

A NEW FLOW INJECTION AND SEQUENTIAL INJECTION SYSTEMS WITH SPECTROPHOTOMETRIC DETECTIONS FOR DETERMINATION MAGNESIUM ION

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ABSTRACT

This research includes the design flow injection and sequential injection systems for determining magnesium ion containing valve is designed locally. The FIA and SIA systems based on the reaction of magnesium with Eriochrome Black T at pH (9-10.5) with an absorption maximum at 520 nm. Various parameters (physical and chemical) affecting the determination have been investigated such as flow rate, reaction coil, volume of reagent (Eriochrome Black T), volume of sample, concentration of Eriochrome Black T. The calibration curve was prepared and the dispersion coefficient, reproducibility, interferences and application were studied. Two methods, flow injection and sequential injection analysis were compared for determination of magnesium by Eriochrome Black T. The linear range was (1-15 mg/L), (0.05-15 mg/L) at sampling rate of 120, 100 sample per hour, the detection limits (0.0221 mg/L), (0.096 mg/L) for FIA and SIA, respectively. Relative standard deviations for (15 mg/L), n = 3 were found (0.0823% for FIA and 0.1221% for SIA). Dispersion coefficient was also measured for the two methods.

Key words: Flow injection, Sequential injection, Eriochrome black T, Magnesium.

INTRODUCTION

Mg(II) ions have indispensable roles in many vital biological events^{1,2}. The relationship of magnesium deficiency and diabetes mellitus has generated discussion in the medical field in the past 10 years³. 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 stamina⁴, so the determination of magnesium in foods and drinking waters is very important.

Magnesium is the eighth most abundant element in the crust of the Earth. The

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determination of alkaline earth metals, particularly magnesium, is of importance for environmental, biological and industrial applications⁵. Magnesium, an abundant mineral in the body, is naturally present in numerous foods, added to other food products, available as a dietary supplement, and present in some medicines (such as anti-acids and laxatives). It is also a cofactor in more than 300 enzyme systems that regulate diverse biochemical reactions in the body⁶⁻⁸. Eriochrome Black T was a reddish-brown powder is dissolved in hot water or slightly soluble in ethanol and acetone, and is used in revealing interactions formation complexes, the molecular weight (439.381 g/mole) and partial formula is ($C_{20}H_{12}N_3O_7SNa$)⁹, and a scientific name:[Sodium salt of 1-(1-hydroxyl-2-naphthylazo)-5-nitro-2-naphthol-4-sulfonic acid]¹⁰.

Use Eriochrome black T estimate many items such as copper, manganese, lead, zinc, cadmium, indium, Gallium, aluminum, cobalt¹¹. Magnesium estimated by a number of ways, including using the method of Micellar-Sensitized Spectrophotometric¹², the solution scanometric method using a reagent titan yellow¹³, fluorometric flow injection using reagent 8-hydroxyquinoline-5-sulfonic acid¹⁴, FIA using potentiometric detection¹⁵, by atomic absorption spectroscopy¹⁶, ion-selective electrode and flow injection analysis¹⁷, UV absorbing chelates with EDTA by capillary electrophoresis¹⁸.

EXPERIMENTAL

Apparatus

Spectrophotometer Labomed.inG single beam, USA, and a spectrophotometer Shimadzu UV-1700 spectrophotometer, Analytical balance sensitive Denver Instrument, Recorder Pen Siemens C 1032, Hitter thermal Ardeas 51, peristaltic pump Germany, Ismatic, files Interaction with the radius of 0.5 mm, homemade valves, pipes load of Teflon, flow cell volume of 450 μ L, pH meter.

