

Spectrophotometric Determination of Palladium(II) Using Thioglycollic Acid

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A simple and sensitive spectrophotometric method is proposed for the determination of palladium(II) in ppm level using thioglycollic acid, as the spectrophotometric reagent. In aqueous medium at a pH of 11, Pd(II) forms a light yellow coloured complex with the proposed spectrophotometric reagent. The optimum concentration range for maximum precision was deduced from Ringbom's plot and was found to be 2.4-6.4 ppm of Pd(II). The mean value of molar absorptivity and Sandell's sensitivity were calculated and was found to $2.0692 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $6.8287 \times 10^{-3} \text{ g/cm}^2$, 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, Thioglycollic acid, Sandell's sensitivity, Molar absorptivity.

INTRODUCTION

Palladium is the most abundant of the platinum group metals in the earth's crust. Palladium finds extensive applications as catalyst in several chemical reactions. Some salts of palladium has been used for the detection of carbon monoxide¹. Palladium complexes like $\text{Pd}(\text{O}_2\text{Me})_2$ are claimed to have antitumor properties². The alloys of palladium with rare earths are used as magnetic materials³ 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 literature survey identifies a large number of spectrophotometric reagents were used for the determination of Pd(II). Many of the methods need extraction after the coloured complex is formed between the reagent and metal palladium or heating and cooling for developing the colour.

The reagents 2-(2-quinolyazo)-5-diethyl amino benzoic acid solution⁴ and 4-(2-pyridylazo) resorcinol⁵ were used for extractive spectrophotometric determination of palladium(II). A highly sensitive method for the determination of Pd(II) in synthetic mixtures and hydrogenation catalysts using benzildithiosemicarbazone was proposed by Reddy *et al.*⁶. The λ_{max} value was 395 nm and Beer's law was obeyed for the range 0.25-3.50 ppm. The reagents thiosalicylic acid and hexylamine

ligand complex⁷ was used for the extractive spectrophotometric determination of palladium. The reagent 5(*p*-dimethylaminobenzylidene)rhodamine⁸ was used as a simple sensitive spectrophotometric reagent for the determination of Pd(II) at 463 and 534 nm.

Sarma *et al.*⁹ proposed a rapid and sensitive extractive method for the determination of Pd(II) in synthetic mixtures and hydrogenation catalysts using pyridoxal-4-phenyl-3-thiosemicarbazone. Beer's law was obeyed for the range 0.4-6.4 g cm⁻³. Anthemidis *et al.*¹⁰ proposed a highly sensitive method for the determination of Pd(II) in hydrogenation and automobile exhaust gas converter catalysts using 2,2'-dipyridyl-2-pyridylhydrazone (DPPH). Reagents like 2-(5-nitro-2-pyridylazo)-5-(*N*-propyl-*N*-3-sulfopropylamino) phenol (5-NO₂-PAPS) and tartaric acid with 5NO₂ PAPS niobium(V) complex¹¹, salicylaldehyde and thiosemicarbazone¹², (2,2'-bipyridyl-2-pyridyl hydrazone)¹³, propericiazine¹⁴, 6-nitro quinoxaline-2,3-dithiol¹⁵, TTA-methyl-propyl ketone¹⁶ and 4-(2-pyridylazo) resorcinol¹⁷ were used for the determination of palladium in microamounts. Many of these reagents need extraction for the determination.

EXPERIMENTAL

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

All chemicals used were of AR grade.

Palladium(II) stock solution: A stock solution of Pd(II) was prepared by dissolving PdCl₂·3H₂O in distilled water and KCl. The stock solution was standardized by standard method¹⁸ and working solutions were prepared by suitable and accurate dilutions of the stock solution.

Reagent solution: The reagent thioglycollic acid (mercapto acetic acid) was used as 2 % ethanolic solution.

Buffer solution: 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 proportions¹⁹.

General procedure: An aliquot of the sample solution containing 0.8-8.0 ppm of palladium(II) was transferred quantitatively into 25 mL standard flask. Excess of 2 % alcoholic solution of thioglycollic acid was added to the flask and made up to mark using buffer solution of pH 10. The solution was mixed very well and the absorbance of the solution was measured at 384 nm using 10 mm matched cells against the reagent blank.

RESULTS AND DISCUSSION

Absorption spectra: The absorption spectra of palladium(II)-thioglycollic acid complex was studied for a wavelength range from 350-500 nm and shown in Fig. 1.

