CHAPTER-I: Introduction

The determination of elements in microgram or even below has become a matter of great importance today and organic compounds serve in a variety of ways to simplify and facilitate procedures in inorganic analysis. During the last few decades heterocyclic azo dyes have received much attention as analytical reagents, with a wide range of applications. Heterocyclic azo dyes are compounds which contain the azo grouping, \(-\text{N= N-}\), in combination with a heterocyclic system and other groups such as aryl, \(-\text{OH}\), \(-\text{SO}_3\text{H}\) and \(-\text{AsO}_3\text{H}_2\), furnishing replaceable \(H\). Applications are due to the fact that a wide variety of azo dyestuffs are already available and also the ease with which the compounds can be synthesized by known methods. Other equally important factors are their valuable analytical properties such as highly sensitive colour reactions, stability and selectivity towards various metal ions. Two well known representatives of this class, PAN and PAR have been used in the spectrophotometric determination of more than fifty elements. They are also good metal indicators in complexometric titrations and have also been used as chromatographic spray reagents. A short account of the various types of heterocyclic azo dyes is given in this chapter.
Synthesis of tris-[2,4,6-(2-hydroxy-1-naphthylazo)]-s-triazine (THNT), tris-[2,4,6-(9-hydroxy-10-phenanthrylazo)]-s-triazine (THPT) and tris-[2,4,6-(2-hydroxy-1-sulpho-1-naphthylazo)]-s-triazine, trisodium salt (THST) are described in this chapter. Properties of the ligands viz., absorption spectra, molar absorptivities and results of elemental analyses are reported. Chemicals, instruments and methods used in the present investigations, including those for finding out the composition of complexes (using spectrophotometric technique) are reported. Preliminary investigations show that these dyes give colour reactions with a number of base metals, but the complexes formed with THNT and THPT are precipitated and are extractable in water-immiscible organic solvents. Some of the complexes of these dyes are unstable also. On the other hand THST is a water-soluble heterocyclicazo dye and the complexes formed with various base metals are also watersoluble. THST has therefore, been explored as an analytical reagent for the spectrophotometric determination of zinc (II), cadmium (II), mercury (II), manganese (II), iron (II), cobalt (II), nickel (II), lead (II), silver (I), thorium (IV), uranyl (II), bismuth (III), indium (III) and antimony (III).

THST complexes of silver, mercury, antimony and thorium have also been utilised as analytical reagents for the indirect determination of certain anions viz.
bromide, iodide, sulphide, thiosulphate, thiourea, thiosemicarbazide and phosphate.

CHAPTER-III: **Spectrophotometric Determination of zinc, Cadmium and Mercury**

This chapter has been divided into three parts. In each part are described investigations on the spectrophotometric determination of zinc, cadmium and mercury respectively.

A. Zinc

The dark brown zinc(II)-TET complex has a constant and maximum absorbance ($\lambda_{\text{max}}$ 510 nm) in the pH range 5.5-7.4. For full colour development of complex two times molar excess of TET is required. Beer's law range and optimum concentration range (as obtained from Ringbom plot) are 0.0-1.45 and 0.2-1.3 ppm respectively. The sensitivity of the colour reaction is $0.00145 \ \mu g \ \text{Zn(II)}/cm^2$, with molar extinction coefficient of $4.75 \times 10^4 \ \text{l.mol}^{-1} \ \text{cm}^{-1}$. Composition of the complex is 1:1 (metal : ligand). Effect of diverse ions has been studied. The reagent has been found to be a highly sensitive as well as selective for zinc (II) masking other metals by cyanide, iodide, thiosulphate, phosphate, arsenate and sulphide.

B. Cadmium

Cadmium (II) forms a dark brown complex with an aqueous solution of TET. The pH range for maximum and constant absorbance ($\lambda_{\text{max}}$ 510 nm) is 5.5-7.0. For complete complexation, two times molar excess of TET is required.
Beer's law range and optimum concentration limit (as obtained from Ringbom plot) are 0.0-2.4 and 0.25-1.7 ppm respectively. Sandell's sensitivity is 0.0021 \mu g Cd(II)/cm², molar extinction coefficient being $5 \times 10^4$ l.mol⁻¹ cm⁻¹. Composition of the complex has been found to be 1:2 (metal:ligand). In order to explore the selectivity of the reagent, a study on the effect of foreign ions in the determination of the metal has also been made.

