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Spectrophotometric Studies of 4-[N'-(4-Imino-2-oxo-thiazolidin-5-ylidene)-hydrazino]-benzenesulfonic acid as a Reagent for the Determination of Palladium

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Abstract

The spectrophotometric behavior of a new, first-time synthesized reagent – 4-[*N'*-(4-imino-2-oxo-thiazolidin-5-ylidene)-hydrazino]-benzenesulfonic acid (ITHBA), has been investigated. A simple, rapid, accurate, selective and sensitive method for the spectrophotometric determination of Pd(II) ions using this reagent was developed. The optimal conditions for the formation of the complexes were found. The molar absorptivity at $\lambda = 438$ nm is 7.5×10^3 L mol^{-1} cm^{-1}, and Beer's law is observed for the concentrations ranging from 0.2–2.2 µg mL^{-1} Pd(II). The effects of extraneous ions were investigated. The method proved to be successful in determination of palladium in the intermetallides and resistor. The accuracy of spectrophotometric palladium assay in real objects with 4-[*N'*-(4-imino-2-oxo-thiazolidin-5-ylidene)-hydrazino]-benzenesulfonic acid has been confirmed by voltammetric or atomic absorption spectroscopy method.

Keywords: Palladium(II); 4-[*N'*-(4-imino-2-oxo-thiazolidin-5-ylidene)-hydrazino]-benzenesulfonic acid; spectrophotometry; azolidones; intermetallides; resistor.

1. Introduction

Palladium is widely used in various fields, especially in catalysis, petroleum, electronics. Owing to its corrosion resistant nature and alloying ability, palladium and its alloys are used in dental and medicinal devices, and in jewelry manufacture.[1,2] The increasing area of the palladium applications stimulates the development of simple and rapid methods for the quantitative determination of palladium(II). For the determination of palladium at micro levels, several analytical techniques such as atomic absorption spectrometry, inductive coupled plasma atomic emission, ion chromatography, X-ray fluorescence spectrometry, and neutron activation are used. However, spectrophotometric methods have gained popularity for palladium determination as advantageous due to their simplicity and low operating costs. A wide variety of spectrophotometric reagents, such as azo dyes, rhodanine derivatives, porphyrin ligands, thiourea derivatives, 8-aminoquinoline derivatives and nitroso dye have been developed for the determination of palladium.[3–20] Many of these reagents have some disadvantages, such as low sensitivity, poor selectivity, durability, extraction, necessity to use high temperature to promote the complexation reaction.

In our previous studies the interaction of Pd(II), Rh(III), Pt(IV), Ru(IV), Ir(IV) ions with a new reagent – 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one, which belongs to the class of azolidones, was investigated. Spectrophotometric methods for determination of platinum metals with this reagent were developed.[21–24]

Azolidones as a new class of organic compounds were discovered in the middle of the 20th century.[25] These reagents are widely used in medicine, due to their wide range of biological activity.[26,27] In this work, we investigated the interaction of palladium(II) ions with first-time synthesized reagent – 4-[*N'*-(4-imino-2-oxo-thiazolidin-5-ylidene)-hydrazino]-benzenesulfonic acid (ITHBA). This reagent also belongs to the class of azolidones and has a similar structure to 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one.

2. Experimental

2. 1. Apparatus

Absorption spectra were obtained using 108 UV/ULAB spectrophotometer and 1.0 cm quartz cells. Absorption was also measured at KFK-3 using 5.0 cm glass cells. All absorbance measurements were performed at ~20 °C.

Voltammetric measurements were performed using an oscillopolarograph CLA-03 with a digital setup equipped with a computer and a three-electrode cell using linear potential sweep. A dropping mercury electrode, a platinum electrode and a saturated calomel electrode served as and indicator, auxiliary, and reference electrodes, respectively.

Atomic absorption measurements were performed using the atomic absorption spectrophotometer AAS-1N at λ = 246.5 nm in the propane-butane-air flame. The monochromatic radiation source was a hollow-cathode lamp produced by "Narva".

^{1}H NMR spectra of compounds dissolved in DMSO-d$_6$ were registered on the spectrometer Bruker Avance (400 MHz), internal reference of TMS.

The pH measurements were carried out with pH-meter model pH-150 M equipped with a combination glass electrode.

2. 2. Reagents

All aqueous solutions for experiments have been prepared using distillated water. All chemicals used in the research were of analytical grade.

The stock solution of Pd(II) was prepared by dissolving metallic palladium (99.999 %) in a mixture of concentrated HNO$_3$ and HCl (1:3). The standard working Pd(II) solutions were prepared by diluting an aliquot of palladium(II) stock solution in 1.0 mol L^{-1} HCl.

