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Flow Injection Determination of Total Water Hardness in Seawater by Using Metal-ligand Buffer and Color-indicator

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ABSTRACT

Flow injection determination of total water hardness (sum of concentrations of calcium and magnesium ions) is proposed, using the reaction of the sample with a metal-ligand buffer solution containing calmagite as an indicator. Seawater injected into a stream of water was merged with a stream of 0.01 M ethylenediaminetetraacetic acid solution (pH 9.5), and the mixed stream was merged with a magnesium–nitorilotriacetic acid buffer solution containing calmagite. The absorbance change of the calmagite–magnesium complex at 535 nm was monitored. About 60 samples/h could be determined by the proposed method. The analytical results obtained by this method were in good accordance with those obtained by the conventional chelatometric titration method.

INTRODUCTION

Total water hardness, i.e., the sum of total concentrations of calcium and magnesium ions, is one of important factors affecting the quality of seawater used for salt industries. Therefore, rapid determination or continuous monitoring of total water hardness is desirable in the quality control of such water. Water hardness is usually determined by the chelatometric titration (American Public Health Association, 1985; Japanese Industrial Standard, K0101, K0102). The titration procedure is quite time-consuming and it is unsuitable for continuous monitoring of water hardness. On the other hand, flow injection analysis (FIA) is promised as a fairly rapid analytical technique (Ruzicka and Hansen, 1988). Recently, several methods for the determination of calcium and magnesium ions by FIA have been reported based on atomic absorption spectrometry (Zagatto et al., 1979; Basson and Van Staden, 1980), spectrophotometry and fluorometry using chromophores (Jacintho et al., 1981; Nakagawa et al., 1983; Wada et al., 1983, 1984). Simultaneous determination of the calcium and magnesium ions was achieved by means of a FIA system with a single spectrophotometric detector (Cante et al., 1987). However, few reports have appeared for direct determination of total water hardness (Yamane and Kamijyo, 1984).

In the previous papers (Ishibashi and Imato, 1986; Ishibashi et al., 1986; Imato et al., 1989, 1990), we have reported the spectrophotometric and potentiometric flow injection determinations of heavy metal and alkaline earth metal ions by using metal ion buffer streams. For the spectrophotometric determination, the metal-ligand buffer solution containing a suitable color-indicator was utilized for a reagent solution of the FIA of metal ions (Ishibashi and Imato, 1986; Imato et al., 1989).

In this paper, we apply the above spectrophotometric flow injection method to the determination of total water hardness of seawater by optimization of the flow condition.

THEORETICAL CONSIDERATIONS

The flow diagram for the determination of metal ions is shown in Fig. 1. The metal ion buffer solution consisting of metal ion, M, and ligand, L, contains a color reagent indicator, In, and it is pumped in one line. In such a solution, the following equilibria hold.

$$C_{ML}/(C_M\, C_L) = K_{ML} \quad (1)$$

$$C_{MIn}/(C_M\, C_{In}) = K_{MIn} \quad (2)$$

where K_{ML} and K_{MIn} are the stability constants of metal-ligand and metal-indicator complexes, respec-

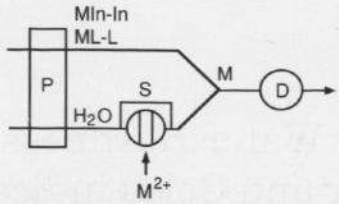

Fig. 1. Flow diagram for determination of metal ions. P: Pump, S: sample injector, M: mixing point, D: detector; ML-L: metal–ligand complex and ligand, MIn-In: metal–indicator complex and indicator.

tively. C_{ML}, C_M, C_L, C_{MIn} and C_{In} are the concentrations of ML, M, L, MIn, and In, respectively. From Equations (1) and (2), the following equation is obtained:

$$C_L/C_{ML} = k\,(C_{In}/C_{MIn}) \quad (3)$$

where $k=K_{MIn}/K_{ML}$.

When a sample solution containing metal ion, M, is injected into the stream of water, the metal ion is distributed to the ligand and the indicator, and the ratios of C_L/C_{ML} and C_{In}/C_{MIn} change according to Equation (3). The change in the ratio of C_L/C_{ML} may be determined by the measurement of the absorbance of the metal-indicator complex used, since it is related to the change in the ratio of C_{In}/C_{MIn} by Equation (3).

