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Selective Liquid–Liquid Extraction of Platinum(IV) from Ascorbate Media by N-n-Octylaniline: Its Separation from Associated Elements and Real Samples

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ABSTRACT

The distribution equilibrium of platinum(IV) species between aqueous ascorbate media and 0.1 mol/L of N-n-octylaniline in xylene was studied as a function of different parameters, such as the concentration of extractant in organic phase, weak organic acid concentration, different diluents, and effect of shaking period on extraction. The quantitative extraction of platinum(IV) was observed with N-n-octylaniline in xylene from 0.01 to 0.02 mol/L of ascorbic acid in the pH range of 0.5 to 1.25. The metal ion was stripped out from organic phase with water and determined spectrophotometrically with stannous chloride. The extraction of platinum(IV) was quantitative in most aromatic solvents, such

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as benzene, toluene, and xylene. The stoichiometry of the extracted species was determined on the basis of slope analysis and found to be 1:3:1 (metal:acid:extractant). As an application, the system was used for selective extraction of platinum(IV) from its binary mixture with Pd(II), Au(III), Rh(III), Ir(III), Os(VIII), Ru(III), Fe(III), Co(II), Ni(II), and Cu(II), and also from its ternary mixture with Pd(II) and Rh(III). The distribution coefficient for platinum(IV) in ascorbate media was of higher magnitude than malonate, salicylate, succinate, tartrate, acetate, and oxalate media. The method developed was successfully applied for the analysis of platinum(IV) in the real samples, such as platinum–rhodium thermocouple wire, pharmaceutical sample cisplatin, and catalysts.

Key Words: Solvent extraction; Platinum(IV) determination; N-n-octylaniline; Ascorbic acid.

INTRODUCTION

The development of new but selective extractants for the separation and concentration of precious metals at trace levels reflects an increasing need for these metals to be recovered and analyzed. High-molecular weight amines (HMWA) have emerged as powerful extractants for many elements. Recently, it has been shown that HMWA are an effective extractants for the extraction of anionic complexes of platinum. The use of n-octylaniline[1−7] in the extraction of noble metals has been described in a number of published research results. The extraction coefficient depends on the method of preparation of n-octylaniline; fairly high equilibration time as well as high reagent concentrations. The method needs multiple extraction and the use of mineral acids, which is not environmentally friendly. Tri-octyl amine (TOA)[8] was used as effective extractant for platinum(IV) from hydrochloric acid media but the method suffers from interference of Pd(II), Ru(III), Cu(II), and SCN^-. Tri-iso-octylamine[9] in carbon tetrachloride was used as a group extractant for the noble metals from 1 mol/L hydrochloric acid media with 2 min of shaking but many ions interfere in the extraction. The platinum(IV) was extracted with a mixture of 0.25 mol/L C_{8-10} alkylaniline hydrochloride[10] and 0.25 mol/L petroleum sulphides in toluene and estimated by atomic absorption spectroscopic method (AAS). Alamine 336, NN-dioctyl-2-picolylamine, N,N,N′N′-tetraoctyl ethylenediamine,[11] and aliquat[11,12] were evaluated as extractants for platinum(IV) from aqueous chloride medium at pH of 1 to 5. All the amines are equally efficient for platinum(IV) but their extraction efficiency decreased with increasing pH.

The advantages of the proposed method over the reported one from this laboratory for platinum(IV) extraction from hydrochloric acid media using N-n-octylaniline[13] are (1) the method is ecofriendly, as the extraction carried from weak organic acid; (2) lower reagent concentration is required; and (3) many metal ions do not interfere. This article deals with the rapid and quantitative extraction of platinum(IV) from 0.015 mol/L of ascorbic acid at pH 1.0 with 0.1 mol/L of N-n-octylaniline in xylene as rapid and quantitative. The proposed method offers extraction separation and determination of platinum(IV) from alloy, catalysts, and pharmaceutical samples, and also from associated elements.

EXPERIMENTAL

Apparatus

An Elico digital spectrophotometer model SL-171 with 1×1 cm quartz cells was used for absorbance measurement; pH measurements were carried out using an Elico digital pH meter model LI 120.

Reagents

Standard solution of platinum(IV) was prepared by dissolving 1×10^{-3} kg of hydrogen hexachloro platinate(IV) hydrate, $H_2PtCl_6{\cdot}6H_2O$ (Johnson and Matthey, UK) in 1 mol/L of hydrochloric acid and was standardized gravimetrically.[14] A working solution was made by appropriate dilution (100×10^{-9} kg). N-n-octylaniline was prepared by the method of Gardlund[15] and its solutions (0.1 mol/L) were prepared in xylene. All the chemicals used were of A.R. grade. Double-distilled water was used throughout.

Extraction Procedure for Platinum(IV)

An aliquot of platinum(IV) solution (3×10^{-3} dm^3 of 100×10^{-9} kg) was mixed with a sufficient quantity of ascorbic acid (0.066×10^{-3} kg) to make its concentration 0.015 mol/L in a total volume of 25×10^{-3} dm^3 of the solution. The pH of the solution was adjusted to 1.0 using dilute hydrochloric acid and sodium hydroxide. The solution was then transferred to a 125×10^{-3} dm^3 separatory funnel, 10×10^{-3} dm^3 of 0.1 mol/L N-n-octylaniline in xylene was added. It was shaken gently for about 1 min. The layers were allowed to separate and the aqueous layer was carefully withdrawn. Platinum(IV) from the organic phase was stripped with water ($2 \times 10 \times 10^{-3}$ dm^3).

