

POTENTIOMETRIC TITRATION OF CALCIUM IN SEAWATER*

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Abstract

By using calcium ion selective electrode (Ca ISE) as indicating electrode, saturated calomel electrode (SCE) as reference electrode and EGTA as titrant, calcium in seawater was determined by potentiometric titration in borate buffer solution. This method can reduce observation errors in the determination of the endpoint, and thus provide better analytical precision ($< 0.08\%$) than present complexometric titration.

Key words: calcium ion selective electrode, calcium, seawater, potentiometric titration

At present, the standard method for determining calcium in seawater is complexometric titration using EGTA [ethyleneglycol-bis(2-aminoethylether)-*N, N, N', N'*-tetraacetic acid] and GHA [glyoxal-bis(2-hydroxyanil)]. This method was first developed by Tsunogai et al. (1968), summarized by Kremling, and edited in *Methods of Seawater Analysis* by Grasshoff (1983). Although the endpoint readings in this method are not quite sharp, and may be affected by overcast weather, with the use of calcium ISE as indicating electrode, SCE as reference electrode and digital voltmeter to indicate the potential changes, the titration endpoint depends on the second differential of potential change to volume, the precision is better than that of the classical method for seawater samples.

1. Principle

EGTA developed by Schwarzenbach can complex with calcium and magnesium. The difference of stability constants of these two complexes is over 5 logarithmic units ($\log K_{\text{Ca-EGTA}} = 11.0$, $\log K_{\text{Mg-EGTA}} = 5.2$), so it is possible that calcium is selectively titrated. Whitfield (1975) proposed that in the presence of a large amount of magnesium, the Nernst response produced by concentration change in direct potential determinations is very small, and that the very complex electrode structure causes potential drift severely limiting the precision of the method. If a titration process is monitored by a selective electrode, the above problem can be overcome, and the determination selectivity will be improved also. If the equivalent point can be exactly determined, the precision of total concentration of a constituent is better than $\pm 0.1\%$. In practice, we use the calcium ISE as indicating electrode, and data are treated by the second differential method. This method provides very satisfactory results for determining of calcium in seawater.

2. Equipment and reagents

Model PZ91 digital voltmeter, Shanghai Electric Meter Factory; magnetic stirrer; Model 402 calcium ISE, Jiangsu Electroanalytical Instrument Factory; Type 232 SCE, Shanghai.

EGTA solution: Dissolve 3.8g EGTA in 30 cm³ of 1 mol/dm³ NaOH solution and dilute to 1.0 dm³ with twice distilled water.

Standard calcium solution (0.0103 mol/dm³ Ca²⁺): Dissolve exactly 1.0309g CaCO₃

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(spectrographically standardized) in a few cm³ of hydrochloric acid and dilute to 1000 cm³ after addition of 6.4037 g MgSO₄ (A.R.), 0.0242g SrCl₂ · 6H₂O (A.R.) and 27.467 g NaCl (G.R.), containing 10.30 mmol/dm³ calcium, 53.20 mmol/dm³ magnesium, and 0.091 mmol/dm³ strontium (final solution salinity is 35.0).

Borate buffer solution: Dissolve 10 g borax (Na₂B₄O₇ · 10H₂O, A. R.) and 30 g NaOH (A. R.) in twice distilled water and dilute to 500 cm³.

Artificial seawater containing no Sr.

Standard CaCl₂ solution.

3. Procedures

Standardization of EGTA solution: Transfer exactly 10.00 cm³ standard calcium solution into a 50 cm³ beaker; add necessary EGTA solution for 96–98% of the endpoint equivalent; stir 30 s, then add 2 cm³ borate buffer; insert calcium ISE and SCE; stir over 5 min; add 30 microlitre of EGTA into the solution; determine the potential difference after 30 s. Then add the second portion of EGTA, repeat the operation until past the equivalent point. The endpoint can be determined from the second differential of potential to volume. The molarity of the EGTA solution M_{EGTA} is calculated as follows:

$$M_{EGTA} = \frac{M_{Ca} \times a}{b}$$

where

M_{Ca} = molarity of the calcium standard solution

a = cm³ of calcium standard solution used

b = cm³ of EGTA solution required

The analysis of the samples is identical to that for the standardization of the EGTA solution, the only difference is to transfer about 10 cm³ of the seawater sample into a pre-weighed beaker covered with polyethylene film and then weigh again to find the weight of the sample. The amount of EGTA solution required is estimated from the salinity of the samples. The concentration of calcium is calculated as follows:

where

a = cm³ of EGTA solution used

M = molarity of EGTA solution

W = sample weight in g corrected to weight in vacuum

4. Results and discussion

The effect of amount of borate buffer is shown in Table 1 which shows that for greatest E_{max} , the most suitable volume of borate buffer is 1.5–2.0 cm³.

