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## Novel analytical approach for spectrophotometric determination of bismuth through measurement of permittance of the copper-ethylenediaminetetraacetate absorbing system

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### ABSTRACT

The absorbance quenching capability of  $\text{Bi}^{3+}$  towards the copper(II)-ethylenediaminetetraacetate,  $[\text{Cu}(\text{II})\text{-EDTA}]^{2-}$  absorbing system, was alternatively exercised for measurement system's permittance in spectrophotometric determination of bismuth. The validity of this method was tested at 725 nm by measuring the clearance of  $[\text{Cu}(\text{II})\text{-EDTA}]^{2-}$  system, which was subsequently formed in the  $\text{Bi}^{3+}$  solution via utilizing surplus EDTA. The linearity of permittance (viz. logarithm of clearance) versus concentration of bismuth was used for determination of bismuth. The effects of some important variables on the determination of bismuth based on proposed method were studied. The average value of system's permittance coefficient was observed as  $0.1488 \text{ lit. g}^{-1}\text{cm}^{-1}$  at pH 1.0 to 1.25 for concentration of bismuth in the range of 0.002 g to 0.080g. The method was successfully applied for determination of bismuth in Trymo tablets. The average accuracy was found good, which was evaluated by comparison of the results obtained with those claimed by the manufacturer.

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### KEYWORDS

Absorbing system;  
Clearance;  
Permittance;  
Permittance coefficient.

### INTRODUCTION

Bismuth and its compounds plays an important role in chemical and biological processes, and is used in semiconductors; cosmetics preparation, alloy and metallurgical additives<sup>[1]</sup>. The bismuth metal is used for preparation of alloys of low melting points, which are characterized by their expansion on cooling<sup>[2]</sup>. Bismuth salts especially the subnitrate being used for medical purposes because those are generally not poisonous and may be taken internally without danger<sup>[2]</sup>.

Because of wide applications, numerous analytical

methods have been investigated for determination of trace quantity of bismuth in various types of sample. These include electrothermal vaporization inductively coupled plasma mass spectrometry<sup>[3,4]</sup>, graphite furnace atomic absorption spectrometry<sup>[5]</sup>, voltammetry with modified carbon paste electrode<sup>[6,7]</sup>, stripping voltammetry<sup>[8-10]</sup> and spectrophotometry<sup>[11-18]</sup>. With most of these sensitive instrumental methods, requires the preconcentration of analyte for quantitation of trace amount of bismuth.

Bismuth with high content was determined by direct EDTA titration, employing thiourea, iodide and

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cupric ion as indicator<sup>[19-23]</sup> for detection of photometric end point. The change in concentration of thiourea and iodide may affect the end point of photometric titration. The information of stability/formation constant ( $\log K_f$ ) of metal-EDTA chelates and their absorption spectra are the parameters<sup>[24]</sup> utilized for simultaneous determination of bismuth and copper in a single photometric titration<sup>[23]</sup>. Although the detection of exact end point by graphical means is tedious and time consuming yet photometric titration methods are consistently used, since the presence of other substances absorbing at the same wavelength does not necessarily cause the interference, in as much as only the change in absorbance is significant<sup>[25]</sup>.

The  $\log K_f$  values<sup>[26,27]</sup> of EDTA complexes of bismuth and copper are reported as 22.8 and 18.7 respectively, which are sufficiently larger indicates both chelates are much more stable; however,  $[\text{Bi(III)-EDTA}]^-$  have more stability than  $[\text{Cu(II)-EDTA}]^{2-}$ . The considerable difference in the stability constant allows bismuth to react with EDTA first in presence of copper consequently, copper ions functioning as an indicator<sup>[23]</sup> in bismuth titration as well as permits for simultaneous<sup>[23]</sup> determination of both metals in a single photometric titration. The same generalized principle was exercised here for spectrophotometric determination of bismuth using copper ion as an indicator for surplus EDTA.

In this method,  $\text{Bi}^{3+}$  solution buffered with chloroacetic acid was treated initially with fixed and excess of EDTA reagent; after quantitative chelation of  $\text{Bi}^{3+}$  as  $[\text{Bi(III)-EDTA}]^-$  the surplus EDTA was utilized for generation of  $[\text{Cu(II)-EDTA}]^{2-}$  absorbing system via adding fixed quantity of  $\text{Cu}^{2+}$  solution. The solution with greater concentration of  $\text{Bi}^{3+}$  left the smaller amount of surplus EDTA (for generation of absorbing system) and vice versa. As a result, the color intensity of  $[\text{Cu(II)-EDTA}]^{2-}$  chelate was observed inversely proportional to the concentration of bismuth. Hence, the permittance<sup>[28]</sup> of the absorbing system was found directly proportional to the concentration of bismuth. Thus, the absorbance quenching<sup>[28]</sup> action of bismuth analyte on to the  $[\text{Cu(II)-EDTA}]^{2-}$  absorbing system was worked out as an alternative way for determination of bismuth.

## EXPERIMENTAL

### Apparatus

- i) Shimadzu UV-Visible spectrophotometer (Model UV-1800) was used with the quartz standard rectangular cuvettes of identical dimension for measurement of % transmittance.
- ii) Equip-tronics pH-meter (Model EQ-610) was used to check the pH of test solutions.

### Reagents and chemicals

All the chemicals used were analytical grade and were used without further purification.

