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Extraction and separation studies of Palladium(II) with 4-(4-methoxybenzylideneimino)-5-methyl-4*H*-1,2,4-triazole-3-thiol in hydrochloric acid medium

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ABSTRACT

A novel method is proposed for the extraction of microgram level concentration of palladium(II) from hydrochloric acid medium with 4-(4-methoxybenzylideneimino)-5-methyl-4H-1,2,4-triazole-3-thiol(MBIMTT) dissolved in chloroform as an extractant. The palladium(II) from the organic phase is stripped with 50 % ammonia solution and determined spectrophotometrically with pyrimidine–2-thiol as a reagent. The method affords the binary separation and determination of palladium(II) from the alloys and synthetic mixture. The method is successfully applied for the separation and determination of palladium from the catalysts. The method is highly selective, simple and reproducible.

Keyword: palladium(II), MBIMTT, Solvent extraction, Catalyst, Spectrophotometry.

INTRODUCTION

The abundance of palladium in the earths crust is $8.5\times 10^{-13}\%$. Palladium is a good catalyst and in hydrogenation and dehydrogenation reactions. Owing to its corrosion resistance properties and easy alloying, palladium and its alloys are also used in chemical industry, medical devices and jewelry manufacture. The increasing application of the platinum group metals 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 future demand. Solvent extraction has become an effective technique in the recovery and separation of palladium[1-3]. The aqueous chemistry of these metals is extremely complex. The important tendency of these metals is to form chlorocomplex in chloride medium. Solvent extraction technique of separation uses the difference in kinetic behavior for the formation of extractable species as well as the strength of electrostatic interactions of their chlorocomplexes with liquid anion exchanger. The inertness of the chlorocomplex of palladium in aqueous medium plays an important role in the extraction from acidic solution by an anion exchange mechanism. Other extractants reported for palladium(II) are 1,12-di-2-thienyl-2,5,8,11-tetrathaidecane[4], dithizone[5], N-benzoyl-N,N’-diethylthiourea[6], hexadecylpyridinium bromide (HDPB)[7], 4-(2-pyridylazo)-resorcinol[8], iso-amyl benzothiazolyl sulfoxide[9]. The methods reported are not so reliable for routine application because these methods suffer due to the drawbacks such as operating condition (emulsion formation leading to problem for the separation, slow equilibrium) and ionic exchanger, nature of diluents, critical pH range etc.

One coordination chemistry property of Pd(II) is that it prefer to coordinate most strongly with polarizable atoms such as sulfur, phosphorous and nitrogen. These ligands are 'soft' bases according to the empirical Pearson classification[10]. Sulphur containing ligands are highly selective for extraction of Pd(II), and have been widely used in the extraction of this species[11-13]. 4-(4-methoxybenzylideneamino)-5-methyl-4*H*-1,2,4-triazole-3-thiol(MBIMTT) is a sulphur containing ligand and it is highly water repellent. It does not form emulsion at the time of extraction. Because of the determination of small amounts of noble metals in minerals containing large amount of base metals is difficult; the effectiveness of MBIMTT has been evaluated as an extractant for palladium(II) from variety of palladium bearing materials and process solutions. MBIMTT has been employed successfully in this laboratory for the extraction of Rh(III), Ru (III) and Au(III) [14-16]. We report here the use of MBIMTT as an extractant for palladium(II) from hydrochloric acid medium.

MATERIALS AND METHODS

Equipments and chemicals

A Shimadzu UV-Visible spectrophotometer (UV-1601) with 1cm quartz cells was used for measurement. pH measurements were carried out with an Elico digital pH meter model LI-120(±0.01). A stock solution of palladium (II) was prepared by dissolving 1g of palladium chloride hydrate (S. D. Fine, India) in dilute AnalaR hydrochloric acid (1mol/dm^3) and diluting to 100ml with distilled water and further standardizing it[17]. A working solution 100 μg ml^{-1} was prepared from it by diluting the stock solution with distilled water. The reagent MBIMTT synthesized by known literature method[14]. MBIMTT (0.1 mol/dm^3) solution was prepared in chloroform. Other standard solutions of different metal ions used to study the effect of foreign ions were prepared by dissolving weighed quantities of respective salts in distilled water or dilute hydrochloric acid. Solutions of anions were prepared by dissolving the respective alkali metal salts in distilled water. All the chemicals used were of AR grade. Double distilled de-ionized water was invariably used throughout the measurements.

