

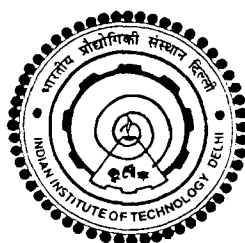
**ANALYTICAL APPLICATIONS OF SOME
THIAZOLYLAZO COMPOUNDS FOR TRACE
DETERMINATION OF TOXIC METALS
IN COMPLEX SAMPLES**

by

ANJU BHALOTRA
Department of Chemistry

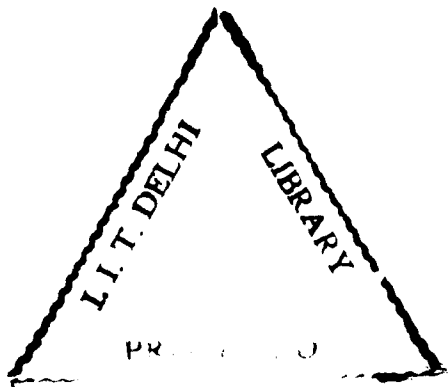
Submitted
in fulfilment of the requirements of the degree of
DOCTOR OF PHILOSOPHY

to the



INDIAN INSTITUTE OF TECHNOLOGY, DELHI
APRIL 2000

I. I. T. DELHI.
LIBRARY
No. TH-2702



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.



B.K. Puri

Professor, Department of Chemistry,

Indian Institute of Technology,

New Delhi- 110016, India.

Acknowledgements

I place on record my deep sense of gratitude to my worthy guide, **Prof. B.K. Puri** who has been a source of unabated inspiration and encouragement to me. He has also rendered invaluable guidance, expert criticism, timely direction and viable solution to the problems during my research work.

I also express my thanks to Prof. M.N. Gupta, Head of the Chemistry Department, I.I.T. Delhi, for providing necessary facilities. I am also grateful to Prof. H.M. Chawla, Chairman DRC, and other members of the faculty for their advice and cooperation.

The financial assistance from Council of Scientific and Industrial Research (CSIR), New Delhi and the various research facilities provided by Indian Institute of Technology, Delhi are gratefully acknowledged.

I am also thankful to Mr. Narain Singh(SLA) for helping in the laboratory work and Mr. Prasad for neat and prompt drafting of figures.

My sincere thanks to my friends Neeti, Padmavathy, Jyotsna, Ipsita, Kanika, Sneha, Chitra and Neena for their valuable support.

I also owe my thanks to my friend and lab colleague Patrick for his full cooperation, fruitful suggestions and timely help during my research work.

I am also thankful to my sister Neerja, brother-in-law Girish for affection and encouragement and little imp, Harshit, who would never fail to cheer me up with his antics.

Extra special thanks go to my parents for their blessings and guidance. They have been a source of emotional boost during my monotonous moments.

Finally I want to thank the Almighty for sustaining and blessing me with knowledge and capacity to learn.

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

CONTENTS

	Page No.
CERTIFICATE	(i)
ACKNOWLEDGEMENTS	(ii)
ABSTRACT	(iv)
LIST OF FIGURES	(vii)
ABBREVIATIONS AND SYMBOLS USED	(x)

CHAPTER I INTRODUCTION

1.1	Organic Complexing Reagents	1
1.2	Thiazolylazo Compounds As Analytical Reagents	6
1.3	Other Applications Of Thiazolylazo Compounds	9
1.4	Third Component In Complexation Reactions	9
1.5	Preconcentration	10
1.6	Determination Techniques	16
1.7	Chemometrics	41
1.8	Present Work	48
	References	50

CHAPTER II DERIVATIVE SPECTROPHOTOMETRIC

DETERMINATION OF Ni, Pd, Rh, V AND Cu IN AQUEOUS PHASE USING 2-(2-THIAZOLYLAZO)- 5-DIMETHYLAMINO BENZOIC ACID

2.1	2-(2-Thiazolylazo)-5-Dimethylaminobenzoic Acid As Reagent	55
2.2	Past work on Spectrophotometric Determination of Nickel, Palladium, Rhodium, Vanadium and Copper	56

2.3	Experimental	65
2.4	Results and Discussion	67
2.5	Zero Crossing Method For Simultaneous Determination Of Nickel and Palladium	79
2.6	Analytical Applications	82
	References	87

CHAPTER III DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF Ni, Co, Cu, Bi, Ir, Rh AND Ru AFTER SOLID PHASE EXTRACTION USING 2-(2- THIAZOLYLAZO)-5-DIMETHYLAMINOPHENOL