- (1) 4.0 L. 0.05M  $\text{Bi}^{3+}$  solution [viz. 10.450 mg  $\text{ml}^{-1}$  of  $\text{Bi}^{3+}$ ] was prepared by dissolving 97.016 g. of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  in minimum quantity of conc.  $\text{HNO}_3$ , followed by dilution with distilled water containing sufficient  $\text{HNO}_3$  to make the final solution in 0.5M  $\text{HNO}_3$ . This solution of  $\text{Bi}^{3+}$  was standardized against standard EDTA solution using chloroacetate buffer and xylene orange indicator and it was further diluted with 0.5M  $\text{HNO}_3$  so as to obtain 10.0 mg  $\text{ml}^{-1}$  of bismuth. Furthermore, the calculated volumes of  $\text{Bi}^{3+}$  stock solution were diluted to 1.0 liter with 0.5M  $\text{HNO}_3$  and 8.0 mg  $\text{ml}^{-1}$ , 6.0 mg  $\text{ml}^{-1}$ , 4.0 mg  $\text{ml}^{-1}$  and 2.0 mg  $\text{ml}^{-1}$   $\text{Bi}^{3+}$  solutions were prepared as an analyte solution of  $\text{Bi}^{3+}$ .
- (2) 4.0 L. 0.1M EDTA solution was prepared by dissolving 148.896 g. of disodium dihydrogen ethylenediaminetetraacetate dihydrate,  $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$  in distilled water. The salt was dissolved by warming the solution nearly to 60-70°C.
- (3) 4.0 L. 0.1M  $\text{Cu}(\text{NO}_3)_2$  solution was prepared by dissolving 96.640g. of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in distilled water. The solutions of EDTA and  $\text{Cu}(\text{NO}_3)_2$  produces  $[\text{Cu(II)-EDTA}]^{2-}$  absorbing system, therefore, they are termed here as absorbing system reagent.
- (4) 4.0 L. 1.0 M  $\text{CH}_2\text{ClCOOH}$  solution was prepared by dissolving 378.0 g. of monochloroacetic acid in distilled water. The solution of chloroacetate was used as buffer.
- (5) 8.0 Liter 0.5M  $\text{HNO}_3$  solution was obtained by diluting 256.0 ml of conc.  $\text{HNO}_3$  with distilled water.
- (6) Trymo tablets manufactured by Raptakos, Brett and Co. Ltd. of batch No T 8030C were used for deter-

mination of bismuth. Manufacturer granted that, each film coated Trymo tablet contains colloidal bismuth subcitrate equivalent to 120 mg of  $\text{Bi}_2\text{O}_3$ .

### Method for determination of bismuth

The analytical performance of the method was tested primarily with the standard test solutions (TS) of bismuth of varying range of concentration and it was initially implemented with the determination of bismuth in the range 0.010 g. to 0.100 g. For preparation of test solutions (TS) of  $\text{Bi}^{3+}$  in this concentration range, 1.0ml, 2.0ml, ..., to 10.0ml aliquots of  $10.0 \text{ mg ml}^{-1} \text{ Bi}^{3+}$  solution were added sequentially into 25ml graduated flasks each containing 5.0ml of  $1.0 \text{ M CH}_2\text{ClCOOH}$  as a buffer solution. To equalize the proton ions concentration, 9.0ml, 8.0ml, ..., to 0.0ml aliquots of  $0.5 \text{ M HNO}_3$  were also added serially into these volumetric flasks numbered as 2 to 11. Then in each flask, 4.0ml of  $0.1 \text{ M EDTA}$  solution was added and reaction mixture was shaken thoroughly for quantitative chelation of  $\text{Bi}^{3+}$  with EDTA and immediately 4.0ml of  $0.1 \text{ M Cu(NO}_3)_2$  solution was added for utilization of the surplus EDTA and generation of the  $[\text{Cu(II)-EDTA}]^{2-}$  absorbing system. The reaction mixtures were further diluted to 25ml with distilled water. Excluding only  $\text{Bi}^{3+}$  solution, the reagent blank (RB) solution<sup>[28]</sup> was prepared in flask No.1 with 10.0ml  $0.5 \text{ M HNO}_3$ . The true blank (TB) or reference solution<sup>[28]</sup> was also prepared in the similar way using 11.0ml of  $10.0 \text{ mg ml}^{-1} \text{ Bi}^{3+}$  solution. The added 4.0ml of  $0.1 \text{ M EDTA}$  was completely utilized for chelation of excess of bismuth ( $0.110 \text{ g. Bi}^{3+}$  present, so no possibility of generation of  $[\text{Cu(II)-EDTA}]^{2-}$  absorbing system in TB solution.

The visible absorption spectrum of  $[\text{Cu(II)-EDTA}]^{2-}$  system (viz. RB solution) was obtained against the TB solution, and a wavelength 725nm was selected for measurement. The % T of RB as well as each TS was measured at 725nm against TB as a reference. The % T of the RB was used for obtaining the clearance<sup>[28]</sup> value of test solutions. The graph of clearance of the absorbing system versus the concentration of  $\text{Bi}^{3+}$  was prepared for testing validity of the method and the linearity of permittance<sup>[28]</sup> of the absorbing system against the concentration of  $\text{Bi}^{3+}$  was used for determination of bismuth. An analogous method was further practiced for quantitation of  $\text{Bi}^{3+}$  in different lower range concentrations of bismuth.