Estimation Procedure for Platinum(IV)

The resulting aqueous phase (strippants) was mixed with 5×10^{-3}dm^3 of concentrated hydrochloric acid and 10×10^{-3}dm^3 of 25% stannous chloride in concentrated hydrochloric acid. The solution was diluted to the mark with water. The absorbance of the resulted solution was measured at 403 nm.[16] The concentration of platinum(IV) was found from a calibration curve.

Determination of Platinum(IV) in Platinum–Rhodium Thermocouple Wire

The proposed procedure was used for the estimation of the platinum(IV) from the platinum base alloy containing more than 10% of iridium and rhodium. These alloys are insoluble in *aqua regia* at atmospheric pressure but can be dissolved in it at elevated temperature in a high-pressure system.[17] More convenient is preliminary fusion of the sample with zinc and dissolution of the melt in hydrochloric acid.[18] A black powder remains, containing the platinum metals in elemental form, ready for an attack by acids or by other appropriate means, prior to distillation (Os or Ru), chlorination (Rh, Ir), or chemical separation, such as by bromate hydrolysis (Pt from Ir and Rh).

A known weight (0.100×10^{-3} kg) of Pt–Rh thermocouple wire[19] was preliminarily fused with zinc powder and the melt was cooled and dissolved in hydrochloric acid. The black powder that remained was treated with 5×10^{-3}dm^3 *aqua regia*. After the reaction was over, the whole solution was heated with two 5×10^{-3} dm^3 portions of concentrated hydrochloric acid until complete removal of the oxides of nitrogen was obtained and diluted with distilled water to 10×10^{-3} dm^3 in a standard volumetric flask.

Procedure for Platinum(IV) in Pharmaceutical Sample

The proposed method was used for the determination of platinum(IV) in pharmaceutical sample such as Kemoplat (cisplatin injection). It is 30 years since Barnett Rosenberg and colleagues published their seminal paper in *Nature* entitled "Platinum Compounds: A New Class of Potent Antitumour Agents."[20] The platinum drugs, cisplatin and carboplatin, are still at the forefront of anticancer therapy.

Kemoplat (cisplatin injection) is an antineoplastic agent with biochemical properties similar to those of bifunctional alkylating agents. The drug covalently binds to DNA bases and disrupts DNA functions. Kemoplat appears to enter cells by diffusion.

A known volume ($2 \times 10^{-3}\,\mathrm{dm}^3$) of cisplatin solution was digested in perchloric acid–nitric acid (10:1) and evaporated to dryness until organic matter was removed.[21] The obtained residue was dissolved in concentrated hydrochloric acid and diluted with glass distilled water to $10 \times 10^{-3}\,\mathrm{dm}^3$ in a standard volumetric flask.

Determination of Platinum(IV) in Catalyst

Noble metals are widely used in homogeneous and heterogeneous catalysis. Their advantages are high activity under mild reaction conditions and improved selectivity, as compared to base metal catalysts. Precious metal catalyst systems are expensive initially because of the metal costs, but since platinum group metals (PGMs) can be recovered, the overall cost of using these catalysts may actually be lower than that of a less active or selective base metal systems. Platinum is used in hydrogenation reactions. The most commonly used catalytic systems for the chemical synthesis are PtO_2, Pt/C and Pt/Al_2O_3.

The sample of the catalyst (Pt/C) containing platinum was weighed ($2 \times 10^{-3}\,\mathrm{kg}$) and transferred in $500 \times 10^{-3}\,\mathrm{dm}^3$ beaker by heating with $30 \times 10^{-3}\,\mathrm{dm}^3$ 6 mol/L hydrochloric acid on a hot plate with a surface temperature of about 373°K. From time to time, a few 10^{-1} dm of 30% H_2O_2 was added to aid in the dissolution of platinum. The volume was maintained with 6 mol/L hydrochloric acid until dissolution was complete. The solution was filtered and then the clear solution was transferred to a $100 \times 10^{-3}\,\mathrm{dm}^3$ volumetric flask.[22]

An aliquot of the sample (alloy, pharmaceutical and catalyst) solution was taken and platinum(IV) was determined using the procedure described earlier. The results of the analysis are given in Table 1.

Table 1. Analysis of real samples for platinum content.

Sample	Manufacturer	Certified value of platinum	Amount of platinum(IV) found by proposed method[a]	RSD (%)
Platinum–rhodium[b] thermocouple wire (Pt, 87; Rh, 13)	Ruia Resistance Wire Pvt. Ltd., Mumbai	87%	86.7%	0.34
Cisplatin (anticancer injection)	Dabur India Ltd., Baddi	1.3 mg	1.295 mg	0.38
Platinum catalyst (fresh reforming)	E. Merck India Ltd., Mumbai	0.3%	0.298%	0.66

[a] Average of five determination.
[b] Masked with tartrate (25×10^{-6} kg).

