Flow-Injection Determination of the Total Water Hardness by Using a Copper(II) Ion-Selective Electrode and a Copper(II) Ion Buffer

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A potentiometric determination of the total water hardness by flow-injection analysis is proposed, which uses both a Cu²⁺ ion-selective electrode detector and a Cu²⁺-ion buffer stream comprising a Cu-EDTA complex and free EDTA. This method is based on potentiometric monitoring of the change in the free Cu²⁺-ion concentration in the buffer with a Cu²⁺-ion-selective electrode, caused by the reaction of Ca²⁺ and Mg²⁺ ions with free EDTA in the buffer. Chloride interference in the measurement of the Cu²⁺-ion concentrations with the Cu²⁺ ion-selective electrode was successfully eliminated by adding triethylenetetramine to the Cu²⁺-ion buffer. The total hardness of seawater samples could therefore be determined at a sampling rate of 30 h⁻¹ and a relative standard deviation of 0.7%. The obtained results using the proposed method were in good accord with those obtained by conventional chelatometric titration.

Keywords Flow-injection analysis, total water hardness, copper(II) ion-selective electrode detector, copper(II) ion buffer solution, seawater

The total water hardness, i.e., the sum of the Ca²⁺ and Mg²⁺ ion concentration, is one of the important factors in assessing the quality of tap water, water for industrial use and other types of water.¹² A rapid determination or a continuous monitoring method of the total water hardness is desirable in the quality control of these types of water. The water hardness is usually determined by chelatometric titration.¹² The titration procedure is generally time-consuming, and is unsuitable for the continuous monitoring of the water hardness. A more rapid method based on a polarographic reduction of the Mg²⁺ ion was reported which utilizes a displacement reaction for the Mg-EDTA complex.³ Potentiometry using a divalent ion-selective electrode with a liquid membrane⁴⁵ was applied to continuous monitoring of the water hardness. However, even an electrode which initially has equal sensitivity to Ca²⁺ and Mg²⁺ ions tends to become more sensitive to the Ca²⁺ ion during prolonged use.⁶ Recently, several methods for the determinations of Ca²⁺ and Mg²⁺ ions by flow-injection analysis (FIA) have been reported based on atomic absorption spectrometry⁷⁻⁸ as well as spectrophotometry⁹⁻¹² using chromogenic and fluorometric reagents. The simultaneous determination of Ca²⁺ and Mg²⁺ ions was achieved by means of an FIA system with a single spectrophotometric detector.¹³ However, few reports have appeared concerning a direct determination of the total water hardness.¹⁴

In previous papers¹⁵⁻¹⁷ we reported on both spectrophotometric and potentiometric flow-injection determinations of heavy metals and alkaline earth metals using metal-ion buffer streams. Regarding the potentiometric determination, a Cu²⁺ ion-selective electrode and a Cu²⁺-ion buffer were used. One of the characteristics of the proposed potentiometric method is that many metal ions which show no direct response to the electrode, but are capable of forming complexes with the buffer ligand, can be determined with equal sensitivity by selecting the buffer ligand and pH. Although this method gives only small response peaks (ca. 10 – 20 mV), it is sufficiently sensitive and precise to detect potential changes of less than 100 µV, since the electrode detector shows a very stable base-line potential in a metal-ion buffer solution.

In this work we apply the above-mentioned potentiometric flow injection method to determine the total water hardness. The Cu²⁺ ion-selective electrode has been known to suffer from interference due to halides, such as chloride ion.¹⁸¹⁹ In this study an elimination of interference from the halides was achieved by adding triethylenetetramine (Trien) to the Cu²⁺-ion buffer. By eliminating chloride interference, the proposed potentiometric flow injection method was successfully applied to determine the total hardness of seawater.

Experimental

Reagents and apparatus

All of the reagents were of analytical grade and used as received. Distilled and deionized water was used throughout. Stock solutions of Ca²⁺ and Mg²⁺ ions were prepared from their nitrates or chlorides, and were
standardized by conventional chelatometric titration. The Cu²⁺-ion buffer was prepared from a stock solution of Cu(NO₃)₂ and the standard EDTA solution. The pH of the Cu²⁺-ion buffer was adjusted to 9.4 by adding 0.1 M ammonia and 0.1 M ammonium nitrate. The pH effect of the Cu²⁺-ion buffer on the sensitivity of the proposed method in determinations of Ca²⁺ and Mg²⁺ ions was examined by using 2-(N-morpholino)ethanesulfonic acid (MES) and 3-(N-morpholino)propanesulfonic acid (MOPS) as pH-adjusting reagents. The Cu²⁺-ion buffer contains 0.5 M KNO₃ and a small amount of Trien.

