POTENTIOMETRIC DETERMINATION OF CALCIUM AND MAGNESIUM IN WATER AND BIOLOGICAL FLUID USING A DIVALENT ION ELECTRODE

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ABSTRACT

A simple and rapid complexometric method was developed for determination of calcium and magnesium in natural waters and biological fluids. The titration was carried out with standard EDTA or EGTA in the presence of a divalent cation electrode at pH 12. Calcium in the samples was determined at pH 10 in the presence of 8-hydroxy-7-iodoquinoline-5-sulfonic acid solution as a masking agent to eliminate interference from magnesium ions.

The method was successfully used for determination of both cations in the concentration range $1x10^{-1}$ to $1x10^{-6}$ M solution, and for estimation of the hardness of water samples in the Kingdom of Saudi Arabia and of biological fluids.

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1. INTRODUCTION

Several procedures have been used for the determination of water hardness due to calcium or magnesium or a mixture of both ions. Calcium has been determined using titrimetric /1/, spectrophotometric /2/, atomic absorption spectrophotometric /3/, gas chromatographic /4/ and potentiometric /5/ methods.

Magnesium has been determined using polarographic /6/, fluorometric /7/, colorimetric /8,9/ and titrimetric /10/ procedures.

The determination of both metals has been carried out by amperometric /11/, densitometric /12/, conductometric /13/, potentiometric /14/, photoelectrometric /15/ and spectrophotometric /16/ methods.

2. INSTRUMENTS, MATERIALS AND METHODS

Potentiometric measurements were made using an Orion research microprocessor pH/millivoltmeter 811 equipped with Orion model 93-32, 93-20 divalent cation and calcium electrodes, a single-junction reference electrode (Orion model 90-01) and a combination pH electrode (Orion model 91-02). A Pye Unicam SP 1800 spectrophotometer was used as an additional analytical tool.

All solutions were prepared with analytical reagent grade chemicals (BDH) using double distilled water.

a) Standard calcium chloride dihydrate $CaCl_2$, $2H_2O$ (0.1 M) solution was prepared by dissolving 14.71 g in one liter. Serial dilutions were made to obtain other concentrations down to $1x10^{-6}$ M.
b) Standard magnesium sulphate (0.1 M) solution was prepared by dissolving 12.04 g in one liter. Serial dilutions were made to obtain other concentrations down to $1x10^{-6}$ M.

c) Standard EDTA solution (0.1 M) solution was prepared by dissolving 37.2 g reagent-grade EDTA in about 200 ml distilled water and diluting to one liter. Serial dilutions were made to obtain other concentrations down to 1×10^{-6}.
d) Standard EGTA solution was prepared from a tetra-sodium ethyleneglycol bis (B-aminoethylether) N, N, N', N' tetra acetate (Na_4 EGTA) solution in the following manner: A (0.1 M) EGTA stock solution was prepared by dissolving an accurately weighed 34.04 g of $C_{14}H_{24}$ N_2O_{10} in a measured volume of sodium hydroxide solution to make the pH about 7.0, completed to one liter and stored in a polyethylene bottle. The stoichiometry of the solution was checked by titration with standard calcium solution; serial dilutions were prepared down to 1×10^{-6} Na_4EGTA.
e) Sodium tartrate solution (5% w/v).
f) Sodium citrate solution (5% w/v).
g) Hydroxylamine hydrochloride solution (10% w/v).
h) 8-Hydroxy-7-iodoquinoline-5-sulfonic acid solution (0.5 w/v).
i) Buffer solution (pH 10.0 at 20°C) was prepared by dissolving 54 g of ammonium chloride in 200 ml of water, followed by 350 ml of 25% ammonium hydroxide, with final dilution of the solution to one liter.
j) Sodium hydroxide solution (1 M).
k) Potassium cyanide solution (5% w/v).