The solution of 4-[*N*'-(4-imino-2-oxo-thiazolidin-5-ylidene)-hydrazino]-benzenesulfonic acid was prepared by dissolving the exact mass of the reagent in water. ITHBA was synthesized by the following procedure: in a 100 ml round-bottomed flask, fitted with a mechanical stirrer 1.16 g (10 mmol) 4-iminotiazolidone-2[28] and 4.0 g of sodium acetate in 80 mL of acetic acid were placed. The mixture was cooled till 0 °C and the diazonium salt (prepared by using 2.1 g (10 mmol) 4-aminobenzenesulfonic acid) was added. The mixture was left for 12–18 h, and then was poured into 200–300 mL of water. The precipitate was filtered, washed with water, and dried at 60 °C. Yield 85 %. ^{1}H NMR (400 MHz, DMSO-d6; δ, ppm): 7.40 d (*J* = 6.4 Hz, 2H, C$_6$H$_4$), 7.51 d (*J* = 6.4 Hz, 2H, C$_6$H$_4$), 8.95 s (H, NH), 9.18 s (H, NH), 10.42 s (H, NH). The purity of reagent is 100 %, which was determined by chromatography-mass spectrometry.

The solutions of Na$_2$B$_4$O$_7$, NaOH were prepared by dissolving of appropriate amount of Na$_2$B$_4$O$_7$, NaOH in

water. The HCl solution was prepared by dilution of concentrated HCl. The universal buffer solutions (UBS) were made by mixing solutions of phosphoric, boric and acetic acids.[29]

2. 3. Procedure

Protolytic equilibria experiment

1.0 mL of 1.0×10^{-3} mol L^{-1} ITHBA, 2.0 mL universal buffer (1.5 mol L^{-1}), and 1.25 mL of 2.0 mol L^{-1} NaCl were placed in a 25.0 mL standard flask and the distilled water was added to a total volume of ~15–20 mL. Then the pH was adjusted by means of 4.0 mol L^{-1} NaOH addition (pH = 2.0–12.0). Next, distilled water was added to complete the volume and its absorption spectrum was measured. For pH = 1.0, the solution was prepared as follows: 1.0 mL of 1.0×10^{-3} mol L^{-1} ITHBA, 1.25 mL of 2.0 mol L^{-1} NaCl solutions were poured into 25.0 mL flask and the distilled water was added to a total volume of ~15–20 mL; then the pH was adjusted by means of 6.0 mol L^{-1} HCl addition; after that, distilled water was added to complete the volume and its absorption spectrum was measured.

Interaction of Pd(II) with ITHBA in water solution

The 1.0 mL of 1.0×10^{-3} mol L^{-1} ITHBA, 1.11 mL of 4.5×10^{-4} mol L^{-1} Pd(II) and 1.25 mL of 2.0 mol L^{-1} NaCl were put into 25.0 mL flasks and the distilled water was added to a total volume of ~15–20 mL. Then the pH was adjusted by means of addition of NaOH and HCl diluted solutions. After that, distilled water was added to complete the volume and its absorption spectrum was measured.

Influence of concentration and nature of the anion

The 1.0 mL of 1.0×10^{-3} mol L^{-1} ITHBA, 1.11 mL of 4.5×10^{-4} mol L^{-1} Pd(II), and the solution of sodium salt with the studied anion were put into 25.0 mL flasks and the distilled water was added to a total volume of ~15–20 mL. Then the pH (pH = 8.0) was adjusted by means of addition of HCl and NaOH diluted solutions. After that, distilled water was added to complete the volume, and the absorbance of the solution was measured relatively to a blank solution at 438 nm. The blank solution contained all the components of the sample with the exception of Pd(II).

Effect of extraneous ions

The 2.5 mL of 1.0×10^{-3} mol L^{-1} ITHBA, 0.5 mL of 4.5×10^{-4} mol L^{-1} Pd(II), 12.5 mL of 0.1 mol L^{-1} Na$_2$B$_4$O$_7$, and appropriate volume of the solution of foreign ion, were put into 25.0 mL flasks and the distilled water was added to a total volume of ~15–20 mL. Then the pH was adjusted by means of addition of HCl and NaOH diluted solutions (pH = 8.0). After that, distilled water was added to complete the volume, and the absorbance of

the solution was measured relative to a blank solution at 438 nm. The blank solution contained all the components of the sample with the exception of Pd(II).

