

CHAPTER VI

**EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF
PALLADIUM(II) WITH 2,6-DIACETYLPIRIDINE BIS-4-PHENYL-3-
THIOSEMICARBAZONE(2,6-DAPBPTSC)**

6.1 Introduction

The abundance of palladium in the earth's crust is 8.5×10^{-13} %. Palladium and its alloys have a wide range of applications both in the chemical industry and in instrument making¹. Environmental contamination by the platinum group elements (PGEs), mainly related to automotive catalytic converters, is exponentially increasing and reliable and accurate quantification is a mandatory task. The wide use of palladium not only in automotive catalytic converters but also as a drug and in food production has led to a more uncontrolled release of these metals in the environment, with respect to the one due to the traditional chemical industry². Several alloys of palladium with cobalt and nickel have been constructed and studied. Palladium-cobalt alloys show catalytic activity in the hydrogenation of nitrile function³. Palladium is one of the precious metals. Owing to its corrosion resistant nature and alloying ability, palladium is an important element in metallurgy. Its alloys are used in dental and medicinal devices and in jewelry manufacture. Moreover, palladium is used in automobile catalysts together with Pt and Rh⁴.

6.2. Review of known methods

As per the review of literature some standard, sensitive and/or selective reagents for the spectrophotometric and extractive spectrophotometric determination of palladium(II) are discussed here.

1,3-bis(hydroxymethyl)benzimidazole-2-thione[BHMBT]⁵ is used for the extractive spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 370 nm in presence of acidic medium and the complex is extracted into methyl isobutylketone. The molar absorptivity of the complex is found to be 1.543×10^4 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed upto 6.0 ppm of palladium(II). The method is successfully used for the determination of palladium(II) in synthetic mixtures, alloys and hydrogenation catalysts.

Zuhri et al⁶ have reported 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol (5-Br-PADAP) for the spectrophotometric determination of palladium(II). The complex

shows maximum absorbance at 585 nm in the pH 3.5. The molar absorptivity of the complex is found to be 3.86×10^4 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed upto 50 ppm of palladium(II).

n-butyl xanthate⁷ is used for the spectrophotometric determination of palladium(II). The complex shows a maximum absorbance at 385 nm in the pH range of 3.8-8.4. The molar absorptivity of the complex is found to be 1.319×10^4 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed in the range 2.5-105.0 ppm of palladium(II). The method is successfully used for the determination of palladium(II) in some alloys.

o-Hydroxyhydroquinonephthalein⁸ is used for the spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 630 nm in acidic medium. The molar absorptivity of the complex is found to be 8.4×10^5 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed in the range 0.02-0.18 of palladium(II).

5-(5-nitro-2-pyridylazo)-2,4-diaminotoluene (5-NO₂-PADAT)⁹ is used for the spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 592 nm in acidic medium. The molar absorptivity of the complex is found to be 1.25×10^5 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed upto 0.9 ppm of palladium(II). The method is successfully used for the determination of palladium(II) in industrial samples.

Toei et al¹⁰ have reported 2-nitroso-5-diethylaminophenol for the extractive spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 486 nm in acidic medium and the complex is easily extractable into chloroform. The molar absorptivity of the complex is found to be 4.38×10^4 lit mol⁻¹ cm⁻¹. The method is successfully applied for the determination of palladium(II) in catalysts for automobile exhaust purifiers.

Pentane-2,4-bis-(*o*-mercaptophenyl)-anil¹¹ is used for the spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 510 nm in the pH range of 1.5-3.0. Beer's law is obeyed in the range 2.0-16.0 ppm of palladium(II).

Gao et al¹² have reported 1-(2-pyridylazo)-2-naphthol(PAN) for the spectrophotometric determination of palladium(II). The complex shows maximum absorbance at

678 nm in the pH range of 1.5-7.5. The molar absorptivity of the complex is found to be 1.2×10^4 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed in the range 0.5-10 ppm of palladium(II). The method is successfully used for the determination of palladium(II) in synthetic samples.

Saxena et al¹³ have reported 4-(2-pyridylazo)-resorcinol for the spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 486 nm in the pH 4.0.

Carbonyl derivatives like oximes, hydrazones, thio- and phenylthiosemicarbazones are also used for the spectrophotometric as well as extractive spectrophotometric determination of palladium(II). Some of sensitive and/or selective methods are discussed below.

α -Benzilmonoxime(BZ)¹⁴ is used for the extractive spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 434 nm in acidic medium and the complex is easily extractable into chloroform. The molar absorptivity of the complex is found to be 1.0×10^4 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed in the range 0.3-13.0 ppm of palladium(II). The method is successfully used for the determination of palladium(II) in synthetic mixtures.

Paria et al¹⁵ have reported α -benzoinoxime for the extractive spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 390 nm in acidic medium and the complex is easily extractable into chloroform. The molar absorptivity of the complex is found to be 3.9×10^3 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed in the range 20.0-200.0 ppm of palladium(II).

2-cis-3,7-dimethyl-2,6-octadien-1-oxime¹⁶ is used for the extractive spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 445 nm in acidic medium and the complex is easily extractable into chloroform. The molar absorptivity of the complex is found to be 2.43×10^3 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed in the range 0.4-40.0 ppm of palladium(II). The method is successfully used for the determination of palladium(II) in industrial samples.

Rao et al¹⁷ have reported 5,6-dimethyl-1,3-indanedione-2-oxime for the spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 370 nm in pH 5.5. The molar absorptivity of the complex is found to be 2.98×10^4 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed in the range 0.15-4.17 ppm of palladium(II). The method is successfully used for the determination of palladium(II) in synthetic samples.

α -Furildioxime¹⁸ is used for the extractive spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 297 nm in acidic medium and the complex is easily extractable into benzene. The molar absorptivity of the complex is found to be 2.25×10^4 lit mol⁻¹ cm⁻¹.

2-Methyl-1,4-naphthoquinone-4-oxime¹⁹ is used for the spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 460 nm in the pH range of 6.5-7.8. The molar absorptivity of the complex is found to be 8.60×10^3 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed in the range 1.58-10.47 ppm of palladium(II). The method is successfully used for the determination of palladium(II) in alloy samples.

Utakar et al²⁰ have reported 2-oxo-4-hydroxy-phenylacetaldehydeoxime(HOHPO) for the extractive spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 420 nm in acidic medium and the complex is easily extractable into chloroform. The method is successfully used for the determination of palladium(II) in synthetic mixtures and real samples.

Other oximes used for the spectrophotometric and extractive spectrophotometric determination of palladium(II) are alkylketoximes²¹, 5-chloro-2,4-dihydroxypropiophenone-oxime²², 5-chlorosalicylaldoxime²³, 2,2-diquinolyl ketoxime²⁴, glyoxime²⁵, 4-heptanoneoxime²⁶, *o*-hydroxyacetophenoneoxime²⁷, 3-hydroxy-2-methyl-1,4-naphthoquinone-4-oxime²⁸, 5-methyl-2,3-hexanedionedioxime²⁹, 3-Phenoxy benzaldoxime³⁰ and salicylaldoxime³¹.