## RESULTS AND DISCUSSION

Ethylenediaminetetraacetic acid (EDTA) is a hexadentate chelating reagent which combines with  $\text{Bi}^{3+}$  and  $\text{Cu}^{2+}$  in 1:1 stoichiometry. EDTA gives remarkably stable chelates with the cage-like structure in which the cation is effectively surrounded by and isolated from solvent molecules<sup>[29]</sup>. The stability of these metal-EDTA chelates is mostly related to complexing ability of the  $\text{Bi}^{3+}$  and  $\text{Cu}^{2+}$  ions with the EDTA and the pH of the solution<sup>[30]</sup>. The earlier literature<sup>[31]</sup> showed the minimum pH needed for satisfactorily chelation of various cations with EDTA; strongly acidic pH (in between 1-2) can be tolerated in the complexation of  $\text{Bi}^{3+}$  with EDTA.

### Stability of $[\text{Cu(II)-EDTA}]^{2-}$ absorbing system

Reaction with 1:1 stoichiometry between of  $\text{Cu}^{2+}$  and EDTA produces intense blue colored  $[\text{Cu(II)-EDTA}]^{2-}$  chelate which was employed as the absorbing system at 745nm for spectrophotometric determination of copper<sup>[32]</sup>. The same chelation reaction in acetate buffer was also utilized for amperometric determination of EDTA<sup>[27]</sup>. The chelating reagent EDTA has great nucleophilic capability to complex the cupric ion over a broad pH range<sup>[33]</sup>; thus, the stability of  $[\text{Cu(II)-EDTA}]^{2-}$  chelate is not affected significantly by the pH of the solution. In this study,  $[\text{Cu(II)-EDTA}]^{2-}$  chelate was generated at pH nearly in between 1.0 to 1.25 to which quantitative chelation of  $\text{Bi}^{3+}$  was also attained. The stability of  $[\text{Cu(II)-EDTA}]^{2-}$  system at this pH is also experimentally beneficial, since the sample solution of bismuth was prepared using strong acids.

### Cupric ion-indicator for surplus EDTA

The sufficient difference (about 4.10) in stability constant ( $\log K_f$ ) value<sup>[26,27]</sup> of EDTA chelate of  $\text{Bi}^{3+}$  ( $\log K_f = 22.8$ ) and  $\text{Cu}^{2+}$  ( $\log K_f = 18.7$ ) reveals that,  $[\text{Bi(III)-EDTA}]^{1-}$  chelate is much more stable<sup>[23]</sup> than  $[\text{Cu(II)-EDTA}]^{2-}$  chelate. Therefore, it was appropriate to utilize the surplus EDTA in the test solutions for generation of  $[\text{Cu(II)-EDTA}]^{2-}$  as the absorbing system, without disturbing the stability of  $[\text{Bi(III)-EDTA}]^{1-}$  chelate. Furthermore, copper chelate exhibits maximum absorption in the visible region where other species in the test solution exhibits nil absorption.

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### Equalization of proton ion concentration

Although the stability of absorbing system is not affected by presence of mineral acids but the variable proton ion concentration in test solutions affects the ionization of EDTA to more or less extent; which reflects its adverse effect on the analytical performance of the method. Even if, test solutions were buffered with 5.0 ml of 1.0M chloroacetic acid solution<sup>[23]</sup>, but the linearity of system's permittance against concentration of bismuth was found good, when 0.5M HNO<sub>3</sub> solution was added in inverse order (as explain in method) to the TS. Moreover, the addition of buffer species ensures quantitative chelation of both metals via controlling the ionization process of EDTA through nullifying the effect of protons released from EDTA during complexation reactions. Though, the volume of 1.0M ClCH<sub>2</sub>COOH (buffer solution) was increased from 5.0ml to 7.0ml or decreased to 3.0ml, the analytical performance of the method was observed unchanged, when the concentration of H<sup>+</sup> ions was equalized by addition of 0.5M. HNO<sub>3</sub>.

### Selection of the wavelength for measurement

The proposed method emphasis on the measurement of permittance<sup>[28]</sup> of the [Cu(II)-EDTA]<sup>2-</sup> absorbing system for quantitative determination of bismuth. The optical density of this absorbing system indicates the concentration of surplus EDTA in test solutions. Therefore, for attending the greater sensitivity, it was necessary to carry out measurement at the system's  $\lambda_{max}$  wavelength. For this purpose, visible absorption spectrum of [Cu(II)-EDTA]<sup>2-</sup> chelate (viz. RB solution) was obtained against the TB solution as a reference, both were prepared as described in experimental section. The spectrum clearly showed that, the [Cu(II)-EDTA]<sup>2-</sup> chelate in chloroacetic acid and nitric acid medium exhibits maximum absorptivity in the region 716 nm to 728 nm (highest at 725 nm). Therefore, measurement of %T was carried out at 725 nm at which all other species are transparent, except the free Cu<sup>2+</sup> ions have little absorbance at this wavelength. Therefore, equivalent amount of free cupric ions were added in TB or reference solution for compensating the background absorbance of unused Cu<sup>2+</sup> ions. Though the concentration of unused / free Cu<sup>2+</sup> ions was not identical in all test solutions, but that does not affect much the linearity

of system's permittance versus concentration of bismuth. In the further part of the experiment, the selected volume of cupric ion, nitric acid and chloroacetic acid solutions were only diluted to 25.0 ml with distilled water for obtaining the TB solution.

