Chapter 1: Introduction

The growth and development of modern technology has resulted in the need for ever more versatile and sensitive analytical reagents. During last few decades heterocyclic azo dyes have received much attention as analytical reagent with a wide range of applications. Heterocyclic azo dyes contain the azo grouping –N=N–, in combination with a heterocyclic system and other groups such as aryl, -OH, -SO₃H etc. furnishing replaceable H. The dyes are easy to prepare and have high stability, sensitivity and selectivity towards metal ions. PAN and PAR are two well known representatives of this class and have used in the spectrophotometric determination of over 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.

Chapter 2: Materials and Methods

Synthesis of the ligand 2,5-dimethyl-4-(2-quinolylazo)phenol (DM-p-QAP) is described in this chapter. Characterisation of the ligand viz. Elemental analysis, IR spectral data and NMR spectra of the ligand are reported here. Properties of the viz. absorption spectra and molar absorptivities are reported. Methods used in the present investigations including those for finding out composition of the complexes using spectrophotometric technique are reported. At the end scope of the present work is given.
Chapter 3: Spectrophotometric Determination of Copper

On addition of ethanolic solution of DM-p-QAP to solutions containing Cu(I) and Cu(II) separately two complexes are formed. The yellowish green Cu(I)-DM-p-QAP complex forms at lower pH’s while purple coloured Cu(II)-DM-p-QAP complex forms at higher pH’s. The chapter is divided into Part I and Part II.

Part I: Cu(I)-DM-p-QAP system – Cu(I) forms a yellowish green coloured complex with DM-p-QAP which shows constant maximum absorbance at $\lambda_{\text{max}}$ 452nm in the pH range 2.25 – 2.75. Five minutes heating in water bath is required for full colour development and after that the complex is stable at least up to 24 hours. The effect of ethanol concentration, ascorbic acid concentration and reagent concentration on the absorbance of the solution and stability of the complex to heat and different time intervals has been studied. Beer’s law limit and optimum concentration ranges obtained from Ringbom plot are 0.0 – 0.762ppm and 0.248 – 0.707 ppm respectively. The sensitivity of the colour reaction is 0.00117µg of Cu(I)cm$^{-2}$, with molar extinction coefficient $5.43 \times 10^4$ Lmol$^{-1}$cm$^{-1}$. Composition of the complex has been found to be 1:2 (M:L). Effect of foreign ions has also been studied. The reagent has been found to be highly selective and has been successfully applied for selective determination of the element in alloys, milk samples and various human blood sera.

Part II: Cu(II)-DM-p-QAP system - Cu(II) forms a purple coloured complex with DM-p-QAP at alkaline pH which is stable at least up to 48 hours in 40% ethanolic medium. The complex shows constant maximum absorbance at $\lambda_{\text{max}}$ 569nm in the pH ranges 9.0 - 11.0. Beer’s law obeyed up to 0.76ppm and optimum concentration range for accurate determination is 0.126 – 0.716 ppm. Sensitivity of the colour system is 0.00076µg of Cu(II)cm$^{-2}$, molar extinction coefficient being $8.34 \times 10^4$ Lmol$^{-1}$cm$^{-1}$. Composition of the
complex is 1:3 (M:L). Effect of diverse ions is also studied. The reagent is made more selective by masking some of the common interferents. The reagent is successfully applied in the determination of the element in some alloys and milk samples. Findings of copper in milk samples as Cu(I) and Cu(II) is also compared.

Chapter 4: Spectrophotometric Determination of Silver(I) and the use of Silver(I) – DM-p-QAP Complex in the Indirect Spectrophotometric Determination of some Anions and Organic Thio compounds.

This chapter is divided into Part I and Part II. Part I deals with the spectrophotometric determination of silver(I) with DM-p-QAP. In Part II investigations on the use of silver(I) – DM-p-QAP complex as an analytical reagent in indirect spectrophotometric determination of some anions and organic thio compounds are reported.

