

The project is divided into two parts :

- A) Synthesis and characterization of N-n-octylaniline
- B) Analytical application of N-n-octylaniline

PART – A

Synthesis and characterization of N-n-octylaniline

High molecular weight amines (HMWA) popularly known as liquid anion exchangers, uniquely combine some of the advantages of liquid-liquid extraction and ion exchange. There are several general features which are essential for an extraction, if it has to achieve the selective extraction of a metal. These are as follows :

- (i) The ability to extract the metal at the desired acidity or pH.
- (ii) To be selective for the required metal.
- (iii) Ease of formation of complex with metal of interest and high solubility of metal organic species in the organic phase.
- (iv) Ease of recovery of the metal from the organic phase.
- (v) It must be stable throughout the principal phases of solvent extraction.
- (vi) It is to be prepared in laboratory in large scale.
- (vii) To have acceptable rates of extraction and stripping.
- (viii) Regeneration of extractant for recycling in economical large scale process.

Due to greater solubility in water, primary amines are used less frequently as compared to secondary amines. In addition, in N-n-octylaniline, the presence of octyl group attached to amino group in aniline renders this amine less soluble in water. There is no emulsion formation.

N-n-octylaniline was prepared by the Gardlund's method [1]. A solution of distilled aniline and n-octylbromide (3:1 molar ratio) was refluxed overnight. After cooling to room temperature, the reaction mixture was made basic with dilute aqueous ammonia. The aqueous layer was repeatedly washed with pentane. The pentane washings were combined with organic layer and treated with 50% aqueous zinc chloride solution. Extraction of resulting solid with pentane, followed by drying with anhydrous potassium carbonate and flash evaporation of pentane yield crude N-n-octylaniline. A pure compound was obtained by fractional distillation on a spinning band column. The yield and boiling range was as follows : 98.5%, 177-178°C at 25 mm pressure (found C, 82.1; H, 11.4; $C_{14}H_{23}N$ requires C, 81.9; H, 11.3%) N-n-octylaniline was found to be 0.89 g/cm³. The p-toluensulphonyl derivative crystallized from alcohol in fan shaped clusters of needles, M.P. 42-43°C (found: N, 4.1; $C_{21}H_{29}O_2NS$ requires N, 3.8%).

Proton resonance assignment for the pure product were made using TMS as an internal standard and chemical shift expressed in δ values. PMR (CCl_4 , 90 MHz, Fig. 1.1) : 0.9 (3H, t, CH_3), 1.3 (12H, br, s, - $(CH_2)_6$ -), 3.0 (2H, t, -NH - CH_2), 3.38 (3H, s, -NH-), 6.5 (5H, m, Ar-H). Purity of the product checked by thin layer chromatographic technique.

Reference :

- [1] Z.G. Gardlund, R.J. Curtius, G.W. Smith, Liquid Crystals Ordered Fluids 2 (1973) 541.