RESULTS AND DISCUSSION

Extraction as a Function of pH

Platinum(IV) was extracted in the pH range of 0.1 to 10 in the presence of 0.015 mol/L ascorbic acid (Table 2). The extraction commenced at pH 0.1 and was quantitative between a pH range 0.5 to 1.25. With an increase in pH, the extraction goes on decreasing and becomes zero at pH 2.5 (Fig. 1). The percentage extraction is calculated using the expression

$$\%E = \frac{\text{Metal extracted}}{\text{Metal taken}} \times 100$$

After stripping from the organic phase, the metal is estimated from a calibration graph as described previously. At a higher pH of extraction, there was the possibility of hydrolysis. This indirectly promotes competing equilibria with the formation of an ion-pair complex, resulting in a decrease in extraction effectiveness. This shows that the equilibrium in the pH range of 0.5 to 1.25 is favorable for the formation of ion-pair complex from an ascorbic acid medium.

Table 2. Extraction behavior of platinum(IV) as a function of pH.

pH	Percentage extraction (% E)	Distribution ratio (D)
0.10	30.0	1.07
0.25	54.0	2.93
0.50	100.0	∞
0.75	100.0	∞
1.00	100.0	∞
1.25	100.0	∞
1.50	50.4	2.54
1.75	20.0	0.63
2.00	8.0	0.22
2.25	3.2	0.08
2.50	0.0	0.0
3.00	0.0	0.0
4.00	0.0	0.0
5.00	0.0	0.0

Extraction as a Function of Organic Acid Concentration

The extraction of platinum(IV) was carried out at pH 1.0 with 0.1 mol/L N-n-octylaniline in xylene in the presence of varying concentrations of ascorbic acid. The extraction commenced with 0.001 mol/L ascorbic acid and became quantitative in the concentration range of 0.01 to 0.02 mol/L ascorbic acid. With increased concentration of ascorbic acid, there was a decrease in the extraction of platinum(IV) (Fig. 2). The decrease in extraction at high organic acid concentration was presumably due to the preferential formation of the ascorbate of the N-n-octylaniline. Therefore, a 0.015 mol/L ascorbic acid was used throughout this work. There was no extraction of platinum(IV) from malonate, salicylate, succinate, tartrate, acetate, and oxalate media.

Effect of N-n-Octylaniline Concentration

To optimize the conditions for extraction of platinum(IV), xylene solutions of N-n-octylaniline with varying concentrations, 0.01 to 0.3 mol/L, were employed (Table 3). It was found that 10×10^{-3} dm^3 of 0.09 mol/L N-n-octylaniline was sufficient for quantitative extraction of 300×10^{-9} kg platinum(IV) from 0.015 mol/L ascorbic acid, but the recommended

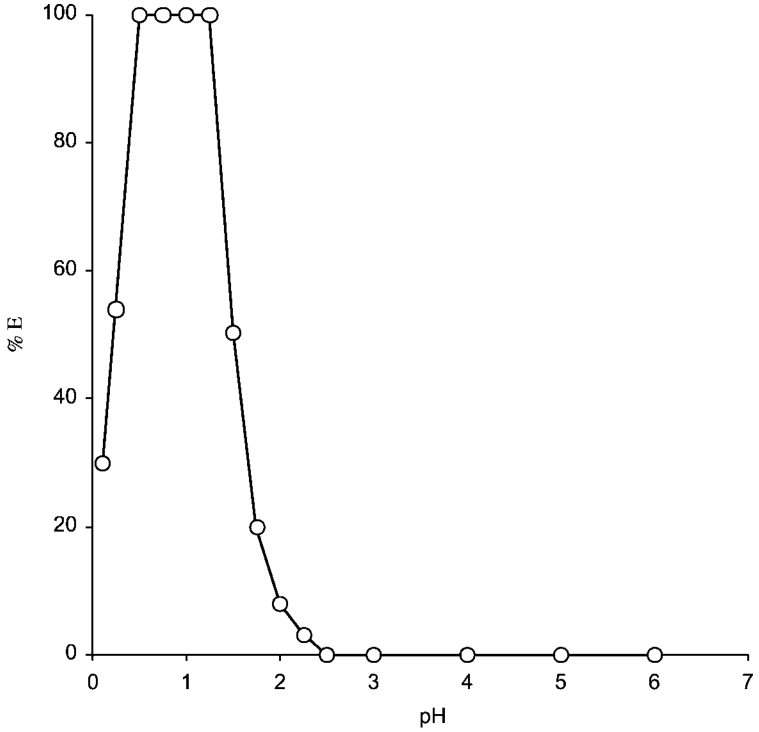

Figure 1. Extraction of platinum(IV) with 0.1 mol/L N-n-octylaniline from 0.015 mol/L ascorbic acid medium as a function of pH. Platinum(IV) $= 300 \times 10^{-6}$ kg.

procedure, 10×10^{-3} dm^3 of 0.1 mol/L N-n-octylaniline in xylene was used to ensure the complete extraction of metal ion. There was no adverse effect of using excess of N-n-octylaniline (0.3 mol/L) (Fig. 3). However, a decrease in concentration of extractant resulted in lower distribution ratio (D) values for platinum(IV).

