



## Studies on Precision and Accuracy In Microdetermination of Transition Metals Using Ternary Complex EAB-CTAB-Metals

SUPARNA DESHMUKH

S. K. Gandhi College, Kada Ashti, Dist. Beed, Maharashtra 414202, India.  
Corresponding author E-mail: suparna.deshmukh@gmail.com

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### ABSTRACT

Complexometric and Analytical studies have been carried out by forming ternary complex between Eriochrome Azuro B, and Cetyl Trimethyl Ammonium Bromide CTAB; and some transition metal ions mainly  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$ . The absorption spectra of Eriochrome Azuro B, EAB; a triphenylmethane dye, has been studied in the presence as well as in the absence of surfactant, Cetyl Trimethyl Ammonium Bromide, CTAB at pH values ranging from pH 1.00 to 12.00. Hypsochromic shift is observed in the absorption spectra in the presence of surfactant. pK values i.e. dissociation constant values are found to be decreased, in the presence of surfactant is observed. Composition of chelates EAB: CTAB: Metal is found to be 1: 1: 1, and effect of foreign ions such as chlorides, nitrates; and sulphates of sodium, potassium and ammonium; has been studied in detail. Stability constants of chelates have been determined. Sensitivity and Stability of chelates formed increases in presence of surfactant. Various analytical parameters including range of adherence to Beer's Law, Molar Extinction constants, Sandells sensitivity, were studied for all systems by its interaction with and without CTAB. Precision and Accuracy of the method suggested for microdetermination of metal ions was determined and found out that method is precise as well as accurate.

**Keywords:** Triphenylmethane Dye, Surfactant, Hypsochromic Shift, Stability, Sensitivity, Precision and Accuracy.

### INTRODUCTION

The property of formation of colored complexes has been successfully applied for the spectrophotometric estimation of metal ions since last few decades. The addition of long chain quaternary salts to the deeply colored solution of dyes, causes a marked color change with the change in wavelength of maximum absorption. Short range electrostatic forces, on the surface of micelle double

layer changes the  $\lambda_{\text{max}}$  and hence hypsochromic shift is observed. The purpose of addition of surfactants to the dyes is thus to decolorize them. It is followed by Sign Rule<sup>1</sup> which is an empirical statement. The interesting property of the aggregates formed is their ability to form colored complexes with various cations. Another advantage is that the determination of microamounts of metal ions can be done with much higher sensitivity in the presence of surfactants. Reaction of triphenylmethane dyes with



4f and 5f metal ions have been a subject matter of study by several workers<sup>2-8</sup>. Studies were carried out on the mechanisms of interactions between dyes, surfactants and metal ions for analysis of metals in solutions<sup>6-10</sup>. Reactions between Cu<sup>2+</sup>, Fe<sup>2+</sup> & Al<sup>3+</sup> with Chrome Azurol S and non ionic surfactants has been studied in detail<sup>11</sup>. Present studies are taken with the aim to determine metals under study with simple and sophisticated instruments like Shimadzu Spectrophotometer at micro levels if present in water as pollutants. With this aim present studies are taken to develop a sensitive process for microdetermination with higher sensitivity by interactions of Triphenylmethane dye EAB, and surfactant Cetyl Trimethyl Aminonium Bromide. Complexation of dye and metal ions under study Cu<sup>2+</sup>, Ni<sup>2+</sup> and Cd<sup>2+</sup> has been discussed in both absence and presence of surfactant. Composition of dye-surfactant complex is determined by adding varying concentration of surfactants to the dye solutions. Higher concentration of mineral salts<sup>12</sup> prevents the micelle formation due to occurrence of inorganic anions which displace dye as counter ions. Hence effect of mineral salts has also been studied.

## EXPERIMENTAL

### Instruments

UV Shimadzu spectrophotometer UV-240 a Japanese Model was used for all absorbance measurements were used. For absorption studies distilled water blanks were used and measurements were done by using Glass cuvettes of 1 cm thickness supplied with the instrument. All pH measurements were done on pH meter with glass electrodes and instrument was operated on 220volts stabilized by AC mains. pH meter used was of Elico make model.

## MATERIALS

The reagents used were of 99.99% purity and of BDH make with analytical reagent grade. For preparing surfactant solution, cetyl trimethyl ammonium bromide was dissolved in 20% aq. methanol. Eriochrome Azurol B powder is dissolved in double distilled water to make dye solution, while standard solutions of metals were prepared by dissolving metal salts in double distilled water.

