

# EXPEDITIOUS EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM(II) FROM CATALYSTS AND ALLOY SAMPLES USING NEW CHROMOGENIC REAGENT

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## ABSTRACT

A simple, rapid and selective method has been developed for the extractive spectrophotometric determination of palladium(II) using 4-(4'-fluorobenzylideneimino)-3-methyl-5-mercapto-1, 2, 4-triazole, (FBIMMT). In hydrochloric acid medium palladium(II) instantly forms stable yellow colored 1:1 complex with FBIMMT at room temperature, which was well extracted in chloroform. The extracted palladium(II)-FBIMMT species showed absorption maximum at 390 nm against reagent blank. The molar absorptivity and Sandell's sensitivity of palladium(II)-FBIMMT in chloroform were found to be  $5.404 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $0.0196 \mu\text{g cm}^{-2}$  respectively. The Beer's law was obeyed up to  $17.5 \mu\text{g mL}^{-1}$  of palladium(II). The optimal concentration range for maximum precision was evaluated from Ringbom's plot and was found to be 5 to  $17.5 \mu\text{g mL}^{-1}$ . To establish the optimum extraction conditions; various experimental parameters such as acidity, reagent concentration, solvents, shaking time, interference of cations and anions have been studied. To determine accuracy and precision of proposed method, determinations were carried out at five identical aliquots. The selectivity of the method was enhanced by the use of masking agents. The stoichiometry of the extracted species was assessed by Job's method, mole ratio method and verified by log-log plot. The present method was successfully applied for the separation and determination of palladium(II) from binary mixtures, multi component synthetic mixtures, synthetic mixtures corresponding to alloys and catalyst.

**Keywords:** Alloy samples, Extraction, FBIMMT, Palladium(II), Spectrophotometry

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## INTRODUCTION

Palladium is a rare element having lustrous silvery-white color and belongs to platinum group metals (PGMs). As compared to rest of platinum group metals, palladium has low density and lower melting point. At ordinary temperature, palladium is strongly resistant to corrosion and to the action of acids. Hence palladium and its alloys find extensive applications in various fields like catalysis, jewelry and cosmetic industries, dentistry, production of surgical instruments, electrical contacts and hydrogen storage material.<sup>1-7</sup> Palladium salts are also used in place of silver compounds in photographic printing papers.<sup>8</sup> The use of palladium and its alloys in various fields is growing continuously. Besides these applications, palladium causes significant allergic reactions as well as contact dermatitis, stomatitis, and periodontal gum diseases.<sup>9-11</sup> Therefore, the need arose for the effective extraction and trace level determination of palladium(II). Many analytical techniques such as X-ray fluorescence spectroscopy,<sup>12-14</sup> atomic absorption spectrophotometry,<sup>15-16</sup> neutron activation analysis<sup>17-18</sup> and spectrofluometry<sup>19</sup> have been used for the

determination of palladium at microgram level. Though these techniques are highly sensitive, are not selective, involve a number of steps, require sophisticated and expensive instruments. The experts are needed to monitor the instruments. The spectrophotometric methods are simpler and become popular technique for extraction and quantitative determination of palladium(II) and other transition metals.<sup>20-22</sup>

The reported methods suffer from limitations such as maximum absorbance in UV region and less selectivity, some methods are non extractive and require surfactant for full-color development, more equilibration time, synergent, heating of aqueous phase for complexation and have narrow Beer's range. According to Pearson's rule sulfur containing ligands form more stable complexes with PGMs, since sulfur containing ligands are soft bases and PGMs are soft acids.<sup>23</sup> Extraction and spectrophotometric determination of palladium(II) was reported using several organic reagents, summarized in Table 1.<sup>24-39</sup> In continuation of our work on the extractive spectrophotometric determination of PGMs,<sup>40-43</sup> we have synthesized new sulfur containing ligand, FBIMMT and aimed to develop simple, selective and rapid spectrophotometric method for trace level determination of palladium(II).

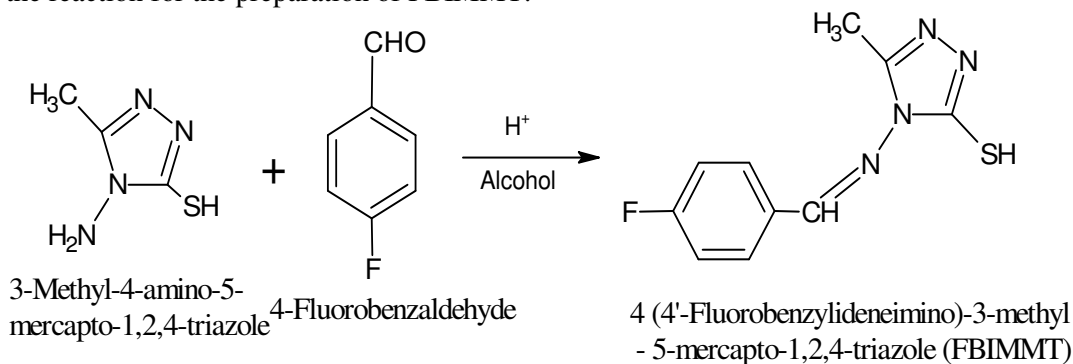
## EXPERIMENTAL

### Apparatus

Microcontroller based UV-Visible digital spectrophotometer Systronics model-117 (200-1100 nm) with 1 cm matching quartz cells was used for absorbance measurement. The pH measurements were made by using Equiptronics digital pH meter model EQ-615. For weighing purposes an electronic balance Contech, CA-123 was used. Calibrated glass wares were used for volumetric measurements.

### Preparation and characterization of 4-(4'-fluorobenzylideneimino)-3-methyl-5-mercapto-1, 2, 4-triazole (FBIMMT)

The reagent FBIMMT was prepared by simple condensation of 3-methyl-4-amino-5-mercapto-1, 2, 4-triazole<sup>44</sup> (2.6 g, 0.02 mol L<sup>-1</sup>) with 4-fluorobenzaldehyde (2.1 mL, 0.02 mol L<sup>-1</sup>). The mixture of 3-methyl-4-amino-5-mercapto-1, 2, 4-triazole and 4-fluorobenzaldehyde in 75 mL of ethanol containing 3 drops of glacial acetic acid was refluxed for 3-4 h. The reaction mixture was poured into ice cold water, filtered and recrystallized from hot 1:2 ethanol. On cooling, white needles were obtained. The scheme-1 shows the reaction for the preparation of FBIMMT.