Part I: Silver (I) –DM-p-QAP system: Silver(I) ions react with ethanolic solution of DM-p-QAP instantaneously to give a dark red coloured complex stable towards sunlight. The complex gives constant maximum absorbance at $\lambda_{\text{max}}$ 574nm in the pH ranges 9.5 – 10.5. In 40% ethanolic medium the complex is stable at least up to 48 hours. Beer’s law is followed up to 1.29 ppm. The optimum concentration range for accurate determination of silver(I) is 0.211 – 1.19 ppm. Sandell’s sensitivity and molar extinction coefficient for the system are 0.0012 $\mu$g of Ag(I)cm$^{-2}$ and 8.93x10$^4$ Lmol$^{-1}$cm$^{-1}$ respectively. Only three moles of the reagent is necessary for full colour development and the stiochiometry of the complex is 1:2 (M:L). Effect of foreign ions is also studied and sensitivity of the colour reaction is compared with some others known for the metal.
Part II: Spectrophotometric determination of some Anions and Organic Thio Compound through Ligand Exchange Reaction

i) **Determination of cyanide:** On addition of cyanide ions to the Ag(I) – DM-p-QAP complex, decrease in absorbance takes place quantitatively and Beer’s law is followed. By making use of this property cyanide ions have been determined by indirect spectrophotometric method. The workable pH range is 9.5 - 10.5. Spectral characteristics do not change with the addition of cyanide, thus determination is carried out at 574nm. Highest sensitivity is obtained when at least 3 fold molar excess of DM-p-QAP to Ag(I) is used. The plot of calibration curve shows linearity up to 0.52 ppm of cyanide ion and optimum range for accurate determination of cyanide is found to be 0.104 – 0.4162 ppm. Stoichiometry of the reaction is ascertained by mole ratio study. It shows that 2 moles of CN\(^-\) ions per mole of the complex are required to decompose the complex fully to form soluble [Ag(CN)\(_2\)]\(^-\), with liberation of DM-p-QAP. Effect of diverse ions is also studied to enhance the utility of the method.

ii) **Determination of iodide:** Iodide ions decompose quantitatively the Ag(I) – DM-p-QAP complex in the ratio 1:1. \(\lambda_{max}\) and pH ranges are 574nm and 9.5 – 10.5 respectively. The range of accurate determination for iodide ion is 0.381 – 1.016 ppm. Effect of diverse ions is also studied to enhance the utility of the method.

iii) **Determination of sulphide:** Sulphide ions decompose quantitatively the Ag(I) – DM-p-QAP complex in the ratio 2:1. \(\lambda_{max}\) and pH ranges are 574nm and 9.5 – 10.5 respectively. The range of accurate determination for sulphide ion is 0.008 – 0.192ppm. Effect of diverse ions is also studied to enhance the utility of the method.

iv) **Determination of thiosulphate:** Thiosulphate ions decompose quantitatively the Ag(I) – DM-p-QAP complex in the ratio 1:1. \(\lambda_{max}\) and pH ranges are 574nm and 9.5 –
10.5 respectively. The range of accurate determination for thiosulphate ion is 0.056 – 1.348 ppm. Effect of diverse ions is also studied to enhance the utility of the method.

v) **Determination of thiourea:** Decomposition behaviour of Ag(I) – DM-p-QAP complex is also studied by adding thiourea. Thiourea decomposes the Ag(I) – DM-p-QAP complex in the ratio 2:1. $\lambda_{\text{max}}$ and pH ranges are 574nm and 9.5 – 10.5 respectively. The range of accurate determination for thiourea is 0.0096 – 0.456 ppm. Effect of diverse ions is also studied to enhance the utility of the method.

**Chapter 5: Spectrophotometric Determination of Nickel and Cobalt**

This chapter has been divided into two parts. The first part deals with the investigations on the spectrophotometric determination of nickel while part II deals with the investigations on the spectrophotometric determination of cobalt.

