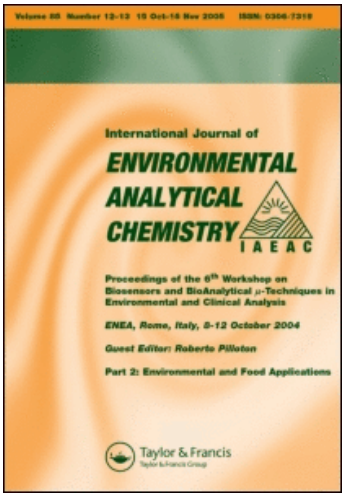

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Arey, Frank K. , Chamblee, J. Wayne and Heckel, Edgar(1980) 'Determination of Calcium and Magnesium by Chelometric Indicator Titrations with the Cupric Ion Electrode', International Journal of Environmental Analytical Chemistry, 7: 4, 285 — 293
To link to this Article: DOI: 10.1080/03067318008071491
URL: http://dx.doi.org/10.1080/03067318008071491

Intern. J. Environ. Anal. Chem., 1980, Vol. 7, pp. 261–271
0306-7319/80/0704-0285 $04.50/0

Printed in Great Britain

Determination of Calcium and Magnesium by Chelometric Indicator Titrations with the Cupric Ion Electrode

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(*Received April 25, 1979; in final form September 19, 1979*)

A chelometric indicator titration technique using the cupric electrode was developed for application in the determination of Ca^{++} and Mg^{++} in estuarine waters and biological samples. This method has uses in both laboratory and field studies. In routine work, the lower limits of determination are about 0.2 ppm for Ca^{++} and for Mg^{++}. If the Mg^{++} ions are in solution with Ca^{++}, the calcium ion concentration must be of the same order of magnitude or smaller than the Mg^{++} concentration. A comparison has been provided between the data obtained by the titration technique and those of atomic absorption measurements.

KEY WORDS: Calcium, magnesium, cupric ion electrode, chelometric indicators, titrimetry, biological samples, estuarine waters.

INTRODUCTION

The usefulness of commercial calcium and divalent ion sensitive electrodes in the analyses of both estuarine waters and biological samples such as the exoskeleton and tissue of the blue crab is limited by the susceptibility of the electrodes to foreign ion interferences and to variations in the ionic strength of the sample solutions. However, a solid-state cupric ion selective electrode can be employed for the determination of calcium and magnesium ions by the application of chelometric indicator titrations. This method requires that a titration with EGTA ([Ethylenebis(oxyethylenenitrilo)]tetraacetic acid) be carried out to determine calcium. In another titration, calcium and magnesium are determined simultaneously using EDTA (disodium ethylenediamine tetra-

acetate) as the chelating agent. The indicator for each titration consists of a small quantity of either EGTA or EDTA cupric chelate.[1] However, the proper selection of the buffer is very important for routine use of this method in the analyses of estuarine waters and biological samples since sensitivity (change of EMF at equivalence point) and rate of electrode response are greatly affected by the composition of the buffer.[2] In this paper we discuss in detail the controlled conditions under which the titration technique may be applied using ordinary titration equipment for the determination of calcium and magnesium in a wide variety of sample material.

EXPERIMENTAL

All measurements were carried out using the Orion cupric ion-sensitive solid-state electrode, Model 94-29, and the Orion Model 90-01 single junction reference electrode. The electrode potentials were measured with the Orion Model 801 digital pH/mV meter in conjunction with Model 751 digital printer. The electrode potentials can also be obtained using any commercial multimeter with an input impedance of at least 10 kΩ capable of measuring potentials in the millivolt range.

All of the chemicals used were Analytical Reagent grade, except for the EGTA, which was Eastman White Label. The buffer for titrations with EGTA contained 37.3 g of KCl and 15 ml of conc. NH_4OH per liter of solution ($pH = 11.0 \pm 0.1$). The buffer used for EDTA titrations contained 40 g of NH_4Cl and 400 ml of conc. NH_4OH per liter of solution ($pH = 10.2 \pm 0.1$). Copper indicator EGTA and EDTA stock solutions were prepared from 0.21 g of $CuCl_2 \cdot 2H_2O$ and 12 ml of 0.1 M EGTA and 4.5 ml of 0.25 M EDTA, respectively. Appropriate amounts of NH_4OH and water were added to make 50 ml of each indicator solution ($pH \simeq 9$).

