FLOW-INJECTION SPECTROPHOTOMETRIC DETERMINATION OF MAGNESIUM WITH XYLYLAZO VIOLET I

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Abstract

Magnesium ion was selectively determined in the presence of calcium ion by a flow-injection spectrophotometric method with sodium [1-azo-2-hydroxy-3-(2,4-dimethylcarboxyanilido)-naphthalene-1´-(2-hydroxybenzene-5-sulfonate)], Xylylazo Violet (XV-I). In the presence of Triton X-100(TX-100), XV-I and its magnesium chelate were dissolved in an aqueous solution, and at pH>8 the maximum absorbance of magnesium chelate was obtained at 515nm. The determination of magnesium in water samples was examined both at pH 9.2 and 11.3. The determination range of magnesium was 2×10^{-6} mol $l^{-1} \sim 1.2 \times 10^{-4}$ mol l^{-1}, and the detection limits corresponding to S/N=3 at pH 9.2 and 11.3 were about 2×10^{-6} mol l^{-1} and 1.2×10^{-6} mol l^{-1}, respectively. The rate of sampling was 80 injections per hour.

Recently, several flow-injection methods have been reported for the spectrophotometric determination of magnesium ion in water samples. Wada et al. reported the method using 1-(2-hydroxyl-3-sulfo-5-chloro-1-phenylazo)-2-naphthol-3,6-disulfonic acid as a chelating reagent for magnesium[1], in which method cyanide was used as a masking agent to remove the interferences from other metal ions. Other methods using 2-(2-hydroxyl-3,6-disulfo-1-naphthylazo)-5-(N,N-diethylamino) phenol[2] and Acidic Chrome Blue K[3] were reported for the simultaneous determination of magnesium and calcium ions. The method with Chlorophosphonazo was also applied to the simultaneous determination of magnesium and calcium ions in river water samples[4]. And also, several sensitive and selective methods for calcium ion have been already reported. However, simple and sensitive methods for the selective determination of magnesium ion by flow-injection analysis have been scarcely reported.

Mann and Yoe have reported the spectrophotometric method for magnesium with sodium [1-azo-2-hydroxy-3-(2,4-dimethylcarboxy-anilido)-naphthalene-1´-(2-hydroxybenzene-5-sulfonate)], Xylylazo Violet I (XV- I), which forms pinkish

chelate with magnesium ion in an ethanolic solution at pH around 9[5]. Though XV-I is selective for magnesium ion, XV-I is less soluble in water, and therefore the alcoholic solution (ethanol: 50% or more) must be used to dissolve the reagent and the chelate formed. In the method with XV-I in alcoholic solution, it took more than 30min to complete the reaction.

Triton X-100 (TX-100) can dissolve and stabilize XV-I in an aqueous medium, and can be used as an alternative dissolving agent. Furthermore, an aqueous reagent solution containing a little amount of TX-100 is stable for at least 3 months when stored in a brown bottle. Watanabe and Tanaka have reported the dual-wavelength spectrophotometric determination of magnesium ion with XV-I in the presence of TX-100 by a batchwise method[6], where it took more than 5min to complete the coloration of magnesium at pH 11, and the absorbance of the reagent blank at 515nm was large.

In this report, the authors aim at developing a sensitive and selective method for the determination of magnesium ion, and investigate the characteristics of Xylylazo Violet I in the presence of TX-100 using a tetraborate buffer solution (pH 9.2) and a phosphate buffer solution (pH 11.3) by flow-injection technique.

Experimental

Reagent
Triton X-100(TX-100), 12%(m/m) solution. TX-100 solution was prepared by dissolving 12g of TX-100(Wako Pure Chemicals Ind.) in 88cm^3 of water.
Xylylazo Violet I (XV-I) solution. XV-I stock solution, 2×10^{-3} mol l^{-1}, was prepared by dissolving 107mg of XV-I (Tokyo Kasei Kogyo Co. Ltd.) in 100cm^3 of the 12%(m/m) TX-100 solution.
Standard solution of magnesium ion. Magnesium chloride (hexahydrate, Wako Pure Chemicals Ind., purity 99.9%) was dissolved in water. The accurate concentration was standardized by the titration method with EDTA.
Buffer solutions. Tetraborate buffer(0.1 mol l^{-1}, pH 9.2) and phosphate buffer solution (0.25 mol l^{-1}, pH 11.3) were used.