3.1	2-(2-Thiazolylazo)-5-Dimethylaminophenol As Reagent	92
3.2	Past Work On Spectrophotometric Determination Of Nickel, Copper, Cobalt, Bismuth, Iridium, Rhodium and Ruthenium	93
3.3	Experimental	103
3.4	Results and Discussion	106
3.5	Analytical Applications	121
	References	128

CHAPTER IV DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF Zn, Mn, Cd, Sc AND Ga AFTER SOLID PHASE EXTRACTION USING 1-(2- THIAZOLYLAZO)-2-NAPHTHOL

4.1	1-(2-Thiazolylazo)-2-Naphthol As Reagent	133
4.2	Past Work On Spectrophotometric Determination Of Zinc, Manganese, Cadmium, Scandium and Gallium	134
4.3	Experimental	142

4.1	Results and Discussion	143
4.5	Analytical Applications	155
	References	161

**CHAPTER V DIFFERENTIAL PULSE POLAROGRAPHIC
DETERMINATION OF Bi, Cd, Cu, In, Pb AND U
AFTER SOLID PHASE EXTRACTION USING 1-(2-
THIAZOLYLAZO)-2-NAPHTHOL**

5.1	Past Work On Polarography As An Analytical Technique	166
5.2	Experimental	178
5.3	Results and Discussion	180
5.4	Analytical Applications	197
	References	203
	Conclusions	207
	List of Publications	208
	Biodata of author	209

LIST OF FIGURES

Figure No.		Page No.
1.1	Structural representation of thiazolylazo compounds.	7
1.2	Coordination of metal with thiazolylazo compound.	7
1.3	Extensive π conjugation in thiazolylazo complexes.	8
1.4	Four fold interactions in solid phase extraction.	14
1.5	Different regions of electromagnetic spectrum.	17
1.6	First derivative spectrophotometry for the quantitative measurement of a small band alone and obscured by a broader overlapping band.	19
1.7	Influence of an impurity (Y) on normal, first and second derivative spectra of a substance(X).	22
1.8	Definition of graphical method.	24
1.9	Definition of zero crossing method.	24
2.1	Acid-base equilibria of TAMB.	55
2.2	Normal and derivative spectra, effect of pH and calibration plot of nickel using TAMB.	71
2.3	Normal and derivative spectra, effect of pH and calibration plot of palladium using TAMB.	72
2.4	Normal and derivative spectra, effect of pH and calibration plot of rhodium using TAMB.	73
2.5	Normal and derivative spectra, effect of pH and calibration plot of vanadium using TAMB.	74
2.6	Normal and derivative spectra, effect of pH and calibration plot of copper using TAMB.	75

2.7	Normal and derivative spectra of nickel, palladium and mixture using TAMB.	81
3.1	Acid-base equilibria of TAM.	92
3.2	Funnel tipped glass column for preconcentration.	102
3.3	Normal and derivative spectra, effect of pH and calibration plot of nickel using TAM.	110
3.4	Normal and derivative spectra, effect of pH and calibration plot of copper using TAM.	111
3.5	Normal and derivative spectra, effect of pH and calibration plot of cobalt using TAM.	112
3.6	Normal and derivative spectra, effect of pH and calibration plot of bismuth using TAM.	113
3.7	Normal and derivative spectra, effect of pH and calibration plot of iridium using TAM.	114
3.8	Normal and derivative spectra, effect of pH and calibration plot of rhodium using TAM.	115
3.9	Normal and derivative spectra, effect of pH and calibration plot of ruthenium using TAM.	116
4.1	Acid-base equilibria of TAN.	133
4.2	Normal and derivative spectra, effect of pH and calibration plot of zinc using TAN.	144
4.3	Normal and derivative spectra, effect of pH and calibration plot of manganese using TAN.	145
4.4	Normal and derivative spectra, effect of pH and calibration plot of cadmium using TAN.	146
4.5	Normal and derivative spectra, effect of pH and calibration plot of scandium using TAN.	147
4.6	Normal and derivative spectra, effect of pH and calibration plot of gallium using TAN.	148

5.1	Differential pulse polarogram, effect of pH and calibration plot of bismuth.	181
5.2	Differential pulse polarogram, effect of pH and calibration plot of cadmium.	182
5.3	Differential pulse polarogram, effect of pH and calibration plot of copper.	183
5.4	Differential pulse polarogram, effect of pH and calibration plot of indium.	184
5.5	Differential pulse polarogram, effect of pH and calibration plot of lead.	185
5.6	Differential pulse polarogram, effect of pH and calibration plot of uranium.	186
5.7	Cyclic voltammograms of Bi, Cd, Cu, In, Pb and U	191