Scheme-1

By using thin layer chromatography, the purity of the FBIMMT was checked. The melting point of the ligand was found to be 190 °C and its structure was confirmed by using <sup>1</sup>H NMR and IR spectra.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.31 (s, 3H, -CH<sub>3</sub>), δ 7.01-7.07 (d, 2H, Ar-H), δ 7.72-7.78 (d, 2H, Ar-H), δ 10.34 (s, 1H, -N=CH), δ 13.15 (s, 1H, -SH); IR (KBr, cm<sup>-1</sup>): 2751 (SH), 1171 (C=S), 1595 (HC=N)

### Standard palladium(II) solution

A standard stock solution of palladium(II) was prepared by dissolving 1.0 g palladium chloride (PdCl<sub>2</sub>, Loba chem.) in 1.0 mol L<sup>-1</sup> HCl and diluted to 250 mL in calibrated volumetric flask with distilled water.

Table-1: Comparison between present method and reported spectrophotometric methods for the determination of palladium(II)

Reagent	$\lambda_{\max}$ ( nm)	Acidity (mol L <sup>-1</sup> ) or pH	Beer's range ( $\mu\text{g mL}^{-1}$ )	Molar absorptivity ( L mol <sup>-1</sup> cm <sup>-1</sup> )	Remarks	Ref.
Hexyl benzimidazolyl sulfide	452	HCl 0.01-0.1	0.01-0.6	$2.08 \times 10^5$	Narrow Beer's range	24
N,N,N',N'-tetra(2-ethylhexyl) thiodiglycolamide	300	HNO <sub>3</sub> 3.0	1.0-15.0	$2.29 \times 10^5$	Absorbance in UV region, 5 min. waiting time	25
3,4,5-Trimethoxybenzaldehyde thiosemicarbazone	370	HCl 0.8	1.0-12.0	$8.35 \times 10^4$	2 min. shaking time	26
Diacetyl monoxime-(p-anisyl)-thiosemicarbazone	440	CH <sub>3</sub> COOH 10.0	0.2-2.0	$3.8 \times 10^4$	Non-extractive	27
<i>o</i> -Methoxyphenyl thiourea	325	HCl 1.0-8.0	0-15.0	$3.38 \times 10^3$	Absorbance in UV region	28
Azure I	647	HCl 4.0	5.0-20.0	-	High interference of Pt(IV), Au(III) , Hg(II)	29
1-Nitroso-2-hydroxy naphthalene-3,6-disulphonate	510	pH 2.0	0.015-0.3	$8.77 \times 10^5$	Heating 5 min.	30
Picramine-epsilon	556	H <sub>2</sub> SO <sub>4</sub> 5.0	0.02-0.04	$2.01 \times 10^4$	Heating 10 min.	31
Dahlia violet	585	H <sub>2</sub> SO <sub>4</sub> 0.02	0.001-0.038	-	Heating 10 min. (100 °C )	32
Thioglycolic acid	384	pH 11.0	2.4-6.4	$2.069 \times 10^4$	Non extractive, interference of many cations	33
Cefixime	352	pH 2.6	0.75-16.5	$1.224 \times 10^4$	Absorbance in UV region	34
3-Hydroxy-2-methyl-1-phenyl-4-pyridone	345	pH 1.5-3.0	0.28-8.0	$1.89 \times 10^4$	Absorbance in UV region, shaking 35 minutes	35
Benzyl dithiosemicarbazone	395	pH 2.5	0.25-3.5	$3.01 \times 10^4$	Narrow Beer's range	36
3-Methoxysalicylaldehyde-4-hydroxybenzoyl hydrazone	412	pH 4.5	0.287- 4.256	$1.03 \times 10^3$	Less sensitive, use of surfactant	37
4-[N'-(4- Imino-2-oxo-thiazolidin-5-ylidene)-hydrazino]- benzenesulfonic acid	438	pH 5.0	0.2-2.2	$7.5 \times 10^3$	Narrow Beer's range, Non extractive	38
<i>o</i> -Methylphenylthiourea	340	HCl 0.8	0.01-15.0	$2.85 \times 10^3$	Absorbance in UV region, less sensitive	39
4-(4'-Fluorobenzylideneimino)-3-methyl-5-mercapto-1, 2, 4-triazole (FBIMMT))	390	HCl 0.6-2.0	4.12-17.5	$5.404 \times 10^3$	Rapid, selective, low reagent concentration, wide Beer's range	PM

PM = Present method

The stock solution was standardized gravimetrically by a known method.<sup>45</sup> The working standard solution of palladium(II) was prepared by proper dilution of the standard stock solution with water.

### FBIMMT solution

The reagent FBIMMT solution (0.01 mol L<sup>-1</sup>) was prepared in chloroform by dissolving 0.236 g of FBIMMT crystals in 100 mL calibrated volumetric flask. The fresh reagent solution was used as and when required. Analytical reagent grade chemicals were used throughout the study. The standard solutions of foreign ions were prepared in water by using their salts.

### Synthetic mixtures and catalyst samples

Synthetic samples of the desired composition were prepared by mixing palladium(II) solution with other metal ions solutions in suitable proportions.

The accurately weighed sample of palladium catalyst (0.1 g) was dissolved in aqua regia, followed by evaporation to moist dryness on a hot plate with the addition of three 5 mL portions of concentrated hydrochloric acid to remove the oxides of nitrogen. Then it was extracted with 10 mL (1.0 mol L<sup>-1</sup>) hydrochloric acid, filtered and diluted to 100 mL with water.

### Recommended procedure

The sample solution (1 mL) containing 100 µg mL<sup>-1</sup> of palladium(II) was taken and acidity was adjusted to 1.0 M with hydrochloric acid in 25 mL volumetric flask. The solution was transferred into 125 mL separating funnel, followed by addition of 10 mL 0.01 mol L<sup>-1</sup> FBIMMT in chloroform. The two phases equilibrated for 10 s. The yellow organic extract was collected over anhydrous sodium sulphate (1 g) to remove the traces of water. The total volume of the organic phase was made 10 mL by adding chloroform, if necessary. The absorbance of the extracted yellow complex was measured at 390 nm against reagent blank. The reagent blank was prepared in the same way without taking palladium(II). A calibration curve was prepared and an unknown amount of palladium(II) was determined from the calibration curve.