2-Acetylthiophene guanylylhydrazone³² is used for the spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 375 nm in pH 12.5. The molar absorptivity of the complex is found to be 0.74×10^4 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed upto 12.0 ppm of palladium(II).

Gangadharappa and Reddy³³ have reported 2-aminoacetophenone isonicotinoyl-hydrazone for the spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 500 nm in the pH range of 3.0-5.0. The molar absorptivity of the complex is found to be 3.0×10^4 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed in the range 0.3-3.0 ppm of palladium(II).

2,2'-bipyridyl-2-pyridyl hydrazone³⁴ is used for the extractive spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 585 nm in the pH range of 2.0-12.0 and the complex is easily extractable into chloroform. The molar absorptivity of the complex is found to be 1.90×10^4 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed in the range 2.0-20.0 ppm of palladium(II).

Nakanishi et al³⁵ have reported Di-2-pyridyl ketone benzoylhydrazone spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 455 nm in acidic medium and the complex is easily extractable into benzene. The molar absorptivity of the complex is found to be 9.38×10^2 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed upto 10.0 ppm of palladium(II).

Di-2-pyridyl methanone-2-(5-nitro) pyridylhydrazone³⁶ is used for the spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 560 nm in acidic medium. The molar absorptivity of the complex is found to be 3.78×10^4 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed upto 2.8 ppm of palladium(II).

Rosales and Ariza³⁷ have reported 1-(2-Pyridylmethylidene)-5-(salicylidene) thiocarbohydrazone spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 505 nm in the pH range of 4.5-9.0. The molar absorptivity of the complex is found to be 1.65×10^3 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed upto 5.0 ppm of palladium(II).

Thiozole-2-carbaldehyde-2-quinolyhydrazone³⁸ is used for the spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 625 nm in acidic medium. The molar absorptivity of the complex is found to be 1.93×10^4 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed upto 4.2 ppm of palladium(II).

Thio- and phenylthiosemicarbazones have emerged as very important analytical reagents for the spectrophotometric and extractive spectrophotometric determination of palladium(II).

Reddy et al³⁹ have reported Benzildithiosemicarbazone for the extractive spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 370 nm in pH 2.5 and the complex is easily extractable into methylisobutyl ketone. The molar absorptivity of the complex is found to be 3.01×10^4 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed in the range 0.25-3.5 ppm of palladium(II).

Narayana et al⁴⁰ have reported benzyloxybenzaldehydethiosemicarbazone(BBTSC) for the extractive spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 365 nm in pH 5.0 and the complex is easily extractable into cyclohexanol. The molar absorptivity of the complex is found to be 0.40×10^4 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed in the range 5.0-60.0 ppm of palladium(II). The method is successfully used for the determination of palladium(II) in synthetic and water samples.

5-Bromosalicylaldehyde-4-phenyl-3-thiosemicarbazone⁴¹ is used for the spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 412 nm in acidic medium. The molar absorptivity of the complex is found to be 1.42×10^4 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed upto 8.0 ppm of palladium(II).

Yamaguchi and Usegi et al⁴² have reported 3,5-dichlorosalicylaldehyde-4-phenyl-3-thiosemicarbazone for the spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 410 nm in acidic medium. The molar absorptivity of the complex is found to be 1.43×10^4 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed upto 8.0 ppm of palladium(II).

2,4-Dihydroxyacetophenonethiosemicarbazone⁴³ is used for the spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 412 nm in pH 3.5. The molar absorptivity of the complex is found to be 1.30×10^4 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed in the range 0.72-12.0 ppm of palladium(II).

Radushev and Statina at al⁴⁴ have reported diphenylthiosemicarbazone for the spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 530 nm in the pH range of 4.0-5.0. The molar absorptivity of the complex is found to be 0.98×10^4 lit mol⁻¹cm⁻¹.

N-Ethyl-3-carbazolecarbaxaledethiosemicarbazone⁴⁵ is used for the extractive spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 410 nm in pH 4.0 and the complex is easily extractable into n-butanol. The molar absorptivity of the complex is found to be 1.64×10^4 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed upto 6.6 ppm of palladium(II). The method is successfully used for the determination of palladium(II) in water and synthetic mixtures.

Sharma at al⁴⁶ have reported pyridoxal-4-phenyl-3-thiosemocarbazone for the extractive spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 460 nm in pH 3.0 and the complex is easily extractable into benzene. The molar absorptivity of the complex is found to be 2.20×10^4 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed in the range 0.4-6.4 ppm of palladium(II). The method is successfully used for the determination of palladium(II) in synthetic mixtures.

3,4,5-trimethoxybenaldehyde thiosemicarbazones⁴⁷ is used for the spectrophotometric determination of palladium(II). The complex shows maximum absorbance at 370 nm in acidic medium. The molar absorptivity of the complex is found to be 8.35×10^4 lit mol⁻¹ cm⁻¹ and the Beer's law is obeyed upto 12 ppm of palladium(II).

A thorough literary survey has revealed that a number of thiosemicarbazones are available for the spectrophotometric and extractive spectrophotometric determination of palladium(II). But many of the thiosemicarbazones are either less sensitive or non-selective. Hence, a new reagent namely 2,6-diacetylpyridinebis-4-phenyl-3-thiosemicarbazone (2,6-DAPBPTSC) is synthesized to the development of a simple, selective and sensitive extractive spectrophotometric method for the determination of palladium(II). In the present investigation, the researcher has studied the reactivity of 2,6-DAPBPTSC with palladium(II) and the results are reported in terms of its maximum absorbance, pH, molar absorptivity and stoichiometry, which provides the basis for judging the potential

utility of 2,6-DAPBPTSC as an analytical reagent for palladium(II). Finally, the developed method is successfully applied for the determination of palladium(II) in spiked samples.

6.3. Results and Discussion

2,6-Diacetylpyridine bis-4-phenyl-3-thiosemicarbazone(2,6-DAPBPTSC) forms a 1:1(M:L) yellowish orange colored complex with palladium(II), which is extracted into isoamylalcohol, from sodium acetate-acetic acid buffer (pH 4.0). The yellowish orange Pd(II)-2,6-DAPBPTSC complex has a maximum absorbance at 410 nm and is stable for 46 hours. The conditions for effective extraction are established after studying the effects of various factors, such as pH, reagent concentration, metal ion concentration and influence of diverse ions, in order to develop a sensitive and selective extractive spectrophotometric method for the determination of palladium(II) at trace levels.

6.3.1. Absorption spectra of reagent and Pd(II)- 2,6-DAPBPTSC complex

The absorption spectrum of Pd(II)-2,6-DAPBPTSC complex was recorded against the reagent blank. Similarly the absorption spectrum of the reagent (2,6-DAPBPTSC) was recorded against the solvent blank. The absorption spectra of both the complex and reagent are shown in Fig. 6.1. From the absorption spectra it is clear that the complex and reagent have shown maximum absorptions at 410 nm and 360 nm, respectively. The reagent has minimum absorbance at the maximum absorbance of the complex and the reagent does not interfere with the determination of palladium(II). Hence, further absorbance measurements of the complex were recorded at 410 nm.