All samples were first diluted with 5 ml of the respective buffer solution. The size of the sample aliquot varied according to the concentration of the particular sample. Ten μl of indicator solution were then added to the sample. Magnetic stirring at $\sim$100 rpm was maintained during the titration, and the sample container was thermally isolated from the stirrer by a cork pad. Constant electrode potentials were obtained approximately one minute after each addition of titrant. To maintain the fast response of the electrode, it is advisable to polish the cupric electrode membrane surface with Orion polishing strips (94-82-01) after every 100 sample titrations.

Blue crab samples required several steps of pretreatment before the titration procedures were carried out. Cleaned and dried exoskeleton

samples were dissolved in 1 ml of conc. $HClO_4$ under reflux heating. This was followed by dilution to 10 ml. An aliquot of this solution was used for the titrations. Tissue from the blue crab was separated from hemolymph by centrifuging and then treated in a similar manner as the exoskeleton. Water samples from the Pamlico River estuary in North Carolina required no pretreatment.

RESULTS AND DISCUSSION

Some representative titration curves of the chelometric indicator titrations of calcium and magnesium ions are shown in Figures 1 and 2. In the titration of calcium ions (Figure 1), for example, 10 μl of a $CuEGTA^{2-}$ solution were added to yield a small amount of Cu^{++} ions which are sensed by the cupric electrode. Actually the indicator complex solution was made to contain excess free Cu^{++}(4%). The titration curve of this indicator is marked "blank" in Figure 1. A total of 2.0 μl of 0.10 M EGTA was required to reach the equivalence point. This volume of titrant must be subtracted from any subsequent titration of a sample for each 10 μl of CuEGTA indicator complex. The amount of EGTA used in the previous titration is 20 times the quantity intended for a titration of the excess 4% of Cu^{++} in CuEGTA. In a corresponding titration with EDTA (Figure 2), 2.59 μl of 0.25 M EDTA solution instead of 0.1 μl (for 10% excess Cu^{++}) were consumed for the indicator CuEDTA. Our investigations have shown that titrant was needed in excess because of the presence of traces of calcium and magnesium in the chemicals which were used to prepare the

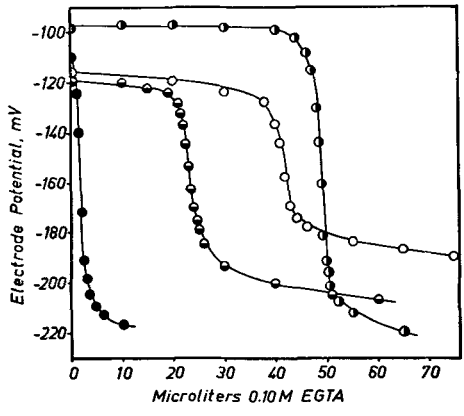

FIGURE 1 Chelometric Indicator Titrations of Calcium Ions. $CuEGTA^{2-}$ Blank (●), 5×10^{-6} moles of Ca^{++} Standard (◑), 6.5 mg of crab tissue (○), 1-ml Pamlico River Water Sample 3 (◒).

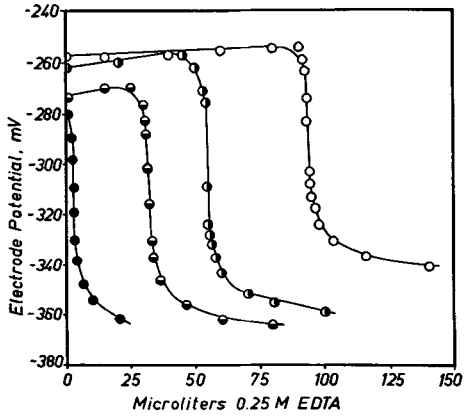

FIGURE 2 Chelometric Indicator Titration of Calcium and Magnesium Ions. $CuEDTA^{2-}$ Blank (●), 1.25×10^{-6} moles of Ca^{++}, 6.25×10^{-6} moles of Mg^{++} Standard (◑), 5.26 mg of crab exoskeleton (○), 0.5-ml Pamlico River Water Sample 4S (◒).