The percentage extraction (%E) and metal distribution ratio (D) were calculated according to equation (1) and (2) respectively.<sup>46</sup>

$$\%E = \frac{[M]_{\text{org.}}}{[M]_{\text{aq. init.}}} \times 100 \dots \dots \dots (1)$$

$$D = \frac{[M]_{\text{org.}}}{[M]_{\text{aq.}}} \dots \dots \dots (2)$$

Where, [M]<sub>aq. init.</sub> = initial conc. of metal in the aqueous phase, [M]<sub>org.</sub> = conc. of the metal ion in organic phase after equilibrium and [M]<sub>aq.</sub> = conc. of the metal ion in the aqueous phase after equilibrium

## RESULTS AND DISCUSSION

The 4-(4'-fluorobenzylideneimino)-3-methyl-5-mercapto-1,2,4-triazole was synthesized and used to develop an extractive spectrophotometric method for determination of palladium(II) at microgram level. In a hydrochloric acid medium (0.6 to 2.0 mol L<sup>-1</sup>) FBIMMT in chloroform readily reacts with palladium(II) and forms a yellow colored complex, soluble in chloroform at room temperature. The extracted palladium(II)-FBIMMT species showed absorption maximum at 390 nm against reagent blank. The extracted complex was stable for more than 24 hours. The method has been employed for extraction and determination of palladium(II) from synthetic mixtures, catalysts and alloy samples. The proposed method offers advantages like a wide range of validity of Beer's law; very less equilibration time, selectivity, reproducibility, and reliability. It does not require heating of aqueous phase, use of synergent and surfactant. Hence the method is rapid reliable, selective and has good potential for its use in the determination of palladium(II) at microgram level.

### Absorption spectra and spectral characteristics

Figure-1 shows absorption spectra of the palladium(II)-FBIMMT complex in 1.0 mol L<sup>-1</sup> hydrochloric acid medium against reagent blank. The absorption measurements were made in the spectral range 380-540 nm. The absorbance curves indicated that the yellow colored palladium(II)-FBIMMT complex in organic phase has an absorbance maximum at 390 nm. All measurements were made at 390 nm against the reagent blank for further spectrophotometric determination of palladium(II). The optimum conditions for the effective extraction of palladium(II) were established by evaluating the effect of acidity, reagent concentration, choice of solvents, equilibration time and interferences of various foreign ions. The spectral characteristics and precision data are given in Table-2.

### Effect of varying experimental conditions

#### Effect of acidity

Acidity is one of the important parameters which affect on the extraction of metal species. Protonated metal species are stable and therefore enhance the color of metal ligand complex. The different mineral acids such as sulphuric acid, hydrochloric acid and nitric acid in the range 0.1-3.0 mol L<sup>-1</sup> were used to investigate the optimum acid concentration for complete extraction of palladium(II)-FBIMMT complex by using 0.01 mol L<sup>-1</sup> reagent in chloroform. The maximum absorbance was observed in the range 0.6-2.0 mol L<sup>-1</sup> hydrochloric acid as shown in Fig.-2. Hence 1.0 mol L<sup>-1</sup> hydrochloric acid concentration was used conveniently for all the subsequent studies.

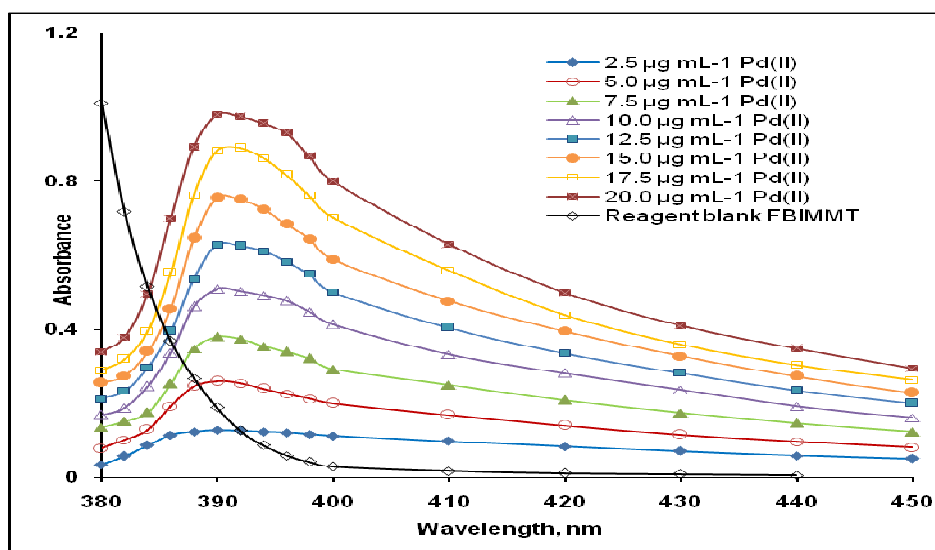


Fig.-1: Absorbance curves for Pd(II)-FBIMMT against a reagent blank and FBIMMT against chloroform. Pd(II) = 2.5-20 µg mL<sup>-1</sup>, HCl = 1.0 mol L<sup>-1</sup>, Equilibration time = 10 s, FBIMMT = 10 mL 0.01 mol L<sup>-1</sup> in chloroform, Wavelength = 380 to 450 nm.

Table-2: Spectral characteristics and precision data of palladium(II)-FBIMMT complex.

Parameters	Optimum range
Solvent	Chloroform
$\lambda_{\max}$	390 nm
Hydrochloric acid concentration	1.0 mol L <sup>-1</sup> (0.6-2.0 mol L <sup>-1</sup> )
Equilibration time	10 s
FBIMMT concentration	0.01 mol L <sup>-1</sup>
Stability of complex	>24 h
Beer's law range	4.13-17.5 µg mL <sup>-1</sup>
Ringbom's optimum concentration range	5.0- 17.5 µg mL <sup>-1</sup>

Molar absorptivity	$5.404 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$
Sandell's sensitivity	$0.0196 \mu\text{g cm}^{-2}$
Relative standard deviation <sup>a</sup>	0.621%
Mean recovery	$99.97 \pm 0.62\%$
Stoichiometry	1:1