### Procedure

In all the experiments of systems under study, a definite sequence was maintained. Surfactant CTAB solution was added to dye solution which was kept for at least 30 min. for complete complexation between dye and surfactant. After 30 mins. time necessary for complete equilibration, the absorbance readings were recorded.

## RESULTS AND DISCUSSION

### Absorption Spectra

By adjusting pH 1.0 to 12.0, absorption spectra of EAB was studied in presence as well as in absence of CTAB. The  $\lambda_{max}$  values obtained at different pH values are summarized below in Table 1.

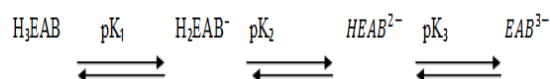
**Table 1: EAB  $\lambda_{max}$  Values At Variable pH Values From 1.0 – 12.0**

pH	$\lambda_{max}$ (nm) of EAB	$\lambda_{max}$ (nm) In Presence of CTAB
1.0 – 2.0	470	480
3.0	460	510
4.0	460	450
5.0	450	420
6.0 -9.0	420	425
10.0- 11.0	425	610
12.0	595	610

Hypsochromic shift is observed At pH 5.0. Hence pH of Study For Using EAB And CTAB is 5.0.

### Dissociation Constant (pK values) of EAB

The EAB contains three replaceable protons in its molecule. Two -COOH groups possess two protons, while third available proton is in -OH group. The dissociation reaction which occurs in the stepwise dissociation of EAB can be represented in equilibrium as follows.



The above equilibrium reaction shows three pK values of EAB. Experiments were carried out for the determination of pK values of EAB alone and in the presence of surfactant, CTAB which are as reported in Table 2. Several sets of solutions of suitable concentrations of dyes were prepared & pH adjusted from 1.0 to 12.0. Spectra of these solutions were recorded from 380 nm to 700 nm

in the entire visible region. Then a graph is plotted between absorbance and pH values at different  $\lambda$  max obtained from spectra. The S-shaped curves are obtained where the lower part of it represents the molecular species and the upper portion represents the ionic species. From these, pK values are calculated for dissociation of dye alone as well as for that with interaction of CTAB. It has shown a decreasing trend in pK values in presence of CTAB. This has been related to an early dissociation of protons of triphenylmethane dyes in the presence of surfactants showing a decrease in the value of their constants. Formation of dye-surfactant complex is indicated by decreased values of pK.

**Table 2: Dissociation Constants of EAB**

pK values	EAB	EAB + CTAB
pK1	3.00	2.70
pK2	5.69	5.04
pK3	11.13	10.84

Lowering of pK values indicates the action of surfactants on EAB.

#### Composition Of EAB-CTAB Complex

The effect of varying concentration of CTAB on EAB absorbance was also studied at pH 5.0 and at 420 nm. The absorbance of EAB decreases linearly upto a definite ratio of EAB:

CTAB, as 1:1, is reached. After this point the addition of surfactant, even in excess amount did not alter the absorbance of EAB to any significant extent. Thus the complex formed can be represented as [EAB(CTAB)]. Successive reaction of CTAB on EAB has been indicated by descending part of the curve. The state of maximum decolorisation is reached after which there is no change in absorbance is observed. Hence, EAB complex can be represented as [EAB(CTAB)].

#### Effect Of Mineral Salts

Caiwen and Quingyue<sup>13</sup> studied the effects of inorganic salts on the color reactions of triphenylmethane dyes in the presence of surfactants, which found to exert some sensitizing effect on the color complex formation between TPM dyes and surfactants. The cations  $K^+$ ,  $Na^+$ ,  $NH_4^+$  did not show any effect on the absorbance of dye-detergent solution. Nitrates has shown some effect at pH 5.0, as the absorbance goes on increasing upto certain extent after which it remains unaltered. The mineral salts selected were the chlorides (KCl, NaCl, and  $NH_4Cl$ ), the nitrates ( $KNO_3$ ,  $NaNO_3$ ,  $(NH_4)NO_3$ ), and sulphates  $K_2SO_4$ ,  $Na_2SO_4$ ,  $(NH_4)_2SO_4$ . To study this in detail, different concentration of salt solutions were added to  $1.0 \times 10^{-3}$  M EAB solution containing  $1.0 \times 10^{-2}$  M CTAB into it.