The flow-injection system comprised two double plunger pumps (Sanuki Kogyo, DM2M-1024 and DMX-2000), a sample injector (Rheodyne, 7125) and a flow-through type Cu²⁺ ion-selective electrode detector (Denki Kagaku Keiki, FLC12). The output signals from a potentiometer (Denki Kagaku Keiki, IOC-10) were fed to a chart recorder (Yokogawa, 3066). Teflon tubing (0.5 mm i.d.) was used for the manifold.

Procedure of analysis

Figure 1 is a schematic diagram concerning the determination of the total water hardness. A sample solution (200 µl) of Ca²⁺ and/or Mg²⁺ ion was injected into a water stream (carrier: CS) and then merged with a stream of 0.5 M NaNO₃ (RS₁) to fix the ionic strength of the stream. This mixed stream was merged with a stream of the Cu²⁺-ion buffer (RS₂). The potential change of an electrode detector located downstream was recorded as a peak. The concentrations of Ca²⁺ and Mg²⁺, or their sum, were determined based on the peak heights.

Results and Discussion

Methodology of analysis and pH effect on the sensitivity

The Cu²⁺-ion buffer comprised the Cu-EDTA complex and free EDTA. The Cu²⁺ ion-selective electrode detector gives a potential value corresponding to the concentration of free Cu²⁺-ion in the Cu²⁺-ion buffer. This potential plays the role of a base line, namely the response to a sample containing no Ca²⁺ or Mg²⁺ ions. The Ca²⁺ or Mg²⁺ ion in the sample injected into the carrier stream (CS) reacts with free EDTA in the buffer stream (RS₂) to form the Ca-EDTA or Mg-EDTA complex after merging of the carrier stream with the buffer stream. The decrease in free EDTA due to its complexation with alkaline earth metals dissociates the Cu-EDTA complex in the buffer stream, resulting in an increase in the free Cu²⁺-ion concentration. The concentration change of the free Cu²⁺-ion is related to the concentrations of the injected Ca²⁺ and Mg²⁺ ions. The concentrations of these alkaline earth metals can thus be indirectly determined by monitoring the change in the Cu²⁺-ion concentration in the buffer stream with the Cu²⁺ ion-selective electrode. In order to measure the total water hardness, the buffer solution should have a pH at which the Mg²⁺ ion can combine with EDTA to an extent equal to the Ca²⁺ ion. At such a pH, the sensitivities of the electrode to Ca²⁺ and Mg²⁺ ions are equal, and the total water hardness can be determined.

Figure 2 shows the theoretical relationship between the potential change, (ΔE) of the Cu²⁺ ion-selective electrode and the concentrations of the Ca²⁺ or Mg²⁺ ion at various
pH of the Cu$^{2+}$-ion buffer. In this case, a flow system with two channels (the carrier stream and the Cu$^{2+}$-ion buffer stream) is assumed for simplicity. The potential change ($\Delta E$) corresponds to the peak height obtained by the assumed flow system without any dispersion of the sample. The following equations, (1) and (2), and the conditional stability constants of the Ca- and Mg-EDTA complexes were used for the calculation:

$$\Delta E = 0.030 \log \left( \frac{[C_{Ca} + k_{CaM}C_{M}]}{C_{Ca0}} \right) \quad (V \text{ at } 25^\circ C) \quad (1)$$

where $C_{Ca0}$ and $C_{Ca}$ are the free Cu$^{2+}$-ion concentration before and after sample injection, respectively. $C_{M}$ is the concentration of free M$^{2+}$ ions such as Ca$^{2+}$ and Mg$^{2+}$ ions, after mixing with the Cu$^{2+}$-ion buffer. $k_{CaM}$ is the selectivity coefficient of the Cu$^{2+}$-ion-selective electrode for the Cu$^{2+}$ ion against the M$^{2+}$ ion. $C_{Ca0}$ is given by one of the roots of the solution of Eq. (2) under the condition that $0 < C_{Ca} < C_{Ca0}$. $C_{Ca0}$ corresponds to the value of $C_{Ca}$ at $C_{M}=0$ in Eq. (2). Since the Cu$^{2+}$-ion-selective electrode does not respond to Ca$^{2+}$ or Mg$^{2+}$ ions directly, it is reasonable to assume that the values of $k_{CaM}$ are zero.

