Spectrophotometric Determination of Magnesium and Calcium with Semimethylxylenol Blue

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Summary—Procedures are described for the spectrophotometric determination of magnesium aud calcium with Semimethylxylenol Blue (SMXB). SMXB reacts with magnesium and calcium to form water-soluble colored complexes. The optimum pH ranges for the color development are pH 10.5-11.1 for magnesium and pH 10.8-11.5 for calcium, and the absorption maxima of the colored solutions lie at 580-583 nm and at 603-605 nm, respectively. Beer's law is obeyed over the range of 0.2-2.0 μg/mℓ of magnesium or calcium and the sensitivities of the determination are 1.6×10^{-3} μg Mg/cm² and 2×10^{-3} μg Ca/cm² for 0.001 of absorbance. The mole ratio of magnesium or calcium and SMXB was estimated to be 1 : 2 by mole ratio and by continuous variation methods. Among the 44 diverse ions examined, beryllium, lead, copper, zinc, cadmium, mercury(II), chromium(III), iron(III), cobalt, and nickel interfered with magnesium and calcium determinations. Copper, zinc, cadmium, mercury(II), cobalt, and nickel, however, could be masked by the addition of potassium cyanide, and the effect of iron(III) was eliminated by triethanolamine.

INTRODUCTION

Semimethylxylenol Blue (SMXB) is obtained as one of the products in the synthesis of Methylxylenol Blue by the Mannich condensation of Paraxylenol Blue, formaldehyde, and iminodiacetic acid. It is a monosubstituted derivative of paraxylenol Blue, while Methylxylenol Blue is a disubstituted derivative.[1] In the preceding papers, we described the spectrophotometric methods for the determination of thorium,[2] iron(III),[3] aluminum,[3] zirconium,[4] gallium,[5] palladium,[6] bismuth(III),[6] and hafnium,[7] using SMXB as a spectrophotometric reagent. In this work, we examined the usefulness of SMXB as the photometric reagent for magnesium and calcium, and recognized that this reagent was a suitable one for these metal ions in respect to the sensitivity and selectivity and could be applied to the determinations of up to 2.0 μg/mℓ of magnesium and calcium. The present method for the determination of calcium is nearly as specific as the methods using such reagents with similar structures to SMXB as Methylxylenol Blue[8] and Methylthymol Blue,[9] and

Received on Sept. 16th, 1993.

has higher sensitivities than these methods. For the magnesium determination, the proposed method also has higher sensitivity than the method using Methylthymol Blue.[10]

This paper describes the fundamental conditions for the spectrophotometric determination of magnesium and calcium with SMXB as a photometric reagent.

EXPERIMENTAL

Reagents

Standard magnesium solution: A solution containing about 1 mg/mℓ of magnesium was prepared by dissolving guaranteed reagent grade magnesium nitrate in a small amount of nitric acid and diluted with distilled water. The concentration of magnesium was determined by the complexometric titration using Eriochrome Black T as an indicator. This solution was diluted as required.

Standard calcium solution: A solution containing about 1 mg/mℓ of calcium was prepared by dissolving guaranteed reagent grade calcium nitrate in a small amount of nitric acid and diluted with distilled water. The concentration of calcium was determined by the complexometric titration using NN as an indicator. This solution was diluted as required.

SMXB solution: A 0.05% SMXB solution was prepared by dissolving in distilled water a weighed amount of the SMXB which was synthesized by the Mannich condensation and purified by means of cellulose column chromatography.[2),3)]

Buffer solution: The pH was adjusted with 0.1 mol/l glycine-0.1 mol/l sodium chloride-0.1 mol/l sodium hydroxide for the determinations of both magnesium and calcium.

All the other reagents used were of guaranteed reagent grade.

Apparatus

A Hitachi-Perkin-Elmer model 139 spectrophotometer with 1 cm glass cells was used for the absorbance measurements, and a Hitachi-Horiba model M-5 glass electrode pH meter for the pH measurements.

Recommended procedures

A sample solution containing 5-50 μg of magnesium or calcium is taken into 25 mℓ volumetric flask. Then 3 mℓ of 0.05% SMXB solution and 10 mℓ of 0.1 mol/l glycine-0.1 mol/l sodium chloride-0.1 mol/l sodium hydroxide buffer solution are added. After making up the volume to 25 mℓ (the final pH:10.9), the absorbances are measured at the wavelength of 581 nm for magnesium and at 604 nm for calcium against the reagent blank as a reference.