The procedure of palladium assay in the intermetallides

The samples of intermetallides (0.1–0.2 g of the intermetallic alloy) were dissolved in 10–20 mL of a mixture of concentrated HCl and HNO₃ (3:1). The resulting mixture was boiled in a beaker in a sand bath for 1–2 h. The dry residue was dissolved in a 2.5 mol L⁻¹ HCl solution and transferred into a 100.0 mL volumetric flask. The working solution was prepared by diluting an aliquot of the stock solution 10 times by 1.0 mol L⁻¹ HCl. For palladium determination 0.5–1.0 mL of analytes' aliquots has been taken and undergone the proper analytical procedure according to the following scheme. The necessary quantities of solutions of ITHBA, the analytes' aliquots and sodium tetraborate were placed into a 25.0 mL volumetric flask and the distilled water was added to a total volume of ~15–20 mL. Then the pH was adjusted by means of addition of NaOH and HCl diluted solutions. After that, distilled water was added to complete the volume and the absorbance measurement was carried out against blank solution at 438 nm in 5.0 cm cells. The palladium content was evaluated using the method of a normal calibration curve (all tests were performed at the alpha level of 5 %; the number of individual measurements n was 3; confidence limits were calculated as means $\pm$ St$_\alpha$/√n, where S is a standard deviation and t$_\alpha$ = 4.30).

The procedure of palladium assay in the resistor

All parts of the resistor, containing platinum group elements, have been transferred into a beaker and dissolved in 20 mL of a mixture of concentrated HCl and HNO₃ (3:1) by heating on a sand bath during 1 h with further decantation. Obtained palladium(II) was transferred into chloride form by means of evaporation of the solution into wet salts and adding 10.0 mL of concentrated HCl until nitrogen oxides stopped discharging. Then the content of the beaker was quantitatively transferred into a 50.0 mL volumetric flask and brought to the mark with distilled water. The working solution was prepared by diluting stock solution 10 times with 1.0 mol L⁻¹ hydroch-

loric acid. For palladium determination 0.5 mL of analytes' aliquots has been taken and undergone the proper analytical procedure according to the following scheme. The necessary quantities of solutions of ITHBA, the analytes' aliquots and sodium tetraborate were placed into a 25.0 mL volumetric flask and distilled water was added to a total volume of ~15–20 mL. Then the pH was adjusted by means of addition of NaOH and HCl diluted solutions. After that, distilled water was added to complete the volume and the absorbance measurement was carried out against blank solution at 438 nm in 5.0 cm cells. The palladium content was evaluated using the method of a normal calibration curve (all tests were performed at the alpha level of 5 %; the number of individual measurements n was 3; confidence limits were calculated as means $\pm$ St$_\alpha$/√n, where S is a standard deviation and t$_\alpha$ = 4.30).

3. Results and Discussion

## 3. 1. Protolytic Equilibria of ITHBA in Water Medium

The analitical reagent, 4-[*N*'-(4-imino-2-oxo-thiazolidin-5-ylidene)-hydrazino]-benzenesulfonic acid, was prepared by azo coupling reaction of 4-iminothiazolidin-2-one with diazotized sulfanilic acid (scheme 1):

It was supposed that 4-(4-imino-2-oxo-thiazolidin-5-ylazo)-benzenesulfonic acid (**B**) or 4-(4-amino-2-oxo-2,3-dihydrothiazol-5-ylazo)-benzenesulfonic acid (**C**) has formed, but from NMR spectroscopy it was apparent that the prepared compound is a tautomeric form **A** (scheme 2). In the ¹H NMR spectra there are free singlets (δ: 8.95. ppm , 9.18 ppm and 10.42 ppm) belonging to an N-H groups of tautomere **A**.

