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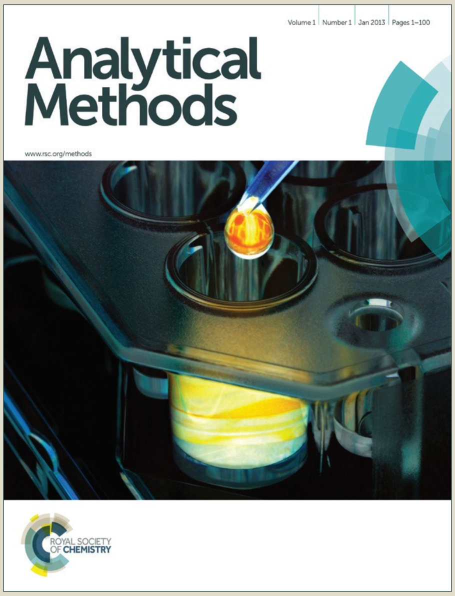

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Development of a solvent extraction system with 4-heptylaminopyridine for the selective separation of platinum(IV) from catalysts, anticancer injection and water samples

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Abstract

In this paper, the solvent extraction of platinum(IV) from ascorbate media (0.007 M) has been studied by equilibrating aqueous phase having pH 1.5 with 10 mL of 0.06 M 4-heptylaminopyridine (4-HAP) as a novel anion exchanger diluted in xylene for 2 min. The extracted metal from organic phase was separated by stripping with water solution (2 X 10 mL). The effect of various parameters, such as pH, extractant concentration, weak acid concentration, equilibrium time, stripping agents, aqueous to organic volume ratio and diluents on the extraction of platinum(IV) was investigated. The extracted species has been evaluated from log $_D$ vs log $_C$ and species appears to be 1:3:1 (metal:acid:extractant). The selectivity of the method was checked by separating platinum(IV) from binary and ternary mixtures of associated metal ions as well as platinum group metals(PGMs). The extraction separation of platinum(IV) has been achieved from catalysts, anticancer injection, Pt-Rh thermocouple wire and water samples.

Keywords

Solvent extraction; Platinum(IV); 4-Heptylaminopyridine; Anticancer injection; Water samples

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1. Introduction

Platinum is a element of platinum group of metals (PGMs) that are available in nature as an arsenite compound or in a sulfide associated with copper, nickel and iron, etc. platinum is employed in various industries in electronic and electrical devices as catalysts, jewelry, dental materials, for production of fuel cells, for plating and coatings, in glass making. As a catalyst, it is widely used in the automobile, chemical and petrochemical industries. The secondary/waste materials containing platinum are generated and discarded during the production and at the end-of-service life. To recover valuables from primary and secondary resources, Pyro/ hydrometallurgical process consisting of roasting and leaching are usually employed to dissolve the metals into an aqueous phase using suitable lixiviants.[1] Cisplatin, cis-diamminedichloroplatinum(II) is an inorganic coordination compound commonly used in the treatment of different solid tumors. However, it is also highly toxic and probable carcinogenic to humans.[2] The presence of cisplatin in water and wastewater has been reported. The excretion via faeces and urine of patients under medical treatment and disposal of unused pharmaceuticals[3-5] effluents from hospitals[6-9] and wastewater is generated during the pharmaceutical manufacturing process[10] represent the major contamination source for this cytostatic.

Efficient and selective extraction/separation of platinum is essential for the recycling of this metals from the secondary resources. The conventional method for the separation of Pt from other PGMs is used by chemical precipitation. Precipitation process are permanent problems, such as high chemical consumption and high labor requirements involved in the steady process, measured kinetics and solid–liquid separation. The chemical precipitation process accumulates environmental pollution is due to use of toxic chemicals. Also, as aqueous chemistry for the extraction and separation of platinum is immensely complicated, practicable hydrometallurgical techniques need to be developed to replace the common chemical precipitation method.[11-13] The solvent extraction technique is one of the most universal method used for the removal, separation and concentration of metallic species from mixed metal aqueous media. The solvent extraction technique has been used commercially in the separation of platinum by using different extractants such as TBP and amine,[14] cyanex 921,[11,15] cyanex 301,[12] trioctyle amine,[14] LIX84I,[16] tetra-n-amyl ammonium chloride,[17] triisooctylamine,[18] tri-*n*-butyl phosphate,[19] aliquat 336,[20] Alamine 300[21] and Cyanex923.[22] Literature investigation suggests that the reported studies have limitations such as poor separation/selectivity and difficult stripping.

The intention of the present work is to reveal some new information about the use of a 4-heptylaminopyridine as a novel extractant for extraction and separation of platinum. The effect of various parameters like equilibration time, diluents, concentration of extractant, organic/aqueous (O/A) phase ratio, acid study, loading capacity, stripping and diverse ions has been investigated. The developed method has been extended for the recovery of platinum from catalyst, Pt-Rh thermocouple wire, anticancer injection(cytoplatin) and water samples. The superiority of the presently employed method is also compared with other reported method (Table 1).

2. Experimental

2.1. Apparatus

UV/VIS Spectrophotometer model-Optizen α (mecasys Co., Ltd/made in Korea) with 1cm quartz cell has used for absorbance measurements and pH measurements are carried out with an Elico Digital pH meter Model LI-120 with a combined glass electrode.

2.2. Reagents

2.2.1. Standard platinum(IV) solution

Standard solution of platinum(IV) was prepared by dissolving 1 g (1 X 10^{-3} Kg) of hydrogen hexachloroplatinate(IV) hydrate, $H_2PtCl_6.H_2O$ (Johnson and Matthey, UK), in 1 M hydrochloric acid and was standardized gravimetrically.[23] A working solution (200 µg/mL) was made by appropriate dilution.

2.2.2. 4-Heptylaminopyridine solution (0.06 M)

To a stirred solution of 4-aminopyridine (0.05 mol) in dry THF (40 mL), sodium amide was added at 0^oC and continued stirring for 30 min. The temperature of the reaction mixture increased to room temperature and 1-bromoheptane was added slowly. The reaction mixture was stirred at the ambient temperature for 1 hr. The reaction mixture was poured to water, NH_4Cl and extracted with chloroform (150 mL). The chloroform extract was dried (Na_2SO_4) and evaporated on a rotary evaporator to yield a residue which was crystallized to afford the corresponding 4-heptylaminopyridine in 75-85 % overall yield[24] and and it's solutions were prepared in xylene. Other standard solutions of diverse ions were prepared by dissolving weighed quantities of their salts in water or dilute HCl[29]. Different synthetic mixtures containing platinum(IV) were prepared by combining with commonly associated metal ions in definite composition[27].All other chemicals and solvents were of AR grade and double distilled water has used throughout the experiments.

