

Reversed phase extraction chromatographic separation of palladium(II) using liquid anion exchanger

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A selective, sensitive, less expensive and more precise method has been developed for separation of palladium(II) with *N-n*-octylaniline, coated on silica gel as a stationary phase. Quantitative extraction of palladium(II) is observed in the acidic medium within the range 0.8–1.2 M nitric acid with 1.5% *N-n*-octylaniline at a flow rate of 0.5 ml/min. The extracted metal ion is stripped with 7.0 M ammonia and determined by spectrophotometric method. The extraction behaviour of palladium(II) has been studied as a function of different parameters such as concentration of mineral acids, reagent, elution time and diverse ions. The method is free from large number of cations and anions. It is applied for separation of palladium(II) from synthetic mixtures corresponding to alloys. A scheme for mutual separation of platinum(IV), palladium(II) and iridium(III) has been developed. Log-log plot of *N-n*-octylaniline concentration versus distribution ratio indicates that probable extracted species is $[\text{RR}'\text{NH}_2^+\text{Pd}(\text{NO}_3^-)_3]_{\text{org}}$.

Key words: extraction chromatography, palladium(II), separation alloys.

INTRODUCTION

Abundance of palladium in Earth's crust is $8.5 \times 10^{-13}\%$. It is used as a catalyst for various organic reactions as well as multi-layer ceramic capacitor (MLCC), photography and jewelry. Palladium alloys have wide range of applications in industry. It is used as low current electrical contact, preliminary telephone equipment and integrated circuit, *etc.* [1], in view of its wide range of applications, the separation of palladium has analytical importance.

Palladium(II) has been extracted using LIX 841 [2], but extraction quality is poor and it requires higher concentration of hydrochloric acid for stripping. Palladium(II) was extracted and separated with aliquot-336 [3], in hydrochloric acid media. Cyanex 471X [tri-isobutyl phosphine sulphide] [4], has been used for separation of palladium(II) by extraction chromatography in nitric acid media using thiourea as a stripping agent. Palladium(II) and platinum(IV) were preconcentrated on Amberlite XAD-7 resin, coated with dimethylglyoxal bis (4-phenyl-3-thiosemicarbazone) [5], using acidic solution in the presence of iodide and it was eluted with dimethylformamide. Palladium(II) has been extracted with various ketones [6], from nitric acid media, which requires 3.0 M ligand concentration above 2.0 M acidity. Silica gel, impregnated with prime JMT, is used for separation of palladium(II)

in sulphuric acid media and eluted using sulphate phases [7]. Palladium(II) was extracted from hydrobromic acid media by hexadecylpyridinium bromide [8], which gives metal recovery 99%. 1-(2-pyridylazo)-2-naphthol [9], has been used for solvent extraction of palladium(II) but in the method, non-ferrous alloys affect the determination of palladium.

In our laboratory *n*-octylaniline has been used for solvent extraction of gallium(III), indium(III), thallium(III), [10], zinc(II), cadmium(II), mercury(II) [11], lead(II) [12]. *n*-Octylaniline and *N-n*-octylaniline has also been used for extraction column chromatography of gallium(III), indium(III), thallium(III) [13], and reversed phase paper chromatographic separation of zinc(II), cadmium(II), and mercury(II) [14]. The *N-n*-octylaniline has also been used for reversed phase paper chromatographic study of cooper(II), silver(I), gold(III) [15], gallium(III), indium(III), thallium(III) [16].

In the present communication selective, sensitive, less expensive and more precise method has been developed for extraction chromatographic separation of palladium (II) is achieved at 1.5% *N-n*-octylaniline in 1.0 M nitric acid and the metal ion was stripped with 7.0 M ammonia. Various parameters are studied such as acid concentration, reagent concentration, effect of flow rate and different ions. The method is extended for separation of palladium(II) from synthetic mixture corresponding to alloys and mutual separation of palladium(II), platinum(IV) and iridium(III) has been achieved.

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EXPERIMENTAL

Apparatus. An Elico spectrophotometer model SL-159 with 10 mm path length quartz cell has been used for absorbance measurements. Control dynamic pH meter is used for pH measurements.

