

**APPLICATION OF ION-SELECTIVE  
ELECTRODES AND SPECTRAL METHODS  
FOR METAL ION ANALYSIS**

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**THESIS**

Submitted in Partial Fulfilment of the Requirements  
of M.Sc. Degree in **Chemistry**

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*Presented by*

**ADEL EL-SAYED MOHAMED ALI**

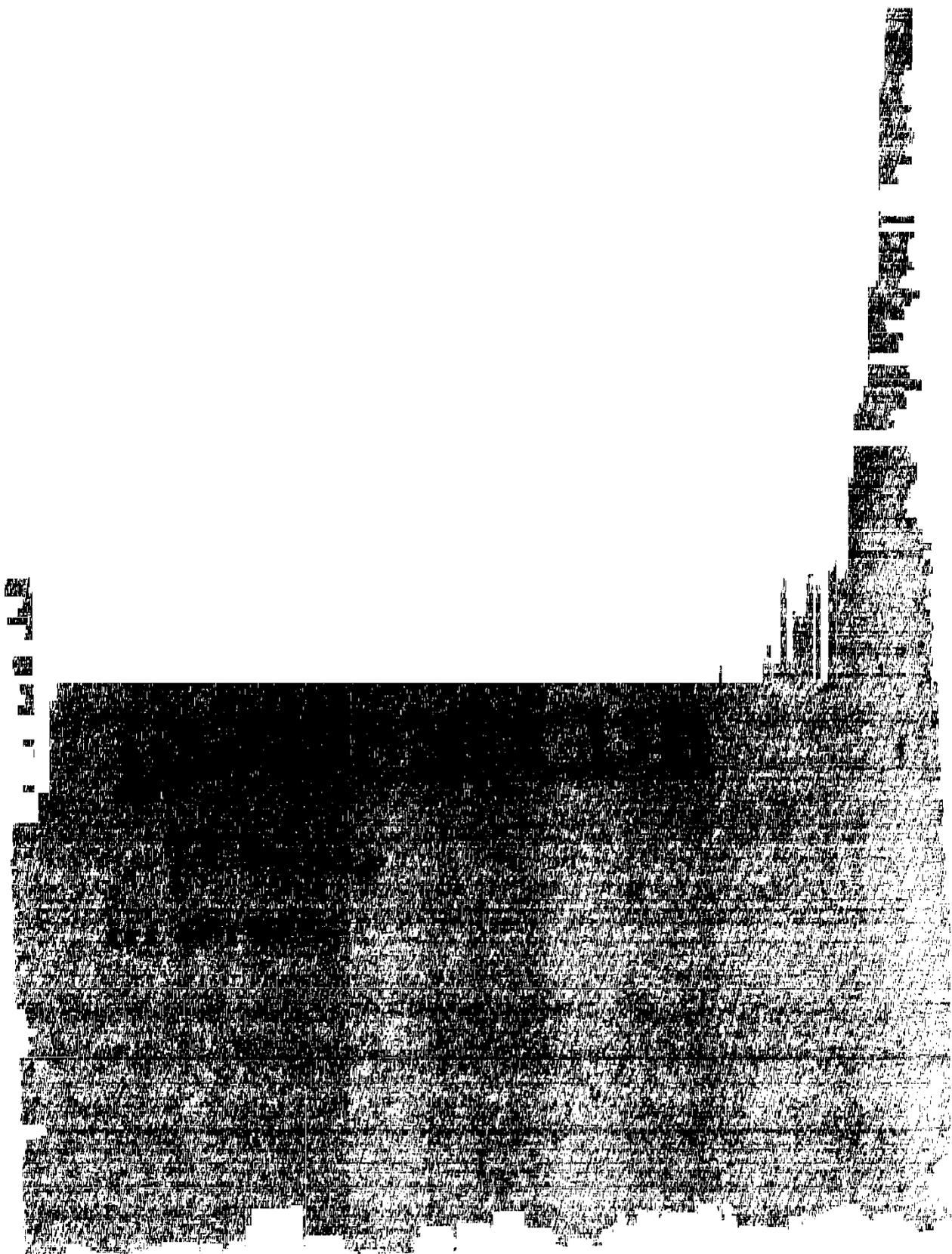
B.Sc. (1983)

**Ain Shams University**

**Faculty of Science**

**Cairo, A.R.E.**

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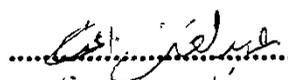
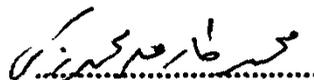
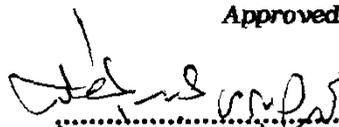
**Thesis Advisors**

