CHAPTER IV

Application of extractants for the extraction of Palladium(II)
4.1 Introduction

Palladium is one of the platinum group metals. It is steel-white, ductile metallic element resembling and occurring with the other platinum group metals (PGMs) and nickel. The abundance of palladium in the earth’s crust is $8.5 \times 10^{-13}\%$ and it exists in various natural minerals, soils, and rocks [1]. For industrial use, it is recovered mostly as a by-product of nickel, platinum and other base metal refining. Its separation from the PGMs depends upon the type of ore in which it is found.

Economically important and viable sources exist in Russia, South Africa and North America. The worldwide mining of palladium is estimated to yield about 260 tonnes/year.

Palladium and its alloys are used as catalysts in the (petro) chemical and, above all, the automotive industries. Demand for palladium in automobile catalysts rose from 24 tonnes in 1993 to 139 tonnes in 1998, as palladium-rich technology was adopted in many gasoline-fuelled cars.

Applications for electronics and electrical technology include use in metallization processes (thick film paste), electrical contacts and switching systems. Palladium alloys are also widely used in dentistry (e.g., for crowns and bridges) [2].

The increasing application of the palladium metal in the industrial process next to their extremely scarcity due to their natural abundance and the complexity of the process used for its extraction and refining, therefore, it is of paramount importance in the development of separation method to recover these metals to meet the present and future demand. Solvent extraction has become an effective technique in the recovery and separation of palladium [3-5].

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 2,2′-dithiodianiline [6], pyridine-2 acetaldehyde salicyloyl hydrazone [7], di-2- pyridyl ketonebenzoyl hydrazone [8], isonitroso benzoylacetone [9], isonitroso thiocamphor [10], butyl dithio carbonate [11], diphenyl thiovioluric acid [12], 2-carboxy-2_-hydroxy-5- methylazobenzene [13], pyridoxal-4-phenyl-3-thiosemicarbazone[14], benzylxy benzaldehyde thiosemicarbazone(BBTSC) [15], N-
ethyl-3-carbazolecarbaxaledehydethio semi-carbazone [16] and benzoin oxime (ABO) [17] have been developed. However, the existing methods suffer from various limitations such as longer extraction periods [6-8], temperature control [11], narrow pH range [11,9,14-16], less stability [9], and interference from other metal ions [6,11,13,17]. Moreover, in some methods [8-10], the extraction is not found to be quantitative. Solvent extraction of Palladium from hydrochloric acid [18] and nitric acid [19] media is reported.

Palladium(II) forms a number of complexes that are soluble in organic solvents because of the labile character of its chloro complex PdCl₄²⁻ towards several hydrophobic ligands [20]. This leads to the formation of several highly extractable complexes at room temperature. Palladium prefers to coordinate most strongly with polarizable atoms which have focused the development of an extracting agent on those with donor atoms such as sulfur, phosphorus and nitrogen.

According to the hard-soft acid-base (HSAB) concept [21], sulfur-containing extractants (soft bases) selectively extract metals classified as soft acids, e.g., Au, Ag, Pd, and Pt, but do not extract base metals. Several sulfur-containing extractants have been tested for the extraction of Pd(II), such as dialkyl(aryl) sulfides [22-24], trialkylphosphine sulfides [25,26], organothiophosphorus [27-29], mercaptobenzothiazole [30], sulfur-containing crown ethers [31], as well as thioether derivatives of calyxarenes [32-34]. Thiourea derivatives containing both sulfur and nitrogen donor atoms form strong complexes with Pd(II). N,N-diphenylthiourea has been investigated as an extractant for preconcentration from hydrochloric acid solutions and subsequent determination of PGM [35]. N-substituted benzoylthiourea [36] and alkylthiourea [37,38] showed high selectivity for Pd (II) in acidic solutions.