Extraction with Various Diluents

Ten systems containing identical amounts (300×10^{-6} kg) of platinum(IV) were prepared and extracted with 10×10^{-3} dm^3 of 0.1 mol/L N-n-octylaniline in each of the various diluents. The extraction of platinum(IV) was quantitative with inert diluents, such as xylene, toluene,

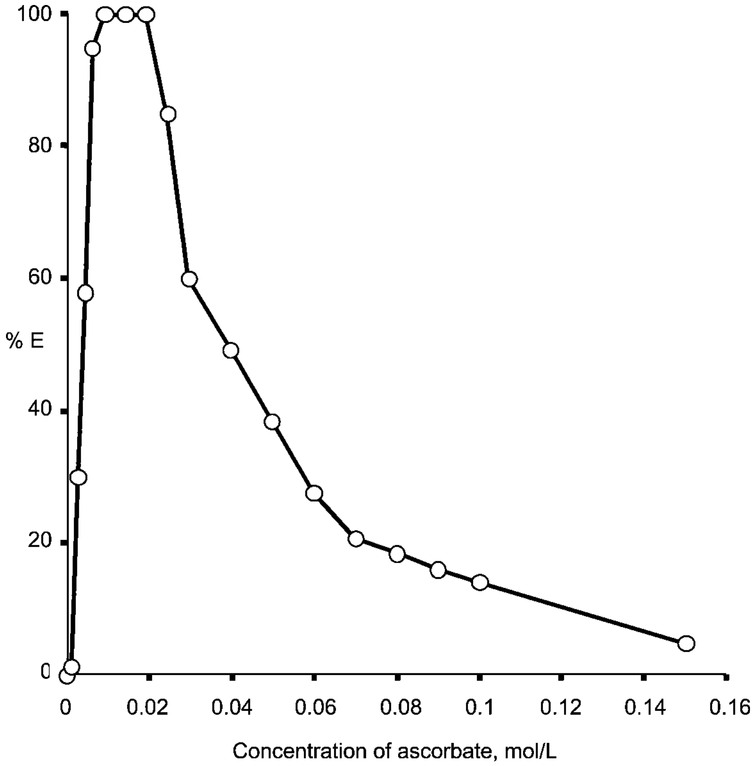

Figure 2. Extraction of platinum(IV) with 0.1 mol/L N-n-octylaniline at pH 1.0 as a function of ascorbic acid concentration, Platinum(IV) = 300×10^{-9} kg.

and benzene, because the ion-pair complex has a high distribution ratio value in these, whereas chloroform (34.8%), carbon tetrachloride (46%), and methyl isobutyl ketone (50.8%) were found to be poor solvents, with no extraction in amyl alcohol, amyl acetate, n-butyl alcohol, and 4-methyl-2-pentanol. Polar solvents, such as chloroform, methyl isobutyl ketone, and carbon tetrachloride, interact with N-n-octylaniline, thus decreasing the reagent concentration. While in benzene, toluene and xylene involve pi electrons, however, interaction of pi electrons with N-n-octylaniline is less and do not affect the reagent concentration. An inert solvent, such as xylene, does not participate in the actual extraction process. It has minimum toxicity as compared to benzene and toluene and offers better phase separation. Hence it was used for further study.

Table 3. Extraction behavior of platinum(IV) as a function of N-n-octylaniline concentration.

Concentration of N-n-octylaniline (mol dm^{-3})	Percentage extraction (% E)	Distribution ratio (D)
0.000	0.00	0.00
0.010	2.4	0.072
0.015	4.4	0.115
0.020	6.4	0.17
0.025	9.2	0.25
0.030	12.0	0.34
0.035	14.4	0.42
0.040	18.0	0.55
0.045	20.0	0.62
0.050	22.4	0.72
0.055	30.0	1.07
0.060	38.0	1.53
0.065	45.2	2.06
0.070	58.4	3.5
0.075	70.0	5.8
0.080	80.0	10.0
0.085	92.4	30.4
0.090	100.0	∞
0.100	100.0	∞
0.150	100.0	∞
0.200	100.0	∞
0.250	100.0	∞
0.300	100.0	∞

Mechanism of the Extraction

Attempts were made to ascertain the nature of the extracted species using log D–log C plots. The graphs of $\log D_{[Pt(IV)]}$ against $\log C_{[N-n-octylaniline]}$ at a fixed ascorbic acid concentration (0.015 mol/L) were found to be linear, having slopes of 1.31, 1.35, and 1.36 at pH 0.75, 1.25, and 1.50, respectively (Fig. 4). Also, plots of $\log D_{[Pt(IV)]}$ against $\log C_{[ascorbate]}$ at fixed N-n-octylaniline concentration (0.1 mol/L) were linear and slope values were found to be 2.88, 3.0, and 2.8 at pH 0.75, 1.25, and 1.5, respectively (Fig. 5). The probable composition of the extracted species was calculated to be 1:3:1 (metal:acid:extractant). In the extraction of platinum(IV) with

