

**DERIVATIVE SPECTROPHOTOMETRY AND DIFFERENTIAL
PULSE POLAROGRAPHY STUDIES OF TRACE TOXIC METALS
IN ENVIRONMENTAL, BIOLOGICAL AND DRUG SAMPLES
AFTER PRECONCENTRATION OF THEIR COMPLEXES**

by

MOHAMMAD ALI TAHER

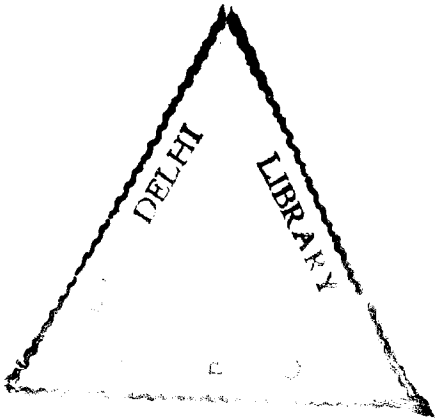
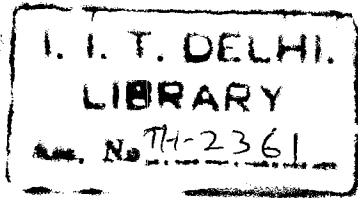
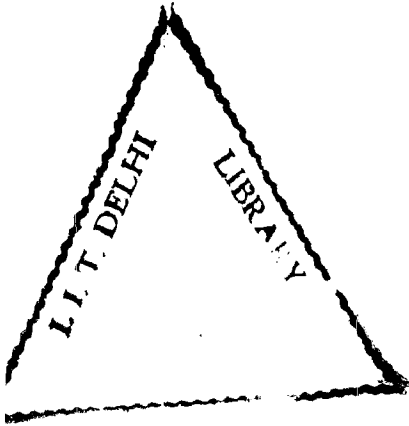
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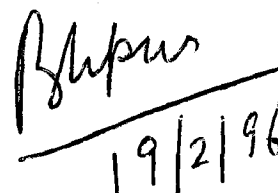
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CERTIFICATE

This is to certify that the thesis entitled "DERIVATIVE SPECTRO-PHOTOMETRY AND DIFFERENTIAL PULSE POLAROGRAPHY STUDIES OF TRACE TOXIC METALS IN ENVIRONMENTAL, BIOLOGICAL AND DRUG SAMPLES AFTER PRECONCENTRATION OF THEIR COMPLEXES" being submitted by Mr. Mohammad Ali Taher to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. Taher has worked under my guidance and supervision and has fulfilled the requirements for 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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SUMMARY

The thesis consists of five chapters. Each chapter has been subdivided into various sections dealing with introduction, experimental, 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, a brief introduction to the fundamentals of derivative spectrophotometry and the present work have also been described in this chapter.

The chemistry and analytical applications of 2-nitroso-1-naphthol-4-sulfonic acid (Nitroso-S) have been described in the second chapter. A systematic survey of the literature relating to extraction-polarographic determination of antimony, tin, cadmium, copper, lead and thallium has been carried out in order to compare these methods with methods developed in the present work. Differential pulse polarography (DPP) has been applied for the determination of trace amount of antimony, tin, cadmium, copper, lead and thallium after adsorption of their 2-nitroso-1-naphthol-4-sulfonic acid onto

microcrystalline naphthalene. The 2-nitroso-1-naphthol-4-sulfonic acid of metal ions are adsorbed onto microcrystalline naphthalene at optimum pH. The metal complexes are desorbed with HCl and determined with a differential pulse polarography. The various parameters such as reversibility of electrode reaction process, effect of pH on adsorption, volume of aqueous phase, and interference of a number of metal ions have been studied. The determination of these metals has been carried out in various complex materials e.g. environmental samples, standard alloys, biological, pharmaceutical and synthetic samples.