$$K_{CaM} = \frac{K_{CaL} - K_{M,M}}{C_{Ca} + [(C_{Ca} - C_{Ca0})K_{CaL} + (2C_{Ca} + C_{M} - C_{Ca} - C_{Ca0})K_{CaL}M_{M} + K_{CaL} - K_{M,L}]C_{Ca}} - (C_{Ca0} - C_{Ca})K_{ML} = 0. \quad (2)$$

In the above equation $K_{CaL}$ and $K_{ML}$ are the stability constants of the Cu-EDTA and M-EDTA complexes, respectively. $C_{Ca}$, $C_{M}$ and $C_{L}$ are the total concentrations of Cu$^{2+}$, M$^{2+}$ and EDTA, respectively.

The sensitivities of the electrode to Ca$^{2+}$ and Mg$^{2+}$ ions increase with an increase in the pH of the Cu$^{2+}$-ion buffer. This is because the increase in pH of the Cu$^{2+}$-ion buffer leads to an increase in the conditional stability constants of the Ca- and Mg-EDTA complexes, and then advances the complex formation of both metals with EDTA. Namely, the concentration of the free Cu$^{2+}$ ion liberated from the Cu-EDTA complex increases with increasing pH. It can be seen from Fig. 2 that potential changes become almost the same for the Ca$^{2+}$ ion above pH 6 as for the Mg$^{2+}$ ion above pH 8. A determination of the total water hardness is therefore expected to be possible at a pH above 8. The theoretical expectation given in Fig. 2 was experimentally verified by using a flow-injection system with two channels (CS and RS$2$), as given in Table 1. The sensitivities to both ions are different at pH 6 - 7, but become identical at pH 8.5 and 9.4. Above pH 8, advancements of the formations of Ca-EDTA and Mg-EDTA complexes are almost the same; the sensitivities to Ca$^{2+}$ and Mg$^{2+}$ ions become equal above pH 8.5.

**Effect of coexisting ions and removal of halides interference**

The effects of the foreign ions usually present in natural water, such as Na$^+$, K$^+$, Cl$^-$ and SO$_4^{2-}$-ions were examined. When the FIA system with two channels (CS and RS$2$), in the absence of a stream of 0.5 M NaNO$_3$ solution (RS$1$) from the manifold of Fig. 1 was used, although the K$^+$ and Li$^+$ ions did not interfere, the Na$^+$ ion present in the sample was found to interfere with the determination of the total water hardness. For example, when 0.01 M Na$^+$ ions coexisted, about a 10% positive error was observed in the determination of $6 \times 10^{-3}$ M Ca$^{2+}$. In principle, any metal ion capable of forming an EDTA complex will interfere with the determination of the total water hardness in the proposed method. The stability constant of the Na-EDTA complex is reported to be $10^{1.66 \pm 0}$. In fact, the injection of a sample of 0.01 M Na$^+$ ion gave a peak height of 2.0 mV for a buffer solution comprising $5 \times 10^{-3}$ M Cu(NO$_3$)$_2$ and $1 \times 10^{-2}$ M EDTA. This peak height is in fair agreement with the value calculated based on the stability constant of the Na-EDTA. Although the degree of error due to the presence of the Na$^+$ ion could be suppressed by decreasing the pH of the Cu$^{2+}$-ion buffer solution, the sensitivities to the Ca$^{2+}$ and Mg$^{2+}$ ions also decreased. Therefore, the error due to the Na$^+$ ion was eliminated in this study by adding a 0.5 M NaNO$_3$ stream (RS$1$) to the system (Fig. 1) without any decrease in the sensitivities to the Ca$^{2+}$ and Mg$^{2+}$ ions. Since the addition of a 0.5 M NaNO$_3$ stream stabilizes the interference effect, the electrode detector does not show any response to a sample containing Na$^+$ ions. In this work, a three-channel system was adopted by using a separated stream of 0.5 M NaNO$_3$. In practice, however, the two-channel system may be sufficient in cases where the RS$_1$ stream contains 0.5 M NaNO$_3$.

It is well known that such halides as Cl$^-$ and Br$^-$ ions interfere with the determination of the Cu$^{2+}$ ion with a Cu$^{2+}$-ion-selective electrode. The cause for this interference involves a precipitation of the halides with Ag$^+$ ion on the sensing membrane surface of the electrode, since the sensing membrane comprises Ag$_2$S and CuS.