reagents. For example, by replacing Fisher Brand NH_4Cl #660 with NH_4Cl #661 in a buffer solution employed for titrations with EDTA, the amount of titrant for the blank could be reduced from 7.75 μl to 4.55 μl of 0.1 M EDTA solution. It is therefore necessary to use the same reagents both for the blank and the samples.

The EMF of the cupric ion-selective electrode in the titrations of Ca^{++} and Ca^{++}/Mg^{++} ions is governed principally by four simultaneous chemical equilibria which can be described as follows.

$$\text{Cu chelate}^{2-} \leftrightharpoons \text{Cu}^{++} + \text{chelate}^{4-} \quad (1)$$

$$\text{Cu}^{++} + 4\,\text{NH}_3 \leftrightharpoons \text{Cu(NH}_3)_4{}^{2+} \quad (2)$$

$$\text{Ca}^{++} + \text{chelate}^{4-} \leftrightharpoons \text{Ca chelate}^{2-} \quad (3)$$

$$\text{Mg}^{++} + \text{chelate}^{4-} \leftrightharpoons \text{Mg chelate}^{2-} \quad (4)$$

Equations (1) and (2) reveal that the free cupric ion concentration is determined by the amounts of chelate and ammonia. In absence of these reagents, the precipitation of copper hydroxide would establish the upper limit of free Cu^{++} ions which can be present in solution. For magnesium ions, large quantities of ammonium ions are needed to form the soluble $Mg(NH_3)_2^{2+}$ in alkaline solution. Otherwise the insoluble $Mg(OH)_2$ is precipitated. If the pH of the solution is adjusted to 11.0 using 15 M NH_4OH exclusively, EDTA will react with approximately 30 percent of

the total magnesium. It may then require an hour or more to reach a stable electrode potential while $Mg(OH)_2$ is slowly converted to $MgEDTA^{2-}$. However, if the solution contains additional NH_4^+ ions (from NH_4Cl), it is possible to determine the magnesium ions quantitatively and to reach a stable electrode potential within a minute after each chelate addition. Here the weak $Mg(NH_3)_2^{2+}$ complex ion is rapidly converted to the rather stable $MgEDTA^{2-}$ chelate in the presence of excess EDTA (Table I).

TABLE I

Pertinent conditional stability constants at 25 ± 5°C (2, 3)

Complex compound	pH	Ionic strength	Stability constant
$CaEDTA^{2-}$	10.2	0.1	2×10^{10}
$CaEGTA^{2-}$	11	0.1	1.0×10^{11}
$CuEDTA^{2-}$	10.2	0.1	3.2×10^{16}
$CuEGTA^{2-}$	11	0.1	2×10^{14}
$Cu(NH_3)_4^{2+}$	10	0.1	1.6×10^{12}
	11	0.1	5.0×10^{12}
$Cu(OH)_n^{2-n}$	10	0	3×10^{15}
	11	0	3×10^{14}
$MgEDTA^{2-}$	10.2	0.1	2×10^{8}
$MgEGTA^{2-}$	11	0.1	1.3×10^{5}
$Mg(NH_3)_2^{2+}$		2.0	1.2
NH_4^+	10	0.1	2.0×10^{9}
	11	0.1	2.5×10^{9}

It is necessary to use different buffer systems for the EDTA and EGTA titrations. The CuEGTA complex is less stable than the CuEDTA complex (Table I). Therefore, a greater concentration of free Cu^{++} can be predicted to be present for EGTA titrations. The proper free Cu^{++} ion concentration is achieved by selecting a certain ratio of NH_4^+ to NH_4OH in the buffer system used. Results of titrations with EGTA and EDTA are shown in Figures 1 and 2, respectively. The more negative EMF's of Figure 2 relative to Figure 1 are due to the fact that a more negative electrode potential corresponds to a smaller free Cu^{++} ion concentration. This observation is in agreement with the prediction based on the stabilities of the two indicator complex species.