We investigated the spectrophotometric characteristics of this reagent. Absorption maximum of the ITHBA depends on pH (Fig. 1). At pH = 1.0–9.0 two absorption maxima are observed at λ = 256 nm and λ = 382 nm (pH = 1.0 λ = 390 nm), pH = 10.0 – three absorption bands: λ = 256 nm, λ = 382 nm and λ = 460 nm, pH = 11.0: λ = 256 nm, λ = 286 nm, λ = 382 nm and λ = 460 nm, pH = 12.0: λ = 250 nm, λ =286 nm and
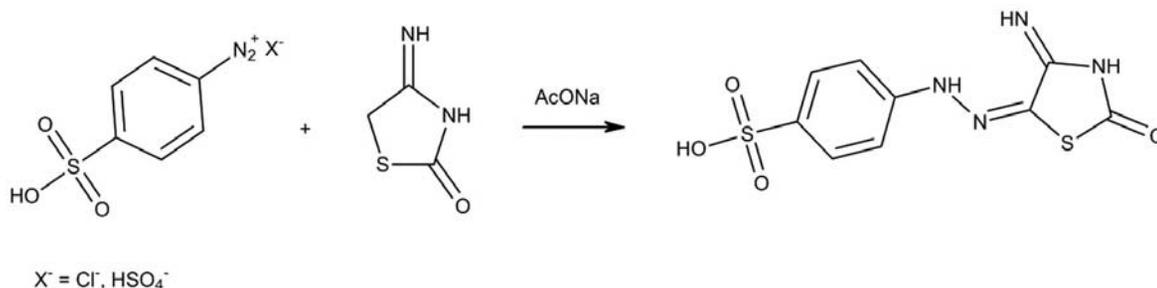
Scheme 1. Synthesis of 4-[N'-(4-Imino-2-oxo-thiazolidin-5-ylidene)-hydrazino]-benzenesulfonic acid
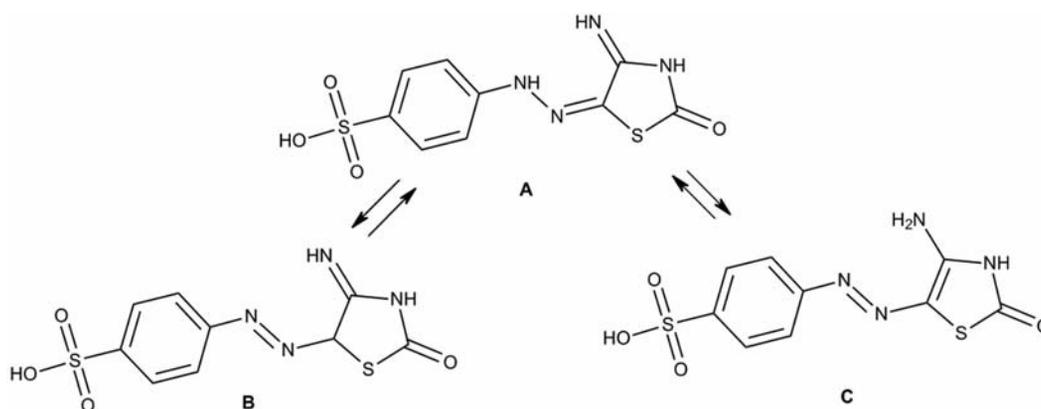
Scheme 2. Tautomeric forms of ITHBA

λ = 460 nm. Beer's law is obeyed at 256 nm and 382 nm (pH = 5.0) over a wide concentration range (Fig. 2). The average effective values of molar absorption coefficients at λ = 256 nm is 1.4×10^4 L mol^{-1} cm^{-1}, and at λ = 382 nm – 2.5×10^4 L mol^{-1} cm^{-1}.
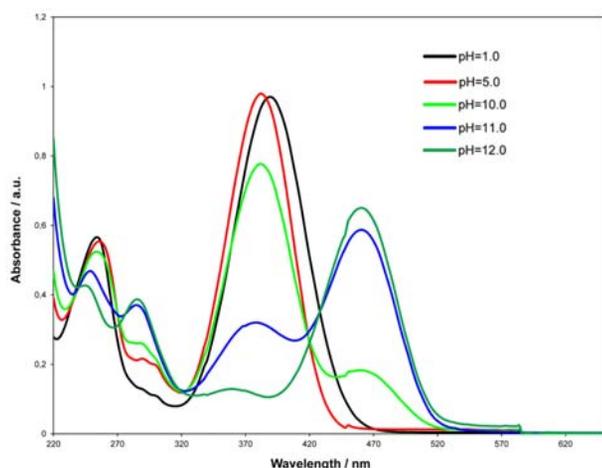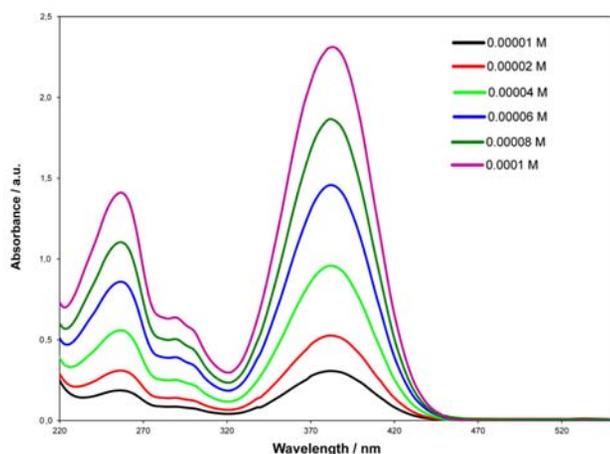

Fig. 1. Absorbance spectra of ITHBA at different pH

3. 2. Investigation of the Interaction of Pd(II) with ITHBA in Water Solution

The ion of Pd(II) forms with ITHBA a yellow complex. Fig. 3 represents absorbance spectra of the dye solution and Pd(II)-ITHBA complex-compound. As seen from the absorption spectra, the absorption maximum of the complex is observed at 382 nm. It is in the same wavelength area as the reagent, but compound of Pd(II) with ITHBA is characterized by the shoulder within the wavelength range of 420–550 nm. According to Fig. 3, the investigation of the interaction between Pd(II) ions and ITHBA was performed at λ = 438 nm. There is virtually no absorption of the reagent and the maximum increases in the value of shoulder. It should be noted that ions of Pt(IV), Rh(III), Ir(IV) and Ru(IV) do not interact with ITHBA.

