1-(5-Benzylthiazol-2-yl)azonaphthalen-2-ol — a new reagent for the determination of Pd(II)

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Abstract: A simple method for the determination of Pd^{2+}-ions using the azo dye 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol (or BnTAN) and toluene or chloroform as extraction media is proposed. The palladium(II) ion interacts with 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol creating a chelate complex. This compound was extracted into toluene and chloroform from the alkaline and acid aqueous solutions respectively. Obtained extracts showed absorbance maxima at 600 and 684 nm. Obedience to Beer's law was established in the range of 0.261 to 0.850 μg mL^{-1} of Pd(II) and the molar absorptivity of the complex of $6.70 \cdot 10^3$ L mol^{-1} cm^{-1} was determined. Optimum reaction conditions for complexation, the effect of variables like time of heating and pH were studied. Detailed studies to check the Pd^{2+} : BnTAN — stoichiometric ratio were carried out. The method was successfully applied for the analysis of Pd(II) in details of electronic devices.

Keywords: extraction, palladium determination, spectrophotometry, thiazolylazonaphthol dyes

Introduction

Among all metals of the platinum group palladium has the greatest number of applications. Because of its chemical stability it is used in medicine, electronics and other branches of industry. For example, palladium covers medical instruments, it takes part in the creation of tooth prostheses, details of pacemakers and even as a component of some medicaments (Tsuji, 2004). Alloys based on palladium are helpful in the production of crucibles for melting of glass. Palladium has found much wider application possibilities in electronics. Even small contents of this metal in devices improve their reliability and continuous operation. Palladium is usually a part of car exhaust oxidation catalysts (Varghese and Khadar, 2011) and it is a great hydrogen absorbent. One volume of this metal can absorb 900 volumes of hydrogen. This fact is perspective for the creation of ecologically clean car engines.

Because of the high importance of palladium, it is necessary to control its quantities in a wide range of concentrations with sufficient reliability, which is the reason of increased interest in the spectrophotometric determination of Pd^{2+} in catalytic, biological, and other materials using thiazolylazo, or triazolylazo reagents (Hovind, 1975; Hallas and Jae-Hong, 1999). Selectivity and stability of the chelates of Pd^{2+} with thiazolylazo reagents have attracted much attention (Lemos et al., 2007). Various spectrophotometric methods for the analysis of Pd^{2+} have been reported (Abalos et al., 2012; Adachi et al., 2004; Ahmed, 2005; Chavan et al., 2013; Guogi et al., 2012; Kuswandi and Narayanaswamy, 1999; Mathew and Innocent, 2010; Mousavi et al., 2004; Raber et al., 1995; Shuangqing et al., 2003; Tupys and Tymoshuk, 2013). However, these analytical methods for the determination of Pd^{2+} lack sensitivity and selectivity.

In this paper, attempting to obtaining a more selective and sensitive spectrophotometric method for Pd^{2+} determination using chelating azo dyes, first the color reaction between Pd^{2+} and 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol (BnTAN, fig. 1) was systematically investigated. This azo dye is a

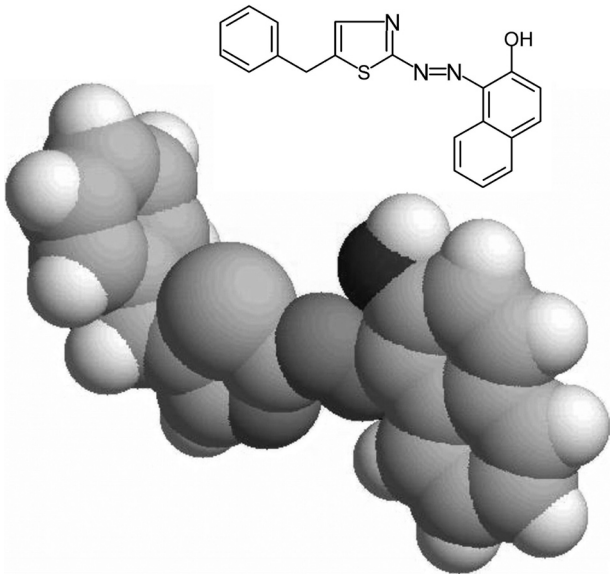

Fig. 1. Molecule of 1-(5-benzylthiazol-2-yl) azonaphthalen-2-ol (structural formula and spacefill illustration).