Chemicals [1]

- (i) The standard stock of magnesium prepared by dissolving 10.1350 g of magnesium sulphate heptahydrate MgSO₄.7H₂O, in water and dilute the solution with distilled water to 1 liter.
- 0.2% of Eriochrome Black T were prepared by dissolving 0.2 g of Eriochrome Black T in 100 mL of methanol in volumetric flask.
- (iii) Buffer solution of prepared pH = 9.6, dissolve 60 g of ammonium chloride NH_4Cl in water, add 120 mL of conc. ammonia solution, and dilute the solution with water to 1 liter.

RESULTS AND DISCUSSION

Determination of the wavelength for maximum absorption

Ultraviolet visible spectroscopy was used to determine the optimum conditions for the complex formation and the result are shown in Fig. 1. The λ_{max} of complex was 520 nm.



Fig. 1: UV-Vis spectroscopy for magnesium complex with EBT

Design of FIA and SIA units

This study included the design of a new injection valve from cheap and available materials, the new valve design consists of four secondary valves, each secondary valve has three outlets through, which the movement and direction of the common chemicals in the chemical reaction control, as shown in Fig. 2 and the works of the new valve in two stages, is full of the stage and injections of the stage and shown in Fig. 3.



Fig. 2: New injection valve



The new valve is integrated with the pump and UV-visible detector and signal recorder for the design of a new system flow injection and sequential injection to estimate the magnesium ion and Figs. (4, 5) illustrate the new designs of the two systems.

The various parameters affecting the unit have been investigated and selected for a final method evaluation. The following results allow the operator to choose different operation conditions. All units depend on a new valve is homemade, this valve using in FIA and SIA systems. Used new designs as shown in the Fig. 4 and 5.



Fig. 4: New design of FIA unit



Fig. 5: New design of SIA unit

Physical parameters in FIA

Effect of the flow rate

The effect of the flow rate on the peak height was studied in the range of 1.0-4.6 mL min⁻¹ (Table 1 and Fig. 6). The flow rate was 3.5 mL min⁻¹ as optimum rate after that the height of peak was reduced due to decreased the sensitivity of measurement in high flow rate because the reaction was no completed when increased the flow rate¹⁹.

Effect of the reaction coil length

Table 2 and Fig. 7 has shown the effect of reaction coil length on the peak height in the range (10-40) cm it was seen that the suitable reaction coil length was 20 cm, since it provided the greatest sensitivity.

Table 1: Effect of the flow rate on the peak height at; Mg conc. = 15 ppm, R. C. L. (reaction coil length) = 30 cm, EBT conc. = 0.002%, sample volume (L_1) = reagent volume (L_2) = 78.50 µL

| Flow rate (mL/min) | Pe | ak height (m | m) | Mean | SD | RSD (%) |
|-----------------------|--------|--------------|--------|--------|--------|---------|
| 1.0000 | 6.7800 | 6.8200 | 6.8100 | 6.8033 | 0.0208 | 0.3057 |
| 2.5000 | 7.1000 | 7.1200 | 7.1300 | 7.1166 | 0.0152 | 0.2135 |
| 3.5000 | 7.2200 | 7.2000 | 7.2200 | 7.2133 | 0.0115 | 0.1594 |
| 4.6000 | 6.9900 | 7.0100 | 7.0300 | 7.0100 | 0.0200 | 0.2853 |

Table 2: Effect of the reaction coil length on the peak height; Mg conc. = 15 ppm, flow rate (3.5 mL min⁻¹), EBT conc. = 0.002%, and sample volume (L1) = Reagent volume (L2) = 78.50 μL

| Reaction coil length cm | Pea | ık height (n | nm) | Mean | SD | RSD (%) |
|----------------------------|--------|--------------|--------|--------|--------|---------|
| 10 | 4.8500 | 4.8800 | 4.8300 | 4.8533 | 0.0251 | 0.5171 |
| 20 | 7.2600 | 7.2800 | 7.2700 | 7.2700 | 0.0100 | 0.1375 |
| 30 | 7.2200 | 7.2000 | 7.2200 | 7.2133 | 0.0115 | 0.1594 |
| 40 | 5.0500 | 5.0100 | 5.0400 | 5.0333 | 0.0208 | 0.4132 |



Fig. 6: Change of peak height with flow rate in FIA unit



Fig. 7: Change of peak height with the reaction coil length in FIA unit.