To establish the optimal condition for complexation, we investigated the influence of acidity on the yield of complex compounds Pd(II)-ITHBA (Fig. 4). The complex is formed over a wide range of pH. The maximum yield of Pd(II)-ITHBA coloured compound was achieved in the range of pH = 7.6–8.3 against sodium
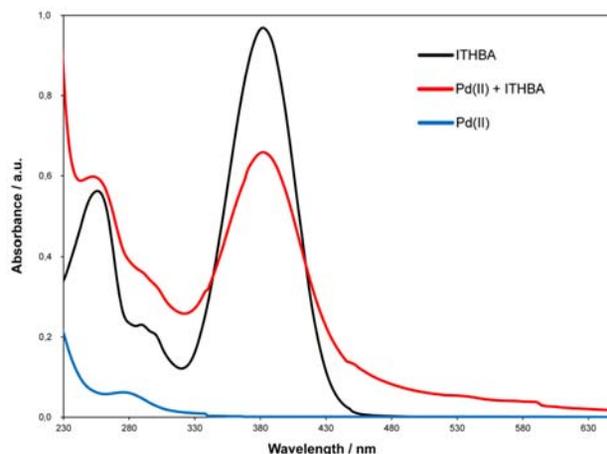

Fig. 2. Absorbance spectra of ITHBA of different molar concentration

Fig. 3. Absorbance spectra of reagent, Pd(II) and complex Pd(II) with ITHBA
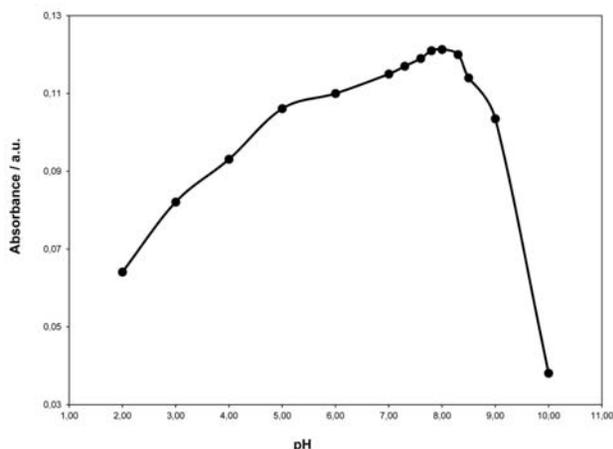
Fig. 4. Effect of acidity on the maximum yield of Pd(II) with ITHBA colored complex

Fig. 5. The method of continuous variations

chloride as a background. For further research, we chose pH = 8.0.

To select the medium in order to create the constant ionic strength the effect of the concentration and nature of anions of sodium salts on the interaction of Pd(II) with ITHBA was researched. In general, the nature of anion has small effect on the photometric characteristics of the complex. The Cl^-, CH_3COO^-, SO_4^{2-}, NO_3^- – have almost no effect on the value of the optical density; PO_4^{3-} – at first increases and later decreases the yield of the complex. As the reaction medium, we chose a solution of sodium tetraborate, because the presence of 0.05 mol L^{-1} solution of $Na_2B_4O_7$ slightly increases the yield of the complex and improves the rapidity of the method.

To establish the optimal conditions for the photometric reaction, we examined the effect of standing time at room temperature and heating time in the boiling water bath (~98 °C) on the yield of the complex. The compound Pd(II)-ITHBA is formed at room temperature, and heating only reduces the magnitude of the analytical signal. The absorbance values remain virtually unchanged for 72 h during storage of the obtained product solution.

Using the mole-ratio method and the method of continuous variations, the correlation between the components in the reaction system was established. The results are illustrated in Fig. 5 and 6. The calculations indi-
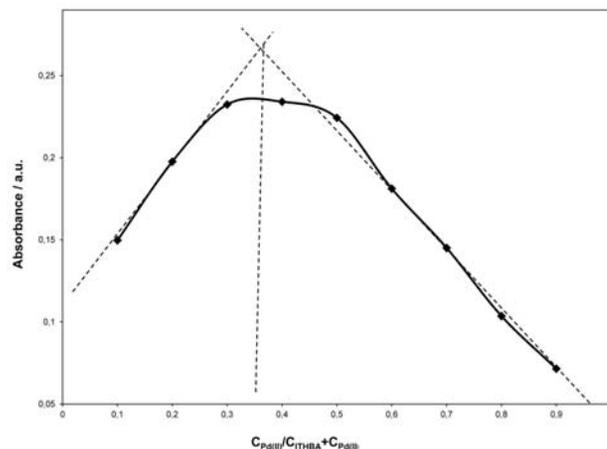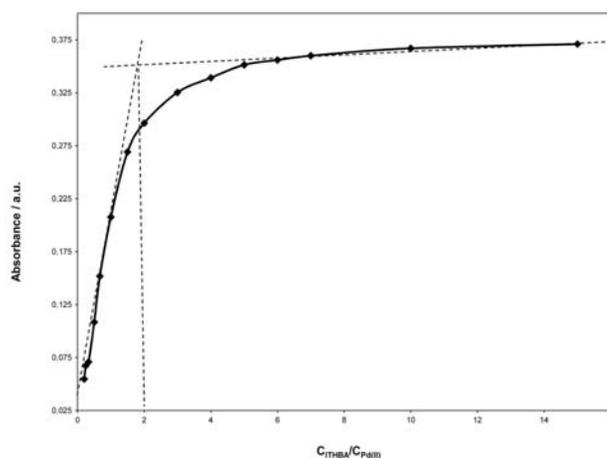