Reagent and chemicals. A stock standard solution of palladium(II) is prepared by dissolving 1.0 g palladium chloride (PdCl_2) (Loba. Chem.) in 1.0 M hydrochloric acid and diluted to 250 ml with distilled water. It is standardized by gravimetric method [17]. A working solution of palladium(II), 25 $\mu\text{g}/\text{ml}$ has been made by diluting the stock standard solution with distilled water. Other standard solutions of different metal ions are prepared by dissolving the respective salt in distilled water and diluted hydrochloric acid. *N-n*-octylaniline has been prepared using method reported by Gardlund [18]. The stock solution of *N-n*-octylaniline is prepared in chloroform. All other chemical used were of an analytical reagent purity grade.

Preparation of anion exchange material. Silica gel (60–120 mesh), obtained from BDH, has been dried at 120°C for 2–3 h and stored in desiccators. It is packed in U tube, through which a stream of nitrogen that has been bubbled through a small Durand bottle, containing about 20.0 ml of dimethyldichlorosilane (DMCS) (Across organic). The passage of DMCS vapour continued for 4 h. The silica gel is then washed with anhydrous methanol and dried. A portion of 5.0 g of this silanated silica gel has been soaked with 1.5% (v/v) *N-n*-octylaniline, previously equilibrated with nitric acid (1.0 M) for 10 min. The solvent has been evaporated to get nearly dried gel. The slurry of *N-n*-octylaniline coated silica gel has been prepared by centrifugation at 2000 rpm and coated silica gel is packed into chromatographic column to give a bed height of 6.0 cm. The bed has been covered with glass wool plug.

General procedure. An aliquot of a solution containing 25.0 μg of Pd (II), made up to 25.0 mL by adjusting concentration of nitric acid 1.0 M, is passed through the column containing silica coated with 1.5% *N-n*-octylaniline at a flow rate of 0.5 ml/min. After extraction, the metal ion is stripped with 25.0 mL aqueous ammonia, evaporated to dryness and determined spectrophotometrically [19].

RESULTS AND DISCUSSION

Effect of acid concentration on extraction. The extraction of palladium(II) has been studied in hydrochloric (0.2 to 2.0 M), hydrobromic (0.2 to 2.0 M), sulphuric (0.015 to 0.96 M), perchloric (0.5 to 2.5 M) and nitric (0.2 to 1.2 M) acid media with 1.5% (v/v) *N-n*-octylaniline. A maximum extraction

of palladium(II) is in hydrochloric 74.35%, in hydrobromic 91.82%, in sulphuric 82.22%, in perchloric 22.02% and in nitric acid 99.65% (Fig. 1).

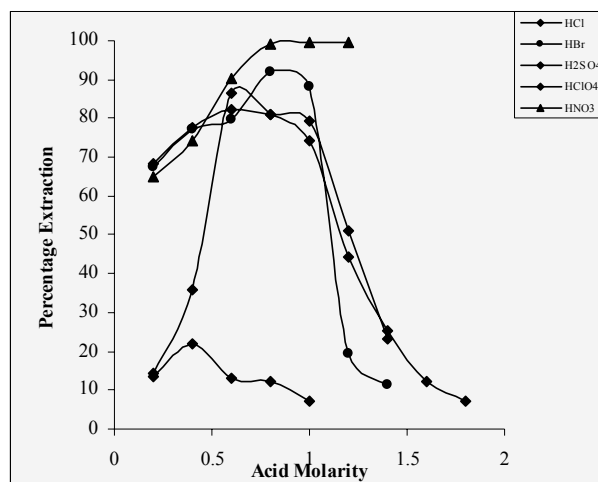


Fig. 1. Extraction behaviour of palladium(II) as a function of acid concentration.

Effect of flow rate. The effect of flow rate on percentage extraction for palladium(II) has been studied from flow rate 0.5 ml/min up to 3.0 ml/min. It is observed that percentage extraction decreases with increase in flow rate. Therefore normal flow rate is kept at 0.5 ml/min for further extraction studies.