When a Cu$^{2+}$-ion buffer without Trien was used for the determination of the total water hardness of a sample containing the Cl$^-$ ion, an anomalous negative peak was observed prior to the normal peak after injection. The

<table>
<thead>
<tr>
<th>pH</th>
<th>Sensitivity (mV/mM-ion)</th>
<th>log $K_{M,EDTA}$</th>
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<tbody>
<tr>
<td></td>
<td>M: Ca$^{2+}$</td>
<td>Mg$^{2+}$</td>
</tr>
<tr>
<td>6.0</td>
<td>0.79</td>
<td>0.62</td>
</tr>
<tr>
<td>7.0</td>
<td>0.93</td>
<td>0.79</td>
</tr>
<tr>
<td>8.5</td>
<td>2.05</td>
<td>2.04</td>
</tr>
<tr>
<td>9.4</td>
<td>2.06</td>
<td>2.05</td>
</tr>
</tbody>
</table>

A two-channel system consisting CS and RS$_2$ was used in this experiment. pH of the RS$_2$ was adjusted to 6.0 with MES buffer, to 7.0 with MOPS buffer and to 8.5 - 9.4 with NH$_4$-NH$_2$NO$_3$ buffers. Sample: $1 \times 10^{-3}$ M - $2 \times 10^{-3}$ M Ca(NO$_3$)$_2$ and Mg(NO$_3$)$_2$, 200 µl. log $K_{M,EDTA}$: taken from ref. 20.
peak heights of the second normal peaks were not proportional to the concentrations of the Ca²⁺ and Mg²⁺ ions. In addition, when the concentration of the Cl⁻ ion in the sample solution was higher than 10⁻² M, only a large negative peak was observed with no second peak. This phenomenon reflects interference from the halides.

One of the authors (N. I.) found that a ligand having a strong complexing ability for the Cu²⁺ ion, such as Trien, is effective for masking any interference from halides as well as some organic ligands. Based on this observation, we added a small amount of Trien to the Cu²⁺-ion buffer; the negative peak then disappeared for samples containing 0.01 M Cl⁻. The presence of 10⁻⁴ M Trien in the Cu²⁺-ion buffer was sufficiently effective for masking any interference of the Cl⁻ ion, even in seawater samples.

**Calibration curve**

The calibration peaks observed by the flow system given in Fig. 1 are shown in Fig. 3 for a concentration range between 0.5×10⁻³ and 3×10⁻³ M. The calibration peaks for the Ca²⁺ ion are almost the same as the corresponding peaks for the Mg²⁺ ion, as expected. This means that a determination of the total water hardness is possible using the flow system described in Fig. 1. The relative standard deviation of ten successive injections of 3×10⁻³ M Ca²⁺ ion was 0.7%. About 30 samples can be analyzed per hour using the present manifold and operating condition.

**Determination of synthetic and seawater samples**

The usefulness of the proposed method has been demonstrated through applications to both synthetic and real seawater samples. Figure 4 gives the response peak for a pure Ca²⁺ solution (1), a mixed solution of Ca²⁺ and Mg²⁺ (2) and a synthetic seawater sample prepared by dissolving main cations and anions present in common seawater (3). Each peak height is the same, and corresponds to the total concentration of Ca²⁺ and Mg²⁺ ions. Coexisting cations and anions do not show any interference with the determination of the total water hardness. Table 2 shows the analytical results concerning the water hardness of seawater. The result obtained by the proposed FIA method is in a good agreement with that by chelometric titration. Figure 5 shows the correlation between chelometric titration and the present FIA method for the determination of the total water hardness. The samples were prepared by adding the Ca²⁺ ion to seawater samples. There is a good correlation between both methods (correlation coefficient of 0.995).

In conclusion, a simple and rapid flow-injection method is proposed for the determination of the total water hardness with a Cu²⁺ ion-selective electrode. Its usefulness was demonstrated by applying it to seawater samples. The proposed method is not interfered with by the presence of halides, and an analysis with a higher sampling rate is possible compared to conventional chelometric titration. This method could be applied...
to continuous monitoring of the total water hardness by continuously mixing a stream of the sample solution with that of a Cu²⁺-ion buffer solution. The measurable concentration range could be varied by an appropriate selection of the concentration of the Cu²⁺-ion buffer. This method can therefore be applied to the determination of different levels of water hardness from tap water and boiler water to seawater.

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References


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