

## COMPLEXOMETRIC TITRATION OF CALCIUM IN THE PRESENCE OF LARGER AMOUNTS OF MAGNESIUM

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**Summary**—A simple and accurate titrimetric determination of calcium in the presence of larger amounts of magnesium is proposed. Calcium is extracted into a small volume of organic solvent as its glyoxal-bis(2-hydroxyanil) complex, and the calcium is titrated with EGTA. The end-point is sharp, and occurs when the red colour of the organic layer vanishes. This method has been successfully applied to the determination of calcium in sea-water with an error less than 0.1%.

In the determination of calcium, the presence of a large amount of magnesium gives difficulties. In the field of chemical oceanography, it is necessary to be able to determine accurately and rapidly the calcium content of sea-water, in which the molar concentration of magnesium is five times that of the calcium.

Several complexometric methods have been reported for the determination of calcium in the presence of a large amount of magnesium. In the most common procedure calcium alone is titrated with EDTA at about pH 13 with Murexide<sup>1-3</sup> or Patton-Reeder's reagent (NN)<sup>4</sup> as an indicator. Sometimes, however, this procedure gives large errors owing to co-precipitation of calcium with magnesium hydroxide and adsorption of the indicator on the precipitate. Some attempts have been made to avoid these errors, *e.g.*, drop by drop addition of EDTA solution,<sup>5,6</sup> back-titration,<sup>7</sup> aging of the precipitate,<sup>8</sup> addition of alkali after the addition of EDTA equivalent to 95% of the calcium,<sup>9</sup> and addition of tartrate<sup>10</sup> or sucrose<sup>11</sup> to prevent the precipitation. In the case of sea-water, however, the present authors failed to reduce the error to less than 0.1% by using these proposed methods. Although calcium may be determined with a high accuracy by titrating it after separation from a mixture by ion-exchange chromatography or precipitation as calcium oxalate, the procedure is time-consuming.

When EGTA [ethyleneglycol-bis(2-aminoethylether)-*N,N,N',N'*-tetra-acetic acid] is used as the titrant<sup>12,13</sup> instead of EDTA, calcium is selectively titrated in the presence of magnesium because of the difference in the stability constants between calcium-EGTA ( $\log K_{\text{Ca-EGTA}} = 11.0$ ) and magnesium-EGTA ( $\log K_{\text{Mg-EGTA}} = 5.2$ ). Unfortunately, a selective indicator for calcium has not been available for use at pH 10, at which magnesium does not precipitate. This problem has been overcome by several methods. Calcium may be titrated after masking magnesium with tartaric acid,<sup>14,15</sup> or magnesium may be titrated while calcium is masked with EGTA.<sup>16,17</sup> Indirect indicators such as zinc-Zincon,<sup>18,19</sup> zinc-PAN<sup>20</sup> or zinc-Murexide<sup>21</sup> have been used. None of these methods, however, seems to be precise enough to detect subtle variations of calcium concentration in sea-water, because the errors are larger than 0.1%. Culkin and Cox<sup>22</sup> adopted a spectrophotometric titration, using zinc-Zincon indicator.

The present authors have tried to determine calcium directly by a visual titration, with high accuracy, in the presence of larger amounts of magnesium. EGTA is used as a titrant and GHA [glyoxal-bis(2-hydroxyanil)], a sensitive and selective reagent for calcium,<sup>23</sup> is used as metal indicator<sup>24</sup> at pH 11.7. If a suitable organic solvent is added to the solution, the calcium-GHA complex is extracted quantitatively and the interference by the magnesium precipitate formed at this pH is very small.

## EXPERIMENTAL

### Reagents

*EGTA standard solutions.* A stock solution, 0.1M, was prepared by dissolving 38 g of EGTA in 300 ml of 1M sodium hydroxide and diluting with distilled water to 1 litre. Aliquots of this solution were taken to prepare 10mM and 5mM or more dilute solutions. The EGTA solutions were standardized against pure zinc or magnesium.

*Borate buffer.* In 500 ml of distilled water were dissolved 10 g of borax, (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10 H<sub>2</sub>O) and 30 g of sodium hydroxide.

*GHA solution, 0.05% in n-propanol.*

*n-Butanol or n-amyl alcohol.*

*Standard calcium solution.* Exactly 1.0309 g of pure calcium carbonate dissolved in hydrochloric acid and diluted to 1 litre after the addition of 13.114 g of magnesium sulphate (MgSO<sub>4</sub>·7H<sub>2</sub>O), 0.0243 g of strontium chloride (SrCl<sub>2</sub>·2H<sub>2</sub>O) and 274.67 g of sodium chloride. The solution was 10.30mM in calcium, 53.20mM in magnesium, 0.091mM in strontium and 470mM in sodium, as in sea-water.