red powder, which is insoluble in water, but soluble in aqueous alcoholic solutions, pure ethanol, methanol, toluene, chloroform, carbon tetrachloride, dimethylsulfoxide and dimethylformamide. Molecular absorption spectrum of the azo dye has a maximum at the wavelength of 490 nm. The Beer's Law is obeyed in a wide range of concentrations and the molar absorptivity at 490 nm is high (approximately $3{,}0 \cdot 10^4$ L mol^{-1} cm^{-1}). Absorptivity at the wavelengths $\lambda \geq 600$ nm is negligible.

Further, a new, sensitive, and selective spectrophotometric determination of Pd^{2+} with a thiazolylazo compound in alkaline and acidic media is proposed.

Materials and Methods

Apparatus and reagents

A ULAB model 108 UV spectrophotometer was used for spectral measurements in cuvettes with the thickness of the absorbing layer of 1 cm. Acidity of the solution was controlled with a pH-meter model pH-150M with a silver chloride electrode and a glass indicative electrode using diluted solutions of NaOH and HCl. Double distilled water was used throughout the experiment. A stock solution of Pd(II) ($9.00 \cdot 10^{-3}$ mol L^{-1}) was prepared by dissolving metal in a mixture of nitric and hydrochloric acids (1:3). Working solution of Pd(II) was prepared by appropriate dilution of the stock solution. A $2.12 \cdot 10^{-3}$ mol L^{-1} alcoholic solution of BnTAN was prepared by the dissolution of an exact of the previously purified sample in pure ethanol. 1-(5-Benzylthiazol-2-yl)azonaphthalen-2-ol was purified by double recrystallization from acetone and ethanol followed by filtration and vacuum distillation. Chloroform, toluene and dry sodium sulfate were used during the extraction and after it. All the chemicals used were of Analytical Reagent grade or the best quality available and they were supplied by LLC "Sfera Sim", Lviv, Ukraine.

Procedure

A known amount of Pd(II) solution was put in a 25 mL measuring flask. The appropriate volume of sodium hydroxide (4.0 mol L^{-1}) or sulfuric acid (3.6 mol L^{-1}) was added to create the required acidity of the solution. Then 0.25—1.00 mL of a 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol alcoholic solution was added to the flask. The solution was kept in a water bath at 95 °C for 30—60 minutes to initiate the complexation reaction. The solution changed its color from orange to green.

After taking the flask from the water bath and cooling the solution was transferred into a separatory funnel (capacity of 50—100 ml). Then, 10.0 mL of chloroform or toluene were added to the funnel and the mixture was shaken for 3—5 minutes (Pethe et al., 2010). The organic extract was removed from the funnel into a previously drained 25.0 mL flask. The procedure in the funnel was repeated using another 10.0 mL of the organic solvent. The volume of the flask with two portions of the extract was filled to the 25 mL mark using pure solvent. Approximately 0.5 g of dry sodium sulfate was added to the obtained solution to prevent the possible impurities of water.

Absorbance of the solution was measured in the wavelengths range from 300 to 850 nm. The quantity of the chelate compound was calculated using the absorbance at the wavelength of 684 nm.

Many solvents have been studied for the determination of Pd(II), e.g. benzene, tetrachloromethane, amyl alcohol, diethyl ether and others; toluene and chloroform were found to be the most appropriate solvents for Pd(II) compounds extraction with BnTAN.

Results and Discussion

Effect of pH

The effect of pH on the absorbance of the azo dye was studied over the range of 0.0—12.0. In the pH range of 1.0—9.0, the dye remained red with the maximum and constant absorbance at the wavelength of 490 nm. Below pH 1.0, it became yellow (maximum absorbance at 450 nm) and above pH 9—10 the color changed to violet (maximum absorbance at 560 nm). Sulfuric acid recommended itself as the best reagent for providing the acidic environment.

