

Micellar-Sensitized Spectrophotometric Determination of Magnesium in Drinking Water

Ramazan Gürkan¹, Halil İbrahim Ulusoy and Mehmet Akçay

University of Cumhuriyet, Faculty of Sciences & Arts, Department of Chemistry, TR-58140, Sivas, Turkey

Received: 08 May 2009; Accepted: 04 June 2009

Abstract

A sensitive and relatively selective spectrophotometric method is proposed for the rapid determination of magnesium using Eriochrome black T (EBT) as a complexing agent in the presence of N-cetyl-N,N,N-trimethylammonium bromide (CTAB). The complex formation reaction between EBT and magnesium (II) is instantaneous in presence of $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer at pH 9.5 after CTAB adds as micellar-sensitized medium and the absorbance as analytical signal remains stable for over 6 h. N-cetyl N,N,N-trimethylammonium bromide as cationic surfactant and Triton X-100 as nonionic surfactant are used for improving the sensitivity and solubility of the analytical system, respectively. The surfactant-sensitizing method allows the determination of magnesium in the concentration range of $0.05\text{-}1.2 \mu\text{g mL}^{-1}$ with a molar absorption coefficient of $8928 \text{ L mol}^{-1} \text{ cm}^{-1}$ and Sandell's sensitivity of 2.82 ng cm^{-2} . The method has a detection limit of $0.012 \mu\text{g mL}^{-1}$ ($\text{DL}=3\text{S}_b/\text{m}$) and quantification limit of $0.054 \mu\text{g mL}^{-1}$ ($\text{QL}=10\text{S}_b/\text{m}$) at an analytical measurement wavelength of 640 nm with a bathochromic shift of 86 nm. The selectivity of chelating reagent was improved by the use of 1 mL masking agent solution containing 0.1 mol L^{-1} EDTA, 0.01 mol L^{-1} triethanolamine and $5000 \mu\text{g NaF mL}^{-1}$. The proposed method has been successfully applied to the determination of magnesium at trace levels in different drinking water samples. The precision (with CV of 2.35%) and the accuracy obtained were highly satisfactory.

Keywords:

Surfactants; CTAB; EBT; bathochromic shift; spectrophotometry; magnesium determination

1. Introduction

Mg(II) ions have indispensable roles in many vital biological events [1]. The relationship of magnesium deficiency and diabetes mellitus has generated discussion in the medical field in the past 10 years [2]. In addition, Mg(II) is involved in a series of metabolism processes in the human body, including the formation of bones and cells. The daily requirement of Mg(II) for an adult is 350 mg for a male and 300 mg for a female. Magnesium deficiency will result in muscle sag and poor stamina [3], so the determination of magnesium in foods and drinking waters is very important.

The significant role of calcium and magnesium has resulted in the publication of many methods for their determination in a wide variety of matrixes [4, 5, 6], especially in natural and drinking waters [8 and 9]. Several techniques such as atomic absorption spectrometry [4, 10] atomic emission spectrometry [7], ICP-OES [11], capillary electrophoresis [9,12], spectrofluorimetry [13], liquid chromatography [14], spectrophotometry [15] combined with chemometrical methodologies [5, 6] have been presented over the years for the determination of these elements.

¹ Phone: (90) 346 219 10 10
ISSN: 1306-3057,

Fax: 0 346 2191186
Moment Publication ©2009

E-mail: rgurkan@cumhuriyet.edu.tr

Flame atomic absorption spectrometry (FAAS) is one of the most sensitive and efficient techniques used for the determination of magnesium [16]. Although, apart from sodium, no significant spectral interferences have been reported in the determination of magnesium, chemical interferences have to be taken into account for the analysis of real samples [16]. Silicon, aluminum and phosphate suppress the signal of Mg in the air-acetylene flame through the formation of stable compounds. Therefore, the addition of releasing agents (lanthanum or vanadium) is necessary for the reduction of these effects. Nevertheless, the interferences from silicon and aluminum persist to this treatment [4]. The interference of sodium becomes detectable when it is present at ten times the concentration of magnesium in an air-acetylene flame and a monochromator of bandpass 0.5 Å [19]. However, such selectivity does not solve the problems of spectral interference of sodium when seawater is analyzed, as the concentration of sodium ion in seawater is about 8–26 times higher than that of the magnesium ion [11].

Common analytical methods applied for the determination of magnesium with FAAS employ solvent extraction as a pre-concentration step, partly because of the low detection limits available, but primarily because of the relatively high abundance of this element in many sample types [17]. The complex of 8-hydroxyquinoline with magnesium, among several other complexes like magneson or Eriochrome black T, has been widely utilized for its determination with FAAS [17]. The complex was subsequently extracted in an organic solvent (mostly 4-methylpentan-2-one) in order to remove the analyte element from the initial matrix [17]. The disadvantage of solvent extraction (toxicity, required volume, etc.) following the formation of the metal-chelate complexes in the usual spectrometric applications has initiated a wide research activity on the development of alternative methods like the use of adsorptive columns [18], co-precipitation [19], cloud point extraction [20], and even micellar-enhanced ultrafiltration [21]. Among the simple and most versatile methods is the micelle-sensitized spectrophotometry without need to pre-separation and pre-concentration from aqueous solution. This technique only requires the direct addition of surfactant into the metal ion complexation media with a selective chromogenic ligand. The similar micellar systems in literature [22, 23, 24] are extensively used to improve the sensitivity and selectivity of numerous analytical reactions, and to solubilize an insoluble complex and/or ligands.