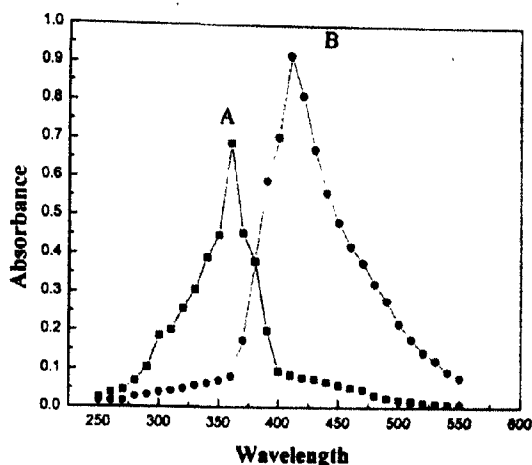


Fig. 6.1 (A) Absorption spectrum of 2,6-DAPBPTSC; (B) Absorption spectrum of Pd(II)-2,6-DAPBPTSC complex: Pd(II)= 1.0 mL of 1.0×10^{-4} M; 2,6-DAPBPTSC= 1.0 mL of 1.0×10^{-3} M and 2.0 mL of pH 4.0.

6.3.2. Effect of pH

To arrive at the optimum pH required for maximum colour development, the effect of pH on the colour intensity was studied. In each case, a mixture containing 1.0 mL of 1.0×10^{-4} M palladium(II), 2.0 mL of suitable buffer, 1.0 mL of 1.0×10^{-3} M 2,6-DAPBPTSC solution was taken and the aqueous phase is adjusted to 10.0 mL with double distilled water. It was shaken with 10.0 mL of portion of isoamylalcohol for one minute. The organic phases was collected into a 25 mL of standard flask and made upto the mark with isoamylalcohol. The same procedure was applied for buffers of different pH values, ranging from 1.0-6.5. The absorbances were measured at 410 nm, using their corresponding reagent blanks and the values are noted in Table 6.1. A plot is executed between the pH and the absorbance, and the same is represented in Fig. 6.2. The plot shows that there is maximum absorbance and constancy in the pH range 3.5-4.5. Hence, pH 4.0 is chosen for further studies, considering this as an optimum pH.

Table 6.1 Effect of pH on Pd(II)- 2,6-DAPBPTSC complex

| S.No. | pH | Absorbance |
|-------|-----|------------|
| 1 | 1.0 | 0.230 |
| 2 | 1.5 | 0.323 |
| 3 | 2.0 | 0.436 |
| 4 | 2.5 | 0.576 |
| 5 | 3.0 | 0.792 |
| 6 | 3.5 | 0.907 |
| 7 | 4.0 | 0.923 |
| 8 | 4.5 | 0.918 |
| 9 | 5.0 | 0.695 |
| 10 | 5.5 | 0.543 |
| 11 | 6.0 | 0.436 |
| 12 | 6.5 | 0.320 |

Pd(II) = 1.0 mL of 1.0×10^{-4} M; 2,6-DAPBPTSC = 1.0 mL of 1.0×10^{-3} M and $\lambda_{\text{max}} = 410$ nm.

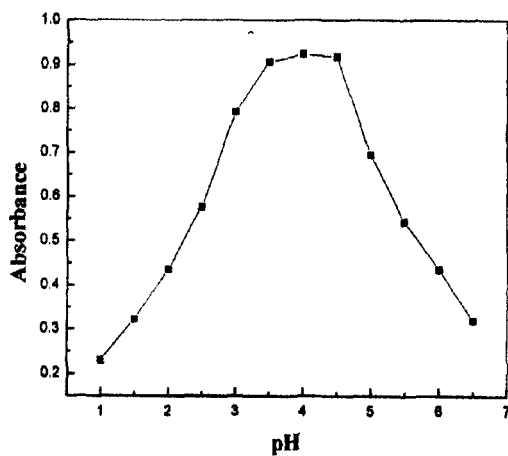


Fig.6.2. Effect of pH on Pd(II)-2,6-DAPBPTSC complex: Pd(II)=1.0 mL of 1.0×10^{-4} M; 2,6-DAPBPTSC= 1.0 mL of 1.0×10^{-3} M and $\lambda_{\text{max}} = 410$ nm

6.3.3. Effect of solvents

The effect of various solvents such as isoamylalcohol, cyclohexanol, chloroform, toluene, benzene, n-butanol, carbontetrachloride, ethyl acetate, butyl acetate, xylene, tributyl phosphate, n-propyl alcohol and methylisobutylketone on the extraction of palladium(II) with 2,6-DAPBPTSC is at pH 4.0 for registering the effect of solvent. Among the various solvents studied, isoamylalcohol is selected as a suitable solvent, because the complex has shown maximum absorbance in it and its greater extraction ability. The results are reported in Table 6.2.

Table 6.2 Effect of solvent on the extraction of Pd(II)- 2,6-DAPBPTSC complex

| Solvent | Absorbance |
|-----------------------|------------|
| cyclohexanol | 0.856 |
| isoamylalcohol | 0.920 |
| methylisobutyl ketone | 0.725 |
| n-butanol | 0.768 |
| chloroform | 0.612 |
| benzene | 0.548 |
| carbontetrachloride | 0.645 |
| xylene | 0.487 |
| hexane | 0.456 |
| butyl acetate | 0.523 |
| ethyl acetate | 0.410 |
| toluene | 0.365 |

Pd(II)=1.0 mL of 1.0×10^{-4} M; 2,6-DAPBPTSC=1.0 mL of 1.0×10^{-3} M; pH=4.0 and $\lambda_{\text{max}} = 410\text{nm}$

6.3.4. Effect of reagent concentration

The effect of reagent concentration was studied, using different aliquots containing constant volumes of 1.0×10^{-4} M palladium(II) solution, 2.0 mL of pH 4.0 buffer solution and 1.0 mL of 2,6-DAPBPTSC solution containing different concentrations ranging from 1.0×10^{-4} to 20.0×10^{-4} M, in order to obtain the maximum colour formation. The total volumes of aqueous each phase was brought to 10.0 mL with double distilled water. The aqueous phases were shaken with 10.0 mL of isoamylalcohol in each case and

the organic phases were collected into 25 mL standard flasks. The organic phases were made up to the mark with isoamylalcohol. The absorbances of the organic phases were measured at 410 nm, against their corresponding reagent blanks and the values are noted in Table 6.3. It is clearly observed from the absorbance values, that a sixteen-fold molar excess of the reagent is sufficient to get maximum color formation of the complex. The plot is shown in Fig. 6.3.