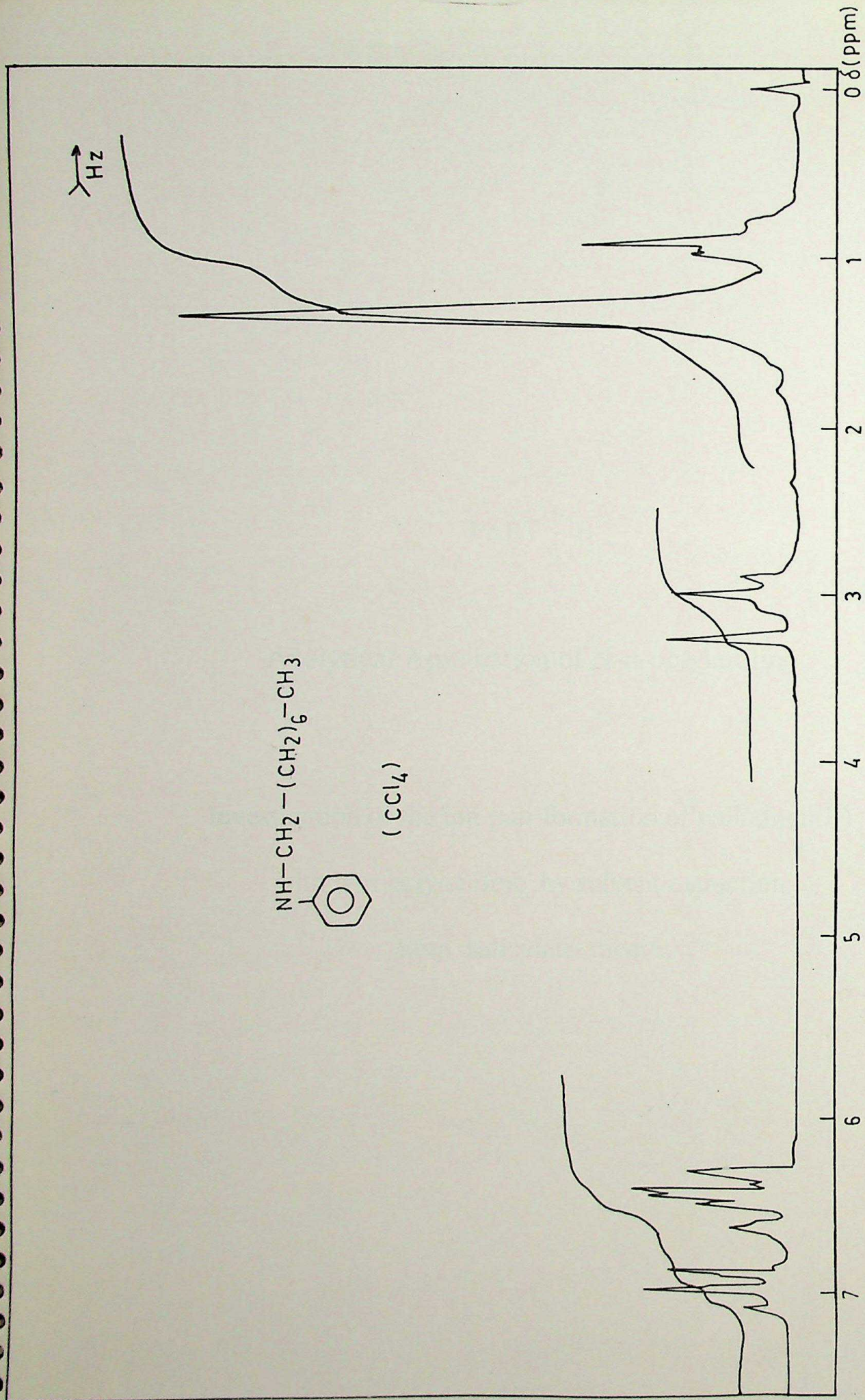


FIG. 1.1 — PROTON MAGNETIC RESONANCE SPECTRA OF N-n-OCTYLANILINE .

PART - B

Analytical Application of N-n-octylaniline

Investigation of the ion-pair formation of palladium(II)

with N-n-octylaniline by solvent extraction

from salicylate media

Palladium is the second most important platinum group metals (PGMs). This metal is often used in place of platinum, where conditions permit, because of its lower price and density. Its freedom from tarnish and resistance to corrosion make it almost as suitable as platinum for contacts in electrical relays. Palladium as a catalyst is effective for both hydrogenation and dehydrogenation reactions. The enforcement of the 1970 Clean Air Act by the Environmental Protection Agency (EPA) led to the introduction of catalytic converters for automobile exhaust gases, starting with the 1975 model cars. General motors also use platinum-palladium monoliths containing approximately 800 ppm of platinum and 400 ppm of palladium.¹ A moderate amount of palladium is used in jewelry and alloys containing 4.5 per cent ruthenium or 4 per cent ruthenium plus 1 per cent rhodium are most commonly recommended. In addition, so-called 'white gold' is an alloy of gold decolourised by the addition of palladium.² Noble metal alloys, wires and solders are used in dentistry because they are nontoxic, biocompatible, stress and wear resistant, noble in the oral environment and have good casting properties³. Palladium alloys are used as replacements for damaged arthritic bones and joints in which there is a load bearing requirement. Palladium(II) complexes have shown some antitumor activity on initial screening, and $\text{Pd}(\text{OH})_2$ was tested in treating obesity.

Great attention has been paid to developing solvent extraction technique in order to replace the conventional highly complicated selective precipitation technique which consume large amounts of energy and labour. Also, these are often insufficient in terms of the achieved separation efficiency. Solvent extraction process is a potential alternative refining technology as well as an ion exchange process. The most important factor in the solvent extraction of metals is extractant selectivity to the specified metal ions to be recovered.

The complex nature of the solution chemistry of Platinum Group Metals (PGMs) has contributed to the difficulty of developing methods for their separation

from binary or multicomponent systems. This problem in solvent extraction procedures for the individual metals is due to the slow reaction of the chloro-complexes. The kinetically labile character of the chloro-complexes of palladium towards a number of hydrophobic anions allows the immediate formation of highly extractable anionic complexes at room temperature. Several studies of the chloro-complexes of the PGMs clearly indicate that the strength of interaction with anion-exchangers is highly dependent on the charge of the complex.⁴ Hence it is worthwhile to develop the solvent extraction procedure in weak organic carboxylic acid media. One of the distinct advantage of the organic acid media is the facility of controlling the concentration of complexing ligand, the ease of adjustment of pH and the wide difference in pH at which various metal form anionic complexes. The comparative ease of stripping of the complexes from the organic phase can be achieved by fully exploiting the differences in reactivity of various metals to backwash in the aqueous phase by mineral acid. It is known that organic acid media offers better separation of metals possibly due to high stability of metal organic acids complexes.

There are several extractants reported for extraction of palladium(II). These are n-octylaniline,⁵⁻⁹ carbamoylphosphonates¹⁰, 1,2-bis (tert-hexylthio) ethane,¹¹ 7-tridecanone oxime,¹² methyl isobutyl ketone (MIBK),¹³ sulphide podand 1,12-di-2-thienyl-2,5,8,11-tetrathiadodecane,¹⁴ 2-ethylhexylaminomethylpyridine¹⁵ triphenylphosphine sulphide,¹⁶ quaternary ammonium salts,¹⁷ monoazadithioether¹⁸ bis(n-octylsulphinyl) ethane¹⁹ methylpyridylidene-O-amino benzenethiol,²⁰ di(2-ethylhexyl) thiophosphoric acid,²¹ diisoamyl sulphide,²² 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester.²³ The available data is sometimes unhelpful. This is because they depend very much on the operating conditions used, such as ionic exchanger diluent nature and pH or salt concentration levels and so are difficult to compare.