RESULTS AND DISCUSSION

Absorption curves

Figure 1 shows the absorption spectra of magnesium and calcium complexes obtained by the recommended procedure. The absorption maxima of the colored solutions of the complexes are at 580-583 nm and at 603-605 nm, respectively.

The effect of pH

The effect of pH on the color development of the complexes was examined according to the recommended procedure, changing the pH of the solution at various values with 0.1 mol/l glycine-0.1 mol/l sodium chloride-0.1 mol/l sodium hydroxide buffer solution. As shown in Fig. 2, the ranges in which the maximum and nearly constant absorbance was obtained were pH 10.5-11.1 for magnesium and pH 10.8-11.5 for calcium.

The stability of the color

The full color development for magnesium or calcium complex occurred immediately after the reagent was added. The colors of the both complexes, once developed, were very stable, and the absorbances remained constant for at least 3 hrs.

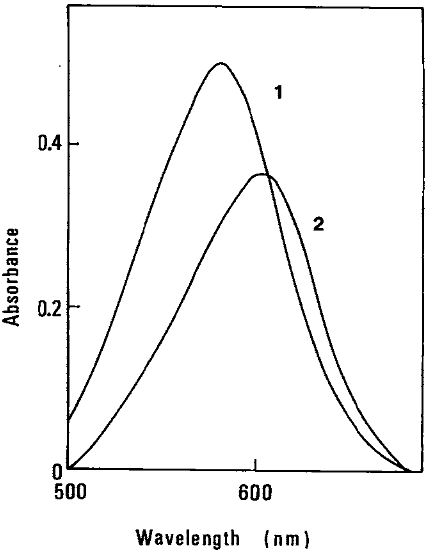

Fig. 1. Absorption curves.
0.05% SMXB: 3 mℓ, pH:10.9,
reference: reagent blank,
(1) Mg 20 μg/25mℓ,
(2) Ca 20 μg/25mℓ.

The effect of the reagent concentration

Various amounts of 0.05% SMXB solution were added to a solution containing 20 μg of magnesium or calcium. The maximum and reasonably constant absorbances were obtained by adding from 1.8 to 6 mℓ of SMXB solution for each element. The results were shown in Fig. 3. In this experiment, therefore, 3 mℓ of 0.05% SMXB solution was used

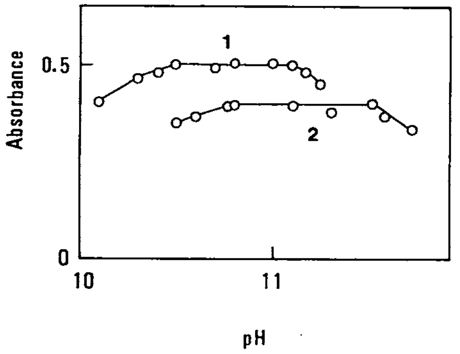

Fig. 2. Effect of pH.
0.05% SMXB: 3 mℓ, reference: reagent blank,
(1) Mg 20 μg/25mℓ, wavelength: 581nm,
(2) Ca 20 μg/25mℓ, wavelength: 604nm.

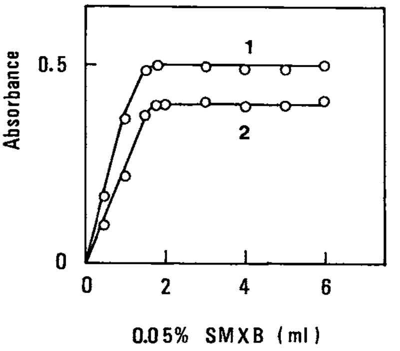

Fig. 3. Effect of the amount of SMXB.
pH: 10.9, reference: reagent blank,
(1) Mg 20 μg/25mℓ, wavelength: 581nm,
(2) Ca 20 μg/25mℓ, wavelength: 604nm.

for the formation of the complexes.

The effect of the amount of the buffer solution

The addition of 3 to 15mℓ of 0.1 mol/l glycine-0.1 mol/l sodium chloride-0.1 mol/l sodium hydroxide buffer solution had no effect on the color intensity of the both magnesium and calcium complexes.