After adding Pd^{2+} ions into the solution, the color turned from yellow to green in an acidic medium and the maximum absorbance was observed at 684 nm (fig. 2). Also a new maximum was found at 594 nm in a basic solution (pH 12). However, further investigations can be done only in the acidic medium because above pH 9, such diverse ions as Cu(II), Cd(II), Co(II), Zn(II) and Hg(II) interact with BnTAN forming stable complexes, which is the reason of the high selectivity of the Pd(II) determination in the pH range of 0.0—1.0.

Effect of Time and Temperature

The completion of the complexation reaction between BnTAN and Pd^{2+} required a long time. The absorption at 490 nm slowly decreased and the maximum at 684 nm increased. In this case, the possibility of accelerating this process by heating the system was analyzed. For this purpose, all solutions were kept in water a bath at 95 °C for 10—120 minutes. The results showed that the absorption spectra reached their

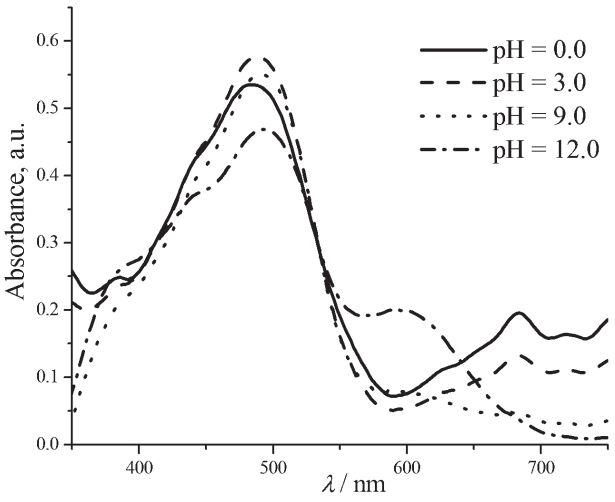

Fig. 2. Absorption spectra of BnTAN in the presence of Pd^{2+} at various pH values.

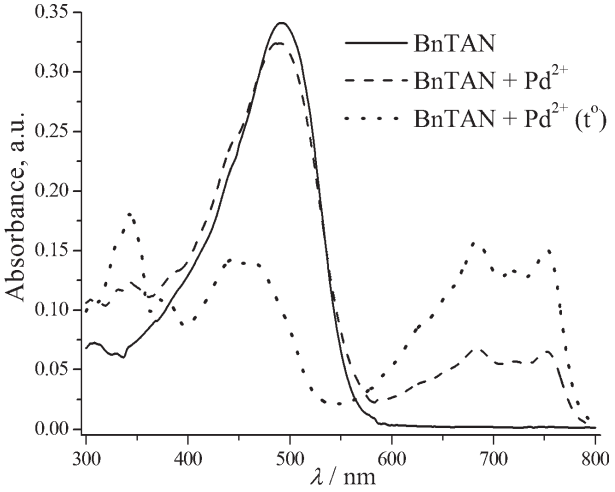

Fig. 3. Absorption spectra of BnTAN in the absence of Pd^{2+} ions; in the presence of Pd^{2+} ions, and after heating of the solution containing Pd^{2+} ions.

maxima at 684 nm after 90 minutes of increasing the temperature (fig. 3).

Analytical characteristic

As it was already mentioned, the colored system showed the maximum absorbance at 684 nm. The Beer's law is obeyed in the range from 0.11 to 2.82 μg mL^{-1}. Molar absorptivity and the Sandell's sensitivity of $6.70 \cdot 10^3$ and 0.0160 μg mL^{-2} respectively, were obtained.

Repeating the 50 μg/25 mL Pd(II) solution analysis following this technique, provided a standard deviation of ±0.0020 and the relative standard deviation of 1.40 %. Also, the limit of quantification and the limit of detection were calculated considering the relations 10σ/s and 3σ/s, respectively. Here, σ is the standard deviation of the blank solution with respect to water, and s is the slope of the calibration curve. According to the obtained data the limit of detection is lower than the minimal limit of the Beer's law dependence. Using the least-squares regression analysis, the intercept, the slope and the correlation coefficient were also evaluated (table 1).