### Procedure

By pipette transfer 20 ml of a sea-water sample into a 100-ml conical beaker and add exactly 20 ml of 10mM EGTA. Stirring the solution, add 4 ml of 0.05% GHA and 4 ml of buffer solution. After stirring for 3 min (with a magnetic stirrer) add 7 ml of n-butanol or 5 ml of n-amyl alcohol, extract the red calcium-GHA complex into the organic layer, and titrate with 5mM EGTA solution. While adding the titrant, stir the solution vigorously and observe the organic layer occasionally, stopping the stirring near the end-point. At the end-point, the colour of the organic layer changes from red to colourless. The amount of calcium is evaluated by multiplying the titre by an empirically determined correction factor allowing for the magnesium and strontium.

## RESULTS AND DISCUSSION

As shown in Table I, the relative standard deviation in the determination of calcium in a sea-water sample was <0.1%. Small amounts of calcium added to a sea-water sample were quantitatively recovered within the limits of analytical error, as shown in Table II.

### Effect of other cations

The effects of the major cationic constituents in sea-water were investigated. The results are shown in Table III.

*Sodium and potassium.* No effects were found in the presence of sodium and potassium at five times the concentrations in sea-water.

*Magnesium.* The presence of magnesium gave slightly lower values for calcium, e.g., by 0.2% with the same amount of magnesium as in sea-water, and the same decrease was observed with an artificial sea-water containing no strontium. In order to eliminate this small but certain error caused by magnesium, it is necessary either to reduce the concentration of magnesium to less than 0.7 g/l. or to make an empirical correction with the standard calcium solution containing the same amount of magnesium as the sample. The correction factor was +0.23% for the magnesium in sea-water.

TABLE I.—Determination of calcium in sea-water sample\*

Sample* <i>ml</i>	9.257 <i>mM</i> EGTA added, <i>ml</i>	4.627 <sub>6</sub> <i>mM</i> EGTA in titration, <i>ml</i>	Ca + Sr found, <i>μmole</i>
20.008	20.002	4.74	207.1 <sub>0</sub>
20.008	20.002	4.76	207.1 <sub>8</sub>
20.008	20.002	4.74	207.1 <sub>0</sub>
20.008	20.002	4.73	207.0 <sub>8</sub>
20.008	20.002	4.74	207.1 <sub>0</sub>
20.008	20.002	4.76	207.1 <sub>8</sub>
Average		4.74	207.1 <sub>2</sub>
Standard deviation			0.06

\* The water was sampled from the surface of the Pacific at 38°01'N, 143°58'E (salinity = 34.58‰).

TABLE II.—Recovery of calcium added to a sea-water sample\*

Sample, <i>ml</i>	Ca added, <i>μmole</i>	Ca + Sr found,† <i>μmole</i>	Recovery of Ca added, <i>μmole</i> %	
20.008	0.00	207.1 <sub>2</sub>		
20.008	1.99	209.0 <sub>0</sub>	1.9 <sub>7</sub>	99 ± 7
20.008	3.98	211.0 <sub>8</sub>	3.9 <sub>8</sub>	99 ± 4
20.008	4.98	212.0 <sub>6</sub>	4.9 <sub>4</sub>	99 ± 3
20.008	9.95	217.0 <sub>0</sub>	9.8 <sub>8</sub>	99 ± 2
20.008	19.90	226.8 <sub>7</sub>	19.7 <sub>8</sub>	99 ± 1
20.008	49.75	256.9 <sub>3</sub>	49.8 <sub>1</sub>	100.1 ± 0.3

\* The sea-water used is the same sample as in Table I.

† Each of the values is the average of five determinations and the 95% confidence limits were ±0.10 *μmole*.

*Behaviour of strontium.* As shown in Table IV, a large portion of strontium added to a sample was determined together with calcium and the recovered strontium was always lower than the added amount by about 10%. The recovery depended also on the concentration of magnesium. When the solution contained no magnesium, all of the strontium–GHA complex was extracted into the organic layer and titrated with 100% recovery. When the concentration of magnesium was as high as 0.25*M*, no strontium–GHA complex was extractable. In the case of sea-water, the effect of strontium can easily be allowed for by comparison with an artificial or standard sea-water of which the chemical composition has been determined, since the concentration of strontium is low and its ratios to calcium and to magnesium are almost constant. The correction factor was –0.77% for the strontium in sea-water. Therefore, the titre for calcium in sea-water must be corrected by multiplying by a factor of 0.9946 (to allow for strontium *and* magnesium). Even taking account of these corrections and other factors reducing the accuracy of the calcium titration, it is unlikely that the error in the determination of calcium in sea-water exceeds 0.1%.

*Heavy metals.* It is unnecessary in the case of sea-water to consider the effects of heavy metals, because of their low concentration, but the usual masking agents may be used, as shown in Table V.