Potentiometric determination of samples of calcium ions

Place 10 ml sample solution for the determination of calcium (concentration range, 1×10^{-1} to 1×10^{-6} M) into a 250 ml beaker equipped with a magnetic stirrer and dilute to 100 ml. Add 10 ml of 10% hydroxylamine hydrochloride solution followed by 10 ml of pH 10 buffer solution. Add 5 ml of 5% potassium cyanide solution, 5 ml of sodium tartrate and 5 ml of sodium citrate or 10 ml of 8-hydroxy-7-iodoquinoline-5-sulfonic acid solution. Place electrodes (calcium cation and reference) in the solution to a depth of about 3 cm. Stir thoroughly and record the potential when stable. Titrate with $1\text{x}10^{-1}$ to $1\text{x}10^{-6}$ M of standard solution of EGTA or EDTA.

In each case plot potential versus added volume of titrant to determine the end point graphically, at the point of maximum slope $\Delta E/\Delta V$ or the point where the second derivatives Δ^2E/Δ^2V become zero (Fig. 1).

Each 1 ml of $1\text{x}10^{-3}$ M EDTA or EGTA = 0.04 mg Ca^{2+}.

Potentiometric determination of mixtures of calcium and magnesium ions.

Transfer equal volumes of the sample solutions containing calcium and magnesium ions into a 250 ml beaker. Add 10 ml of 10% hydroxylamine hydrochloride solution and adjust the pH to 12 with N sodium hydroxide (about 5 ml). Add 5 ml of potassium cyanide, dilute to about 100 ml, and place the electrodes (divalent cation and reference) in the solution to a depth about 3 cm. Stir thoroughly, and record the potential when stable. Titrate with $1\text{x}10^{-1}$ to $1\text{x}10^{-6}$ M of standard solution of EDTA or EGTA according to the molarity of the calcium and magnesium solutions used.

In each case plot potential versus added volume of titrant to determine the end point graphically, at the point of maximum slope $\Delta E/\Delta V$ or the point where the second derivatives Δ^2E/Δ^2V become zero.

The magnesium content can be determined from the difference in the titre between the two procedures A and B.

Each 1 ml of $1\text{x}10^{-3}$ M EDTA or EGTA = 0.0243 mg Mg^{2+}.

3. RESULTS AND DISCUSSION

Ma and Hassan /17/ used a potentiometric method to determine calcium and magnesium ions in water samples and biological fluids. The calcium ion selective electrode sensitively measures the activity of calcium ions.

Magnesium ion was masked with citrate ion and the pH was adjusted to 8 with dilute strong acid or base, and the sample was titrated with EGTA or EDTA. Other masking agents can be used to eliminate the interference of many metal cations. Large amounts of ferric ions could be reduced with hydroxylamine hydrochloride or ascorbic acid. Potassium cyanide has been used to mask cadmium, zinc, copper, iron(II), cobalt and nickel /18,19/.

It is well known that water hardness is frequently caused by the presence of calcium and magnesium ions in the water samples, but it may be induced by some other polyvalent ions, such as aluminium, barium, iron, manganese, strontium and zinc. Because hardness ions other than calcium and magnesium are generally present at insignificant concentrations in natural waters, it is customary to consider the total calcium and magnesium ionic concentration as equivalent to the hardness.

In this experiment calcium and divalent electrodes could be used to determine calcium ions potentiometrically by titration with EDTA or EGTA. 8-Hydroxy-7-iodoquinoline-5-sulfonic acid, or a sodium citrate-tartrate mixture are used to eliminate the interference of magnesium ions. Table 1 shows the average percent recoveries and the relative mean deviations to be 99.30 or 99.33 and 0.24 or 0.27 for calcium ion determination in the concentration range of $1x10^{-2}$ to $1x10^{-6}$ M solution, with the masking agent 8-hydroxy-7-iodoquinoline-5-sulfonic acid or sodium citrate tartrate mixture respectively. For magnesium ion determination in the concentration range of $1x10^{1}$ to $1x10^{-6}$ M solution, these values are 99.39 or 99.34, and 0.31 or 0.28 for the above reagents, respectively.