The concentration of the metal-indicator complex is calculated by using the following mass balance equations together with Equations (1) and (2).

$$C_M^T = C_M + C_{ML} + C_{MIn} \quad (4)$$

$$C_L^T = C_L + C_{ML} \quad (5)$$

$$C_{In}^T = C_{In} + C_{MIn} \quad (6)$$

where C_M^T, C_L^T and C_{In}^T are the total concentrations of metal ion, ligand, and indicator, respectively.

C_{MIn} is given from C_M, one of the roots of Equation (7), which is derived from Equations (1), (2) and (4)–(6), under the condition $0 < C_M < C_M^T$.

$$K_{ML}K_{MIn}C_M^3 + [K_{ML} + K_{MIn} + K_{ML}K_{MIn}(C_L^T + C_{In}^T - C_M^T)]C_M^2 + [K_{ML}C_L^T + K_{MIn}C_{In}^T - (M_{ML} + K_{MIn})C_M^T + 1]C_M - C_M^T = 0 \quad (7)$$

In Fig. 2, the relationship between the concentrations of injected metal ion and of the metal-indicator complex is shown by calculating from Equations (2), (6) and (7). Figure 2 shows the so-called calibration curves for the proposed method. The total concentrations of L and In are taken as 5.0×10^{-2} M and 2.0×10^{-5} M, respectively, as an example. The stability constants of the calmagite complexes with magnesium and calcium (transition points of calmagite) are shown in Table 1 together with those of nitrilotriacetic acid (NTA) complexes with magnesium and calcium. In calculation of the calibration curves in Fig. 2, the numerical value of K_{MIn} is assumed for simplicity to be 1.0×10^5 [$dm^3\ mol^{-1}$] and the values of K_{ML} are varied from 1.0×10^3 to 1.0×10^6 [$dm^3\ mol^{-1}$]. When the values of K_{MIn} and K_{ML} are the same, i.e., k, in Equation (3) is unity, the calibration curve becomes linear. This means that the metal in the sample is distributed to the ligand, L, and the indicator, In, so that the ratio C_{ML}/C_L is almost equal to that of C_{MIn}/C_{In}. On the other hand, the calibration curves are convex and concave in the case of K_{MIn} >

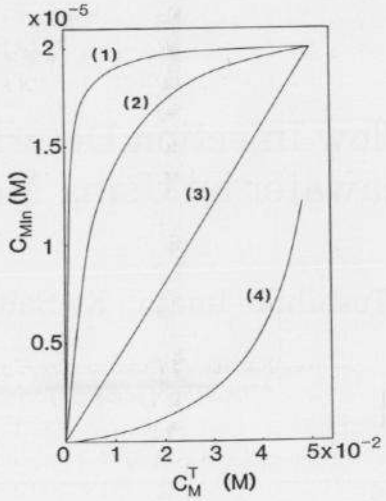

Fig. 2. Theoretical relationship between concentrations of metal ion and meta–indicator complex. Conditional stability constants K_{ML} and K_{MIn} used for calculation. $K_{MIn} = 1.0\times10^5$. K_{ML}: (1) 1.0×10^3, (2) 1.0×10^4, (3) 1.0×10^5, (4) 1.0×10^6. $C_L^T = 5.0\times10^{-2}$ M and $C_{In}^T = 2.0\times10^{-5}$ M are assumed.

TABLE 1

Stability constants of NTA complex with magnesium and calcium and transition points of calmagite

	pH			
	7	8	9	10
$K_{Mg\text{-}NTA}$	$10^{2.6}$	$10^{3.6}$	$10^{4.5}$	$10^{5.2}$
Mg_{trans}	$10^{1.6}$	$10^{3.4}$	$10^{4.7}$	$10^{5.7}$
$K_{Ca\text{-}NTA}$	$10^{3.6}$	$10^{4.6}$	$10^{5.5}$	$10^{6.2}$
Ca_{trans}	$10^{7.3}$	$10^{8.4}$	$10^{9.3}$	$10^{10.2}$

*Values are taken from Rigbom (1963).

K_{ML} and $K_{MIn} < K_{ML}$, respectively. This is due to the fact that the metal ion is bound preferentially to the indicator in the former case, and to the ligand in the latter case. The reason for the choice of the calmagite–NTA–magnesium system is described in the section of results and discussion.

