京都電子工業株式会社
KYOTO ELECTRONICS MANUFACTURING CO.,LTD.

Application Note

Determination of calcium and magnesium in water

Industry	:	Chemicals
Instrument	:	Automatic potentiometric titrator
Measurement method	:	Chelatometric titration
Standards	:	ASTM D511-03

1. Scope

This Application Note describes an example of the measurement of calcium and magnesium ions' concentrations in water, based on ASTM D511-03.
Water hardness is used as an index of calcium and magnesium concentrations in water. In general, hardness is defined as the value obtained by converting the calcium and magnesium concentrations into the equivalent concentration (mg/L) of calcium carbonate ($CaCO_3$). The concentration values in these measurements are also denoted in this way.
The measurement was made by chelatometric titration, and the end point was determined by automatically detecting the color change of the indicator with a photometric sensor.
Titration is used to determine the combined calcium and magnesium and also the calcium concentration. The magnesium concentration is then calculated from the difference between the combined and the calcium concentration.

2. Precautions

In chelatometric titration, the reactivity of the sample with titrant change with the pH of the sample solution, so adjust the pH as specified on the standard.

3. Post-measurement procedure

Clean the photometric sensor carefully in pure water. Then wipe away any moisture and store it in a dry place.

4. Apparatus

Main unit : Automatic potentiometric titrator (photometric preamplifier : PTA),
Photometric sensor : Bandpass filter wavelength 630nm

5. Reagents

Titrant : 0.01mol / L EDTA solution
Indicator : Eriochrome Black T (EBT) indicator solution;
Dissolve 0.4 g of EBT in 100 mL of pure water.

Murexide indicator ;
Pulverize and mix 0.1 g of murexide and 20 g of sucrose.

Additional reagent : Buffer Solution, ammonium Chloride-Ammonium Hydroxide ;
Dissolve 6.76 g of ammonium chloride, 57 mL of 28 % ammonia water, and 0.5 g of EDTA magnesium salt in pure water. Add water to make the total volume 100 mL.

Sodium hydroxide solution (80g/L) ;
Dissolve 8.0 g of sodium hydroxide in 80 mL of pure water. Leave it to cool to room temperature, and then add pure water to make the total volume 100 mL.

0.5mol/L-Ammonium chloride solution ;
Dissolve 2.67 g of ammonium chloride in pure water, and make the total volume 100 mL.

6. Procedure

- Calibration of Photometric sensor -

1) Press the [Calibration] button.
2) Set the channel/unit to “Ch3/% T.”
3) Immerse the photometric sensor’s detector in pure water. Wait for the displayed transmittance value to stabilize. After the transmittance value has stabilized, perform calibration with this value as 100 % transmittance.
4) Gently insert the shutter into the cell window and block off the light. After the displayed value stabilizes, perform calibration using this value as 0 % transmittance.
Transmittance depends on the shape of the container, so perform calibration in the same shape beaker and with the same amount of pure water as sample measurement is performed.

- pH calibration of combined glass electrode -

1) Press the [Calibration] button.
2) Set the channel/unit to “Ch1/pH.”
3) Immerse the electrode’s liquid junction in pH standard solutions with a pH of 7 and 9 and perform calibration.

- Combined Amount of Calcium and Magnesium -

1) Introduce 50 mL[*1] of the sample in a beaker.
2) Add with 28 % ammonia water, adjusting the pH to between 7 and 10.
3) Add 1 mL of an ammonia buffer solution with a pH of 10. Then add a 0.5 mol/L ammonium chloride solution or 28 % ammonia water, adjusting the pH to 10.0 ± 0.1.
4) Add four drops of the EBT indicator.
5) Titrate with 0.01 mol/L EDTA solution.

- Calcium concentration -

1) Introduce 50 mL[*1] of the sample in a beaker.
2) Add 1 mL of an 80 g/L sodium hydroxide solution, adjusting the pH to between 12 and 13.
3) Add 0.2 g of the murexide indicator.
4) Titrate with 0.01mol / L EDTA solution.

[*1]: If the titration volume exceeds 15 mL or titration takes longer than 5 minutes, reduce the amount of sample introduced.
When reducing the amount of sample, add sufficient pure water so that the sensor’s detector is immersed.