**Prof. Dr. M.S. Abdel-Mottaleb**

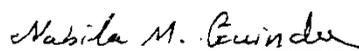
**Prof. Dr. M.T.M. Zaki**

**Dr. Abdel-Ghani Ragheb**

**Approved**



**Prof. Dr. N.M. Guindy**



**Head of Chemistry Department**

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### NOTE

Beside the work carried out in this thesis, the student had attended post-graduate courses for one year in Analytical and Inorganic Chemistry including the following topics:

1. Advanced instrumental analysis.
2. Advanced separation techniques.
3. Inorganic reaction mechanism.
4. Group theory and its applications.
5. Organometallic chemistry.
6. Advanced electrochemistry.
7. Nuclear and radiation chemistry.
8. Computer science and its application in chemistry.

He had successfully passed an examination in these topics.

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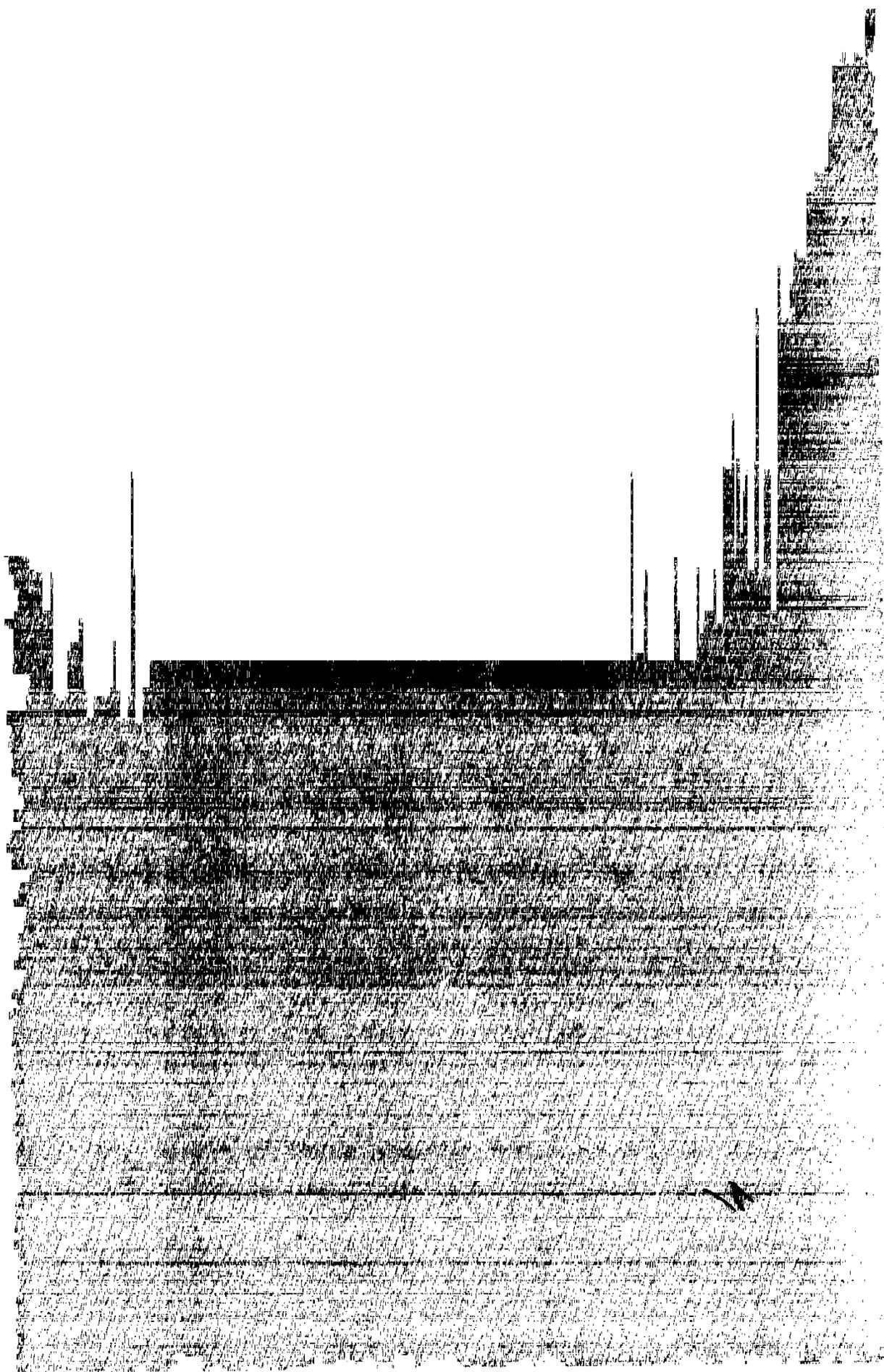
