

**TRACE DETERMINATION OF SOME TOXIC METALS IN
COMPLEX SAMPLES AFTER SOLID PHASE
EXTRACTION AS THEIR METAL-2-(-5-BROMO-2-
PYRIDYLAZO)-5-DIETHYLAMINOPHENOLATES**

By
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DEPARTMENT OF CHEMISTRY

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

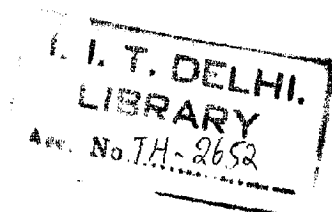
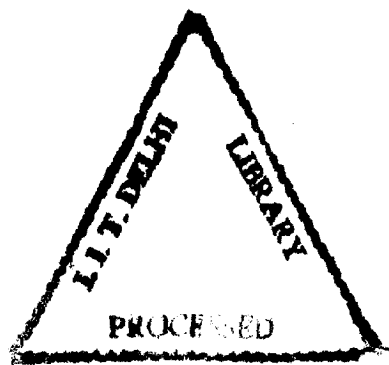
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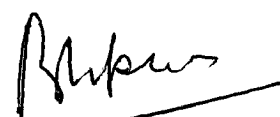
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CERTIFICATE

This is to certify that the thesis entitled "**TRACE DETERMINATION OF SOME TOXIC METALS IN COMPLEX SAMPLES AFTER SOLID PHASE EXTRACTION AS THEIR METAL-2-(-5-BROMO-2-PYRIDYLAZO)-5-DIETHYLAMINOPHENOLATES**" being submitted by **Mr. J. Patrick Pancras** to the Indian Institute of Technology, Delhi, for the award of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by him. Mr. J. Patrick Pancras 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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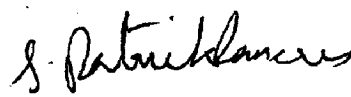
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ABSTRACT

The thesis has been divided into four chapters and each chapter has been further subdivided into various sections.

The first chapter starts with a discussion on the importance of preconcentration in trace analysis. Some of the widely used preconcentration techniques have been briefed. The new solid-phase extraction techniques i.e. 'Solid-liquid separation after liquid-liquid extraction' and 'separation of metals by co-precipitation of their chelates onto microcrystalline naphthalene' have been discussed. General introduction to organic reagents in analytical chemistry with special reference to the chemistry of N-heterocyclic azo dyes as complexing agents and their analytical applications have been included. The chelating behaviour and acid-base equilibrium of the title reagent 2-(-5-bromo-2-pyridylazo)-5-diethylaminophenol have also been incorporated. Besides, statistical treatment of data and the scope of the present work have also been given.

The second chapter starts with a brief introduction to derivative spectrophotometric determination of analytes in uv/visible region. This has been followed by a summary of the literature for the extraction/direct spectrophotometric determination of Co, V, Zr, Sb, Pd, U, Ir and Rh. The preparation of the adsorbent, buffer solutions and metal ion solutions has also been described. The optimum conditions for the preconcentration such as pH, reagent concentration, amount of

extracting solid, effect of counter ion, shaking time and aqueous phase volume have also been discussed. The possibility for the simultaneous determination of 'Ir and Rh' and 'V and Zr' has been explored using derivative spectrophotometry. Effect of various diverse ions on the preconcentration and derivative spectrophotometric determination of metal ions of interest has been studied. The accuracy and applicability of these methods developed have been verified by analyzing various standard environmental, biological and alloys samples.

The third chapter starts with a brief introduction to different voltammetric techniques such as d.c. polarography, differential pulse polarography and cyclic voltammetry for the determination of electro-active metals. Literature relating to extraction-polarographic determination of Bi, Pb, In, Cd, Ni, Zn and Mn has been high-lighted to compare these methods with those developed in the present work. The preparation of the adsorbent, buffer solutions and metal ion solutions has also been discussed. Various parameters like the effect of pH on adsorption, reagent concentration, buffer volume, amount of naphthalene/benzophenone, aqueous phase volume and effect of diverse ions have been studied in detail for the adsorptive extraction of metals such as Bi, Pb, In, Cd, Ni, Zn and Mn. After the adsorptive extraction, the metal ions were stripped with HCl of appropriate concentration. Differential pulse polarogram was run after the addition of a supporting electrolyte, if required. The reversibility mechanism of the electrode reduction was established using cyclic voltammetric studies at the

mercury drop working electrode. The accuracy and applicability of the proposed method have been evaluated by employing the developed procedure on various alloys, environmental and biological samples.

The fourth chapter starts with a brief introduction to the atomic absorption spectrometric determination of Cu, Fe, Ni, Cr and Zn. This has been followed by a systematic literature survey relating to the FAAS determination of the above mentioned metal ions. Conditions for the extraction of Cr-5-Br-PADAP into molten naphthalene method has been discussed. Column method has been developed for Ni, Cu, Zn and Fe. The adsorbent 5-Br-PADAP-TPB-naphthalene has been prepared and used for the column preconcentration. In all the cases, the whole complex along with the adsorbent was dissolved in 10 ml of DMF and the final solution was directly aspirated into the flame of AAS. Various parameters like pH, flow rate, aqueous phase volume, reagent concentration, amount of naphthalene, and effect of diverse ions have been studied. The characteristic concentration for both, DMF medium(developed method) and aqueous medium(after stripping the metal with acid) have been compared. The developed method has been applied for the determination of these metals in Alloys, biological samples, environmental samples and waste water samples.

The thesis has been appended with the list of publications and reprints of the papers published.

CONTENTS

CERTIFICATE	(i)
ACKNOWLEDGEMENTS	(ii)
ABSTRACT	(iii)
CHAPTER I: INTRODUCTION	1
1.1 Preconcentration	2
1.2 The Novel Solid Phase Extraction	8
1.3 Organic reagents in Analytical Chemistry	9
1.4 Statistical Treatment of Data	19
1.5 Present Work	24
References	26
CHAPTER II: DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF V, Co, Sb, Zr, Rh, Ir, Pd and U	
2.1 Derivative Spectrophotometry	32
2.2 Past Work on spectrophotometric Determination of V, Co, Sb, Zr, Rh, Ir, Pd and U	45
2.3 Experimental	58
2.4 Results and Discussion	62
2.5 Simultaneous Determination	81
2.6 Sample Analysis	91
References	100

CHAPTER III: DIFFERENTIAL PULSE POLAROGRAPHIC DETERMINATION OF Bi, Pb, In, Cd, Ni, Zn and Mn

3.1	Introduction to Polarography	107
3.1A	Analytical Aspects	122
3.2	Past Work on Polarography as an Analytical Technique	126
3.3	Experimental	139
3.4	Results and Discussion	143
3.5	Sample Analysis	163
	References	170

CHAPTER IV: ATOMIC ABSORPTION SPECTROMETRIC DETERMINATION OF Cu, Fe, Ni, Zn and Mn

4.1	Fundamental Concepts of AAS	175
4.2	Past Work on Spectrophotometry and Flame AAS Determination of Cu, Fe, Ni, Zn and Mn	186
4.3	Experimental	192
4.4	Results and Discussion	195
4.5	Application to Analysis of Complex materials	205
	References	211
	List of publications	216