Effect of the EBT volume

The influence of the EBT volume on the peak height was investigated by injecting different volumes (39.2500-157.000) μ L. The peak height increased to the maximum at (78.50) μ L and after that volume, the peak height decreased. So (78.50) μ L was chosen for further work as shown in (Table 3 and Fig. 8).

Table 3: Effect of the volume EBT on the peak height at; Mg conc. = 15 ppm, flow rate = 3.5 mL min⁻¹, EBT conc. = 0.002%, sample volume (L₂) = 78.50 μ L and R.C.L (reaction coil length) = 20 cm

| Reagent volume (µL) | Pea | ak height (m | ım) | Mean | SD | RSD (%) |
|------------------------|--------|--------------|--------|--------|--------|---------|
| 39.2500 | 5.2300 | 5.2600 | 5.2700 | 5.2533 | 0.0208 | 0.3959 |
| 78.5000 | 7.2600 | 7.2800 | 7.2700 | 7.2700 | 0.0100 | 0.1375 |
| 117.750 | 6.5500 | 6.5000 | 6.5400 | 6.5300 | 0.0264 | 0.4042 |
| 157.000 | 5.1200 | 5.0500 | 5.0200 | 5.0633 | 0.0513 | 1.0131 |

Effect of sample volume

The influence of the various volume (39.25-157.0 μ L) of sample was observed. sample volume that exhibited the greatest peak height was found to be 117.75 μ L and it was chosen as the optimum (Fig. 9 and Table 4).

Table 4: Effect of the reagent volume on the peak height at; Mg conc. = 15 ppm, flow rate = 3.5 mL min⁻¹, EBT conc. = 0.002% M, reagent volume (L_1) = 78.50 µL and R.C.L (reaction coil length) = 20 cm

| Sample volume (µL) | Peak height (mm) | | | Mean | SD | RSD (%) |
|--------------------|------------------|--------|--------|--------|--------|---------|
| 39.2500 | 5.8300 | 5.8000 | 5.8400 | 5.8233 | 0.0208 | 0.3571 |
| 78.5000 | 7.2600 | 7.2800 | 7.2700 | 7.2700 | 0.0100 | 0.1375 |
| 117.750 | 9.2800 | 9.2700 | 9.2800 | 9.2766 | 0.0057 | 0.0614 |
| 157.000 | 9.0700 | 9.1000 | 9.0500 | 9.0733 | 0.0251 | 0.2766 |



Fig. 8: Change of peak height with the reagent volume in FIA unit



Fig. 9: Change of peak height with the sample volume in FIA unit

Chemical parameters

Effect of the reagent concentration

The reagent concentration was varied in the range (0.001-0.005)% in order to maximize the peak height. Table 5 and Fig. 10 has shown the effect of reagent concentration on the peak height of the magnesium (II). The maximum peak height was obtained with 0.005% reagent and after that concentration, the peak height decreased and form double peak therefore, the 0.005% reagent was chosen for further work.

Table 5: Effect of the reagent concentration on the peak height at; Mg conc. = 15 ppm, flow rate = 3.5 mL min⁻¹, R.C.L (reaction coil length) = 20 cm, sample volume $(L_1) = 117.750 \ \mu$ L and reagent volume $(L_2) = 78.50 \ \mu$ L

| Reagent conc. (%) | Peak height (mm) | | | Mean | SD | RSD (%) |
|-------------------|------------------|--------|--------|--------|--------|---------|
| 0.0010 | 7.7800 | 7.8100 | 7.8100 | 7.8000 | 0.0173 | 0.2217 |
| 0.0020 | 9.2800 | 9.2700 | 9.2800 | 9.2766 | 0.0057 | 0.0614 |
| 0.0040 | 11.620 | 11.580 | 11.620 | 11.610 | 0.0230 | 0.1981 |
| 0.0050 | 13.520 | 13.510 | 13.510 | 13.513 | 0.0057 | 0.0421 |