The third chapter consists of a brief introduction to the analytical applications of 1-(2-pyridylazo)-2-naphthol as a complexing reagent. A systematic survey of literature has also been cited for those metal ions which are studied in this chapter. Differential pulse polarographic methods has been developed for bismuth, cadmium, copper, indium, lead and uranium. The 1-(2-pyridylazo)-2-naphthol (PAN) of these metals are adsorbed onto microcrystalline naphthalene at optimum pH. After desorption with HCl, these metals were determined by a differential pulse polarography. Lead and cadmium have also been studied in this chapter and a selective polarographic method has been developed for simultaneous determination of these metals. The various parameters such as reversibility of electrode reaction process, effect of pH on adsorption, volume of the aqueous phase, and interference of a number of metal ions have been studied. The developed method has been applied for the trace determination of these metals in various standard alloys, environmental, synthetic and biological samples.

The fourth chapter consists of a systematic survey of the literature relating to extraction-spectrophotometric and derivative spectrophotometric determination of cobalt, copper, manganese, nickel, silver and vanadium in order to compare these methods with methods developed in the present work. The preparation of the adsorbent, buffer solution and metal ions solution have also been described. Adsorption behaviours of cobalt, copper, manganese, nickel, silver and vanadium with 2-nitroso-1-naphthol-4-sulfonic acid-tetradecyldimethylbenzylammonium chloride onto microcrystalline naphthalene or in the column method and their subsequent determination by derivative spectrophotometry have been described. After adsorption, the metal complexes are dissolved in dimethylformamide (DMF) and determined with derivative spectrophotometry. The column method using 2-nitroso-1-naphthol-4-sulfonic acid-tetradecyldimethylbenzylammonium-naphthalene adsorbent has also been used for cobalt. Various parameters like the effect of pH on adsorption, aqueous phase volume, reagent concentration, naphthalene and diverse ions have been studied. The developed method has been applied for the trace determination of these metals in various standard alloys, biological and synthetic samples.

The last chapter deals with the systematic survey of the literature relating to extraction-spectrophotometric and derivative spectrophotometric determination of iridium, iron, palladium and rhodium. The preparation of the adsorbent, buffer solution and metal ions solution have also been described. Adsorption behaviours of copper, iridium, iron, manganese, palladium, rhodium and vanadium with 1-(2-pyridylazo)-2-naphthol (PAN) onto microcrystalline

naphthalene or in the column method has also been discussed. After adsorption, the metal complexes are dissolved in dimethylformamide and determined with derivative spectrophotometry. The column method using (PAN)-naphthalene adsorbent have been used for iron and palladium only. Various parameters like effect of pH on adsorption, aqueous phase volume, reagent concentration, naphthalene and diverse ions have been studied. The developed method has been applied for the trace determination of these metals in various standard alloys, biological and synthetic samples.

The thesis has been appended with the reprints of three research papers published and the list of research papers submitted out of this research work.

ABBREVIATIONS AND SYMBOLS USED

μA	microampere
V	volt
v	scan rate
i	current in μA through the system
i_d	diffusion current
E	potential in volts
t	drop time in second
m	rate of flow of mercury in mg sec^{-1}
$E_{1/2}$	half-wave potential
i_p	peak or summit current
E_p	peak or summit potential
i_{pa}	anodic peak current
i_{pc}	cathodic peak current
E_{pa}	anodic peak potential
E_{pc}	cathodic peak potential
n	number of electrons involved in the electrode reaction process
S.C.E	standard calomel electrode
D	diffusion coefficient in $\text{cm}^2 \text{sec}^{-1}$
$E_{3/4}$	potential at, $i=3/4 i_d$
$E_{1/4}$	potential at, $1/4 i_d$
T	temperature in degree absolute
R	gas constant

F	Faraday
C-V	current voltage
A	absorbance
λ	wavelength
ϵ	molar absorptivity, $\text{L mol}^{-1} \text{cm}^{-1}$
nitroso-S	2-nitroso-1-naphthol-4-sulfonic acid
PAN	1-(2-pyridylazo)-2-naphthol
TDBA	tetradecyldimethylbenzylammonium
DMF	dimethylformamide

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