Table 6.3 Effect of reagent concentration on Pd(II)- 2,6-DAPBPTSC complex

| Concentration of reagent, $\times 10^{-4}$ M | No of folds of reagent concentration with respect to metal | Absorbance |
|-------------------------------------------------|---------------------------------------------------------------|------------|
| 1.0 | 1 | 0.220 |
| 2.0 | 2 | 0.290 |
| 3.0 | 3 | 0.375 |
| 4.0 | 4 | 0.449 |
| 5.0 | 5 | 0.530 |
| 6.0 | 6 | 0.600 |
| 7.0 | 7 | 0.684 |
| 8.0 | 8 | 0.750 |
| 9.0 | 9 | 0.840 |
| 10.0 | 10 | 0.924 |
| 11.0 | 11 | 1.024 |
| 12.0 | 12 | 1.073 |
| 13.0 | 13 | 1.120 |
| 14.0 | 14 | 1.135 |
| 15.0 | 15 | 1.150 |
| 16.0 | 16 | 1.164 |
| 17.0 | 17 | 1.169 |
| 18.0 | 18 | 1.171 |
| 19.0 | 19 | 1.173 |
| 20.0 | 20 | 1.173 |

Pd(II)= 1.0 mL of 1.0×10^{-4} M; 2,6-DAPBPTSC =1.0 mL of 1.0×10^{-4} to 20.0×10^{-4} M; pH=4.0 and λ_{\max} =410 nm

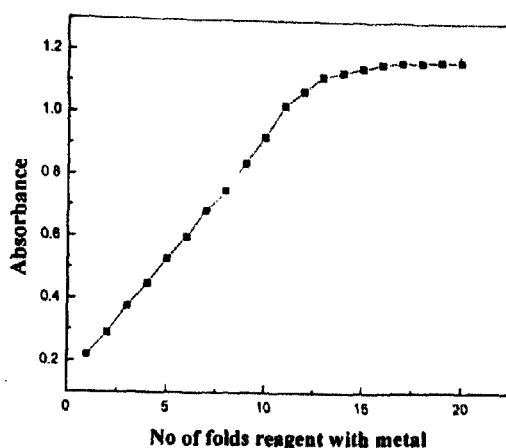


Fig. 6.3 Effect of reagent on Pd(II)-2,6-DAPBPTSC complex: Pd(II)= 1.0 mL of 1.0×10^{-4} M; 2,6-DAPBPTSC = 1.0 mL of 1.0×10^{-4} to 20.0×10^{-4} M; pH=4.0 and $\lambda_{\text{max}} = 410$ nm.

6.3.5. Applicability of Beer's law

Various aliquots containing different concentrations of palladium(II) ranging from 1.0×10^{-5} to 16.0×10^{-5} M (1.06-17.02 ppm), 2.0 mL of pH 4.0 buffer and 1.0 mL of 2,6-DAPBPTSC reagent (16.0×10^{-4} M) solution were taken and their volumes adjusted 10.0 mL with double distilled water. The aqueous phases were shaken with isoamylalcohol in each case and the organic phases were collected into 25 mL standard flasks. The organic phases were made up to the mark with isoamylalcohol. The absorbances of all the solutions were recorded at 410 nm, against their corresponding reagent blanks. The obtained results were noted in Table 6.4. A graph plotted between the amount of palladium(II) and its absorbance is shown in Fig.6.4. It can be observed from the graph that a linear plot passing through the origin obeys Beer's law in the concentration range 1.06 - $12.72 \mu\text{g mL}^{-1}$ (ppm) of palladium(II). The molar absorptivity of the complex is calculated and noted as $1.156 \times 10^4 \text{ lit mol}^{-1} \text{cm}^{-1}$ and the Sandell's sensitivity of the complex is $0.0092 \mu\text{g cm}^{-2}$. The correlation coefficient value of the Pd(II)-2,6-DAPBPTSC complex, with an independent variable as concentration in $\mu\text{g mL}^{-1}$ and a dependent variable as absorbance, is found to be 0.962. This indicates a satisfactory linearity between the two variables.

Table 6.4 Applicability of Beer's law to Pd(II)- 2,6-DAPBPTSC complex

| Concentration of metal, $\times 10^{-5} \text{M}$ | Amount of metal, ppm | Absorbance |
|------------------------------------------------------|----------------------|------------|
| 1 | 1.06 | 0.123 |
| 2 | 2.12 | 0.232 |
| 3 | 3.18 | 0.350 |
| 4 | 4.24 | 0.470 |
| 5 | 5.30 | 0.580 |
| 6 | 6.36 | 0.700 |
| 7 | 7.42 | 0.810 |
| 8 | 8.48 | 0.930 |
| 9 | 9.54 | 1.050 |
| 10 | 10.60 | 1.165 |
| 11 | 11.66 | 1.270 |
| 12 | 12.72 | 1.386 |
| 13 | 13.78 | 1.400 |
| 14 | 14.84 | 1.409 |
| 15 | 15.90 | 1.412 |
| 16 | 16.96 | 1.415 |

Pd(II)=1.0 mL of 1.0×10^{-3} to 16.0×10^{-3} M; 2,6-DAPBPTSC=1.0 mL of 15×10^{-4} M; pH=4.0 and $\lambda_{\text{max}}=410$ nm.

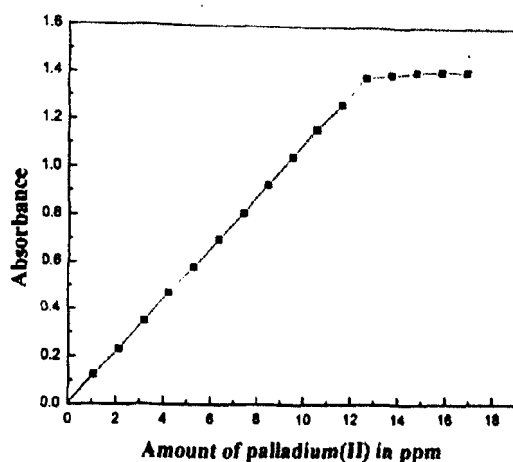


Fig. 6.4 Applicability of Beer's law to Pd(II)-2,6-DAPBPTSC complex: Pd(II)=1.0 mL of 1.0×10^{-3} to 16.0×10^{-3} M; 2,6-DAPBPTSC=1.0 mL of 16.0×10^{-4} M; pH = 4.0 and $\lambda_{\text{max}} = 410\text{nm}$

6.3.6. Ringbom plot for Pd(II)- 2,6-DAPBPTSC complex

Ringbom plot is the standard adopted to know the optimum range of the concentration for a system, which emaciates Beer's law. The values are noted in Table 6.5. The plot is drawn between $\log C$ of Pd(II) and $(1-T)$ [where T is the transmittance]. The plot has a sigmoid shape with a linear segment at intermediate concentration values ranging from $3.02\text{-}4.06 \mu\text{g L}^{-1}$. The slope of the plot from Fig.6.5 is 0.740. Based on this value at 1% photometric error, the ratio between the relative error in concentration and the photometric error is 3.110. Hence, the relative error in concentration is 0.031.