These procedures are compared with the EDTA titrimetric method (reference method) stated by Suess /20/ for calcium determination at pH 12 to 13 in the presence of murexide as indicator. At the same time total hardness caused by calcium and magnesium could be determined at pH 10.0 with EDTA after precipitation of the interfering ions as insoluble sulphides with sodium sulphide, using Eriochrome Black T as indicator. The mentioned methods are compared with the reference methods statistically,

Table 1

Potentiometric Determination of Calcium and Magnesium Ions with EGTA

Concentration of Calcium (m mole)	Recovery %		Concentration of Magnesium (m mole)	Recovery %	
	8-Hydroxy-7-iodoquinoline 5-sulfuric acid	Sodium citrate and tartrate		8-Hydroxy-7-iodoquinoline 5-sulfuric acid	Sodium citrate and tartrate
0.04	99.06	99.05	0.05	99.07	99.06
0.07	99.07	99.08	0.10	99.09	99.08
0.11	99.18	99.20	0.15	99.22	99.19
0.15	99.31	99.35	0.20	99.41	99.36
0.18	99.52	99.58	0.25	99.72	99.61
0.22	99.63	99.71	0.30	99.81	99.72
average mean	99.30	99.33		99.39	99.34
relative mean deviation	0.24	0.27		0.31	0.28
t*	1.08	1.10		1.22	1.30

*t calculated, while the tabulated is 2.02 for 40 degrees of freedom at 95% significance level.

using Student's t test at 95% significance level. It is clear from the data in Table 1 that no significant differences occur between the proposed and the reference methods at 40 degrees of freedom.

The potentiometric techniques are characterized by their simplicity and rapidity; they are easy in application, not time consuming and can be used for coloured solutions; they have high sensitivity when used for both small amounts of calcium and magnesium ions down to $1x10^{-6}$ M solution and high concentration up to $1x10^{-1}$ M of either ion. The sharpness of the end point shows no variation as it can be obtained graphically by a sudden change in potential in the plot of electromotive force reading against the volume of the titrating solution as shown in Fig. 1. The presence of 8-hydroxy-7-iodoquinoline-5-sulphonic acid or a sodium citrate-tartrate mixture prevents precipitation of magnesium as hydroxide and formation of its chelate, making the solution much more clear than the addition of sodium sulphide.

The recommended procedures have been used to determine calcium and magnesium in water samples in the Kingdom of Saudi Arabia and also in samples of urine as an example of biological fluids. The results are given in Tables 2 and 3. It is clear from the tables that house water supplies of Dammam, Rahimah and Jeddah city and tanker waters fall within the category of soft water. Dammam College's water varied from soft to hard, while Northern Province house water and Zamzam well water may be considered as hard. Determination of calcium and magnesium is very essential because certain metabolic disorders, particularly those involving calcium, result in the deposition of metabolites either in the renal tissue itself or as calculi. It is often very difficult to distinguish between the various forms of calcium disorders, and this could be identified by determination of calcium ions in total plasma, or serum calcium levels, or urinary excretion of calcium. The study is restricted to the analysis of these cations in female urine and it is found that calcium hardness is in the range of 19.3 ± 0.2 to 37.5 ± 0.1 mg while magnesium hardness per 24 hours is in the range of 4.1 ± 0.1 to 7.8 ± 0.01 mg. These results tend to be lower than 200 mg per 24