Recommended method

An aqueous solution containing 100 μg of palladium (II) and enough hydrochloric acid and water were added to give final concentration of 1 mol/dm^3 with respect to hydrochloric acid in a total volume of 25 ml. The resulting solution was transferred to 125 ml separating funnel. The aqueous phase was equilibrated once with 10 ml of 0.1 mol/dm^3 MBIMTT solution in chloroform for 30 second. The phase was allowed to separate and the metal from the organic phase was backstripped with two 5-ml portions of 50 % ammonia solution. The extract was evaporated to moist dryness and leached with dilute hydrochloric acid to form the solution. Palladium(II) was estimated spectrophotometrically with pyrimidine-2-thiol[18-19].

RESULTS AND DISCUSSION

Extraction of palladium(II) as a function of acid concentration

The extraction of 100 μg palladium(II) was carried out from different acid medium with 0.1 mol/dm^3 MBIMTT in chloroform keeping the aqueous to organic volume ratio 2.5:1. The extraction was found to be complete from hydrochloric acid. Palladium(II) was extracted over the 0.2- 10 mol/dm^3 acidity range with hydrochloric acid with 0.1 mol/dm^3 MBIMTT in chloroform. It was observed that extraction increased in the acidity of the aqueous solution and became quantitative at 1 mol/dm^3 hydrochloric acid. It was incomplete in sulphuric acid due to emulsion formation. The extraction was quantitative in nitric acid medium in the 6-7 mol/dm^3 range, but third-phase formation took place above this range of acidity. Hence, the hydrochloric acid system was used for further studies.

Effect of reagent concentration

Palladium(II) was extracted over the 0.5-3 mol/dm^3 acidity range with hydrochloric acid with varying concentrations of MBIMTT. The reagent concentration was varied from 1×10^{-5} – 2 mol/dm^3 (Table 1). It was observed that extraction increased in the acidity of the aqueous solution and became quantitative at 1 mol/dm^3 hydrochloric acid. It was found that 0.1 mol/dm^3 reagent in chloroform was needed for quantitative extraction of Pd(II) from 1 mol/dm^3 hydrochloric acid.

Effect of equilibration time

Variation of the shaking period from 5 seconds to 5 minutes showed that a minimum 10 second equilibration time is adequate for quantitative extraction of palladium(II) from hydrochloric acid media. As a general procedure, 30 second of equilibration time is recommended in order to ensure complete extraction of palladium(II) hydrochloric acid medium. Prolonged shaking up to 5 minutes has no adverse effect on the efficiency of extraction.

Effect of stripping agents

Palladium loaded in the organic phase was stripped with various stripping agents, such as1 mol/dm^3 HCl, 1 mol/dm^3 HNO_3, 1 mol/dm^3 NaOH, 50% NH_3, 1 mol/dm^3 Na_2SO_3. The stripping was observed in only with NaOH, 50% NH_3, and Na_2SO_3 as stripping agent. It was found the stripping was less than 50% when NaOH solution and 40% when Na_2SO_3 was used as stripping agent. The stripping was quantitative when 50% NH_3 solution was used. Hence, 50% NH_3 solution is suitable strippent for palladium.

Effect of diluents

The extractions were performed from 1 mol/dm^3 hydrochloric acid medium using 0.1 mol/dm^3 MBIMTT in various solvents as diluents. It was found that 0.1 mol/dm^3 MBIMTT solution in carbon tetrachloride, chloroform, xylene, toluene and benzene provides quantitative extraction of palladium(II). The extraction of palladium(II) was found to be incomplete in isobutyl methyl ketone (50 %), isoamylalcohol (48.8 %), while no extraction in n-butanol and 4-methyl-2-pentanol. Chloroform is recommended for further extraction procedure because it offers better phase separation.

