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Spectrophotometric determination of palladium(II) using a nitrogen, sulphur and oxygen donor triazine

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ABSTRACT

A simple and sensitive spectrophotometric method is proposed for the determination of palladium (II) in ppm level using 4-amino-3-mercapto-6-methyl-1, 2, 4-tirazine (4-H)-5-one, a nitrogen, sulphur and oxygen donor triazine, as the spectrophotometric reagent. In aqueous medium at a pH of 11, Pd(II) forms a light yellow colored complex with the proposed spectrophotometric reagent. The optimum concentration range for maximum precision was deduced from Ringbom's plot and was found to be 5.6 – 10 ppm of Pd(II). The mean valve of molar absorptivity and Sandell's sensitivity were calculated and was found to be 2.1121 x 10^4 $Lmol^{-1}$ cm^{-1}, and 5.3287 x 10^{-3} ìg/cm^2 respectively. The composition of Pd(II)-AMMT complex was found to be of ML_2. The interference of various cations and anions were studied also studied.

Key words: Spectrophotometry, palladium determination, triazine, Sandell's sensitivity, molar absorptivity.

INTRODUCTION

Palladium is the most abundant of the platinum group metals in the earth's crust. The major applications of the metal are in the electronic industry where it is used as an alloy with silver, as an electrical contact material[1]. Palladium finds extensive applications as catalysts in many chemical reactions. Palladium complexes like $Pd(O_2Me)_2]_3$ are claimed to have antitumor properties[2]. Palladium is also has been used for the construction of astronomical and fine instruments. Considering these extensive and excellent applications of palladium, a reliable and accurate spectrophotometric method is developed for the micro level determination of palladium. The study of literature reveals the usage of a large number of reagents for the spectrophotometric determination of Pd(II). Many of the methods need heating, cooling or extraction after the colored complex is formed between the reagent and metal palladium.

Weizu Yang et al conduct an experiment for the solid phase extraction and spectrophotometric determination of Pd(II) with 2-(2-quinolyazo)-5-diethyl amino benzoic acid solution[3]. Beer's law was obeyed in the range of 0.01-1.2 mg/ml at 628nm and the molar absorptivity value was calculated as 1.4310 x 10^5 L mol^{-1}. Palladium forms an anionic chelate with the reagent 4-(2-pyridylazo) resorcinol[4] which is extractable with xylometazolonium cation into chloroform in the pH range 7.2 – 7.8. The coloured species exhibits maximum absorbance at 520nm and obeyed Beer's law in the range 0.8 -5.30 µg / ml of palladium. Reddy B. K. et al proposed a highly sensitive method for the determination of Pd(II) in synthetic mixtures and hydrogenation catalysts using

Benzildithiosemicarbazone[5]. The experiment was done successfully at pH 2.5 at a ëmax value of 395nm and Beer's law was obeyed for the range 0.25 – 3.5 ppm. Extractive spectrophotometric method for the determination of palladium using thiosalicylic acid and hexylamine ligand complex[6] was done by A. K. Chhakker and L. R. Kakker. 5(p-dimethylaminobenzylidiene) Rhodamine[7] was used as a simple sensitive spectrophotometric reagent for the determination of Pd(II) at 463 nm and 534nm. The experiment was done successfully at a pH of 3.

A rapid and sensitive extractive method for the determination of Pd(II) in synthetic mixtures and hydrogenation catalysts using pyridoxal-4-phenyl-3thio semicarbazone[8] was proposed by Sharma L. S. Beer's law was obeyed for the range 0.4 – 6.4 ìgcm^{-3}. Anthemidis. A. N. et al proposed a highly sensitive method for the determination of Pd(II) in hydrogenation and automobile exhaust gas converter catalysts using 2, 2[1] dipyridal-2-pyridylhydrazone (DPPH)[9]. Selective spectrophotometric determination of cobalt, nickel, palladium, copper, ruthenium, molybdenum using isoamylxanthate[10] in presence of surfactants was done by AK Malik et al. Maximum absorbance was found at 400nm and 350nm and the experiment was done successfully at pH range 5-5.8. Reagents like 2-(5-nitro-2-pyridylazo)-5-(N propyl-N-3-sulfopropylamino) phenol (5-No2. PAPS) and tartaric acid with 5NO_2 PAPS niobium (V) complex (11), salicyladehyde and thiosemicarbazone[12], (2, 2[1]-bipyridyl 2-pyridyl hydrazone)[13], propericiazine[14], 6-nitro quinoxaline 2,3-dithiol[15], TTA-methyl-propyl ketone[16] and 4-(2-pyridylazo) resorcinol (17) were used for the determination of palladium in microamounts. Many of these reagents need extraction for the determination. G. H. Ayres and B. L. Tuffly proposed a highly sensitive method for the determination of Pd(II) using bromide[18] to give the orange red colour at pH 3. The system confirms to Beer's law upto 200 ppm of palladium.