### Analytical performance of the method

The test solutions of bismuth prepared as mentioned in above method, provides an excellent evidence that, at the fixed and excess concentration of EDTA, the blue color intensity of [Cu(II)-EDTA]<sup>2-</sup> absorbing system is directly proportional to the concentration of surplus EDTA and inversely proportional to the concentration of bismuth. Since, the concentration of surplus EDTA left after complexation of Bi<sup>3+</sup> was inversely proportional to the concentration of Bi<sup>3+</sup> in test solutions. After measurement of %T at 725nm of each TS and RB against TB as a reference, the clearance of test solution was calculated<sup>[28]</sup> and plotted against the concentration of bismuth for testing the validity of the method. This graph (Figure 1) illustrates that, at fixed wavelength and concentration of EDTA, the clearance of the absorbing system of constant path-length exhibits an exponential increase with concentration of Bi<sup>3+</sup>. The clearance of the absorbing system instigates at value 1 on Y-axis and increases exponentially with the arithmetic increase in

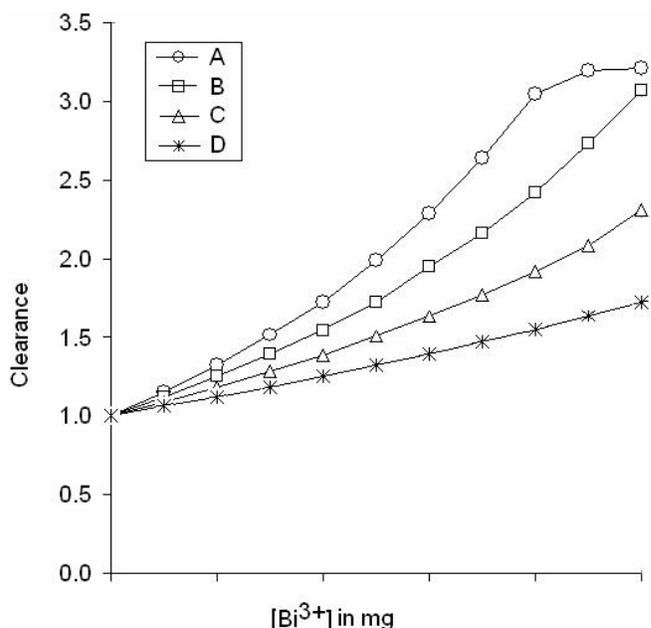


Figure 1 : The graph of clearance (Cr) against the concentration of bismuth; the curve A for 10.0mg to 100.0mg; curve B for 8.0mg to 80.0mg; curve C for 6.0mg to 60.0mg; curve D for 4.0mg to 40.0mg of Bi<sup>3+</sup>.

concentration of the bismuth (Figure 1). Furthermore, the graph of permittance<sup>[28]</sup> (viz. logarithm of clearance) of the absorbing system is plotted versus concentration of the  $\text{Bi}^{3+}$ , also demonstrates that, system's permittance is directly proportional to concentration of the bismuth (Figure 2; TABLE 1).

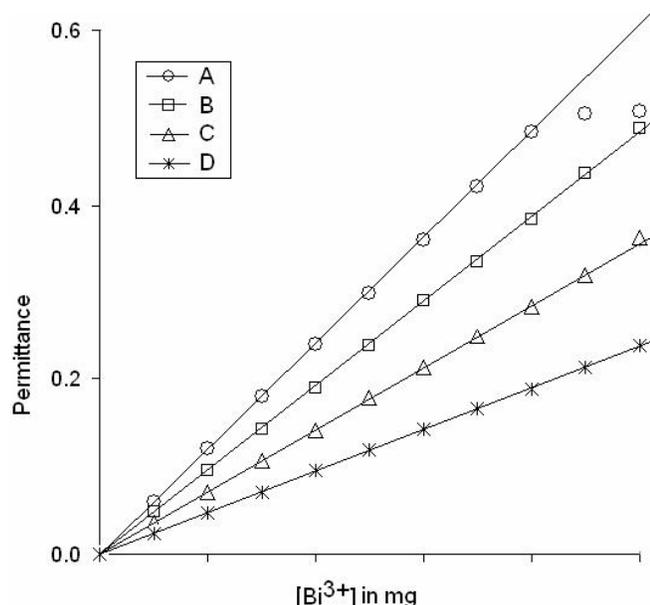


Figure 2 : The graph of permittance (Pr) against the concentration of bismuth; the curve A for 10.0mg to 100.0mg; curve B for 8.0mg to 80.0mg; curve C for 6.0mg to 60.0mg; curve D for 4.0mg to 40.0mg of  $\text{Bi}^{3+}$ .

