

FOREWORD

Recent advances in analytical chemistry are characterised by great progress toward more powerful methods of separation, equalling in significance the development brought about in instrumental methods of determination. Problems of chemical analysis almost always involve two steps : Separation of the desired constituent and measurement of the amount or concentration of this constituent. Much worthy research has been dedicated to the development of more discriminatory methods of estimation, such as spectrophotometric, spectrographic etc. with a view to minimizing the need for separation steps preceding the measurement step. But despite the availability of the modern, more discriminating methods of measurement, successful and effective solutions to many analytical problems depend heavily on separation processes.

Solvent extraction claims a significant position among the separation techniques because of its ease, simplicity, speed and applicability to both tracer and macro amounts of metal ions. The objective of these analytical liquid-liquid extraction procedures lies in the extrapolation to full-scale commercial hydrometallurgical processes from the technical point of view. The methods are highly operative on numerous metallurgical separation systems involving extraction from mine waste and dump leach liquors.

The present thesis is the outcome of a series of investigations carried out to study the separation and spectrophotometric determination of cobalt(II), platinum(IV), palladium(II), copper(II), Bismuth(III), Iron(II), Nickel(II), by using the analytical reagents such as 4-nitrosoresorcinol, cetyltrimethylammoniumbromide (CTAB), Phenylthiohydantoic acid (PTHA), 2-hydroxy-1-naphthaldoxime, Cacotheline and 2-mercaptobenzoic acid. Auxiliary ligands namely iodide, bromide, pyridine and some of its methyl substituted derivatives and solvents like chloroform, benzene, carbon tetrachloride, ethylacetate were made use of during the investigatory operations.

The main aim of this thesis involves the development of analytical methods for separation and spectrophotometric determination of different heavy metals with the help of various organic reagents. Some of the methods are promising from the stand point of separation of the aforesaid metals from each other. References to the literatures survey have been presented so as to indicate, to some extent, the subject matter of each.

This thesis is divided into seven chapters. A brief chapter-wise summary of the work done is given below:

CHAPTER - I

The first chapter deals with the discussion of basic principles of solvent extraction and separation of metal ions

followed by a discussion of spectrophotometry, the analytical basis adopted throughout the course of the work. The chapter ends with a brief outline of the proposed investigation and References.

CHAPTER - II

This chapter describes the use of phenylthiohydantoic acid (PTHA) as an analytical reagent for extraction, separation and spectrophotometric determination of cobalt and palladium. Cobalt forms a complex with PTHA extractable into chloroform. Absorbance of the metal complex shows a linear response over a concentration of 10 ppm of cobalt with molar absorptivity $1.123 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 480 nm. The system tolerates a number of diverse ions. Cobalt has been estimated in synthetic mixtures using the proposed method.

The method has been compared with some other existing methods. The Pd-PTHA complex shows λ_{max} at 370 nm with molar absorptivity $1.303 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. The method provides excellent recovery of the metal in presence of almost all the common ions. The method has been compared with some other existing methods.

CHAPTER - III

In this chapter the use of 2-hydroxy-1-naphthaldoxime as a simple and sensitive reagent for the extraction and spectrophotometric determination of nickel, cobalt and palladium has been described.

Nickel forms a complex with 2-hydroxy-1-naphthaldoxime extractable into carbon tetrachloride. Absorbance of the metal complex shows a linear response over a concentration of 10 ppm of nickel with molar absorptivity $1.202 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 380 nm.

The system tolerates a number of diversions. Nickel has been estimated in synthetic mixtures using the proposed method. The method has been compared with some other existing methods.

A selective spectrophotometric method for the determination of cobalt with 2-hydroxy-1-naphthaldoxime has been devised. Beer's law is obeyed over 10 ppm of cobalt with molar absorptivity $0.826 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 400 nm. The method provides excellent recovery of the metal in presence of almost all the common ions tested. The method has been compared with some other existing methods.

Palladium forms a complex with 2-hydroxy-1-naphthaldoxime extractable into chloroform. Beer's law is obeyed over 15 ppm of palladium with molar absorptivity $0.865 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 400 nm. The method provides excellent recovery of the metal in presence of a large number of diverse ions tested. The method has been compared with some other existing methods.

CHAPTER - IV

This chapter describes the use of cetyltrimethylammonium bromide as an analytical reagent for the extraction and spectrophotometric determination of bismuth and copper.

Bismuth-CTAB complex shows a linear response over a concentration of 25 ppm of bismuth with molar absorptivity $0.822 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 490 nm. The system tolerates a number of diverse ions. Bismuth has been estimated in synthetic mixtures using the proposed method. The method has been compared with some other existing methods.

For Cu-CTAB complex the Beer's law is obeyed over 10 ppm of copper with molar absorptivity $1.064 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 360 nm. The method provides excellent recovery of the metal in presence of almost all the common ions tested. The method has been compared with some other existing methods.

CHAPTER - V

This chapter includes the uses of iodide, bromide and pyridine bases as analytical reagents for the extraction and spectrophotometric determination of palladium, platinum and copper.

Palladium forms a complex with potassium iodide and pyridine bases extractable into chloroform. Beer's law is obeyed over 1-10 ppm of palladium with maximum absorbance at 354-365 nm. The method provides excellent recovery of the metal in presence of almost all the common ions tested. The method has been compared with some other existing methods.

Platinum forms complex with KI and pyridine bases extractable into chloroform. Beer's law is obeyed over 5-50 ppm of platinum with

λ_{max} at the region 345-485 nm. The system tolerates a number of diverse ions. Platinum has been estimated in synthetic mixtures using the proposed method. The method has been compared with some other existing methods.

A selective spectrophotometric method for the determination of copper with potassium bromide/potassium iodide and pyridine bases has been devised. Beer's law is obeyed over 5-50 ppm of copper with λ_{max} at 320-360 nm. The method provides excellent recovery of the metal in presence of almost all the common ions tested. The method has been compared with some other existing methods.

CHAPTER - VI

This chapter describes the use of 2-mercaptobenzoic acid as an analytical reagent for spectrophotometric determination of palladium.

The Pd(II)-2-mercaptobenzoic acid complex showed λ_{max} at 420 nm. The system conforms to Beer's law over 10 ppm of palladium with molar absorptivity $1.725 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. Palladium has been estimated in synthetic mixtures using the proposed method. By this method, the interferences of most of the diverse ions were overcome and this has been compared with some other existing methods.

CHAPTER - VII

A spectrophotometric method for the determination of iron(II) with Cacotheline has been presented.

The absorbance of the Fe(II)- Cacotheline complex was measured at 530 nm. The system conforms to Beer's law over 2-50 ppm of iron with molar absorptivity $1.49 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$. The method provides excellent recovery of the metal in presence of almost all the common ions tested. The method has been compared with some other existing methods.

Many obviously inferior reagents and methods are included since the treatment of the subject is intended to be complete. Their inclusion is justified because of two considerations : in future no time need be lost in attempting analytical methods that in the past have been demonstrated as unsatisfactory; and further, an inferior method may, with suitable modifications, be made useful for certain ^{other} purposes.