In the present study, a simple, sensitive, relatively selective, accurate and precision method for the determination of magnesium in drinking water samples by spectrophotometry is described based on the formation of the magnesium (II)-EBT complex in micellar medium. In order to improve the sensitivity and solubility of analytical system, N-cetyl-N,N,N-trimethylammonium bromide as cationic surfactant and TritonX-100 as nonionic surfactant were used, respectively. The method was applied to the determination of magnesium in three different commercial drinking water samples. The results were evaluated by spiking standard magnesium solutions into the samples under the optimal conditions and it was concluded that the results found by using the proposed method was at quantitative acceptable recovery levels.

2. Experimental

2.1. Reagents and solutions

All reagents used were of analytical grade and the bidistilled water was used throughout analysis.

Stock magnesium solution (1000 µg mL⁻¹): Prepared by dissolving 10.30 g of MgSO₄·7H₂O (Merck) in water and diluting to volume with water in a 1000 mL volumetric flask.

Erichrome Black T solution (5×10^{-4} mol L⁻¹): Prepared by dissolving 0.0233 g of Na-EBT (Merck) in 100 mL of ethanol-water mixture (80+20, v/v).

Masking agent solutions: 100 mL 0.1 mol L⁻¹ EDTA (Na-EDTA, Merck), 100 mL 5000 µg mL⁻¹ NaF and 100 mL 0.01 M Triethanolamine.

N-cetyl-N,N,N-trimethylammonium bromide (CTAB) solution (7.3×10^{-3} mol L⁻¹): Prepared by dissolving, mixing properly and diluting the appropriate amount of cationic surfactant in 100 mL water.

Triton X-100 solution (7.3×10^{-3} mol L⁻¹): Prepared by dissolving, mixing properly and diluting the appropriate amount of nonionic surfactant in 100 mL water.

Sodium dodecyl sulphate (SDS) solution (7.3×10^{-3} mol L⁻¹): Prepared by dissolving, mixing properly and diluting the appropriate amount of anionic surfactant in 100 mL water.

NH₃/NH₄Cl buffer solution (0.200 mol L⁻¹, pH 9.5): Prepared by dissolving 0.3852 g solid NH₄Cl in approximately 50 mL water, mixing with 3.96 mL concentrated NH₃ solution and diluting to 100 mL with water.

2.2. Instrumentation

In this study, a Shimadzu Model UV-Visible 160 spectrophotometer equipped with a 1 cm quartz cell was used for absorbance measurements. In order to control the temperature of reaction medium with an accuracy of $\pm 0.1^\circ\text{C}$, a Grant LTG-6G model thermostatic water bath regulated at the desired temperature operating in the range of -20 and 100°C was used. A stopwatch was used for recording the reaction time. A pH meter consisting of a glass-calomel electrode double was used to determine pH values of solutions. All solutions were preheated to a suitable working temperature before the initiation of the complex formation reaction in micellar medium. The absorbance measurements were made at a working wavelength of 640 nm.

2.3. General procedure

Aliquots of standard solution of magnesium, 2 mL 0.2 mol L⁻¹ pH 9.5 buffer solution, 1 mL of masking agent solution (0.1 mol L⁻¹ EDTA, 5000 µg mL⁻¹ NaF or 0.01 mol L⁻¹ triethanolamine), 1 mL of EBT solution, finally 0.3 mL of CTAB and 0.1 mL of Triton X-100 solution were added to a series of 10-mL standard flask and the mixture shaken thoroughly at room temperature when a complete and stable red colour was formed almost instantaneously. The solutions were made up to the mark with water. The absorbance was measured at 640 nm against the corresponding reagent blank prepared under identical conditions but without magnesium and the calibration curve was obtained with working standard solutions in the range of 0.05–1.2 µg mL⁻¹. Concentration of magnesium in test solutions was calculated from the regression equation computed from the Beer's law data as a reference. Additionally, for the Mg content of drinking water samples and the accuracy of the method, the "recovery" test was used by spiking commercial water with Mg, i.e. known quantity of standards was determined (µg mL⁻¹), than was added to different kinds of samples where magnesium quantity had previously been measured.

3. Results and Discussion

3.1. Spectral characteristics of Mg(II)-EBT complex

The absorption maximum was obtained for magnesium-EBT complex in water at 554 nm. Investigations on the effect of various surfactants on the absorbance of magnesium-EBT

complex were carried out. The surfactants used were CTAB as cationic surfactant, SDS as anionic surfactant and TritonX-100 as nonionic surfactant. The study was performed using 2 mL 0.200 mol L⁻¹ pH 9.5 NH₃/NH₄Cl buffer solutions, 0.3 mL 7.3x10⁻⁴ mol L⁻¹ surfactant, 0.7 mL 5x10⁻⁴ mol L⁻¹ EBT and 1 mL 10 µg mL⁻¹ Mg²⁺ ion. The absorbance values and corresponding molar absorptivities at absorption maxima of magnesium complexes in these media are given in Table 1. The best increase in the absorbance of the complexes occurred only in the presence of CTAB. CTAB was used as a micellar forming surfactant throughout this work. The magnesium (II) ions and EBT form a red complex with an absorption maximum in micellar medium at 640 nm. The reaction between EBT and magnesium (II) is rapid and the metal complex formed is stable for at least 6 h. The use of CTAB as cationic surfactant leads to a maximum increase in the absorbance signal and as a result the analytical determination sensitivity is also increased. Addition of CTAB was accompanied by a bathochromic shift of the absorbance of the Mg (II)-EBT complex and an increase in its molar absorptivities; 640 nm was selected as the wavelength to be measured. In the presence of CTAB, magnesium-EBT complex has a low solubility in water, which can be overcome by adding TritonX-100 as nonionic surfactant. Before the absorbance measurement, a meaningful shift in analytical wavelength was not obtained with adding Triton X-100.