Trioctylamine [39,40] and n-octylamine [41,42] have been used for the extraction of palladium(II) using various organic solvents such as chloroform, benzene, carbon tetrachloride, methyl iso butyl ketones, o-xylene from nitrate, chloride, iodide, acetate, or succinate medium. Palladium complex with isopropyl, phenyl, isoprophenyl and with acetylenes [43] are known to extract palladium(II). Many dyes [44,45] in the presence of sulphate, bromide, or pyridine have been used to extract palladium(II) in to organic solvents. The organic compound containing
amino group [46-48], aniline compound [49,50], pyridine and its derivatives have been used to extract palladium(II) under diverse conditions of pH and in the presence of a particular anion. The dimethyl compound is preferred for the colorimetric estimation of palladium(II) as it gives the most stable color. Palladiazo (arsenoazo) and quinazinazo have been used to extract palladium(II) from sulphuric acid into chloroform [51-53]. These complexes can be extracted using solution of diphenyl guanidinum chloride or quaternary ammonium chloride salt into butanol or higher alcohols. Dithiozone [54] is another common extractant and has been effectively used for the quantitative extraction of palladium(II) from acid solution. Dialkyl, dialkyl ammonium and trialkyl dithiocarbamate have been employed by several workers [55-58], small amount of these type reagent can extract palladium(II) quantitatively in to carbon tetrachloride and many other solvents in the pH range 4 -11.0.

TBP [59,60] in the presence of bromide, iodide, chloride or nitrate has been used for the separation of palladium(II) from other metals by solvent extraction. TOPO [61,62] and TPP [63,64] in MIBK and 1, 2 dichloromethane have also been used to extract palladium(II) into various solvents. Some other organophosphorous reagents [65-67] have been also used to extract palladium (II) under various conditions. There are several other useful chelating extractants coordinating through oxygen and/or nitrogen. The organic compound containing pyridylazo group such as (1-12 pyridyl azo) -2 napthol [68,69] 4-(pyridyl azo) resorcinol (PAR) [70-74], etc have been used as effective reagents for the extraction of palladium(II) into various solvents. Some of the other extractants like organic compounds containing phenylazo [75-77] and derivatives of pyrazolone [78], and other containing azo group [79,80] have been successfully employed for the separation and or photometric determination of palladium.

Various oximes have been used for the extraction palladium(II), Dimethylglyoxime (DMG) [81-84] has been most frequently used among them, in which palladium(II) was extracted from acidic media in to chloroform, α benzyl monoxime [85], α furyldioxime [86,87], salicyladoxime [88], and naphthodoxime [89] are some of the other oximes have been extracted by acenaphthene quinine monoxime and their derivatives [90-92] into chloroform. Some alkyl pyridine
ketoxime [93-95] have also proved to be very effective in the extraction of palladium(II).

Extractive spectrophotometric methods find many advantages over direct spectrophotometric determination of metal ions. Selective separation of the metal ions, concentration and enrichment study can be achieved by extraction methods. 4-(4-ethoxybenzylideneamino)-5methyl-4H-1,2,4-triazole-3-thiol (EBIMTT) is a sulphur containing ligand and is highly water repellent. It does not form emulsion at the time of extraction. Because of the determination of trace and ultra trace level amounts of noble metals in minerals containing large amount of base metals is difficult; the effectiveness of EBIMTT has been evaluated as an extractant for palladium(II) from variety of palladium bearing materials and process solutions.

The various extraction methods for palladium describing the nature of the aqueous phase, organic phase, interference and special features have been summarized in Table 4.2.

The part 4.3 includes the method of extraction of palladium(II) with EBIMTT-I in chloroform from 1M hydrochloric acid which is rapid and quantitative from a variety of palladium bearing materials. The method proposed here offers extraction, separation and determination of palladium(II) from associated elements and from synthetic mixtures.

The part 4.4 includes the method of extraction of palladium(II) with EBIMTT-II in chloroform from 1M hydrochloric acid. The method proposed here offers extraction, separation and determination of palladium(II) from associated elements.
### 4.2 Summary of the methods used for solvent extraction of Palladium(II)