Fig. 10: Change of peak height with reagent concentration in FIA unit

Study of the dead volume

Experiment was conducted to study the dead volume, which indicates the fact composition of the complex within the innovative system. Wherever, the dead volume is

small, it means best result. Two experiments were done (i) in the first, the reagent was injected in one loop and in the another loop is inject H_2O instead of sample Mg ion and there was response estimated about 1.35 mm and (ii) in the second experiment sample was injected and in another loop H_2O instead of reagent and there was no response, then injected Mg ion and reagent in order to complex formation and measured peak height. The result is shown in Fig. 11.



Fig. 11: Study of the dead volume in FIA unit

Calibration curve in FIA method

Calibration curve was prepared at the optimum conditions of complex ion and change in the ion concentration (Table 6 and Fig. 12). The calibration curve is linear in the range of (1-15) mg/L and the detection limit is 0.0221 mg/mL.

| Table 6: | Effect of the concentration of Mg conc. with peak height at; flow rate = 3.5 |
|----------|---|
| | mL min ⁻¹ , R.C.L (reaction coil length) = 20 cm, sample volume (L ₁) =117.750 |
| | μ L and reagent volume (L ₂) = 78.50 μ L, EBT conc. = 0.005% and peak height |
| | of reagent = 1.354 mm |

| Mg conc. (ppm) | Peal | k height (mi | n) | Mean* | SD | RSD (%) | | |
|--|--------|--------------|--------|--------|--------|---------|--|--|
| 1.0000 | 2.1200 | 2.1000 | 2.1200 | 2.1133 | 0.0115 | 0.5441 | | |
| 3.0000 | 4.3300 | 4.3400 | 4.3600 | 4.3433 | 0.0152 | 0.3499 | | |
| 5.0000 | 5.4300 | 5.4100 | 5.4500 | 5.4300 | 0.0200 | 0.3683 | | |
| 8.0000 | 7.5200 | 7.5500 | 7.5000 | 7.5233 | 0.0251 | 0.3336 | | |
| 10.000 | 8.6100 | 8.6500 | 8.6200 | 8.6266 | 0.0208 | 0.2411 | | |
| 15.000 | 12.150 | 12.140 | 12.160 | 12.150 | 0.0100 | 0.0823 | | |
| *Removal the reagent peak height from all peaks height | | | | | | | | |



Fig. 12: Calibration curve of Mg ion with EBT in FIA Unit

Repeatability

Repeatability was established through re-injection the same concentration of magnesium complex. The concentration of magnesium ion was 15 ppm and 0.005% from EBT. Fig. 13 shows the repeatability of magnesium complex. The efficiency of the proposed FIA unit for the determination of magnesium was reflected from the results of repeatability and the detection of limit was (0.0221 mg/L) depend on the repeatability results as (Table 7 and Fig. 13).

Table 7: Repeatability for 15 ppm of magnesium ion in FIA unit

| No. of peak height | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | Mean | SD | RSD (%) |
|-----------------------|-------|-------|------|------|-------|-------|------|------|------|------|--------|--------|------------|
| Peak height mm | 13.51 | 13.51 | 13.5 | 13.5 | 13.51 | 13.51 | 13.5 | 13.5 | 13.5 | 13.5 | 13.507 | 0.0051 | 0.0377 |

Sequential injection analysis (SIA)

Physical parameters

Effect of the flow rate

The effect of the flow rate on the peak height was studied in the range of 1.0-6.5 mL min⁻¹ (Table 8. and Fig. 14). The flow rate was 5.6 mL min⁻¹ as optimum rate because of the stability of the pump, peak shape and sampling time and highest sensitivity. After that the peak height decreased with the increasing flow rate²⁰.