Table 6.5 Ringbom plot for Pd(II)- 2,6-DAPBPTSC complex

| Amount of palladium(II), $\mu\text{g L}^{-1}, C$ | Log C | Absorbance | Transmittance | (1-T) |
|-----------------------------------------------------|-------|------------|---------------|-------|
| 1060 | 3.02 | 0.123 | 0.884 | 0.116 |
| 2120 | 3.32 | 0.232 | 0.792 | 0.208 |
| 3180 | 3.50 | 0.350 | 0.704 | 0.296 |
| 4240 | 3.62 | 0.470 | 0.625 | 0.375 |
| 5300 | 3.72 | 0.580 | 0.559 | 0.441 |
| 6360 | 3.80 | 0.700 | 0.496 | 0.504 |
| 7420 | 3.87 | 0.810 | 0.444 | 0.556 |
| 8480 | 3.93 | 0.930 | 0.394 | 0.606 |
| 9540 | 3.98 | 1.050 | 0.349 | 0.651 |
| 10600 | 4.02 | 1.165 | 0.311 | 0.689 |
| 11660 | 4.06 | 1.270 | 0.280 | 0.720 |
| 12720 | 4.10 | 1.386 | 0.250 | 0.750 |
| 13780 | 4.14 | 1.400 | 0.246 | 0.754 |
| 14840 | 4.17 | 1.409 | 0.244 | 0.756 |
| 15900 | 4.20 | 1.412 | 0.243 | 0.757 |
| 16960 | 4.23 | 1.415 | 0.242 | 0.758 |

Pd(II)= 1060-16960 $\mu\text{g L}^{-1}$; 2,6-DAPBPTSC=1.0 mL of 15×10^{-4} M; pH=4.0 and $\lambda_{\text{max}} = 410$ nm.

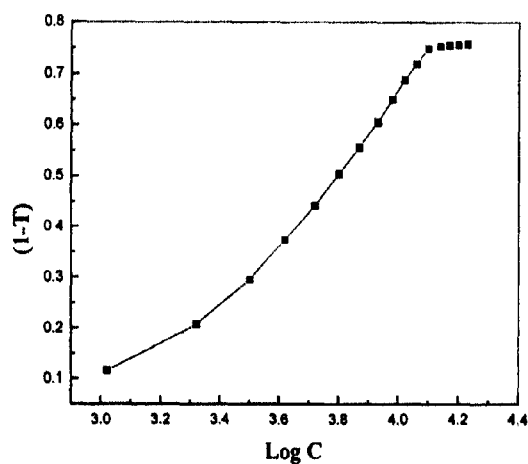


Fig. 6.5 Ringbom plot for Pd(II)-2,6-DAPBPTSC complex: Pd(II)= 1060-16960 $\mu\text{g L}^{-1}$; 2,6-DAPBPTSC= 1.0 mL of 15.0×10^{-4} M; pH = 4.0 and $\lambda_{\text{max}} = 410$ nm

6.3.7. Precision, accuracy and detection limit of the method

To assess the precision and accuracy of the method, determinations were carried out for a set of five measurements, with different concentrations of Pd(II), under optimum conditions. Calculations had revealed that the standard deviation of method was not more than 0.001 and the relative standard deviation was less than 0.371%. It is evident from these results, that the method is precise, besides being accurate. The detection limit, C_{\min} is determined as the amount of palladium(II) corresponding to three times the standard deviation of the blank values and a value of $0.00785 \mu\text{g L}^{-1}$ is obtained.

6.3.8. Determination of the composition of Pd(II)- 2,6-DAPBPTSC complex

Job's method of continuous variation, molar ratio method and Asmus' method were employed to elucidate the composition of the complex.

6.3.8.1. Job's method of continuous variation

Equimolar solutions of palladium(II) and 2,6-DAPBPTSC (1.5×10^{-3} M) were used to determine the metal to ligand ratio by job's method of continuous variation. The absorbance values were recorded at 410 nm using their corresponding reagent solution as blanks. The values are reported in Table 6.6 and the corresponding graph drawn between absorbance and $V_M / V_L + V_M$ (where V_L and V_M are the volumes of the reagent and the metal, respectively) is shown in Fig.6.6. From the graph, it is observed that one mole of palladium(II) reacts with one mole of ligand, shows the composition of metal to ligand complex is 1:1.

Table 6.6 Job's method of continuous variation

| Volume of Pd(II), V_M , mL | Volume of 2,6-DAPBPTSC, V_L , mL | V_M/V_{M+V_L} | Absorbance |
|---------------------------------|---------------------------------------|-----------------|------------|
| 0.2 | 1.8 | 0.1 | 0.520 |
| 0.4 | 1.6 | 0.2 | 0.902 |
| 0.6 | 1.4 | 0.3 | 1.240 |
| 0.8 | 1.2 | 0.4 | 1.512 |
| 1.0 | 1.0 | 0.5 | 1.620 |
| 1.2 | 0.8 | 0.6 | 1.492 |
| 1.4 | 0.6 | 0.7 | 1.297 |
| 1.6 | 0.4 | 0.8 | 0.820 |
| 1.8 | 0.2 | 0.9 | 0.440 |

$[Pd(II)] = [2,6-DAPBPTSC] = 1.5 \times 10^{-3} M$; $pH = 4.0$ and $\lambda_{max} = 410 \text{ nm}$.

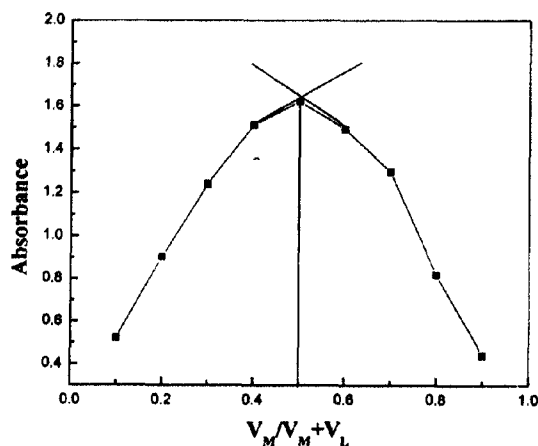


Fig. 6.6 Job's method of continuous variation: $[Pd(II)] = [2,6-DAPBPTSC] = 1.5 \times 10^{-3} M$; $pH = 4.0$ and $\lambda_{max} = 410 \text{ nm}$

6.3.8.2. Molar ratio method

In molar ratio method, different aliquots containing 1.0 mL of $1.0 \times 10^{-3} M$ palladium(II), 2.0 mL of sodium acetate-acetic acid buffer ($pH = 4.0$) and varying concentrations (0.25×10^{-3} to $2.0 \times 10^{-3} M$) of 2,6-DAPBPTSC were used to determine the metal ligand ratio. The absorbances of the solutions were recorded at 410 nm against their respective reagent blanks. The values are noted in Table 6.7. A plot (Fig.6.7.) is drawn between the absorbance and the concentration of the reagent. From the obtained

curve, it is confirmed that one mole of palladium(II) complexes with one mole of 2,6-DAPBPTSC.

