

Extractive Spectrophotometric Determination of Pd(II) with Sodium salt of hexamethyleneiminecarbodithioate

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ABSTRACT

The reagent NaHMICdt·2H₂O has found to be a good chelating agent for the spectrophotometric determination of various metal ions. The present investigation deals with spectrophotometric determination of Pd(II) by using NaHMICdt·2H₂O. The reagent reacted with Pd(II) to give yellow complex extractable into toluene. Pd (II) was extracted quantitatively in the pH range 0.5-2.0. Pd(II)-HMICdt complex showed λ_{max} at 435 nm. The extracted species has a 1:2 (M:L) stoichiometry. Beer's law is obeyed in the range of 0.2-0.8 $\mu\text{g ml}^{-1}$ of Pd (II). The molar absorptivity and the sandells sensitivity were found to be $0.754 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.0140 \mu\text{g mol}^{-1} \text{ cm}^{-2}$ respectively. The effect of divers ion on the extraction of Pd(II) has been investigated. The proposed method is highly sensitive, selective, and simple and rapid has been applied for accurate determination of palladium in synthesis mixtures and real samples.

Keywords: Palladium; Sodium hexamethyleneiminecarbodithioate; Extractive Spectrophotometry; Synthetic mixture; Real Samples

1. INTRODUCTION

It is well known that precious metals which possess special physical and chemical properties are important materials and have been applied widely in industry and technology recently [1-5]. Palladium has extensive applications in various fields like catalysis, pharmaceuticals, petroleum, electronics, jewelers etc. Therefore, its separation and estimation at trace level is of significant importance. Especially, the demand amount of platinum group metals (PGMs) has increased a lot in industry. To satisfy these demands, new methods for

their recovery from ores and spent materials have been prompted [6-8]. However, in consideration of the low natural abundance of the precious metals, traditional production methods, such as precipitation and reducing process methods, do not meet their tremendously increasing demand in industries and other spheres. Solvent extraction has been proved to be a very efficient and practicable approach for extraction and recovery of the precious metals leached from their low graded sources or spent catalysts [9,10]. Many of these techniques are either time consuming or require sophisticated and expensive instruments. Extractive spectrophotometric methods are simpler techniques and have been widely used for determination of palladium. Palladium forms intensely colored complexes with hydrazones, dyes, dithiocarbonates, oximes, and thio compounds.

Using this property a number of extractive spectrophotometric methods of palladium determination with various reagents such as di-2-pyridyl-methanone-2-(5-nitro)pyridyl hydrazine [11], pyridine-2-acetaldehyde salicyloyl hydrazine [12], di-2-pyridyl ketonebenzoyl hydrazine [13], Isonitroso benzoylacetone [4], o-butyldithiocarbonate [15], pyridoxal-4-phenyl-3-thiosemicarbazone [16], Benzyloxy benzaldehyde thiosemicarbazone (BBTSC) [17], N-ethyl-3-carbazolecarbaxaldehydethiosemicarbazone [18] and α -benzoin oxime (ABO) [19], N,N,N',N'-tetra(2-ethylhexyl) thiodiglycolamide (T(2EH)TDGA) [20].

However, the existing methods suffer from various limitations such as longer extraction periods [11-13], temperature control [15], narrow pH range [12-16,18], less stability [14], and interference from other metal ions [11,15,19].

Moreover, in some methods [13,14], the extraction is not quantitative. In the present method an analytical reagent hexamethyleneiminecarbodithioate was used for the extractive spectrophotometric determination of Pd(II). New analytical method can be employed for efficient determination of Pd(II) at μg level. The result of analysis obtained were employed with those obtained by known method with certify value of palladium. The proposed method is sensitive rapid and free from many limitations.