Reagent blank was used thereafter as a reference because it showed absorption at this wavelength.

Table 1 Influences of some surfactants on the absorbance of magnesium-EBT complex (Optimum conditions: 2 mL 0.200 mol L⁻¹ pH 9.5 NH₃/NH₄Cl buffer solution, 0.3 mL 7.3x10⁻⁴ mol L⁻¹ Surfactant, 0.7 mL 5x10⁻⁴ mol L⁻¹ EBT and 1 mL 10 µg mL⁻¹ Mg²⁺ ion)

| Surfactant | Nature of Surfactant | λ_{\max} (nm) | $\Delta\lambda_{\max}^{**}$ (nm) | Absorbance | ϵ_{\max} (L mol ⁻¹ cm ⁻¹) | Stability (hour) |
|--------------|----------------------|-------------------------------------|-------------------------------------|------------|---|---------------------|
| In water | - | 554 ^a (563) ^b | - | 0.797 | 6.01x10 ³ | 3 |
| SDS | Anionic | 615 ^a (562) ^b | 61 | 0.851 | 7.62x10 ³ | - |
| CTMAB* | Cationic | 640 ^a (646) ^b | 86 | 0.855 | 8.93x10 ³ | 6 |
| Triton X-100 | Nonionic | 627 ^a (575) ^b | 19 | 0.811 | 6.78x10 ³ | - |

* The best surfactant increasing its sensitivity and relatively selectivity according to those of complex in aqueous solution.

** It shows that the absorption maximum of the metal-complex shifted to longer wavelength.

^a In the presence of 0.2 mg L⁻¹ Mg²⁺

^b In the presence of 2 mg L⁻¹ Mg²⁺

3.2. Effect of pH

The effect of pH on the formation of the magnesium-EBT complex in presence of CTAB was examined at 640 nm using various buffer solutions of different pH values ranging from 6.0 to 11.0. The results are given in Fig. 1 (a). The magnesium-EBT-CTAB ternary complex begins to form at approximately pH 6.0, with maximal and constant absorbance being reached at pH 9.5. After pH 9.5, a precipitation and turbidity was formed under experimental conditions. In order to overcome this problem, Triton X-100 was added into the Mg(II)-EBT-CTAB ternary complex system. In the light of these findings, all subsequent studies were carried out at pH 9.5 using NH₃/NH₄Cl buffer. The effect of the buffer concentration on the magnesium-EBT complex was studied within buffer concentration range from 0.05 to 0.35 mol L⁻¹ and according to the results a maximum increase was observed in

the absorbance signal in the buffer concentration of 0.2 mol L^{-1} . Thus, a concentration of 0.2 mol L^{-1} was chosen for the procedure (Fig.1 (b)).

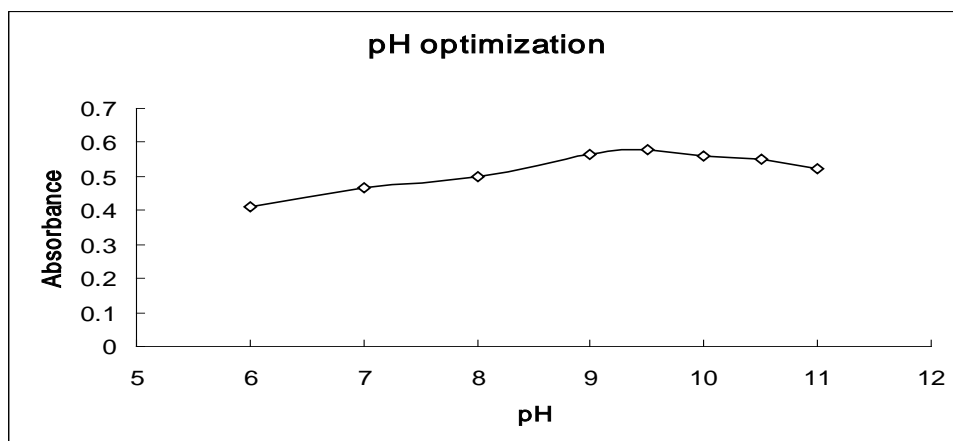


Fig.1 (a) The pH effect on the absorbance of Mg (II)-EBT complex in the presence of cationic surfactant CTAB at 640 nm