<table>
<thead>
<tr>
<th>System</th>
<th>Aqueous phase</th>
<th>Organic Phase</th>
<th>Interference</th>
<th>Special features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di-octyl Sulphonide</td>
<td>HNO₃ 0.5-1.5M</td>
<td>Xylene</td>
<td>-</td>
<td>i) Pd(II) was back extracted with a mixture of NaCO₃ + NH₃ [96]</td>
</tr>
<tr>
<td>Bis-(2-ethylhexyl) Sulphoxide</td>
<td>HCl 1.0-4.0 M</td>
<td>Kerosene</td>
<td>Shaking for 30min</td>
<td>i) Pd(II) was back extracted with 1.0 M HCl and determined by AAS [97]</td>
</tr>
<tr>
<td>N,N-Dialkyl-N-benzoyl thiourea</td>
<td>pH-3</td>
<td>Toluene or decane</td>
<td>Shaking for 10 min</td>
<td>i) Separation from Cu, Fe, Ni [98]</td>
</tr>
<tr>
<td>Thiobenzenilide</td>
<td>HCl 0.5M</td>
<td>Chloroform</td>
<td>-</td>
<td>i) Method suitable for separation of noble metals from base metals[99]</td>
</tr>
<tr>
<td>3- Hydroxy-4-(4-H-tatrazol-5-ylazo) naphthale-2,7 sulphonic acid</td>
<td>Aqueous Cl Solution</td>
<td>Chloroform</td>
<td>Shaking for 10 min</td>
<td>i) Pd was back extracted with 0.2 M HClO₄. ii) Method was applied to determined Pd in sludge [100]</td>
</tr>
<tr>
<td>Benzothiozole-2-thiol</td>
<td>HCl 1-6 M</td>
<td>MIBK</td>
<td>-</td>
<td>i) Method is applied for determination of Pd in geological samples [101]</td>
</tr>
<tr>
<td>N,N-disubs-</td>
<td>HCl</td>
<td>Toluene</td>
<td>-</td>
<td>i) Palladium is separated</td>
</tr>
<tr>
<td>Compound</td>
<td>Concentration</td>
<td>Extractant</td>
<td>Methodology</td>
<td>Notes</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>---------------</td>
<td>---------------</td>
<td>------------------------------------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>Tituted benzoyl thio urea</td>
<td>1-6 M</td>
<td>HCl, 0.1M, pH 2.4</td>
<td>Shaking for 20 min</td>
<td>Method suitable for extraction of Pd and Pt from Pt, Ru or Rh [102]</td>
</tr>
<tr>
<td>Bis-(2,4,4-tri-methylphenyl) phosphino dithioic acid</td>
<td>HCl, 0.1M, pH 2.4</td>
<td>Chloroform</td>
<td>Shaking for 20 min</td>
<td>Method suitable for extraction of Pd and Pt from Pt, Ru or Rh [103]</td>
</tr>
<tr>
<td>Benzothiazolethiol (BT)</td>
<td>Aqua-regia</td>
<td>Isobutyl Methyl Ketone</td>
<td>Many metal ions co-extracted</td>
<td>Pd extracted from geological samples and determined by AAS [104]</td>
</tr>
<tr>
<td>Derivative of benzo-thiazole</td>
<td>pH 5.0</td>
<td>MIBK</td>
<td>-</td>
<td>A procedure developed for extraction, separation of Pd, Hg, Pb, Cu, and Cd [105]</td>
</tr>
<tr>
<td>Bis-(2-ethylhexyl) sulfoxide</td>
<td>HNO₃, 8.0 M</td>
<td>Toluene</td>
<td>-</td>
<td>Pd is back extracted with 0.2M sodium thiosulphate, Pd recovered from synthetic nuclear waste solution [106]</td>
</tr>
<tr>
<td>Bis-(2-butylethioethyl) sulfide</td>
<td>HNO₃, 3.0 M</td>
<td>Chloroform</td>
<td>-</td>
<td>Pd separated from U(VI) and Pu(IV) Recovery of Pd(II)= 86% [107]</td>
</tr>
<tr>
<td>Triphenyl Phosphine</td>
<td>HCl, 1-8 M</td>
<td>1,2-Dichloroethane</td>
<td>Shaking for 60 min</td>
<td>Determined by spectrophotometrically after evaporation of organic phase [108]</td>
</tr>
<tr>
<td>Tributyl Phosphate</td>
<td>HCl, 1 M</td>
<td>Ethyl Acetate</td>
<td>Fe interfere</td>
<td>Extraction mechanism was studied.</td>
</tr>
<tr>
<td>Extractant</td>
<td>Acid/ Salt</td>
<td>Strip</td>
<td>Method/ Conditions</td>
<td></td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------------</td>
<td>-------</td>
<td>--------------------------------------------------------</td>
<td></td>
</tr>
</tbody>
</table>
| Tributyl Phosphate (TBP)      | HCl, 0.5 M | Ethyl Acetate | ii) Recovery= 95.7-99.4% <sup>[109]</sup>  
 i) Pd was back-extracted with thiourea (0.2%) + HCl (0.5M) <sup>[110]</sup>. |
| Tri-n-octylamine              | HCl, 11.5 M| Benzene    | i) SnCl<sub>2</sub> accelerates the extraction of Pd <sup>[111]</sup>  |
| N-n-Octylaniline              | HCl, 3M    | Chloroform / DIBK | i) Group extractant for noble metals  
 ii) Noble metals separated from base metals  
 iii) Extracted metals back-extracted with suitable strippent,  