<sup>a</sup>Average of five determinations

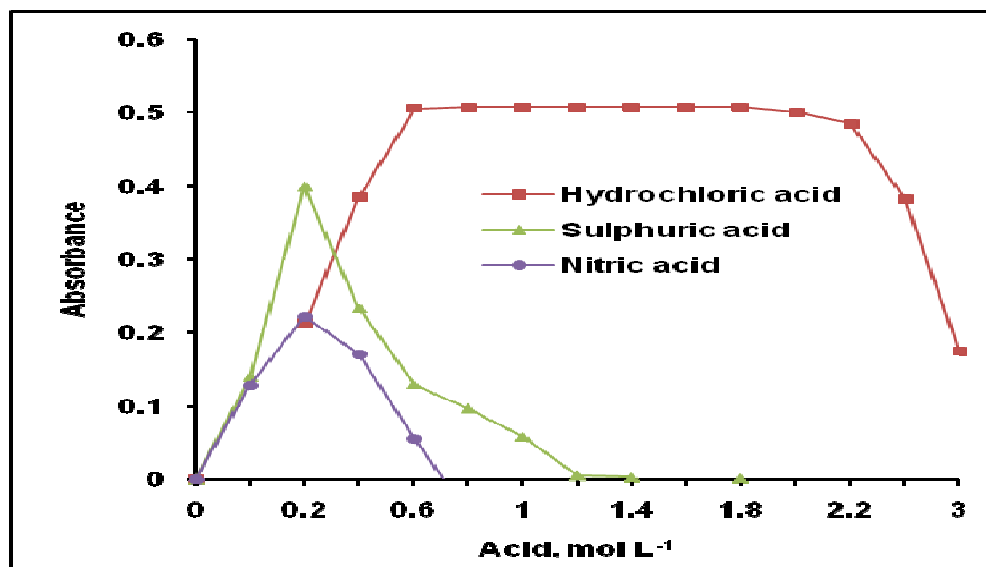


Fig.-2: Effect of acid concentration on the absorbance of Pd(II)-FBIMMT complex.

Pd(II) =  $10 \mu\text{g mL}^{-1}$ , FBIMMT =  $10 \text{ mL } 0.01 \text{ mol L}^{-1}$  in chloroform, Equilibration time = 10 s,  $\lambda_{\text{max}} = 390 \text{ nm}$ .

### Effect of solvent

In the extraction of palladium(II), solvent plays very significant role in complexation of palladium(II) with the ligand. Therefore, the effect of various solvents on the extraction of palladium(II) was studied. For this purpose solution of FBIMMT ( $0.01 \text{ mol L}^{-1}$ ) was prepared in different solvents and the effect of solvents on the percentage extraction at 390 nm was observed. Results obtained are shown in Fig.-3.

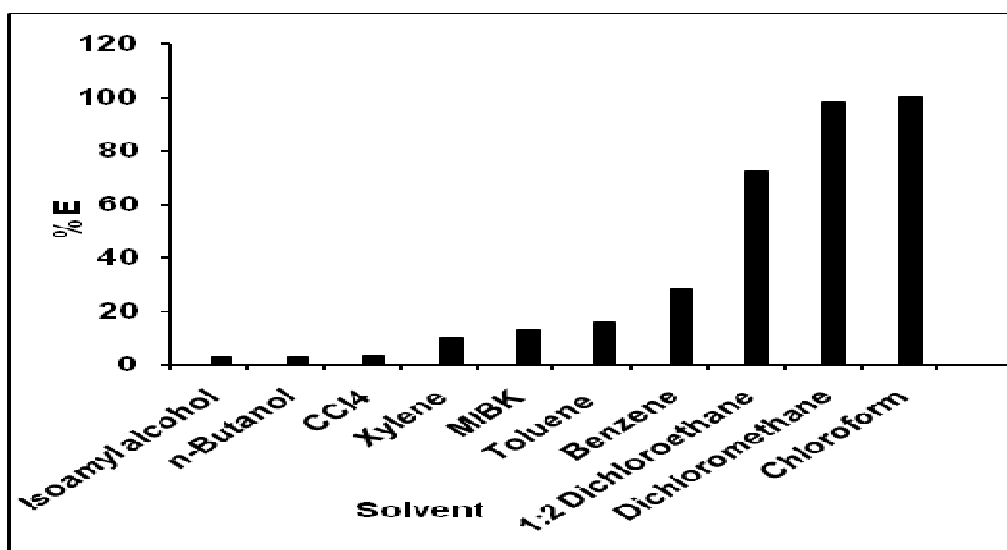


Fig.-3: Effect of solvents on % extraction of Pd(II)-FBIMMT complex.

Pd(II) =  $10 \mu\text{g mL}^{-1}$ , HCl =  $1.0 \text{ mol L}^{-1}$ , FBIMMT =  $10 \text{ mL } 0.01 \text{ mol L}^{-1}$ , Equilibration time = 10 s,  $\lambda_{\text{max}} = 390 \text{ nm}$ .

### Effect of FBIMMT concentration

The effect of ligand concentration for the extraction of palladium(II) was studied at 1.0 mol L<sup>-1</sup> hydrochloric acid. The different molar concentrations of FBIMMT in chloroform in the range 0.0005-0.015 mol L<sup>-1</sup> were prepared and added to 100 µg palladium(II) solutions. The absorbance of the organic phase was measured according to recommended procedure at 390 nm against respective reagent blank. It was found that 10 mL 0.005 mol L<sup>-1</sup> reagent in chloroform was sufficient to complete complexation and extraction of palladium(II)-FBIMMT complex (Figure 4). Excess concentration of reagent did not affect the extraction and sensitivity of palladium(II) determination, hence 10 mL of 0.01 mol L<sup>-1</sup> of reagent in chloroform was used for further studies.