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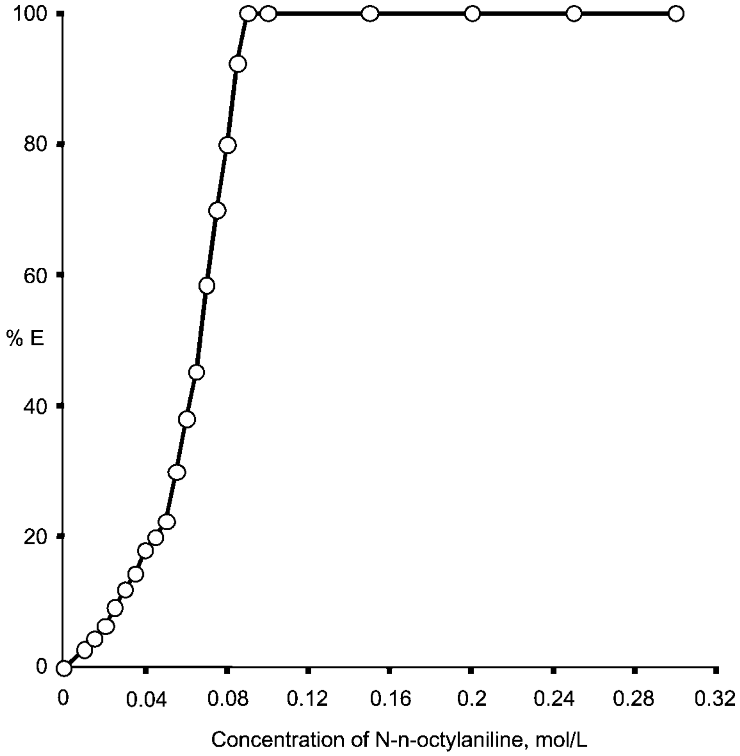

Figure 3. Extraction of platinum(IV) at pH 1.0 from 0.015 mol/L ascorbic acid medium as a function of N-n-octylaniline concentration. Platinum(IV) = 300×10^{-9} kg.

ascorbate medium, first platinum(IV) was reduced to platinum(II),[23] then it was converted into platinum(II) ascorbate as an anion and interacted with $RR'NH_2{}^+$. Hence, the probable extracted species in xylene is $[RR'NH_2{}^+ \cdot Pt(C_6H_7O_6)_3{}^-]_{org}$. The mechanism of extraction is given as:

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

$$[Pt(Ascorbate)_3]^-_{(aq)} + [RR'NH_2{}^+Ascorbate^-]_{(org)}$$
$$= [RR'NH_2{}^+ \cdot Pt(Ascorbate)_3{}^-]^0_{(org)} + Ascorbate^-_{(aq)} \tag{2}$$

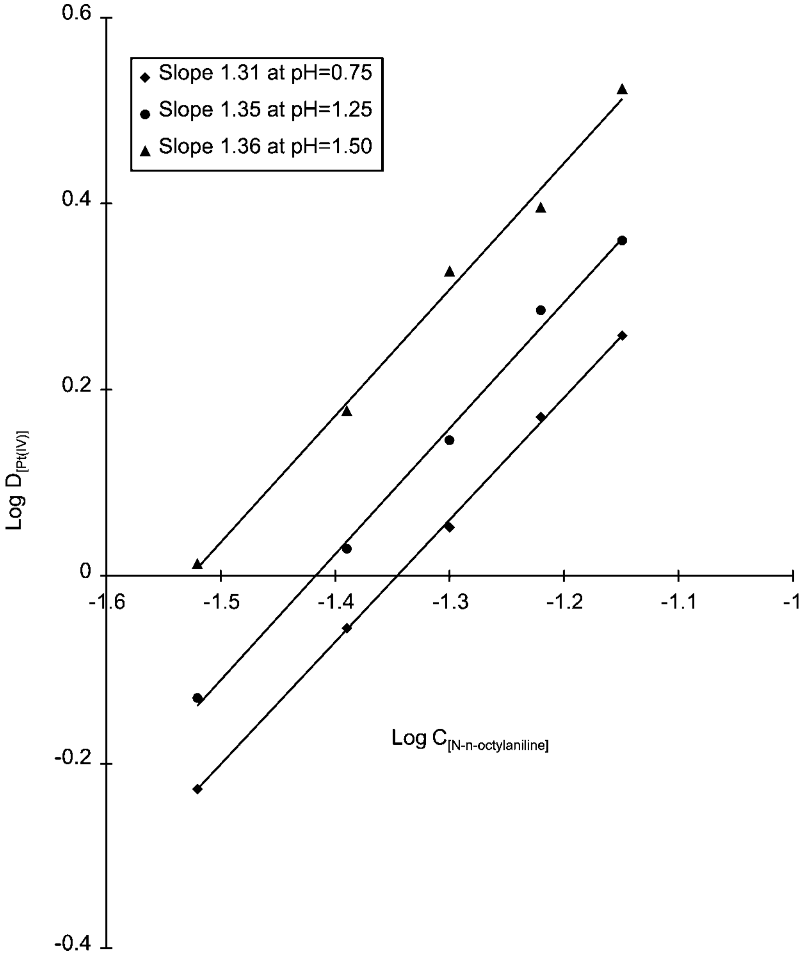

Figure 4. Log–log plot of distribution ratio log D [Pt(IV)] vs. log C [N-n-octylaniline] at pH 0.75, 1.25, and 1.50.