 iv) Method was applied for analysis of sluges, flotation concentration , rocks and catalysts <sup>[112-117]</sup> |
| Tri-iso-Octylamine            | HCl, 4M    | Carbon tetrachloride | i) Co-extracted iron can be masked with potassium dihydrogen phosphate  
 ii) Method proposed for extraction of noble metals <sup>[118]</sup> |
| N-Octylaniline                | HCl, 3 M H<sub>3</sub>BO<sub>3</sub>, BeCl<sub>2</sub> | DIBK | i) Pd(II) was back extracted with 7 M HClO<sub>4</sub>  
 ii) Method suitable for extraction of PGMs except Os <sup>[119]</sup> |
| 1,1-diantipyrinyl butane      | H<sub>2</sub>SO<sub>4</sub> + KCN | Dichloroethane | i) Method proposed for extraction of noble metals <sup>[120]</sup> |
| 4-Octylamino-pyridine         | NO<sub>2</sub> | Carbon Tetrachloride | i) Pd was selectively stripped with 1M NaOH  
 ii) Method also useful for extraction of |
<table>
<thead>
<tr>
<th>Extractant</th>
<th>Acid/Buffer</th>
<th>Solvent</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>N,N,N,N,N-Tetra(2-ethylhexyl) thioglycolamide</td>
<td>HNO₃</td>
<td>n-dodecane</td>
<td>i) Pd determined from high level liquid waste (HLLW) solutions [122]</td>
</tr>
<tr>
<td>Liquid cation exchanger Versatic – 10</td>
<td>Acetate buffer, pH -6</td>
<td>Benzene</td>
<td>i) Pd was back extracted by conc. HCl [123]</td>
</tr>
<tr>
<td>7-Trideca-none oxime</td>
<td>HCl, 0.01 M+ NH₄Cl</td>
<td>Toluene</td>
<td>i) The extraction equilibrium and kinetics of Pd are given [124]</td>
</tr>
<tr>
<td>Quinoline – 8 – ol</td>
<td>Ascorbic Acid (5%)</td>
<td>Chloroform</td>
<td>i) Pd was back extracted with 0.1M NaOH [125]</td>
</tr>
<tr>
<td>Aza- analogue of Dibenzo-18-crown -5</td>
<td>HCl, 0.1 - 1.0 M,</td>
<td>Chloroform</td>
<td>i) Method free from interference of PGMs and gold [126]</td>
</tr>
<tr>
<td>C₈–10 Alkylaniline hydrochlorid</td>
<td>HCl, 50 %</td>
<td>Toluene</td>
<td>i) Extraction of Pd in presence of petroleum sulfides</td>
</tr>
<tr>
<td>Alkylaniline hydrochlorid</td>
<td>HCl</td>
<td>Toluene</td>
<td>ii) Extraction and separation of Pd and Pt described [127]</td>
</tr>
<tr>
<td>1-phenyl-3-Methyl -4-benzoyl -5 –</td>
<td>Acetate buffer pH – 5.2</td>
<td>MIBK</td>
<td>i) Extraction technique is suitable for the analysis of industrial waste solution</td>
</tr>
<tr>
<td>Compound</td>
<td>Interfering Acid</td>
<td>Solvent</td>
<td>Extraction Conditions</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------</td>
<td>---------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>pyrazolone (N-alkyl amino) diaacetamide</td>
<td>Picric acid</td>
<td>Shaking for 30 min</td>
<td>i) Pd separated from alkali metal ions [130]</td>
</tr>
<tr>
<td>2-ethyl hexylamino methyl pyridine</td>
<td>HCl</td>
<td>Toluene</td>
<td>-</td>
</tr>
<tr>
<td>Alamine 336</td>
<td>Aqueous Cl\text{-}mediated media pH - 1-5</td>
<td>5 % isodecanol</td>
<td>-</td>
</tr>
<tr>
<td>Bis(isovaleryl-acetone) ethylene diimine</td>
<td>NaHCO$_3$ buffer pH - 8</td>
<td>Cylohexane</td>
<td>Cu (II) and Ni (II) Coextracted</td>
</tr>
<tr>
<td>Triphenyl phosphene sulphide</td>
<td>HNO$_3$</td>
<td>Benzene</td>
<td>Shaking for 45 min</td>
</tr>
<tr>
<td>α- benzoin oxime</td>
<td>HNO$_3$ 0.1 - 4.0 M</td>
<td>Solvesso100</td>
<td>-</td>
</tr>
<tr>
<td>Triphenyl Phosphene</td>
<td>HNO$_3$</td>
<td>Chloroform</td>
<td>Shaking for 60 min</td>
</tr>
<tr>
<td>Aliquot 336</td>
<td>Acetate buffer pH-3-6</td>
<td>Chloroform</td>
<td>-</td>
</tr>
<tr>
<td>Kelex 100</td>
<td>HCl 1.0 M + SCN\text{-}</td>
<td>Toluene</td>
<td>Extraction for 60 hr</td>
</tr>
<tr>
<td>Isobutyl methyl ketone</td>
<td>HCl 2-3 M + SCN\text{-}</td>
<td>MIBK</td>
<td>-</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>------</td>
<td>------------</td>
<td>---</td>
</tr>
<tr>
<td>N-Benzyl-aniline</td>
<td>HCl</td>
<td>Chloroform</td>
<td>-</td>
</tr>
<tr>
<td>Alkylamine hydrochlorid</td>
<td>HCl 6M</td>
<td>Toluene</td>
<td>Shaking for 30 min</td>
</tr>
<tr>
<td>1,12-Di-2-Thyenyl2,5,8,11-Tetrathio dodecane</td>
<td>Aqua Regia</td>
<td>Chloroform</td>
<td>Shaking for 15 min</td>
</tr>
</tbody>
</table>