Table 8: Effect of the flow rate on the peak height at; Mg conc. = 10 ppm, R.C.L (reaction coil length) = 20 cm, EBT conc. = 0.005%, sample volume (L_1) = reagent volume (L_2) = 78.50 µL

| Flow rate (mL/min) | Peak height (mm) | | | Mean | SD | RSD (%) |
|--------------------|------------------|--------|--------|---------|--------|---------|
| 1.0000 | 3.4400 | 3.4000 | 3.4500 | 3.4300 | 0.0264 | 0.1641 |
| 2.5000 | 2.3500 | 2.3700 | 2.3800 | 2.3660 | 0.0152 | 0.6424 |
| 3.5000 | 3.2500 | 3.2500 | 3.2300 | 3.2430 | 0.0115 | 0.3546 |
| 4.6000 | 17.880 | 17.840 | 17.870 | 17.8630 | 0.0208 | 0.1164 |
| 5.6000 | 20.350 | 20.360 | 20.360 | 20.3560 | 0.0057 | 0.0273 |
| 6.5000 | 19.660 | 19.680 | 19.650 | 19.6630 | 0.0152 | 0.0773 |



Fig. 13: Repeatability of magnesium for 15 ppm with EBT



Fig. 14: Change of peak height with flow rate in SIA unit

Effect of the reaction coil length

Table 9 and Fig. 15 shows effect of the reaction coil length on the peak height in the range (10-30) cm. It was seen that the suitable reaction coil length was 20 cm, since it provided the greatest sensitivity.

Table 9: Effect of the reaction coil length on the peak height; Mg conc. = 10 ppm, flow rate (5.6 mL min⁻¹), EBT conc. = 0.005%, sample volume (L₁) = reagent volume (L₂) = 78.50 μL

| Reaction coil length (cm) | Pea | k height (mi | m) | Mean | SD | RSD (%) |
|------------------------------|---------|--------------|---------|---------|--------|---------|
| 10 | 13.0200 | 13.0300 | 13.0100 | 13.0100 | 0.0100 | 0.0768 |
| 20 | 20.3500 | 20.3600 | 20.3600 | 20.3560 | 0.0057 | 0.0273 |
| 30 | 13.2500 | 13.2600 | 13.2800 | 13.2630 | 0.0152 | 0.1148 |



Fig. 15: Change of peak height with the reaction coil length in SIA unit

Effect of the EBT volume

The influence of the EBT volume on the peak height was investigated by injecting different volumes (39.25-157.0) μ L. The peak height increased to the maximum at (78.50) μ L and after that volume, the peak height decreased. So (78.50) μ L was chosen for further work as shown in (Table 10 and Fig. 16).

| Table | 10: | Effect of the volume EBT on the peak height at; Mg conc. = 10 ppm, flow |
|-------|-----|---|
| | | rate = 3.5 mL min ⁻¹ , EBT conc. = 0.005%, sample volume (L ₁) = 78.50 μ L |
| | | and R.C.L (reaction coil length) = 20 cm |

| Reagent volume (µL) | Pe | ak height (m | m) | Mean* | SD | RSD (%) |
|------------------------|---------|--------------|---------|---------|--------|------------|
| 39.2500 | 15.000 | 15.000 | 15.020 | 15.006 | 0.0115 | 0.0766 |
| 78.5000 | 20.3500 | 20.3600 | 20.3600 | 20.3560 | 0.0057 | 0.0273 |
| 117.750 | 19.400 | 19.410 | 19.430 | 19.413 | 0.0152 | 0.0782 |
| 157.000 | 13.540 | 13.550 | 13.530 | 13.543 | 0.0100 | 0.0738 |



Fig. 16: Change of peak height with the reagent volume in SIA unit

Effect of sample volume

The influence of the various volume (39.25-117.75 μ L) of sample was observed. sample volume that exhibited the greatest peak height was found to be 78.50 μ L and it was chosen as the optimum (Fig. 17 and Table 11).