Effect of Time on Extraction

When two immiscible phases were equilibrated for a period of 6 s to 20 min, the extraction was quantitative over periods longer than > 15 seconds. But in this work, 1-min equilibration time was recommended to ensure the complete

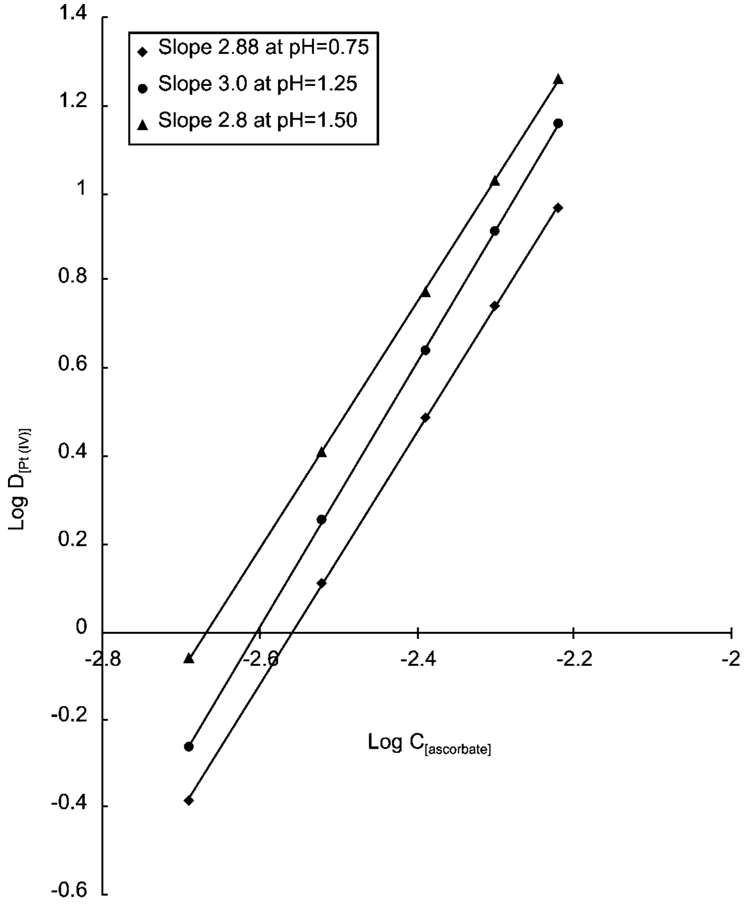

Figure 5. Log–log plot of distribution ratio log D [Pt(IV)] vs. log C [ascorbic acid] at pH 0.75, 1.25, and 1.50.

extraction of platinum(IV). However, a prolonged shaking period (> 15 min) was found to have an adverse effect on the extraction and should be avoided (Fig. 6).

Loading Capacity of N-n-Octylaniline

The concentration of platinum(IV) was varied to determine the loading capacity of N-n-octylaniline. It was found that the loading capacity of 10×10^{-3} dm^3 of 0.1 mol/L N-n-octylaniline in xylene was 3×10^{-6} kg.

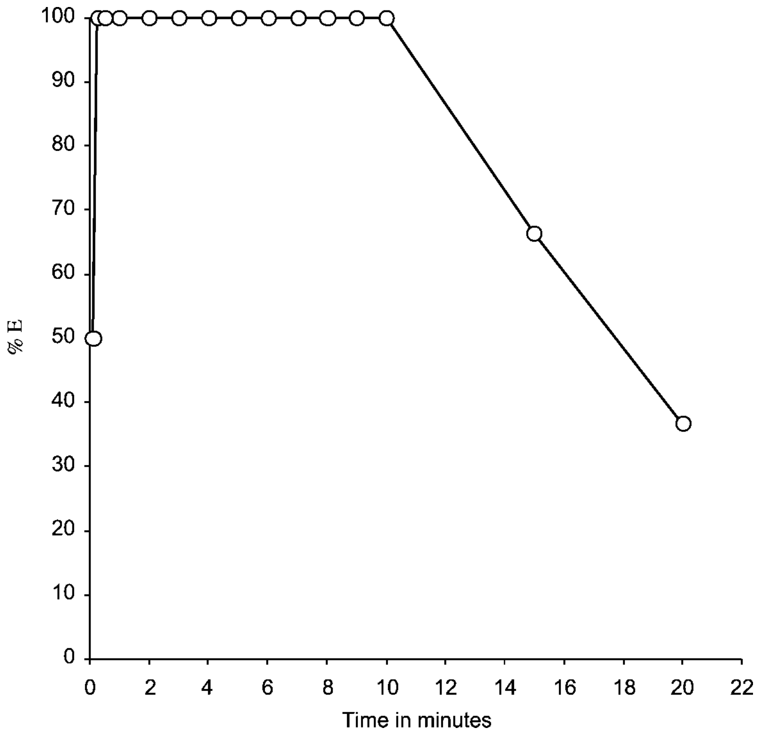

Figure 6. Extraction of platinum(IV) with 0.1 mol/L N-n-octylaniline at pH 1.0 from 0.015 mol/L ascorbic acid medium as a function of time. Platinum (IV) = 30×10^{-9} kg.