4.3 Extraction of Palladium(II) with EBIMTT-I from hydrochloric acid media.

4.3.1 Experimental

**General Procedure:**

An aqueous solution containing 100μg palladium(II) and enough hydrochloric acid and water were added to give final concentration of 1M with respect to hydrochloric acid in 25 ml. The resulting solution was transferred to 125 ml separating funnel. The aqueous phase was equilibrated once with 10 ml of 0.1M EBIMTT solution in chloroform for 30 seconds. It was allowed to separate and the metal from the organic phase was back stripped with two 5 ml portions of 50% ammonia solution. The extract was evaporated to moist dryness. The residue was dissolved in minimum amount of dilute hydrochloric acid to form the solution. Palladium(II) was estimated spectrophotometrically with pyrimidine -2-thiol [145].

4.3.2. Results and discussion:

**Effect of acidity:**
The extraction of palladium(II) was carried out from different acid media with 0.1M EBIMTT in chloroform keeping the aq: org ratio 2.5:1. The extraction was quantitative from 1-8M hydrochloric acid. The extraction was found to be quantitative in very high concentration of nitric acid but was incomplete in sulphuric acid. Hence the use of 1 M hydrochloric acid is used for further studies.

**Effect of concentration of extractant:**

In order to optimize the conditions for extraction of palladium(II), chloroform solutions of extractant with varying concentration (0.01- 0.20 M) were employed. It was found that 10 ml of 0.05 M extractant is sufficient for quantitative extraction of 100μg palladium(II) from hydrochloric acid media, but in recommended procedure 0.1 M extractant in chloroform was used to ensure the complete extraction of metal ion. There was no adverse effect if one can use excess of extractant. However, a decrease in concentration of extractant resulted in lower distribution ratio, D, values for palladium(II). (Figure 4.3.1).

**Effect of Equilibration time on Extraction:**

The effect of time was observed on the system for a period of 5s to 30min (hand shaking) the extraction was found quantitative over the periods longer than 10 seconds. But to ensure the complete extraction of Palladium(II) 1 min equilibration time was recommended. However, a prolonged shaking period doesn’t have any adverse effect on the extraction.

**Nature of extracted species:**

The composition of complex was confirmed by using log D- log C plot. The graph logD [Palladium(II)] versus log C[EBIMTT] at 4 mol/dm³ hydrochloric acid was found to be linear and having slope of 1.34 (Fig4.3.2). Hence, the probable composition of extracted species in chloroform has been found to be 1:1, [palladium(II): EBIMTT].