MATERIAL AND METHODS

Apparatus

Beckman Du-6 spectrophotometer was used with 10mm quartz cell for the absorbance and transmittance measurement. For measuring the pH of the buffer solutions prepared Elico pH meter was employed.

Reagent and Solutions

All chemicals used were of AR grade.

Palladium (II) Stock Solution

A stock solution of Pd(II) was prepared by dissolving $PdCl_2 3H_2O$ in distilled water and KCl. The stock solution was standardized by standard method (19) and working solutions were prepared by suitable and accurate dilutions of the stock solution.

Reagent Solution

The reagent 4-amino-3-mercapto-6-methyl-1, 2, 4-triazine (4-H)-5-one (AMMT) was prepared by the reported procedure (20).

Buffer Solutions

Buffer solutions of suitable pH were prepared by mixing Potassium Chloride, Hydrochloric acid, Sodium Hydroxide potassium hydrogen phthalate, potassium hydrogen – phosphate, borax, Sodium bicarbonate in proper proportions[21].

Procedure

To an aliquot of the sample solution containing 5.6 – 10.4 ppm of Pd(II), an excess of 0.1% alcoholic solution of 4-amino-3-mercapto 6. methyl-1, 2, 4-triazine (4H)-5-one was added and made up to the mark using buffer solution of pH 11 in 25 ml standard flask. The solution was mixed very well and the absorbance of the solution was measured at 384 nm, using 10mm matched cells against the reagent blank.

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectra of Pd(II)-AMMT compex was studied for a wavelength range from 340nm to 480nm and shown in figure 1. The coloured Pd(II)-AMMT complex had a maximum absorption at 384nm and at this wavelength the absorbance of the reagent is very small and hence negligible. The complex formation reaction between Pd(II) and the reagent AMMT was found to be fast and the maximum colour was developed instantaneously at room temperature. In aqueous medium at a pH of 11, Pd(II) forms a light yellow colored complex with

