ANALYTICAL APPLICATIONS OF SOME THIAZOLYLAZO COMPOUNDS FOR TRACE DETERMINATION OF TOXIC METALS IN COMPLEX SAMPLES

by

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Submitted
in fulfilment of the requirements of the degree of
DOCTOR OF PHILOSOPHY

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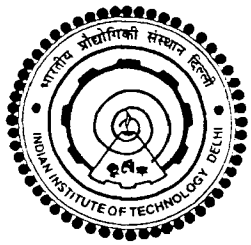

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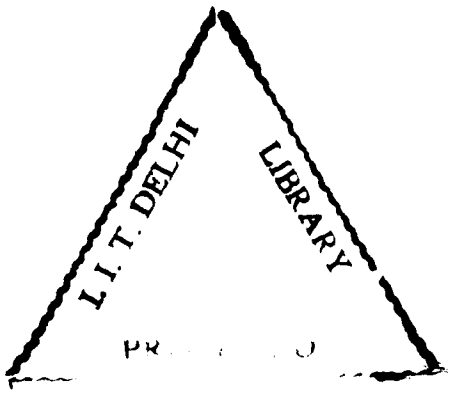

Dedicated to my parents

CERTIFICATE

This is to certify that the thesis entitled **"ANALYTICAL APPLICATIONS OF SOME THIAZOLYLAZO COMPOUNDS FOR TRACE DETERMINATION OF TOXIC METALS IN COMPLEX SAMPLES"** being submitted by **Miss Anju Bhalotra** to the Indian Institute of Technology, Delhi, for the award of degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by her. Miss Anju Bhalotra has worked under my guidance and supervision, and has fulfilled the requirements for the submission of the 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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Anju Bhalotra

Anju Bhalotra

ABSTRACT

The thesis deals with trace analysis of toxic metal ions by exploring the analytical potential of thiazolylazo compounds. The outcome of the experiments are development of methods for rapid, sensitive and reliable determination of metal ions at trace levels. The thesis has been divided into five chapters and each chapter has been further subdivided into various sections.

The first chapter deals with the general introduction to organic chelating agents with special emphasis on chemistry and analytical properties of thiazolylazo compounds. The advantages of using third component for the trace analysis of metal ions have also been discussed. This has been followed by brief theory about various preconcentration techniques and their merits and demerits with special reference to the novel solid phase extraction technique i.e. separation of metals by co-precipitation of their chelates onto microcrystalline naphthalene. An introduction to the fundamentals of derivative spectrophotometry, polarography, differential pulse polarography and cyclic voltammetry has also been described in this chapter. The importance of 'chemometrics' in analytical chemistry has also been briefed. The scope of present work has also been given.

The second chapter highlights the past work on the reagent 2-(2-thiazolylazo)-5-dimethylaminobenzoic acid. The spectrophotometric methods reported in the literature for the aqueous phase determination of Ni, Rh and Cu and extraction/direct determination of Pd and V have been briefed and the existing gaps explored. In this chapter, nature, sources and preparation of various starting materials, namely ligand, buffer solutions, metal ion solutions

and their standardization have been described. Various parameters viz. effect of pH, buffer volume, reagent concentration, the amount of third component have also been studied. The simultaneous determination of palladium and nickel using derivative spectrophotometry technique has also been studied. The effect of diverse ions on the quantification of above metal ions has also been reported. The analytical performance was evaluated by determining the linear range, sensitivity, detection limit, correlation coefficient and relative standard deviation. The accuracy and applicability of these methods developed have been verified by analyzing various standard alloys, biological and environmental samples.

The third chapter starts with the survey of the literature on the reagent 2-(2-thiazolylazo)-5-dimethylaminophenol. This has been followed by past work on the extraction spectrophotometric determination of Ni, Cu, and Rh and direct/extraction spectrophotometric methods of Bi, Co, Ir, and Ru. The materials used and general procedure followed for the determination of Ni, Co, Cu, Bi, Ir, Rh and Ru have been described. Various parameters viz. pH, buffer volume, reagent concentration, amount of naphthalene, flow rate, aqueous phase volume, amount of adsorbent, choice of counter ion and solvents are optimized. The various analytical parameters have also been calculated. The effect of diverse ions has also been studied for the above metal ions in order to determine their contents in various alloys, environmental and biological samples.

In fourth chapter, a systematic survey of the literature relating to 1-(2-thiazolylazo)-2-naphthol has been described. The direct/extraction spectrophotometric methods reported in literature for the determination of Zn,

Mn, Cd, Sc and Ga have been discussed in order to compare with the present work. The materials and procedure used for the quantification of the above metals have been described. Various parameters similar to those mentioned in Chapter III have been evaluated for the above metal ions and conditions have been developed for their determination in various standard alloys, environmental and pharmaceutical samples.

The fifth chapter starts with the literature relating to extraction-polarographic determination of Bi, Cd, Cu, In, Pb and U in order to compare these methods with those developed in the present work. The preparation of metal ion solutions, buffer solutions and other solutions has also been discussed. Various parameters like the effect of pH on adsorption, reagent concentration, buffer volume, amount of adsorbent, amount of counter ion, aqueous phase volume, and effect of diverse ions have been studied in detail for the adsorptive extraction of above metals. After adsorptive extraction, the metal ions were stripped with HCl of appropriate concentration. The differential pulse polarograms were recorded in presence of suitable supporting electrolyte. The reversibility of the electrode reaction process of these metal ions was established by cyclic voltammetry. The various analytical parameters were also calculated. The developed method has been tested successfully for the estimation of these metal ions in various alloys, biological, environmental and pharmaceutical samples.

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

ABBREVIATIONS AND SYMBOLS USED

μA	microampere
nA	nanoampere
V	volt
v	scan rate
i	current in microampere through the system
i_d	diffusion current
E	potential in volts
t	droptime in seconds
m	rate of flow of mercury in mg/sec
$E_{1/2}$	halfwave potential
i_p	peak or summit current
i_{pc}	cathodic peak current
i_{pa}	anodic peak current
E_p	peak or summit potential
E_{pc}	cathodic peak potential
E_{pa}	anodic peak potential
D	diffusion coefficient in cm^2/sec
n	number of electrons involved in the electrode process
T	temperature in absolute scale
R	gas constant
A	absorbance

C-V	current-voltage
λ	wavelength
ε	molar absorptivity, L mol^{-1} cm^{-1}
DMF	dimethylformamide
ATPB	ammonium tetraphenylborate
TAMB	2-(2-thiazolylazo)-5-dimethylaminobenzoic acid
TAM	2-(2-thiazolylazo)-5-dimethylaminophenol
TAN	1-(2-thiazolylazo)-2-naphthol
SLS	sodium lauryl sulphate
CTMAB	cetyltrimethylammonium bromide
TDBA	tetradecyldimethylbenzylammonium

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