Calibration curves

The calibration curves for magnesium and calcium which were prepared by the recommended procedure are shown in Fig. 4. Linear relationships between the absorbance and the concentration were held over the range of 0.2-2.0 μg/mℓ of magnesium and calcium. The relative standard deviations for five replicate determinations were 1.1% for 20 μg of magnesium and 0.9% for 20 μg of calcium, and the molar absorptivities calculated from the curves were 1.52×10^4 and 2.0×10^4, respectively.

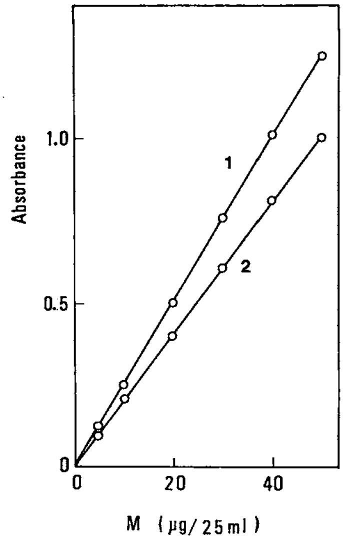

Fig. 4. Calibration curves. 0.05% SMXB: 3 mℓ, pH:10.9, reference: reagent blank, (1) Mg, wavelength: 581 nm, (2) Ca, wavelength: 604 nm.

The effect of diverse ions

Table 1 shows the effect of diverse ions on the determination of 20 μg of magnesium or calcium. The both elements could be determined within 5 % errors in the presrence of 500 μg each of 25 cations such as alkali metals, strontium, aluminum, tin(Ⅳ), arsenic(Ⅴ), bismuth(Ⅲ), lanthanoids, thorium, and palladium and in the presence of 10 mg each of 4 anions such as sulfate, oxalate, citrate, and tartrate. On the other hand, beryllium, lead, copper, zinc, cadmium, mercury(Ⅱ), chromium(Ⅲ), iron (Ⅲ), cobalt, and nickel interfered with both determinations, but copper, zinc, cadmium, mercury(Ⅱ), cobalt, and nickel could be masked by the addition of potassium cyanide, and the effect of iron(Ⅲ) was eliminated by triethanolamine.

The composition of the complexes

The compositions of the magnesium and calcium complexes were examined at pH 10.9 by the mole ratio and the continuous variation methods, measuring the absorbances at the wavelengths of 560 and 581 nm for magnesium and at 580 and 604 nm for calcium. In the mole ratio method, various amounts of SMXB were added to a constant amount of magnesium or calcium, 5.72×10^{-4} mol/l. In the continuous variation method, on the other hand, the total moles of magnesium and SMXB or calcium and SMXB were held constant at 2.86×10^{-3} mol/l. As the results were shown in Fig. 5 and 6, both the equivalence points in the mole ratio method and the maximum points of the absorbances in the continuous variation method indicated that the mole ratio between magnesium or calcium and SMXB was 1 : 2.