2. EXPERIMENTAL

2.1 Apparatus

All absorbance measurements were carried out on Bousch and Lomb spectronic 20 spectrophotometer. A digital elico pH meter (Model LI -120) with combined glass electrode was used to determine the pH of the solution. The stock solution of Pd(II) was prepared by dissolving calculated amount of palladium chloride in double distilled water containing 10 ml of concentrated hydrochloric acid. The solution was diluted to 250 ml with doubly distilled water and standardized [21].

The reactant hexamethyleneimine brought from Lancaster was used without further purification. The ligand sodium salt of hexamethyleneiminecarbodithioate dehydrate was prepared by method reported in the literature [22].

2.2 Reagents

Stock solution of the reagent (0.15 %) was prepared by dissolving NaHMICdt·2H₂O (0.15 g) in ethanol. The pH 2.0 was adjusted by using HCl and NH₃ solution of order. Cation and anion were prepared by dissolving there AR grade salts in doubly distilled water with a few drops of suitable acid. Synthetic mixtures were prepared by using standard solution of Palladium and desired metal ions. Analytical grade chemicals were used unless otherwise stated. Doubly distilled water was used throughout the experimental work.

2.3 Recommended Procedure

To an aliquot containing 50 μg Pd(II), 1 ml of 0.15 % HMICdt in ethanol was added. The pH of solution was adjusted by required volume of Ammonia and HCl. It was diluted to 10 ml with distilled water and the complex was extracted with toluene (10 ml) equilibrated mixture for 1 min organic extract was collected in 10 ml standard volumetric flask and made up to the mark with fresh solvent and absorbance was measured at 435 nm against similarly prepared reagent blank. The amount of Pd(II) was detected from the standard calibration curve.

3. RESULTS AND DISCUSSION

3.1 Absorption spectra

The yellow colored complex shows absorbance maximum at 435 nm (Figure 1) where reagent has no significant absorbance. Hence all absorbance measurements were carried out at 435 nm against reagent blank.

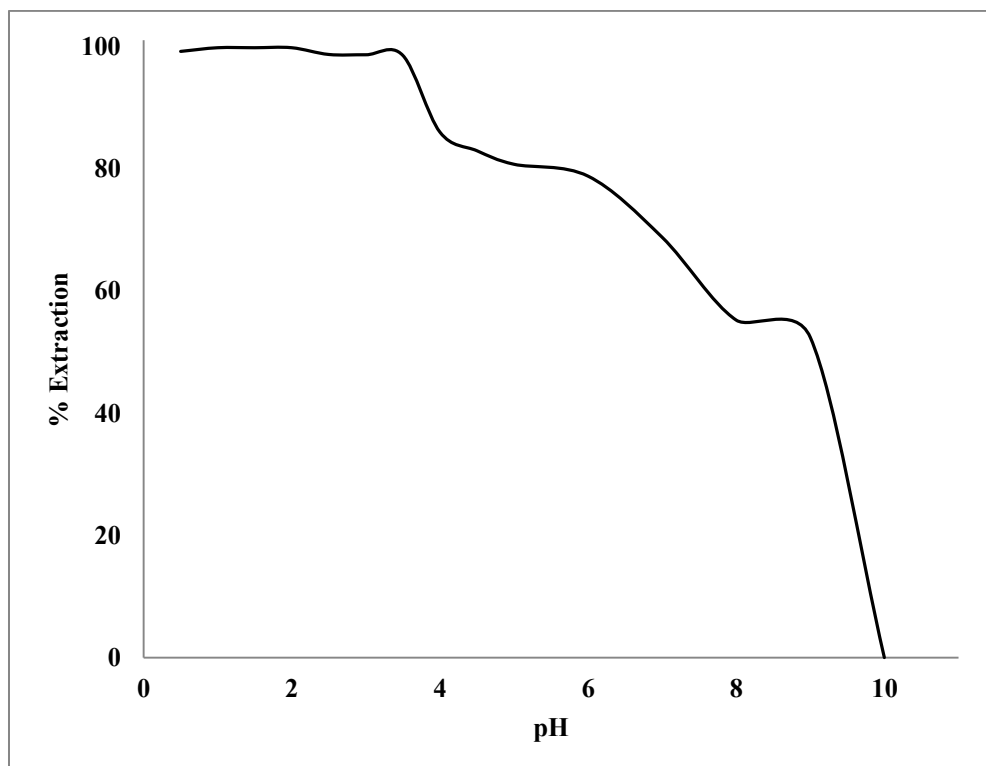


Fig. 1. Effect of pH on Extraction recovery of Pd(II)