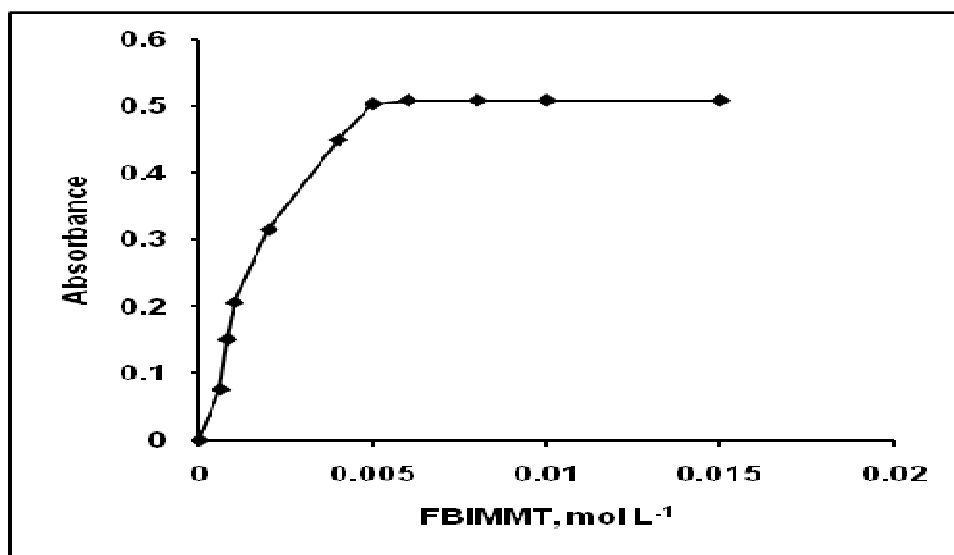


Fig.-4: Effect of reagent concentration on absorbance of Pd(II)-FBIMMT complex.  
Pd(II) = 10 µg mL<sup>-1</sup>, HCl = 1.0 mol L<sup>-1</sup>, FBIMMT in 10 mL chloroform, Equilibration time = 10 s,  
 $\lambda_{\max}$  = 390 nm.

### Effect of shaking time

It is often required to investigate the trace amounts of metal ions with high efficiency in a minimum time. Shaking plays an important role in getting an equilibrium between the organic and aqueous phase. For this reason, shaking time varied from 5 s to 2 min. It was observed that extraction of palladium(II) by FBIMMT (0.01 mol L<sup>-1</sup>) in chloroform was found to be very rapid and occurs in 6s quantitatively. Therefore in present investigation 10 s shaking time was recommended for quantitative extraction of palladium(II) in the organic phase.

### Validity of Beer's law and sensitivity

Determination of palladium(II) at trace level, the absorbance of a solution containing different amount of metal ion under the optimum condition was measured at 390 nm and a calibration curve was constructed. It was found that at optimized reaction conditions of the palladium(II)-FBIMMT complex obeyed Beer's law up to 17.5 µg mL<sup>-1</sup> of palladium(II) as shown in Fig.-5, with optimum concentration range 5.0-17.5 µg mL<sup>-1</sup> of the metal as evaluated from a Ringbom's curve, a plot of log C<sub>[Pd(II)]</sub> versus % transmittance (Fig.-6). The Ringbom's plot showed the sigmoid curve. The steepest portion of the curve indicates the optimum concentration range where the error is minimal.<sup>47</sup> The molar absorptivity and Sandell's sensitivity were found to be 5.404 × 10<sup>3</sup> L mol<sup>-1</sup>cm<sup>-1</sup> and 0.0196 µg cm<sup>-2</sup>, respectively. Molar absorptivity and Sandell's sensitivity values suggest that the method is moderately sensitive.<sup>48</sup>

### Stoichiometry of the complex

The composition of palladium(II)-FBIMMT complex was determined by Job's continuous variation method, mole ratio method and was confirmed by log-log plot method.

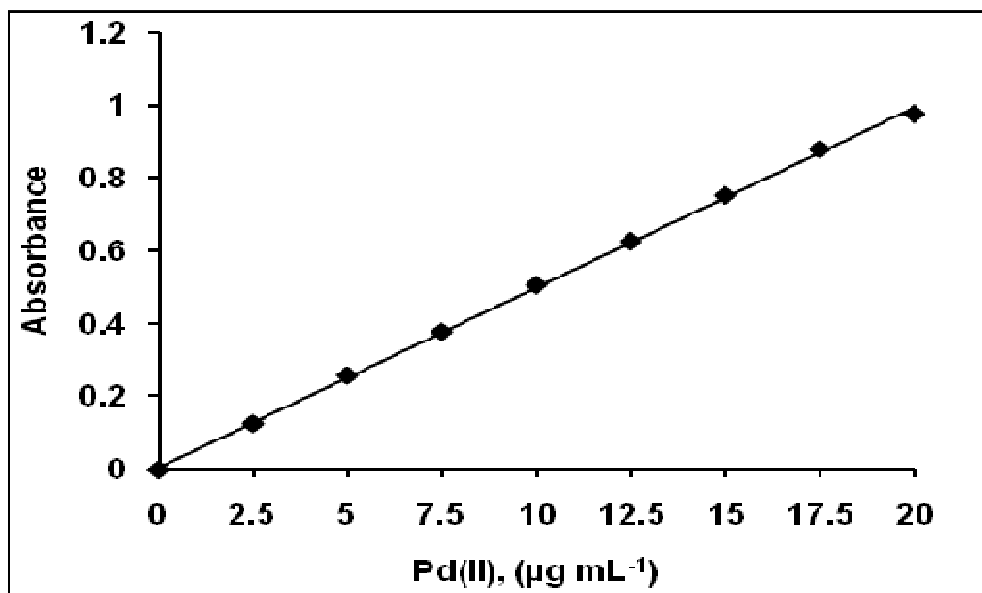


Fig.-5: Validity of Beer's law for Pd(II)-FBIMMT complex.

Pd(II) = 2.5-20  $\mu\text{g mL}^{-1}$ , HCl = 1.0  $\text{mol L}^{-1}$ , FBIMMT = 10 mL 0.01  $\text{mol L}^{-1}$  in chloroform, Equilibration time = 10 s,  $\lambda_{\text{max}} = 390 \text{ nm}$ .

