FOREWORD

The present thesis submitted for the degree of Doctor of Philosophy (Science) of the University of North Bengal, deals with "Solvent Extraction of Nickel(II), Palladium(II), Platinum(IV) & Rh(III)." The work has been done by the candidate at the Department of Chemistry, University of North Bengal. Portions of the work appearing in Parts I,II,& III have already been published (1. Z.Anal.Chem, 274,127 (1975); 2. Anal.Chim. Acta, 74, 197 (1975); 3. Indian J.Chem, 13, 743 (1975); 4. Z.Anal.Chem, 276, 205 (1975) 5. Z.Anal.Chem, (1975) (in press) 6. Z.Anal.Chem, (1975) (in press)) which deals with the solvent extraction and seperations of the said elements.

This thesis is divided into four parts and opens with a general introduction of liquid-liquid extraction. Here the theoretical aspects of solvent extraction are described with special reference to the method of extraction, classification into ion association and chelate extraction systems and the equilibria involved. Then a description of techniques of extraction is given followed by examples of ion association and chelate extraction systems. The xanthate and different oxime compounds are particularly emphasized here. They produce characteristic colour reactions with the metal ions. This permits extraction and colorimetric determination in the organic phase in one step.

Parts I, II, III and IV are divided into some other sub-sections. In every sub-section a brief review of the different methods is given, followed by experimental details of the work, results and discussion.

References cited in the thesis have been taken from original or translated papers, reviews and sometimes from text books or chemical abstracts.

PART - I : NICKEL (II)

Section 1 : The rapid extraction followed by the spectrophotometric determination of microamounts of nickel with potassium xanthates is described. The yellow brown chelates are extractable into chloroform and determined at 415 and 475 nm. 1 : 2 complexes (metal : ligand) are formed in both the cases and are quite stable. The results are fairely precise and reproducible. Effect of pH, reagent concentration, interference of same diverse ions on the extraction behaviour are tested.

Section 2 : A spectrophotometric method has been developed for the extraction and determination of nickel at microgram levels. Nickel for~~o~~m~~e~~s a red complex with benzil-α-monoxime extractable into chloroform quantitatively from aqueous solution of pH 7-10. A wave length of 400 nm was chosen for calibration and estimation. Effect of pH, reagent concentration, diverse ions etc. have been studied.

PART - II : PALLADIUM (II)

Section 1 : Liquid-liquid extraction behaviour of palladium(II) with ethyl acetate has been studied. Thiocyanate complex of palladium is extractable with ethyl acetate. Maximum extraction is about 87% from 3M HCl medium. Presence of ammonium chloride as an salting-out agent enhances the extraction to above 95% . Intereferences of the diverse ions on the extraction behaviour have been investigated.

Section 2 : Extraction behaviour of Pd(II) with the reagents, triethylamine, pyridine, α- methyl pyridine and s-trimethyl pyridine has been studied. Iodo complex of Pd is extractable into triethyl amine whereas palladium chloride itself is extracted with pyridine and substituted pyridines. Chloroform has been used as the diluent. Effect of acidity, reagent concentraion, foreign ion etc. have been tested.

Section 3 : Xanthate compounds have been used as colorimetric reagents for palladium. Xanthates give yellow coloured chelates extractable into chloroform. The colour systems are quite stable for a long period and conform Beer's law. Potassium ethyl xanthate extracts palladium from 10M HCl medium to pH 8.0 where as other xanthates extract from pH 1-7. The results are more or less accurate. The process is a rapid one.

Section 4 : The reagent -α- benzoin oxime has been used for the extraction studies of Pd(II). The metal ion~~s~~ gives a light yellow complex extractable into chloroform from aqueous solution of pH 1-6. Spectrophotometric method has been applied to determine palladium at 390 nm. Beer's law is obeyed over the concentration range of 5-30 mg Pd per 100 ml. The nature of the complex has been investigated.

Section 5 : The rapid extraction and spectrophotometric determination of microamounts of palladium with diacetyl monoxime is described. The yellow complex in chloroform obeys Beer's law at 320 nm over a concentration range of 0.9 µg Pd/ml. pH 4-5 is recommended for quantitative extraction. Effect of pH, period of extraction, diverse ions etc. are tested.

PART - III : PLATINUM (IV)

Section 1 : A method is proposed for the extraction and spectrophotometric determination of platinum(IV) with -α-benzoin oxime into chloroform. The reagent developes a brown colour with platinum in hot condition. Quantitative extraction occurs at pH 3.0.

Beer's law is obeyed at 450 nm over a concentration range of 5-40 µg Pt(IV) per ml. The results are accurate to within ± 2% . The composition of the complex has been determined by mole ratio method.

<u>Section 2 :</u> Extraction behaviour of Pt(IV) with benzil-α-monoxime is described. Alike α- benzoin oxime the reagent gives a brown chelate when heated with Pt on a water bath. Chloroform is the extracting solvent. Spectrophotometric measurements have been performed at 440 nm. Platinum can be determined in presence of a number metals.

PART - IV : RHODIUM (III)

<u>Section 1 :</u> A method is devised for the extraction and direct photometric determination of rhodium(III) with α-benzoin oxime. The yellow chelate formed in hot condition is extractable into chloroform at pH 4-8. Optical density measurements are carried out at 390 nm. The system conformes Beer's law for 5-35 µg per ml. Nature of the complex has been studied. The results are accurate to within ± 2.5 % .

<u>Section 2 :</u> Extraction and spectrophotometric determination of rhodium(III) with benzil-α-monoxime is described. Alike the previous method Rh(III) forms an yellow complex with the reagent

on worming and is extracted into chloroform from aqueous solutions of pH 0.5-6. Absorbance measurements have been performed at 400 nm at which wave length Beer's law is obeyed over the concentration range of 1-9 µg Rh per ml. Rhodium has been determined in presence of a number of diverse ions. The method proposed shows an accuracy to within ± 3.1% .