Determination of Trace Amount of Pd(II) and Ni(II) with Newly Synthesized Pyrozlon Azo Bromo Phenol by Spectrophotometric Methods

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Abstract: A sensitive and selective method has been developed for the determination of palladium(II) and nickel(II). A new reagent and two complexes have been prepared in aqueous solutions. The method is based on the chelation of metal ions with 4-(4- antipyryl azo) -2-bromo phenol (APBP) to form an intense color soluble products, that are stable and have a maximum absorption at 498 nm and at 433.5 nm and $\epsilon_{\max}$ of 0.21×10^4 and 0.38×10^4 $\text{L mol}^{-1} \text{cm}^{-1}$ for Pd(II) Ni(II) respectively. A linear correlation of (0.2 - 3) and (0.6 -2.2) ppm for Pd(II) Ni(II) respectively. The stoichiometry of both complexes was found to be 1:2 (metal:ligand). The effect of various cations and anions on Pd(II) and Ni(II) determination have been investigated. The stability constants Pd(II) and Ni(II) were 0.37×10^8 , 0.38×10^8 L mol^{-1} respectively. The conductivity measurements for complexes are consistent with those expected for an electrolyte. The optimum conditions for full color development for described methods were applied satisfactorily to synthetic mixtures samples and biological samples.

Introduction

Palladium finds very important and extensive use in alloys, catalysts and in low voltage electrical contacts. Hence, its recovery, purification and determination palladium have been reported¹⁻⁵. Azo -dyes widely used in analytical chemistry because of their ability to form coloured complex with many metal ion in water. In recent years they have been employed in sorption spectroscopic test method more extensively then in conventional spectrophotometry⁶. The literature survey reveals different analytical methods for the determination of Pd(II) in

Jewelry and biological samples; these methods⁷ (ETAAS), flame atomic absorption (FAAS)⁸, optical test strip for spectrophotometry⁹ and stripping voltammetry¹⁰. Azo compounds are known to be involved in a number of biological reactions such as inhibition of DNA, RNA and protein synthesis, carcinogenesis and nitrogen fixation¹¹. Azo pyrazole derivatives and its metal complexes can be used as inkjet, they have got fastness properties for dyeing papers¹² and process high dyeing power on fibers¹³. They can also be used in subtractive photographic process and for the production of color transparencies and color pictures¹⁴ and have many applications¹⁵. Various methods for the assay of nickel(II) have been reported: adsorptive stripping voltammetry^{16,17}, reverse phase high performance liquid chromatography^{18,19}, flame and electrothermal atomic absorption²⁰⁻²², flow injection and flow injection-inductively coupled plasma optical emission spectrometry^{23,24} and simple spectrophotometric methods²⁵⁻²⁸. The aim of the present work is to develop an easy, rapid method for the determination of palladium(II). The method is based on the reaction of 4-(4'-antipyryl azo)-2-bromophenol (APBP), which forms coloured complexes which form coloured complexes with Pd(II) and Ni(II) ions.

Experimental

All chemicals used were of analytical grade.

Apparatus

Spectrophotometric measurements were made with Shimadzu UV-Visible -1700 double beam spectrometer using (1.0) cm glass cells. The pH measurements were performed with AWTW pH-meter 720. Electric molar conductivity measurements were carried out at room temperature using an Alpha digital conductivity model -800. Vibration spectra were recorded by Testscan Shimadzu FT-IR 8000 series.

Preparation of reagent (APBP)

The reagent was prepared by coupling resorcinol with diazotized 4-amino antipyrin in alkaline alcoholic solution. A diazonium solution was prepared by taking 1 g 4-amino antipyrin in 15 mL of ethanol and concentrated hydrochloric acid with 5 mL of distilled water and adding sodium nitrite solution dropwise at 0-5 °C. 2-Bromophenol 1.2 g was dissolved in 50 mL of ethanol and 30 mL of 0.1 M were added at (-5 °C). The mixture was left to stand overnight. The precipitate was filtered off and recrystallized from ethanol²⁹ Scheme 1.

Scheme 1. Preparation of reagent APBP

Preparation of palladium(II) complex

The complex was prepared by stoichiometric amount from ligand in 50 mL of ethanol then added drop wise with stirring to a stoichiometric amount 1:2 for palladium salt in (25) mL hot distilled water. The solid product thus formed off, washed with ethanol and dried.