2.2.3. Stannous chloride solution (25% w/v)

Stannous chloride (25 g) was dissolved in 25 mL of conc. hydrochloric acid and diluted with water to 100 mL.

2.3. Extraction procedure

An aliquot of 200 µg of platinum(IV) solution has been mixed with 0.0308 gm of ascorbic acid to make its concentration 0.007 M in a total volume of 25 mL of the solution. The pH of the aqueous solution was adjusted to 1.5 by dil. sodium hydroxide and hydrochloric acid solution. The solution was then transferred to a 125 mL separating funnel and shaken with 10 mL of 0.06 M 4-heptylaminopyridine in xylene for 2 min. After separating the two phases, the aqueous phase is discarded and the organic phase was stripped with two 10 mL portions of water solution. After being stripped with water platinum(IV) has entered into the aqueous phase quantitatively. The stripped aqueous phase was evaporated to moist dryness and extracted into dil. hydrochloric acid.

2.4. Estimation procedure for platinum(IV)

The resulting aqueous phase was mixed with 5 mL of concentrated hydrochloric acid and 10 mL of 25% stannous chloride. The solution was diluted to the mark with water in 50 mL volumetric flask. The absorbance of the resultant solution was measured at 403 nm[25] The concentration of platinum(IV) was calculated in terms of percentage extraction (% E).

A percentage extraction (% E) and a metal distribution ratio (D) are calculated according to (1) and (2), respectively:

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

Where $[M]_{aq.,\ init}$.represents the initial concentration of metal ion in the aqueous phase. $[M]_{aq}$. and $[M]_{org.}$ are the total concentrations of metal ion in the aqueous and organic phases after the equilibrium, respectively.

$$D = \frac{{}^{V_W}\!/\!{}_{V_o} \times \%E}{(100 - \%E)} \qquad (2)$$

Where V_w = Volume of aqueous phase, V_o = Volume of organic phase and D = Distribution ratio.

3. Results and Discussion

3.1. Extraction of platinum(IV) as a function of pH

Extraction of platinum(IV) was performed between pH 0.10 and 6.0 at a fixed concentration of 0.007 M ascorbic acid with a 0.06 M solution of 4-heptylaminopyridine in xylene. The extraction was found to be quantitative between a pH range 0.5 to 2.0. With an increase in pH above 2.0 the extraction goes on decreasing. Hence, the extraction of platinum(IV) was carried out at pH 1.5 for all extraction experiments (Fig. 1). The decrease in extraction with increase in pH value was due to hydrolysis of the ion-pair complex.

3.2. Extraction as a function of weak organic acid concentration

The extraction behavior of platinum(IV) from ascorbic acid, sodium salicylate, sodium malonate and sodium succinate at pH 1.5 with 0.06 M 4-heptylaminopyridine in xylene was studied. The extraction initiated in 0.001 M ascorbic acid and became quantitative in the concentration range of 0.005 to 0.01 M. With increased concentration of ascorbic acid, there was a decrease in the extraction of platinum(IV). This may be due to formation of stable 4-heptylaminopyridine-ascorbate species. Therefore, a 0.007 M ascorbic acid has used throughout this work. There was incomplete extraction of platinum(IV) from malonate, salicylate, and succinate media (Fig. 2).

3.3. Effect of extractant concentration

The effect of extractant concentration in the range 0.01 to 0.1 M of 4-heptylaminopyridine in xylene was studied for the extraction of 200 µg platinum(IV) from 0.007 M ascorbic acid. It was found that 10 mL of 0.055 M extractant was sufficient for quantitative extraction of 200 µg platinum(IV) from 0.007 M ascorbic acid. However, in recommended procedure 10 mL 0.06 M 4-heptylaminopyridine in xylene was used to ensure the complete extraction of metal ion. There was no adverse effect of using excess of 4-heptylaminopyridine (Fig. 3).

3.4. Effect of diluents

The extraction of 200 µg platinum(IV) from 0.007 M ascorbic acid media using 0.06 M 4-heptylaminopyridine in various aliphatic and aromatic diluents, like n-hexane, benzonitrile, kerosene, cyclohexane, benzyl alcohol, toluene, xylene, dichloroethane, chloroform, and carbontetrachloride was tested. The extraction of platinum(IV) was quantified with inert diluents, such as xylene and toluene because the ion-pair complex has a high distribution ratio value in these solvents. Whereas carbontetrachloride (47%), kerosene (52.4%) and chloroform (89.7%) were found to be poor solvents, while there was no extraction in n-hexane, benzonitrile, benzyl alcohol, dichloroethane and cyclohexane. No correlation between dielectric constant and percentage extraction was observed. In the present study, xylene has used as diluent as it is cheap, no emulsion formation and phase separation took place rapidly.

3.5. Effect of equilibration time

The extraction behavior of platinum(IV) from ascorbic acid media with 0.06 M 4-heptylaminopyridine in xylene has been measured at the different equilibration time of 6 s to 20 min. It has observed that, under the optimized experimental conditions, a minimum 25 second time interval is required for attaining equilibrium in the sense to extract platinum(IV) quantitatively. In the recommended procedure 2 min. equilibration time was recommended for ensuring the complete extraction of platinum(IV). However, a prolonged shaking period was found to have an adverse effect on the extraction and should be avoided (Fig. 4). This may be due to the dissociation of the ion-pair complex.

3.6. Stripping of platinum(IV) from loaded organic phase

Back stripping is the process of reverse of extraction. Therefore, stripping of platinum(IV) from loaded organic phase was carried out using NH_3, ammonia buffer (pH 10), H_2O, HCl, HNO_3, H_2SO_4, NaCl, KOH and NaOH (Table 2). The Stripping of platinum(IV) was quantified with water. The stripping was found to be incomplete with NaCl (12.7%), NH_3 (20.6%), ammonia buffer (pH 10) (27%), NaOH (35.8%), KOH (42.3%), HCl (52.3%) and HNO_3(55.9%). In recommended procedure, two 10 mL portions of water was used for the complete stripping of loaded organic phase.