Fig. 6. The mole-ratio method

cate the formation of the complex with a ratio of components Pd(II):ITHBA = 1:2. It was found that 5-fold excess of the reagent is required for full colour development. The value of effective molar absorption coefficients is 7.5×10^3 L mol^{-1} cm^{-1}; conditional stability constants is 7.9×10^{10}.

After analyzing the experimental data and literature sources it can be assumed that the palladium ions interact with ITHBA as shown in scheme 3.
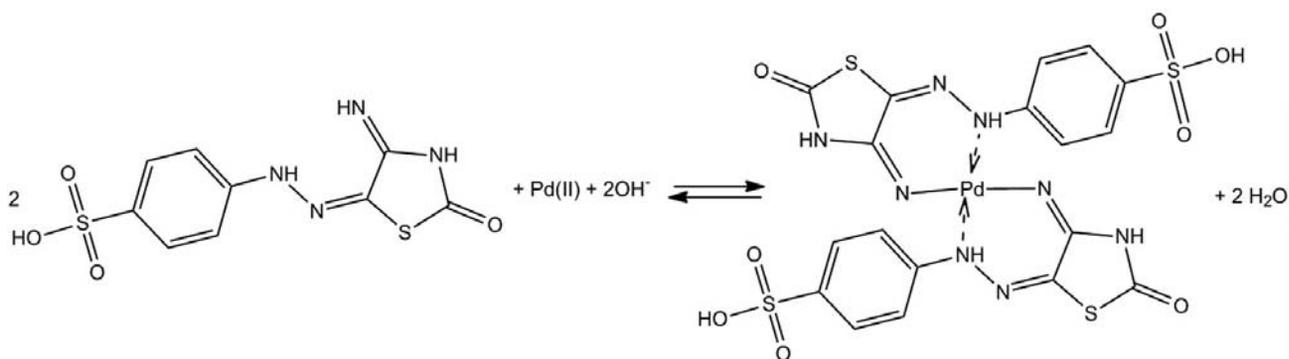
Scheme 3. Proposed reaction of Pd-ITHBA complex formation

It has been established that the magnitude of the analytical signal in determining Pd(II) with ITHBA linearly depends on the concentration of metal in the solution. The metrological characteristics of spectrophotometric determination of palladium(II) with ITHBA are given in table 1.

Table 1. The metrological characteristics of spectrophotometric determination of the Pd(II) with ITHBA (C(ITHBA) = 1.0×10^{-4} mol L^{-1}; C(Na$_2$B$_4$O$_7$) = 0.05 mol L^{-1}; pH = 8.0; λ = 438 nm; l = 5.0 cm; n = 5; P = 0.95)

Characteristic	Value
Linearity range, C$_{Pd(II)}$, μg mL^{-1}	0.2–2.2
Calibration equation, C$_{Pd(II)}$, μg mL^{-1}	$\Delta A = 0.03 + 0.27 \times C$
Limit of detection, C$_{Pd(II)}$, μg mL^{-1}	0.07
Limit of determination, C$_{Pd(II)}$, μg mL^{-1}	0.2
Correlation coefficient, R	0.9997

3. 3. Investigation of the Effect of Foreign Ions

The selectivity of developed technique was tested in determination of palladium(II) in the presence of platinum group elements, alkali-earth, heavy metals and other metals as well as some anions. The results of the selectivity investigation are shown in table 2. The technique is characterized by good selectivity towards many metals, such as Pt(IV), Rh(III), Ni(II), Co(II), Cu(II), Ag(I) and other metals, which often occur in the Pd-containing objects of study. The anions, which were researched also did not interfere much, and, therefore, they can be used to mask certain metals to improve selectivity.