Table 1 Effect of amount of buffer^{a)}

Amount of buffer (cm ³)	9.531 mmol/dm ³ EGTA used (cm ³)	ΔE_{max} (mV)	pH mixture before titration
1.0	10.850	3.7–5.0	11.0
1.5	10.846	10.4–11.5	12.3
2.0	10.835	10.1–10.5	12.5
2.5	10.825	9.5–9.7	> 12.5
3.0	10.818	8.5–8.7	> 12.5

a) sample: Artificial seawater containing Sr. SCE(+); Ca ISE(-)

The potential change at 30 and 60 seconds after addition of EGTA solution are shown in Table 2.

Table 2 Potential change with time

V_{EGTA} (cm ³)	10.70	10.73	10.76	10.79	10.82	10.85	10.88	10.91
E_{30} (mV)	99.7	104.5	110.3	117.8	127.6	137.8	143.6	147.0
ΔE_{30} (mV)	4.8	5.8	7.5	9.8	10.2	5.8	3.4	
E_{60} (mV)	99.8	104.6	110.5	118.0	128.2	139.0	144.7	148.0
ΔE_{60} (mV)	4.8	5.9	7.5	10.2	10.8	5.7	3.3	

The second differential of the 30" and 60" data showed that all the endpoint volumes were about 10.823 cm³, so we took 30" as the reading time.

Effect of major cations and result of standard addition are shown in Table 3 and Table 4.

Table 3 Potentiometric titration of calcium in the presence of major cations in seawater

Sample (cm ³)	Metal (mmol/dm ³)	Concentration factor ^{a)}	10.16 mmol/dm ³		Deviation (%)
			[Ca] (mmol/dm ³)	EGTA Used, (cm ³)	
10.00 ₆	—	—	10.30	10.14	/
10.00 ₆	Na 940	2	10.30	10.13	-0.1
10.00 ₆	K 20	2	10.30	10.14	0.0
10.00 ₆	Mg 53.2	1	10.30	10.14	0.0
10.00 ₆	Mg 106.4	2	10.30	10.13	-0.1
10.00 ₆	Artificial seawater containing no Sr		10.30	10.05	-0.9
10.00 ₆	Artificial seawater containing 0.091 mmol/dm ³ Sr		10.30	10.14	0.0

a) The concentration factor for a metal means the ratio of its concentration in the sample to that in seawater

Table 4 Result of standard addition

s	Ca added (μmol)	Ca found (μmol)	Recovery (μmol)	of Ca added (%)
35	0.00	102.30		
	4.90	107.20	4.90	100.0
	19.61	121.92	19.62	100.1
18	0.00	50.29		
	4.90	55.15	4.86	99.2
	19.61	69.89	19.60	99.9
8	0.00	25.90		
	4.90	30.76	4.86	99.2
	19.61	45.46	19.56	99.7

Each of the above values is the average of two determinations.

Results of determinations on two samples by this method are shown in Table 5.

Table 5 Sample determination (Ca, 10⁻³)

Sample	1	2	3	4	5	6	Average	Relative deviation
1	408.9	408.8	408.8	408.3	408.8	/	408.7	0.058%
2	375.2	374.9	374.5	374.6	374.6	375.0	374.8	0.074%

sample: 1. Chinese standard seawater, G-137, s=34.969; 2. Zhanqiao seawater of Qingdao, 1995.11.11 pm., s=31.662

CONCLUSION

The method presented here is rapid, accurate and sensitive, and if the EGTA solution can be standardized to less than 0.05%, the error in the determination of calcium in seawater by this method is less than 0.08%. This method can also economize on a lot of organic solvents.

References

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