3.7. Effect of aqueous to organic volume ratio

The results of contacting different volume ratios of aqueous to organic phases have been studied. The result indicates that a preferred aqueous/ organic (A/O) phase ratio in this study was 2.5:1. This is evident from the sharp increase in the separation efficiency as well as the distribution ratio of platinum(IV), when the phase ratio (A/O) changed from 10:1 to 5:1. This may simply be due to the unavailability of reagent for metal extraction and so acrowding effect occurs at a low phase ratio. However, in the recommended procedure, the phase ratio was maintained as 2.5:1.

3.8. Metal loading capacity of extractant

Loading capacity of 0.06 M 4-heptylaminopyridine was determined by contacting 10 mL of organic phase for 2 min. repeat with the 25 mL of aqueous phase containing varied concentration of platinum(IV). The maximum loading capacity of 10 mL 0.06 M solution of 4-heptylaminopyridine in xylene was found to be 2000 µg platinum(IV).

3.9. Mechanism of the extraction of platinum(IV)

Attempts are made to ascertain the nature of the extracted species using log D–log C plots. The graphs of $\log D_{[Pt(IV)]}$ against $\log C_{[4\text{-}HAP]}$ at a fixed ascorbic acid concentration (0.007 M) were found to be linear, having slopes of 0.78 and 0.77 at pH 2 and 2.25, respectively (Fig. 5). Also, plots of $\log D_{[Pt(IV)]}$ against $\log C_{[\text{Ascorbic acid}]}$ at fixed 4-heptylaminopyridine concentration (0.06 M) were linear and slope values were found to be 2.78 and 2.87 at pH 2 and 2.25, respectively (Fig. 6). The probable composition of the extracted species was calculated to be 1:3:1 (metal:acid:extractant). In the extraction of platinum(IV) with ascorbate medium, the first platinum(IV) was reduced to platinum(II)[26] then it was converted into platinum(II) ascorbate species as an anionic complex and interacted with $RR'NH_2^+$. Hence, the probable extracted species in xylene are $[RR'NH_2^+.Pt(C_6H_7O_6)_3^-]_{org}$. The mechanism of extraction is:

$$RR'NH_{(org)} + H^+\text{ascorbate}_{(aq)}^- \rightleftharpoons [RR'NH_2^+\text{ascorbate}^-]_{(org)} \tag{1}$$

$$H_2Pt^{IV}Cl_6 \xrightarrow[\text{Reducing agent}]{\text{Ascorbic acid}} Pt^{II}Cl_4^{2-} + 2\ HCl \tag{2}$$

$$Pt^{2+} + 3\ \text{ascorbate}^- \rightleftharpoons [Pt(\text{ascorbate})_3]_{(aq)}^- \tag{3}$$

$$[Pt(\text{ascorbate})_3]_{(aq)}^- + [RR'NH_2^+\text{ascorbate}^-]_{(org)} \rightleftharpoons [RR'NH_2^+\ Pt(\text{ascorbate})_3^-]_{(org)} + \text{ascorbate}_{(aq)}^- \tag{4}$$

Stripping mechanism:

$$[RR'NH_2^+\ Pt(\text{ascorbate})_3^-]_{(org)} + H_2O \rightleftharpoons RR'NH + H_3O^+ + Pt(\text{ascorbate})_3^- \tag{5}$$

3.10. Effect of various foreign ions on percentage extraction

The effect of various diverse ions were tested, when platinum(IV) was extracted with 4-heptylaminopyridine in xylene. The tolerance limit of individual diverse ions were determined with an error less than ± 2%. It was observed that the method is free from interference from a large number of cations and anions (Table 3). The only species showing interference in the procedure were Pd(II), Rh(III), iodide, thiocyanate, thiourea, and thiosulphate. However, the interference due to coextraction of Pd(II) and Rh(III) were eliminated by masking with tartrate. However, thiocyanate, thiosulphate and thiourea make very strong complexes with platinum(IV). This is due to soft acid and soft base combination while iodide ion forms strong anionic species with platinum(IV).

4. Applications

4.1. Separation and determination of platinum(IV) from binary mixtures

The separation of Pt(IV) from some commonly associated metal ions like Ru(III), Os(VIII),Ir(III), Rh(III), Au(III), Fe(III), Co(II), Ni(II), Hg(II), Cd(II), Zn(II), Pd(II), Bi(III), Te(IV), and Ag(I) using 4-heptylaminopyridine was achieved by taking advantage of the difference in the extraction conditions of metal such as, the pH of the aqueous phase, reagent concentration and use of masking agent (Table 4). All the added metal ions were remained quantitatively in aqueous phase from which they were determined spectrophotometrically by standard methods.[27-32] Rhodium(III) and Pd(II) were interfered due to their coextraction with Pt(IV). Rhodium(III) and Pd(II) were separated from Pt(IV) by masking with 10 mg tartrate. The masked metal ion from the aqueous phase was demasked with perchloric acid and determined spectrophotometrically with the standard method.[27,32]

4.2. Separation of platinum(IV) from ternary synthetic mixtures

Platinum(IV) is one of the platinum group metals (PGMs), and therefore, it was separated from Ru(III), Ag(I); Rh(III) and Pd(II). The Rh(III) and Pd(II) was masked by the tartrate as masking agent. Other platinum group metals were not extracted with the optimum extraction condition of platinum(IV). Platinum(IV) was also isolated from the Os(VIII), Te(IV); Ir(III), Bi(III); Au(III), Zn(II);Fe(III), Cd(II); Co(II),Hg(II); Ni(II), Ru(III);Hg(II), Os(VIII); Cd(II), Ir(III); Zn(II), Cd(II); Pd(II), Fe(III); and Ag(I), Bi(III). The results are found to be quantitative (Table 5).

4.3. Analysis of platinum(IV) from real samples

4.3.1. Determination of platinum(IV) in catalysts sample

The catalyst (0.1 g) was dissolved in 5 mL *aqua regia.* The solution was evaporated to moist dryness. Two 3 mL portions of hydrochloric acid were added and evaporated till all the nitric acid was removed. The residue was extracted in 1 M hydrochloric acid. The solution was filtered and the filtrate was diluted to 100 mL. An aliquot of this diluted solution was analyzed for platinum(IV) content by the proposed method. It is found that there is a good agreement with the certified value (Table 6).