N-n-octylaniline is a secondary amine, the presence of an octyl group attached to an amino group in aniline renders this amine less soluble in water. There is no emulsion formation and it has the potential of being prepared on a large scale. We have recently reported solvent extraction of some platinum group metals (PGMs) with N-n-octylaniline from hydrochloric acid media.²⁴⁻²⁷

In this work, N-n-octylaniline – salicylate system was studied to investigate the extraction of aqueous palladium(II) solution at pH 3.0 and different concentration of salicylate ion with solution of N-n-octylaniline in xylene. The stripping of palladium(II) from the resultant pregnant organic solutions at pH 3.0, was analysed using ammonia, hydrochloric acid, nitric acid, perchloric acid, sodium nitrate, sodium hydroxide, potassium hydroxide, water, acetate buffer (pH=4.7) and ammonia buffer (pH 10.0) aqueous solutions of various concentrations. The relative efficiency of the stripping agents is compared. The proposed method is used for rapid and selective separation of palladium(II) from associated elements. It is also tested for the separation and determination of palladium(II) from real samples such as alloy, and catalysts.

Procedure

Apparatus - Systronics spectrophotometer – 106 with a set of 1 cm quartz cells were used for absorbance measurements. A Elico digital pH meter model LI-120 was used for pH measurements.

Standard Palladium(II) solution - A stock solution of palladium(II) was prepared by dissolving 1 g of palladium chloride hydrate (Johnson Matthey, UK) in dilute analar hydrochloric acid (1M) and diluting to 250 mL with distilled water and standardised.²⁸ A working solution of 100 µg/mL was made from it by diluting the stock solution with distilled water.

N-n-Octylaniline was prepared by the method of Gardlund et al.²⁹ and its solutions (0.1M) were prepared in xylene.

All the chemicals used were of AR grade. Doubly distilled water was used throughout.

Extraction procedure for palladium(II) – An aliquot of 1 mL of palladium(II) solution (100 $\mu\text{g/mL}$) was mixed with sufficient quantity of sodium salicylate (0.100 gm) to make its concentration 0.025 M in a total volume of 25 mL of the solution. The pH of solution was adjusted to 3.0 by using dilute hydrochloric acid and sodium hydroxide. The solution was transferred into a 125 mL separatory funnel and shaken with 10 mL of 0.1 M (2.303%, v/v) N-n-octylaniline in xylene for 1 min. After the equilibration, mixture was allowed to separate and the metal from the organic phase was stripped with two 10 mL portions of ammonia solution (7M). The extracts were evaporated to moist dryness in order to remove excess of ammonia. The residue was dissolved in 3 mL aqua regia evaporated with two 5 mL portion of concentrated hydrochloric acid to remove oxides of nitrogen. The residue was dissolved in 0.1 M hydrochloric acid and determined palladium(II) spectrophotometrically by pyrimidine-2-thiol.³⁰

Results and Discussion

Extraction condition - The extraction of palladium(II) was studied at various pH (1-10) in presence of 0.025 M sodium salicylate with different concentrations of N-n-octylaniline in xylene (0.01 M – 0.25 M). The results showed that > 0.09 M N-n-octylaniline in xylene extracts palladium(II) quantitatively in the pH range of 2.5 – 3.25 (fig.1).

The extraction of palladium(II) was carried out at pH 3.0 with 0.1 M N-n-octylaniline in xylene in presence of varying concentration of sodium salicylate, sodium succinate and sodium malonate as weak carboxylic acid media (Table 1). The extraction commenced with 0.005 M sodium salicylate and became quantitative in the concentration range of 0.015 M – 0.03 M sodium salicylate. With increased concentration of sodium salicylate there is decrease in the extraction of palladium(II). The decrease in extraction at high weak acid

concentration is presumably due to preferential formation of the salicylate of the N-n-octylaniline. Therefore a 0.025 M of sodium salicylate was used throughout this work. The extraction was found to be incomplete (43%) in sodium succinate media while there was no extraction of palladium(II) from sodium malonate.

Choice of solvents - The studies were then performed to find out the most suitable solvent for the extraction of the ion-pair complex of palladium(II). It was found that a 0.1 M solution of N-n-octylaniline in benzene, toluene, xylene, chloroform amyl alcohol provides quantitative extraction of palladium(II). The extraction of palladium(II) was incomplete if N-n-octylaniline is dissolved in carbon tetrachloride (54%), n-butyl alcohol (65.6%) and methyl isobutyl ketone (62.5%) while no extraction in amyl acetate and 4-methyl-2-pentanol. On safety ground, xylene was preferred to other solvents. It does not participate in the actual extraction process. However, N-n-octylaniline causes ion-pair formation of the palladium(II)-salicylate complex and promotes extraction.