Chemical parameters

Effect of the reagent concentration

The reagent concentration was varied in the range (0.001-0.01)% in order to maximize the peak height. Table 12 and Fig. 18 show the effect of reagent concentration on the peak height of the magnesium (II). The maximum peak height was obtained with 0.005% reagent and after that concentration, the peak height decreased and form double peak therefore, the 0.005% reagent was chosen for further work.

Table 11: Effect of the reagent volume on the peak height at; Mg conc. = 10 ppm, flow rate = 5.6 mL min⁻¹, EBT conc. = 0.005%, reagent volume (L₁) = 78.50 μ L and R.C.L (reaction coil length) = 20 cm

| Sample volume (µL) | Pea | ak height (m | ım) | Mean* | SD | RSD (%) |
|-----------------------|---------|--------------|---------|---------|--------|---------|
| 39.2500 | 16.8600 | 16.8400 | 16.8700 | 16.8560 | 0.0152 | 0.0901 |
| 78.5000 | 20.35 | 20.36 | 20.36 | 20.356 | 0.0057 | 0.0273 |
| 117.750 | 6.7100 | 6.7000 | 6.6700 | 6.6933 | 0.0208 | 0.2273 |

Table 12: Effect of the reagent concentration on the peak height at; Mg conc. = 10 ppm, flow rate = 5.6 mL min⁻¹, R.C. L (reaction coil length) = 20 cm, sample volume (L₁) = reagent volume (L₂) = 78.50 μ L

| Reagent conc. (%) | Pea | ık height (n | nm) | Mean* | SD | RSD (%) |
|-------------------|--------|--------------|--------|--------|--------|---------|
| 0.0010 | 9.4700 | 9.5100 | 9.4800 | 9.4860 | 0.0208 | 0.1216 |
| 0.0020 | 11.130 | 11.100 | 11.130 | 11.120 | 0.0173 | 0.1037 |
| 0.0030 | 14.690 | 14.690 | 14.670 | 14.683 | 0.0115 | 0.0785 |
| 0.0040 | 17.650 | 17.660 | 17.680 | 17.663 | 0.0152 | 0.0860 |
| 0.0050 | 20.350 | 20.360 | 20.360 | 20.356 | 0.0057 | 0.0273 |
| 0.0100 | 10.820 | 10.760 | 10.780 | 10.776 | 0.0305 | 0.1410 |



Fig. 17: Change of peak height with the sample volume in SIA unit



Fig. 18: Change of peak height with reagent concentration in SIA unit.

Calibration curve in SIA method

Calibration curve was prepared at the optimum conditions of complex ion and change in the ion concentration (Table 13 and Fig. 19). The calibration curve is linear in the range of (0.05-15) mg/L and the detection limit is 0.0096 mg/mL.

| C | | | | | | |
|--------------------|-------------|--------------|--------------|--------|--------|---------|
| Mg conc. (ppm) | Pea | k height (1 | nm) | Mean* | SD | RSD (%) |
| 0.0500 | 1.4100 | 1.4400 | 1.4000 | 1.4166 | 0.0208 | 1.4683 |
| 0.1000 | 1.5400 | 1.5600 | 1.5900 | 1.5633 | 0.0251 | 1.6119 |
| 0.5000 | 2.3300 | 2.3600 | 2.3500 | 2.3466 | 0.0152 | 0.6477 |
| 1.0000 | 3.2300 | 3.2500 | 3.2300 | 3.2366 | 0.0115 | 0.3553 |
| 3.0000 | 5.3800 | 5.3700 | 5.3900 | 5.3800 | 0.0100 | 0.1858 |
| 5.0000 | 9.3400 | 9.3600 | 9.3800 | 9.3730 | 0.0200 | 0.2136 |
| 8.0000 | 13.020 | 13.020 | 12.970 | 13.003 | 0.0288 | 0.2214 |
| 10.000 | 15.780 | 15.770 | 15.770 | 15.773 | 0.0057 | 0.0351 |
| 12.000 | 18.600 | 18.550 | 18.560 | 18.570 | 0.0264 | 0.1421 |
| 15.000 | 24.950 | 25.010 | 24.970 | 24.976 | 0.0305 | 0.1221 |
| * Removal the reag | ent peak he | ight from al | l peaks heig | ht | | |