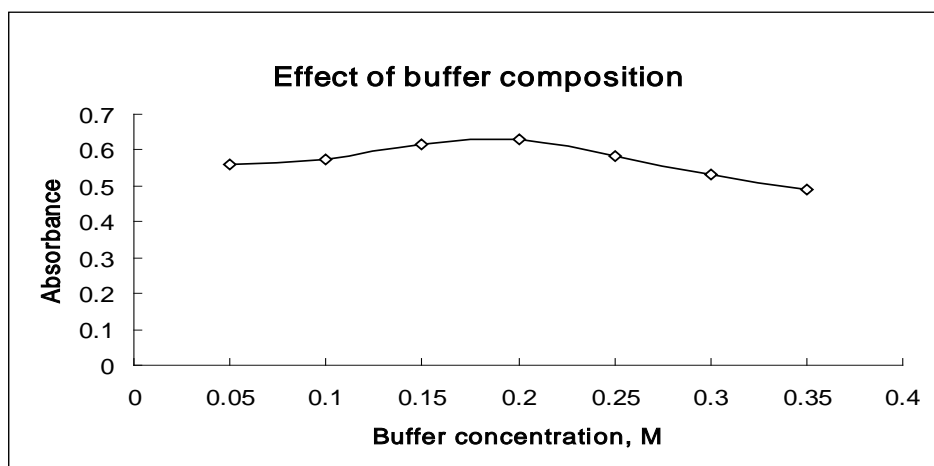


Fig.1 (b) The effect of buffer composition on the absorbance of Mg (II)-EBT complex in the presence of cationic surfactant CTAB at 640 nm

3.3. Effect of the type and amount of surfactants

The desired complex and ligand has good water solubility in alkaline media, but sensitivity of its complex in the absence of surfactants is low. In order to improve the sensitivity and selectivity of complex formation reaction, the effect of type and concentration of different surfactants on the reaction were examined. To ensure the effect of the types of surfactants, TritonX-100 as nonionic surfactant, SDS as anionic surfactant and CTAB as cationic surfactant on the absorbance of complex were studied. The results showed that TritonX-100 must be present in analytical system in a minimum concentration of $5.48 \times 10^{-5} \text{ M}$ to avoid precipitation and turbidity. When this surfactant is present in the lower and higher concentrations, a decrease was observed on the absorbance signal. Thus, the concentration of $5.48 \times 10^{-5} \text{ mol L}^{-1}$ was chosen as optimum value for the analytical procedure (Fig.2 (b)). The effect of CTAB concentration on the determination of magnesium was studied in the concentration range of 1.825×10^{-5} - $7.3 \times 10^{-4} \text{ mol L}^{-1}$. The results are shown in Fig.2 (a). When CTAB is present in a minimum concentration of $2.19 \times 10^{-4} \text{ mol L}^{-1}$, the absorbance signal is maximal and constant. CTAB affects the absorbance signal in the lower and higher

concentrations due to decrease in sensitivity. Therefore, the concentration of 2.19×10^{-4} mol L⁻¹ was chosen as optimum value for the further study (Fig.2 (a)).

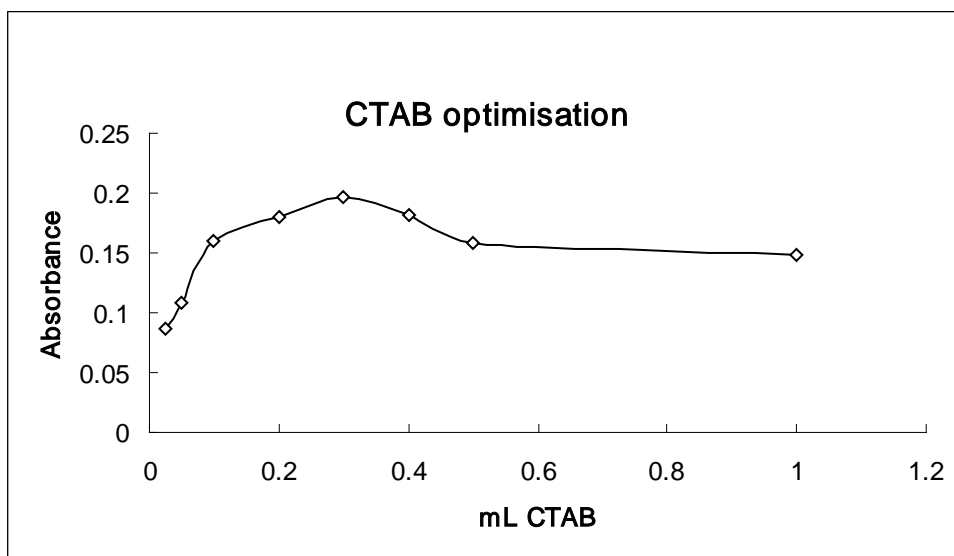


Fig.2 (a) The effect of CTAB concentration the absorbance of Mg (II)-EBT complex in the presence of cationic CTAB at 640 nm

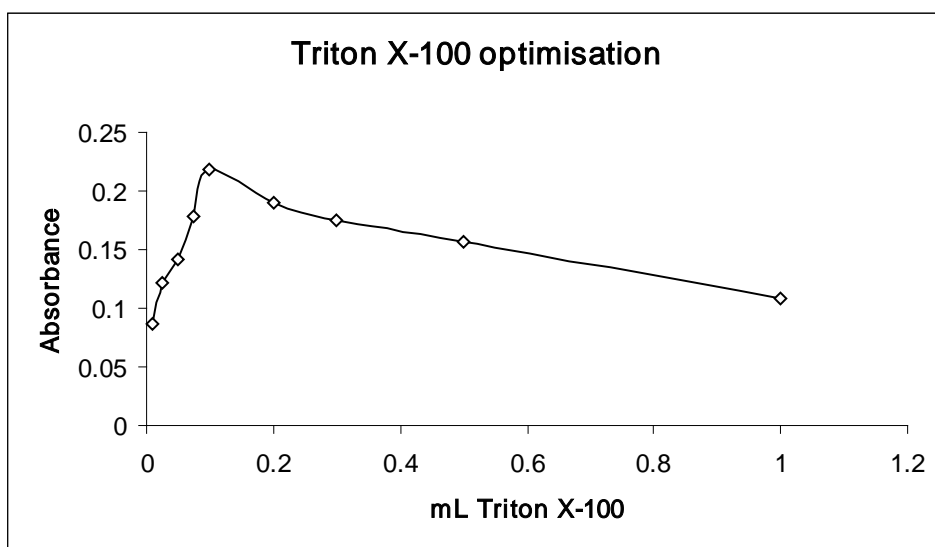


Fig.2 (b) The effect of TritonX-100 concentration on the absorbance of Mg (II)-EBT complex in the presence of cationic CTAB at 640 nm