Tab. 1. Spectral characteristics and precision of the presented method.

Parameter	Results
λ_{max} (nm)	684
Limits of Beer's law (μg mL^{-1})	0.11 to 2.82
Molar absorptivity (L mol^{-1} cm^{-1})	$6.70 \cdot 10^3$
Limit of detection (μg mL^{-1})	0.096
Limit of quantification (μg mL^{-1})	0.160
Sandell's sensitivity (μg mL^{-2})	0.0160
Standard deviation	±0.0020
Relative standard deviation (%)	1.40
Regression equation $Y = A + BX$ ([X] = μg mL^{-1})	
Intercept A	0.0058
Slope B	0.063
Correlation coefficient R (n = 5)	0.9961

Extraction efficiency

Extraction efficiency of the absorbing solution was determined by four replicate analyzes of Pd(II) standard solutions following the proposed procedure. However, these four aqueous solutions were extracted using 1, 2, 3, and 4 portions of 10 mL of chloroform, respectively. Assuming that that the extraction efficiency of the fourth solution is 100 %, the amount of Pd^{2+} ions removed from the water was evaluated (table 2). It is obvious that triple extraction is sufficient to transfer Pd(II) quantitatively into the extragent and double extraction also provides good extraction efficiency.

Tab. 2. Dependence of the extraction efficiency on the number of extraction stages (10 ml of $CHCl_3$).

Extraction stages	Extraction efficiency, (%)
1	81.20
2	95.60
3	98.80
4	100.00

Pd(II): BnTAN stoichiometric ratio

Another important part of the investigation was the determination of the stoichoiometric ratio in which Pd(II) and BnTAN interact forming a chelate complex. For this purpose, two classical methods were used: mole-ratio method and

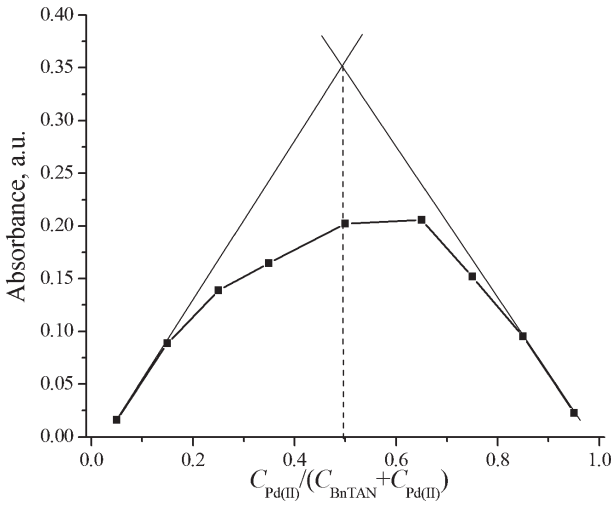

Fig. 4. Method of continuous variations for Pd(II)-BnTAN complex.

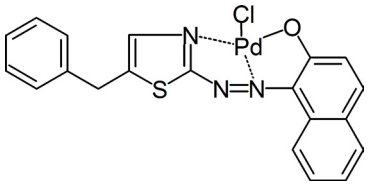

Fig. 5. Structure of Pd(II)-BnTAN complex.

method of continuous variations (Job's method) (figure 4).

The analysis provided the evaluated stoichiometric ratio of 1.0 (Tupys et al., 2013), which means that one molecule of an azo dye interacts with one Pd^{2+} ion. Such a complex is less stable than compounds of Co(II), Cd(II), Zn(II), and Cu(II) (Chavan, 2010) with BnTAN because the stoichiometric ratio for these complexes is 1:2. They include two ligands of the dye, the molar absorptivity of such complexes is higher compared to that of the Pd(II) and BnTAN chelate complex. For example, 3,4,5-trimetoxybenzaldehide thiosemicarbazone forms a 1:2 complex with Pd(II) with the molar absorptivity of $8{,}35 \cdot 10^4$ L mol^{-1} cm^{-1}.

Complex structure and reaction mechanism

Using the computer program SpectroCalc-Complex, the stability constant of the complex was calculated as $\beta = 3.65 \cdot 10^5$ (lg $\beta = 5.56$). Based on this and on the previously obtained data, the structure of the complex was proposed (figure 5). As it can be seen in the figure below, the Pd^{2+} ion forms two five-membered cycles with BnTAN.