Nature of extracted species

The composition of complex was confirmed by using log D- log C plot. The graph log $D_{[Pd(II)]}$ versus log $C_{[MBIMTT]}$ at 4 mol/dm^3 hydrochloric acid was found to be linear and having slope of 1.3(fig.1). Hence, the probable composition of extracted species in chloroform has been found to be 1:1, [Pd(II): MBIMTT].

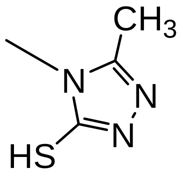
The probable extracted species is,

$$\left[RCHNR'H_2^{++}\ PdCl_4^{2-} \right]_{org}$$

Where

R = $C_6H_5OCH_3$

R'=



The extraction mechanism can be explained as follows:

$$\left[RCHNR' \right]_{org} + 2HCl_{(aq)} \rightleftharpoons \left[RCHNR'H_2^{++}\ 2Cl^- \right]_{org}$$

$$\left[RCHNR'H_2^{++}\ 2Cl^- \right]_{org} + PdCl_4^{2-}{}_{(aq)} \rightleftharpoons \left[RCHNR'H_2^{++}\ PdCl_4^{2-} \right]_{org} + 2Cl^-_{(aq)}$$

Loading capacity of MBIMTT

The loading capacity of the extractant was determined by the repeated contact of organic phase with a fresh feed solution of the metal of some concentration. For a 10 ml of 0.1 solution of MBIMTT in chloroform at 1 hydrochloric acid medium and a Aq/Org phase ratio of 2.5:1, the maximum loading capacity for palladium(II) was found to be 4.5 mg.

Effect of Diverse Ions

Various ions were used in order to asses the tolerance of these ions on the extraction of palladium(II). Palladium(II) was extracted in the presence of different diverse ions (Table 2). The tolerance limit was set as the amount of foreign ions cause ±2 % errors in recovery of palladium. The results showed that in the extraction and determination 100 µg of the palladium, these ions did not interfere at the level tested. The reproducibility of palladium extraction investigated from six replicate measurement was found to be 99.00± 0.95%.

Application

Binary separation of palladium(II) from base metals

The method allowed separation and determination of palladium(II) from a binary mixture containing either iron (III), cobalt(II), nickel(II), and copper(II). The separation of palladium(II) from iron(III), cobalt(II), nickel(II), and copper(II) by its extraction with 0.1 mol/dm^3 MBIMTT in chloroform at 1 mol/dm^3 hydrochloric acid. Under these condition all the base metals remain quantitatively in the aqueous phase and these base metals determined spectrophotometrically with thiocyanate[17], 1-nitroso-2 naphthol[17], DMG[17], and pyrimidine-2-thiol[20] respectively. Palladium is stripped from the organic phase with two 5ml portion of 50 % ammonia solution. The extract was evaporated to moist dryness and leached with 1 mol/dm^3 hydrochloric acid to form the solution. 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 3).

Separation of palladium(II) from multicomponent synthetic mixture

In its natural occurrence palladium is always associated with the noble and base metals, hence its separation from these metals is of great importance. Under the optimum condition for extraction of palladium(II), there is quantitative extraction of Au(III), Pt(IV) and Rh(III). But the coextracted metal ions cannot be backstripped by 50 % ammonia solution. Thus the MBIMTT reagent is made selective towards palladium(II) by taking advantage of the strippent used. The proposed method allows the selective separation and determination of palladium from many metal ions (Table 4).

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 real samples were not available; hence the synthetic mixtures were prepared corresponding to the composition of alloy. The results of the analysis are reported in (Table 5). The average recovery of palladium(II) has been found to be 99.5%.

Table: 1 Extraction behavior of palladium(II) as a function of MBIMTT concentration.