Preparation of nickel(II) complex

The complex was prepared by stoichiometric amount from ligand in 50 mL of ethanol then added drop wise with stirring to a stoichiometric amount 1:2 for nickel salt in 25 mL hot distilled water. The solid product thus formed off, washed with ethanol and dried.

Reagents*Palladium(II) stock solution (1000 $\mu\text{g}\cdot\text{mL}^{-1}$)*

0.3330 g of PdCl_2 was dissolved in 10 mL of 1 M HCl and diluted to 100 mL using distilled water, working standard Pd(II) solution were prepared by dilution of the appropriate volume of standard Pd(II) solution (100 $\mu\text{g}/\text{mL}$) with distilled water.

Nickel(II) stock solution (200 $\mu\text{g}\cdot\text{mL}^{-1}$)

0.4033 g of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ was dissolved in 500 mL of distilled water, working standard Ni(II) solution were prepared by dilution of the appropriate volume of standard Ni(II) solution (100 $\mu\text{g}/\text{mL}$) with distilled water.

4-(4- Antipyril azo) -3-Bromo phenol (1×10^{-4} M)

0.0086 g of Regent (APBP) was dissolved in 250 mL of ethanol working (APBP).

Foreign ion solutions (100 $\mu\text{g}\cdot\text{mL}^{-1}$)

These solutions were prepared by dissolving an amount of the compound in distilled water completing the volume in a volumetric flask.

Recommended procedure for determination of Pd (II) and Ni(II)

In to a series of 10 mL calibrated flask, increasing volume of Pd(II) and Ni(II) working solutions (100 $\mu\text{g}\cdot\text{mL}^{-1}$) to the range of the calibration curve was transferred, 2.0 mL of 5×10^{-4} M of (APBP) for both ions was added. The pH (4.0, 8.0) for Pd(II) and Ni(II) was adjusted by NH_3 and CH_3COOH for Pd(II) and 0.05 M HCl and NaOH for Ni(II) respectively. The complexes formed were solubilized in water and diluted up to 10 mL with distilled water. The concentration range 0.2-3 $\mu\text{g}/\text{mL}$ and 0.6-2.2 $\mu\text{g}/\text{mL}$ of Pd(II) and Ni(II), respectively. Measure the absorbance at 498 nm for Pd(II) and at 498 nm for Ni(II) complexes against a reagent blank.

Results and Discussion

Properties of APBP and its metal chelates APBP is a bidentate with coordination of azo group nitrogen and carbonyl groups; it has following structure (Scheme 2)

Scheme 2. Structure of 4-(4- antipyril azo)-2-bromophenol (APBP)

Owing to the large conjugated, the compound showed excellent chelation ability to form metal chelates. APBP and its metal chelates can be easily dissolved in aqueous solutions.

Mechanism of reagent reaction

The reaction sequence in procedure of reagent involves tow steps. First, 4-amino antipyrine react with nitrite to form diazonium ion; the second including the diazanium ion is coupling with 2-bromophenol to form dark yellow azo dye¹⁶ (Scheme 1). The effect of various parameters on the absorbance intensity of the formed products was studied and the reaction conditions were optimized.

Absorption spectra

The results of this investigation indicated that the reactions of Pd(II) and Ni(II) with 4(4-pyrazolon azo)-2-bromophenol yields highly soluble colored complexes which can be utilized as a suitable assay procedure for determination of Pd(II) and Ni(II). These colored complexes have a maximum a absorption at 498 nm for Pd(II) and at 498 nm for Ni(II), the blank at these wavelengths shows zero absorbance Figure 1 & 2.

Figure 1. Absorption spectra of (R-Pd) treated as described under procedures and measured against a reagent blank and R the reagent blank against ethanol

Figure 2. Absorption spectra of (R-Ni) treated as described under procedures and measured against a reagent blank and R the reagent blank against ethanol

The effect of various parameters on the absorption intensity of the formed products was studied and the reactions condition were optimized.

Effect of pH

To establish the optimum condition (stability of the product from the reaction of palladium(II) ion with the azo reagent, minimum blank value and relatively rapid reaction rate), the effect of pH (2.5-9) was studied. Only pH 4.0 and 8.0 was found to be optimum for Pd(II) and Ni(II) respectively. Alkaline and acid results in low sensitivity and was not stable for Pd(II) and Ni(II) respectively. pH change on the electronic absorption spectra of the complex was studied by adding a small amount of NH_3 and CH_3COOH and 0.05 M HCl and 0.05 M NaOH. The UV-Visible spectra of complexes gives the band centered at 498 nm for Pd(II) and at 433.5 nm for Ni(II). The bands appearing in the range of 270-320 nm are attributed to $\pi \rightarrow \pi^*$ transition. The other band observed in the region of 498 and nm is attributed to $n \rightarrow \pi^*$ electronic transition³⁰⁻³² for Pd(II) and Ni(II) respectively Figure 3 Table 1.