C. Mercury:

Mercury (II) ions interact with an aqueous solution of THT to form two complexes, a dark red complex at low pH with $\lambda_{\text{max}}$ 550 nm and a blue complex at high pH with $\lambda_{\text{max}}$ 633 nm. The maximum and constant absorbance of the dark red complex is attained at pH 6.8-7.9 while blue complex has maximum absorbance above pH 10.6 and thus 3-8 ml of 0.04N sodium carbonate concentration is required to maintain the appropriate pH in the later case. Beer's law validity and optimum concentration range for accurate determination for dark red complex are 0.0-3.8 and 0.48-3.0 ppm respectively and for a blue complex are 0.0-3.63 ppm and 0.48-2.7 ppm respectively. Sandell's sensitivity of the colour reaction for the dark red complex is 0.0038 \mu g Hg(II)/cm², the molar extinction coefficient being $5.28 \times 10^4$ l.mol⁻¹ cm⁻¹. For the blue complex Sandell's sensitivity is 0.003 \mu g Hg(II)/cm² with a molar extinction coefficient $6.69 \times 10^4$ l. mol⁻¹ cm⁻¹. Only 4 moles of the reagent for the dark red complex and 10 moles of the reagent for the blue complex are needed for full colour development. The stoichiometries of the complexes determined by Job's method of continuous variations are, 1:2 (metal:ligand) for the dark red complex and 1:3 for the blue complex. The effect for diverse ions has also been studied in both the cases.
In this chapter, spectrophotometric determination of manganese, iron, cobalt and nickel are reported.

A. Manganese:

A dark brown complex of THT with manganese (II) ($\lambda_{\text{max}}$, 520 nm) has the maximum and constant absorbance in the pH range 5.8-7.3. For full colour development 2-times molar excess of THT is necessary. Beer's law range and optimum concentration range (as obtained from Ringbom plot) are 0.0-1.20 and 0.16-1.0 ppm respectively. Sandell's sensitivity for the colour reaction is $0.001 \mu g \text{Mn(II)}/cm^2$ with a molar extinction coefficient $5.5 \times 10^4 \text{Lmol}^{-1}\text{cm}^{-1}$. Composition of the complex is 2:3 (metal:ligand). The method is highly selective as the coloured complexes of the most of the other metal ions are masked by EDTA, cyanide, sulphide, thiosulphate, phosphate and arsenate easily.

B. Iron:

Iron (II) interacts with an aqueous solution of THT to form a dark red complex with maximum absorbance at 530 nm ($\lambda_{\text{max}}$) in the pH range 5.3-6.8. The colour development is instantaneous and absorbance remains constant up to 24 h. Beer's law is obeyed up to 0.9 ppm and the limit for accurate determination of the metal is 0.16-0.8 ppm. Sandell's sensitivity:
and molar extinction coefficient for the system are 0.0011 μg Fe(II)/cm² and 5x10⁴ l.mol⁻¹ cm⁻¹ respectively. Job's method of continuous variations reveals its composition to be 2:3 (metal:ligand). Effect of diverse ions on complex formation has also been studied. The reagent has been found to be a highly sensitive as well as selective for iron(II) masking other metals by iodide, acetylacetone, sulphide, thiosulphate, phosphate and arsenate. Zinc(II) and manganese (II) interfere.

C. Cobalt (II):

Cobalt (II) forms a dark brown complex with an aqueous solution of THT (λ max 500 nm) in the pH range 4.5-6.5. Full colour development of complex requires 4-times molar excess of THT. Beer's law range and optimum concentration range (as obtained from Ringbom plot) are 0.0-1.30 and 0.15-1.10 ppm respectively. Sandell's sensitivity for the colour reaction is 0.0016/μg Co(II)/cm², molar extinction coefficient being 3.7x10⁴ l.mol⁻¹ cm⁻¹. In order to explore the selectivity of the reagent, the effect of foreign ions in the determination of the metal has also been investigated.

D. Nickel:

A wine red coloured complex is formed by interaction of an aqueous solution of THT with nickel(II) exhibiting λ max at 570 nm, at pH 6.6-7.3. 3-Times molar excess of THT is required for complete complexation. Beer's law validity
and optimum concentration range for accurate determination are 0-1.2 and 0.13-1.1 ppm respectively. The sensitivity and the molar extinction coefficient are \( 0.0014 \, \text{mg} \, \text{M(II)} / \text{cm}^2 \) and \( 4.2 \times 10^4 \, \text{l.mol.}^{-1} \, \text{cm}^{-1} \) respectively. The stoichiometry of the complex is 2:1 (metal:ligand), as determined by Job's method. Effect of foreign ions has also been studied to assess the selectivity of the method.

CHAPTER-V: Spectrophotometric Determination of Lead, Silver, Thorium and Uranium

In this chapter, spectrophotometric determination of lead, silver, thorium and uranium has been explained.