Nature of the extracted species - The probable composition of extracted species is ascertained by plotting the graphs of $\log D_{[Pd(II)]}$ against $\log C_{[N-n-octylaniline]}$ at fixed sodium salicylate concentration (0.025 M). The graphs are found to linear and having the slopes of 0.88 and 0.92 values respectively (fig.2). Also plots of $\log D_{[Pd(II)]}$ against $\log C_{[salicylate]}$ at fixed N-n-octylaniline concentration (0.1 M) were linear and the slope values are found to be 2.83 and 2.59 respectively (fig.3). The probable composition of the extracted species is calculated to be 1:3:1 (metal:acid:extractant). The possible mechanism of the ion-pair complex extracted appears to be protonated N-n-octylaniline which form cationic species as $RR'NH_2^+$ while salicylate combines with palladium(II) to form anionic species as $Pd(C_7H_5O_3)_3^-$ and both of them associate to form ion-pair of the type $[RR'NH_2^+ Pd(C_7H_5O_3)_3^-]_{org}$ and being neutral constitutes extractable species.

Effect of stripping agents - A variety of stripping agents were used for the stripping of palladium(II) from the organic extract. The results are shown in Table

2, from which it is clear that all of the solutions examined (2 x 10 mL) only ammonia is effective to strip palladium(II) from the organic layer.

Palladium(II) was extracted from 10 mL to 40 mL aqueous solution containing 0.025 M sodium salicylate with 10 mL of 0.1M N-n-octylaniline in xylene. The extraction was quantitative when aqueous to organic volume ratio was in the range 1:1 to 4:1 and above this ratio the extraction decreased.

The extraction period showed that minimum of 30 s equilibration time was adequate for quantitative extraction of palladium(II) from salicylate media at pH 3.0. However, for general procedure 1 min equilibration time was recommended in order to ensure the complete extraction of metal ion.

The loading capacity of 10 ml of 0.1 M N-n-octylaniline is 2 mg of palladium(II).

Effect of foreign ions - The effect of a large number of foreign ions on the extraction of 100 µg of palladium(II) with the proposed reagent was investigated following the recommended procedure. The tolerance limit was set at the amount of the foreign ion that could be present to give an error less than $\pm 2\%$ in the recovery of palladium(II) (Table-3). It was observed that the method is free from interference from a large number of cations and anions. The only species showing interference in the procedure were tartrate, oxalate, EDTA and ascorbate due to formation of strong metal chelates, while thiourea, thiocyanate and thiosulphate form very strong complexes with palladium(II) because platinum group metals (PGMs) belong to the soft metal which possess a strong affinity to ligands containing donating type sulphur atoms which act as soft bases.³¹ hence the proposed method permits the separation of palladium(II) in presence of a large number of foreign ions.

Applications

Separation of palladium from binary mixture - The method permits separation and determination of palladium(II) from binary mixtures containing either Pt(IV), Os(VIII), Ru(III), Rh(III), Ir(III), Au(III), Cu(II) Fe(III), Co(II), Ni(II) or Sb(III).

Aliquots containing 100 μg of palladium(II) with added metal ion were adjusted to pH 3.0 and 0.025 M sodium salicylate concentration to total volume of 25 ml. The mixture was transferred into a 125 mL separatory funnel. It was then equilibrated with 10 mL of 0.1 M N-n-octylaniline in xylene for 1 min. Under this condition palladium(II) was alone extracted into organic layer as an ion-pair complex, leaving behind added metal ion in the aqueous phase. After quantitatively separating the organic layer the aqueous layer was analysed for added metal ion content by standard methods (Table-4). From the organic extract palladium(II) was quantitatively stripped back using two 10 mL portions of 7 M ammonia. The back-extracts were evaporated to moist dryness in order to remove excess of ammonia. Palladium(II) was determined spectrophotometrically with pyrimidine-2-thiol.

Determination of palladium(II) in synthetic solution corresponding to alloys –

The proposed method was applied to the extraction and determination of palladium(II) from salicylate media at pH 3.0 in various synthetic mixture corresponding to alloys. The results were found to be in good agreement with the amounts of palladium(II) added (Table 5).

Determination of palladium in catalysts - A known weight of catalyst (BDH) was dissolved in a mixture of 9 mL and 3 mL of concentrated hydrochloric and nitric acid, respectively. After the reaction was over the solution was heated with a two 5 mL portions of concentrated hydrochloric acid until complete removal of oxides of nitrogen. The residue was dissolved in 10 mL of 1 M hydrochloric acid and filtered to remove carbon or barium sulphate. The residue was washed with dilute hydrochloric acid. The filtrate and washings 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 analysis are collected in Table-6.

The method is highly selective, rapid, reproducible and permits the rapid separation and determination of micro amounts of palladium(II). The average recovery of palladium(II) was 99.8 %. Each determination took 15-20 min.

Conclusion

The results of the experiment indicate that N-n-octylaniline in salicylate form extracts palladium(II) at pH 3.0 in xylene. The extraction mechanism corresponds to an anion exchange in which a ion-pair complex of stoichiometric formula $[RR'NH_2^+ Pd (C_7H_5O_3)_3^-]_{org}$ is formed in the organic phase. 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 palladium(II). The satisfactory recovery of palladium(II) from these samples also indicated that the developed method is suitable for the separation and concentration of palladium(II) from a solution of complex composition. It permits the separation of palladium(II) from other platinum group metals (PGMs), gold and base metals; which are commonly associated with its natural occurrence. N-n-octylaniline can be synthesized at low cost, with high yield, in the best purity and recovered for reuse without loss of extraction efficiency. The method is simple, rapid, highly selective and reproducible.