4.3.2. Analysis of anticancer injection(Cytoplatin)

The method permits the separation and determination of platinum(IV) from anticancer injection (Cytoplatin). A known volume (10 mL) of cisplatin solution was digested in perchloric acid /nitric acid (10:1) and evaporated to dryness until organic matter was removed. The obtained residue was dissolved in concentrated hydrochloric acid and diluted with water to 10 mL in a standard volumetric flask. An aliquot of the sample solution was taken and platinum(IV) determined using the recommended procedure (Table 7).

4.3.3. Analysis of Pt-Rh thermocouple wire for platinum content

The proposed procedure was used for the estimation of the platinum(IV) from Pt-Rh thermocouple wire (Table 7). A known weight (0.100) of thermocouple wire was preliminary fused with zinc powder and the melt was cooled and dissolved in hydrochloric acid. The black powder remained was treated with 5 mL *aqua regia.* After the reaction was over, the whole solution was heated with two 5 mL portions of concentrated hydrochloric acid until complete removal of oxides of nitrogen and diluted with water to 10 mL in standard volumetric flask. An aliquot of sample solution was taken and platinum(IV) was determined by using the recommended procedure.

4.3.4. Determination of platinum(IV) in water samples

In order to investigate the accuracy and applicability of the method, it was used for determination of platinum(IV) in water samples collected from different sources. The water samples collected were filtered through Whatmann filter paper No. 40 to remove suspended matter, impurities etc., and then boiled for 5 min. to remove chlorine and dissolved gases. Then water samples were spiked with 200 μg of platinum(IV) and the developed method is applied for determination of platinum(IV) in spiked water samples. The results were in good agreement with amount added (Table 8).

5. Conclusions

4-Heptylaminopyridine has been proved to be a sensitive, selective extractant for separation of platinum(IV) from commonly associated metal ions. The developed method is simple, reproducible and required less time for separation of platinum(IV). The important features of the proposed methods are,

i. Low concentration of extractant is required for quantitative extraction of platinum(IV).
ii. 4-Heptylaminopyridine forms ion-pair complex with platinum(IV) in ascorbic acid medium.
iii. Extraction of platinum(IV) have been carried out without any addition of synergent or modifier at room temperature.
iv. Ecofriendly strippant (water) is used for stripping of platinum(IV); here in method has been proves one of the principles of green chemistry.
v. The developed method is free from interference of a large number of diverse ions which are commonly associated with platinum(IV). The selectivity was also enhanced by use of suitable masking agents.
vi. The developed method is reproducible, simple and used for extraction of platinum(IV) from binary, ternary metal ion mixtures.
vii. The developed method is successfully used for extraction of platinum(IV) from real samples such as catalysts, Pt-Rh thermocouple wire, anticancer injection and water samples.

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Table Caption

Table 1

Comparison of the present method with earlier reported solvent extraction methods for extraction of platinum(IV)

Extractant	Solvent	Acidity/pH	Stripping agent	Determination method	Equilibrium time, min.	Ref.
Cyanex 923	Toluene	1 M HCl	5 M $HClO_4$	ICP-OES	4	32
Aliquat 336	Kerosene	pH 3.4	Thiourea	ICP-OES	5	33
DMDCHTDMA	1,2-DCE	8 M HCl	1 M HCl	AAS	30	34
Cyanex 302	Kerosene	Chloride	HNO_3	ICP-OES	30	35
Aliquat 336	Kerosene	HCl+HNO_3	$Na_2S_2O_3$	AAS	30	20
Alamine 308	Kerosene	1 M HCl	5.0 M HCl +0.75 M Thiourea	ICP-OES	60	18
4-HAP	Xylene	0.007 M Ascorbic acid pH 1.5	water	Spectrophotometry	2	P.M

P.M = Present Method

Table 2

Extraction of platinum(IV) with stripping agents

Pt(IV) = 200 µg, pH = 1.5, Ascorbic acid = 0.007 M, 4-HAP = 0.06 M in xylene, contact time = 2 min, aq.**:** org. = 2.5:1

Stripping agent	Percentage Extraction, (% E)	Distribution ratio, (D)
Ammonia (1-10 M)	20.6	0.64
Ammonia buffer(pH 10)	27.0	0.92
HCl(1-10 M)	52.3	2.74
Water	100	∞
HNO_3 (1-10 M)	55.9	3.16
NaCl(0.1-1.3 M)	12.7	0.36
KOH(0.1-1.5 M)	42.3	1.83
NaOH(0.1-1.5 M)	35.8	1.39

Table 3

Effect of foreign ions on the extractive determination of platinum(IV)

Pt(IV) = 200 µg, pH = 1.5, Ascorbic acid = 0.007 M, 4-HAP = 0.06 M in xylene,

contact time = 2 min, Strippant = Water, aq.**:** org. = 2.5:1

Amount tolerated (mg)	Diverse ion added
25	Ca(II), Zn(II), malonate, fluoride
15	U(VI), Mo(VI), Tl(III), tartrate, citrate, oxalate, acetate, bromide
10	Ti(IV), V(V), Ni(II), Cd(II), Pb(II), Te(IV), Mg(II), Be(II), EDTA, nitrate
5	Hg(II), Cr(III), Cr(VI), Fe(II), Fe(III), Bi(III), Se(IV), succinate, salicylate, chloride
3	Rh(III)[a],Os(VIII), Au(III)
2	Re(VII), Pd(II)[a],Ru(III), Ag(I), Ir(III)
0	Iodide, thiocyanate, thiourea, thiosulphate

[a] Masked with 10 mg tartrate

Table 4

Separation of platinum(IV) from binary mixtures

Metal ion	Amount taken (µg)	Average Recovery (%)[a]	Chromogenic ligand	Reference
Pt(IV)	200	99.4		
Ru(III)	200	97.9	Thiourea	28
Pt(IV)	200	99.4		
Fe(III)	60	99.1	Thiocyanate	27
Pt(IV)	200	99.1		
Ni(II)	40	98.5	DMG	27
Pt(IV)	200	99.3		
Co(II)	300	98.1	Thiocyanate	27
Pt(IV)	200	99.1		
Pd(II)[b]	100	97.1	4’-ChloroPTPT	32
Pt(IV)	200	99.1		
Os(VIII)	300	98.8	Thiourea	28
Pt(IV)	200	98.8		
Ir(III)	40	98.2	Hydro bromic acid	27
Pt(IV)	200	98.9		
Au(III)	200	98.8	Stannous chloride	28
Pt(IV)	200	98.9		
Rh(III)[b]	200	99.3	Potassium iodide	27
Pt(IV)	200	99.0		
Hg(II)	100	99.2	PAN	29
Pt(IV)	200	99.1		
Zn(II)	60	99.4	PAR	29
Pt(IV)	200	99.1		