3.2 Effect of pH and Acidity

The extraction of Palladium as function of pH Pd(II) was extracted by NaHMICdt·2H₂O in toluene over the pH range of 1-10 it was found that the complex would be quantitatively extracted in the pH range 0.5-2.0, where the percentage extraction was found to be over 99.75 % (Figure 2).

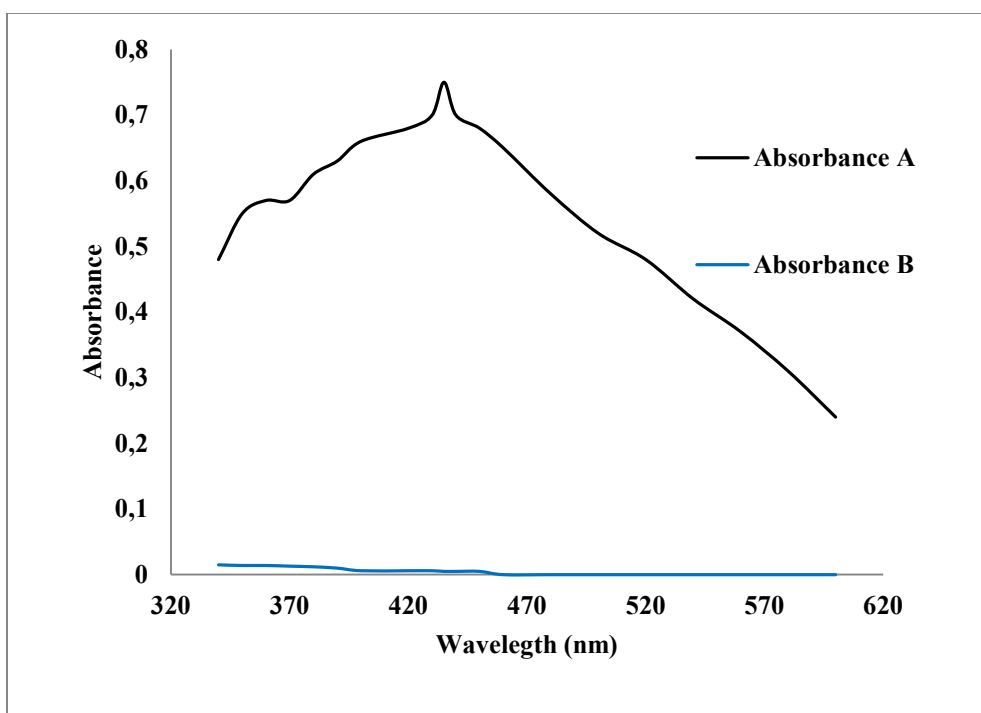


Fig. 2. Absorption spectra of Pd-HMIMcd complex (A) and reagent blank NaHIMCdt (B) in Toluene.

Therefore all extraction was carried out at pH 2.0. The extraction was also carried out in presence of various acid it was found that the extraction is quantitative in presence of 0.01 N HCl (Table 1).

Table 1. Recovery of Pd(II) in various acids

	Acids	Extraction Recovery (%)
1	0.01 M HCl	99.65
2	0.1 M HCl	83.55
3	0.01 M H ₂ SO ₄	86.65
4	0.1 M H ₂ SO ₄	71.11
5	0.01 M HNO ₃	98.77
6	0.1 M HNO ₃	68.77
7	0.01 M CH ₃ COOH	97.67
8	0.01 M CH ₃ COOH	80.69

3.3 Effect of Solvent

Various organic solvents were tried to get maximum extraction of Pd(II) with HMICdt. The result shows that among various solvent, toluene was found to be the most suitable solvent for its quantitative extraction (Table 2).