Apparatus
The diagram for a flow injection system is shown in Fig.1. The system was assembled by using a double-plunger micropump(Sanuki Kogyo, DMX-2000), a six-way sample injection valve with a loop (Sanuki Kogyo), a visible detector with a 10-mm micro flow cell (8μl, Soma Kogaku, S-3250) and a strip-chart recorder (Toa Electronics, FBR 251A). The flow lines were made of PTFE tubing (0.5mm

i.d.). A recording spectrophotometer (JASCO,Ubest-35) was used to examine the fundamental conditions for the stable coloration of magnesium chelate and the reaction time necessary for the formation of magnesium chelate.
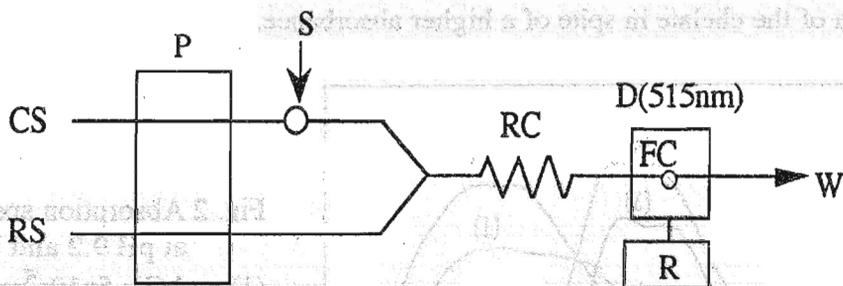

Fig. 1 Flow diagram for magnesium determination
CS,carrier solution; RS,reagent solution; S,sample injection (100μl); R,recorder; P,pump (0.8cm^3 min^{-1}); D,detector (515nm); FC,flow cell(8μl,10-mm path); RC,reaction coil (0.5mm i.d. x100cm, kept in a water bath at room temperature).

Procedure for the determination of magnesium

Distilled water was used as a carrier stream. A solution containing 2x10^{-4} mol l^{-1} XV-I, 1.2%(m/m) TX-100 and 0.05 mol l^{-1} tetraborate buffer(pH 9.2) or a solution containing 1x10^{-4} mol l^{-1} XV-I , 0.6%(m/m) TX-100 and 0.05 mol l^{-1} phosphate buffer(pH 11.3) was used as a reagent stream. Sample solutions were injected into the carrier with a six-way injection valve, and the peaks caused by absorbance increase at 515nm with an increase in magnesium concentration were recorded.

Results and Discussion

Effect of pH on the formation of magnesium chelate

The effect of pH of solutions was examined by varying the pH from 3.5 to 11.5. In acidic media, it was difficult to form a magnesium chelate. In alkaline media at pHs above 8, the formation of magnesium chelate gradually increased, and the maximum absorption wavelengths of XV-I and magnesium chelate were 620nm and 515nm, respectively. The apparent molar absorptivities increased with an increase in pH up to 10, and were almostly constant at pH from 10 to 11.5. Figure 2 shows the absorption spectra of XV-I and the magnesium chelate at pH 9.2 and 11.3. Though the absorbance difference between the reagent blank and the chelate solutions was large at 620nm, the absorbance of the reagent blank was higher than that of the chelate, and the negative peaks were obtained by injecting