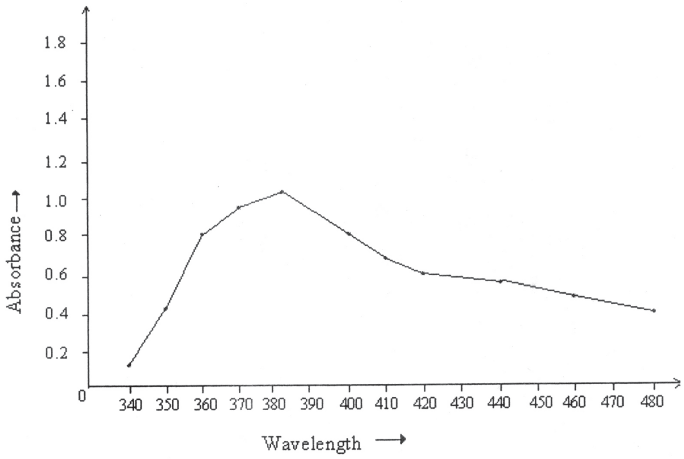

Fig. 1: Absorption spectrum for Pd(II)-AMMT system

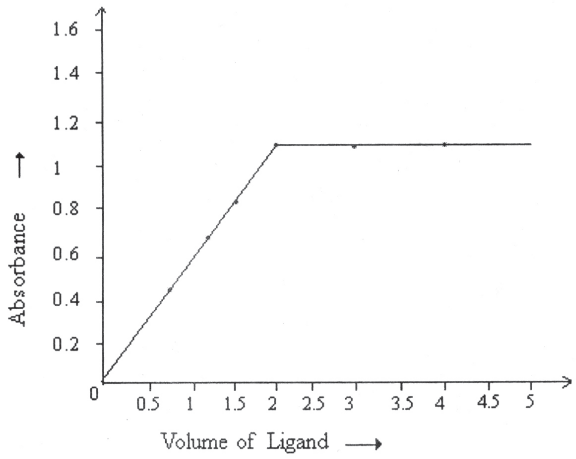

Fig. 2: Mole-ratio graph for Pd(II)-AMMT system

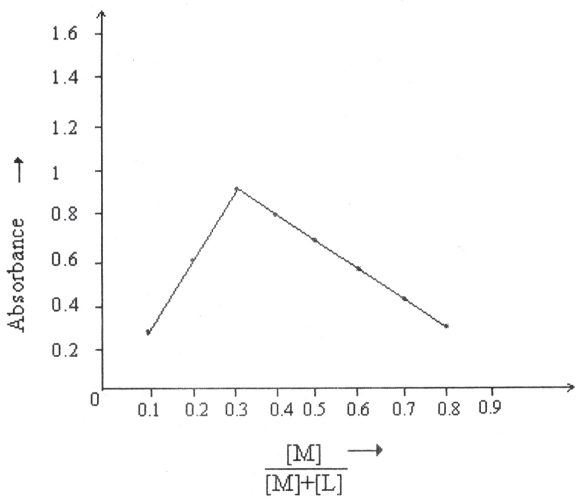

Fig. 3: Continuous - variation graph for Pd(II)-AMMT system

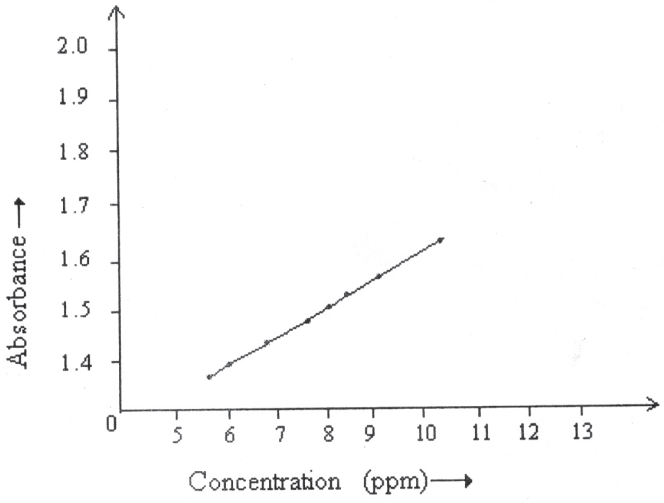

Fig. 4: Verification of Beer's law for Pd(II)-AMMT system

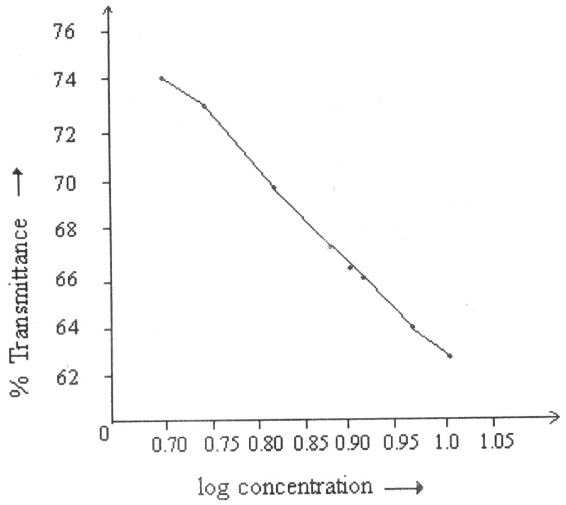

Fig. 5: Ringbom's plot for Pd(II)-AMMT system

AMMT reagent. The colour of the complex was stable for at least 24 hours and there was not any considerable change in the absorption value.

Composition of the complex

The composition of Pd(II)-AMMT complex was studied using Mole ratio method[22] and Job's method of continuous variation[23]. In mole ratio method (Fig. 2) a break was observed when the Pd(II) – AMMT ratio was 1:2, indicating a ML_2 type complex formation. The plot of Job's method (Fig. 3) also confirms the formation of a ML_2 type composition for the complex.

Effect of pH

A series of buffer solutions of pH ranging from 1 to 13 were prepared[21] and using these buffer solutions the variation of absorbance of Pd(II) – AMMT complex was studied. It was observed that the absorbance value was maximum for the coloured complex at a pH of 11. Hence for all subsequent studies, the pH was obtained at the optimum level of 11.

Effect of Metal Concentration

The effect of metal concentration on the intensity of the colour development was investigated

by treating the Pd(II) solution with various amounts of the reagent. When 1 ml of 0.1% solution of AMMT was added to 6 ppm of Pd(II) solution, maximum and constant absorbance was noted.

Beer's Law and Optimum Range and Sensitivity

The adherence of the Pd(II) – AMMT system to the Beer's law was studied by measuring of varying Pd(II) concentration. A graph was drawn by plotting absorbance against concentration of metal ion and from the plot it could be noted that at 384 nm, the Beer's law was valid up to 10.4 ppm of Pd(II) (Fig. 4).

Table 1: Effect of Foreign Ions on Absorbance

Foreign ions	Absorbance
Pd_{11}	0.616
Na_{I}	0.599
Zr_{IV}	0.455
Mg_{11}	0.544
Cu_{11}	0.612
Ca_{11}	0.594
Zn_{11}	0.581
$Po_{4\ 11}$	0.607
$CH_3\ COO^-$	0.633

The optimum concentration range for maximum precision was deducted from Ringbom's Plot [24], by plotting the percentage transmittance values against the log [M]. The linear portion of the curve indicates that the range was 5.6 – 10. ppm of Pd(II), (Fig. 5).

The molar absorptivity was calculated by measuring the absorbance of solutions at different concentration levels of Pd(II). The mean value was found to be 2.1121×10^4 $Lmol^{-1}$ cm^{-1}. The Sandell's sensitivity (25) was also calculated and was found to be 5.3287×10^{-3} ìg/cm^2.

Effect of Foreign Ions

The effect of foreign ions was studied by adding known quantities of an ion in question to an aliquot of standard Pd(II) – AMMT complex solution. The data is summarized in the Table 1. The studies clearly showed that almost all anions did not provide any interference in the determination. Cations like Zr(IV), Mg(II), offered serious interference.

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