Effect of *N-n*-octylaniline concentration. The concentration of *N-n*-octylaniline in chloroform is varied from 0.1% up to 2.5% (v/v) over nitric acid range 0.2 to 1.2 M for palladium(II). It is extracted quantitatively with 1.5% (v/v) *N-n*-octylaniline in 1.0 M nitric acid media. The increase in *N-n*-octylaniline concentration increases the percentage extraction. Log-log plot of *N-n*-octylaniline concentration versus distribution ratio at 0.4 M and 0.6 M nitric acid gives slope 1.0 indicating that the probable extracted species is $[\text{RR}'\text{NH}_2^+ \text{Pd}(\text{NO}_3)_3]_{\text{org}}$ (Fig. 2).

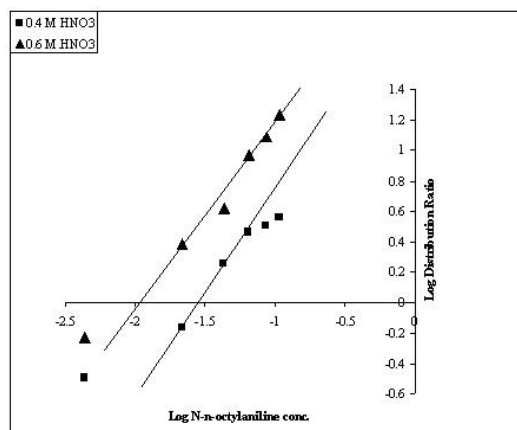


Fig. 2. Log-log plot *N-n*-octylaniline concentration versus distribution ratio.

Effect of diverse ions. The extraction of palladium(II) in presence of cations and anions has been carried out according to recommended procedure to examine their interferences. The tolerance limit is set at the amount required to cause $\pm 2\%$ error in recovery of palladium(II). For 25 μg of palladium(II) there is no interference from 400 μg chromium(VI); 200 μg of tin(II) and molybdenum(VI); 100 μg of mercury(II), cobalt(II), bismuth(III), nickel(II), uranium(VI), iron(II), cadmium(II), cerium(IV) and vanadium(V); 75 μg of titanium(IV); 50 μg of magnesium(II), copper(II), rhodium(III), gold(III), ruthenium(III), osmium(VIII), silver(I), manganese(II), strontium(II), platinum(IV), lead(II), iron(III), selenium(IV) and iridium(III); 25 μg of gallium(III), indium(III), thallium(III) and aluminium(III). 500 μg of citrate and tartrate; 300 μg of oxalate and acetate; 250 μg of thiourea; 200 μg of thiosulphate, fluoride, EDTA and malonate (Table 1).

Analysis of synthetic mixture corresponding to alloy. Validity of the method is confirmed by applying method for separation of palladium(II) from synthetic mixtures corresponding to alloy. The composition of alloy has been prepared for 'Golden-coloured silver alloy resistance to tarnishing, iridium alloy, oaky alloy, solder alloy, jewelry alloy, stibio palladinite mineral, jewelry alloy (Pd-Au

alloy), Pd-Ag alloy and Pd-Cu alloy' in laboratory and the proposed method was applied for separation of palladium(II). The results are reported in Table. 2.

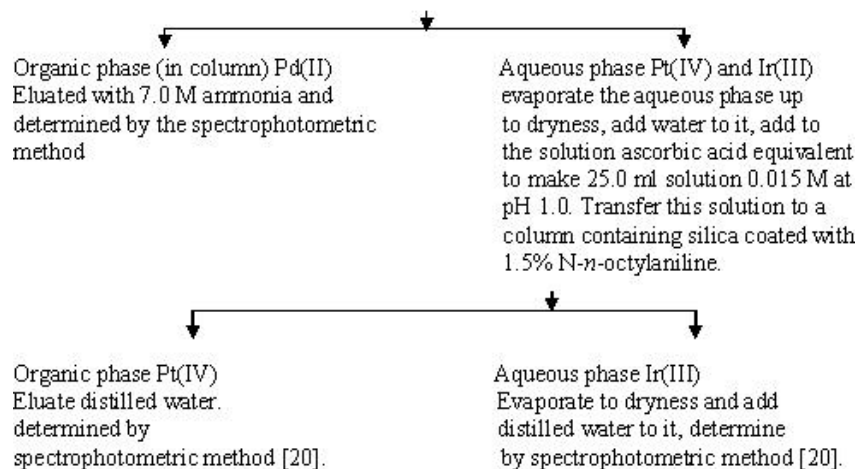
Table 1. Effect of various ions on the extraction of palladium(II). Pd(II) 25 μg , Organic phase N-n-octylanilin 1.5% in chloroform, Eluent 7.0 M ammonia.