3. 4. Determination of Palladium in Model Systems and Real Objects

The accuracy of palladium(II) spectrophotometric determination with ITHBA has been tested using the "in-

Table 2. Tolerance ratios of extraneous ions during the spectrophotometric determination of Pd(II) in the presence of 4-[N'-(4-imino-2-oxo-thiazolidin-5-ylidene)-hydrazino]-benzenesulfonic acid (C(ITHBA) = 1.0×10^{-4} mol L^{-1}; C(Pd(II)) = 9.0×10^{-6} mol L^{-1}; C(Na$_2$B$_4$O$_7$) = 0.05 mol L^{-1}; pH = 8.0; λ = 438 nm; l = 5.0 cm)

Extraneous ion	C$_{Pd(II)}$:C$_{ion}$	Extraneous ion	C$_{Pd(II)}$:C$_{ion}$	Extraneous ion	C$_{Pd(II)}$:C$_{ion}$
Ru(IV)	1:1	Cu(II)	1:50	Ca(II)	1: >200
Ir(IV)	1:2	Pb(II)	1:>200	Mg(II)	1: >200
Rh(III)	1:15	Cd(II)	1: >200	C$_2$O$_4^{2-}$	1: >200
Pt(IV)	1:15	Zn(II)	1:40	F$^-$	1: >200
Au(III)	1:10	Hg(II)	1:15	SiO$_3^{2-}$	1: >200
Ni(II)	1: >200	Ga(III)	1:50	EDTA	1:25
Co(II)	1: >200	Sn(II)	1:40	Sal$^-$	1: >200
Ag(I)	1:40	Yb(III)	1:15	Citr^{3-}	1: >200
Fe(III)	1:15	Al(III)	1:40	Tart^{2-}	1: >200
Mn(II)	1: >200	Ba(II)	1: >200	PO$_4^{3-}$	1: >200

Table 3. Accuracy of the spectrophotometric determination of Pd(II) with ITHBA in model solutions, n = 3; P = 0.95

Content of matrix solution	Added Pd(II), μg	Found Pd(II), $\bar{x} \pm \dfrac{s \times t_\alpha}{\sqrt{n}}$, μg	RSD, %
0.48 mg Pt(IV), 1.32 mg Ni(II), 2.0 mg Co(II)	24	23.6 ± 1.0	1.7
0.23 mg Rh(III), 0.13 mg Fe(III), 0.29 mg Cu(II)	24	24.8 ± 1.7	2.8
0.04 mg Ir(IV), 0.49 mg Ag(I), 2.53 mg Cd(II)	24	24.5 ± 1.4	2.3

Table 4. Results of the determination of palladium(II) in the alloy, n = 3, P = 0,95

Intermetallides		Spectrophotometry			Voltammetry	
	ω_{Pd}^{calc}, %	$\overline{\omega}_{Pd}^{pr} \pm \dfrac{S \times t_\alpha}{\sqrt{n}}$, %	RSD, %	$\overline{\omega}_{Pd}^{pr} \pm \dfrac{S \times t_\alpha}{\sqrt{n}}$, %	RSD, %
Yb$_{40}$Pd$_{38}$Sn$_{22}$	29.8	29.5 ± 1.0	1.4	30.2 ± 0.8	1.1
Yb$_{40}$Pd$_{40}$Ga$_{20}$	33.9	34.6 ± 1.4	1.6	34.3 ± 0.6	0.7

troduced-determined" method on model solutions. As it is shown in table 3, the method has good reproducibility and accuracy of the determination.

In addition, the developed techniques of palladium spectrophotometric determination have been applied to palladium assay in the intermetallides and the resistor SP5-35B (table 4, 5).

Obtained data are in a good agreement with the content of palladium in the studied objects determined by voltammetric and atomic absorption spectroscopy methods (AAS), within the error of the photometric determination. Concomitant ions in the solutions did not affect the performed analyses.

Characteristics of some spectrophotometric methods for the determination of palladium are shown in table 6.

Some of these methods are inferior in metrological characteristics to the method, which is proposed in this paper. The proposed technique unlike some presented in Table 6 does not need an organic solvent or highly acidic media, the reaction occurs immediately, the determination is not

Table 5. Results of the determination of palladium(II) in the resistor, $n = 3$, P = 0,95

Method	Found content Pd(II),	
	$\bar{x} \pm \dfrac{s \times t_\alpha}{\sqrt{n}}$, mg	**RSD, %**
AAS	23.3 ± 1.4	2.5
Spectrophotometry	23.7 ± 0.4	0.7

Table 6. Comparison of the present method with other spectrophotometric methods for the determination of palladium(II)