The electrode response of the cupric ion-selective electrode used in this investigation could be presented by the Nernst equation (1.5 M KCl reference electrode filling solution)

$$E = (0.320 \pm 0.006) + (0.029 \pm 0.003) \log a_{Cu^{++}} \quad (5)$$

where $a_{Cu^{++}}$ represents the activity of cupric ions. Because the Cu^{++} ion concentration is low, it is possible to substitute the concentration of Cu^{++} for the activity of Cu^{++}.

The chelometric titration of Ca^{++} ions with EGTA using CuEGTA as the indicator is based on the equilibrium:

$$CuEGTA^{2-} + 4\,NH_3 + Ca^{2+} \rightleftharpoons CaEGTA^{2-} + Cu(NH_3)_4^{2+} \quad (6)$$

Also present in the system is a small quantity of free Cu^{++} which is formed by the partial dissociations of both the $CuEGTA^{2-}$ and the $Cu(NH_3)_4^{2+}$ complex. Neglecting some minor deviations which arise from protolytic side reactions of the complexing agents, the Cu^{++} concentration can be calculated from equation (7). The equation is derived from the stability constants[2,3] of the complexes of $Cu(NH_3)_4^{2+}$ and NH_4^+.

$$[Cu^{++}] = (K^4_{NH_4^+}/K_{Cu(NH_3)_4^{2+}})[Cu(NH_3)_4^{2+}]([H^+]/[NH_4^+])^4 \quad (7)$$

The substitution of Eq. (7) into Eq. (5) yields a Nernst equation for the electrode potential which applies to a chelometric titration using the cupric electrode. It is interesting to note that the electrode potential depends on the type of complexing agent only to the extent that EGTA controls the concentration of $Cu(NH_3)_4^{2+}$ ions. Equation (7) also demonstrates the importance of the presence of NH_4^+ ions in the solution as well as the need for adjusting the pH of the system with a base like NH_4OH if no additional NH_4^+ ions are added. The reason for this is the fact that, in the absence of NH_4^+ ions, EGTA cannot lower the Cu^{++} ion concentration to any extent because the stability constants of $CuEGTA^{2-}$ and $Cu(OH)_n^{2-n}$ are of the same order of magnitude (Table I). Consequently, the concentration of free Cu^{++} must be reduced by NH_4^+ through the formation of $Cu(NH_3)_4^{2+}$ complex ions.

Using Eqs. (5) and (7), it is possible to calculate the EMF of the cupric electrode. As an example, a solution of 5 ml buffer and 10 μl of 0.025 M $CuEGTA^{2-}$ contained 2.0×10^{-6} M $Cu(NH_3)_4^{2+}$, 1.1×10^{-11} M H^+ (pH = 10.95) and 4.0×10^{-3} M NH_4^+. According to Eq. (7), the free Cu^{++} concentration in this solution amounted to 8.9×10^{-16} M, and the electrode potential became -116 mV (Eq. 5). The experimental EMF was found to be -109 mV as shown in Figure 1 for the sample "blank". The

concentration of $Cu(NH_3)_4^{2+}$ can be equated with the concentration of the 4% excess Cu^{++} ions of the indicator since the concentrations of contaminant ions anticipated are of the same order of magnitude, but the stabilities of their EGTA chelates are lower than that of $CuEGTA^{2-}$.

The mathematical treatment applicable to titrations with EDTA for the determination of Ca^{++} and Mg^{++} is similar to that of the Ca^{++}–EGTA system.

The titration curves of Figures 1 and 2 exhibit steep slopes in the regions of the equivalence points. Potential changes between 75 and 120 mV were observed which are typical for chelometric titrations of Ca^{++} and Mg^{++} using the cupric electrode.[4] The application of this electrode for such titrations is superior to that of titrations using the calcium ion selective electrode. Tackett[5] and Hadjiioannou and Papastathopoulos[6] observed rather flat slopes in the region of the equivalence point by employing calcium ion selective electrodes. The change of the EMF for the sloping portion of the titration curves apparently did not exceed 40 mV. We experienced a greater dependence upon the ionic strength of the sample solution and also some sodium ion interference in experiments with calcium ion sensitive electrodes (Orion's 92-20 and 93-20) in comparison to the behavior exhibited by the cupric electrode.