**Effect of Stripping Agents:**

Palladium(II) loaded in the organic phase was stripped with various stripping agents such as 1M HCl, 1M HNO₃, 1M NaOH, 50% NH₃, 1M Na₂CO₃. The stripping was observed only with NaOH, 50% NH₃, 1M Na₂CO₃. It was found that stripping was less than 50% with NaOH solution and 40% when Na₂CO₃ was used as
stripping agents. It was quantitative when 50% NH$_3$ solution was used. Hence, 50% NH$_3$ (1:1 ammonia) solution is suitable stripent for palladium (Table 4.3.1).

**Effect of diverse ions:**

Palladium(II) was extracted in the presence of different diverse ions (Table 4.3.2). The tolerance limit was set as the amount of foreign ions cause ±2% error in the recovery of palladium. The results showed that in the extraction and determination 100μg of the palladium(II), these ions did not interfered at the level tested. The reproducibility of palladium extraction investigated from six replicate measurements was 99.00 ± 0.95%.

**Application:**

**Analysis of synthetic mixtures:**

The separation of palladium(II) from the platinum group metals and other metals is very difficult. A solution containing 100μg of palladium(II) was taken and known amount of other metals were added. Under the optimum extraction conditions of palladium(II), there is a quantitative extraction of Au(III), Pt(IV), Ru(III) and Rh(II). But the co-extracted metal ions cannot be back-stripped by 1:1 ammonia solution. Thus, the reagent (EBIMTT) is made selective towards palladium(II) by taking an advantage of the stripant used. (Table 4.3.3)

**Binary separation of palladium (II) from iron (III), cobalt (II), nickel (II) and copper(II):**

The method allowed separation and determination of palladium(II) from a binary mixture containing either iron(III), cobalt(II), nickel(II) and copper(II). In a typical experiment, solution containing 100μg of palladium(II) was taken and known amounts of other metals were added. The separation of palladium(II) from iron(III), cobalt(II), nickel(II) and copper(II) was accomplished with 0.1 M EBIMTT in chloroform at 1M hydrochloric acid. Palladium(II) was estimated spectrophotometrically with pyrimidine-2-thiol. The recovery of palladium(II) and that added ions was 99.5% and results are reported in (Table 4.3.4).

**Analysis of alloys:**

To ascertain the selectivity of the reagent, the proposed method was successfully used in the determination of palladium(II) from alloys. The synthetic
mixture was prepared corresponding to the composition of alloy. The results of the analysis are reported in (Table 4.3.5). The average recovery of palladium(II) was 99.5%.

**Fig 4.3.1** Extraction of Palladium(II) as a function of EBIMTT-I concentration

![Extraction Graph](image1)

**Fig 4.3.2** Log-log plot of distribution ratio (DRh) versus EBIMTT-I concentration at 4 mol/dm³ HCl

![Log-log Plot](image2)
Table 4.3.1 Effect of different stripping agents

<table>
<thead>
<tr>
<th>Stripping agent</th>
<th>Concentration</th>
<th>Extraction(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>1M-6M(2×10 ml)</td>
<td>-</td>
</tr>
<tr>
<td>HNO₃</td>
<td>1M-6M(2×10 ml)</td>
<td>-</td>
</tr>
<tr>
<td>NH₃</td>
<td>1:1 (2×10 ml)</td>
<td>99.9</td>
</tr>
<tr>
<td>NaOH</td>
<td>1 mol.dm⁻³ (2×5 ml)</td>
<td>50</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>(2×10 ml)</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 4.3.2 Effect of foreign ions on the extraction of Pd (II) with EBIMTT -I

<table>
<thead>
<tr>
<th>Foreign ions</th>
<th>Amount tolerated (mg)</th>
<th>Foreign ions</th>
<th>Amount tolerated (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(II)</td>
<td>10</td>
<td>Pb(II)</td>
<td>5</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>15</td>
<td>Hg(II)</td>
<td>5</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>20</td>
<td>Ni(II)</td>
<td>5</td>
</tr>
<tr>
<td>Bi(III)</td>
<td>20</td>
<td>Co(II)</td>
<td>15</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>5</td>
<td>Sn(II)</td>
<td>5</td>
</tr>
<tr>
<td>Ca(II)</td>
<td>20</td>
<td>Be(II)</td>
<td>20</td>
</tr>
<tr>
<td>Mo(VI)</td>
<td>5</td>
<td>Ba(II)</td>
<td>20</td>
</tr>
<tr>
<td>Pt(II)</td>
<td>0.5</td>
<td>Cu(II)</td>
<td>5</td>
</tr>
<tr>
<td>Au(III)</td>
<td>1</td>
<td>Pt(IV)</td>
<td>1</td>
</tr>
<tr>
<td>Sb(III)</td>
<td>5</td>
<td>Cd(II)</td>
<td>5</td>
</tr>
<tr>
<td>Fluorid</td>
<td>200</td>
<td>Sr(II)</td>
<td>10</td>
</tr>
<tr>
<td>EDTA</td>
<td>100</td>
<td>Oxalate</td>
<td>200</td>
</tr>
<tr>
<td>Iodide</td>
<td>100</td>
<td>Acetate</td>
<td>100</td>
</tr>
<tr>
<td>Mg(II)</td>
<td>20</td>
<td>Bromide</td>
<td>100</td>
</tr>
</tbody>
</table>
Table 4.3.3 Analysis of synthetic mixtures