Effect of Aqueous to Organic Volume Ratio

The results of contacting different volume ratios of organic to aqueous phases have been studied. The results indicate that a preferred aqueous/organic (A/O) phase ratio in this study was 5:1 or less. This is evident from the sharp increase in the separation efficiency as well as 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 a crowding effect occurs at a low phase ratio. However, in the recommended procedure, the phase ratio was maintained as 2.5:1.

Effect of Stripping Agents

Platinum(IV) was stripped with different strengths of mineral acids, bases, and salts after its extraction. The stripping of platinum(IV) was quantitative with water. The stripping was found to be incomplete with nitric acid (25%), ammonia (50%), and sodium chloride (72%), whereas platinum (IV) was not stripped with hydrochloric acid, sulphuric acid, sodium hydroxide, potassium hydroxide, acetate buffer ($pH = 4.5$), and ammonia buffer ($pH = 10.0$).

Effect of Various Diverse Ions on Percentage Extraction

The effect of various diverse ions was tested, when platinum(IV) was extracted with N-n-octylaniline in xylene. The tolerance limit of individual diverse ions was 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 4). The only species showing interference in the procedure were Pd(II), Rh(III), iodide, thiocyanate, thiourea, and thiosulphate. However, the interference of Pd(II) and Rh(III) was eliminated by masking with tartrate. Thiocyanate and thiourea form very strong complexes with platinum(IV).

Table 4. Effect of various diverse ions on percentage extraction of 300×10^{-9} kg of platinum(IV) from $0.015\,\mathrm{mol\,dm^{-3}}$ ascorbic acid with $0.1\,\mathrm{mol\,dm^{-3}}$ N-n-octylaniline in xylene.

Tolerance limit (10^{-6} kg)	Diverse ion added
0	Iodide, thiocyanate, thiourea, thiosulphate
2	Rh(III)[a], Ir(III), Ru(III), Re(VII), Ag(I)
3	Hg(II), Pd(II)[a], Au(III), Os(VIII)
5	Cr(III), Cr(VI), Fe(II), U(VI)
10	Ti(IV), V(V), Mn(II), Fe(III), Ni(II), Cd(II), Ba(II), Pb(II), Sn(II), Bi(III), Se(IV), Te(IV), EDTA
15	Co(II), Cu(II), Mg(II), Ca(II), Be(II), oxalate, acetate
20	Zn(II), Mo(VI), Tl(III), citrate, bromide, fluoride, nitrate
25	Tartrate

[a] Masked with tartrate.

This is due to soft acid and soft base combination while iodide ion forms strong anionic species.

APPLICATIONS

Separation and Determination of Platinum(IV) from Binary Mixtures Containing Pd(II), Au(III), Rh(III), Ir(III), Os(VIII), Ru(III), Fe(III), Co(II), Ni(II), and Cu(II)

The suitability of the developed method was examined by applying it to the separation and determination of platinum(IV) in a variety of binary mixtures containing commonly associated metals (Table 5).

It was found that Au(III), Ir(III), Os(VIII), Ru(III), Fe(III), Co(II), Ni(II), and Cu(II) remained unextracted under the acidic conditions with platinum(IV) using 0.015 mol/L ascorbic acid with $10 \times 10^{-3}\,\mathrm{dm}^3$, 0.1 mol/L N-n-octylaniline. The pregnant organic phase was stripped with water ($2 \times 10 \times 10^{-3}\,\mathrm{dm}^3$) and platinum(IV) was determined by the stannous chloride method as recommended in the procedure. The raffinate-containing added metal ion was estimated by standard procedure.[16,24,25]

The proposed method was also extended for separation of platinum(IV) from Pd(II) and Rh(III) by masking these with tartrate (25×10^{-6} kg). The masked metal ion remained in the aqueous phase while platinum(IV) was extracted selectively into the organic phase with N-n-octylaniline in xylene. It was stripped from the organic phase with water and estimated as per the given procedure. The aqueous phase containing added metal ion was demasked with $2 \times 5 \times 10^{-3}\,\mathrm{dm}^3$ concentrated hydrochloric acid, and after reducing the volume of the aqueous phase, estimated by standard procedures.[16,26]

Separation of Platinum(IV) from Ternary Mixture

The selectivity of extraction was also achieved by the use of a suitable masking agent for added metal ion. When a ternary mixture containing platinum(IV), palladium(II), and rhodium(III) was extracted from $0.015\,\mathrm{mol\,dm}^{-3}$ ascorbic acid with $10 \times 10^{-3}\,\mathrm{dm}^3$ 0.1 mol/L N-n-octylaniline in xylene at pH 1.0 by masking Pd(II) and Rh(III) with tartrate (25×10^{-6} kg), it was found that platinum(IV) was extracted; whereas Pd(II) and Rh(III) remained unextracted. Platinum(IV) was stripped with water ($2 \times 10 \times 10^{-3}\,\mathrm{dm}^3$) and estimated as per the recommended procedure.

Table 5. Separation of platinum(IV) from binary mixtures.