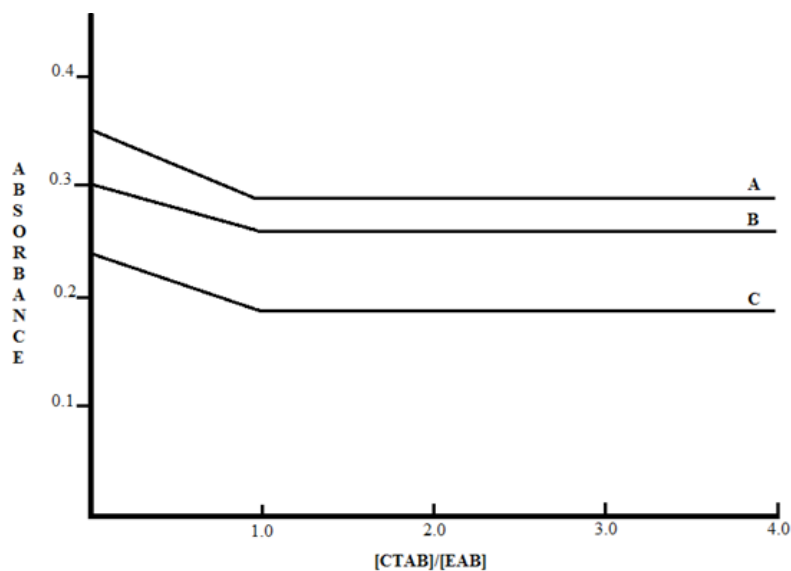


Fig. 1. Composition Of EAB-CTAB Complex

**Absorption Spectra of the Complexes and Chelates**

For systems of EAB, EAB+Metal ion, EAB+CTAB; EAB + Metal ion+CTAB the absorption spectra are studied at pH 5.0. The nature of complexes and chelates formed between EAB and metal ions  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$ , has been discussed in the presence of surfactant CTAB and were compared with those formed in absence of CTAB. Absorption Spectras obtained are same as represented in Fig. 2. In alkaline range the metals under study were

found to be susceptible for hydrolysis. Hence the complexation is studied in the lower range of pH 3.0 to pH 6.0. The bathochromic shift is observed in the absorption spectras of chelates of metals  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  in the presence of surfactant CTAB, with increase in their values of absorbance. Bathochromic shift for chelates is observed due to the dissociation of protons of the dye EAB after its interaction with surfactant CTAB, and the metals selected for study.

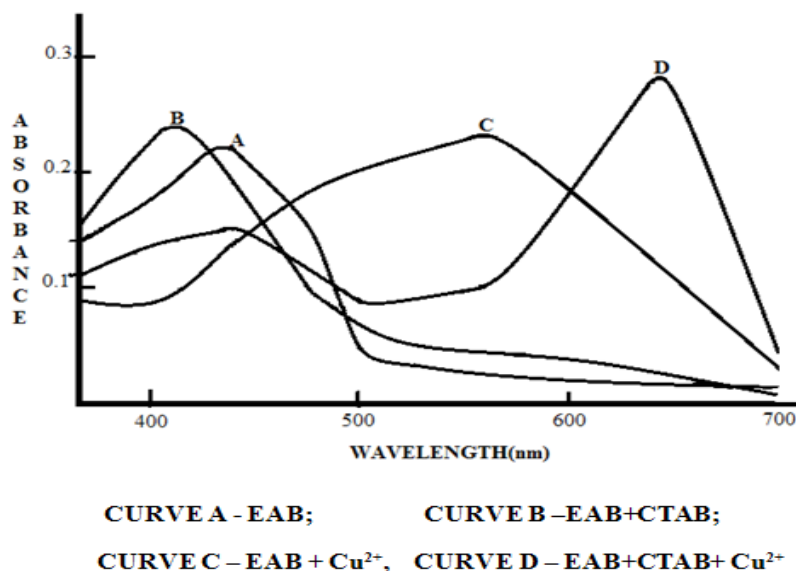


Fig. 2. Representative Absorption Spectrum Of  $\text{Cu}^{2+}$  At pH 5.0

**Table 3:  $\lambda$  max of EAB its complexes at pH 5.0**

complex system	$\lambda$ max (nm)
EAB	450
EAB+ CTAB	420
EAB + $\text{Cu}^{2+}$	560
EAB +CTAB + $\text{Cu}^{2+}$	640
EAB + $\text{Ni}^{2+}$	530
EAB+ CTAB + $\text{Ni}^{2+}$	630
EAB + $\text{Cd}^{2+}$	540
EAB+ CTAB + $\text{Cd}^{2+}$	640