into the flow-injection system. Therefore, the measurement was carried out at 515nm. Figure 3 shows the absorbance change of the magnesium chelate with time at pH 9.2 and 11.3. It was found that at pH 9.2 the reaction of chelate formation was accomplished within 30 s, whereas at pH 11.3 it took about 130s to reach stable coloration of the chelate in spite of a higher absorbance.
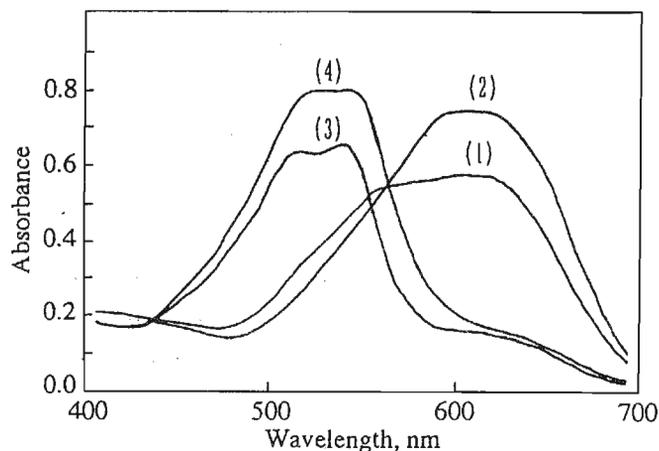

Fig. 2 Absorption spectra
at pH 9.2 and 11.3.
(1) and (3): 5×10^{-5} mol l^{-1}
XV-I, pH 9.2.
(2) and (4): 5×10^{-5} mol l^{-1}
XV-I, pH 11.3.
(3) and (4):
Mg^{2+}, 2×10^{-4} mol l^{-1}.

Effect of the concentration of nonionic surfactants as a dissolving agent
    The effect of the concentration of TX-100 on the dissolution and the formation of the magnesium chelate at pH 9.2 was examined by varying the TX-100 concentration from 0.005% to 0.5%(m/m) for 3×10^{-5} mol l^{-1} XV-I. At concentrations above 0.20% (m/m) of TX-100, the minimum absorbance for the reagent blank and the identical absorbance for 1×10^{-5} mol l^{-1} magnesium were obtained at 515nm, and the absorbances were stable for at least 1h. For safety, the reagent solution containing 1.2%m/m TX-100 and 2×10^{-4} mol l^{-1} XV-I was used as the reagent stream in the flow injection system.

Examination of experimental variables for flow-injection measurement
    The flow rates of the carrier and the reagent streams were identical and fixed to 0.8 ml min^{-1}, considering the sampling time and the pump performance used in this work. The length of a reaction coil and the sample volume injected at pH 9.2 were examined, and were fixed to 100cm and 100μl, respectively; such conditions provided the highest sensitivity for the determination of magnesium ion, and allowed an injection rate of 80 h^{-1}.
    The effect of concentrations of XV-I was examined by varying from 5×10^{-5}

mol l^{-1} to 2×10^{-4} mol l^{-1}. The peak height for magnesium ion increased with increasing the concentration of XV-I. At concentrations above 1×10^{-4} mol l^{-1} when a 3×10^{-5} mol l^{-1} magnesium solution was injected, the peak height was greatest and constant. A 2×0^{-4} mol l^{-1} XV-I solution was used for safety and lower background noise.