Table 13: Effect of the concentration of Mg conc. with peak height at; flow rate = 5.6 mL min⁻¹, R.C.L. (reaction coil length) = 20 cm, sample volume (L_1) = reagent volume (L_2) = 78.50 µL, EBT conc. = 0.005% and reagent peak height = 4.583 mm



Fig. 19: Calibration curve of Mg ion with EBT in SIA Unit.

Repeatability

Repeatability was established through re-injection the same concentration of magnesium complex. The concentration of magnesium ion was 10 ppm and 0.005% from EBT. Fig. 20 shows the repeatability of magnesium complex. The efficiency of the proposed SIA unit for the determination of magnesium was reflected from the results of repeatability and the detection of limit was (0.0096 mg/L) depend on the repeatability results as (Table 14 and Fig. 20).

| No. of peak height | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | Mean | SD | RSD (%) |
|-----------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|--------|------------|
| Peak height mm | 20.36 | 20.35 | 20.36 | 20.36 | 20.35 | 20.36 | 20.35 | 20.36 | 20.36 | 20.35 | 20.353 | 0.0048 | 0.0236 |

Table 14: Repeatability for 10 ppm of magnesium in SIA unit



Fig. 20: Repeatability of magnesium for 10 ppm with EBT

Determination of dispersion

To measure the dispersion value in different sample zones of (10 and 15) ppm magnesium ion for FIA and (5 and 8 ppm) for SIA, two experiments were carried out. In the first experiment, after mixing of reactants (EBT and magnesium ion) that passes through manifold unit gives continuous response. This indicates non-existence of dispersion effect by convection or diffusion. This measurement represents (H^{o}). The second experiment includes injecting different concentration of Mg ions (10 and 15 ppm) for FIA and (5 and 8 ppm) for SIA and signal recorded as H_{max} . The value dispersion (D) from this experiment can be calculated from this equation:

$$\mathsf{D} = \frac{\mathrm{H}^{\mathrm{o}}}{\mathrm{H}_{\mathrm{max}}}$$

These values fall in limit state of dispersion (Table 15 and 16).

Table 15: Determination of dispersion of Mg ion in FIA Unit

| Respon | Dispersion (D) | | | |
|------------------|--|---|--|--|
| \mathbf{H}^{0} | H _{max} | $\mathbf{D} = \mathbf{H}^0 / \mathbf{H}_{\text{max}}$ | | |
| 9.95 | 8.623 | 1.1538 | | |
| 12.61 | 12.156 | 1.0373 | | |
| | Respon H ⁰ 9.95 12.61 | Response (mm) H ⁰ H _{max} 9.95 8.623 12.61 12.156 | | |

 Table 16: Determination of dispersion of Mg ion in SIA Unit

| Mg concentration | Respon | Dispersion (D) | | |
|------------------|----------------|------------------|---|--|
| (mg/L) | H ⁰ | H _{max} | $\mathbf{D} = \mathbf{H}^0 / \mathbf{H}_{\text{max}}$ | |
| 5ppm | 9.4500 | 9.3660 | 1.0089 | |
| 8ppm | 13.120 | 12.993 | 1.0097 | |