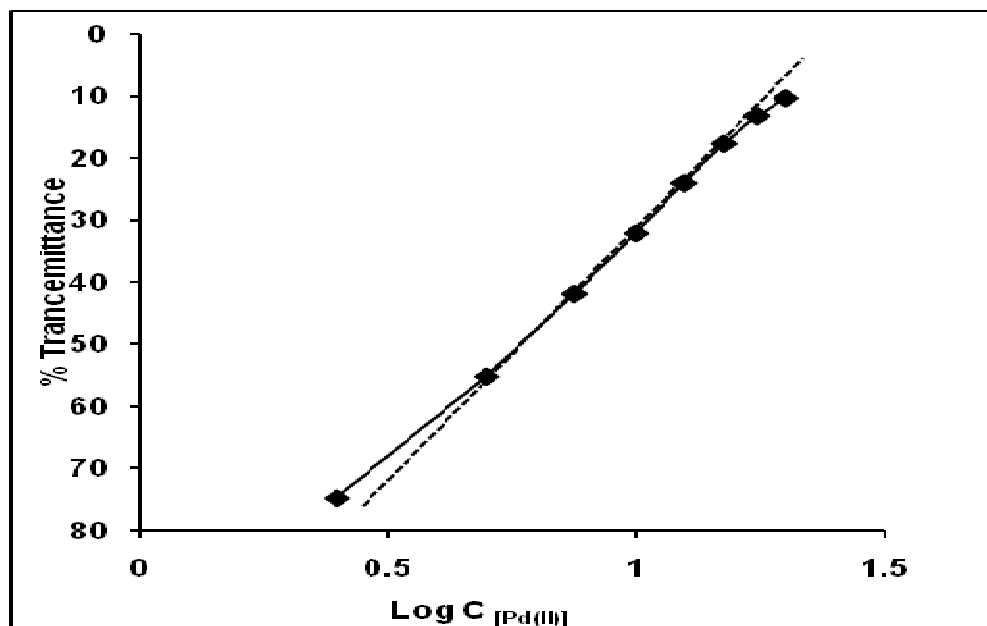


Fig.-6: Ringbom's plot for Pd(II)-FBIMMT complex. Pd(II) = 2.5-20  $\mu\text{g mL}^{-1}$ , HCl = 1.0  $\text{mol L}^{-1}$ , Equilibration time = 10 s, FBIMMT = 10 mL 0.01  $\text{mol L}^{-1}$  in chloroform,  $\lambda_{\text{max}} = 390 \text{ nm}$ .

### Job's continuous variation method

Equimolar solutions of palladium(II) and FBIMMT in chloroform were used to determine the metal to ligand ratio in the complex. The acidity of palladium(II) solution was adjusted to 1.0  $\text{mol L}^{-1}$  with hydrochloric acid in a total volume of 25 mL and the solution was transferred to 125 mL separating funnel. FBIMMT in chloroform was mixed with complementary proportions containing varying amount of palladium(II). The absorbance of an organic extract was measured at 390 nm against the reagent blank



prepared in a similar way without taking palladium(II). The plot of absorbance versus mole fraction ( $M/M+L$ ) indicates that the stoichiometry of palladium(II)-FBIMMT complex is 1:1 (Fig.-7).

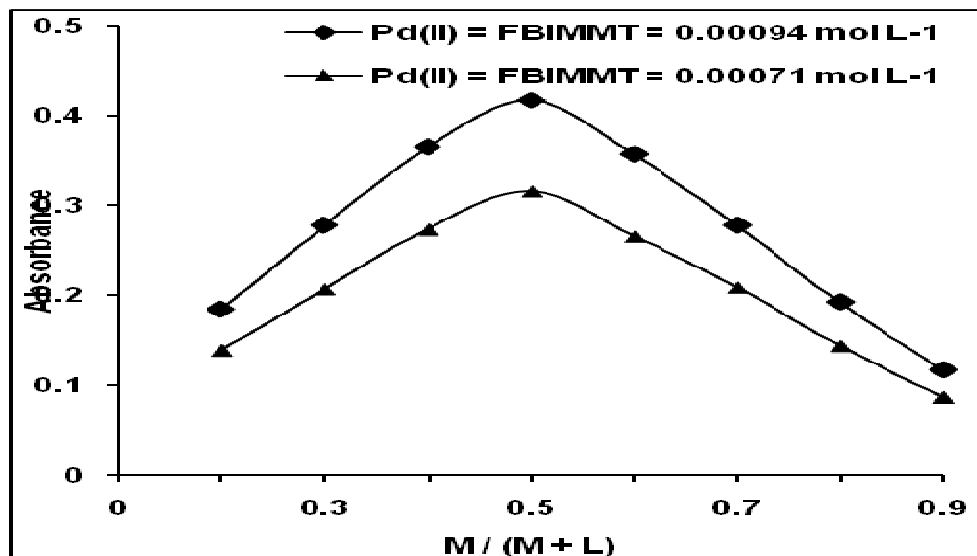


Fig.-7: Job's plot of continuous variation for composition of Pd(II)-FBIMMT complex.

$[M] = [L] = 0.00094 \text{ mol L}^{-1}$  and  $0.00071 \text{ mol L}^{-1}$ , FBIMMT in chloroform,  $\text{HCl} = 1.0 \text{ mol L}^{-1}$ , Equilibration time = 10 s,  $\lambda_{\text{max}} = 390 \text{ nm}$ .

#### Mole ratio method

Equimolar solutions of palladium(II) and FBIMMT ( $9.4 \times 10^{-4} \text{ mol L}^{-1}$ ) were used. Series of solutions were prepared by keeping the concentration of palladium(II) same (5.0 mL). The acidity of the solution was adjusted to  $1.0 \text{ mol L}^{-1}$  with hydrochloric acid in 25 mL volumetric flask. Then this solution was transferred to 125 ml separating funnel. The varying amount of reagent in chloroform ( $9.4 \times 10^{-4} \text{ mol L}^{-1}$ , 1.0-10.0 mL) were used for extraction of palladium(II)-FBIMMT complex in the organic phase. By adjusting total volume of organic phase to 10 mL with chloroform, the absorbance was measured at 390 nm against corresponding reagent blank. The graph of absorbance versus the mole ratio ( $L / M$ ) showed a break where the palladium(II) to FBIMMT ratio was 1:1 (Fig.-8).