Table 6.7 Molar ratio method

| No. of moles of 2,6-DAPBPTSC per one mole of Pd(II) | Absorbance |
|-----------------------------------------------------|------------|
| 0.25 | 0.375 |
| 0.50 | 0.607 |
| 0.75 | 0.840 |
| 1.00 | 1.103 |
| 1.25 | 1.206 |
| 1.50 | 1.298 |
| 1.75 | 1.380 |
| 2.00 | 1.470 |

Pd(II) = 1.0 mL of 1.0×10^{-3} M; 2,6-DAPBPTSC = 1.0 mL of 0.25×10^{-3} to 2.0×10^{-3} M; pH = 4.0 and $\lambda_{\text{max}} = 410$ nm.

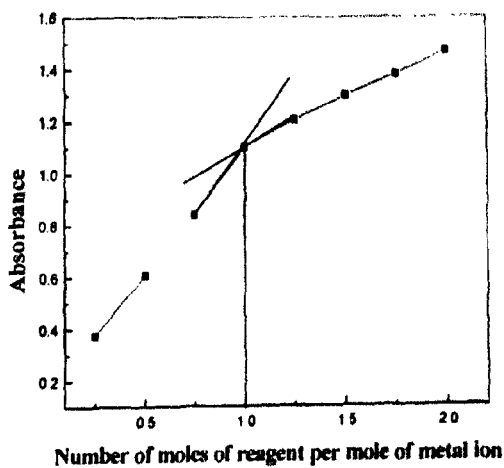


Fig.6.7 Molar ratio method: Pd(II) = 1.0 mL of 1.0×10^{-3} M; 2,6-DAPBPTSC = 1.0 mL of 0.25×10^{-3} to 2.0×10^{-3} M; pH = 4.0 and $\lambda_{\text{max}} = 410$ nm.

6.3.8.3. Asmus' method

For Asmus' method the data obtained from molar ratio method was used. $1/m$ values (where 'm' is extinction modulus) were calculated by dividing the optical density with the cell width, along with $1/V$, $1/V^2$ and $1/V^3$ which are given Table 6.8. The plots between $1/m$ and $1/V$, $1/V^2$ and $1/V^3$ are indicated in Fig.6.8. Among the plots between $1/m$ and $1/V$, $1/V^2$ and $1/V^3$, only the plot between $1/m$ and $1/V$ is linear indicating that the composition of the complex is 1:1 (M: L).

Table 6.8 Asmus' method

| Volume of 2,6-DAPBPTSC, (V) | Absorbance (m) | $1/m$ | $1/V$ | $1/V^2$ | $1/V^3$ |
|-----------------------------|----------------|-------|-------|---------|---------|
| 0.25 | 0.375 | 2.66 | 4.00 | 16.00 | 64.00 |
| 0.50 | 0.607 | 1.64 | 2.00 | 4.00 | 8.00 |
| 0.75 | 0.840 | 1.19 | 1.33 | 1.77 | 2.37 |
| 1.00 | 1.103 | 0.90 | 1.00 | 1.00 | 1.00 |
| 1.25 | 1.206 | 0.82 | 0.80 | 0.64 | 0.51 |
| 1.50 | 1.298 | 0.77 | 0.66 | 0.44 | 0.29 |
| 1.75 | 1.380 | 0.72 | 0.57 | 0.32 | 0.18 |
| 2.00 | 1.470 | 0.68 | 0.50 | 0.25 | 0.12 |

Pd(II)= 1.0 mL of 1.0×10^{-3} M; 2,6-DAPBPTSC= 1.0 mL of 0.25×10^{-3} to 2.0×10^{-3} M; pH=4.0 and $\lambda_{\max} = 410$ nm.

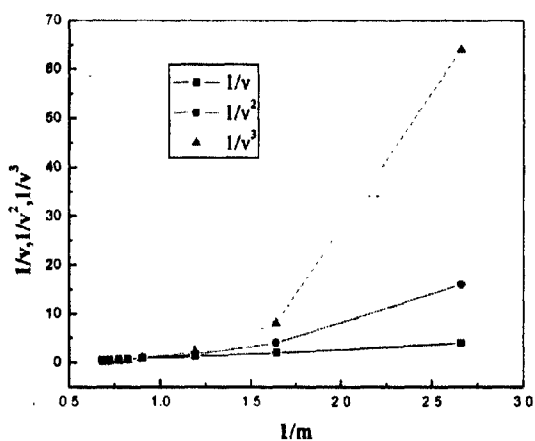


Fig.6.8 Asmus' method: Pd(II)= 1.0 mL of 1.0×10^{-3} M; 2,6-DAPBPTSC= 1.0 mL of 0.25×10^{-3} to 2.0×10^{-3} M; pH=4.0 and $\lambda_{\max} = 410$ nm.

6.3.8. Calculation of instability constant of Pd(II)-2,6-DAPBPTSC complex

The instability constant of Pd(II)-2,6-DAPBPTSC complex was calculated by using Asmus' method. The absorbance values were obtained at 410 nm for the solutions containing fixed volumes of palladium(II) (1.0 mL of 1.0×10^{-3} M) and 2.0 mL of pH 4.0 buffer with different known volumes of 0.25-2.0 mL of 1.0×10^{-3} M of 2,6-DAPBPTSC. The instability constant of Pd(II)-2,6-DAPBPTSC complex is calculated to be 1.667×10^{-4} at room temperature.

6.3.9. Effect of foreign ions on extraction of Pd(II)- 2,6-DAPBPTSC complex

Interference of a number of cations and anions is studied in the color absorbance of the Pd(II)-2,6-DAPBPTSC complex. A change in absorbance of ± 0.0025 was taken as the tolerance limit for interference. In respect of some interfering ions, an increased tolerance limit was achieved by the addition of masking agents such as thiosulphate, citrate, acetate and tartate. Increasing the amounts of masking agents proportionately could mask higher amounts of interfering ions. In this study, cations like As(III), As(V), Mg(II), Mn(II), Zr(IV), Sb(III), Ca(II), Sr(II), Ba(II) and Tl(III) do not interfere, even when present upto $5500 \mu\text{g mL}^{-1}$ and cations like Bi(III), Hg(II), Be(II), Th(VI), U(VI), Al(III), and V(V) are tolerated upto $3000 \mu\text{g mL}^{-1}$, but Co(II), Cu(II), Ni(II), Zn(II), Fe(II), Fe(III), Cd(II) and Mo(VI) do interfere with the determination of palladium(II), when present in more than $2000 \mu\text{g mL}^{-1}$. The interference of Cu(II) can be eliminated by using 1.0 mL 0.2 % thiosulphate as a masking agent. The interference of Co(II) and Ni(II) can be eliminated by using 1.0 mL 0.2 % thiocyanate as a masking agent. Fe(II) and Fe(III) are masked with 1.0 mL of 3% of sodium fluoride. The interference of Zn(II) and Cd(II) can be eliminated by using 1.0 mL of 0.5% of citrate solution. Anions like, bromide, chloride, fluorine, thiosulfate and thiourea do not interfere when present upto $3000 \mu\text{g mL}^{-1}$, with the determination of palladium(II) in the method. Oxalate and phosphate interfere, even when present in trace amounts. These results are given in Table 6.9.