Palladium(II) = 100 µg; Aq/Org = 25:10

[HCl]/ mol.dm^{-3}	MBIMTT/ mol.dm^{-3}	Percentage Extraction / %E	Distribution ratio(D)
0.5	0.00001	11.0	0.30
	0.0001	23.8	0.78
	0.001	59.7	3.70
	0.01	74.5	7.34
	0.1-0.25	100	∞
1	0.0000.1	40	1.66
	0.0001	71.6	6.30
	0.001	91.7	27.62
	0.01-0.25	100	∞
2	0.00001	68.4	5.46
	0.0001	91.6	27.60
	0.001-0.25	100	∞
3	0.00001	14.0	0.40
	0.0001	44.00	1.96
	0.001	50.00	2.50
	0.01	83.6	12.74
	0.1	91.7	27.62
	0.15-0.25	100	∞

Analysis of the real sample

The proposed method is applicable for the determination of palladium content in the palladium catalysts. Dissolution of sample is carried out by using literature method[21-22]. A known weight of catalyst (BDH) was dissolved in a mixture of 9 ml and 3 ml of concentrated hydrochloric acid and nitric acid, respectively. After the reaction was over the solution was heated with a two ml portion of concentrated hydrochloric acid until the complete removal of oxides of nitrogen. The residue was dissolved in 10 ml of 1 mol/dm^3 hydrochloric acid and filter to remove carbon or barium sulphate. The residue was washed with dilute hydrochloric acid. The filtrate and washing were collected and diluted with distilled water in standard volumetric flask. An aliquot of the sample solution was taken and palladium(II) was determined by using the above described procedure. The results of the analysis are collected in (Table 6). The average recovery of palladium(II) was 99.4 %.

Table: 2 Effect of diverse ions on the extractive determination of palladium(II)

Pd(II) = 100 μg; aqueous phase = 1 mol/dm^3 HCl; Aq/Org = 25:10; extractant = 0.1 mol/dm^3 MBIMTT in Chloroform

Tolerance limit (mg)	Foreign ion added
100	Fluride, Citrate, Oxalate, Acetate, EDTA, Malonate, Bromide, Iodide
20	Ca(II), Ba(II), Be(II), Mg(II), Fe(III)
15	Mn(II), Fe(II), Cr(III), Co(II)
10	Mo(VI), Sr(II), Ti(IV), Ce(IV)
5	U(VI), Mn(VII), Sb(III), Zn(II), Pb(II), Hg(II), Ni(II), Sn(II), Cu(II)
0.5	Pt(IV), Rh(III), Au(III), Ru(III)

Table: 3 Binary separation of palladium(II) from iron(III), cobalt(II), nickel(II) and copper(II)

Composition of Metal ions, /μg	Recovery* Pd(II) %	Relative Standard Deviation%.
Pd(II), 100; Fe(III); 15000	99.6	0.13
Pd(II), 100; Co(II), 10000	99.7	0.07
Pd(II), 100; Ni(II), 5000	99.6	0.11
Pd(II), 100; Cu(II), 5000	99.8	0.13

**-average f six determinations*

Table: 4 Analysis of synthetic mixture

Composition (μg)	Palladium found /μg	Recovery* /'%	R.S.D. /%
Pd, 100; Pt,500	99.6	99.8	0.05
Pd, 100; Au,500	99.8	99.9	0.07
Pd, 100; Ru,500	99.4	99.7	0.07
Pd, 100; Rh,500	99.6	99.8	0.05
Pd, 100; Pt,500; Ru,500	99.2	99.6	0.06
Pd, 100; Pt,500; Au,500	99.4	99.7	0.07
Pd, 100; Pt,500; Rh,500	99.4	99.7	0.07
Pd, 100; Pt,500; Ru,500; Au, 500	99.6	99.8	0.05
Pd, 100; Pt,500; Rh,500; Au, 500	99.2	99.6	0.06
Pd, 100; Pt,200; Ru,200; Au, 200; Fe,2000; Co, 2000; Ni, 2000; Cu, 2000	99.4	99.7	0.07