Metal ion	Amount taken (10^{-9} kg)	Average percentage recovery[a]	Chromogenic ligand	Reference number
Pt(IV)	300	99.9	4′-chloro PTPT	26
Pd(II)[b]	100	99.9		
Pt(IV)	300	99.9	Stannous chloride	16
Au(III)	200	99.8		
Pt(IV)	300	99.9	Stannous chloride + potassium iodide	16
Rh(III)[b]	200	99.8		
Pt(IV)	300	99.9	Stannous chloride + hydrobromic acid	16
Ir(III)	50	99.9		
Pt(IV)	300	99.9	Thiourea	16
Os(VIII)	300	99.8		
Pt(IV)	300	99.8	Thiourea	16
Ru(III)	300	99.8		
Pt(IV)	300	99.8	Thiocyanate	16
Fe(III)	10,000	99.7		
Pt(IV)	300	99.9	Thiocyanate	24
Co(II)	15,000	99.8		
Pt(IV)	300	99.9	DMG	24
Ni(II)	10,000	99.9		
Pt(IV)	300	99.9	4′-chloro PTPT	25
Cu(II)	15,000	99.8		

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

The aqueous phase containing tartrates of Pd(II) and Rh(III) and excess of ascorbic acid were decomposed by the addition of concentrated hydrochloric acid ($2 \times 5 \times 10^{-3}$ dm^3). Then, the solution was adjusted to 0.025 mol/L with sodium malonate. Rh(III) was extracted quantitatively with 10×10^{-3} dm^3 of 0.1 mol/L N-n-octylaniline at pH 9.5. Rhodium(III) from organic phase was stripped with 1 mol/L hydrochloric acid ($2 \times 10 \times 10^{-3}$ dm^3) and estimated spectrophotometrically with stannous chloride–potassium iodide method.

The aqueous phase containing malonate was decomposed with concentrated hydrochloric acid and residue extracted into 0.1 mol/L hydrochloric acid. The solution was made to 0.025 mol/L with respect to sodium salicylate. Pd(II) was extracted with 10×10^{-3} dm^3 of 0.1 mol/L

Table 6. Separation of platinum(IV) from ternary mixture.

Metal ion	Amount taken (10^{-9} kg)	Aqueous phase (25×10^{-3} dm^3)	Stripping agent ($2 \times 10 \times 10^{-3}$ dm^3)	Determination method	Recovery percentage[a]
Pt(IV)	300	0.015 mol dm^{-3} ascorbate pH = 1.0	Water	$SnCl_2$	99.9
Pd(II)[b]	100	0.025 mol dm^{-3} salicylate pH = 3.0	7.0 mol dm^{-3} ammonia	4′-chloro PTPT	99.8
Rh(III)[b]	200	0.025 mol dm^{-3} malonate pH = 9.5	1.0 mol dm^{-3} HCl	$SnCl_2$ + KI	99.9

[a] Average of five determination.
[b] Masked with tartrate.

N-n-octylaniline in xylene at pH 3.0. Palladium(II) from organic phase was stripped with 7 mol/L ammonia ($2 \times 10 \times 10^{-3}$ dm^3) and estimated spectrophotometrically with 4′-chloro PTPT[26] (Table 6).

Analysis of Synthetic Mixtures

The method was applied for the analysis of synthetic mixtures. Synthetic mixtures corresponding to alloys were prepared and analyzed for platinum(IV) content. Platinum(IV) was recovered quantitatively from ascorbate medium by the proposed method. The results are given in Table 7.

The method is selective and permits rapid separation and determination of microamounts of platinum(IV). The average recovery of platinum(IV) was 99.5%. Each determination took 10 to 15 min.

CONCLUSION

The proposed extractive separation procedure is simple, rapid, selective, and suitable for the separation of platinum(IV) from other PGMs, gold(III), and base metals. The extraction mechanism corresponds to an anion exchange, in which a complex of stoichiometric formula $[RR'NH_2{}^+ \, Pt\,(C_6H_7O_6)_3{}^-]_{org}$ is formed in the organic phase. The use of nontoxic solvents, like xylene was

Table 7. Analysis of synthetic mixtures corresponding to alloy.

Serial number	Alloy	Platinum(IV) taken (10^{-9} kg)	Platinum(IV) found by proposed method[a] (10^{-9} kg)	Average percentage recovery	RSD percentage
1	Pt–Rh[b] catalyst on alumina	150	149.9	99.9	0.06
2	Pt–Pd[b] catalyst on alumina	150	149.8	99.8	0.13
3	Pt–Pd[b]–Rh[b] catalyst on alumina	150	149.9	99.9	0.06
4	Pt–catalyst on alumina	300	299.9	99.9	0.03
5	Pt–Rh[b] monolith on cordierite	150	149.8	99.8	0.13
6	Pt–Pd–Rh[b] monolith on cordierite	150	149.9	99.9	0.06

Composition of synthetic mixtures corresponding to alloy in percentage:

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

[a] Average of five determinations.

[b] Masked with tartrate.

favorable. N-n-octylaniline can be synthesized at low cost with high yield and in the best purity and recovered for reuse without loss of extraction efficiency. The time needed for equilibration is very short (15 s) as compared with other reported HMWA. Another important feature of the proposed method is that a large number of foreign ions were tolerated in high ratios. The developed method is reliable, as can be seen from the complete agreement of the results observed for the analysis of various practical samples with added ions or certified values.

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