The Pd(II)-thioglycollic acid complex has a maximum absorption at 384 nm and at this wavelength the absorbance of the reagent is very small and hence negligible. The complex formation reaction between Pd(II) and thioglycollic acid was found to be fast and the maximum colour was developed instantaneously at room temperature.

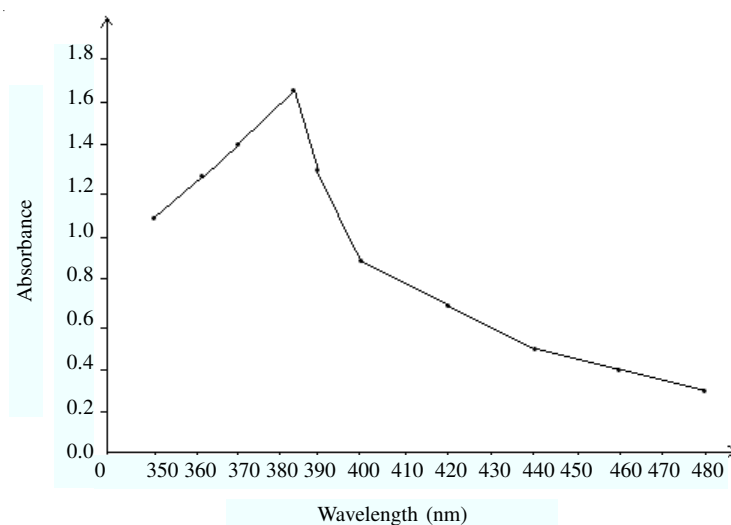


Fig. 1. Absorption spectrum for Pd(II)-thioglycollic acid system

In aqueous medium at a pH of 10, palladium(II) forms a yellow coloured complex with thioglycollic acid. The colour of the complex was stable for at least 24 h and no considerable change was observed in the absorption value.

Composition of the complex: The composition of Pd(II)-thioglycollic acid complex was studied using mole ratio method²⁰ and Job's method of continuous variation²¹. In mole ratio method (Fig. 2) a break was observed when the Pd(II)-thioglycollic acid ratio was 1:2, indicating a ML_2 type complex formation. This was confirmed by the literature^{22,23}. 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 solution of pH ranging from 1-13 were prepared¹⁹ and using these buffer solution the variation of absorbance of Pd(II)-thioglycollic acid complex was studied. It was observed that the absorbance value was maximum for the coloured complex at a pH of 10. Hence for all subsequent studies, the pH was maintained at the optimum level of 10.

Effect of metal concentration: The effect of metal concentration on the intensity of the colour development was investigated by treating the palladium(II) solution with various amounts of the reagent. When 1 mL of 2 % solution of thioglycollic acid was added to 5 ppm solution, maximum and constant absorbance was observed.