If the sample contains interfering ions, perform the following treatment before adding the indicator.

Iron : Add 1 mL of a 30 g/L hydroxyl ammonium chloride solution.
Cobalt, Nickel, Copper, Zinc, Cadmium and Mercury : Add 2 mL of an 80 g/L sodium cyanide solution.

Manganese : Add 1 or 2 small crystals of potassium ferrocyanide.

7. Calculation

Concentration (mg $CaCO_3$ / L) = C1 × K1 × TF × EP1 / S

C1	:	Concentration conversion coefficient = 100.1
K1	:	Unit Conversion coefficient = 10
TF	:	Factor of Titrant = 1.0119
EP1	:	Titration volume (mL)
S	:	Sample volume (mL)

Using the formula above, calculate the combined calcium and magnesium and the calcium concentration.
The difference between the combined and calcium concentrations corresponds to the magnesium concentration.

7. Example

— Parameter —

<Titr. Mode> : Auto Int.
<Titr. Form> : Level Stop

<Titr. Para.>

Max Volume	: 20 (mL)
Channel/Unit (Ctrl.)	: Ch3, %T
Channel/Unit (ref.)	: Ch1, pH
pH Polarity	: Standard
Titr. Type Check	: None
Direction	: Auto
Wait Time	: 0 (s)
Dose Mode	: None

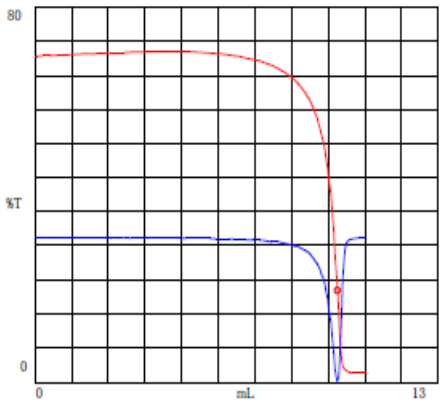
<Ctrl. Para.>

Number of EP	: 1
End Sense	: Auto
Gain	: 1
Data Sampling	: Auto
Ctrl. Speed	: Standard
Other Control	: Standard
Auto Intermit mode	: Standard
Stirrer Speed	: 4

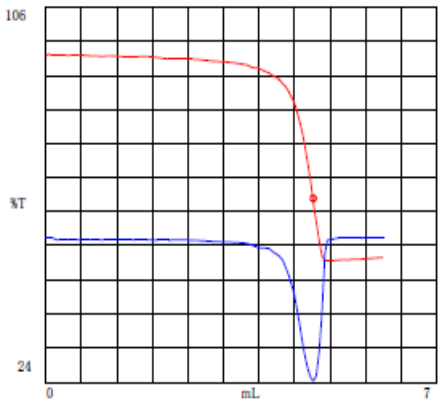
(The measurement parameters and titration curve are an example for using KEM's potentiometric titrator. They may vary depending on the model.)

— Example of Titration curve —

・Combined Amount of Calcium and Magnesium concentration



・Calcium concentration



— Measurement results —

Table 1 Measurement results of Combined Amount of Calcium and Magnesium (sample : 50mL)

	Titration volume (mL)	Concentration (mg $CaCO_3$/L)
1	9.7632	199.35
2	9.7768	199.63
3	9.7605	199.29
Mean		199.42
SD		0.15
RSD (%)		0.07

Table 2 Measurement results of Calcium-Magnesium concentrations (sample : 50mL)

	Titration volume (mL)	Calcium (mg $CaCO_3$/L)	Magnesium (mg $CaCO_3$/L)
1	4.7889	97.78	101.64
2	4.7870	97.74	101.68
3	4.7781	97.56	101.86
Mean		97.69	101.73
SD		0.10	0.10
RSD (%)		0.10	0.10

9. Summary

The measurement results showed good repeatability with a relative standard deviation of less than 0.1 %. Highly precise measurements can be performed using an automatic potentiometric titrator. General samples may need to be examined to determine whether measurement is feasible. If you have any questions, please contact us.

10. Reference

ASTM D511-03 Standard test methods for Calcium and Magnesium in Water