Table 6.9 Effect of foreign ions on the extraction of Pd(II)-2,6-DAPBPTSC complex

| Foreign Ion | Tolerance Limit, $\mu\text{g/mL}$ | Foreign Ion | Tolerance Limit, $\mu\text{g/mL}$ |
|--------------------|-----------------------------------------------------|--------------------|-----------------------------------------------------|
| As(III), | 5500 | V(V) | 3000 |
| As(V) | 5500 | Zn(II) | 2000 |
| Mn(II) | 5500 | Fe(III) | 2000 |
| Mg(II) | 5500 | Ni(II) | 2000 |
| Ca(II) | 5500 | Cu(II) | 2000 |
| Sb(III) | 5500 | Co(II) | 2000 |
| Sr(II) | 5500 | Thiosulfate | 3000 |
| Ba(II) | 5500 | Thiourea | 3000 |
| Zr(IV) | 5500 | Fluoride | 3000 |
| Tl(III) | 5500 | Citrate | 1500 |
| Hg(II) | 3000 | Borate | 1500 |
| Bi(III) | 3000 | | |
| Be(II) | 3000 | | |
| Th(VI) | 3000 | | |
| U(VI) | 3000 | | |
| Al(III) | 3000 | | |

6.4. Applications

The developed extractive spectrophotometric method for palladium(II) is applied for its determination in water, synthetic and catalyst samples.

6.4.1. Determination of palladium(II) in Water samples

The present method is applied for the determination of palladium(II) in water samples. The concentration of palladium(II) was determined by adopting the procedure described in general procedure. The data obtained in the analyses of water samples are given in Table 6.10.

Table 6.10 Determination of palladium(II) in water samples

| S. No | Palladium (II) added ^b | Amount of Palladium(II) found ^a | | | | | |
|----------|-----------------------------------|--------------------------------------------|-----------------------------|----------------|---------|--------|--------|
| | | Reported method ^b | Present method ^b | Present method | | | |
| | | | | S.D. | R.S.D.% | T-test | F-test |
| Sample 1 | 6.0 | 5.69 | 5.67 | 0.02 | 0.342 | 7.86 | 4.89 |
| Sample 2 | 8.0 | 7.62 | 7.56 | 0.032 | 0.418 | 4.92 | 2.59 |
| Sample 3 | 10.0 | 9.83 | 9.75 | 0.036 | 0.363 | 2.00 | 5.25 |
| Sample 4 | 11.0 | 11.92 | 11.85 | 0.032 | 0.271 | 2.20 | 3.82 |

^a Average of five determinations, ^b Concentration in µg/mL.

6.4.2. Analysis of palladium(II) in synthetic mixtures

Various synthetic mixtures were prepared and analyzed for Pd(II) by employing the proposed recommended procedure⁴⁸. The data obtained in the analyses of water samples are given in Table 6.11.

Table 6.11 Determination of palladium(II) in synthetic mixtures

| Synthetic mixture composition | Amount of palladium(II) found ^a | | | | | | |
|-------------------------------------------------------------|--------------------------------------------|-------------------------|-----------------------------|----------------|----------|--------|--------|
| | Palladium (II) added ^b | AAS method ^b | Present method ^b | Present method | | | |
| | | | | S.D. | R.S.D. % | T-test | F-test |
| 25 Fe(III) + 12.5 Co(II) + 25 Cu(II) | 3.00 | 2.98 | 2.99 | 0.008 | 0.27 | 1.17 | 4.67 |
| | 4.00 | 3.98 | 3.99 | 0.010 | 0.25 | 0.89 | 5.33 |
| | 5.00 | 4.99 | 4.98 | 0.012 | 0.24 | 1.73 | 4.97 |
| 2.0 Fe(III) + 10 Ru(III) + 5 Pb(IV) + 10 Ir(IV) | 3.00 | 2.97 | 2.98 | 0.012 | 0.41 | 0.85 | 3.58 |
| | 4.00 | 3.98 | 3.97 | 0.016 | 0.39 | 0.42 | 1.19 |
| | 5.00 | 4.98 | 4.97 | 0.016 | 0.32 | 0.59 | 4.79 |
| 20 Ni(II) + 10 Co(II) + 5.0 Au(II) | 10.0 | 9.98 | 9.96 | 0.012 | 0.12 | 1.71 | 3.58 |
| 25 Pt(IV) + 10 Ru(III) + 20 Ir(IV) + 20 Rh(III) + 10 Zr(IV) | 4.00 | 3.97 | 3.98 | 0.018 | 0.45 | 0.66 | 2.55 |
| | 5.00 | 4.97 | 4.98 | 0.016 | 0.32 | 0.59 | 4.79 |
| | 6.00 | 5.96 | 5.97 | 0.016 | 0.27 | 0.51 | 5.99 |
| 2.0 Ni(II) + 12 V(V) + 5 Pb(IV) | 6.00 | 5.98 | 5.97 | 0.017 | 0.29 | 0.51 | 5.45 |
| | 7.00 | 6.97 | 6.99 | 0.021 | 0.30 | 1.10 | 2.66 |
| | 8.00 | 7.95 | 7.98 | 0.026 | 0.32 | 1.27 | 3.18 |

^a Average of five determinations, ^b Concentration in µg/mL.

6.4.3. Analysis of palladium(II) in catalyst samples

About 0.3 g of the every catalyst sample was treated twice with 10.0 mL portions of aquaregia. Each solution was then evaporated to 5.0 mL after cooling the solution was diluted with 20.0 mL of double distilled water and filtered into a 250mL calibrated flask. The residue was washed first with 20.0 mL of 2.0 M nitric acid and then the solution was made upto the mark with double distilled water. Suitable aliquots of this solution were taken and analyzed for palladium(II), using the recommended procedure⁴⁸. The data obtained in the analyses of catalyst samples are given in Table 6.12.

Table 6.12 Determination of palladium(II) in hydrogenation catalysts

| Catalyst | Amount of palladium(II) found ^a | | | | | | |
|--------------------------|--------------------------------------------|----------------------------|--------------------------------|----------------|----------|--------|--------|
| | Palladium(II) Claimed ^b | AAS method ^b | Present method ^b | Present method | | | |
| | | | | S.D. | R.S.D. % | T-test | F-test |
| Pd-CaCO ₃ | 5.00 | 4.95 | 4.98 | 0.021 | 0.424 | 1.31 | 4.54 |
| Pd-BaCO ₃ | 5.00 | 4.96 | 4.99 | 0.015 | 0.302 | 2.03 | 3.34 |
| Pd-BaSO ₄ | 5.00 | 4.98 | 4.97 | 0.019 | 0.381 | 0.56 | 3.21 |
| Pd-Activated charcoal | 10.00 | 9.95 | 9.98 | 0.021 | 0.211 | 1.20 | 5.71 |

^aAverage of five determination, ^bConcentration in %

6.5. Conclusions

The present investigations proved that 2,6-DAPBPTSC is a promising complexing agent for palladium(II) and its subsequent determination by extractive spectrophotometry was rapid and precise. The method has good sensitivity when compared to other existing extractive spectrophotometric determination methods. The selectivity of this method is improved by using masking agents for Co(II), Ni(II), Fe(II), Fe(III), Cu(II), Zn(II), Mo(IV) and Cd(II). It has been successfully applied for the determination of palladium(II) in water, synthetic and catalyst samples.