3.4. Effect of reagent concentration

The effect of EBT amount on Mg-EBT complex formation was studied in both the aqueous solution and cationic micellar medium at optimum pH value. The results are clearly seen in Figure.3. It was found that the absorbance signal increased with increasing reagent concentration in both media in the studied concentration range. It is clearly seen that the absorbance is higher for the same reagent concentration in the cationic surfactant medium. A maximum and constant absorbance value was obtained with at least three fold-excess reagent concentrations from those of magnesium. When EBT/Mg (II) concentration ratio is 5.25 fold, the maximum reproducible absorbance values were obtained with an EBT/Mg (II) ratio

changing between 3 and 30. However, both the absorbance of complex and repeatability of method was decreased in the higher CTAB:Mg(II) concentration ratios.

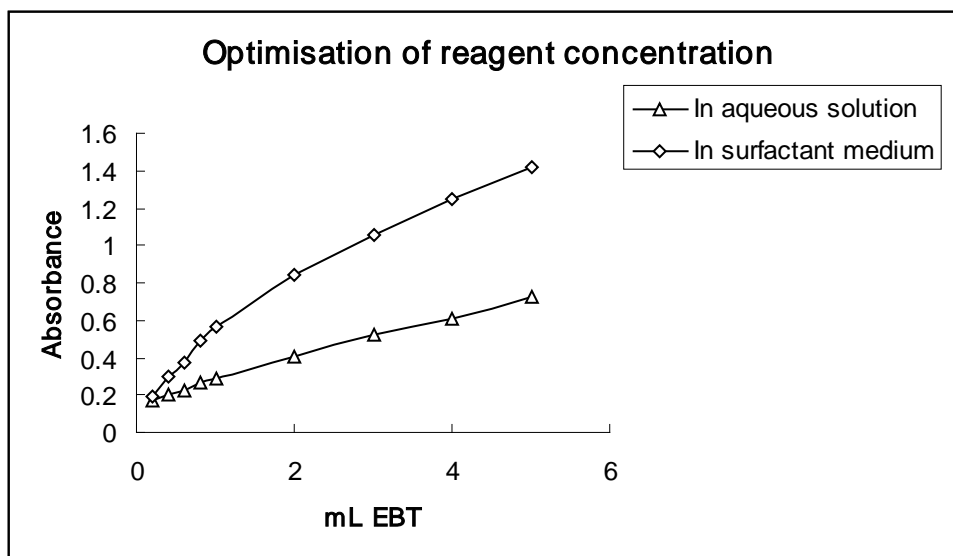


Fig.3 The effect of EBT concentration on the absorbance of Mg (II)-EBT complex in aqueous solution and surfactant medium at 554 nm and 640 nm, respectively, at pH 9.5

3.5. Composition of Mg(II)-EBT complex

The positive charge of the cationic surfactant would attract the negatively charged complex or mixed ligand complex forming 1:2 (mole ratio) complex of CTAB and Mg(II)-EBT. The mole ratio of Mg(II) to EBT in the binary metal-chelate complex was determined by means of Job's method [25] and a mole ratio of 1:2 was found. Job's method is based on the following fact: *if a series of solutions is prepared, each containing the same total number of moles of Mg(II) and EBT or Mg(II)-EBT and CTAB, but a different ratio, R, of moles EBT to moles Mg(II), the maximum amount of product, Mg-EBT or Mg-EBT-CTAB complex, is obtained in the solution in which $R=k$ (the stoichiometric ratio).* To implement Job's method experimentally, one prepares a series of solutions containing a fixed total number of moles of Mg(II) and EBT (or Mg-EBT and CTAB), but in which the R is systematically varied from large to small (or small to large), and measures the amount of product obtained in each solution. One then plots amount of product versus R, and obtains a maximum at the initially-unknown value of k. The composition of ternary complex was studied with initially excess of CTAB by using the continuous variation method, which is also called as Job's method. For ternary complex system, approximately a mole ratio of 1:2 was found by using Job's method and changing magnesium concentration, respectively. Because the complete break point in plot depends on the magnesium concentration used, it can not be reached to a net conclusion by changing the concentration of EBT in mole ratio method. A development of maximum colour was reached at a Mg(II)/EBT molar concentration ratio near 1:2 ratio ; but a complete ratio is depended on magnesium concentration. Additional information on the composition of ternary complex was also obtained by using the continuous variation method applied to the surfactant at equal-molar concentrations and the complex was formed at 1:2 molar ratios in a similar way. As a result, a binary Mg(II)-EBT complex/CTAB at 1:2 mole ratio was found. Thus, it was concluded that the ternary complex was a Mg(II)-EBT-CTAB complex having 1:2:2 mole ratio.