TABLE 1 : The results obtained at 725nm in quantitative determination of bismuth in the range from 6.0mg to 60.0mg

6.0 mg ml <sup>-1</sup> of $\text{Bi}^{3+}$ (ml)	Conc. of $\text{Bi}^{3+}$ (g)	%T at 725nm (25.0ml)	Clearance $\text{Cr} = \frac{\%T_{\text{TS}}}{\%T_{\text{RB}}}$	Permittance $\text{Pr} = \log \text{Cr}$	a' at 25.0 ml dilution	a' at 1.0 lit. dilution (lit.g <sup>-1</sup> cm <sup>-1</sup> )
0.0	RB	0.000	31.16	1.000	0.0000	--
1.0	TS	0.006	33.85	1.086	0.0360	5.99
2.0	TS	0.012	36.64	1.176	0.0704	5.86
3.0	TS	0.018	39.87	1.280	0.1070	5.95
4.0	TS	0.024	43.11	1.384	0.1410	5.87
5.0	TS	0.030	46.94	1.506	0.1779	5.93
6.0	TS	0.036	50.93	1.634	0.2134	5.93
7.0	TS	0.042	55.31	1.775	0.2492	5.93
8.0	TS	0.048	60.03	1.927	0.2848	5.93
9.0	TS	0.054	65.16	2.091	0.3204	5.93
10.0	TS	0.060	72.06	2.313	0.3641	6.07
Average Values:					5.939	0.1485

Figure 1 also demonstrates that, the absorbing system of fixed reagents concentration, when contain the greater concentration of  $\text{Bi}^{3+}$  shows more curvature in

the clearance curve. The larger concentration of  $\text{Bi}^{3+}$  left smaller amount of surplus EDTA in test solutions; consequently, generates more resolved %T readings with respect to %T reading of RB solution. The resolution in %T reading =  $(\%T_{\text{TS}} - \%T_{\text{RB}})$ . Comparatively, greater concentration of system's reagents when employed for determination of trace concentration of bismuth, the resolution in %T reading was observed poor and the clearance curve appeared nearly as a straight line.

Curve 'A' in figure 1 and figure 2 shows the deviation, which is obtained when the method was tested for quantitation of bismuth in the range 10.0mg to 100.0mg. The 4.0ml of 0.1M EDTA is sufficient to chelate only 83.6 mg of bismuth (viz. 8.0ml 0.05M  $\text{Bi}^{3+}$ ). The concentration of  $\text{Bi}^{3+}$  when equal to 90.0mg or 100.0mg, no surplus EDTA left in the TS; consequently, these TS were identical to TB, so the absorbing system shows deviation from linearity. This system's deviation from the linearity is also confirmation of quantitative chelation of bismuth with EDTA.

#### Effect of analyte concentration on permittance

Permittance is the inability of the test solution (absorbing system with quencher analyte) to absorb the light of specific wavelength with respect to reagent blank (absorbing system only) solution<sup>[28]</sup>. Therefore, excluding only  $\text{Bi}^{3+}$  analyte, the composition of RB solution was kept identical in every respect to TS. With the fixed concentration of absorbing system's reagents [viz. 4.0ml of 0.1M EDTA and 4.0ml of 0.1M  $\text{Cu}(\text{NO}_3)_2$ ]; analytical performance of the method was tested with different standard solutions of bismuth of known concentration. It was observed that, permittance of the absorbing system was dependent only on the concentration of bismuth, since the extent of chelation reaction that occurred between  $\text{Bi}^{3+}$  and excess of EDTA is totally subjective to the concentration of  $\text{Bi}^{3+}$  only. As a result, concentration of the surplus EDTA as well the optical density of copper-chelate was inversely proportional to the concentration of bismuth in test solutions. Thus, at fixed wavelength and concentration of reagents, the permittance of the absorbing system was observed directly proportional to the concentration of  $\text{Bi}^{3+}$  analyte (Figure 2; TABLE 1).

#### Permittance and permittance coefficient

The relationship<sup>[28]</sup> between the system's

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permittance (Pr) and concentration (c) of quencher analyte can be written as shown below and was used for determination of proportionality constant ( $a'$ ) of 1.0cm path length (b) absorbing system.

$$\text{Pr} = a' b c \text{ (when conc. of analyte, c in g/L) or} \quad (1)$$

$$\text{Pr} = \varepsilon' b c \text{ (when conc. of analyte, c in mol/L)} \quad (2)$$

The proportionality constant  $a'$  is termed here as permittance coefficient or  $\varepsilon'$  as molar permittance coefficient of the absorbing system; in order to distinguish that from absorptivity (a) or molar absorptivity ( $\varepsilon$ ) the proportionality constant term used in Beer's law.

At 25.0ml final dilution of test solutions, the proportionality constants shown in TABLE 1 are calculated by using equation (1). At a fixed wavelength, and concentration of absorbing system's reagents, the proportionality constants were remained same for various concentration of bismuth analyte. But the values proportionality constants were observed decreasing with increase in final dilution volume of test solutions, since the number of absorbing species per unit path length in the solution decreases with dilution. For result reported in TABLE 1, the average proportionality constant is 5.939 at 25.0 ml for final volume dilution when doubled from 25.0 ml to 50.0 ml, the proportionality constant is decreased from 5.939 to 2.973 (nearly equal to half). Thus, for a one liter final dilution, the proportionality constant becomes (nearly equal to 0.1485) permittance coefficient for a solution of absorbing system containing unit concentration of analyte; when measured in a cell of unit path length. Consequently, the dimensions of permittance coefficient are  $\text{lit.g}^{-1}\text{cm}^{-1}$ . For every different standard solution of bismuth with the absorbing system permittance coefficient was observed nearly as constant (TABLE 1 and TABLE 2). Increase in dilu-

**TABLE 2 : The permittance coefficient of the absorbing system at 725nm for the different range of concentration of bismuth**

Concentration of bismuth (g)	Average Pro. Const. at 25.0ml	Average Pr. coeff. $\text{Lit g}^{-1}\text{cm}^{-1}$
0.010 to 0.080	5.986	0.1497
0.008 to 0.080	5.996	0.1499
0.006 to 0.060	5.940	0.1485
0.004 to 0.040	5.922	0.1481
0.002 to 0.020	5.916	0.1479
Avg. Values $\rightarrow$	5.952	0.1488

tion volume decreases the value of proportionality constant. Similar circumstance was observed with the permittance of the absorbing system. The permittance values for a series of different standard solution of bismuth with the absorbing system (TABLE 1) were also decreased nearly equal to half when dilution is doubled. But along with the dilution, concentration of reagents is also doubled, then permittance values were nearly similar to those are observed in double dilution.