Such a structure can be obtained only in an acidic medium using a solution of Pd(II) in 2.00 mol L^{-1} HCl. In this case, Pd(II) exists only in two possible forms: $[PdCl_3(H_2O)]^-$ and $[PdCl_2(H_2O)_2]$ (Babkova and Ivanov, 1988). Thus, the solution of H_2SO_4 was added to activate Pd(II) and the system with BnTAN was heated in a boiling water bath.

Therefore, there are only two possible complexation reaction mechanisms between Pd(II) and BnTAN (or HR). As BnTAN can change its form in an acid solution ($HR + H^+ = H_2R^+$) has also to be considered:

$$[PdCl_3(H_2O)]^- + HR = \\ = [ClPd—R] + H^+ + 2Cl^- + H_2O \quad (1)$$

$$[PdCl_3(H_2O)]^- + H_2R^+ = \\ = [ClPd—R] + 2H^+ + 2Cl^- + H_2O \quad (2)$$

$$[PdCl_2(H_2O)_2] + HR = \\ = [ClPd—R] + H^+ + Cl^- + 2H_2O \quad (3)$$

$$[PdCl_2(H_2O)_2] + H_2R^+ = \\ = [ClPd—R] + 2H^+ + Cl^- + 2H_2O \quad (4)$$

Organic reagent purity determination

An additional chromatographic experiment was carried out to confirm the degree of the BnTAN purity employing the mass spectrometric detection. The molar weight of BnTAN was Mr = 344.4. as it

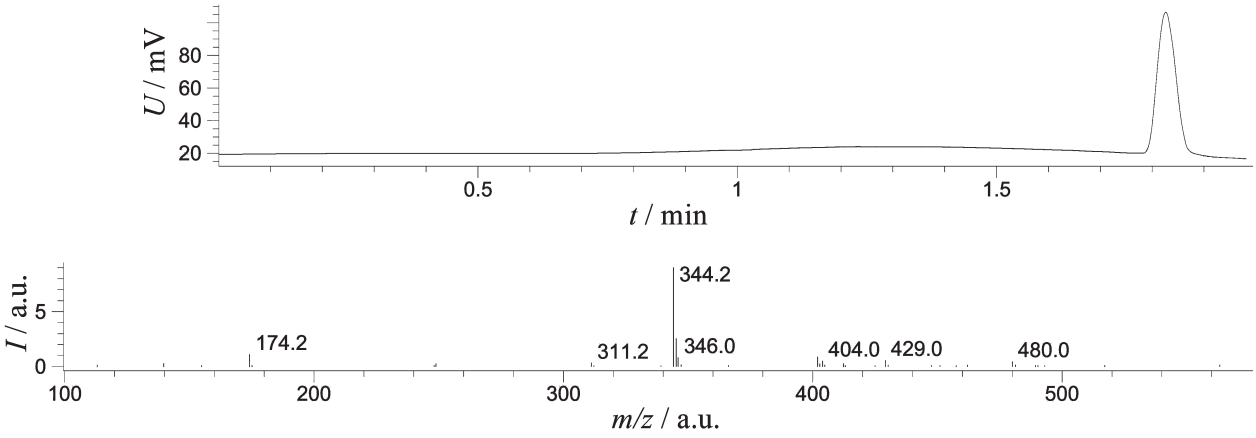

Fig. 6. Chromatogram with mass spectrometric detection for the determination of BnTAN purity.

can be seen from the figure 6, and only one maximum on the chromatogram with a strong analytical signal was observed, which means that there is one substance with a respective molar weight of 344.2, this maximum refers to BnTAN. Also, using the computer processing of the chromatogram, the content of pure benzylthiazo in the substance was calculated as 93.19 %.

Effect of foreign species

The effect of all possible diverse ions that can interfere with the Pd(II) determination was studied by an addition of a known amount of diverse ions into the absorbing solution before the sampling, and then Pd(II) was analyzed following the procedure at pH 0.0. The tolerance limit was considered as a value causing a ±5 % change in the absorbance (table 3).