Table 2. Recovery of Pd(II) in various solvents.

	Solvent	Extraction Recovery (%)
1	Toluene	99.75
2	Chloroform	85.42
3	Benzene	71.91
4	Iso- amyl alcohol	69.00
5	Iso -butyl alcohol	58.69
6	n-butyl alcohol	49.20
7	Methyl isobutyl ketone	38.40
8	Carbontetra Chloride	16.66
9	n-butyl acetate	15.96
10	Xylene	14.23
11	Nitrobenzene	12.26
12	Pentanol	11.24

3.4 Effect of HMICdt. Concentration

The effect of NaHMICdt·2H₂O concentration on extraction of Pd(II) was studied. It was observed that 1 ml of 0.15 % solution of NaHMICdt·2H₂O was sufficient for quantitative extraction of Pd(II). Excess of reagent concentration did not affect on the extraction. Hence 1 ml of 0.15 % reagent was used for further studies.

3.5 Effect of Equilibration time

The colour development was insisting, however shaking was varied from 10-120 second after reagent addition. The minimum shaking time required for quantitative extraction of Pd(II) was 60 second. While longer extraction time did not effect the % extraction. Hence 60 second of shaking time was fixed for further studies.

3.6 Colour Stability of the Extracted Species

The color stability of Pd(II)-NaHMICdt complex was studied by measuring absorbance at 435 nm at definite time intervals. The complex was quantitative stable and remained constant for seven days.

3.7 Calibration curve

The absorbance of the extracted species was a linear function of Pd(II) concentration in the range of 0.2-8.0 ppm at 435 nm. The optimum working range obtained from Ringbom's plot was found to be 1.778-7.24 ppm that confirms the beer's range (Figure 3). The molar absorptivity sandell's sensitivity of the method was found to be $0.754 \times 10^4 \text{ mol}^{-1} \cdot \text{cm}^{-1}$ and $0.0140 \mu\text{g} \cdot \text{ml}^{-1} \cdot \text{cm}^{-2}$ at 435 nm respectively.