Table 1. Effect of diverse ions on the determinations of magnesium and calcium

Ion	A		B		Ion	A		B	
	Amount added (μg)	Mg found (μg)	Amount added (μg)	Ca found (μg)		Amount added (μg)	Mg found (μg)	Amount added (μg)	Ca found (μg)
Li^{+}	500	20.0	500	20.1	Y^{3+}	500	20.3	500	19.7
K^{+}	500	20.0	500	20.0	La^{3+}	500	20.2	500	20.0
Be^{2+}	20	17.9	20	18.1	Ce^{3+}	500	20.1	500	20.3
Mg^{2+}	—	—	20	33.4	Zr^{4+}	500	20.3	500	20.5
Ca^{2+}	20	29.9	—	—	Th^{4+}	500	20.1	500	20.2
Sr^{2+}	500	20.8	500	20.7	V (V)	500	19.8	500	19.8
Ba^{2+}	500	20.6	500	20.4	Cr^{3+}	20	16.9	20	14.4
Al^{3+}	500	19.8	500	19.9	Mo (VI)	500	20.0	500	20.2
Ga^{3+}	500	20.1	500	19.5	W (VI)	500	20.0	500	20.0
In^{3+}	500	20.1	500	20.3	Mn^{2+}	100	19.7	100	19.5
Tl^{+}	500	20.4	500	20.4	Fe^{3+}	20	16.8	20	17.4
Sn^{4+}	500	19.7	500	19.9	〃	100[b)]	19.5	100[b)]	19.4
Pb^{2+}	20	17.5	20	16.3	Co^{2+}	20	24.8	20	25.7
As (V)	500	19.9	500	19.5	〃	500[a)]	20.7	500[a)]	20.6
Sb^{3+}	500	20.2	500	20.1	Ni^{2+}	20	25.5	20	29.3
Bi^{3+}	500	20.5	500	20.1	〃	500[a)]	20.6	500[a)]	20.4
Cu^{2+}	20	16.2	20	17.8	Rh^{3+}	500	20.1	500	20.0
〃	500[a)]	20.1	500[a)]	19.6	Pd^{2+}	500	20.8	500	20.6
Au^{3+}	500	19.8	500	19.7	Pt (IV)	500	20.0	500	19.7
Zn^{2+}	20	18.1	20	18.8	Ir^{4+}	500	20.0	500	19.9
〃	500[a)]	20.0	500[a)]	19.6	F^{-}	1 (mg)	19.4	1 (mg)	19.2
Cd^{2+}	20	18.3	20	18.4	PO_4^{3-}	1 〃	19.6	1 〃	19.6
〃	500[a)]	19.8	500[a)]	19.9	SO_4^{2-}	10 〃	20.0	10 〃	20.0
Hg^{2+}	20	18.4	20	18.1	Oxalate	10 〃	19.5	10 〃	19.8
〃	500[a)]	19.8	500[a)]	19.5	Citrate	10 〃	19.8	10 〃	19.4
Sc^{3+}	500	19.2	500	19.4	Tartrate	10 〃	19.7	10 〃	19.8

A: Effect on the magnesium determination (20 μg of magnesium was taken).
B: Effect on the calcium determination (20 μg of calcium was taken).
a): 1 mℓ of 5 % potassium cyanide solution was added.
b): 1 mℓ of 40% triethanolamine solution was added.

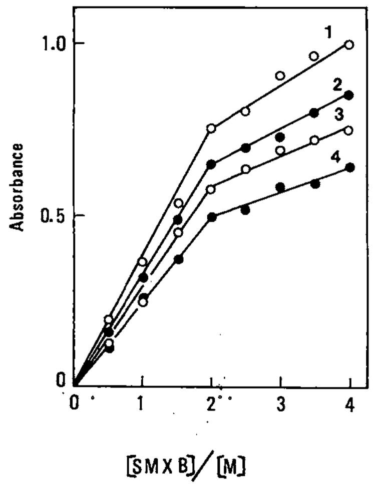

Fig. 5. Mole ratio method. pH: 10.9, [Mg] (mol/l)−(1), (2): 5.72×10^{-4}, [Ca] (mol/l)−(3), (4): 5.72×10^{-4}, wavelength (nm)−(1): 581, (2): 560, (3): 604, (4): 580.

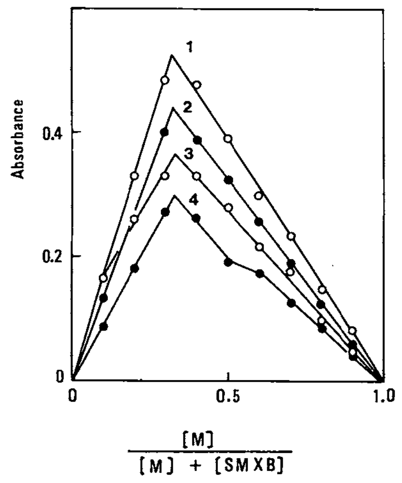

Fig. 6. Continuous variation method. pH:10.9, [Mg]+[SMXB] (mol/l)−(1), (2): 2.86×10^{-3}, [Ca]+[SMXB] (mol/l)−(3), (4): 2.86×10^{-3}, wavelength (nm)−(1): 581, (2): 560, (3): 604, (4): 580.

CONCLUSIONS

From this study, SMXB is recommended as a spectrophotometric reagent for magnesium or calcium determination, because of its good sensitivity and selectivity. The reproducibilities of the methods, expressed by the relative standard deviations of the absorbances which were obtained from five repeat determinations, were 1.1% for 20 μg of magnesium and 0.9% for 20 μg of calcium. The molar absorptivities calculated from the calibration curves were 1.52×10^4 and 2.0×10^4, respectively. By the addition of potassium cyanide and triethanolamine, many diverse ions which interfere with the both magnesium and calcium determinations are masked.

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