Tab. 3. Tolerance limits of interfering ions in Pd(II) determination using BnTAN.

Ion	C(ion):C(Pd^{2+})	Ion	C(ion):C(Pd^{2+})
Na^{+}	>50*	Zn^{2+}	40
K^{+}	>50	Ru^{4+}	10
Mg^{2+}	45	Rh^{3+}	10
Al^{3+}	>50	Ir^{4+}	10
Ca^{2+}	>50	Pt^{4+}	10
Ti^{3+}	50	Os^{4+}	10
Cr^{3+}	50	Ba^{2+}	>50
Mn^{2+}	50	Hg^{2+}	15
Fe^{2+}	>50	Pb^{2+}	25
Fe^{3+}	>50	Sb^{5+}	10
Co^{2+}	10	Ag^{+}	40
Ni^{2+}	30	Cd^{2+}	5
Cu^{2+}	50	Ce^{4+}	1

* ">" means that higher concentration correlations were not investigated.

According to the results obtained in the acidic medium, metals that most commonly occur with Pd e.g. Ni, Cu, Co and Fe do not interfere in the determination of Pd(II). However, some other noble metals (Ir, Pt, Os) or heavy metals (Ce) should be masked or determined using other methods. In this particular case, EDTA has been proven as a good masking reagent for such ions as Zn^{2+}, Cd^{2+} etc.

Application

Determination of Pd(II) in synthetic mixtures

Before applying the new technique of Pd(II) determination it was necessary to improve its validity with synthetic mixtures. These solutions were prepared by an addition of a known amount of the Pd(II) standard solution. Also, the same concentration of Co(II) and five times higher concentration of aluminum were supplied as possible diverse ions. The investigation was carried out three times under the same conditions.

Results of the analysis show that the theoretical amount of Pd(II) in model solutions correlates with the experimental results and the uncertainty of the obtained data is acceptable (table 4). Moreover, no effect of foreign species was observed.

Determination of Pd(II) in resistor SP5-35B

To check the validity of the method, it was applied for Pd(II) analysis in a real sample and the obtained data were compared with those obtained by other methods. The analytical object was a resistor SP5-35B that, according to literature data, contained a small amount of palladium. Voltammetric and spectrophotometric (using azolidones) measurements provided the concentration of Pd^{2+} ions in the solution prepared by dissolving the object in a mixture of HCl and HNO_3 of approximately $4{,}23 \cdot 10^{-4}$ mol L^{-1}.

Tab. 5. Determination of Pd(II) in a resistor.

Pd(II) found		Mean (µg L^{-1})
Reported method (µg L^{-1})	Present method (µg L^{-1})	
4.23	4.47	4.33 (±0.60)
	4.51	
	4.08	

Application of the proposed technique using BnTAN gave a similar result. The extraction into chloroform provided the Pd(II) concentration in the resistor of $4{,}33 \cdot 10^{-4}$ mol L^{-1} (table 5), which is similar as the result of another method (Lozynska and Tymoshuk, 2013). Thus, the extraction-photometric method can be easily applied in the laboratories of analytical chemistry.

Tab. 4. Results of the analysis of model solutions.

Solution	C_{Pd}:C_{ion}	Known amount of Pd, µg	Pd found, µg	Mean, µg	S_r, %
Pd-Co-Al	1:1:5	13.88	14.27	13.99 (±1.64)	4.7
			13.20		
			14.50		

Conclusions

In the proposed work, a simple, selective and inexpensive extraction method coupled with spectrophotometry for the determination of Pd(II) has been introduced. Though a number of sophisticated techniques, like the use of dymethylglyoxime, for the determination of Pd^{2+} ions are available, a method based on the application of 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol (BnTAN) as a new selective reagent proves to be a perspective one. Considering the popularity of spectrophotometry in laboratories of developing countries, this extraction-photometric method can be easily applied due to such advantages like simple handling and low costs of instruments. Also, chemistry of tiazolylazonaphthols is studied in detail as they include functional groups used against cancer in medicine as well as in optical recording materials (Shuangquing et al., 2001).

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