Effect of reagent concentration

Various concentrations of APBP solution were added to a fixed amount of Pd(II) and Ni(II) 2 mL and 2 mL of 5×10^{-4} M where found enough to develop the color to its full intensity and give a minimum blank value and were considered to be optimum for the concentration range (0.2-3.0) (0.6 -2.2) $\mu\text{g/mL}$ of Pd(II) and Ni(II) respectively Figure 4.

Figure 3. Effect of pH

Figure 4. Effect of concentration

Effect of reaction time

The color intensity reached a maximum after the Pd(II) and Ni(II) has been reacted immediately with APBP therefore one minute development time was selected as optimum in the general procedure. The color obtained was stable for a least 24 h Figure 5.

Effect of temperature

The effect of temperature on the colour intensity of the product was studied. In practice, the same absorbance was obtained when the colour was developed at room temperature (30-40 °C) a loss in color intensity and stability were observed, therefore it is recommended that the colour reaction should be carried out at room temperature for both complexes Figure 6.

Figure 5. Effect of time

Figure 6. Effect of temperature

Order of addition of reagents

To obtain the optimum results, the order of addition of materials should be followed as give by the procedure, otherwise a loss in stability was observed.

Calibration graph

At optimum conations, a linear calibration graphs for Pd(II) and Ni(II) were obtained, that Beers low is obeyed over the concentration range of 0.2-3.0 ppm and 0.6-2.2 ppm with a correlation coefficient 0.9986 and 0.9861 respectively. The results of analytical performance are summarized in Table 1.

Table 1. Analytical characteristics of Pd-APBP and Ni-APBP complexes

Characteristic	Pd (II)	Ni(II)
Absorption maxime, nm	498 nm	433.5 nm
Berr's low range, µg/mL	0.2-3.0	0.6-2.2
Ph range	4-7	7-9
Sandell 'S sensitivity µg.cm ⁻²	0.05	0.015
Molar absorptivity, L.mole ⁻¹ .cm ⁻¹	0.21x10 ⁴	0.38x10 ⁴
Stability constant, L.mol ⁻¹	0.37x10 ⁸	0.38x10 ⁸

Interferences

The effect of diverse ions in the determination of these metal ions was studied. To test of diverse ions were determined by the general procedure, in the presence of their respective foreign ions. In the experiment, a certain amount of standard palladium(II) or nickel(II) solution, coexisting ion solution and masking agent (or absence of masking agent) were added. The results are listed in Table 2.

Table 2. Effect of foreign ions

Foreign ion	Amount added µg/mL	Interferences with Pd(II)	Interferences with Ni(II)
Fe ⁺³	100	-100	+36
Fe ⁺²	100	-89	+29
V ⁺⁵	100	-23.6	-3.2
Mo ⁺³	100	+12.7	+4.6
W ⁺²	100	+5.4	+3.2
Ag ⁺¹	100	+14.5	+1.6
Cr ⁺³	100	+1.8	+2.1
CO ⁺²	100	+25.4	+15
Hg ⁺²	100	+10.9	+1.1
Cd ⁺²	100	+2.7	+4.3
Pd ⁺²	100	+25.4	+21.4
Cu ⁺²	100	+36.3	+16.8
Cl ⁻¹	100	+63.3	-44
SO ₄ ⁻²	100	+81.8	+1.4
CO ₃ ⁻²	100	+69	+16
NO ₃ ⁻²	100	+69	+20

In the experiment, a certain amount of standard palladium(II) solution coexisting ion solution and masking agent (or absence of masking agent) were added. It is found that large amount of W²⁺, Cr³⁺, Cd²⁺, Na₂HPO₄, tartaric acid and citric acid do not interfere in the

determination of Pd(II) and Ni(II) by comparing in the presence of masking agents Na_2HPO_4 , tartaric acid and citric acid test cations. It's found that Cu^{++} , Co^{++} , Mo^{++} , V^{5+} , Ag^+ and Fe^{3+} interfere seriously. However, their interferences are masked efficiently by addition of 1 mL of (0.1 M) NaHPO_4 , 0.5 mL of (0.1 M) tartaric acid and 0.5 mL of (0.5 M) citric acid.