Foreign ion	Tolerance limit, μg	Foreign ion	Tolerance limit, μg
Co(II)	100	Mo(VI)	200
U(VI)	100	Cr(VI)	400
Ni(II)	100	Pb(II)	50
Bi(III)	100	W(IV)	150
Hg(II)	100	Ti(IV)	75
Pt(IV)	50	Ir(III)	50
Ga(III)	25	In(III)	25
Tl(III)	25	Al(III)	25
Fe(II)	100	Mg(II)	50
Cu(II)	50	Rh(III)	50
Sn(II)	200	Ru(III)	50
Cd(II)	100	V(V)	100
Fe(III)	50	Ag(I)	50
Se(IV)	50	Sr(II)	50
Ce(IV)	100	Mn(II)	50
Os(VIII)	50	Au(III)	50
Oxalate	300	H ₂ O ₂	0.5 ml
Acetate	300	Citrate	500
Tartrate	500	Fluoride	200
Thiourea	250	Malonate	200
Thiosulphate	200	E.D.T.A.	200

Table 2. Analysis of synthetic mixture corresponding to alloy Pd(II) 25 μg , organic phase N-n-octylaniline 1.5% in chloroform, eluent 7.0 M ammonia.

Sample alloy, % composition	Sample solution taken equivalent to Pd(II) μg	Pd(II) found, μg	Mean μg	Average recovery, %	Relative errors, %
Low melting dental alloy (Pd 34.0, Au 10.0, Co 22.0, Ni 34.0)	50	49.4, 49.9, 49.6	49.6	99.1	0.9
Golden colored silver alloy (Pd 25.5, In 21.0, Cu 18.0, Ag 35.0)	25	24.8, 24.8, 24.7	24.8	99.2	0.8
Iridium alloy (Pd 3.5, Cu 8.01, Pt 55.51, Fe 3.51, Rh 7.01, Ir 28.01)	25	24.7, 24.9, 24.8	24.8	99.2	0.8
Oaky alloy (Pd 18.2, Pt 18.2, Ni 54.2, V 9.1)	50	49.6, 49.7, 49.6	49.6	99.1	0.9
Solder alloy (Pd 30.0, Pt 10.0, Au 60.0)	50	49.4, 49.9, 49.6	49.6	99.1	0.9
Jewelry alloy (Pd 95.0, Ru 4.0, Rh 1.0)	100	99.2, 99.0, 99.1	99.1	99.1	0.9
Stibio palladinite mineral (Pd 75.0, Sb 25.0)	100	99.3, 99.0, 99.0	99.1	99.1	0.9
Jewelry alloy (Pd-Au alloy) (Pd 50.0, Au 50.0)	100	99.8, 99.0, 99.4	99.4	99.4	0.6
Pd-Ag alloy (Pd 60.0, Ag 40.0)	100	99.4, 99.6, 99.2	99.4	99.4	0.6
Pd-Cu alloy (Pd 60.0, Cu 40.0)	100	99.6, 99.6, 99.1	99.4	99.4	0.6

In 25 ml vol. flask add 25 µg Pd(II) + 50 µg Pt(IV) + 50 µg Ir(III) + HNO₃ to make 1.0 M solution and transfer it in a column containing silica coated with 1.5% N-*n*-octylaniline.



Scheme. 1. Mutual separation scheme for palladium(II), platinum(IV) and iridium(III).

