PREFACE

In the past thirty years, there has been considerable progress in atomic absorption spectrometry (AAS), an analytical instrumental probe which may be used directly for the determination of about 70 elements at the trace level. This has given a great boost for working in the field of analytical chemistry. But a considerable number of elements may not be determined directly by AAS or may have low sensitivity in the conventional instrumentation for atomization, viz. flame, electrothermal, hydride generation or cold vapour atomization. In order to extend the range of application of AAS and to increase the attainable sensitivity for those elements where it is inadequate for trace analysis, much attention has been devoted recently to the development of indirect AAS methods of analyses of many elements. Thus non-metals or organic compounds or radicals which form organometallic complexes or insoluble salts with metallic ions or show certain chemical interferences in the determination of some metals can be subjected to indirect AAS determination. The success of indirect methods of analyses by AAS and their applicability to practical analyses, depends
on the degree to which the selectivity for the determination of the species concerned can be retained via the chemical reaction utilized before the final atomization and absorbance measurement. Even if some loss of selectivity is experienced owing to the nature of the initial chemical reaction employed, this may be compensated by enhanced sensitivity of the method developed in AAS.

The present work has been aimed to determine the analytes based on complex formation in presence of another ligand, either as an ion-pair or as an inner-metallic complex, extraction of the complex into an organic solvent and aspiration of the organic phase into flame AAS or autoinjected into electrothermal AAS (ETAAS). Then the concentration of the metal is determined and hence indirectly the analyte concentration is determined at the trace level.

The present dissertation proposes new indirect AAS methods for the determination of four inorganic anions and three organic compounds in diverse matrices. There are 9 Chapters in the dissertation; of which first two chapters introduce to the principle of AAS and all about indirect AAS technique, while Chapters 3-9 describe the experimental part.

Chapter 1 gives a brief description on the theory, instrumentation and analytical performances of atomic absorption spectrometry.
Chapter 2 includes a comprehensive review of about 300 references on the indirect AAS methods available for certain non-metals, organic compounds and certain less AAS sensitive metals, including its application in various fields of our interest.

An indirect method for the determination of inorganic sulphate in human blood serum by AAS has been described in Chapter 3. In this method, sulphate forms a stable ion-association complex, \([\text{Cu(neocuproine)}_2\text{SO}_4]\) in neutral medium which can be extracted into isobutyl methyl ketone (IBMK) with an efficiency greater than 98.0%.

Chapter 4 proposes the determination of free cyanide in industrial waste effluents. In an alkaline medium, cyanide forms a stable complex species \([\text{Cu(BPTC)(CN)}]^-\) (where BPTC = 2-benzoyl pyridine thiosemicarbazone) which can be extracted into a mixture of IBMK-isopentyl alcohol (7:1) with an efficiency greater than 98.0%. The extract can be analysed directly for copper (and hence indirectly for cyanide) by flame AAS.

The same complex species \([\text{Cu(BPTC)}]^+\) has also been utilized for thiocyanate determination in biological fluids by indirect AAS and detailed experimental work has been presented in Chapter 5. The complex is extracted into isopentyl acetate and aspirated into air-\(\text{C}_2\text{H}_2\) flame of the AAS and copper content in the organic extract measured and related to thiocyanate concentration.
Chapter 6 presents the determination of perchlorate by indirect AAS based on the formation of ion-association complex \([\text{Co(BPTC)}_2]^+\text{(ClO}_4\text{)}\), extraction of the ion-pair into IBMK in acidic medium and subsequent determination of cobalt in organic phase. The method was applied for perchlorate determination in human blood serum samples spiked with perchlorate, urine and commercial chlorate sample.

The same complex species \([\text{Co(BPTC)}_2]^+\) has also been used for anionic surfactant (as sodium dodecyl sulphate, SDS) determination. The method was successfully applied for its determination in waste water, commercial liquid detergents and toothpastes. The results have been presented in Chapter 7.

Chapter 8 describes an AAS method for determination of cationic surfactants in waste and hair rinsers. The method involves an ion-pair formation between cationic surfactant and hexanitro cobaltate(III) anion, extraction of the ion-pair into 1,2-dichloroethane and determination of cobalt concentration in organic phase by ETAAS, thus indirectly determining cationic surfactant concentration.

Salicylic acid (SA) has been determined in pharmaceuticals viz. ointments via the ion-pair formation with \([\text{Co(BPTC)}_2]^+\) and the work is presented in Chapter 9. The ion-pair was extracted into IBMK, the organic phase aspirated into flame AAS, the cobalt content determined and hence indirectly salicylic acid was determined.
The novelty of the present methods depicted above may be described as follows: sulphate, in its sensitivity and unique applicability; cyanide, in its selectivity to determine free cyanide; thiocyanate, in its unique application to determine smoker-nonsmoker status; perchlorate, due to its better limit of detection and sensitivity values than the existing methods; anionic detergents, in its low blank value and wide range of analyte determination; and salicylic acid, nevertheless, provides an alternative to the existing methods, which is not interfered by a large number of organic compounds.