : 1	0.2–5.0	Cu ²⁺ , Co ²⁺ , V ⁵⁺ , Ag ⁺ , Fe ³⁺
4-(4'-Antipyril azo)-2-bromo phenol [8]	pH = 4.0–7.0	498	2.1×10^3	1 : 2	0.2–3	–
Sulphochlorophenol-azorhodanine [10–12]	8 mol·L ⁻¹ H ₃ PO ₄ + 5 mol·L ⁻¹ H ₂ SO ₄ ; 1 mol·L ⁻¹ HCl, 1–2 h	520; 520	1.2×10^5 ; 5.0×10^4	–	–	Pt ⁴⁺ , Rh ³⁺
5-Hydroxyimino-4-imino-1,3-thiazolidin-2-one [18, 20]	pH = 5.0, acetate buffer, 10 min (~98°C)	350	5.9×10^3	1 : 1	0.6–6.4	Pt ⁴⁺ , Ru ⁴⁺ , Rh ³⁺ , Ir ⁴⁺ , Fe ³⁺ , Cu ²⁺
4-(<i>N</i> '-(4-Imino-2-oxo-thiazolidin-5-ylidene)-hydrazino)-benzene-sulfonic acid [23]	pH = 7.6–8.3	438	7.5×10^3	1 : 2	0.2–2.2	Ir ⁴⁺ , Ru ⁴⁺
1-(2-Benzothiazolyl-azo)-2-hydroxy-3-naphthoic acid [32]	5.0 mol·L ⁻¹ HCl and cetyl trimethyl ammonium bromide	669	2.61×10^5	1 : 2	0.02–0.85	Ni ²⁺ , Co ²⁺
Cefixime [33]	Methanol-distilled water medium, pH = 2.6 Na ₂ HPO ₄ -citric acid buffer	352	1.224×10^4	2 : 1	0.75–16.50	Cu ²⁺ , Zn ²⁺ , Cd ²⁺ , Ni ²⁺
2-(2-Quinolylazo)-5-diethylaminobenzoic acid [34]	1.0 mol·L ⁻¹ HCl, 1% cetyl trimethyl-ammonium bromide	625	1.51×10^5	1 : 2	0.01–0.6	Co ²⁺ , Ni ²⁺
Benzoyloxybenzaldehydethiosemicarbazone [35]	pH = 5.0, cyclohexanol	365	4.0×10^3	1 : 1	5–60	Ni ²⁺ , Cu ²⁺
4-(2'-Furalidene-imino)-3-methyl-5-mercapto-1,2,4-thiazole [36]	pH = 5.4, <i>n</i> -butanol	410	1.4×10^3	1 : 1	17–50	Cu ²⁺ , Cr ⁺⁶ , Mn ⁺⁷ , S ₂ O ₃ ²⁻ , CH ₄ N ₂ S
4-(6-Bromo-2-benzothiazolylazo) pyrogallol [37]	Dimethylformamide	580	–	–	0.6–15.0	–
4-(<i>N</i> '-(4-Imino-2-oxo-thiazolidine-5-ylidene)-hydrazino)-benzoic acid	pH = 7.0, universal buffer	450	4.3×10^3	1 : 1	0.64–10.64	Pt ⁴⁺ , Ru ⁴⁺ , Rh ³⁺ , Ir ⁴⁺

determination. The most influence of the metals of the platinum group can be explained by the similar electronic structure of the outer electronic levels of platinum metals, which compete with the palladium ions in the process of formation of a colored complex compound. The anions that

were studied do not affect the determination of Pd(II), even when present in 100-fold excess, so they can be used to mask certain metals to improve selectivity.

This method has higher selectivity than most of the earlier reported spectrophotometric methods (Table 2)

TABLE 3: Determination of Pd(II) with *p*-ITYBA in synthetic solutions ($C_{p\text{-ITYBA}} = 7.50 \cdot 10^{-5} \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{NaCl}} = 0.10 \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{UBS}} = 0.020 \text{ mol}\cdot\text{L}^{-1}$; $V = 25 \text{ mL}$; $\text{pH} = 7.0$; $l = 1 \text{ cm}$; $\lambda = 450 \text{ nm}$; $n = 3$, $P = 0.95$).

