

Fluorometric Flow Injection Determination of Magnesium Using 8-Hydroxyquinoline-5-sulfonic Acid

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Abstract

A flow injection method for the determination of magnesium was developed, which is based on the complex formation between Mg(II) and 8-hydroxyquinoline-5-sulfonic acid (HQSA) and fluorometric monitoring (excitation at 365 nm and emission at 500 nm). Maximum emission was observed near pH 9. The addition of ethylene glycol-bis(β -aminoethyl ether)-N,N,N',N'-tetraacetic acid (EGTA) resulted in 30% reduction of the peak height for magnesium but the peak for calcium disappeared completely. A linear calibration curve was obtained in the range of 1×10^{-5} to 2×10^{-3} mol dm⁻³ and the detection limit of magnesium was about 1×10^{-6} mol dm⁻³. The relative standard deviation of the peak height was 0.4%, when 2×10^{-4} mol dm⁻³ Mg(II) was injected 12 times successively. The proposed method was applied to the determination of magnesium in tap water and a commercial drinking water and satisfactory results were obtained.

Keywords: magnesium; fluorometric flow injection method; 8-hydroxyquinoline-5-sulfonic acid; tap water

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Introduction

The determination of magnesium and calcium in water, physiological fluid, chemicals and so on is important from various aspects such as biological and industrial standpoints. Atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry can be used effectively for this purpose. However, these methods need large and expensive instruments. Flow injection analysis (FIA) has been often applied to those metals because of its simplicity and high reliability. Most of them¹⁻³ were based on spectrophotometric monitoring of chelates formed. Some researches⁴⁻⁶ attempted simultaneous determination of both metals by spectrophotometric FIA methods. Recently fluorometric detection has been used in FIA because of its high sensitivity. Wada *et al.*⁷ used Quin 2 for the FI determination of calcium. Chimpale *et al.*⁸ and Thuy *et al.*⁹ used Calcein for the FI determination of calcium and magnesium.

The authors' final purpose is construction of a high sensitive fluorometric FIA system for the simultaneous determination of both metals in environmental samples. As the first step, fluorometric FI determination of magnesium was tried, which was based on the complex formation between magnesium and HQSA.

Experimental

Figure 1 shows the home-made flow injection system for the determination of magnesium. Two plunger-type pumps (Sanuki Co., DM2M-1024) were used to feed the reagent solution and to carry the sample band (10 μ l) injected through an injector (Rheodyne 7725). A 2×10^{-3} mol dm⁻³ HQSA solution daily prepared by dissolving HQSA in 0.1 mol dm⁻³ phosphate buffer (pH 9), was fed by pump A. Water, used as the carrier of the sample band, was fed by pump B. For masking Ca(II), a 2×10^{-3} mol dm⁻³ EGTA solution was also prepared freshly before use, which was fed by pump B. Flow rates were set at 0.25 ml min⁻¹. After passing through the reaction coil (0.5 mm i.d. \times 50 cm), the complex formed was monitored by a fluorometric detector (JASCO Co., FP 110) equipped with a medium pressure mercury lamp (excitation at 365 nm, emission at 500 nm). The dispersion was estimated as about 14 from the peak

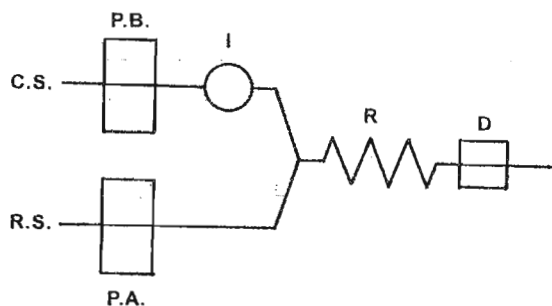


Fig. 1. Schematic diagram of the flow injection system for determination of Mg(II).

P.A.: pump A, P.B.: pump B, C.S.: carrier solution (water or 2×10^{-3} mol dm⁻³ EGTA solution), R.S.: reagent solution (2×10^{-3} mol dm⁻³ HQSA solution, pH 9), I: injector, R: reaction coil, D: fluorometric detector.

width observed. This suggests the sample band was diluted highly while it passed through the reaction coil.

Results and Discussion

Figure 2 shows the fluorescence intensity of Mg-HQSA complex as a function of pH of the reagent solution. Maximum emission was observed near pH 9. The reason why the optimum pH was lower than that obtained in a batch system (pH 10 to 10.5)¹⁰ is uncertain. This difference may be attributed to a difference in the composition of buffer solutions and a small difference in monitoring wavelength. The effect of the concentration of HQSA on the peak height was investigated in region of 5×10^{-4} to 2×10^{-3} mol dm⁻³. The peak height increased with increase in the concentration of HQSA but the detection limit and the linear response range were almost the same. In this study, a 2×10^{-3} mol dm⁻³ HQSA solution in phosphate buffer at pH 9 was used.