Reagent	Conditions	λ_{max}, nm	ε_{max}, L mol^{-1} cm^{-1}	Linear Range, µg mL^{-1}	Interfering ions
Dimethylglyoxime[4,7]	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	25–125; 100–800	Pt(II), Fe(II), Ir(III), Au(III)
o-Hydroxyacetophenone thiosemicarbazone[5]	pH=6.0, H$_2$O and dimethylformamide	370	9.0×10^3	0.4–10.6	Fe(III), Ag(I), Sn(II)
1-(2-Pyridylazo)-2-naphtol[6]	pH = 1.5–7.5, CHCl$_3$, 90°C	678	1.2×10^4	0.5–10	Ni(II), Fe(II), Fe(III)
β-Nitroso-α-naphthol[7]	pH = 1.0–2.0, CHCl$_3$, toluene	308; 385; 370	$(2.1–2.2) \times 10^4$	1–5; 0.1–10	Cu(II), Co(II), Ni(II), Cr(III), Fe(III), CN$^-$
Palladiazo[7,8]	pH = 3.5, *n*-butanol	640, 675	5.7×10^4	0.2–5.0	Pb(II), Bi(III), Cl$^-$, REE
Sulphochlorophenolazo-rhodanine[9–12]	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(IV), Rh(III)
4-Phenylthiosemicarba-zide[13]	Oleic acid surfactant	300	4.9×10^3	2.0–4.5	–
2-(2-Benzothiazolylazo)-5-dimethylamino-4-tolylarsonic acid[14]	Sulphuric or nutric acid and ethanol, 10 min	718	6.7×10^4	0–1.6	–
α-Furildioxim[7]	0.1–1.4 mol L^{-1} HCl, CHCl$_3$	380	2.2×10^4	1–3	–
Dithizone[7,15]	H$_2$SO$_4$, CCl$_4$	635	3.6×10^4	to 4	Ag(I), Au(III), Cu(II), S^{2-}
Nitroso-R-salt[7,16]	pH = 5.57 to 0.1 mol L^{-1} HCl; 0.05 mol L^{-1} HNO$_3$, 2.6 N CH$_3$COOH	510; 520–560	1.2×10^4; 9.7×10^4	1.3–4.3; 0.1–2.6	Co(II), Cl$^-$
4-(4'-Antipyriyl azo)-2-bromo phenol[17]	pH = 4.0–7.0	498	2.1×10^3	0.2–3	Cu(II), Co(II), V(V), Ag(I), Fe(III)
4-(2'-Furalideneimino)-3-methyl-5-mercapto-1,2,4-thiazole[18]	pH = 5.4, *n*-butanol	410	1.4×10^3	17–50	Cu(II), Cr(VI), Mn(VII)
Benzyloxybenzaldehyde-thiosemicarbazone[19]	pH = 5.0, cyclohexanol	365	4.0×10^3	5–60	Cu(II)
Propionyl promazine phosphate[20]	pH = 0.8-4.0	490–500	7.1×10^3	0.2–21	V(V), Ce(IV), Au(III)
4-[*N*'-(4-Imino-2-oxo-thiazolidin-5-ylidene)-hydrazino]-benzene-sulfonic acid	pH = 7.6–8.3	438	7.5×10^3	0.2–2.2	Ir(IV), Ru(IV)

interfered by many concomittant metals (Pt(IV), Rh(III), Ni(II), Co(II), Cu(II), Fe(III), Ag(I) etc.), sufficient sensitivity.

4. Conclusions

The spectrophotometric properties of ITHBA were researched and it was found out that this reagent forms a complex compound with Pd(II). A new simple method of spectrophotometric determination of palladium(II) ions with ITHBA, which is characterized by high selectivity, good sensitivity, reproducibility, accuracy and rapidness was elaborated. It is shown that this is a good method for the determination of palladium(II) when compared to some other spectrophotometric methods reported earlier. The proposed method has been successfully applied to the determination of palladium in intermetallides and resistor SP5-35B.

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Povzetek

Raziskovali smo spektrofotometrične lastnosti novega, prvič sintetiziranega reagenta – 4-[*N*'-(4-imino-2-okso-tiazolidin-5-iliden)-hidrazino]-benzensulfonske kisline (ITHBA). Razvili smo preprosto, hitro, točno, selektivno in občutljivo metodo za spektrofotometrično določitev Pd(II) ionov z uporabo tega reagenta. Poiskali smo optimalne pogoje za tvorbo kompleksa. Molarna absorptivnost pri λ = 438 nm je $7,5 \times 10^3$ L mol^{-1} cm^{-1}, Beerov zakon velja za koncentracije med 0,2–2,2 μg mL^{-1} Pd(II). Raziskovali smo vpliv drugih ionov. Metoda se je izkazala za uspešno pri določevanju paladija v intermetalidih in uporih. Točnost spektrofotometrične metode za paladij z 4-[*N*'-(4-imino-2-okso-tiazolidin-5-iliden)-hidrazino]-benzensulfonsko kislino v realnih vzorcih smo potrdili z voltametrično ali atomsko absorpcijsko spektroskopsko metodo.