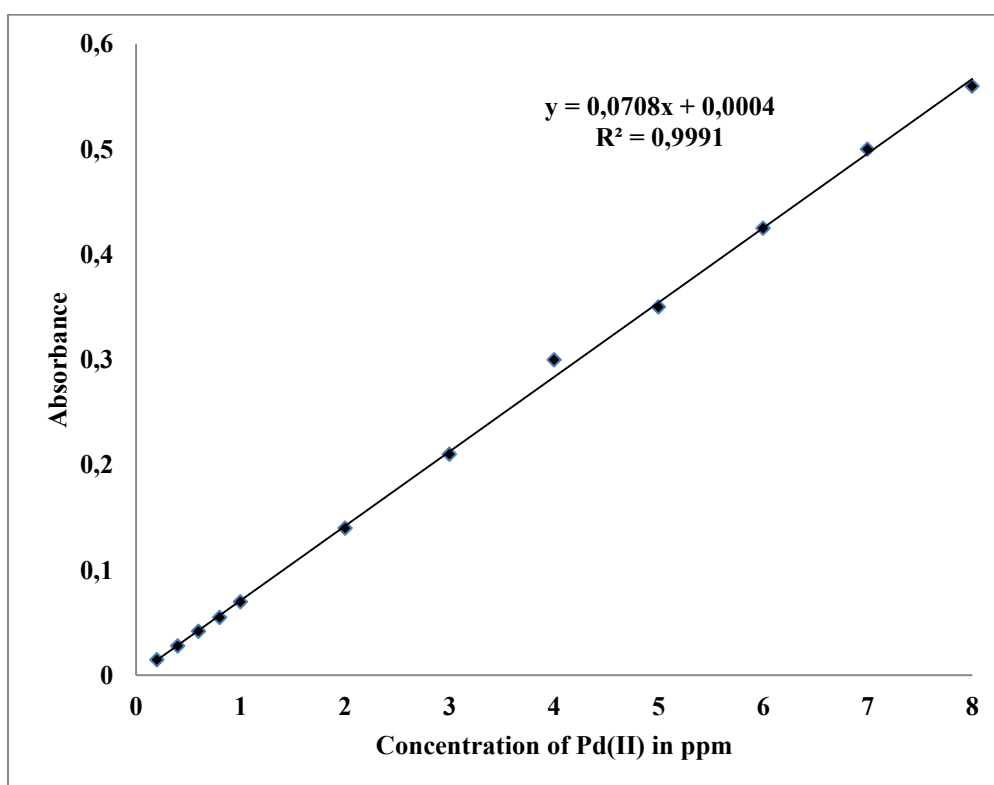


Fig. 3. Calibration Curve Pd(II).

3.8 Effect of Foreign ions

The tolerance level for the divers ions investigated were as follows F^- , Cl^- , Br^- , I^- , NO_3^- , SO_4^{2-} , SO_3^{2-} , ClO_3^- , BrO_3^- , IO_3^- , $\text{S}_2\text{O}_8^{2-}$, SCN^- , Acetate, Citrate, Tartarate, Oxalate, Urea (20 mg each). Li(I), Na(I), K(I), Ca(II), Mg(II), Sr(II), Mo(VI), Sb(III), Ba(II), Cd(II), Mn(II), Zn(II), Ni(II), & Sb(III) (10 mg each). Ti(III), V(IV), Pd(II), & Hg(II) (5 mg each). Co (II) interferes and masked with EDTA. The tolerance limit was set as the amount of foreign ion that causes an error of not more than +2 % in the recovery of metal ion.

3.9 Precision and Accuracy

The precision and accuracy of the method were determined the average of ten determination with 50 µg Pd(II) was found to be 49.931 µg with standard deviation 0.3836 and the deviation from mean at 95 % confident limit was ± 0.1037 . The native of extraction complex was determined by job's continuous variation method and was found to be 1:2 (M:L) i.e Pd(II) - HMICdt was confirmed by mole ratio 1:2. The reaction is,



3.10 Application

3.10.1 Synthetic mixture

The developed method has been employed for estimation of Palladium in various synthetic mixture and real samples. A number of synthetic mixtures containing 50 µg Palladium and other commonly associated metal ions were prepared by mixing there solution and analyzed according to developed method (Table 3).

Table 3. Determination of Pd(II) in various synthetic, Alloys Samples.

Name of Sample	Pd(II) Found by Present Method*	Certified Value	Recovery (%)
Synthetic Mixture#			
Pd ²⁺ (50 µg) + Co ²⁺ (50 µg)	49.97	50	99.94
Pd ²⁺ (50 µg) + Ni ²⁺ (100 µg)	49.98	50	99.96
Pd ²⁺ (50 µg) + Cu ²⁺ (50 µg)	49.99	50	99.98
Pd ²⁺ (50 µg) + Ag ¹⁺ (100 µg)	49.96	50	99.92
Pd ²⁺ (50 µg) + Cd ²⁺ (100 µg)	49.97	50	99.94
Alloys Samples®			
Pd-Ag Alloy#			
(ITA LAB)	29.09	29.11	99.93

Values are in µg, * Mean of Five determinations, ® Values in percentage

3.10.2 Analysis of alloys (White metal)

The developed method has been employed for estimation of Palladium in various real samples like pd-Ag alloy. Definite amount of alloy was dissolved in concentrated nitric acid and solution was evaporating to dryness. The dried residue was taken up in dilute nitric acid. The solution was filtered off and washed with hot dilute nitric acid and finally washed with hot water then filtrate was collected and dilute to 100 ml with distilled water. A definite aliquot of the above solution was used to extract and to determine palladium by developed method. The results obtained were compared with those of AAS (Table 3).