Acknowledgements

SSK is grateful to the U.G.C. New Delhi for sponsoring minor research project. The authors express their gratitude to Dr. K.J. Patil, Professor and Head, Department of Chemistry for his valuable discussion and kind encouragement.

References

- 1 Silve Kallmann & Paul Blumberg, *Talanta*, 27 (1980) 827.
- 2 Hampel C A, "Rare Metals Handbook", Second Edition, Robert E Krieger Publishing Co INC, Huntington, NY 1971, pp. ———
- 3 Meyers R A, "Encyclopedia of Physical Science and Technology" Academic Press Inc, New York 1987, pp15.
- 4 Al-Bazi S J & Chow A, *Talanta*, 31 (1984) 815.
- 5 Varilyeva A A, Yudelevich I G, Gindin L M, Lanbina T V, Shulman R S, Kotlarevsky I L & Andrievsky V N, *Talanta*, 22 (1975) 745.
- 6 Pohlandt C, Nat Inst Metallurgy, Randburg, *S Afr Rept* No 1881 (1977).
- 7 Pohlandt C & Hegetschweller M, Nat Inst Metallurgy, Randburg, *S Afr Rept* No 1940 (1978).
- 8 Pohlandt C, *Talanta*, 26 (1979) 199.
- 9 Gedye R N, Bozic J, Durbano P M & Williamson B, *Talanta*, 36 (1989) 1055.
- 10 Govski B, Kuca L & Petrzilova H, *J Radioanal Nucl Chem*, 91 (1985) 305.
- 11 Yoshinari Baba, Toshiya Eguchi & Katsutoshi Inoue, *Bull Chem Soc Jpn*, 59 (1986) 1321.
- 12 Katsutoshi Inoue, Yoshinari Baba, Kazuhara & Tetsuji Oka, *Bull Chem Soc Jpn*, 61 (1988) 803.
- 13 Brooks R R & Lee B S, *Anal Chim Acta*, 204 (1988) 333.
- 14 Elwira Lachowicz & Malgorzata Czapiuk, *Talanta*, 37 (1990) 1011.
- 15 Yoshinari Baba & Toshihiro Fukumoto, *Chem lett*, (1992) 727.

- 16 Daoud J A, El-Reefy S A & Aly H F, *J Radioanal Nucl Chem Lett*, 166 (1992) 441.
- 17 Kondo Kazuo, Ourachi Tomoya, Kaneiwa Toshie & Matsumoto Michiaki, *Solvent Extr Res Dev Jpn*, 7 (2000) 176.
- 18 Chayama Kenji, Kurihara Chieko, Tsuji Haruo & Sekido Elichi, *Bunseki Kagaku*, 47 (1998) 1077.
- 19 Huanvan Li, Xiaowen Zhu, Jinghong Wu, Wanyi Xu & Yaobing Lin, *Fenxi Huaxue*, 27 (1999) 708.
- 20 Bag S P, Mukherjee J & Siladitya B, *Indian J Chem, Sect A*, 37A (1998) 185.
- 21 Rovira M, Hurtado L, Cortina J L, Arnaldos J & Sastre A M, *Solvent Extr Ion Exch*, 16 (1998) 545.
- 22 Jianmin Yu, Zhenfen Yang, Shijie Liu & Huaxiang Gu, *Guijinshu*, 18 (1997) 45.
- 23 Bandekar S V & Dhadke P M, *Sept Purif Technol* 13 (1998) 129.
- 24 Lokhande T N, Anuse M A & Chavan M B, *Talanta*, 46 (1998) 161.
- 25 Lokhande T N, Anuse M A & Chavan M B, *Talanta*, 47 (1998) 823.
- 26 Lokhande T N, Kolekar G B, Anuse M A & Chavan M B, *Sep Sci Technol* 35 (2000) 153.
- 27 Lokhande T N & Anuse M A, *J Saudi Chem Soc*, 4(1) (2000) 1.
- 28 Beamish F E & Van Loon J C, Analysis of Noble Metals : Overview and Selected Methods, *Academic Press*, London 1977 pp i31.
- 29 Gardlund Z G, Curtis R J & Smith G W, *Liq Crystals Ordered fluids*, 2 (1973) 541.

- 30 Anuse M A & Chavan M B, *Chem Anal* (Warsaw), 29 (1984) 409.
- 31 Pearson R G, *J Am Chem Soc*, 85 (1963) 3533; *J Chem Educ*, 45 (1968) 581, 643.
- 32 Sandell E B, *Colorimetric Determination of Traces of Metals*, 3rd Ed Interscience Publ New York, 1965, pp 726, 702, 781, 769, 519, 503, 524.
- 33 Anuse M A, Kuchekar S R & Chavan M B, *Indian J Chem*, 25A (1986) 1041.
- 34 Zygmunt Marczenko, *Spectrophotometric Determination of Elements*, Ellis Horwood Limited, Chichester, 1976 pp 229, 370, 125, 413.

Table 1 - Extraction behaviour of palladium(II) as a function of organic acid concentration.