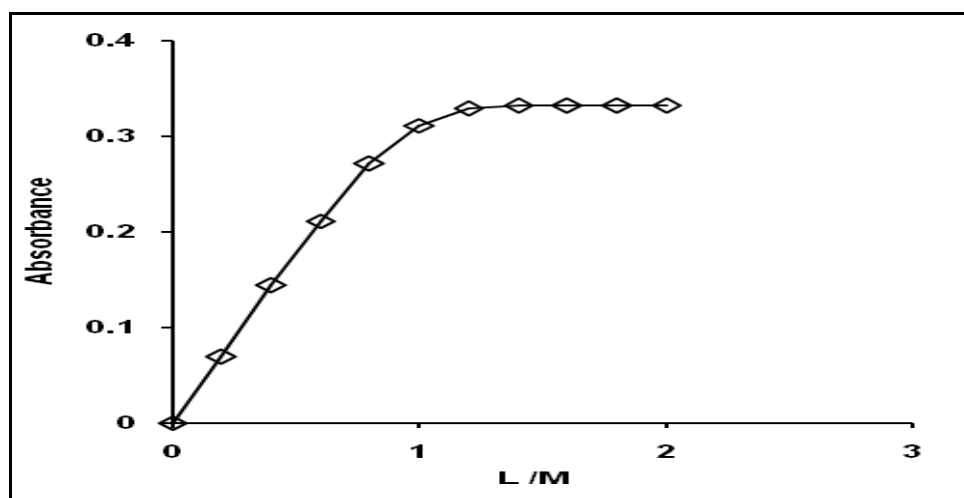
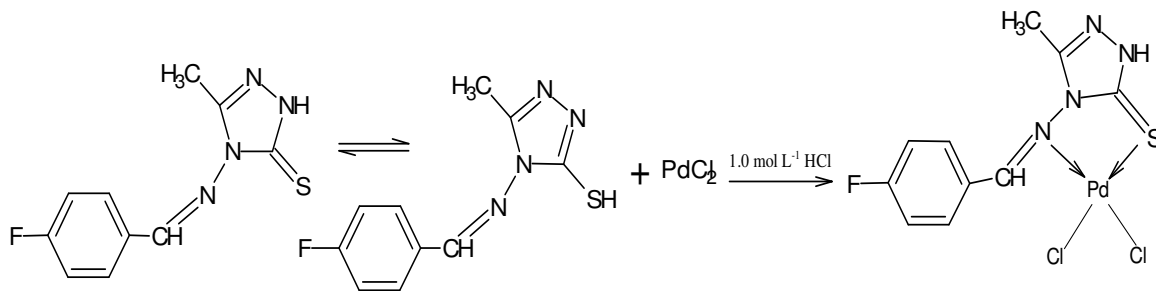


Fig.-8: Mole-ratio method for determination of the composition of the complex.

$\text{Pd(II)} = 0.00094 \text{ mol L}^{-1}$ ,  $\text{FBIMMT} = 0.00094 \text{ mol L}^{-1}$  in chloroform,  $\text{HCl} = 1.0 \text{ mol L}^{-1}$ , Equilibration time = 10 s,  $\lambda_{\text{max}} = 390 \text{ nm}$ .

### Log-log plot method

The plot of  $\text{Log } D_{[\text{Pd(II)}]}$  against  $\text{Log } C_{[\text{FBIMMT}]}$  at  $0.4 \text{ mol L}^{-1}$  hydrochloric acid (Fig.-9), the number of ligand molecules coordinated to the metal ion in the extracted species were confirmed. Where  $D$  denotes the distribution ratio of palladium(II) between two phases and  $C$  is the equilibrium concentration of FBIMMT in the organic phase. The linear plot with slope 0.984 suggests that the Pd(II) to FBIMMT ratio is 1:1. The ligand FBIMMT exists in tautomeric form,<sup>49-50</sup> it binds with palladium(II) through nitrogen of azomethine group and sulfur of thione group as shown in Scheme-2.



Scheme-2

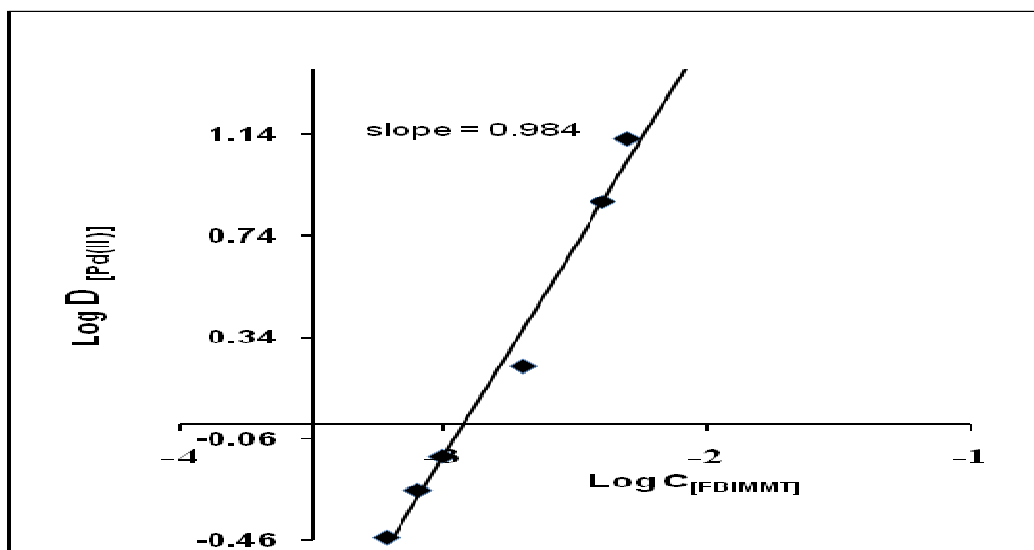


Fig.-9: Plot of  $\text{Log } D_{[\text{Pd(II)}]}$  versus  $\text{Log } C_{[\text{FBIMMT}]}$  for determination of the composition of the complex.  $\text{Pd(II)} = 10 \mu\text{g mL}^{-1}$ ,  $\text{HCl} = 0.4 \text{ mol L}^{-1}$ , FBIMMT in chloroform, Equilibration time = 10 s,  $\lambda_{\text{max}} = 390 \text{ nm}$ .

### Effect of foreign ions

The influence of the various foreign ions on the absorbance values of palladium(II)-FBIMMT complex was studied to find selectivity of proposed method. The large amounts of commonly associated cations and anions do not interfere with absorbance values. The tolerance limit of the ions showed minimum deviation ( $\pm 2\%$ ) in absorbance. By using suitable masking agents, the interference of some cations was removed (Table-3).

### Precision and accuracy

The precision and accuracy of the present method were evaluated by analyzing five identical solutions containing  $100 \mu\text{g}$  palladium(II) by recommended procedure. The average of five determinations is 99.97 and the variation from mean was found to be  $\pm 0.621$  at 95% confidence limit. These values indicate that the method has good accuracy and reproducibility.

Table-3: Effect of foreign ions on the extractive spectrophotometric determination of Pd(II).