Cd(II)	10	98.5	PAR	29
Pt(IV)	200	98.5		
Bi(III)	300	97.8	Potassium iodide	27
Pt(IV)	200	98.8		
Te(IV)	40	98.9	4'-BromoPTPT	31
Pt(IV)	200	98.8		
Ag(I)	150	99.0	2',4'-dinitroAPTPT	30

[a] Average of five determinations

[b] Masked with 10 mg tartrate

Table 5

Separation of platinum(IV) from ternary synthetic mixtures

Composition (μg)	**Average recovery (%)[a]**	**RSD (%)**
Pt(IV), 200; Ru(III), 200; Ag(I), 150	99.9	0.09
Pt(IV), 200; Rh(III)[b], 200; Pd(II)[b], 100	99.9	0.12
Pt(IV), 200; Os(VIII), 300; Te(IV), 40	99.8	0.09
Pt(IV), 200; Ir(III), 40; Bi(III), 300	99.7	0.18
Pt(IV), 200; Au(III), 200; Zn(II), 60	99.8	0.13
Pt(IV), 200; Fe(III), 60; Cd(II), 10	99.9	0.15
Pt(IV), 200; Co(II), 300; Hg(II), 100	99.8	0.09
Pt(IV), 200; Ni(II), 40; Ru(III), 200	99.9	0.17
Pt(IV), 200; Hg(II), 100; Os(VIII), 300	99.8	0.09
Pt(IV), 200; Cd(II), 10; Ir(III), 40	99.9	0.09
Pt(IV), 200; Zn(II), 60; Cd(II), 10	99.9	0.17
Pt(IV), 200; Pd(II)[b], 100; Fe(III), 60	99.9	0.10
Pt(IV), 200; Ag(I), 150; Bi(III), 300	99.9	0.09

[a] Average of five determinations

[b] Masked with 10 mg tartrate

Table 6

Determination of platinum(IV) from catalysts

Catalyst	Pt(IV) taken (µg)	Pt(IV) found by proposed method (µg)[a]	Average, % recovery	RSD (%)
Pt-Pd-Rh[b] monolith on cordierite[1]	200	199.6	99.8	0.1
Pt–Rh[b] monolith on cordierite[2]	200	199.4	99.7	0.18
Pt–catalyst on alumina[3]	200	199.2	99.6	0.21
Pt–Pd[b]–Rh[b] catalyst on alumina[4]	200	199.6	99.8	0.1
Pt–Pd[b] catalyst on alumina[5]	200	199.4	99.7	0.13
Pt–Rh[b] catalyst onalumina[6]	200	199.4	99.7	0.15

Composition of synthetic mixtures corresponding to alloy in percentage:

1. Pt, 0.03–0.20; Pd, 0.03–0.15; Rh, 0.005–0.05
2. Pt, 0.03–0.25; Rh, 0.005–0.03
3. Pt, 0.3–0.8
4. Pt, 0.03–0.20; Pd, 0.03–0.150; Rh, 0.005–0.05
5. Pt, 0.03–0.15; Pd, 0.02–0.12
6. Pt, 0.03–0.25; Rh, 0.005–0.03.

[a] Average of five determinations
[b] Masked with tartrate

Table 7

Analysis of platinum(IV) from drug and thermocouple sample

Sample	Amount taken	Amount of Pt(IV) found[a]	RSD, (%)
Cytoplatin (anticancer injection)	200 μg/mL	198.2 μg/mL	0.35
Platinum–rhodium[b] thermocouple wire (Pt, 87; Rh, 13)	200 μg/mL	197.4 μg/mL	0.25

[a] Average of five determinations
[b] Masked with 10 mg tartrate

Table 8

Determination of platinum(IV) in water samples

Sample	Platinum(IV) spiked (μg)	Platinum(IV) found (μg)	Average recovery[a] (%)	RSD (%)
Distilled water[b]	200	199.86	99.9	0.04
Tap water[b]	200	199.80	99.9	0.06
Waste water[b]	200	199.66	99.8	0.29
River water[c]	200	199.40	99.7	0.33

[a] Average of five determinations
[b] Department of Chemistry, R. R. College, Jath Dist-Sangli
[c] Panchganga river Kolhapur

Figure Captions:

Fig. 1 Effect of pH on extraction of platinum(IV)

Pt(IV) 200 µg, ascorbic acid = 0.007 M, aq.: org. = 2.5:1, 4-HAP = 0.06 M in xylene, equilibrium time = 2.0 min, strippant = water (2 X 10 mL)

Fig. 2 Effect of weak organic acid concentration on extraction of platinum(IV)

Pt(IV) 200 µg, pH= 1.5, aq.: org. = 2.5:1, 4-HAP = 0.06 M in xylene, equilibrium time = 2.0 min, strippant = water (2 X 10 mL)

Fig. 3 Effect of 4-HAP concentration

Pt(IV) 200 µg, pH= 1.5, aq.: org. = 2.5:1, ascorbic acid = 0.007 M, equilibrium time = 2.0 min, strippant = water (2 X 10 mL)

Fig. 4 Effect of Equilibration Time

Pt(IV) 200 µg, ascorbic acid = 0.007 M, pH= 1.5, aq.: org. = 2.5:1, 4-HAP = 0.06 M in xylene, strippant = water (2 X 10 mL)

Fig. 5 Log-Log plot of log $D_{[Pt(IV)]}$ versus log $C_{[(4\text{-}HAP)]}$

A. Pt(IV) 200 µg, pH= 2, aq.: org. = 2.5:1, ascorbic acid = 0.007 M, equilibrium time = 2.0 min, strippant = water (2 X 10 mL)