Effect of interfering ions

The effect of seriously interfering cations (Na⁺, Al³⁺, Fe³⁺, Cu²⁺, Ca²⁺, and Ni²⁺) and anions (Cl⁻, CO₃²⁻, F⁻ CH₃COO⁻ and SO₄²⁻) for determination of magnesium at was studied. The concentrations of Interfering Ions was in 15 and 50 ppm. The evident was not interferences with magnesium complex expect Al³⁺, Ca²⁺, Fe³⁺ at 50 ppm were interference. This interfering ion of Al³⁺ and Fe³⁺ can be removed by using masking agent where the interfering ion was masked by adding 2.0 drop from 100 ppm of F^- . This interfering ion of Ca^{2+} can be removed by using masking agent where the interfering ion was masked by adding 3.0 drop from 100 ppm of sodium citrate⁹.

Applications

The proposed method was applied for the determination of magnesium ion in aqueous samples and pharmaceutical samples. The recoveries of known concentrations of magnesium ion were investigated. Table 17 shows the results of the recovery.

| Pharmaceutical samples in FIA | The take value (ppm) | The found value (ppm) | Recovery (%) |
|-------------------------------|-------------------------|--------------------------|-----------------|
| Ballox | 5.0000 | 4.6620 | 93.2400 |
| Barkalox | 5.0000 | 4.8970 | 97.9400 |
| Meravit | 5.0000 | 4.9110 | 98.2200 |
| Maalus | 5.0000 | 4.9630 | 99.2600 |
| Moxal | 5.0000 | 4.9550 | 99.1000 |
| Pharmaceutical samples in SIA | The take value (ppm) | The found value (ppm) | Recovery (%) |
| Ballox | 1.0000 | 0.9760 | 97.6000 |
| Barkalox | 1.0000 | 0.9910 | 99.1000 |
| Meravit | 1.0000 | 0.9330 | 93.3000 |
| Maalus | 1.0000 | 0.9950 | 99.5000 |
| Moxal | 1.0000 | 0.9910 | 99.1000 |
| Aqueous samples in FIA | The take value (ppm) | The found value (ppm) | Recovery (%) |
| Rawdatain | 3.0000 | 2.8110 | 93.7000 |
| Al-Waha | 10.000 | 9.7460 | 97.4600 |
| Fadak | 8.0000 | 7.4280 | 92.8500 |
| Nawar | 4.0000 | 3.6910 | 92.2750 |

Table 17: Applications FIA and SIA methods for determination magnesium

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| Aqueous samples in SIA | The take value (ppm) | The found value (ppm) | Recovery (%) |
|---------------------------|-------------------------|--------------------------|--------------|
| Rawdatain | 1.0000 | 0.9650 | 96.5000 |
| Al-Waha | 1.0000 | 0.9810 | 98.1000 |
| Fadak | 1.0000 | 0.9620 | 96.2000 |
| Nawar | 1.0000 | 0.9920 | 99.2000 |

Comparison between two units FIA and SIA

The comparison for the two methods are used for determination of magnesium as in Table 19.

 Table 18: Optical characteristics, precision and accuracy of the spectrophotometric determination of magnesium ion with FIA and SIA methods

| Optical characteristics | FIA Method | SIA Method |
|--|------------|------------|
| Concentration linearity range (ppm) | 1 – 15 | 0.05 - 15 |
| λ_{\max} (nm) | 520 | 520 |
| Detection limit (ppm) practically | 0.0221 | 0.0096 |
| Correlation coefficient | 0.9930 | 0.9950 |
| Relative standard deviation (%), determination for (15 mg/L), $n = 10$ | 0.0823% | 0.1221% |
| Desperation coefficient for concentration 10 ppm | 1.1538 | |
| Desperation coefficient for concentration 15 ppm | 1.0373 | |
| Desperation coefficient for concentration 5 ppm | | 1.0089 |
| Desperation coefficient for concentration 8 ppm | | 1.0097 |
| Sampling rate (sample/h) | 120 | 100 |

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