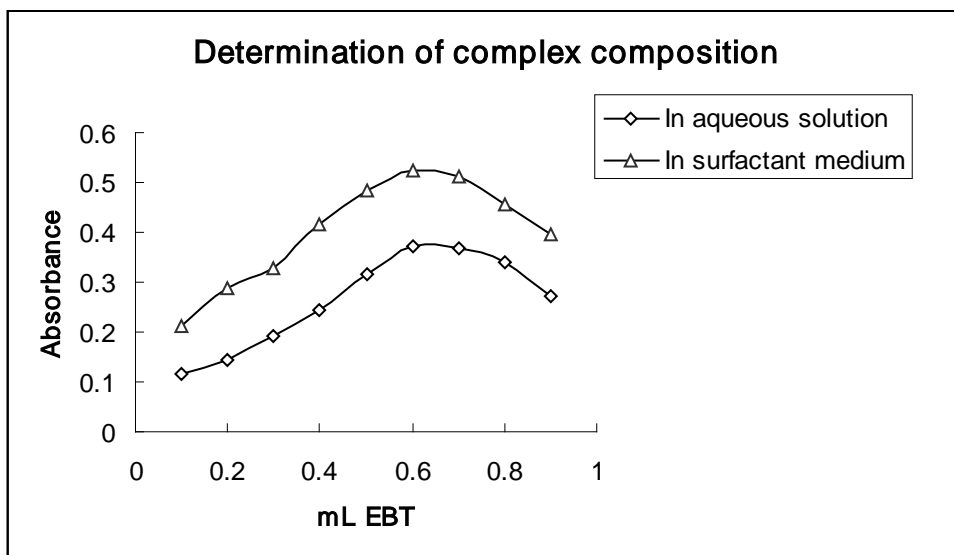


Fig. 4 (a) The determination of Mg(II)-EBT complex composition in aqueous solution and surfactant medium at 554 nm and 640 nm, respectively, at pH 9.5 by using Job's method

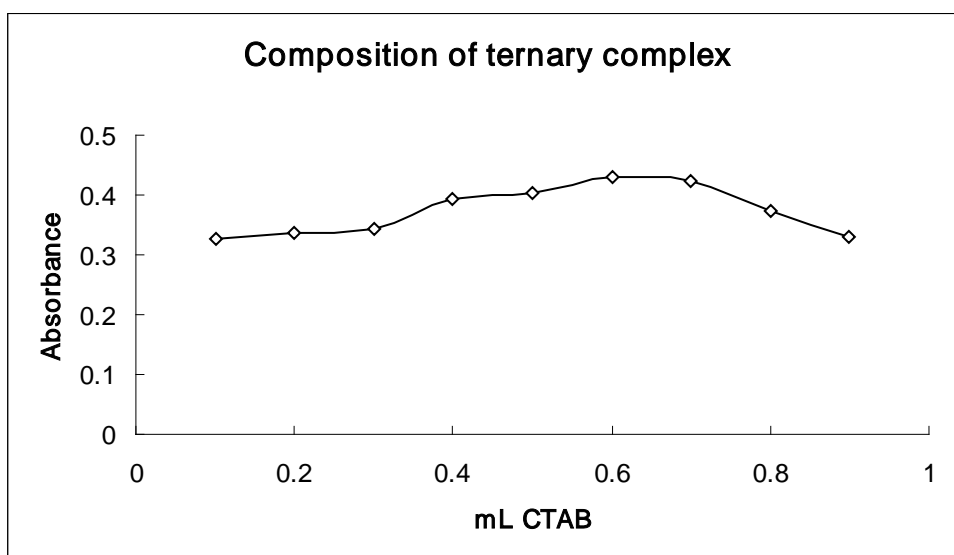


Fig. 4 (b) The determination of Mg(II)-EBT-CTAB ternary complex composition in presence of CTAB at 640 nm in $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer medium (0.2 M, pH 9.5) by using Job's method

3.6. Effect of the reaction temperature and time

The dependency of the absorbance on equilibrium temperature was studied in the temperature range of 20-60 °C, and it was found that the complex formation equilibrium remained a maximum and constant value in the temperature range of 25-45 °C. In order to make a surfactant-sensitized spectrophotometric measurement in a fast and easy way and to fulfill the complex formation reaction, the equilibrium temperature and time must be optimized. It is observed in Figure 6 that the absorbance decreased at higher temperatures. Thus, a temperature of 25 °C was chosen as optimal value because of being operating-easy. Also, the dependency of absorbance on equilibrium time was studied in the time range of 0.5-30 min and it was found that the complex formation equilibrium or the color development of the complex is complete in the first 5 min and the color is stable for at least 6 h in terms of

good reproducibility of absorbance. An equilibrium time of 5 min was chosen as an optimum value for complex formation equilibrium.