The complexes between HQSA and various metal ions showed signal with different level, as pointed out by Soroka *et al.*¹¹ in its application to the post column reactions of chromatographic eluates. Fe(II and III), Cu(II), Mn(II), Ni(II), Co(II) and Bi(III and IV) gave the negative peaks. On the other hand, Ca(II), Pb(II), Zn(II), Al(III) as well as Mg(II) gave the positive peaks. The relative peak height of the complex of the latter group was as follows: Mg(II) 100, Ca(II) 4.4, Pb(II) 0.8, Zn(II) 33, Al(III) 17 for 1×10^{-3}

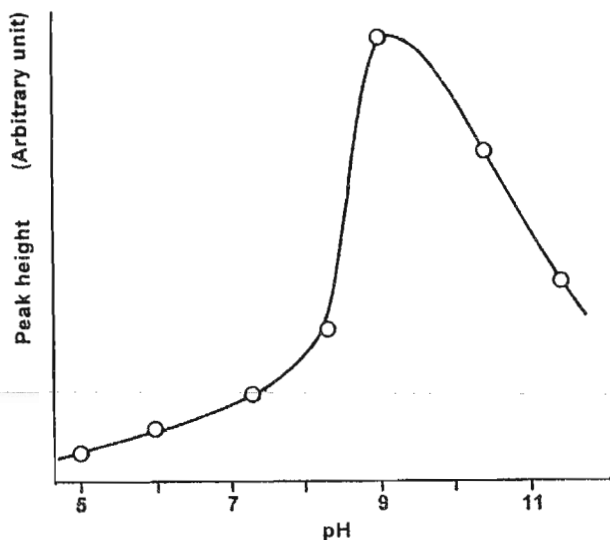


Fig. 2. Effect of pH of reagent solution on peak height.

10 μ l of 1×10^{-3} mol dm $^{-3}$ Mg(II): injected.

mol dm $^{-3}$ metal ion injected. Magnesium gave the highest peak at pH 9 but interference from other metal ions could not be neglected. For the purpose of masking, a 2×10^{-3} mol dm $^{-3}$ EGTA solution was used as the carrier solution instead of water. Every metal ion in the presence of EGTA gave reduced peak height compared to that obtained without any masking agent; Mg(II) 70%, Ca(II) 0.0%, Pb(II) 64%, Zn(II) 64%, Al(III) 36%. It is remarkable that the calcium peak disappeared completely. From our calculation based on the stability constants¹² of complexes between some metal ions and HQSA or EGTA and the estimated dispersion value, it was expected that the peaks for calcium and zinc should disappear completely and the magnesium peak height would decrease by 20%. The results for calcium and magnesium were almost in accord with our estimations but that of zinc was inconsistent with our calculation.

Figure 3 shows the calibration curve for Mg(II) obtained in the presence and absence of EGTA. The sigmoid-shaped lines suggested by Wallach and Steck¹³ were observed and the linear range was 1×10^{-5} to 2×10^{-3} mol dm $^{-3}$ or 1×10^{-5} to 2.5×10^{-3} mol dm $^{-3}$, respectively. Taking into account the large dispersion value, the curved region in the higher concentration reflects self-quenching rather than the too low