**Chelates Composition**

The stoichiometric ratio was determined for studying stability of complexes of metal ions under study. It was ascertained by applying job's method of continuous variation. It is observed that the composition of the complexes of metal ions under study with EAB remains unaltered even in the

presence of surfactant. Composition studies revealed that, EAB forms complexes at Metal: Ligand ratio as 1:1 with metal ions  $\text{Cu}^{2+}$  &  $\text{Ni}^{2+}$  and with ions  $\text{Cd}^{2+}$  it is obtained as 1:2 which remains unaltered even in its chelates with CTAB.

**Stability Constant**

The stability constants are represented by log K values of chelates. The stability constants are as reported in Table 4.

Results revealed that the log K values obtained for chelates of EAB are higher for its systems obtained with CTAB as compared to that obtained without surfactant. This is attributed to the reaction of surfactant with EAB which dissociates protons from phenolic group of EAB, and association of metal ions to it at the pH of study and thereby increasing the value of stability constant in its

**Table 4: Composition and Stability Constant (LogK) of Chelates**

Chelates	$\lambda$ max (nm)	Composition M:EAB:CTAB	LogK value By Job's method
Cu <sup>2+</sup> -EAB	560	1:1	3.7
Cu <sup>2+</sup> -EAB-CTAB	640	1:1:1	4.5
Ni <sup>2+</sup> -EAB	530	1:1	4.1
Ni <sup>2+</sup> -EAB - CTAB	630	1:1:1	5.1
Cd <sup>2+</sup> -EAB	540	1:2	9.7
Cd <sup>2+</sup> -EAB-CTAB	640	1:2:2	10.1

presence.

#### Analytical applications

Throughout the experimentations, a same sequence of addition is followed which is obtained by taking many trials on different combinations. According to selected sequence, to the TPM dye i.e EAB solution surfactant solution was added. This was then kept for half an hour for complete equilibration. On formation of dye - detergent complex metal solution was added to the complex. After stable chelate formation, color shows stability upto 3 to 4 hours. It was observed very less effect from 25°C to 60°C on all systems under study after temperature variations.

#### pH range of stability

For studying effect of pH on stability of metal chelates, the dye : surfactant : metal ratio was taken as 3:15:1 i.e. 1:5:0.33 & from pH 3 to pH 6.5 the effect was studied for all EAB chelates. Total volume of the system was kept as 25ml. The stable pH range

was selected at which absorbance values showed constancy. Such range was selected as pH range of stability for chelates under study.

#### Beer's Law and Photometric Ranges

Beer's Law is studied for getting linear relationship between concentration and absorbance of the systems under study in presence as well as absence of metal ions under study. This study was carried out by taking constant concentrations of reagents and adding different concentrations of metal ions to it at pH 5.0 and at ascertained  $\lambda$ max of chelates. By plotting graphs on the basis of Ringbom plots, log of metal ion concentration Vs. % transmittance, the effective photometric range was evaluated.

#### Sandell's Sensitivity and Molar Absorptivity of the Chelates

Sensitivity of colour reaction, as defined by Sandell ; for chelates is given by  $\log I_0/I_t$ , is as given in Table 5. Along with it values for pH range of stability, Beer's Law Range, Photometric range of analysis are also listed below.