Foreign ions (Anions and cations)	Amount tolerated (mg)
Oxalate, citrate, bromide, thiocyanate, acetate, and tartarate	100
Iodide, Fluoride, Succinate and Sulphate ions	50
Ba(II), Ca(II), Mg(II), Cd(II), Sb(III), Al(III) and V(V)	10.0
Co(II), Mn(II), Ni(II), Pb(II), Zn(II), Fe(III) and Tl(III)	5.0
Ir(III) and Bi(III)	4.0
La(III) and Hg(II)	2.0
Ag(I) <sup>a</sup> , Sn(II) <sup>b</sup> , Cu(II), Ga(III), In(III), Ru(III), Rh(III), Pt(IV), U(VI), Zr(IV) <sup>b</sup> and Os(VIII)	1.0
Se(IV) and Te(IV)	0.5
Au(III) <sup>c</sup>	0.1

<sup>a</sup>Masked with 50 mg iodide, <sup>b</sup>Masked with 50 mg oxalate, <sup>c</sup>Masked with 50 mg thiocyanate.

## Applications

### Separation and determination of palladium(II) from synthetic mixtures

To check selectivity of the present method, the separation and determination of palladium from associated metal ions were carried out following the recommended procedure. The proposed method permits separation of palladium(II) from associated metal ions such as Cu(II), Mg(II), Co(II), Ni(II), Mn(II) Pt(IV) and Os(VIII) due to difference in the complexation conditions for each metal ions. Under the set condition of recommended procedure, associated metal ions were found quantitatively in the aqueous phase. Firstly aqueous phase was evaporated just to dryness. The residue was treated with concentrated hydrochloric acid repeatedly followed by evaporation. Then this moist dry salt was dissolved in water and diluted to suitable volume. The metal ions were estimated by standard methods.<sup>51-53</sup> The results are reported in Table-4.

Furthermore, to evaluate the applicability of proposed method, the multi component synthetic mixtures were analyzed by employing recommended procedure. The results obtained were in conformity with theoretical amount of palladium(II) taken ( Table-5).

### Determination of palladium(II) in catalysts

The utility of proposed method was also assessed by determination of palladium(II) in palladium catalyst samples. An appropriate aliquot (catalyst solution) was taken for the analysis of palladium content and analysis was carried out by recommended procedure. The results obtained by present method were in good agreement with the certified values (Table-6).

To evaluate the analytical applicability of the present method, the synthetic alloy samples were prepared based on the composition of some alloys such as low melting dental alloy, jewelry alloy, stibiopalladinite minerals, okey alloy, golden colored silver alloy and Pd-Cu alloy. The amount of palladium(II) was determined by using recommended procedure from synthetic mixtures of these alloy samples. The results obtained were summarized in Table-7.

Table-4: Separation and determination of palladium(II) from binary synthetic mixtures

Metal ions	Amount taken(μg)	Average recovery (%)	#RSD (%)	Chromogenic ligand	Ref.
Pd(II)	100	99.95	0.62	FBIMMT	-
Cu(II)	100	99.34	0.48	NBIMMT	51
Pd(II)	100	99.57	0.33	FBIMMT	-
Mg(II)	100	99.30	0.84	Titan yellow	52
Pd(II)	100	99.38	0.54	FBIMMT	-
Co(II)	100	99.58	0.36	Thiocyanate	52
Pd(II)	100	99.40	0.56	FBIMMT	-
Ni(II)	100	99.70	0.36	DMG	52
Pd(II)	100	99.15	0.85	FBIMMT	-
Mn(II)	100	99.87	0.33	Permanganate	52

Pd(II)	100	99.65	0.85	FBIMMT	-
Pt(IV)	100	99.80	0.28	Tin Chloride	52
Pd(II)	100	99.61	0.29	FBIMMT	-
Os(VIII)	100	99.74	0.37	2-NBATCH	53

\*Average of five determinations; #Relative standard deviation

Table-5: Determination of palladium(II) from multi component synthetic mixtures

Composition ( $\mu\text{g}$ )	Recovery*(%)	#RSD(%)
Pd(II), 100; Fe(III), 1000; Cu(II), 1000	99.8	0.11
Pd(II), 100; Ni(II), 1000; Co(II), 1000	99.7	0.10
Pd(II), 100; Fe(III), 1000; Cu(II), 1000; Ni(II), 1000; Co(II), 1000	99.8	0.05
Pd(II), 100; Os(III), 300	99.9	0.07
Pd(II), 100; Ru(III), 300	99.8	0.16
Pd(II), 100; Rh(III), 300	99.8	0.12
Pd(II), 100; Ir(III), 300	99.7	0.14
Pd(II), 100; Pt(IV), 100	99.9	0.07

\*Average of five determinations; #Relative standard deviation

Table-6: Determination of palladium(II) in catalysts

Catalyst sample	Pd(II) taken ( $\mu\text{g mL}^{-1}$ )	Recovery* (%)	#RSD (%)
Lindlar hydrogenation catalyst (Pd on $\text{CaCO}_3$ 5 %)	100	99.75	0.37
Lindlar hydrogenation catalyst (Pd on $\text{CaCO}_3$ 10 %)	100	99.49	0.56
Hydrogenation catalyst (Pd on $\text{BaSO}_4$ 10 %)	100	99.48	0.55
Hydrogenation catalyst (Pd on asbestos 5 %)	100	99.63	0.42
Hydrogenation catalyst (Pd on asbestos 10 %)	100	99.56	0.45

\*Average of five determinations #Relative standard deviation

Table-7: Determination of palladium(II) from synthetic mixtures of corresponding alloys

Alloy	Composition (%)	Recovery* (%)	RSD (%)
Low melting dental alloy	Pd,34; Au <sup>a</sup> ,10; Co,22; Ni,34	99.62	0.37
Jewellery alloy	Pd,50; Au <sup>a</sup> ,50	99.79	0.16
Stibiopalladinite minerals	Pd,75; Sb,25	99.89	0.15
Okey alloy	Pd,18; V,9.1; Pt,18.2; Ni,54.2	99.59	0.41
Golden coloured silver alloy	Pd,25.5; Cu,18; In,21; Ag <sup>b</sup> ,35	99.85	0.18
Pd-Cu alloy	Pd,60; Cu,40	99.72	0.26

\*Average of five determinations; #Relative standard deviation

<sup>a</sup>Masked with 50 mg thiocyanate, <sup>b</sup> Masked with 50 mg iodide

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