4. CONCLUSION

The proposed method can be used for determination of Pd at trace level. Method has advantage of reliability, reproducibility, and good sensitivity, simple instant color development and minimum interference. The method has been successively applied for the separation of Palladium at trace level in synthetic mixtures and real samples. The result obtained in the good agreement with the certify value and were compared with those obtained by known method.

References

- [1] Singhal G., Bhavesh R., Kasariya K., Sharma A., Singh R., *J Nanopart Res* 13 (2011) 2981-2988.
- [2] Cadete Santos Aires F. J., Kurzina I., Garcia Cervantes G., Bertolini J. C., *Catal Today* 117 (2006) 518-524.
- [3] Moreno-Alvarez S. A., Martinez-Castanon G. A., Nino-Martinez N., Reyes-Macias J. F., Patino-Marin N., Loyola-Rodriguez J. P., Ruiz F., *J Nanopart Res* 12 (2010) 2741-2746.
- [4] Iwase A., Kato H., Kudo A., *Catal Lett.* 108 (2006) 7-10.
- [5] Nagy G., Hancsok J., Varga Z., Polczmann G., Kallo D., *Top Catal.* 45 (2007) 195-201.
- [6] Chassary P., Vincent T., Marcano J. S., Macaskie L. E., Guibal E., *Hydrometallurgy* 76 (2005) 131-147.
- [7] Barakat M. A., Mahmoud M. H. H., *Hydrometallurgy* 72 (2004) 179-184.
- [8] Kramer J., Driessen W. L., Koch K. R., Reedijk J., *Hydrometallurgy* 64 (2002) 59-68.
- [9] Rane M. V., Venugopal V., *Hydrometallurgy* 84 (2006) 54-59.
- [10] Mhaske A. A., Dhadke P. M., *Hydrometallurgy* 61 (2001) 143-150.
- [11] Kanetake T., Otomo M., *Anal Sci.* 4 (1988) 411-416.
- [12] Sinha S. H., Sawant A. D., *Bull Chem Soc Jpn.* 65 (1992) 1622-1625.
- [13] Nakanishi T., Otomo M., *Anal Sci.* 1 (1985) 161-164.
- [14] Desai B. J., Shinde V. M., *Fresenius Z Anal Chem.* 295 (1979) 412-413.
- [15] Kumar A., Gautam M., Puri B. K., *Microchem. J.* 33 (1986) 256-263.
- [16] Sarma L. S., Kumar J. R., Reddy K. J., Kumar A. K., Reddy A. V., *Anal Sci.* 18 (2002) 1257-1261.
- [17] Narayana S. L., Reddy K. J., Reddy S. A. N., Kumar J. R., Reddy A. V., *J. Chin Chem Soc.* 54 (2007) 1233-1241.
- [18] Reddy K. J., Kumar J. R., Ramachandraiah C., Reddy A. V., *Environ Monit Assess* 136 (2008) 337-346.
- [19] Dakshinamoorthy A., Singh R. K., Iyer R. H., *J Radioanal Nucl Chem.* 177 (1994) 3 27-333.

- [20] Ruhela R., Sharma J. N., Tomar B. S., Panja S., Tripathi S. C., Hubli R. C., Suri A. K., *Radiochim Acta* 98 (2010) 209-214.
- [21] Jeffer G. H., Bassette J., Mendham J. A., Dennej R. C., *Vogel Textbook of Quantitative Chemical Analysis*, 5th edn, English Language Book Society, England (1984).
- [22] Singh A. K., Sharma S., *Microchem J.* 35 (1987) 365-368.

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