A. Lead

Lead (I\(^{+}\)) ions interact with an aqueous solution of THT to form two complexes, a dark red complex at neutral pH with \( \lambda_{\text{max}} \) 545 nm and a blue complex at high pH with \( \lambda_{\text{max}} \) 620 nm. The maximum and constant absorbance of the dark red complex is attained at pH 6.2-7.3 while blue complex has maximum absorbance above pH 11.0 and thus the effect of sodium carbonate concentration has been carried out in the latter case. Beer's law validity and optimum concentration range for accurate determination for dark red complex are 0-4.3 and 0.70-3.60 ppm respectively, for the blue complex are 0.0-4.25 and 0.80-3.4 ppm respectively. Sandell's sensitivity of the colour reaction for dark red complex is \( 0.0048 / \mu \text{g Pb(I\(^{+}\)} / \text{cm}^2 \) with the molar extinction coefficient \( 4.30 \times 10^4 \, \text{l.mol.}^{-1} \, \text{cm}^{-1} \). For
the blue complex Sandell's sensitivity is \( 0.0046 \mu g \text{Pb(II)/cm}^2 \), with the molar extinction coefficient \( 4.45 \times 10^{14} \text{l.mol.}^{-1}\text{cm}^{-1} \). Only five moles of the reagent for the red complex and seven moles of the reagent for the blue complex are needed for full colour development. The stoichiometries of the complexes as determined by Job's method of continuous variations are 1:2 (metal:ligand) for the dark red complex and 2:3 for the blue complex. The method is sensitive as well as selective at high pH. Most of the metal ions do not absorb at \( \lambda_{\text{max}} 620 \text{ nm} \). Effect of diverse ions has also been studied in both the cases.

B. Silver

An intense dark red complex absorbing at \( \lambda_{\text{max}} 538 \text{ nm} \) is formed by interaction of THT with silver (I) at pH 5.8-7.6. Beer's law validity and optimum concentration range for accurate determination of silver are 0.0-5.6 and 0.32-5.2 ppm, respectively. The system is highly sensitive, the Sandell's sensitivity being \( 0.0043 \mu g \text{Ag(I)/cm}^2 \) with a molar extinction coefficient \( 2.5 \times 10^{14} \text{l.mol.}^{-1}\text{cm}^{-1} \). Composition of the complex has been found to be 1:1 (metal:ligand). The method is highly selective for the determination of silver (I). Most of the metals have been masked by DTA but bismuth (III) and antimony (III) interfered. The sensitivity of the method is compared to those of some well known methods at the end.

C. Thorium

Thorium (IV) ions interact with an aqueous solution of THT to form an intense dark red complex in the pH range...
4.8-7.0 absorbing maximum 535 nm. Beer's law and optimum concentration ranges are 0.0-5.2 and 0.7-4.8 ppm respectively. The sensitivity of the colour reaction is $0.0063 \mu g \text{Th(IV)}/\text{cm}^2$, with the molar extinction coefficient $3.70 \times 10^4 \text{l.mol}^{-1} \text{cm}^{-1}$. 3-Times molar excess of THT is required for full colour development of complex. Composition of the complex has been found to be 1:3 (metal:ligand). The effect of foreign ions has been studied in order to explore the selectivity of the reagent.

D. Uranium:

A dark red coloured complex of uranyl (II) with THT has maximum absorbance at $540 \text{nm}$ and is developed in the pH range 3.8-6.0. Beer's law is valid upto 6.20 ppm in the colour system and the optimum concentration range, as obtained from Ringbom plot, is 0.60-4.20 ppm. Sandell's sensitivity of the colour reaction is $0.0039 \mu g \text{UO}_2(II)/\text{cm}^2$ with the molar extinction coefficient $6.1 \times 10^4 \text{l.mol}^{-1} \text{cm}^{-1}$ and the composition of the complex as determined by Job's method of continuous variations is 2:3 (metal:ligand). For complete complexation 2-times molar excess of THT is required. Effect of diverse ions on complex formation has also been studied.

CHAPTER-VI: Spectrophotometric Determination of Bismuth, Indium, and Antimony

A. Bismuth:

The dark red bismuth (III)-THT complex has a constant and maximum absorbance $(\lambda_{\text{max}}^5 530 \text{nm})$ in the pH range 4.0 - 6.5. The colour development is instantaneous and absorbance
remains constant up to 24 h. Beer's law is obeyed up to 3.80 ppm and the limit for accurate determination of the metal is 0.56-3.00 ppm. Sandell's sensitivity and molar extinction coefficient for the system are $0.0038 \mu g \text{Bi(III)}/cm^2$ and $5.5 \times 10^4 \text{mol.}^{-1} \text{cm}^{-1}$ respectively. Job's method of continuous variations reveals its composition to be 2:3 (metal:ligand). Two times molar excess of THT is required for full colour development. Effect of diverse ions on complex formation has also been studied. At the end, the sensitivity of the colour reaction of THT with the metal is compared with other well known methods.