The titrations curves involving crab tissue and exoskeleton (Figures 1 and 2) were obtained from solutions of relatively high ionic strength ($\approx$1 M). Nevertheless the response of the cupric electrode is fast, and steady electrode potentials were obtained within one minute after titrant addition. In a few instances, we increased the NH_4Cl content of the buffer for EDTA titrations by 30% to obtain a faster time response. It is recommended that the sample be diluted to a greater extent than previously suggested if the pretreatment of the sample introduces a rather large quantity of spectator ions thus increasing the ionic strength of the solution.

In Table II the results obtained from chelometric titrations are compared with those from determinations using atomic absorption spectrophotometry. These samples were selected on the basis of covering a broad concentration range and requiring very different procedures of pretreatment. The average deviation of the titration data from AA data for Ca^{++} samples is 5.7%. The corresponding deviations for Mg^{++} samples is 25%. However, the Mg^{++} water samples exhibit a deviation of only 6.5%. These percentage deviations have been confirmed by a larger number of samples than those shown in Table II.[4] All titration data are lower than the corresponding AA data. We have no explanation for this phenomenon at the present time. The average experimental error for

TABLE II

Comparison of Ca^{++} and Mg^{++} data obtained from chelometric indicator titrations with those obtained from atomic absorption spectrophotometric measurements

Sample	Ca^{++} concentration, ppm		Mg^{++} concentration, ppm	
	Titration	AA spectr.	Titration	AA spectr.
Tissue (T) or Exoskeleton (E) samples from blue crabs				
A4(T)	341	335	13	39
B5(E)	2,914	3,210	270	405
D2(E)	9,062	9,600	194	575
Water samples from Pamlico River, North Carolina				
4P	149	158	422	425
4S	206	211	517	525
3	92.3	98.8	262	288
9N	27.7	30.1	63.0	75
10S	5.85	6.24	5.7	6

routine analysis of river water samples using the chelometric titration technique is 2% for Ca^{++} samples and 3% for Mg^{++} samples. Large experimental errors are observed for the Mg^{++} concentrations of crab samples due to the fact that Mg^{++} is obtained from the difference of EDTA and EGTA titrations. Furthermore the Mg^{++} concentrations are only about 1/20 of those of Ca^{++}, i.e. the Mg^{++} content of the samples is in the same order of magnitude as the experimental error in the determination of Ca^{++} ions. The data show that a titration method is not useful under these circumstances. However, the Mg^{++} content of estuarine water samples can be determined rather accurately because the molar concentrations of magnesium are about 5 times those of calcium.

In routine work, the lower limit of determination in a chelometric titration for Ca^{++} ions is about 0.2 ppm (5×10^{-6} M). This limit depends only upon the quantity of available material and the ionic strength of the sample. The same limit can be obtained for Mg^{++} ions if the Ca^{++} concentration is of the same or lesser order of magnitude as the Mg^{++} concentration. These concentrations can be extended to lower limits with some minor modifications, e.g. employing more diluted reagent solutions and larger sample sizes, accounting for the time response of the electrode by extrapolating the EMF's to infinite time using standard computer techniques, controlling the temperature during the titration, etc.

The determination of Ca^{++} and Mg^{++} by chelometric titrations using the cupric electrode is most useful when standard titration equipment is to

be used or in field studies where the equipment must be powered by batteries. This method can also be used for reliable Ca^{++} and Mg^{++} ion water analysis when AA equipment is unavailable from a financial standpoint.

Acknowledgement

We are indebted to Mrs. Martha Jones for the determinations of Ca^{++} and Mg^{++} by atomic absorption spectrophotometry.

The support of this research by the Marine Science Council of the University of North Carolina, the Institute for Coastal and Marine Resources of East Carolina University, and the University of North Carolina Sea Grant College Program is gratefully acknowledged.

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