**- average six determination*

Table: 5 Analysis of alloys

Alloy	Composition (%)	Palladium taken(μg)	Palladium found*(μg)	Recovery(%)	R.S.D.(%)
Low melting dental alloy	Pd, 25; Au, 10; Co,22, Ni, 34	170	169	99.5	0.09
Stibio palladinite Mineral	Pd, 75; Sb, 25	150	149	99.6	0.08
Jewellery alloy (Pd-Ru alloy)	Pd, 95.5; Ru, 4.5	191	190	99.8	0.05
Jewellery alloy (Pd-Au alloy)	Pd, 50; Au, 50	100	99	99.8	0.08
Pd-Cu alloy	Pd, 60; Cu, 40	120	119	99.6	0.11
Pd- Ag alloy	Pd 60; Ag 40	120	119	99.6	0.11
Golden colored silver alloy resistant to transhing	Pd, 25.5; In, 21; Cu,18; Ag, 35	102	101	99.8	0.08

**- average six determination*

Table:6 Analysis of real samples (catalysts)

Catalyst Sample	**Palladium taken (µg)**	**Recovery*(%)**	**R.S.D.(%)**
Hydrogenation catalyst (Pd on $BaSO_4$, 10%)	100	99.8	0.05
Lindlar hydrogenation catalysts (Pd on $CaCO_3$,5%)	100	99.6	0.08
Lindlar hydrogenation catalysts (Pd on $CaCO_3$,10%)	100	99.7	0.12
Hydrogenation catalysts (Pd on asbestos,5%)	100	99.5	0.10
Hydrogenation catalysts (Pd on $CaCO_3$,10%)	100	99.5	0.45

**- average six determination*

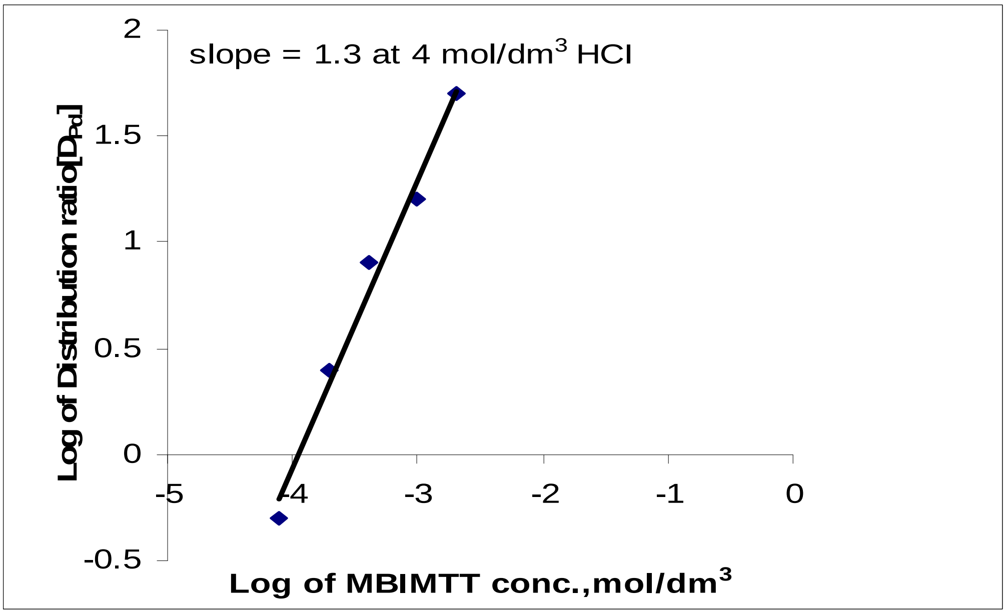


Fig.1 Log-log plot of distribution ratio (D_{Pd}) versus MBIMTT concentration at 4 mol/dm^3 HCI

CONCLUSION

These results underline the potential of the proposed method for the quantitative, selective extraction of palladium(II) with MBIMTT containing low concentration of palladium. It is free from interference from the large number of diverse ions which are associated with palladium(II) in its natural occurrence. The important features of this method are low reagent concentration is required, and the time required for the equilibrium is very short (30 seconds).The method is effective to determine and separate the palladium content from the catalyst. The method is applicable to the analysis of palladium(II) in synthetic mixtures and corresponding to alloys. The method is very simple, selective and reproducible.

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