

**DIFFERENTIAL PULSE POLAROGRAPHIC STUDIES
OF TOXIC METALS AFTER PRECONCENTRATION
OF THEIR COMPLEXES ON NAPHTHALENE**

By

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DOCTOR OF PHILOSOPHY



to the
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Dedicated to
my father
late R.M. Dwivedi

CERTIFICATE

This is to certify that the thesis entitled "**DIFFERENTIAL PULSE POLAROGRAPHIC STUDIES OF TOXIC METALS AFTER PRECONCENTRATION OF THEIR COMPLEXES ON NAPHTHALENE**" being submitted by **Mr. Rajesh Kumar Dubey** to the **Indian Institute of Technology, Delhi**, for the award of the degree **Doctor of Philosophy** in Chemistry, is a record of bonafied research work carried out by him. Mr Rajesh Kumar Dubey has worked under my guidance and supervision and has fulfilled the requirements of the submission of this thesis, which to my knowledge, has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.



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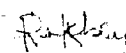
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SUMMARY

The thesis consists of three chapters. Each chapter has been subdivided into various sections dealing with introduction, experimental, and results and discussion.

The first chapter deals with the general introduction of organic reagents. A brief introduction to the new techniques of separation, that is, 'Solid-liquid Separation after Liquid-liquid Extraction and Separation of Metals by Coprecipitation of their Chelates onto Microcrystalline Naphthalene' has been discussed. This chapter also includes a brief discussion on column preconcentration techniques using various adsorbents. Besides these, a brief introduction to the fundamentals of D.C.Polarography, Differential Pulse Polarography, Cyclic Voltammetry and analytical aspects of polarography and the scope of the present work have also been described in this chapter.

The chemistry and analytical applications of dithiocarbamates with special reference to potassium morpholine-4-dithiocarbamate has been described in the second chapter. A systematic survey of the literature relating to extraction-polarographic determination of As, Bi, Cd, Co, Cu, In, Mo, Mn, Ni, Pb, Tl, V and Zn, has been carried out in order to compare these methods with the methods developed in the present work. The method of preparation and standardization of potassium morpholine-4-dithiocarbamate, synthesis of morpholine-4-dithiocarbamate (MCDT)-cetyltrimethylammonium bromide (CTMAB)-naphthalene, preparation of metal ion solutions, buffer solutions of different pH values have been described in this chapter. Differential pulse polarography (DPP) has been applied for the determination of As, Bi, Cd, Co, Cu, In, Mn, Mo, Ni, Pb, Tl, V and Zn after adsorption of their morpholine-4-carbodithioates onto microcrystalline naphthalene. The

morpholine-4-carbodithioates of metal ions are adsorbed onto microcrystalline naphthalene at optimum pH. The metal complexes are desorbed with 1 M HCl and determined with a differential pulse polarograph. The column method using MCDT-CTMAB-naphthalene have also been used to improve the preconcentration factor. The various parameters such as reversibility of electrode reaction process, effect pH on adsorption, pH on differential pulse polarogram, volume of aqueous phase, and interference of a number of metal ions have been studied. Based upon the difference in E_p value or pH, conditions have been developed for the simultaneous determination of metals e.g. Pb and Cd, Zn and Mn and Cu and Bi. The determination of these metals has been carried out in various complex materials e.g. environmental samples (industrial effluents, soil, sludge, waste water and flyash) petroleum and kerosene oil, standard alloys, biological, pharmaceutical and synthetic samples.

The last chapter consists of a brief introduction to the analytical applications of oxine as a complexing reagent. A systematic survey of literature have also been cited for those metal ions which are studied in this chapter. Differential pulse polarographic method has been developed for Ga, Nb, Rh, Ru, Sn and V which, either do not form morpholine-4-carbodithioates or their morpholine-4-carbodithioates are not adsorbed onto microcrystalline naphthalene. The 8-hydroxyquinolines (oxinates) of these metals are adsorbed onto microcrystalline naphthalene at optimum pH. After desorption with 10 mL of 1 M hydrochloric acid for Cd, Pb and Ga, 2 M HCl for U, Ru and Rh, 3.5 M HCl for Sn and 11 M HCl for Nb, these metals were determined by a differential pulse polarograph. Pb and Cd have also been studied in this chapter and a selective polarographic method has been developed for simultaneous determination of Pb, Cd and Sn. The various parameters such as reversibility of electrode reaction process, effect pH on adsorption, pH on differential

pulse polarogram, volume of the aqueous phase, and interference of a number of metal ions have been studied. The developed method has been applied for the determination of these metals in various standard alloys, environmental and synthetic samples.

The thesis has been appended with the reprints of four papers published out of this work and the list of publications.

CONTENTS

Page No.

CHAPTER 1 INTRODUCTION

1.1	Metal Chelates and Organic Complexing Reagents	1
1.2	A Brief Introduction to Polarography	11
1.3	Analytical Aspects	26

CHAPTER 2 COPRECIPITATION STUDIES OF MORPHOLINE-4-DITHIOCARAMATES OF As, Bi, Cd, Co, Cu, In, Mn, Mo, Ni Pb, Tl, V and Zn

2.1	Chemistry of Potassium Morpholine 4-Dithiocarbamate	31
2.2	Past work on Polarography as an Analytical Technique	34
2.3	Experimental	56
2.4	Results and Discussion	60
2.5	Analysis of Metal Ions in Complex Materials	81

CHAPTER 3 COPRECIPITATION STUDIES OF OXINATES OF Cd, Ga, Nb, Pb, Rh, Ru, Sn and U

3.1	Quinoline-8-ol as an Analytical Reagent	101
3.2	Past Work and Polarographic Estimation of Ga, Nb, Rh, Ru, Sn and U	102
3.3	Experimental	109
3.4	Results and Discussion	111
3.5	Analysis of Metal Ions in Complex Materials	128
	REFERENCES	135

LIST OF PUBLICATIONS