Palladium(II) = 100 μ g

pH = 3.0

N-n-Octylaniline = 0.1 M in xylene

Strippant = 1 M Ammonia (2x10 ml)

Concentration of Acid, M	Sodium salicylate		Sodium succinate	
	% E ^a	D ^b	% E ^a	D ^b
0.000	0.00	-	0.00	-
0.005	51.9	2.69	11.0	0.31
0.01	90.4	23.54	24.4	0.81
0.02	100.0	∞	25.5	0.86
0.03	100.0	∞	27.0	0.92
0.04	90.0	22.5	31.0	1.12
0.05	72.0	6.43	40.0	1.67
0.06	50.8	2.58	43.0	1.89
0.07	45.0	2.05	43.0	1.89
0.08	32.5	1.20	42.0	1.81
0.09	20.0	0.63	37.0	1.47
0.10	10.0	0.27	32.8	1.22

a = Percentage extraction, b = Distribution ratio

Table 2 - Choice of electrolyte solution for the stripping of palladium(II) from the organic extract.

Palladium(II) = 100 μ g

aq : org = 2.5 : 1

pH = 3.0

Sodium salicylate = 0.025 M

N-n-octylaniline = 0.1 M in xylene

Stripping solution used	Concentration M	% Stripped ^a
Ammonia	1 – 10	100
Hydrochloric acid	1 – 5	6.0
Sulphuric acid	1 – 5	7.6
Nitric acid ^b	1 – 5	Nil
Perchloric acid	1 – 5	Nil
Sodium nitrate	1 – 3	58.6
Sodium hydroxide	0.1	15.5
Potassium hydroxide	0.01 – 3.0	12.4
Water	-	9.0
Acetate buffer solution	pH 4.7	29.1
Ammonia buffer solution	pH 10.0	100.0

a = 2 x 10 mL of each strippent was taken.

b = Organic extract decomposes in presence of nitric acid

Table 3 : Effect of foreign ions on the extraction of 100 µg palladium(II) at pH 3.0 in 0.025 M sodium salicylate with 0.1 M N-n-octylaniline dissolved in xylene.

Ratio of ions Palladium : ions	Amount tolerated, mg	Foreign ion
1 : 300	30	Citrate
1 : 250	25	Zn(II), iodide, malonate
1 : 200	20	Tl(III), Mo(VI), Cu(II), Te(IV)
1 : 150	15	Cd(II), Mg(II), U(VI), Be(II), Ca(II), Se(IV), Co(II)
1 : 100	10	Mn(II), Fe(III), Pb(II), V(V), Ni(II), Bi(III), Sn(II), Ba(II), Ce(IV), Sb(III)
1 : 30	3	Hg(II), Cr(VI), Fe(II)
1 : 20	2	Ag(I)
1 : 10	1	Au(III), Ru(III), Os(VIII)
1 : 6	0.6	Pt(IV)
1 : 5	0.5	Rh(III), Ir(III)
-	0.0	Tartarate, oxalate, EDTA, thiourea, thiocyanate, thiosulphate, ascorbate

Table 4 - Separation of palladium(II) from binary mixture

Metal ion	Amount taken, μg	Average % Recovery*	Chromogenic ligand	Reference
Pd(II)	100	99.9	Stannous chloride	32
Pt(IV)	300	99.8		
Pd(II)	100	99.8	Thiourea	32
Os(VIII)	300	99.7		
Pd(II)	100	99.9	Thiourea	32
Ru(III)	300	99.8		
Pd(II)	100	99.9	Stannous chloride	32
Rh(III)	300	99.9		
Pd(II)	100	99.9	Stannous chloride + hydrobromic acid	32
Ir(III)	100	99.9		
Pd(II)	100	99.9	Stannous chloride	32
Au(III)	200	99.7		
Pd(II)	100	99.9	4'-chloro PTPT	33
Cu(II)	20,000	99.9		
Pd(II)	100	99.9	Thiocynate	32
Fe(III)	10,000	99.9		
Pd(II)	100	99.9	Thiocynate	34
Co(II)	15,000	99.9		
Pd(II)	100	99.9	DMG	34
Ni(II)	10,000	98.8		
Pd(II)	100	99.9	Iodide	34
Sb(III)	2,000	99.9		

* Average of five determinations

Table 5 : Analysis of palladium(II) in synthetic mixtures corresponding to alloys

Alloy*	Palladium(II) taken μg	Palladium(II) found by proposed method μg	Mean	Average Recovery %	RSD, %
Dental alloy ^a	100	99.9 99.9 99.8 99.9 99.8	99.86	99.86	0.14
Dental alloy ^b	600	599.8 599.9 599.8 599.8 599.9	599.84	99.97	0.02
Dental alloy ^c	600	599.9 599.9 599.8 599.7 599.7	599.8	99.96	0.03
Golden coloured silver alloy ^d	255	254.9 254.9 254.9 254.8 254.9	254.88	99.95	0.04
Stibio Palladinite mineral ^e	150	149.9 149.9 149.7 149.7 149.8	149.80	99.86	0.13
Pt-Pd-Rh ^f catalyst	150	149.8 149.8 149.9 149.8 149.8	149.82	99.88	0.12