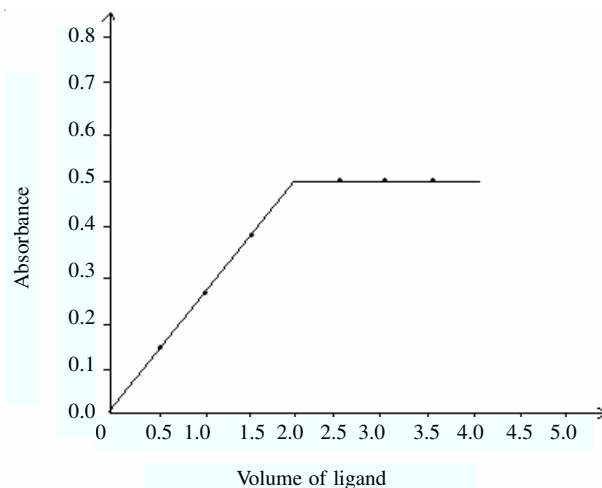


Fig. 2. Mole-ratio graph for Pd(II)-thioglycollic acid system

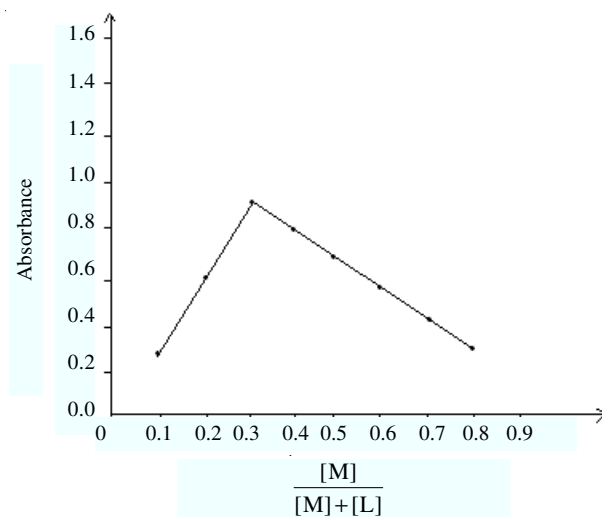


Fig. 3. Continuous-variation graph for Pd(II)-thioglycollic acid system

Beer's law and optimum range: The adherence of the Pd(II)-thioglycollic acid system to the Beer's law was studied by measuring the absorbance value of solution of varying Pd(II) concentration. A graph was drawn by plotting absorbance against concentration of metal ion. A straight line graph was obtained which passes through the origin at zero ppm concentration from the plot, it could be noted that at 384 nm the Beer's law was valid upto 8 ppm of palladium(II) (Fig. 4).

The optimum concentration range for maximum precision was deduced from Ringbom's plot²⁴. The percentage transmittance was plotted against the logarithm of metal concentration. The linear portion of the curve indicates that the range was 2.4-6.4 ppm of Pd(II) (Fig. 5).

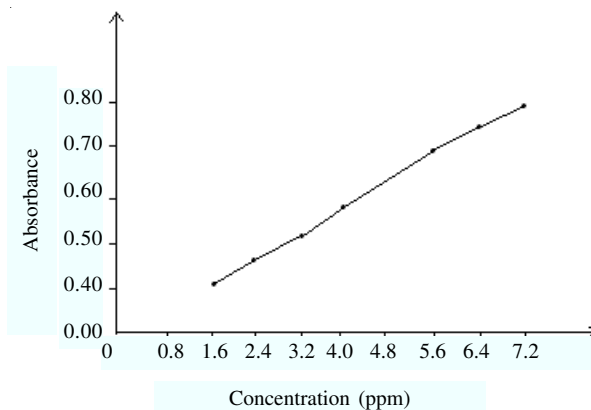


Fig. 4. Verification of Beer's law for Pd(II)-thioglycollic acid system

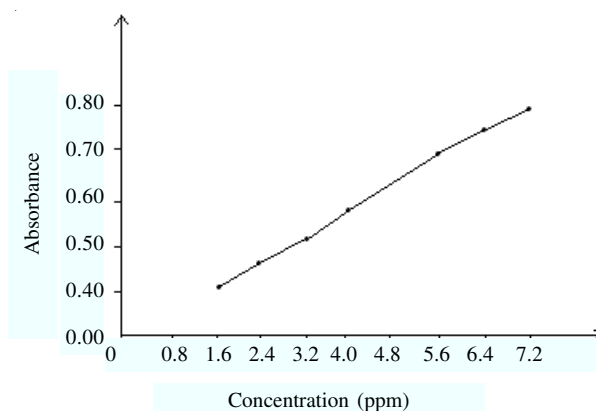


Fig. 5. Ringbom's plot for Pd(II)-thioglycollic acid system

Molar absorptivity and sensitivity: By measuring the absorbance of solution at different concentration levels of palladium(II), the molar absorptivity was calculated. The mean value was found to be $2.0692 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. The Sandell's sensitivity²⁵ was calculated and was found to be $6.8287 \times 10^{-3} \text{ g/cm}^2$.

Effect of foreign ions: The interference effect of foreign ion in the absorbance of Pd(II)-thioglycollic acid complex was studied. Many cations offered interference in the determination. Zirconium and majority of the alkali metal cations and anions did not provide any strong interference to the determination. But majority of the transition metal posed 2-5 % interference in the absorbance.

Conclusion

The proposed method is simple, rapid and sensitive. The reagent provides precise and accurate, results upto 8 ppm of Pd(II). The proposed reagent, thioglycollic acid is easily available. The method does not need any extraction or heating for colour development. The absorbance value of the Pd(II)-thioglycollic acid complex does

not vary much with time. The molar absorptivity and Sandell's sensitivity value are at par with the earlier reported methods.

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