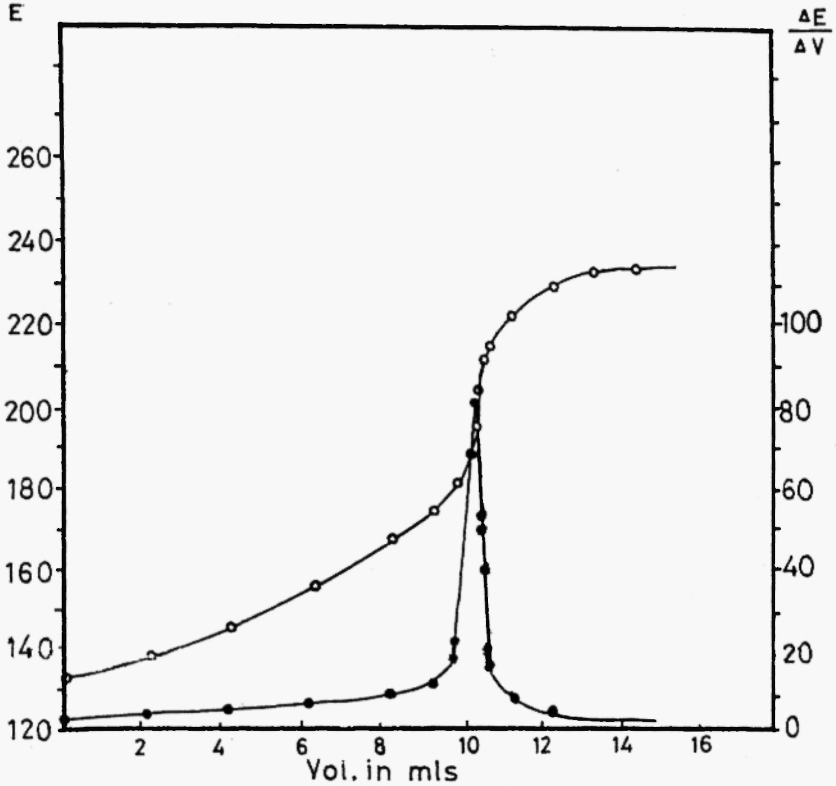

Fig. 1: Potentiometric determination of Ca^{2+} using a divalent electrode and EDTA as titrant (1×10^{-3} M solution).

○ E, millivolts

● ΔE/ΔV, first derivative

hours, the normal urinary calcium excretion /21/. The only interpretation of these results is that most of the population is using sanitary bottled-water, which is characterized by calcium concentration in the range of 4.4 to 18 mg/l, while magnesium concentration is in the range of 5 to 30.6 mg/l.

Table 2

Potentiometric determination of calcium and magnesium hardness in water

Water samples	Calcium hardness mg/l^{-1}	Magnesium hardness mg/l^{-1}
1. Eastern Province		
a. Dammam City		
House taps	35.01 ± 0.30	11.30 ± 0.20
College taps	180.01 ± 0.40	90.90 ± 0.20
Tanker water	7.10 ± 0.30	2.20 ± 0.30
b. Rahimah City	12.50 ± 4.00	2.50 ± 0.20
2. Northern Province		
House taps	106.00 ± 0.40	90.30 ± 0.50
3. Western Province		
a. Jeddah City		
House taps	17.10 ± 0.40	5.60 ± 0.40
b. Zamzam well	131.00 ± 0.50	36.50 ± 0.20

*Each result is the mean of three experiments ± standard deviation

Table 3

Potentiometric determination of calcium and magnesium hardness in urin

Sample No.	Calcium hardness mg	Magnesium hardness mg
1	32.10 ± 0.11	5.00 ± 0.08
2	37.50 ± 0.01	4.10 ± 0.10
3	13.25 ± 0.13	5.90 ± 0.12
4	72.03 ± 0.20	4.90 ± 0.12
5	24.02 ± 0.10	5.80 ± 0.10
6	25.61 ± 0.13	4.90 ± 0.22
7	25.60 ± 0.12	4.89 ± 0.22
8	30.30 ± 0.10	5.71 ± 0.13
9	28.20 ± 0.04	7.75 ± 0.01
10	27.20 ± 0.13	5.81 ± 0.11

* Each result is the mean of three experiments ± standard deviation ar represents the normal urinary excretion of calcium and magnesium per 2 hours.

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