EXPERIMENTAL

Reagents and apparatus

All reagents were of analytical grade and used as received. Distilled and deionized water was used throughout the work. Stock solutions of calcium and magnesium ions were prepared from their nitrates or chlorides, and were standardized by the conventional chelatometric titration. The magnesium ion buffer was prepared from the stock solution of magnesium nitrate and the standard NTA solution. The pH of the magnesium ion buffer and an ethylenediaminetetraacetic acid (EDTA) solution was adjusted to 9.5 by adding 0.1 M ammonia and 0.1 M ammonium nitrate.

The flow injection analysis system consisted of two double-plunger pumps (Sanuki Kogyo, DM2M-1024 and DMX-2000), a sample injector (Rheodyne, 7125), and a spectrophotometric detector (Soma Optics Ltd., S-3250) with a flow-through cell (8 μL, 10 mm light pathlength). The output signal from the spectrophotometric detector was fed to a chart recorder (Yokogawa, 3066). Teflon tubing (0.5 mm i.d.) was used for manifolds.

Procedure of analysis

Figure 3 shows the schematic flow diagram for the determination of total water hardness. The sample solution of the calcium and/or magnesium ion was injected into a water stream (CS), and was merged with a stream of 0.01 M EDTA solution (RS_1). This mixed stream was merged with the stream of the NTA–magnesium buffer (RS_2). The absorbance change of the calmagite–magnesium complex at 535 nm was monitored by the spectrophotometric detector located downstream, and it was recorded as a peak signal. Concentrations of calcium and magnesium ions or the sum of them were determined from peak heights.

RESULTS AND DISCUSSION

Choice of indicator in the batch system

As described in the theoretical considerations, it is desirable that the stability constant of the indicator–metal complex should be close to that of the ligand–metal complex used in the buffer solution. As shown in Table 1, the stability constants of calmagite–magnesium and NTA–magnesium complexes are almost the same in the pH range 8–10. The suitability of the above combination for the present method was examined in the batch system. Figure 4 shows the absorption spectra of calmagite in a mixed solution prepared by adding the magnesium chloride solution with various concentrations to the NTA–magnesium buffer solution. The wavelength of maximum absorbance for calmagite–magnesium complex is located at 535 nm, and the absorbance at 535 nm increases with the increase in the concentration of magnesium ion. This result is in good agreement with the expectation described in the theoretical considerations.

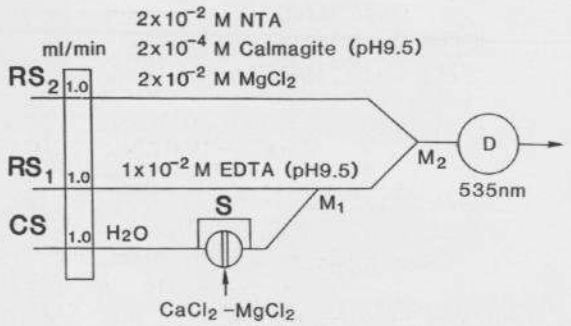

Fig. 3. Flow diagram for determination of total water hardness. CS: Carrier (water), 1.0 ml/min, RS_1: 1.0×10^{-2} M EDTA (pH 9.5), 1.0 ml/min, RS_2: 2.0×10^{-2} M NTA + 2.0×10^{-2} M $MgCl_2$ + 2×10^{-4} M Calmagite (pH 9.5), 1.0 ml/min. S: Injector (10 μl or 200 μl), D: spectrophotometric detector (535 nm). Coil length and diameter: S-M_1 30 cm × 0.5 mm i.d., M_1-M_2 120 cm × 0.5 mm i.d., M_2-D 240 cm × 0.5 mm i.d.