Mutual separation of palladium(II), platinum(IV) and iridium(III). In 25.0 mL volumetric flask 25 µg palladium(II), 50 µg platinum(IV), 50 µg iridium(III) were transferred, nitric acid has been added to make total solution 1.0 M with respect to nitric acid and this solution was transferred to column containing silica coated with N-*n*-octylaniline. Palladium (II) is extracted in column, which is stripped with 7.0 M ammonia and determined by spectrophotometric method [20]. Platinum(IV) and iridium(III) are eluted in aqueous solution. Aqueous solution was evaporated to dryness, after addition of distilled water and ascorbic acid to make 25.0 ml solution, 0.015 M at pH 1.0. It is transferred to a column containing silica coated with 1.5% N-*n*-octylaniline equilibrated with 0.015 M ascorbic acid at pH 1.0. Iridium(III) was not extracted and it was eluted in aqueous phase, which is evaporated to dryness and is estimated by spectrophotometric method [20]. Column containing platinum(IV) is eluted with distilled water and determined by spectrophotometric method [20] (Scheme 1, Table 3).

Table 3. Mutual separation of palladium(II), platinum(IV) and iridium(III). N-*n*-octylaniline 1.5%.

Metal ion	Amount taken, µg	Amount found,* µg	Recovery, %	RSD, %
Pd(II)	25	24.85	99.43	0.47
Pt(IV)	50	49.53	99.06	0.40
Ir(III)	50	49.50	99.00	0.66

* - Average of three determinations.

CONCLUSION

Literature survey revealed that some of the existing methods have drawbacks as:

- Palladium(II) was quantitatively extracted with very high concentration of hydrochloric acid (11.5 M) as a chloro-complex in the presence of tin(II) chloride by tri-*n*-octylamine (TOA) [21].

- Palladium(II) was extracted with 1.0 M *n*-octylaniline in chloroform from 3 M hydrochloric acid but the method requires multiple extractions for quantitative recovery of metal ion [22].

- Effectiveness of *n*-octylaniline in this extraction depends on its method of preparation [23].

- Extraction of palladium using hexaacetato calix(6) arene but the methods have major interferences from copper and chromium [24].

- Extraction of palladium(II) and other VIII group metals using 2-hydroxy-4-*sec*-octanoyl diphenylketoxime [26], but for its quantitative recovery high hydrochloric acid concentrations were used.

The proposed extraction chromatographic separation of palladium(II) has advantages over other reported method.

- The method is simple, rapid, reproducible and reliable.

- Extraction of palladium(II) requires low concentration of N-*n*-octylaniline.

- It permits mutual separation of palladium(II), platinum(IV) and iridium(III).

- The method is free from large number of foreign ions.

- The method gives separation of palladium(II) from alloys.

- Silica gel is used as good solid support because of the higher stability towards stationary phase.

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РАЗДЕЛЯНЕ НА ПАЛАДИЙ(II) ЧРЕЗ ХРОМАТОГРАФСКА ЕКСТРАКЦИЯ С ОБЪРНАТА ФАЗА С ИЗПОЛЗВАНЕ НА ТЕЧЕН АНИОНООБМЕННИК

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(Резюме)

Разработен е селективен, чувствителен, евтин и точен метод за разделяне на паладий(II) с *N-n*-октиланилин, нанесен на силикагел като постоянна фаза. Наблюдава се количествена екстракция на паладий(II) в кисела среда (0.8–1.2 М азотна киселина) с 1.5% *N-n*-октиланилин при скорост на потока 0.5 ml/min. Екстрахираният метален йон се реекстрахира с 7.0 М амоняк и се определя спектрофотометрично. Изследвана е екстракцията на паладий(II) като функция на различни параметри като концентрация на минералната киселина, реагенти, време на елуиране и различни йони. Методът не се влияе от голям брой катиони и аниони. Приложен е за разделяне на паладий(II) от изкуствени смеси, съответстващи на сплави. Разработена е схема за разделяне на платина(IV), паладий(II), и иридий(III) един от друг. Логаритмичната зависимост на концентрацията на *N-n*-октиланилин от коефициента на разпределение показва, че вероятната екстрахирана форма е $[\text{RRNH}_2^+\text{Pd}(\text{NO}_3)_3]_{\text{орг}}$.