Fig.5 The effect of the complex formation equilibrium time on the absorbance of Mg(II)-EBT complex in surfactant medium at 640 nm and at pH: 9.5 under optimum conditions

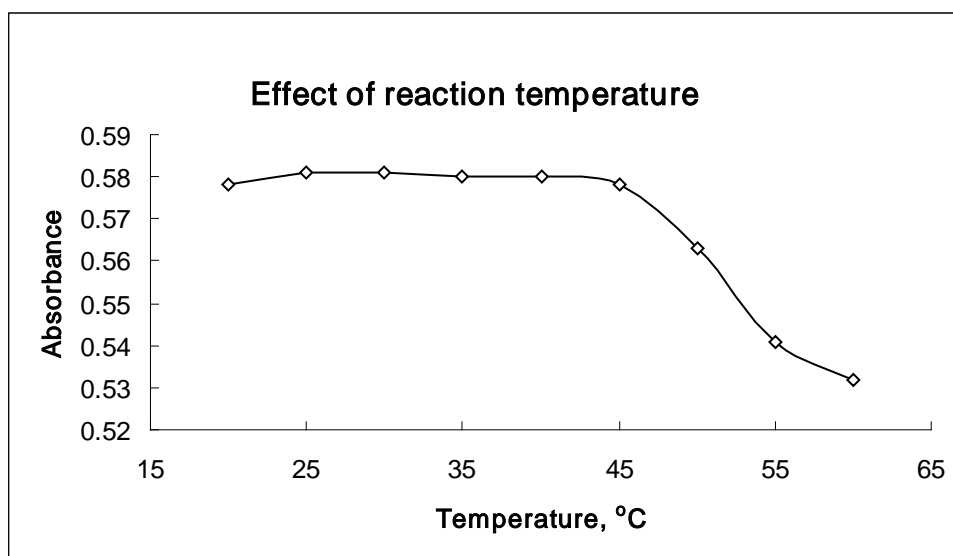


Figure 6 The effect of the complex formation equilibrium temperature on the absorbance of Mg(II)-EBT complex in surfactant medium at 640 nm and at pH: 9.5 under optimum conditions

3.7. Effect of interfering ions

EBT is not highly selective reagent for the spectrophotometric determination of magnesium at trace levels. However, in order to mask the interfering ions, the use of masking agent solutions such as EDTA (0.1 mol L^{-1}), triethanolamine (0.01 mol L^{-1}) and NaF ($5000 \mu\text{g mL}^{-1}$) highly increases the selectivity of complex formation reaction. These independent

masking solutions lead to a change of $\pm 5\%$ in absorbance when adding 1 mL masking solution for a final volume of 10 mL.

To study the effect of potential interfering metal cations on the determination of magnesium ion at optimum conditions, according to the proposed method a solution containing both interfering cations and magnesium ion was treated. The selectivity of the reaction was investigated by using independently masking reagent solutions such as EDTA for Fe(II), Mn(II), Cu(II), Ca(II), Cr(III), Cd(II), Zn(II) and Pb(II), NaF for Fe(III) and Al(III) and triethanolamine for only Fe(III). The tolerance limit was accepted as a change of $\pm 5.0\%$ in absorbance value in which the magnesium ion solution of $0.7 \mu\text{g mL}^{-1}$ gives at optimum conditions. It is clear that the best serious interference is insoluble metal hydroxide salts in higher alkaline pH values from 9.5 and metal cations which have formed the stable complexes with reagent. The tolerable limits for these interfering species are given in Table 2 in both the presence and absence of masking agents. Also, it was found that Cl^- , Br^- , SO_4^{2-} , NO_2^- , NO_3^- , HCO_3^- , HPO_4^{2-} , CH_3COO^- and F ions as anionic interfering species did not interfere in the determination of $0.7 \mu\text{g mL}^{-1}$ Mg(II) in both the aqueous solution and micellar medium.

Table 2 Tolerance limits of possible interfering ions in the surfactant-sensitized spectrophotometric determination of $0.7 \mu\text{g mL}^{-1}$ Mg^{2+} ion in the optimum conditions

| Interfering ion | In aqueous medium: [Interfering ion] / [Mg^{2+}] | In surfactant medium: [Interfering ion] / [Mg^{2+}] |
|---|--|---|
| NH_4^+ , Na^+ , Li^+ and K^+ | 250 | 1000 |
| Ca^{2+} | 25 | 70 (100) ^a |
| Cd^{2+} and Pb^{2+} | 3 | 15 (50) ^a |
| Cr^{3+} and Zn^{2+} | 15 | 50 (100) ^a |
| Al^{3+} | 0.28 | 1 (4) ^b |
| Fe^{3+} | 0.4 | 2 (8) ^b ve (50) ^c |
| Fe^{2+} and Mn^{2+} | 0.1 | 0.5 (145) ^a |
| Cu^{2+} | 0.2 | 1 (45) ^a |
| HPO_4^- | 32 | 64 |
| SO_4^{2-} | 15 | 50 |
| F^- , Br^- , HCO_3^- and Cl^- | 100 | 500 |
| NO_2^- , NO_3^- and CH_3COO^- | 50 | 150 |

^a After the addition of 1 mL 0.1 M EDTA solution

^b After the addition of 1 mL $5000 \mu\text{g mL}^{-1}$ NaF solution

^c After the addition of 1 mL 0.01 M Triethanolamine solution

3.8. Analytical application of the proposed method

The calibration graph was constructed in the above-mentioned optimum conditions. In the proposed method, Beer's law is obeyed from 0.05 to $1.2 \mu\text{g mL}^{-1}$, with a detection limit of $0.012 \mu\text{g mL}^{-1}$, a quantification limit of $0.054 \mu\text{g mL}^{-1}$ and with a coefficient of variation of 2.35% (for ten repetitive measurements at a confidence level of 95%). The calibration curves were made as described in the experimental procedure and good correlation coefficients (r : 0.9966) were found. The molar absorption coefficient and Sandell's sensitivity as a measure of the method sensitivity was also calculated and a molar absorption coefficient of $6007.2 \text{ L mol}^{-1}\text{cm}^{-1}$ and Sandell's sensitivity of $4 \mu\text{g cm}^{-2}$ were obtained in the