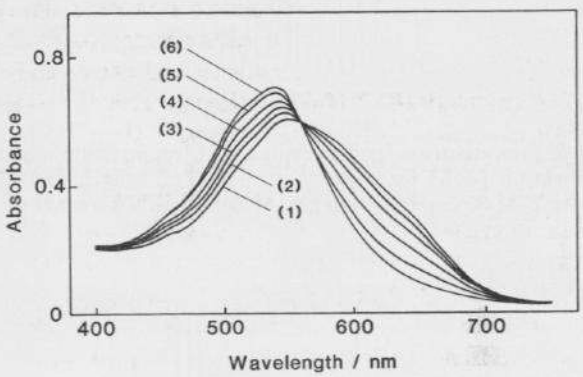

Fig. 4. Change of absorption spectra of calmagite on addition of magnesium ion to magnesium ion buffer containing calmagite. Absorbance was measured for the 1:1 mixtures of the solution (I) and (II). Solution (I): 1.0×10^{-2} M NTA + 5.0×10^{-3} M $MgCl_2$ + 1.0×10^{-4} M Calmagite (pH 9.5). Solution (II): (1) H_2O, (2) 1.0×10^{-3} M $MgCl_2$, (3) 2.0×10^{-3} M $MgCl_2$, (4) 3.0×10^{-3} M $MgCl_2$, (5) 4.0×10^{-3} M $MgCl_2$, (6) 5.0×10^{-3} M $MgCl_2$.

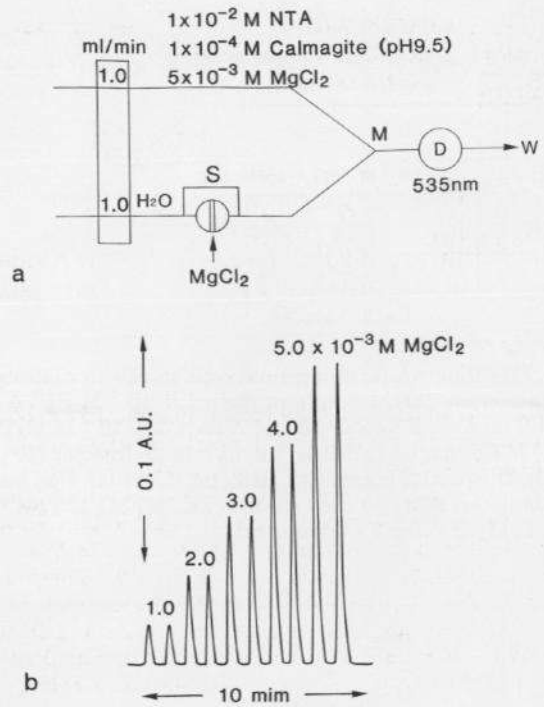

Fig. 5. Flow diagram for determination of magnesium ion and calibration peaks for magnesium ion. Coil length and diameter: S-M 30 cm × 0.5 mm i.d., M-D 150 cm × 0.5 mm i.d.

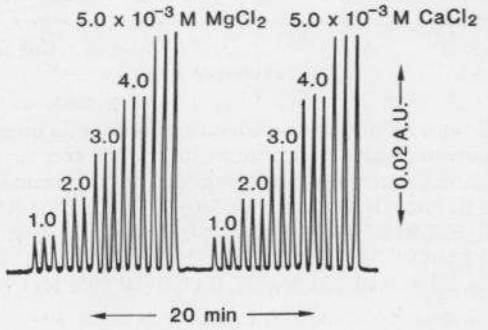

Fig. 6. Response peaks for calcium and magnesium ions. Manifold is identical to Fig. 3. RS_1: 1.0×10^{-2} M $MgCl_2$ + 1.0×10^{-2} M NTA + 2.0×10^{-4} M Calmagite (pH 9.5). RS_2: 5.0×10^{-3} M EDTA (pH 9.5). Sample volume: 200 µl.

Calibration curves for magnesium ion in the flow system

The flow system as shown in Fig. 5 (a), was constructed on the basis of the results of the batch system. The NTA–magnesium buffer solution containing calmagite was used in the analysis of magnesium ion. Figure 5 (b) shows the FIA peaks for the determination of magnesium ion. The peak height was linear to the concentration of magnesium ion. The sampling rate of about 100 samples/h was achieved by the present flow system.