B. Pt(IV) 200 µg, pH= 2.25, aq.: org. = 2.5:1, ascorbic acid = 0.007 M, equilibrium time = 2.0 min, strippant = water (2 X 10 mL)

Fig. 6 Log-Log plot of log $D_{[Pt(IV)]}$ versus log $C_{[(ascorbic\ acid)]}$

A. Pt(IV) 200 µg, pH= 2, aq.: org. = 2.5:1, 4-HAP = 0.06 M in xylene, equilibrium time = 2.0 min, strippant = water min, strippant = water (2 X 10 mL)

B. Pt(IV) 200 µg, pH= 2.25, aq.: org. = 2.5:1, 4-HAP = 0.06 M in xylene, equilibrium time = 2.0 min, strippant = water min, strippant = water (2 X 10 mL)

Fig. 1 Effect of pH on extraction of platinum(IV)

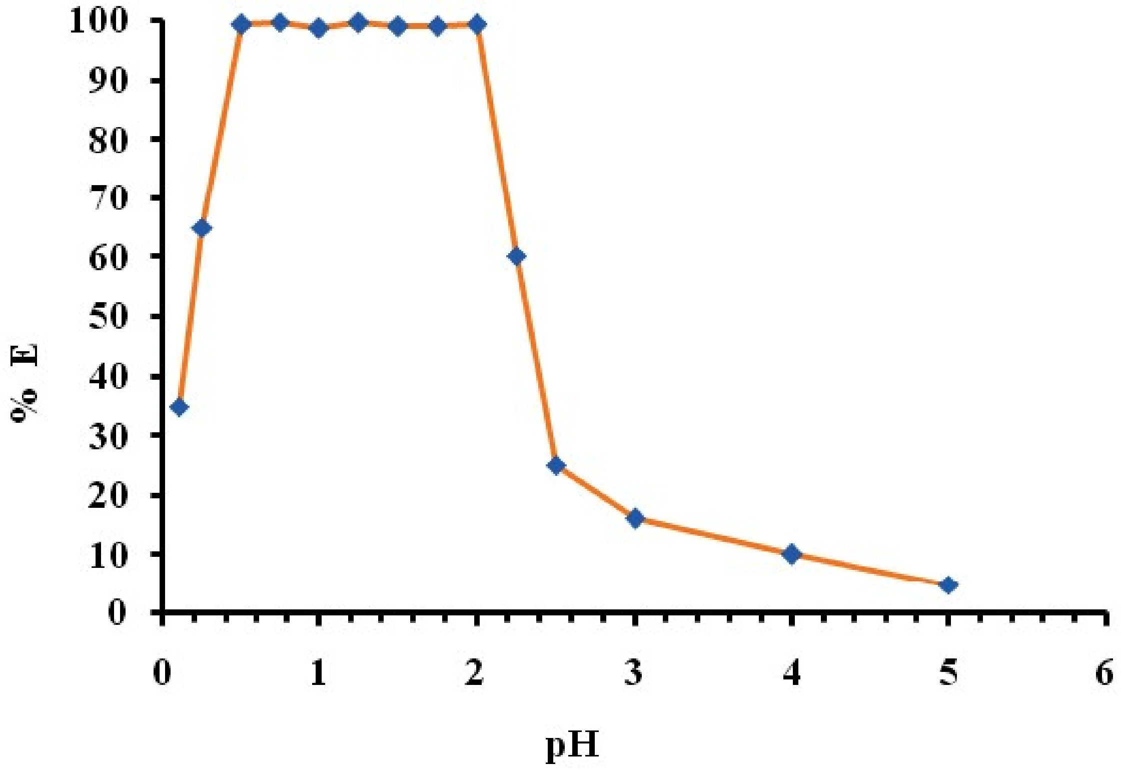


Fig. 2 Effect of weak organic acid concentration on extraction of platinum(IV)