**Part I: Nickel (II) – DM-p-QAP system** – Nickel(II) interacts with an ethanolic solution of DM-p-QAP to form a blood red complex with maximum absorbance at 617nm in the pH range 8.5 – 9.00. The system is studied in 40% ethanolic medium. Colour development is instantaneous and the complex is stable at least up to 48 hours. For full colour development five times molar excess of the reagent is needed. Beer’s law is obeyed up to 1.29 ppm and the limit of accurate determination of the metal is 0.704 – 1.29 ppm. Sandell’s sensitivity and molar extinction coefficient for the system are 0.0018 µg of Ni(II) cm$^{-2}$ and 3.17 x 10$^4$ Lmol$^{-1}$ cm$^{-1}$ respectively. Job’s method of continuous variation reveals its composition to be 1:2 (M:L). Effect of diverse ions on the complex is also studied. To enhance the utility of the reagent Ni(II) has been determined in some alloys and chocolates and candies. At the end sensitivity of the colour reaction is compared with others well known for the metal.

**Part II: Cobalt(II) – DM-p-QAP system** – An ethanolic solution of DM-p-QAP forms a purple violet coloured complex with Co(II). The complex is stable in more than 30%
ethanol and the system is, therefore, studied in 40%(v/v) ethanol. Colour development is instantaneous and the complex shows constant maximum absorbance at $\lambda_{\text{max}}$ 584nm in the pH range 8.5 – 9.00. For full colour development five times molar excess of the reagent is required. Beer’s law limit and optimum concentration limit as obtained from Ringbom plot are 0.00 – 0.765 ppm and 0.173 – 0.716 ppm respectively. Composition of the complex is 1:3 (M:L). Sandell’s sensitivity for the colour reaction is 0.00102 µg of Co(II)cm$^{-2}$ and molar extinction coefficient is $5.75 \times 10^4$Lmol$^{-1}$cm$^{-1}$. Effect of foreign ions in the determination of the metal is also investigated. To enhance the utility of the reagent Co(II) has been determined in some vitamin tablets. At the end sensitivity of the colour reaction is compared with others well known for the metal.

Chapter 6: Spectrophotometric Determination of Cadmium and Mercury

This chapter has also been divided into two parts. The first part deals with the investigations on the spectrophotometric determination of cadmium while the second part deals with the investigations on the spectrophotometric determination of mercury.

Part I: Cadmium (II) – DM-p-QAP system – Cadmium forms a maroon coloured complex with ethanolic solution of DM-p-QAP which is stable at least up to 48 hours in 40%(v/v) ethanolic medium. The complex shows constant maximum absorbance at $\lambda_{\text{max}}$ 593nm in the pH range 8.85 – 9.35. For full colour development six times molar excess of the reagent is necessary. The composition of the complex as ascertained by Job’s method of continuous variation is 1:2 (M:L). Beer’s law is valid up to 2.697 ppm and the optimum concentration range as obtained from Ringbom plot is 0.668 – 2.483 ppm. Sandell’s sensitivity of the colour reaction is 0.00308 µg of Cd(II)cm$^{-2}$ with molar extinction coefficient $3.62 \times 10^4$Lmol$^{-1}$cm$^{-1}$. Effect of foreign ions is studied. To enhance the utility, the metal is determined in tobacco leaves and its products. At the end sensitivity of the colour reaction is compared with others well known for the metal.
Part II: Mercury(II) – DM-p-QAP system – DM-p-QAP forms a blood red coloured complex with Hg(II) instantaneously at alkaline pH in 40%(v/v) ethanolic medium. The complex is unstable and the colour starts fading away as soon as it is formed. However addition of 1mL of 1M NaNO₂ solution stabilises the complex at least for three hours. The complex shows constant maximum absorbance at $\lambda_{\text{max}}$ 582nm and the workable pH range is 7.50 – 8.50. For full colour development 10 times molar excess of the reagent is needed. The composition of the complex as ascertained by Job’s method of continuous variation is 1:2 (M:L). Beer’s law is valid up to 2.407 ppm and the optimum concentration range as obtained from Ringbom plot is 0.5956 – 2.213 ppm. Sandell’s sensitivity of the colour reaction is 0.00352 µg of Hg(II)cm² with molar extinction coefficient $5.68\times10^4$Lmol⁻¹cm⁻¹. Effect of foreign ions is studied. At the end sensitivity of the colour reaction is compared with some others well known for the metal.

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