<table>
<thead>
<tr>
<th>Amount of metal ions (µg)</th>
<th>Palladium found (µg)</th>
<th>Recovery(^a) (%)</th>
<th>R.S.D (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(II)100+Au(III)500</td>
<td>99.2</td>
<td>99.7</td>
<td>0.04</td>
</tr>
<tr>
<td>Pd(II)100+Pt(IV)500</td>
<td>99.1</td>
<td>99.2</td>
<td>0.06</td>
</tr>
<tr>
<td>Pd(II)100+Rh(III)200</td>
<td>99.1</td>
<td>99.6</td>
<td>0.08</td>
</tr>
<tr>
<td>Pd(II)100+Pt(IV)200+Rh(III)200</td>
<td>98.7</td>
<td>99.7</td>
<td>0.07</td>
</tr>
<tr>
<td>Pd(II)100+Au(III)500+Rh(III)200</td>
<td>99.8</td>
<td>99.9</td>
<td>0.07</td>
</tr>
<tr>
<td>Pd(II)100+Pt(IV)200+Au(III)500</td>
<td>99.5</td>
<td>99.8</td>
<td>0.05</td>
</tr>
<tr>
<td>Pd(II)100+Pt(IV)200+Au(III)500+Fe(III)200+Co(III)2000</td>
<td>99.2</td>
<td>99.4</td>
<td>0.04</td>
</tr>
<tr>
<td>Pd(II)100+Pt(IV)500+Au(III)500+Rh(III)200+Fe(III)200+Co(III)2000</td>
<td>98.8</td>
<td>99.6</td>
<td>0.08</td>
</tr>
</tbody>
</table>

\(^a\)=Average of six determination

Table 4.3.4 Binary separation of palladium(II) from iron(III), cobalt(II), nickel(II) and copper(II)

<table>
<thead>
<tr>
<th>Composition of metal ions, (µg)</th>
<th>Recovery Pd(II) (%)</th>
<th>R.S.D (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(II)100; Fe(III)15000</td>
<td>99.6</td>
<td>0.13</td>
</tr>
<tr>
<td>Pd(II)100; Co(II)10000</td>
<td>99.7</td>
<td>0.07</td>
</tr>
<tr>
<td>Pd(II)100; Ni(II)5000</td>
<td>99.6</td>
<td>0.11</td>
</tr>
<tr>
<td>Pd(II)100; Cu(II) 5000</td>
<td>99.8</td>
<td>0.13</td>
</tr>
</tbody>
</table>
# Table 4.3.5 Analysis of alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Palladium taken, (µg)</th>
<th>Palladium found* (µg)</th>
<th>Recovery (%)</th>
<th>R.S.D (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low melting dental alloy</td>
<td>Pd,25; Au,10; Co,22; Ni,34</td>
<td>170</td>
<td>168.83</td>
<td>99.31</td>
<td>0.07</td>
</tr>
<tr>
<td>Stibio palladinite mineral</td>
<td>Pd,75; Sb,25</td>
<td>150</td>
<td>148.83</td>
<td>99.22</td>
<td>0.07</td>
</tr>
<tr>
<td>Jewellery alloy (Pd-Au alloy)</td>
<td>Pd,50; Au,50</td>
<td>100</td>
<td>99.86</td>
<td>99.86</td>
<td>0.11</td>
</tr>
<tr>
<td>Pd-Cu alloy</td>
<td>Pd,60; Cu,40</td>
<td>120</td>
<td>119.5</td>
<td>99.58</td>
<td>0.10</td>
</tr>
<tr>
<td>Pd-Ag alloy</td>
<td>Pd,60; Ag,40</td>
<td>120</td>
<td>119.66</td>
<td>99.9</td>
<td>0.06</td>
</tr>
</tbody>
</table>

*a Average of six determinations

## 4.4 Extraction and spectrophotometric determination of Palladium(II) with EBIMTT-II:

### 4.4.1 Experimental

**Procedure:** The liquid-liquid extraction and the spectrophotometric method followed for the determination of the metal ions were the same as described in 4.3.1 of this chapter.