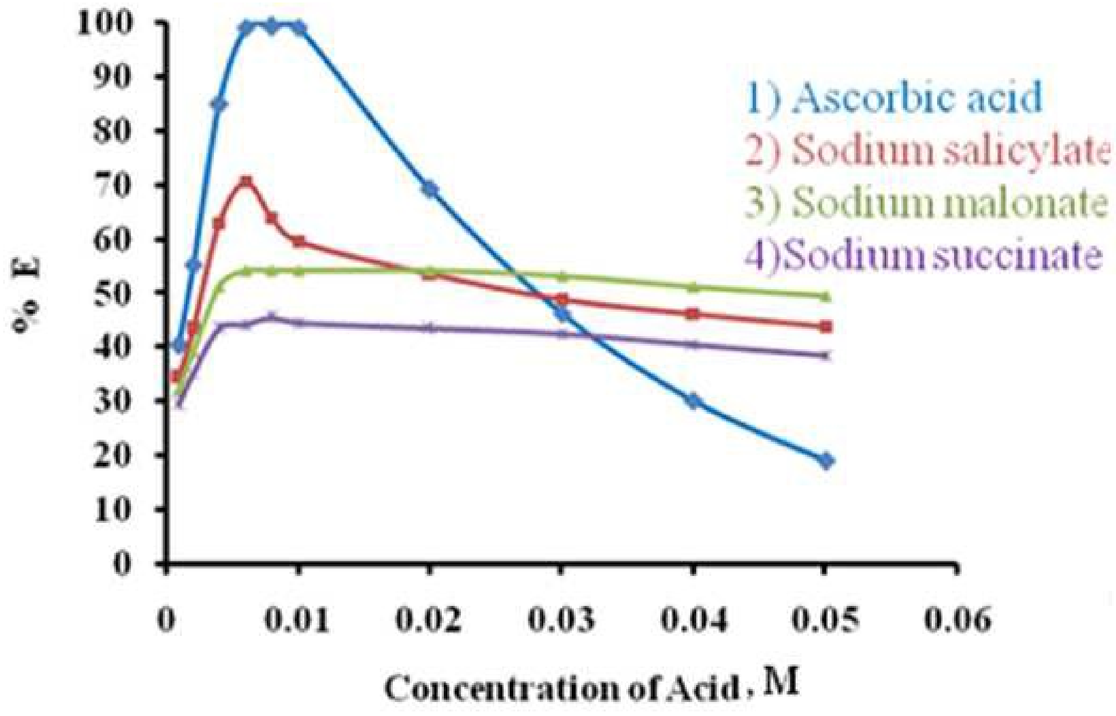


Fig. 3 Effect of 4-HAP concentration

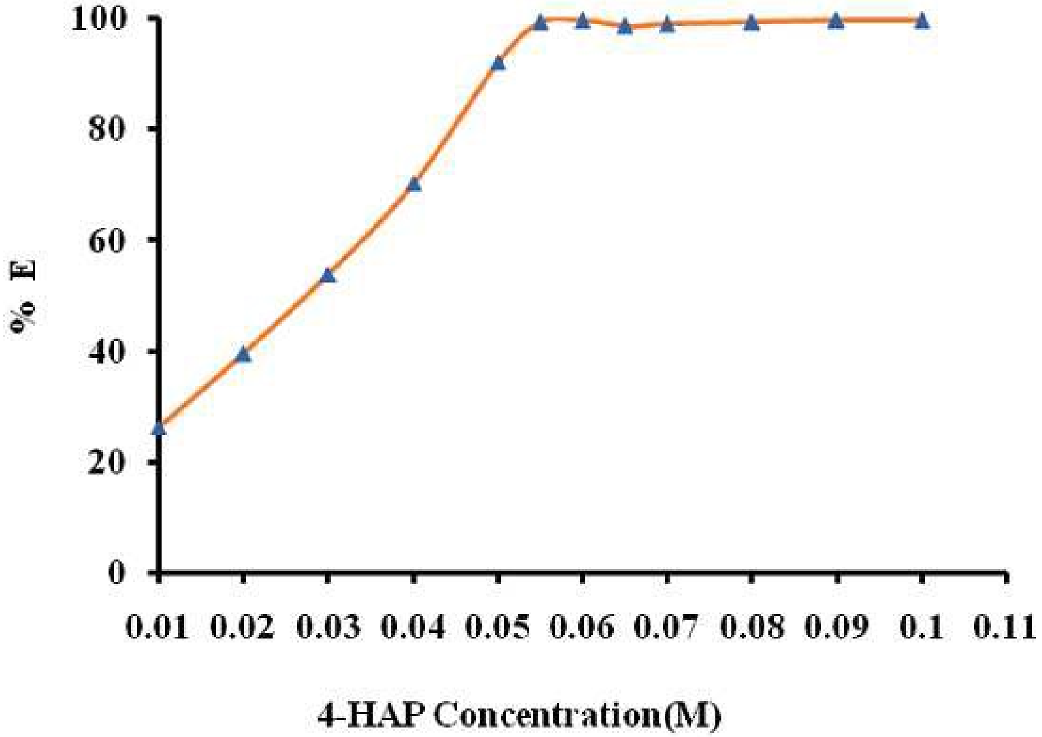


Fig. 4 Effect of Equilibration Time

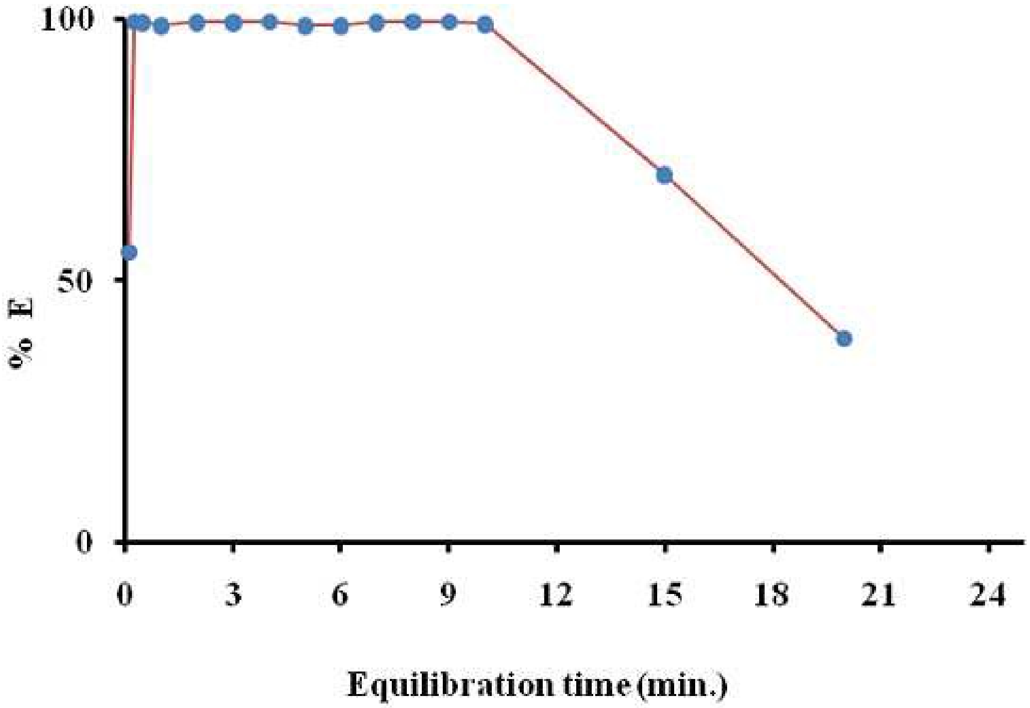


Fig. 5 Log-Log plot of log D $_{[Pt(IV)]}$ versus log C $_{[(4\text{-}HAP)]}$

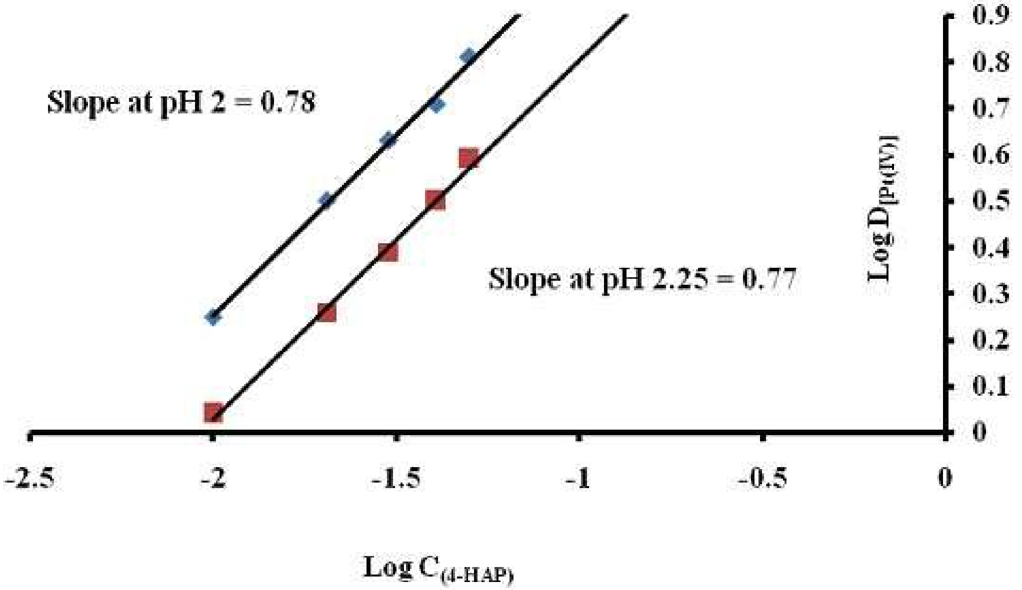