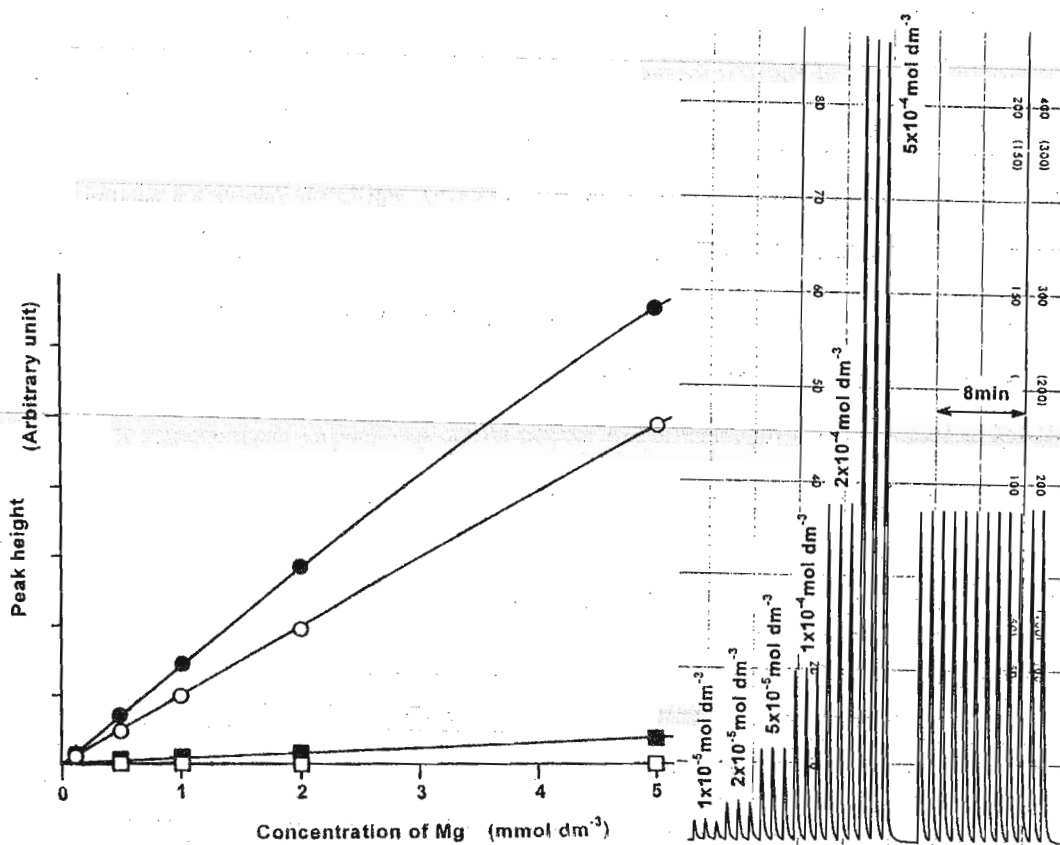


Fig. 3. Calibration curves for Mg(II) and Ca(II) with or without masking agent, EGTA.

● : Mg(II) measured in the absence of EGTA, ○ : Mg(II) measured in the presence of $2 \times 10^{-3} \text{ mol dm}^{-3}$ EGTA, ■ : Ca(II) measured in the absence of EGTA, □ : Ca(II) measured in the presence of $2 \times 10^{-3} \text{ mol dm}^{-3}$ EGTA.

Fig. 4. Some results of FIA measurement of Mg(II) standard solutions and reproducibility obtained by repeated injections of $2 \times 10^{-4} \text{ mol dm}^{-3}$ Mg(II).

concentration of HQSA compared to Mg(II). The detection limit of Mg(II) was about $1 \times 10^{-6} \text{ mol dm}^{-3}$ in both cases, which was comparable to the values observed in a spectrophotometric FIA³ and in a fluorometric FIA⁸. Since the contribution of the sample volume to the band broadening was very small under the present conditions, it must be possible to increase the sample volume about three times without any remarkable band broadening additionally; the peak height must increase and a lower detection limit should be obtained. Figure 3 also shows the masking effect of EGTA for Ca(II). These results suggest the

proposed method can be applied to the determination of Mg(II) in the presence of Ca(II). Figure 4 shows the typical flow patterns of Mg(II) in the range of 1×10^{-5} to 2×10^{-4} mol dm⁻³. The relative standard deviation of the peak height was 0.4% for twelve determinations of 2×10^{-4} mol dm⁻³ Mg(II), as seen in Fig. 4. This method was applied to the artificial mixture of Mg(II) and Ca(II). Mg(II) was determined accurately in the presence of ten times higher concentration of Ca(II), as shown in Table 1 (a). The proposed method was also applied to tap and commercial drinking water samples. As shown in Table 1(b), there was good agreement between the results from FIA and volumetric titration.

Based on these results, a fluorometric FIA method for the simultaneous determination of Ca(II) and Mg(II) based on a single injection and a single detection is under investigation.

Table 1. (a) Determination of Mg(II) in the presence of Ca(II).

Sample	Added (mol dm ⁻³)		Observed (mol dm ⁻³)
	Mg(II)	Ca(II)	Mg(II)
1	5.0×10^{-3}	5.0×10^{-3}	4.75×10^{-3}
2	5.0×10^{-4}	5.0×10^{-3}	5.08×10^{-4}
3	5.0×10^{-4}	5.0×10^{-4}	5.17×10^{-4}

(b) Determination of Mg(II) in tap water and a commercial drinking water.

Sample	FIA (mol dm ⁻³)	Titration (mol dm ⁻³)*
Tap water		
Ohtsu city	1.16×10^{-4}	1.16×10^{-4}
Kyoto city	1.12×10^{-4}	1.18×10^{-4}
Uji city	1.14×10^{-4}	1.21×10^{-4}
Osaka city	1.41×10^{-4}	1.52×10^{-4}
Kyoto Univ.	2.31×10^{-4}	2.34×10^{-4}
A commercial drinking water	1.24×10^{-3}	1.21×10^{-3}

*Difference between the value determined for Mg+Ca by titration with EDTA using EBT indicator and the value determined for Ca by EDTA titration using NN indicator

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