B. Indium:

Indium (III) ions interact with THT to form two complexes; a dark red complex at low pH (3.4-4.7) with $\lambda_{\text{max}}$ 530 nm and a bluish pink complex at high pH ($\approx$ 10.5) with $\lambda_{\text{max}}$ 620 nm. Beer's law validity and optimum concentration range for accurate determination for dark red complex are 0.0-1.80 and 0.24-1.40 ppm respectively and for bluish pink complex are 0.0-1.3 and 0.24-1.1 ppm respectively. Sandell's sensitivity of the colour reaction for dark red complex is $0.0013/\mu g \text{In(III)}/cm^2$, the molar extinction coefficient being $8.40 \times 10^4 \text{mol.}^{-1} \text{cm}^{-1}$ for the bluish pink complex, Sandell's sensitivity is $0.0014/\mu g \text{In(III)}/cm^2$ with the molar extinction coefficient $7.9 \times 10^4 \text{mol.}^{-1} \text{cm}^{-1}$. Only 3 moles of the reagent for dark red coloured complex and 4 moles of the reagent for bluish pink coloured complex are needed for full colour development. The stoichiometries of the complexes, found by Job's method of continuous variations, are 1:2 (metal : ligand) for dark red complex and 1:3 (metal:ligand) for bluish pink complex.
methods are highly sensitive. To increase the selectivity other metals are masked by iodide, fluoride, thiosulphate, thiocyanate, phosphate and arsenate. Manganese (II) and bismuth (III) interfere in the determination of indium (III).

C. Antimony:

Antimony (III) forms a dark red coloured complex with THT at pH 3.3-7.0 (λ max 535 nm). Beer's law and optimum concentration ranges are 0-4.5 and 0.4-3.2 ppm respectively. The sensitivity of the colour reaction is 0.029 μg Sb(III)/cm² with molar extinction coefficient 4.16x10⁻¹ l.mol⁻¹cm⁻¹. Composition of the complex has been found to be 1:1 (metal:ligand). Only four moles of THT are required for complete complexation. The method is sensitive as well as selective for antimony (III) as most of the metal ions are masked by EDTA.

CHAPTER-VII: Spectrophotometric Determination of Some Anions and Organic Thio Compounds Through Ligand Exchange Reactions

A. Determination of bromide and iodide:

These two halide ions decompose the silver (I)-THT complex quantitatively in aqueous medium replacing THT molecules to form stable silver halides. The decrease in absorbance of silver(I)-THT complex at 538 nm by addition of bromide or iodide has been made the basis for the indirect determination of these two halides. Experimental conditions are the same as that of the method for the silver(I). Under these conditions 5-120 μg
of bromide and 6-137 μg of iodide in a total volume of 25 ml can be determined accurately. Stoichiometric behaviour of the decomposition of silver(I) complex with these halides are 1:1.6 \( (\text{Ag-THT} : \text{Br}^-) \) and 1:1 \( (\text{Ag-THT} : \text{I}^-) \) respectively, probably due to the formation of \( \text{AgBr}_2^- \) species in the case of bromide and \( \text{AgI}^- \) in the case of iodide. These stoichiometries have been explained in terms of the stability constants of the species formed.

B. Determination of sulphur compounds:

(1) Sulphide:

Sulphide ions decompose the antimony (III)-THT complex quantitatively to form stable antimony (III) sulphide through ligand exchange reaction in solution. The decrease in absorbance of the antimony (III) complex at 535 nm is directly proportional to the concentration of the sulphide ion added. Under the optimum conditions for the formation of the antimony (III) complex, 0.13-2.1 μg/ml of sulphide ions can be accurately determined.

(II) Thiosulphate:

Thiosulphate ions decompose the mercury (II)-THT complex quantitatively in the pH range 6.8-7.9, thus the thiosulphate ions have been determined indirectly through ligand exchange reaction in aqueous solution. Under the optimum conditions for the formation of mercury (II)-THT complex, thiosulphate decompose in 1:1 ratio and 0.2-1.57 μg/l of the anions can be determined.
(Hi) Thiourea and thiosemicarbazide

These two compounds also decompose the mercury (II)-THT complex in 1:1 ratio. The base of the method for determination is the ligand exchange reaction. Under the optimum conditions, 2.25-28.5 µg/25 ml of thiourea and 2.75-31.75 µg/25 ml of thiosemicarbazide can be determined accurately.

C. Determination of phosphate

Phosphate replaces THT molecules from thorium (IV)-THT complex forming stable thorium (IV) phosphate at pH 4.8 - 7.0. The decomposition behaviour has been studied at pH 5.0 in an acetate buffer and thus 0.22 - 2.6 µg/ml of phosphate ions have been determined accurately. The stoichiometry of the reaction is 1:1.33 \([\text{Th(IV)-THT : PO}_4^{3-}]\) apparently due to the formation of the \([\text{Th}_3(\text{PO}_4)_4]\) species.