Conductivity measurements

The solubility of the complexes in dimethyl sulfoxide and ethanol permitted of the molar conductivity of 10^{-3} M solution at 25 °C and by comparison, the electrolytic nature for complexes. The low values of the molar conductance data listed in Table 3 indicate that the complexes are non electrolytes.

Table 3. Conductivity values of complexes

Complex	Molar conductivity, $\text{S mole}^{-1} \text{cm}^2$	
	DMSO	Ethanol
$\text{Pd}(\text{APBP})_2\text{XH}_2\text{O}$	0.72	1
$\text{Ni}(\text{APBP})_2\text{XH}_2\text{O}$	2.4	4.1

Composition of the complexes

The FT-IR bands of the (APBP) and its palladium(II) complex with their probable assignment are give in Table 4. The stretching band of $\nu(\text{N}=\text{N})$ in the free ligand is observed at 1557 cm^{-1} . This band is shifted to lower with low intensity 1510 cm^{-1} frequency value upon complexation. Also the FT-IR spectrum of the ligand revealed a sharp band at 1645 cm^{-1} due to $(\text{C}=\text{O})$. This band is shifted to lower with low intensity 1593 cm^{-1} frequency in the complex indication to the metal ion^{33,34}. The bonding of oxygen to the metal ion provided by the occurrence of bands at 515 cm^{-1} as the result of $\nu(\text{M}-\text{O})$ ³⁵.

Table 4. Selected IR data of (APBP) and its complexes with Pd(II) & Ni(II)

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{N}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$ azo
H_2L	1645s	1557m	1645s	-	-
$[\text{Pd}(\text{HL})_2]\text{XH}_2\text{O}$	1531s	150m	515w	515w	430w
$[\text{Ni}(\text{HL})_2]\text{XH}_2\text{O}$	1535s	1520m	1585s	520w	435w

S: sharp, m: medium, w: weak

The composition of complexes was studied in the excess of reagent solution by the mole - ratio method. A break at a 1:2 (M:L) mole ration suggested the formation of both complexes where $\text{M}=\text{Pd}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{L}=\text{APBP}$ under the given condition Figure 7, 8.

Figure 7. Mole-ratio method of Ni -Complex

Figure 8. Mole-ratio method of Pd -Complex

On the basis of FT-IR and stoichiometric data the structure of complex can be suggested as follows Figure 9.

Figure 9. The proposed structural formula of complexes with (APBP)

Application

The proposed method was applied to the determination of Pd(II) in synthetic mixtures and results displayed in Table 5.

Table 5. Determination of Pd(II) in synthetic mixtures and Ni(II)

Composition of mixture $\mu\text{g.mL}^{-1}$	Found by present method $\mu\text{g.m}^{-1}$	%R.S.D of the Pd(II) and Ni(II) complex
$Pd^{++}(1), Mo^{++}(10), Co^{++}(10), Cd^{++}(10)$	0.99	1.8
$Pd^{++}(1), V^{+5}(10), Pb^{++}(10)$	0.98	1.7
$Pd^{++}(1), Cu^{++}(10), Ni^{++}(10)$	1.02	2.3
$Pd^{++}(1), Fe^{++}(10), Ag^{++}(10)$	1.04	2.2
$Ni^{++}(1), Fe^{++}(10), Co^{++}(10), Pd^{++}(10)$	0.96	1.8
$Ni^{++}(1), Fe^{++}(10), Mo^{++}(10), Cd^{++}(10)$	0.97	1.2

Determination of Pd(II) and Ni(II) in blood of human

The samples were collected from AL-Sadder hospital in Al-Kufa city in Iraq. 1 mL of blood were mixed with 1.5 mL of H_2O_2 and 4 mL of 5% HNO_3 . Samples were left for 60 min and then ready for UV-Visible spectrophotometric analysis³⁶ Table 6.

Table 6. Pd(II) and Ni(II) levels ($\mu\text{g.mL}^{-1}$) in blood samples

Ions in blood of human	Amount found by spectrophotometric method, $\mu\text{g.mL}^{-1}$	Amount found by atomic absorption method, $\mu\text{g.mL}^{-1}$
Pd(II)	0.020	0.018
Ni(II)	0.012	0.011

Conclusion

This method using APBP was successfully applied for the determination of palladium(II) and nickel(II). Because of the selectivity and sensitivity of the method, its application can be determination of those ions environmental and industrial samples.

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