REFERENCES

1. Lokhande, T.N., Anuse, M.A. and Chavan, M.B., *Talanta*, **46**, 163, 1998.
2. Dong, X., Han, Y., Hu, Q., Chen, H. and Yang, G., *J. Braz. Chem. Society*, **17**, 189, 2006.
3. Bagherian, G., Chamjangali, M.A. and Eskandari, H., *J. Spectrochimica Acta, Part A*, In Press, 2006.
4. Pourreza, N. and Rastegarzadeh, S., *Canadian J. Anal. Sci. and Spectro.*, **49**, 314, 2004.
5. Gaikwad S.H. and Anuse, M.A., *Indian J. Chem. Tech.*, **10**, 447, 2003.
6. Abu Zuhri, A.Z., Shraydeh, B.F. and Shalabi, J., *Anal. Lett.*, **19**, 99, 1986.
7. Kumar, A., Gautam, M. and Puri, B. K., *Microchimical J.*, **33**, 256, 1986.
8. Yamaguchi, T., Inoue, M., Miyachi, K., Tominaga, H. and Fujita, Y., *Anal. Sci.*, **20**, 387, 2004.
9. Yang, H., Zhang, G., Zhang, L., Liu, G. and Zhang, X., *Talanta*, **43**, 747, 1996.
10. Toei, K., Motomizu, S. and Hamada, S., *Anal. Chim. Acta*, **101**, 169, 1978.
11. Chatterjee, A.B., Das, S.R. and Bag, S.P., *Microchimica Acta*, **79**, 115, 1983.
12. Gao, J., Peng, B., Fan, H., Kang, J. and Wang, X., *Talanta*, **44**, 837, 1997.
13. Saxena, K.K., Agarwala, B.V. and Dey, A.K., *Microchimica Acta*, **57**, 694, 1969.
14. Ensafi, A.A. and Eskandari, H., *Microchemical J.*, **63**, 266, 1999.
15. Paria, P.K. and Majunda, S.K., *Z. Anal. Chem.*, **279**, 207, 1976.
16. Chand, M., Lata, P. and Meena, N., *J. Indian Chem. Soc.*, **80**, 861, 2003.
17. Rao, D.M., Reddy, K.H. and Reddy, D.V., *Talanta*, **38**, 1047, 1991.

18. Peshkova, V.M., Shlenskaya, V.I. and Sokolov, S.S., *Tr. Khom. Po. Analit. Khim.*, **11**, 328, 1960.
19. Kamini, S. and Kumar, S.S., *Bull. Chem. Soc., Japan*, **60**, 1135, 1987.
20. Utekar, S.S., Jadhav, S.B. and S P Malve, S.P., *Indian J. Chem. Tech.*, **9**, 424, 2002.
21. Holland, W.J., Dimenna, R.A. and Walker, R.J., *Microchim. Acta*, **60**, 183, 1972.
22. Sharma, K.N., Rastogi, S.N., Jetley, U.K., Shukla, M., Rehman, E. and Singh, J., *Sci. Phy. Sci.*, **1**, 46, 1989.
23. Milosevic, R., Radulovic, D. and Tvanovic, D., *Arh. Farm.*, **36**, 275, 1986.
24. Stupavsky, S. and Holland, W.J., *Microchim. Acta*, **60**, 122, 1972.
25. Holland, W.J. and Soules, D., *Anal. Lett.*, **2**, 167, 1969.
26. Holland, W.J. and Walker, R.J., *Microchim. Acta.*, **61**, 193, 1973.
27. Poddar, S.N., *Anal. Chim. Acta*, **28**, 586, 1963.
28. Sharma, R.K., Shrivah, K. and Sindhvani, S.K., *Analyst*, **112**, 175, 1987.
29. Tandel, P.S., Jadhav, B.S. and Malve, P.S., *Indian J. Chem.*, **40**, 1128, 2001.
30. Lokhande, R.S., Nemade, H.G., Chaudhary, A.B. and Hundiwale, D.G., *Asian J. Chem.*, **13**, 596, 2001.
31. Peshkova, V.M., Shlenskaya, V.I. and Rashevskaya, A.I., *Vestn. Moskov. Univ. Ser. Fiz. Mat.*, **9**, 83, 1954.
32. Kawatkar, S.G. and Sathe, E.S., *Acta Ciencia Indica*, **22**, 1, 1996.
33. Gangadharappa, M. and Reddy, P.R., *J. Indian Chem. Soc.*, **83**, 1130, 2006.
34. Stratis, J.A., Anthemidis, A.N. and Vasilikiotis, G.S., *Analyst*, **109**, 373, 1984.

35. Nakanishi, T. and Otomo, M., *Anal. Sci.*, **1**, 161, 1985.
36. Kanetake, T. and Otomo, M., *Anal. Sci.*, **4**, 411, 1988.
37. Rosales, D. and Ariza, J.L.G., *Analyst*, **111**, 449, 1986.
38. Nakagawa, T., Doi, K. and Otomo, M., *ibid.*, **110**, 387, 1985.
39. Reddy, B.K., Reddy, K.J., Kumar, J.R., Kumar, A.K. and Reddy, A.V., *Anal. Sci.*, **20**, 925, 2004.
40. Narayana, S.L., Reddy, K.J., Reddy, S.A., Kumar, J.R. and Reddy, A.V., *J. Chin. Chem. Soc.*, **54**, 1233, 2007.
41. Usegi, K., Nagahiro, T., Kumagai, T. and Nishioka, H., *Chim. Acta Ture.*, **19**, 245, 1991.
42. Yamaguchi, S. and Usegi, K., *Analyst*, **110**, 1241, 1985.
43. Kumar, C.J., Sharma, L.S. and Reddy, A.V., *Asian J. Chem.*, **9**, 218, 1997.
44. Radushev, A.V. and Statina, I.A., *Zh. Anal. Khim.*, **28**, 2360, 1987.
45. Reddy, K.J., Kumar, J.R., Chandraiah, C.R., Reddy, S.A. and Reddy, A.V., *Envi. Moni. and Asses.*, **136**, 337, 2008.
46. Sarma, L.S., Kumar, J.R., Reddy, K.J., Kumar, A.K. and Reddy, A.V., *Anal. Sci.*, **18**, 1257, 2002.
47. Khader, A.M.A. and Prasad, K.S., *Tr. J. Chem.*, **20**, 222, 1996.
48. Vogel, A. I.; "A text book of Quantitative Inorganic Analysis, 3rd ed." Longmann, Green, London. 1961.