### 4.4.2 Results and discussion

**Nature of extracted species:**

The composition of complex was confirmed by using log D- log C plot. The graph log D [Palladium(II)] versus log C[EBIMTT-II] at 4 mol/dm³ hydrochloric acid was found to be linear and having slope of 1.31 (Fig 4.4.1). Hence, the probable composition of extracted species in chloroform has been found to be 1:1, [Palladium(II): EBIMTT-II].

### 4.4.3 Application

The present method has been successfully applied for the determination of palladium(II) in a series of synthetic mixtures of various compositions, and also in a number of alloy samples.

**Analysis of synthetic mixtures:**
A solution containing 100μg of palladium(II) was taken and known amount of other metals were added. Under the optimum extraction conditions of palladium(II), there is a quantitative extraction of Au(III), Pt(IV), Ru(III) and Rh(III). But the co-extracted metal ions cannot be back-stripped by 1:1 ammonia solution. Thus, the reagent (EBIMTT-II) is made selective towards palladium(II) by taking an advantage of the stripant used. (Table 4.4.1)

**Analysis of alloys:**

To ascertain the selectivity of the reagent, the proposed method was successfully used in the determination of palladium(II) in alloys. The synthetic mixture was prepared corresponding to the compositions of alloy. The results of the analysis are reported in (Table 4.4.2). The average recovery of palladium(II) was 99.5%.

**Conclusion:**

We have reported here the use of EBIMTT-I and EBIMTT-II as extractants for palladium(II) from hydrochloric acid medium. On the basis of extraction studies performed, it was observed that both the extractants contains ‘S’ as a donor atom which is very selective and effective. EBIMTT-I having the oxygen containing side chain is more effective than EBIMTT-II.

The effectiveness of extractants has been evaluated for palladium(II) from variety of palladium bearing materials. The important features of this method are that, they permit selective separation of palladium(II) from other platinum group metals and base metals which are generally associated with it. It is free from interference from a large number of foreign ions, low reagent concentration is required and time needed for equilibration is very short for, about 30 seconds.
Fig 4.4.1 Log-log plot of distribution ratio (DPd) versus EBIMTT-II concentration at 4 mol/dm$^3$ HCl

Table 4.4.1 Analysis of synthetic mixtures

<table>
<thead>
<tr>
<th>Amount of metal ion (µg)</th>
<th>Pd found (µg)</th>
<th>Recovery$^a$ (%)</th>
<th>R.S.D (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(II)100+Au(III)500</td>
<td>99.4</td>
<td>99.8</td>
<td>0.03</td>
</tr>
<tr>
<td>Pd(II)100+Pt(IV)500</td>
<td>99</td>
<td>99.2</td>
<td>0.04</td>
</tr>
<tr>
<td>Pd(II)100+Rh(III)200</td>
<td>99</td>
<td>99.6</td>
<td>0.03</td>
</tr>
<tr>
<td>Pd(II)100+Pt(IV)500+Au(III)500+Rh(III)200+Fe(III)2000+Co(III)2000</td>
<td>98.2</td>
<td>99.6</td>
<td>0.08</td>
</tr>
</tbody>
</table>

$^a$=Average of six determinations

Table 4.4.2 Analysis of alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Pd taken, (µg)</th>
<th>Pd found$^a$ (µg)</th>
<th>Recovery (%)</th>
<th>R.S.D (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jewellery alloy (Pd-Au alloy)</td>
<td>Pd,50; Au,50</td>
<td>100</td>
<td>99.8</td>
<td>99.8</td>
<td>0.12</td>
</tr>
<tr>
<td>Pd-Cu alloy</td>
<td>Pd,60; Cu,40</td>
<td>120</td>
<td>119</td>
<td>99</td>
<td>0.14</td>
</tr>
</tbody>
</table>

$^a$=Average of six determinations
References:


84) W.F. Davis, Talanta, 16 (1969) 330.