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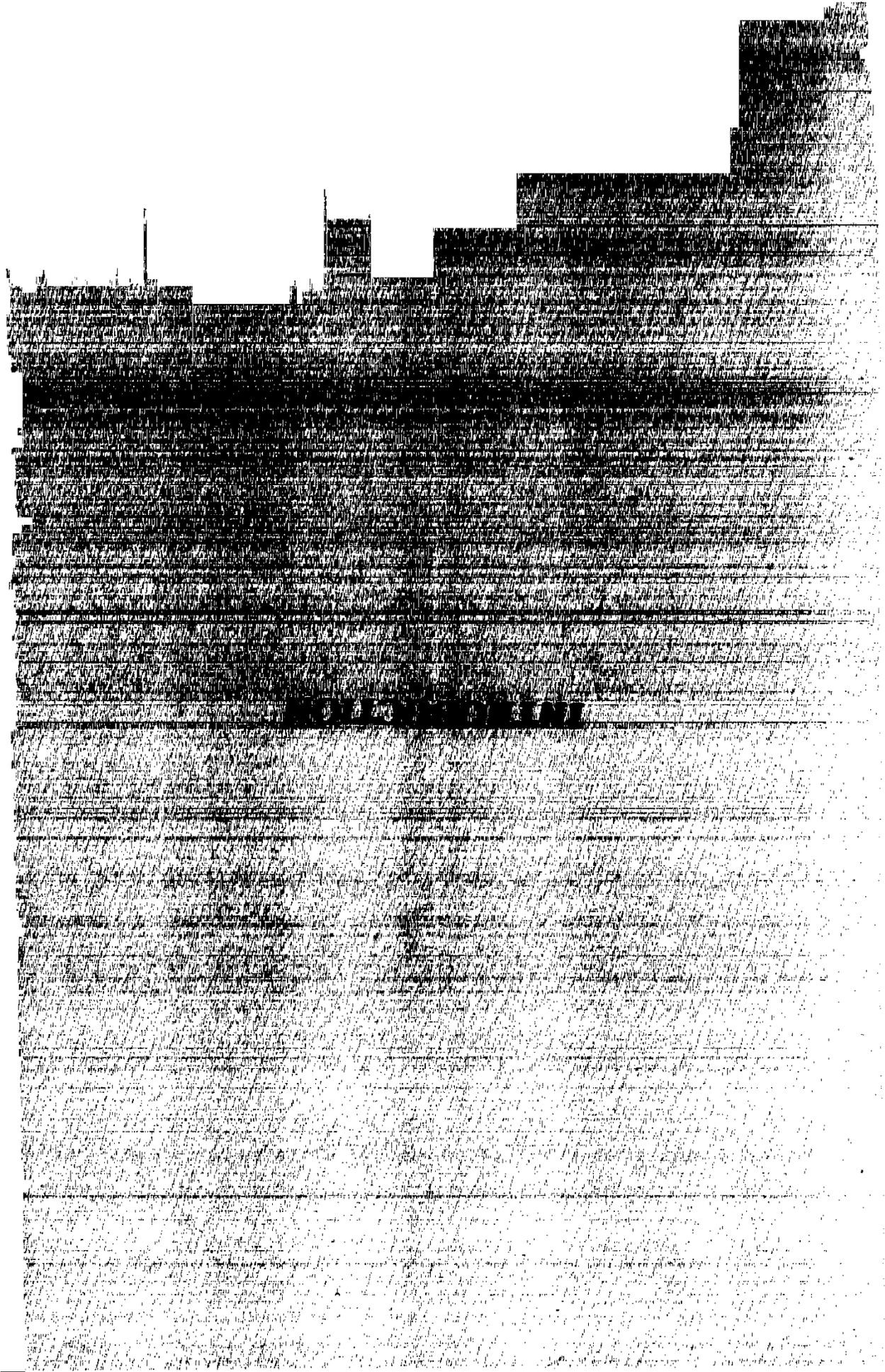
### AIM OF THE WORK

The aim of the present work is to investigate spectrophotometrically, the complexes formed by reaction of zinc(II) with hematoxylin and murexide in aqueous medium. The influence of cationic, anionic and nonionic surfactants, on the spectral characteristics of the binary chelates will be examined. The effect of pH, reagent and surfactant concentrations, standing time and diverse ions will be studied to select the optimum experimental conditions for zinc(II) determination. The stoichiometry of the formed chelates in aqueous and micellar media, and their molar absorptivities will be determined. The applicability of the proposed methods will be tested by determining zinc in aluminium metal and some aluminium-base alloys.