* Composition of alloys in percentage

a = Ag, 5-15; Au, 50-60; Pd, 3-10; Pt, 3-7

b = Pt, 18-35; Pd, 60-75; Rh, 0.8-3; Fe, 20-50; Pb, 0.5-3.0

c = Ag, 10-50; Pd, 10-60; Pt, 0-2; Ru, 0-0.5, d = Pd, 25.5; In, 21; Cu, 18; Ag, 35,

e = Pd, 75; Sb, 25, f = Pt, 0.03 - 0.20; Pd, 0.03 - 0.15; Rh, 0.005 - 0.05

Table 6 : Analysis of palladium(II) in catalysts

Catalyst	Amount found by iodide ³⁴ μg/mL	Amount found by proposed method* μg/mL	Recovery %	RSD, %
PdCl ₂ on carbon	50	49.9	99.8	0.20
Pd on carbon (10% Pd)	50	49.8	99.6	0.40
Pd on carbon (5% Pd)	50	49.9	99.8	0.20
Pd on BaSO ₄	50	49.9	99.8	0.20
Pd on CaCO ₃	50	49.8	99.6	0.40

* Average of five determinations.

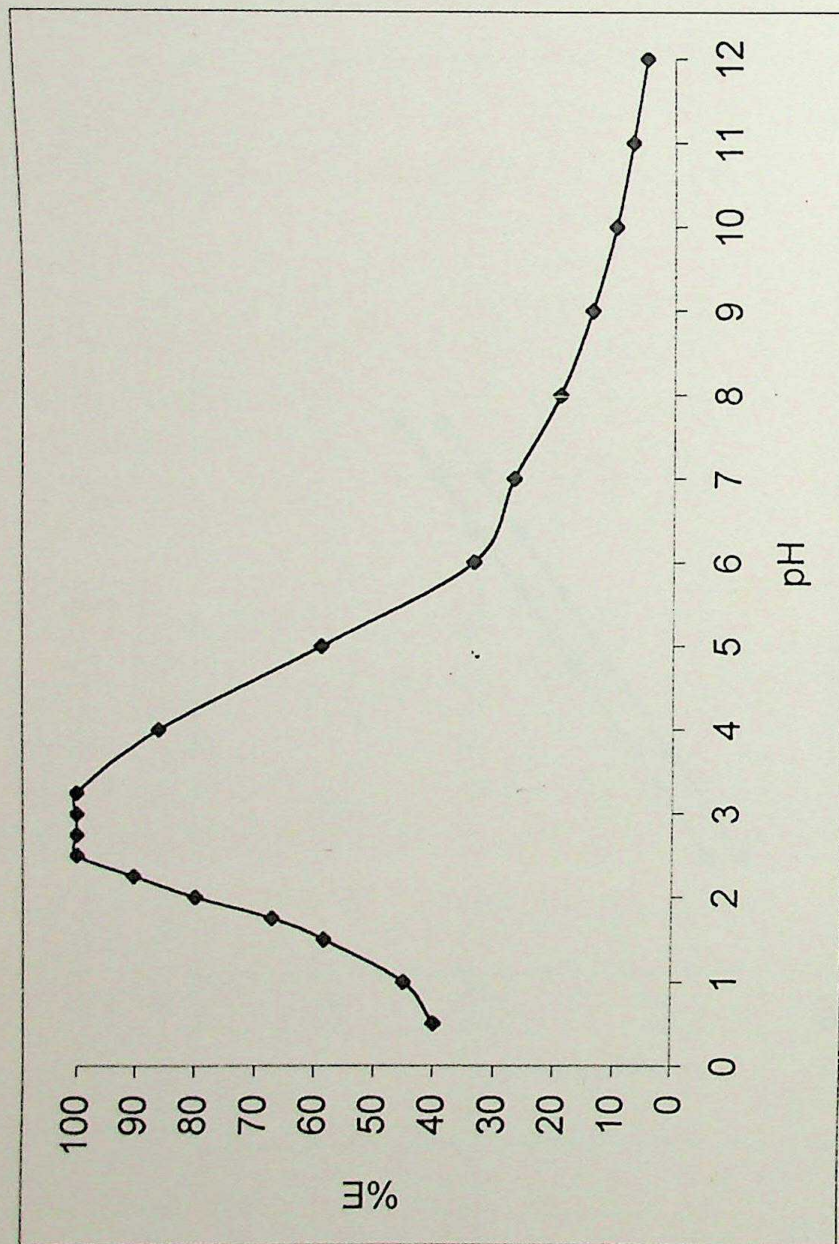


Figure 1 Extraction behaviour of Palladium(II) as a function of pH from 0.025 M sodium salicylate solution with 0.1 M N-n-octylaniline.