### Effect of reagent's concentration on permittance and permittance coefficient

This study was carried out through quantitative determination of bismuth in the range 0.006 g. to 0.060 g. with different volumes of absorbing system reagents. The standard solutions of bismuth in this concentration range were prepared separately with the volume 3.0 ml, 4.0 ml, 5.0 ml and 6.0 ml of 0.1M EDTA and 0.1M  $\text{Cu}(\text{NO}_3)_2$  reagents; in addition 3.0ml of 1.0M buffer solution was also used at 25.0ml final dilution of TS. The results of this assay at 725nm (summarized in TABLE 3) interpret that, even if the concentrations of reagents are altered, the permittance is constant for a fixed concentration of bismuth. That means the permittance of the absorbing system is dependent only on concentration of the analyte and is independent on the concentration of reagents. Moreover, at the fixed wavelength (725nm), the permittance coefficient at ev-

**TABLE 3 : The results obtained at 725nm, in the quantitation of  $\text{Bi}^{3+}$  from 6.0mg to 60.0mg with 3.0ml, 4.0ml, 5.0ml and 6.0ml volumes of 0.1M EDTA and 0.1M  $\text{Cu}(\text{NO}_3)_2$  reagents.**

Conc. $\text{Bi}^{3+}$ (g)	Pr. (3.0ml)	$a'$ $\text{lit.g}^{-1}\text{cm}^{-1}$	Pr. (4.0ml)	$a'$ $\text{lit.g}^{-1}\text{cm}^{-1}$	Pr. (5.0ml)	$a'$ $\text{lit.g}^{-1}\text{cm}^{-1}$	Pr. (6.0ml)	$a'$ $\text{lit.g}^{-1}\text{cm}^{-1}$
0.000	0.0000	--	0.0000	--	0.0000	--	0.0000	--
0.006	0.0365	0.1519	0.0357	0.1486	0.0331	0.1381	0.0355	0.1479
0.012	0.0706	0.1471	0.0713	0.1486	0.0719	0.1497	0.0672	0.1400
0.018	0.1108	0.1539	0.1069	0.1485	0.1071	0.1488	0.1069	0.1484
0.024	0.1439	0.1499	0.1420	0.1479	0.1428	0.1487	0.1419	0.1478
0.030	0.1801	0.1500	0.1789	0.1491	0.1785	0.1487	0.1784	0.1487
0.036	0.2180	0.1514	0.2161	0.1500	0.2157	0.1498	0.2134	0.1482
0.042	0.2506	0.1492	0.2516	0.1498	0.2528	0.1505	0.2511	0.1495
0.048	0.2872	0.1496	0.2872	0.1496	0.2886	0.1503	0.2869	0.1494
0.054	0.3248	0.1504	0.3267	0.1512	0.3250	0.1505	0.3236	0.1498
0.060	0.3601	0.1500	0.3651	0.1521	0.3654	0.1522	0.3594	0.1498
Average Values $\rightarrow$		0.1504	--	0.1496	--	0.1488	--	0.1480

ery different concentration of  $\text{Bi}^{3+}$  as well as the volume of system's reagents is also nearly constant. The change in permittance coefficient was observed by a factor of 0.0008 with the unit change in the volume of absorbing system's reagents (TABLE 3). This value is very small can be ignored.

Further, it was also observed that, the resolution in %T readings is decreases with increase in the volume/concentration of system's reagents. Although the resolution in the %T readings does not affect the values of clearance and permittance of the system, but poor resolution decreases the sensitivity (minimum analyte quantifying capacity) of the method. When trace concentration of bismuth (about 0.1 mg) when tested with higher volume (10.0ml of 0.1M EDTA and 0.1M  $\text{Cu}(\text{NO}_3)_2$ ) of reagents, the %T reading of this TS was observed nearly equal to %T reading of RB; as a result the clearance value was nearly equal to 1 and permittance equal to zero. Therefore, by considering the analyte concentration, the volume/concentration of the absorbing system reagents was selected in such way that the absorbing system should produce the better resolution and good sensitivity.

### Effect of wavelength (Selected for analysis) on permittance and permittance coefficient

The value of proportionality constant, absorptivity (a) or molar absorptivity ( $\epsilon$ ) in Beer's law is governed by the wavelength selected for analysis; for the fixed concentration and path length of the absorbing species; it is greatest at the wavelength ( $\lambda_{\text{max}}$ ) where the absorbing species shows maximum absorbance. In Beer's law, the solution of absorbing species of fixed concentration and path length when measured at different wavelengths produces the different values of absorbance as well as absorptivity. This notion was also observed true in the proposed method and it was proved through measuring the same standard solutions of bismuth with the absorbing system at different wavelengths.