Synthetic solutions composition, μg	Added Pd(II), μg	Found Pd(II), $\bar{x} \pm ((S \times t_{\alpha})/\sqrt{n})$, μg	S_r , %
60.7 Ir(IV) + 32.16 Rh(III)	66.5	69.8 ± 5.6	3.2
63.17 Ru(IV) + 60.96 Pt(IV)	66.5	69.1 ± 4.8	2.8
32.16 Rh(III) + 63.17 Ru(IV)	66.5	65.3 ± 4.7	2.9

towards many cations and anions, such as: Rh(III), Ru(IV), Ga(III), Au(III), Cu(II), Co(II), Ni(II), and others.

3.7. Determination of Pd(II) in Model Solutions. The correctness of spectrophotometric methods for the Pd(II) determination using *p*-ITYBA was verified by analyzing model solutions in the “added-found” method. The results are shown in Table 3.

The main problem of photometric methods for the palladium determination is their insufficient selectivity towards platinum metals. In order to show a possibility of palladium determination using *p*-ITYBA in the presence of platinum metals ions, we added them into the model solutions. The concentration of palladium in the studied solutions was determined by a calibration curve.

As can be seen from the obtained results, there are good reproducibility and accuracy (no systematic error); therefore, the developed method for the palladium determination using *p*-ITYBA can be effectively used in the analysis of various industrial and natural objects.

3.8. Determination of Palladium in a Catalyst. Palladium and its alloys are often used as catalysts in chemical reactions, in particular in the reactions of hydration and the production of pharmaceutical preparations [38]. Palladium exhibits better catalytic properties in the processes of hydrogenation of organic substances than nickel [39].

The developed method for spectrophotometric determination of Pd(II) by means of *p*-ITYBA was used to determine the contents of the palladium in the palladium-rhodium catalyst on a ceramic basis. As the amount of rhodium in this catalyst is about 0.1% [31], it did not interfere with the determination. There was no need to use masking agents, since rhodium and silicate ions do not interfere with the determination of palladium in large quantities. The results of the analysis are presented in Table 4.

As can be seen from Table 4, the results of palladium determination using the spectrophotometric method are well consistent with its content determined by the voltammetric method per reduction peak of its ammonium complexes [7]. The value of the relative standard deviation does not exceed the error in spectrophotometry; therefore, the presence of ions in the solution does not affect the results of the analysis.

The developed method, which is described in this paper, has better selectivity when compared to some

TABLE 4: Results of spectrophotometric determination of palladium(II) in a catalyst using *p*-ITYBA ($C_{p\text{-ITYBA}} = 7.50 \cdot 10^{-5} \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{NaCl}} = 0.10 \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{UBS}} = 0.020 \text{ mol}\cdot\text{L}^{-1}$; $\text{pH} = 7.0$; $\lambda = 450 \text{ nm}$; $l = 1.0 \text{ cm}$; $n = 3$; $P = 0.95$).

Method	$\omega_{Pd}^{pr} \pm ((S \times t_{\alpha})/\sqrt{n})$, %	S_r , %
Spectrophotometry with <i>p</i> -ITYBA	2.18 ± 0.08	1.4
Voltammetry	2.06 ± 0.09	1.8

spectrophotometric methods shown in Table 2. This method is rapid, sufficiently sensitive, and does not need extraction or use of masking agents.

4. Conclusions

The proposed method of spectrophotometric determination of Pd(II) using *p*-ITYBA is simple, rapid, reproducible, sufficiently sensitive, selective, and inexpensive. This method does not require the use of heating and extraction, which greatly simplifies the determination. These advantages allow using the developed method in routine analysis for Pd(II) determination in various objects.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

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Supplementary Materials

The supplemental information includes additional figures showing the composition of the Pd(II)-*p*-ITYBA complex and ^1H NMR spectrum. (*Supplementary Materials*)

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