TABLE III.—Titration of calcium in the presence of major cations in sea-water

Sample, <i>ml</i>	[Metal], <i>mM</i>	Concentration factor*	[Ca], <i>mM</i>	10·187 <i>mM</i> EGTA used, <i>ml</i>	Deviation %
20·00	—	—	10·30	20·23	
20·00	Na, 2350	5	10·30	20·23	0·0
20·00	K, 50	5	10·30	20·22	-0·0
20·00	Mg, 270	5	10·30	19·86	-1·8
20·00	Mg, 108	2	10·30	20·13	-0·5
20·00	Mg, 54	1	10·30	20·19	-0·2
20·00	Mg, 27	0·5	10·30	20·23	0·0
20·00	Artificial sea-water containing no Sr		10·30	20·19	-0·2
20·00	Artificial sea-water containing 0·091 <i>mM</i> Sr		10·30	20·34	

\* The concentration factor for a metal means the ratio of its concentration in the sample to that in sea water.

TABLE IV.—Recovery of strontium added to a sea-water sample\*

Sample, <i>ml</i>	Sr added, $\mu$ mole	Ca + Sr found, $\mu$ mole	Recovery of Sr added	
			$\mu$ mole	%
20·008	0·0	207·1 <sub>2</sub>		
20·008	1·6	208·3 <sub>2</sub>	1·2 <sub>0</sub>	75 ± 12
20·008	4·0	210·6 <sub>7</sub>	3·5 <sub>5</sub>	89 ± 4
20·008	8·0	214·2 <sub>8</sub>	7·1 <sub>4</sub>	89 ± 2
20·008	12·0	217·6 <sub>7</sub>	10·5 <sub>5</sub>	88 ± 2
20·008	16·0	221·1 <sub>2</sub>	14·0 <sub>0</sub>	88 ± 1
20·008	20·0	224·8 <sub>6</sub>	17·6 <sub>4</sub>	88 ± 1

\* The sea-water used is the same sample as in Table I.

TABLE V.—Determination of calcium in the presence of heavy metals

Sea-water, <i>ml</i>	[Metal] added, <i>ppm</i>	Masking agent	Ca + Sr found <i>mM</i>
20·00	—	—	10·3 <sub>5</sub>
20·00	Co, 100	KCN	10·3 <sub>6</sub>
20·00	Cu, 100	KCN	10·3 <sub>5</sub>
20·00	Fe(II), 100	KCN	10·3 <sub>4</sub>
20·00	Fe(III), 100	KCN	10·3 <sub>3</sub>
20·00	Fe(III), 100	TEA*	10·3 <sub>2</sub>
20·00	Al, 100	TEA	10·3 <sub>3</sub>
20·00	Mn, 50	TEA	10·3 <sub>2</sub>

\* TEA = triethanolamine.

### The metal indicator GHA

GHA is unsuitable in two respects: since the GHA-calcium complex is rather unstable in solution, the titration must be finished as quickly as possible, certainly within 20 min, and the development of the colour being slow, the organic solvent must be added 3 min after the addition of the indicator and the buffer solution. The n-propanol used as the solvent for GHA also facilitates the extraction of the calcium-GHA complex, being miscible with n-butanol or n-amyl alcohol as well as with water. Methanol or ethanol can also be used.

### CONCLUSION

If the EGTA solution can be standardized with an error less than 0.05%, the error in the determination of calcium in sea-water by this method is less than 0.1%. Magnesium in concentration below 27mM does not interfere, and in greater amounts may be corrected for by calibration with a standard calcium solution containing a known amount of magnesium. Strontium is only partially titrated, but can be corrected for.

The method presented here is not only rapid and accurate but also highly sensitive, because calcium is extracted into a small volume of organic phase, and it is, therefore possible to determine small amounts of calcium in natural waters.

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**Résumé**—On propose une méthode simple et précise de détermination titrimétrique du calcium en présence de quantités plus grandes de magnésium. On extrait le calcium dans un petit volume de solvant organique sous forme de son complexe avec le glyoxal bis (2-hydroxy-anile) et titre le calcium à l'EGTA. Le point final est net, et correspond à la disparition de la coloration rouge de la couche organique. On a appliqué cette méthode avec succès au dosage du calcium dans l'eau de mer avec une erreur inférieure à 0,1%.

**Zusammenfassung**—Eine einfache und genaue titrimetrische Bestimmung von Calcium in Gegenwart größerer Mengen Magnesium wird vorgeschlagen. Calcium wird in eine kleine Menge organischen Lösungsmittels als Komplex mit Glyoxal-bis(2-hydroxyanil) extrahiert und das Calcium mit EGTA titriert. Der Endpunkt ist scharf und besteht darin, daß die rote Farbe in der organischen Schicht verschwindet. Diese Methode wurde mit Erfolg auf die Bestimmung von Calcium in Meerwasser angewandt; der Fehler war kleiner als 0,1%.

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