The  $[\text{Cu}(\text{II})\text{-EDTA}]^{2-}$  absorbing system in chloroacetic acid and nitric acid medium was showed the  $\lambda_{\text{max}}$  at 725nm. Along with  $\lambda_{\text{max}}$  wavelength, the test solutions were measured at 600nm, 665nm, and 800nm. The results of this assay (summarized in TABLE 4) elucidate that, for the fixed concentration of bismuth in the absorbing system of constant path length, gener-

ates the different values of permittance at different wavelengths. Correspondingly, the magnitude of permittance coefficient ( $a'$ ) was also absolutely administrated by the wavelength selected for analysis. The magnitude of both of these quantities was observed maximum at system's  $\lambda_{\text{max}}$  wavelength.

**TABLE 4 : The results obtained at 600nm, 665nm, 725nm and 800nm in the quantitation of  $\text{Bi}^{3+}$  from 6.0mg to 60.0mg with 4.0ml volumes of 0.1M EDTA and 0.1M  $\text{Cu}(\text{NO}_3)_2$  reagents**

$[\text{Bi}^{3+}]$ (g)	Pr. at 600nm	$a'$ lit.g <sup>-1</sup> cm <sup>-1</sup>	Pr. at 665nm	$a'$ lit.g <sup>-1</sup> cm <sup>-1</sup>	Pr. at 725nm	$a'$ lit.g <sup>-1</sup> cm <sup>-1</sup>	Pr. at 800nm	$a'$ lit.g <sup>-1</sup> cm <sup>-1</sup>
0.000	0.0000	--	0.0000	--	0.0000	--	0.0000	--
0.006	0.0093	0.0389	0.0275	0.1145	0.0358	0.1490	0.0274	0.1144
0.012	0.0187	0.0389	0.0551	0.1149	0.0716	0.1492	0.0534	0.1112
0.018	0.0279	0.0387	0.0842	0.1170	0.1025	0.1423	0.0830	0.1152
0.024	0.0374	0.0389	0.1097	0.1143	0.1443	0.1503	0.1115	0.1162
0.030	0.0478	0.0398	0.1379	0.1150	0.1786	0.1488	0.1393	0.1161
0.036	0.0567	0.0393	0.1662	0.1154	0.2167	0.1505	0.1626	0.1129
0.042	0.0663	0.0395	0.1936	0.1152	0.2521	0.1501	0.1959	0.1166
0.048	0.0772	0.0402	0.2307	0.1201	0.2881	0.1501	0.2285	0.1190
0.054	0.0901	0.0417	0.2570	0.1190	0.3256	0.1507	0.2546	0.1179
0.060	0.1015	0.0423	0.2886	0.1203	0.3664	0.1527	0.2894	0.1206
Avg. Values →	0.0399	--	0.1166	--	0.1494	--	0.1160	--

Thus, the permittance is the property of absorbing system governs by the concentration of absorbance quencher analyte<sup>[28]</sup>, is fixed at the fixed wavelength. Furthermore, the absorbing system was produced better resolved %T readings only at its  $\lambda_{\text{max}}$  wavelength. Therefore, the quantitative assay of quencher analyte should be carried at the system's  $\lambda_{\text{max}}$ -wavelength for better sensitivity; since the small quench in system's absorbance (by the trace concentration of analyte) is well detectable at this wavelength.

### Relative error in absorbing system's clearance and permittance

Many theoretical and experimental investigations have been carried out on precision<sup>[34,35]</sup> and accuracy<sup>[36]</sup> in the molecular absorption spectrophotometry. For minimum relative error it is essential to confine the %T reading of absorbing system in the range<sup>[27,36]</sup> between '20% to 60%'. The specific volume/ concentration of absorbing system (or its reagents) on reaction with analyte, when generates %T readings exactly in between '20% to 60%'; that volume may be termed here as absorbing system's best volume; since it generates %T

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readings which are valid for minimum relative error.

With the best volume of absorbing system, the %T value of the RB starts nearly at 20% and for test solution with highest concentration of the analyte, TS<sub>max</sub> (TS<sub>max</sub> is not the TB); %T value nearly ends at 60%. Under such a condition, theoretically the clearance values for this set of %T readings are in between 1.000 (for RB) to 3.000 (for TS<sub>max</sub>); and corresponding permittance values are in between '0.0000 to 0.4771'.

Thus, the absorbing system with its any specific volume/concentration on reaction with analyte, when generates clearance values in the range in between '1.000 to 3.000' are considered valid for minimum relative error; even though the instrument output of %T may of may not be in between '20% to 60%'. When the instrument output %T is not occurred in the range of '20% to 60%'; the factors those introduce the relative error in the %T reading of the RB solution, exactly the same factors (with little bit more or less magnitude) introduce the relative error in the %T readings of TS. The clearance values of the TS, when calculated<sup>[28]</sup> using %T reading of RB solution (TABLE 1), the effect of relative error associated with each %T reading gets cancelled out to more extent. For the RB solution the relative error associated with clearance is gets cancelled to 100%; since clearance of RB (is equal to 1.000) is the ratio of identical readings of %T.

The valid %T reading may be obtained by increasing or decreasing the volume/concentration of absorbing system or its reagents and controlling the dilution of test solutions. The result reported in TABLE 1, shows %T reading in between 31.16 % to 72.06% when test solutions diluted to 25.0ml fixed volume and same solutions when diluted to 50ml of fixed volume, generates %T readings nearly in between 52.74 % to 80.01%. In both the set of readings, many %T readings are above to 60% and the average proportionality constants are 5.939 and 2.973 corresponding at 25ml and 50.0ml dilution, but for both the set of reading the average values of permittance coefficient are 1.485 and 1.486 lit g<sup>-1</sup>cm<sup>-1</sup> respectively, which are constant.