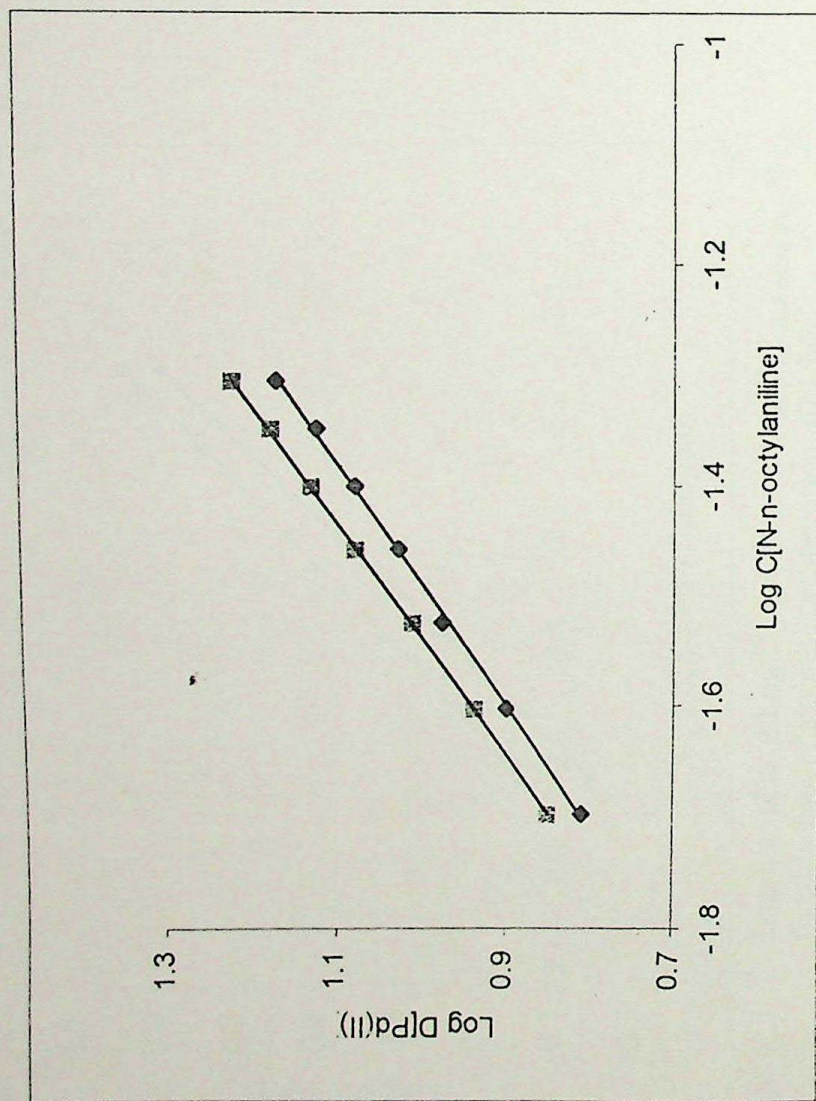


Figure 2 Log-log plot of $\text{Log } D_{[\text{Pd(II)}]}$ against $\text{Log } C_{[\text{N-n-octylaniline}]}$ at fixed sodium salicylate concentration (0.025 M).

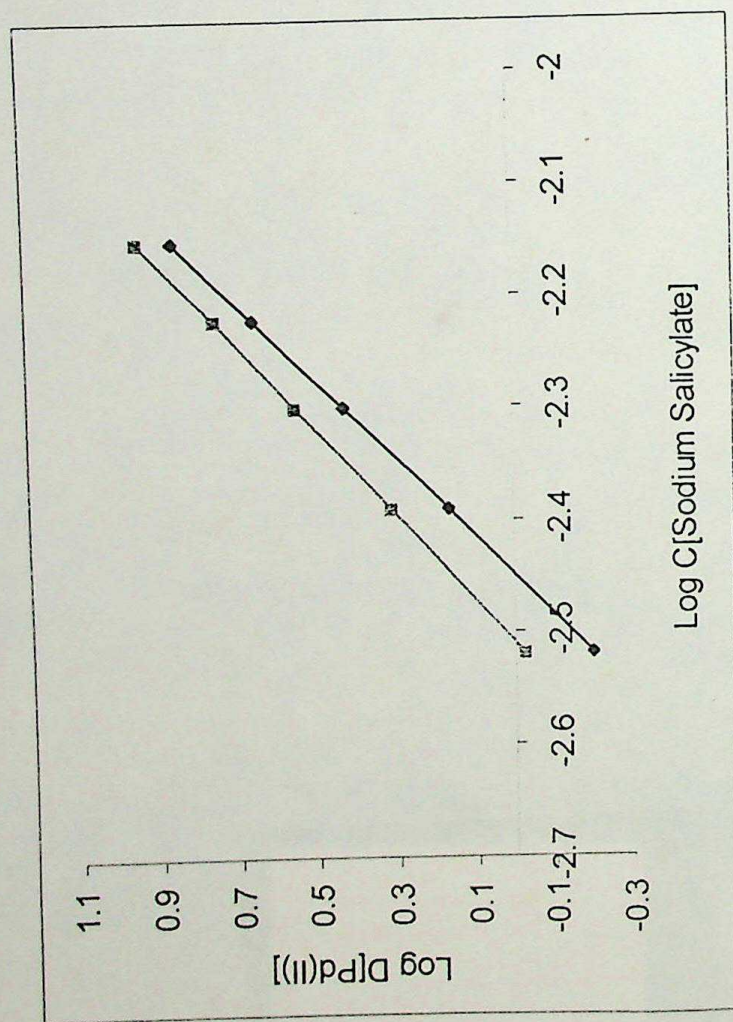


Figure 3 Log-log plot of $\text{Log } D_{[\text{Pd(II)}]}$ against $\text{Log } C_{[\text{sodium salicylate}]}$ at fixed N-n-octylaniline concentration (0.1 M).