concentration range of 0.1–1.2 $\mu\text{g mL}^{-1}$ in absence of CTAB at 554 nm while a molar absorption coefficient of 8928 $\text{L mol}^{-1}\text{cm}^{-1}$ and Sandell's sensitivity of 2.82 ng cm^{-2} are obtained in the concentration range of 0.05–1.2 $\mu\text{g mL}^{-1}$ in presence of CTAB at 640 nm. The proposed method was applied to the determination of magnesium in synthetic samples containing calcium ions at known amounts for five replicate analyses. As is seen in Table 3, magnesium was determined with an error at an acceptable level in the presence of calcium ions at 50 fold more excess concentration. Additionally, the proposed method was successfully applied to the determination of magnesium in three different commercial drinking water samples. The drinking water samples were supplied from commercial firms marketing various marked natural drinking water having different compositions. The results are shown in Table.4. Although the recoveries are partly high, they are between acceptable limits. It is seen that the proposed method is useful for the determination of magnesium in real samples in view of analytical point.

Table 3 Determination of magnesium by the proposed surfactant-sensitized spectrophotometric method in presence of calcium as interfering ion in the optimum conditions

| Sample | Added ($\mu\text{g mL}^{-1}$) | | Observed ($\mu\text{g mL}^{-1}$) | |
|--------|---------------------------------|--------|------------------------------------|----------------------|
| | Mg(II) | Ca(II) | Mg(II) | ^a Error % |
| 1 | 0.20 | 5 | 0.21 | 5.0 |
| 2 | 1.00 | 10 | 1.02 | 2.0 |
| 3 | 1.00 | 15 | 1.03 | 3.0 |
| 4 | 1.00 | 30 | 1.04 | 4.0 |
| 5 | 1.00 | 50 | 1.06 | 6.0 |

^aCalculated for five replicate analyses.

Table 4 Determination of magnesium in three different commercial drinking water samples by using the proposed surfactant-sensitized spectrophotometric method

| Samples | Added Mg(II), $\mu\text{g mL}^{-1}$ | Found Mg(II), $\mu\text{g mL}^{-1}$ | % Recovery |
|-----------------------------|-------------------------------------|-------------------------------------|------------|
| Drinking water ¹ | - | 0.24 ± 0.03 | - |
| | 0.3 | 0.55 ± 0.02 | 103.3 |
| | 0.5 | 0.74 ± 0.01 | 100 |
| Drinking water ² | - | 0.27 ± 0.02 | - |
| | 0.3 | 0.58 ± 0.02 | 103.3 |
| | 0.5 | 0.78 ± 0.01 | 102 |
| Drinking water ³ | - | 0.19 ± 0.03 | - |
| | 0.3 | 0.49 ± 0.02 | 100 |
| | 0.5 | 0.69 ± 0.01 | 100 |

¹The specific properties of Erikli marked drinking water: 7 ppm Cl^- , 4 ppm Ca^{2+} , 1.2 ppm Mg^{2+} , 10.1 ppm SO_4^{2-} , 0.5 ppm F, pH: 7.3, hardness: 1.5 F°, free chloride (Cl_2) and free ammonia (NH_3) is no present. A drinking water sample of 2 mL was treated for analysis.

²The specific properties of Fatsu marked drinking water: 15 ppm Cl^- , 14 ppm Ca^{2+} , 1.4 ppm Mg^{2+} , 12 ppm SO_4^{2-} , pH: 6.2, hardness: 4.1 F°, nitrite and free ammonia (NH_3) are no present. A drinking water sample of 2 mL was treated for analysis.

³ The specific properties of Damla marked drinking water: 15 ppm Cl^- , 5.2 ppm Ca^{2+} , 2 ppm Mg^{2+} , 4 ppm SO_4^{2-} , pH: 7, hardness: 1.5 F°, nitrite and free ammonia (NH_3) are no present. A drinking water sample of 1 mL was treated for analysis.

4. Conclusions

This study presents a new spectrophotometric method for determining magnesium in different natural drinking water samples in micellar medium. The proposed method has some advantages over the classical spectrophotometric method:

- (1) The proposed method is very simple and rapid. The method doesn't need any prior separation or solvent extraction. Moreover, the method also has much wider range of linear concentration in micellar medium than that of method performed in aqueous solution.
- (2) The proposed method has high selectivity. All the interfering ions studied, especially cationic species, which always seriously interfere with the determination of magnesium and calcium with this reagent, don't interfere with the determination of magnesium in the micellar medium.
- (3) The proposed method is highly sensitive in micellar medium. The molar absorption coefficient and Sandell's sensitivity values are $8928 \text{ L mol}^{-1}\text{cm}^{-1}$ and 2.82 ng cm^{-2} , respectively. As little as $0.012 \mu\text{g mL}^{-1}$ can be detected.
- (4) The proposed method is inexpensive. The instruments can be used even in a small laboratory or commercial firm. The reagents required for this surfactant-sensitized spectrophotometric method are available commercially or can be synthesized in a simple way.

So, the proposed method is very convenient for the direct determination of the concentration of magnesium in drinking water samples and can be used as a routine method for the environmental evaluation and analysis even in a small laboratory or firm.

Acknowledgements

The authors are grateful to Chairman of Chemistry Department, Prof. Ferda CANDAN for providing the facilities which made it possible to undertake the experimental work in its research laboratories.

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