Consequently, for the determination of analyte at a trace level, sensitivity of the method can be increased simply by decreasing the concentration of absorbing system or its reagents. Thus, any suitable volume of the absorbing system on reaction with analyte, if generates

instrument output of %T with a greater resolution and fulfils the requirement of minimum relative error for clearance, then that volume is better than the best volume of absorbing system.

### Application of the method

The proposed method was applied for determination of bismuth in the pharmaceutical formulation such as Trymo tablets. The sample (1 tablet) was slowly heated in fuming hood with 10ml of conc. HCl followed by addition of 4ml of conc. HNO<sub>3</sub>. The organic matter was destroyed by treatment with 8ml of 70% perchloric acid. (Boiling perchloric acid can result in serious explosions.) Sample dissolution was carried out for about 18-20 minutes till maximum of the acid was get evaporated. The solution was diluted to 45ml with distilled water containing sufficient HNO<sub>3</sub>. After adjusting the pH equal to the pH (=0.58) of standard bismuth solution (containing 2.0mg ml<sup>-1</sup>Bi<sup>3+</sup>) the solution was finally diluted to 50.0ml. The different fractions were used for determination of bismuth with the recommended procedure. The sample solution has little turbidity which gets dissolved on addition of EDTA solution. The permittance values of sample solution and the average value of permittance coefficient (5.952) at 25.0ml dilution were used for determination of bismuth using equation (1). The results of this determination are shown in TABLE 5.

**TABLE 5 : Results obtained at 725nm in quantitation of bismuth in trymo tablet, with 4.0ml of volumes of absorbing system's reagents**

Bismuth taken (mg)	n	Bismuth found (mg)*	Bismuth found in tablet (mg)
2.15	3	2.16	108.0
4.30	3	4.29	107.30
6.45	3	6.46	107.7
8.60	3	8.60	106.5
10.75	3	10.75	107.5
12.90	3	12.85	107.1
15.05	3	15.03	107.4

Average value → 107.5

\*Average value of three (n) determinations

### Interferences in bismuth determination

The interfering ions can be classified into two groups. The first group is composed of those cations whose

EDTA chelates in acidic medium are sufficiently stable comparative to bismuth chelate. EDTA chelates of  $\text{Fe}^{3+}$  and  $\text{Co}^{3+}$  are more stable than  $\text{Bi}^{3+}$  chelate, consequently  $\text{Fe}^{3+}$  and  $\text{Co}^{3+}$  are the serious interfering cations in  $\text{Bi}^{3+}$  determination. The second type of interfering ion includes those cations which do not compete with bismuth but with copper for the EDTA. These are the cations which forms more stable chelate than copper chelate, particularly no any divalent cation at such strong acidic pH 1 to 1.25, forms more stable chelate than copper chelate. The cations whose EDTA chelate is less stable than copper chelate, particularly the aluminum, barium, calcium, cerium, copper, lead, magnesium, manganese, molybdenum, nickel, silver and zinc does not interferes in bismuth determination. This type of interference can be predicted from the formation constant<sup>[27]</sup> of the EDTA chelates of the cations. In the previous literature<sup>[23,37]</sup> the inference study was already completed.

## CONCLUSIONS

The proposed method for determination of bismuth is based on the measurement of concentration of surplus EDTA through generating the copper-EDTA chelate as the absorbing system. The absorbing system was found excellent for bismuth determination because of its formation and stability at high acidic pH 1 to 1.25, to which quantitatively chelation of  $\text{Bi}^{3+}$  was attained. Many divalent metal cations do not complexed by EDTA at this pH, which makes the process selective. Because of the larger difference in the stability constant of EDTA chelate of  $\text{Bi}^{3+}$  and  $\text{Cu}^{2+}$ , the stability of  $\text{Bi}^{3+}$ -chelate is not affected because of the addition of relative larger amount of  $\text{Cu}^{2+}$  ions; consequently, the linearity of system's permittance against the concentration was maintained even at low concentration (2.0mg) of  $\text{Bi}^{3+}$ . The lower concentration of bismuth (less than 1.0 mg) is not determined in this experiment, but it is possible through decreasing the volume/concentration of system's reagents; since permittance and permittance coefficient are not preside over the concentration of reagents.

The present proposed method is very simple, easy to carry out and do not involve the step of solvent extraction for preconcentration of analyte (bismuth). It is also sensitive [up to 2.0mg of  $\text{Bi}^{3+}$  tested with 4.0ml

volumes of 0.1M EDTA and 0.1M  $\text{Cu}(\text{NO}_3)_2$ ] and produces the reproducible results with good accuracy. The method also found excellent over the photometric titration of bismuth with EDTA; because the graphical method of determination of end point is tedious and time consuming. When the proportionality constant at specific dilution (or permittance coefficient) is determined by using a series of standard solutions of known concentration, the concentration analyte is determined directly using equation (1). The proposed method also neglects a step of standardization of reagents, since it involves the measurement of permittance of TS with respect to permittance of RB. The maintenance of the identical proton ion concentration in RB with respect to test/sample solutions is the only care must be taken for the good linearity.

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