Effect of temperature on the formation of magnesium chelate

In the present coloration reaction, the chelate formation reaction is a little slow as is shown in Fig.3. To improve the reaction rate, the temperature of the reaction coil kept in a heating water bath was varied. As shown in Fig.4, the peak height increased with increasing the temperature of the water bath in the procedures both at pH 9.2 and 11.3, and was almost constant at near 55°C. The baseline of the background became noisy above 50°C, because of the change in temperature of the flow cell. In such cases, a 100cm cooling coil kept in water at room temperature was useful for diminishing the noisiness of the baseline. The peak height at 55°C was about two times as high as that at 25°C. In this work, however, the measurement of magnesium ion was carried out, while the reaction coil was kept in the water bath at room temperature, because of the enough sensitivity for the determination of magnesium ion in water samples, the simplicity of the system and the stable background.
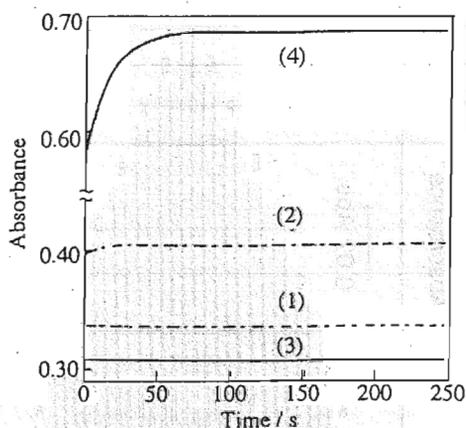
Fig. 3 Time course for the formation
of magnesium chelate.
(1) and (2): 5×10^{-5} mol l^{-1} XV-I , pH 9.2.
(3) and (4): 5×10^{-5} mol l^{-1} XV-I , pH 11.3.
(2) and (4): Mg, 2×10^{-5} mol l^{-1}. $\lambda = 515$ nm.
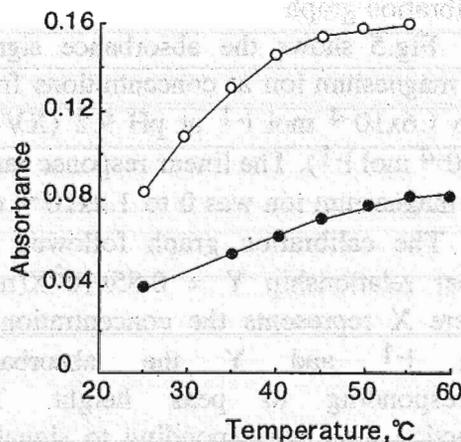
Fig. 4 Effect of temperature.
Mg^{2+}: 2×10^{-5} mol l^{-1} ;
● pH 9.2, 1×10^{-4} mol l^{-1} XV-I,
○ pH 11.3, 2×10^{-4} mol l^{-1} XV-I.
$\lambda = 515$ nm.

Effect of foreign ions

The effect of foreign ions was examined using the reagent solutions described above at pH 9.2 and pH 11.3. The results are shown in Table 1. There were some interferences from Mn^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+} at concentrations above 1×10^{-6} mol l^{-1}. However, such metal ions are commonly present at concentrations below 1×10^{-6} mol l^{-1} in river and sea waters and fertilizers. In the presence of 1×10^{-5} mol l^{-1} Fe^{3+}, the recoveries for 5×10^{-5} mol l^{-1} magnesium ion using the reagent

Table 1 Effect of foreign ions on the determination of magnesium

Foreign ion	Added (mol l^{-1})	Recovery, %	
		pH 11.3	pH 9.2
None	-	100.0	100.0
Cu^{2+}	1×10^{-6}	101.2	105.6
Co^{2+}	1×10^{-6}	100.6	97.3
Zn^{2+}	1×10^{-6}	101.2	110.6
Ni^{2+}	1×10^{-6}	101.5	104.1
Mn^{2+}	1×10^{-6}	101.2	99.0
Fe^{3+}	1×10^{-5}	102.9	99.1
Ca^{2+}	1×10^{-4}	109.4	104.8

solutions of pH 11.3 and pH 9.2 were 102.9% and 99.1%, respectively. For 1×10^{-4} mol l^{-1} Ca^{2+}, the recovery at pH 9.2 was better than that at pH 11.3, and was 104.8%. From these results, the determination of magnesium ion in samples will be carried out at pH 9.2 by the flow-injection method.

Calibration graph

Fig.5 shows the absorbance signals for magnesium ion at concentrations from 0 to 1.6×10^{-4} mol l^{-1} at pH 9.2 (XV-I : 2×10^{-4} mol l^{-1}). The linear response range for magnesium ion was 0 to 1.2×10^{-4} mol l^{-1}. The calibration graph followed the linear relationship $Y = 0.85 \times 10^{3} X (mg)$, where X represents the concentration in mol l^{-1} and Y the absorbance corresponding to peak height. The detection limit corresponding to signal to noise ratio of 3(S/N=3) for magnesium ion was about 2×10^{-6} mol l^{-1} and the relative standard deviation (n = 8) was 0.20% for 3×10^{-5} mol l^{-1} of magnesium.