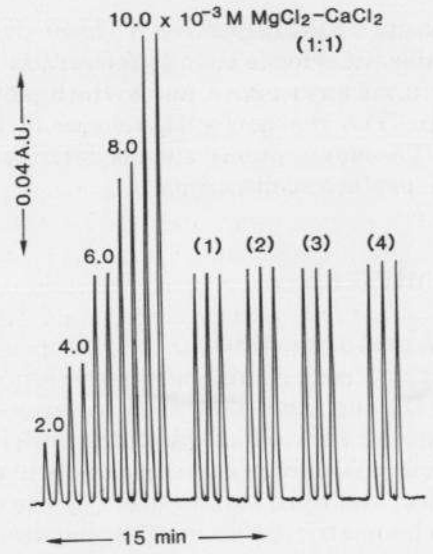

Fig. 7. Response peaks for standard solution, synthetic seawater and real seawater. (1) Standard sample 1.0×10^{-2} M $CaCl_2$ + 5.0×10^{-2} M $MgCl_2$ + 1×10^{-2} M KCl. (2) Standard sample 1.0×10^{-2} M $CaCl_2$ + 5.0×10^{-2} M $MgCl_2$ + 5.2×10^{-1} M NaCl. (3) Synthetic seawater — cations: Ca^{2+}: 1.0×10^{-2} M, Mg^{2+}; 5.0×10^{-2} M; Na^+: 5.2×10^{-1} M, K^+: 1.0×10^{-2}M. Anions: Cl^-: 6.0×10^{-1} M, SO_4^{2-}: 2.5×10^{-2}M. (4) Seawater (sampled at shore of Shikanoshima island in Fukuoka Prefecture, Japan). Flow system is identical with Fig. 3. The injected sample was prepared by 1/10-fold dilution of each sample solution.

Determination of total water hardness of seawater

In the flow system of Fig. 5 (a), the sensitivity to the calcium ion is lower than that to the magnesium ion because of less matching in the stability constants of the calmagite–calcium and NTA–calcium complexes, as shown in Table 1. EDTA was determined by the flow system shown in Fig. 5 (a) using the decrease in the concentration of the calmagite–magnesium complex by the following reaction:

$$\text{Mg–Calmagite} + \text{EDTA} \rightarrow \text{Mg–EDTA} + \text{Calmagite} \quad (8)$$

Fortunately, EDTA reacts with calcium and magnesium ions to the same extent above pH 9. Therefore, the calcium ion can be determined as well as the magnesium ion with the same sensitivity, when the decrease in the concentration of EDTA is utilized by introducing a stream of EDTA solution to the manifold of Fig. 5 (a). Indeed, the response peak heights of magnesium and calcium ions are almost equal in their peak heights, as shown in Fig. 6, which were obtained by the manifold shown in Fig. 3.

The usefulness of the proposed method has been

demonstrated by the application to synthetic and real samples of seawater. Figure 7 shows the response peak for standard solutions prepared by mixing calcium and magnesium ions (1) and (2), synthetic seawater sample prepared by dissolving dominant cations and anions present in common seawater (3), and real seawater (4). Peak heights of (1) to (3) are equal, and it corresponds to the total concentration of calcium and magnesium ions. This means that coexisting cations and anions show no interference for the determination of total water hardness. In this case, the sample was diluted by 1/10-fold. Table 2 shows that the obtained results by the proposed FIA method are in good agreement with those by the chelatometric titration method. It was possible to determine total water hardness of seawater without any dilution of the sample when the sample volume was reduced to 10 μl, since the sample is diluted by about 1/10-fold in the carrier stream. The relative standard deviation for peak heights was examined by 10 repeated injection and was 0.6%. The sampling rate was about 60 samples/h for the present manifold.

TABLE 2

Total water hardness of seawater

Analytical method	Total water hardness ($CaCO_3$ mg/l sample)
Chelate titration	6110
Proposed FIA	6200

Seawater was sampled at the shore of Shikanoshima island in Fukuoka Prefecture (Japan).
Manifold is the same as in Fig. 3.

CONCLUSIONS

The simple and rapid flow injection method for the determination of total water hardness was demonstrated by its application to a real seawater sample. The dominant ions existing in seawater did not interfere with the proposed method, and analysis of a higher sampling rate was possible in comparison with the conventional chelatometric titration method. This method could be applied to continuous monitoring of total water hardness by continuous mixing of a stream of a sample solution with that of NTA–magnesium buffer solution. The measurable concentration range can be varied by appropriate selection of the concentrations of the magnesium ion buffer and the EDTA solution. Therefore, this method can be applied to the determination of different levels of total water hardness from tap water to boiler water.

ACKNOWLEDGEMENT

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