#### Spectrophotometric Microdeterminations of Cu (II), Ni(II), and Cd (II), with EAB and CTAB

Concentration of metal ions under study are taken as that mentioned in effective photometric range of determination and the pH of the EAB solution, pH of systems with this concentration was adjusted to pH 5.0. Dye-surfactant solution was kept for 30 min. for complete decolorisation and complexation. Total volume of the systems was maintained at 25 ml with distilled water. Absorbances are recorded at maximum wavelength of study

**Table 5: pH range, Beer's Law obeying range, Effective Photometric Range, Sensitivity and Molar Absorptivity at pH 5.0**

Chelates	pH range	Beer's law Range In ppm	Photometric Range	Sandell Sensitivity SX10 <sup>-2</sup>	Molar absorptivity EmX10 <sup>-3</sup>	$\lambda$ max (nm)
Cu(II)-EAB	3.2-4.4	0.22-0.36	0.20-0.74	2.7	9.5	560
Cu(II)EABCTAB	3.5-5.0	0.69-1.98	0.69-1.41	3.8	13.1	640
Ni (II) - EAB	3.8-4.2	0.95-1.1	1.14-3.24	2.8	10.6	530
Ni(II)EABCTAB	4.5-5.5	1.04-3.52	1.56-3.55	3.9	14.5	630
Cd(II) - EAB	4.2-4.8	0.75-4.22	1.55-3.36	10.2	3.5	540
Cd(II)EABCTAB	5.0-6.0	1.12-5.99	2.82-4.46	17.9	5.83	640

Spectrophotometric Microdeterminations of Cu (II), Ni(II), and Cd (II), with EAB and CTAB

on Shimadzu double beam Spectrophotometer. Concentration of metal ion present in unknown solution or analyte can be obtained by comparing absorbance with standard spectras studied with same conditions. The mean absorbance, mean deviation and relative mean deviation are also found out. The value of most probable analytical errors is determined with root mean square deviation; for ten replicate determinations ranges between 0.0008 to 0.0037 at the confidence limit of  $t=99.5\%$ . If the number of determinations are further increased that would subsequently decrease the value of

$t\alpha$ . Consequently, a point would be reached when increase in precision will be too small to justify the expenditure of labour, time and reagents involved in increased number of determinations. On the basis of root mean square deviation ( $\sigma$ ); the most probable error ( $\epsilon$ ), the difference between arithmetic mean ( $X$ ); and the true or most expected value ( $X_t$ ) of absorbance for the systems under study, conclusions are drawn. Precision and accuracy data calculated are given in following table. The expected diminish in the probable errors would also decrease the level of confidence limit, hence ten replicate determinations have been done in present studies.

**Table 6: Precision Data For Absorbance Measurement**

System	$X$	$\sigma$	$\epsilon$	$X-\epsilon$	$X+\epsilon$
Cu(II)-EAB	0.893	0.008	0.0094	0.8836	0.902
Cu(II)EABCTAB	0.076	0.002	0.0023	0.0737	0.078
Ni (II) - EAB	0.566	0.005	0.0058	0.56	0.572
Ni(II)EABCTAB	0.058	0.002	0.0023	0.0557	0.114
Cd(II) - EAB	0.537	0.006	0.007	0.53	0.544
Cd(II)EABCTAB	0.064	0.003	0.0035	0.0605	0.068

**Table 7: Accuracy Data For Absorbance Measurement Expressed as ( $\Delta < \epsilon$ )**

System	$X$	$X_t$	$\Delta = X_t - X$	$\epsilon$
Cu(II)-EAB	0.893	0.791	-0.102	0.0094
Cu(II)EABCTAB	0.076	0.076	0.000	0.0023
Ni (II) - EAB	0.566	0.470	-0.096	0.0058
Ni(II)EABCTAB	0.058	0.055	-0.003	0.0023
Cd(II) - EAB	0.537	0.523	-0.014	0.0070
Cd(II)EABCTAB	0.064	0.065	0.001	0.0035

## CONCLUSION

Characteristics of a best reagent is to exhibit properties like stability of the compounds formed, specificity and sensitivity of the color reactions. Triphenylmethane dye, Eriochrome AzuroI B, posses all these properties of good reagent. Stable colored complexes of the metal ions under study i.e,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$ , formed with EAB, has found out to increase stability as well as sensitivity of their determination at micro level in the solution containing surfactant, CTAB. The addition

of surfactants to TPM dye has been observed to cause hypsochromic shift due to which there is decrease in dissociation constant while that in the presence of metal ions under study with surfactant and a bathochromic shift has been observed with considerable change in  $\lambda_{\text{max}}$  which causes increase in stability constants of the chelates formed. The metal ions  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$ , can be effectively detected spectrophotometrically, at micro levels, by using this method. The standard deviation values are also evaluated which are the results of ten replicate determinations. The precision and accuracy studies are carried out on microdeterminations and data is reported which shows that the method proposed is both precise as well as accurate.

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