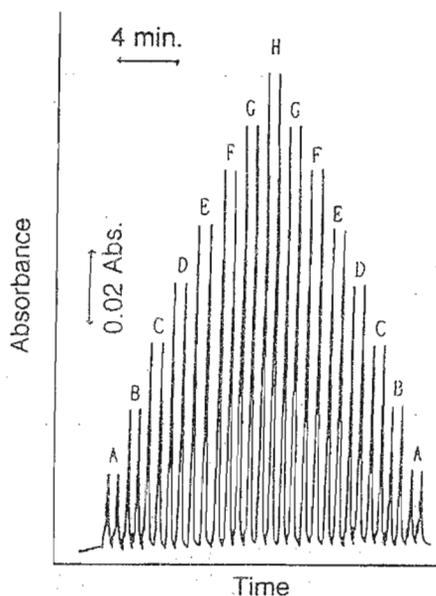For the calibration graph of $(0-1) \times 10^{-4}$ mol l^{-1} of magnesium ion at pH 11.3,

Fig. 5 Flow-injection signals for magnesium. Standard magnesium solution(10^{-5} mol l^{-1}): A,2; B,4; C,6; D,8; E,10; F,12; G,14; H,16.

the linearity was good, and the detection limit (S/N=3) was about 1.2×10^{-6} mol l^{-1}. The relative standard deviation (n = 6) was 0.58% for 2×10^{-5} mol l^{-1} magnesium.

Determination of magnesium ion in water samples

In case of water sample analysis, the sensitivity of the procedure at pH 9.2 is enough for the determination of magnesium. Table 2 shows the analytical results for the determination of magnesium ion in various water samples. Water samples, which were diluted to 2-fold~300-fold, were injected. They are in good agreement with the results obtained by the chelatometric titration with EDTA. The relative standard deviations (n = 8) were 0.26-0.66%.

Table 2 Determination of Magnesium in water samples

Sample	Titration[d]	Mg^{2+}, 10^{-4} mol l^{-1}	
		This work	
		pH 11.3 (RSD, %)[e]	pH 9.2 (RSD, %)[e]
Zasu River[a]	1.12	1.09 (0.31)	1.07 (0.65)
Asahi River[a]	0.68	0.62 (0.39)	0.62 (0.58)
Tap water[a]	0.65	0.63 (0.62)	0.60 (0.65)
Sea water[b]	466	438 (0.31)	477 (0.42)
Fertilizer 1[c]	11.8	11.3 (0.31)	12.6 (0.26)
Fertilizer 2[c]	21.2	22.9 (0.66)	24.1 (0.36)

a : Samples diluted to 2-fold ~5-fold were injected.
b : Sample diluted to 300-fold was injected.
c : Samples (about 2.5g) were dissolved in 500ml of 0.45 mol l^{-1} sulfuric
   acid, and these solutions diluted to 100-fold were injected. Fertilizer 1
   NH_3-N 15.80%, K_2O 15.54%; Fertilizer 2 NH_3-N 8.72%, P_2O 18.61%,
   K_2O 14.87%.
d : These were obtained by EDTA titration method.
e : Figures in parentheses are the relative standard deviations for n=8.

Conclusion

The proposed method is very sensitive for magnesium. The interference from calcium ion is very scarce, and therefore the proposed method will be preferably applicable to fertilizers and sea water samples, in which calcium content is less than magnesium content. In a practical sense, the procedure at pH 9.2 is recommended because the borax buffer solution can be easily prepared.

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キシリルアゾバイオレット I を用いるマグネシウムの
フローインジェクション － 吸光光度定量

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要旨

カルシウムイオンの存在下でのマグネシウムイオンの高感度，選択的な定量について検討した．キシリルアゾバイオレットI（XV·I）を発色キレート剤として用いた．非イオン界面活性剤（Triton X-100）の存在下で，マグネシウムキレートは水に可溶化し，pH8以上でキレートは515nmに極大吸収波長を示した．マグネシウムイオンの定量をpH 9.2と11.3で検討した．いずれのpHでも，$2 \times 10^{-6} \sim 1.2 \times 10^{-4}$Mの濃度範囲のマグネシウムイオンが定量できることが分かった．実際試料として，河川水，海水及び肥料中のマグネシウムの定量を行い，良好な結果を得た．