Moreover, potentiometric methods for the determination of silver(I), palladium(II) and gold(III) in their individual states or in binary mixtures, by titration with a standard solution of potassium iodide, using the iodide ion-selective electrode as sensor, will be investigated. The effect of foreign ions and analate pH, on the shape of the titration curves and the success of the analysis will be studied.

**PART I**

**Spectrophotometric Determination of Zinc(II)  
in Aqueous and Micellar Media**



## INTRODUCTION

### A. Spectrophotometric Determination of Zinc(II) in Aqueous Medium:

Several spectrophotometric methods for the determination of zinc(II) were reported. Dithizone, Zincon, PAN, Methylthymol Blue, Xylenol Orange, Semimethylthymol Blue and PAR were the most commonly used reagents.

The dithizone method is the most sensitive extraction-spectrophotometric method for zinc determination. The molar absorptivity of the zinc-dithizone complex in carbon tetrachloride was  $9.26 \times 10^4$  l.mol.<sup>-1</sup>cm<sup>-1</sup> at 538 nm. Using the correct pH and masking agents, the dithizone method proved to be specific for zinc<sup>[1,2]</sup>. Thiosulphate was commonly utilized as a masking agent. At pH 4.0-5.5 (acetate buffer), thiosulphate formed stable complexes with Cu, Ag, Hg, Bi, Pb and Cd, thus preventing the reactions of those metal ions with dithizone. At higher concentrations of those metals, it was advisable to add small amounts of cyanide as masking agent. Thiourea, dithiocarbamates and iodide were also used for masking interfering metal ions<sup>[3,4]</sup>.

Moreover, McClellan and Sabel<sup>[5]</sup> separated zinc from nickel and Cobalt by taking advantage of the difference of extraction rate of these metals with dithizone. On the other hand, Manita<sup>[6]</sup> determined zinc with dithizone in a one phase alcohol-water system, at pH 11, using an alcoholic solution of dithizone.

The dithizone method has been used to determine zinc in some metals and alloys<sup>[3,7-9]</sup>, silicate rocks<sup>[10]</sup>, urine<sup>[11]</sup>, soil<sup>[12]</sup>, and

plant material<sup>[13]</sup>. Moreover, di-2-naphthylthiocarbazon which is an analogue of dithizone was also used for the determination of zinc<sup>[14]</sup>.

Zincon(2-carboxy-2'-hydroxy-5'-sulphoformazyl benzene) was first introduced by Yoe and Rush<sup>[15,16]</sup> as reagent for zinc. In slightly alkaline solution of pH 9, the formed blue complex exhibited a molar absorptivity of  $2.0 \times 10^4 \text{ l.mol.}^{-1}\text{cm}^{-1}$  at 625 nm. However a large number of metals interfered making it necessary to separate the zinc first<sup>[17,18]</sup>. Zincon had been used for zinc determination in biological materials<sup>[19,20]</sup>, plant materials<sup>[21]</sup>, water<sup>[22,23]</sup>, and lubricating oils<sup>[24]</sup>.

Kish et al.<sup>[25]</sup> reported a method for zinc determination based on reaction with Malachite Green. The molar absorptivity of the formed chelate ranged between  $5 \times 10^4$  and  $1.2 \times 10^5 \text{ l.mol.}^{-1}\text{cm}^{-1}$ , depending on the solvent used. This method was further modified by Dong and Yue<sup>[26]</sup>, who determined zinc by extracting the ion-association complex formed by reaction of the anionic zinc(II)-thiocyanate chelate with the cationic malachite green dye into toluene. The ion association complex was formed over a wide pH range (3-7). The method adhered to Beer's law in the concentration range 0-1.1  $\mu\text{g/ml}$  of zinc and was applied to the determination of zinc in drinking water.

Goldstein et al.<sup>[27]</sup> reported a method for the determination of zinc using 4-(2-pyridylazo)-resorcinol (PAR). The molar absorptivity