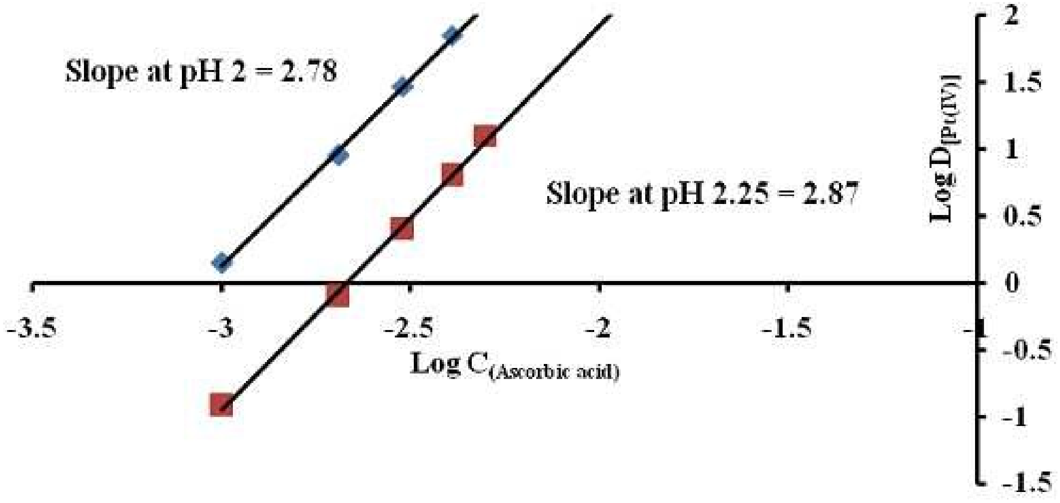
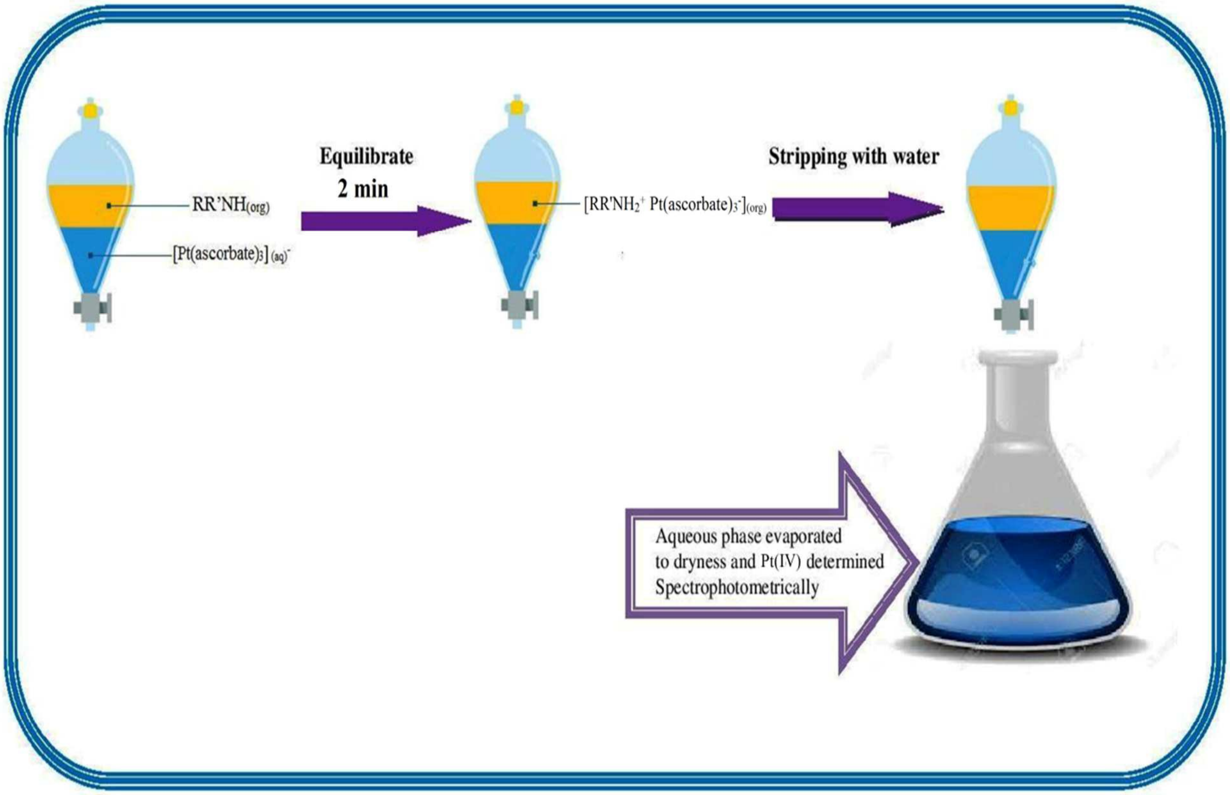


Fig. 6 Log-Log plot of log D $_{[Pt(IV)]}$ versus log C $_{[(ascorbic\ acid)]}$




RR'NH(org)
[Pt(ascorbate)3] (aq)-
Equilibrate
2 min
[RR'NH2+ Pt(ascorbate)3-](org)
Stripping with water
Aqueous phase evaporated
to dryness and Pt(IV) determined
Spectrophotometrically