
Application Bulletin

Of interest to: Laboratories for water and drink analysis
 General analytical laboratories

A 1, 2, 7, 8

Complexometric simultaneous determination of calcium and magnesium in water samples and beverages with the aid of an ion-selective calcium electrode

Summary

The following describes a potentiometric method for the simultaneous complexometric determination of the calcium and magnesium ions in a sample with Na₂EDTA as titrant. The Ca-ISE is used for indication. For a better differentiation of the Ca and Mg potential jumps an auxiliary complexing agent is used that masks Fe³⁺ and Al³⁺ simultaneously. Fixing the pH value at pH 8.5 prevents disturbances that could appear through precipitation of CaCO₃. In water samples the method is suitable for the automatic determination of all hardnesses (carbonate, Ca, Mg, total and permanent hardness). The determination of Ca and Mg in beverages (fruit and vegetable juices, wine) is also described.

Instruments and accessories

- 726 Titroprocessor with 685 Dosimat or 700 Dosino, 751 GPD Titrino or 736 GP Titrino with 685 Dosimat or 700 Dosino
 - Titration Stand for attachment to above titrators:
 - 2.728.0040 Magnetic Swing-out Stirrer or
 - 2.727.0100 Titration Stand with built-in magnetic stirrer, rinsing pump and rinsing head or
 - 2.727.0010 Titration Stand with rinsing pump and rinsing head + 2.722.0010 Rod Stirrer with controller and stirrer propeller
 - 2x 6.3014.223 Exchange Unit for Titrinos and Dosimats or 6.3031.XXX Dosing Units for Dosinos
 - 1x 6.3014.253 Exchange Unit (for auxiliary complexing solution)
 - 6.0239.100 Combined glass electrode with cable 6.2104.020*
 - 6.0504.100 Ion selective Ca electrode with cable 6.2104.020
 - 6.2106.030 Jumper cable (for 726 only)
 - Printer with suitable 6.2125.0X0 printer cable (except for 2.726.0020 and 2.726.0120)
- * its reference system is also used for the Ca-ISE

Reagents

- **Acid titrating reagent**
 $c(\text{HCl}) = 0.1 \text{ mol/L}$
- **Alkaline titrating reagent**
 $c(\text{Na}_2\text{EDTA}) = 0.05 \text{ mol/L} + c(\text{KOH}) = 0.1 \text{ mol/L}$
- **Buffered auxiliary complexing solution**
 $c(\text{acetyl acetone}) = 0.1 \text{ mol/L} + c(\text{TRIS}) = 0.2 \text{ mol/L}$
(TRIS = trishydroxymethylaminomethane)
- **w(HCl) = 0.2g/g (20%)**
for Ca/Mg in fruit juices etc.
- **w(NaOH) = 0.2g/g (20%)**
for Ca/Mg in fruit juices etc.

Analysis

Water samples

The sample (100 mL) is measured into the titration vessel and titrated with HCl in a first titration (comb. glass electrode).

The auxiliary complexing agent (15 mL) is added with the auxiliary Dosimat and, after a short waiting time, the Ca and Mg are titrated in a second titration with Na_2EDTA (Ca-ISE). The first potential jump represents Ca, the difference between the second and the first potential jump Mg.

Calculations (with 100 mL sample)

1. Titration:

Acid-binding capability (ABC)/acid capacity = $EP1;2;\text{mmol/L}$

Carbonate hardness = $EP1*0.5;2;\text{mmol/L}$

2. Titration:

Calcium hardness = $EP1*0.5;2;\text{mmol/L}$

Magnesium hardness = $(EP2-EP1)*0.5;2;\text{mmol/L}$

Remaining (permanent) hardness = total hardness - carbonate hardness; 2; mmol/L

In the formula, ";2" means 2 decimal places.

Remarks

The volume of the added auxiliary complexing solution can be optimised for the magnesium content. The rule of thumb is that the ratio Mg/acetylacetonone should be approx. 0.05.

Calcium electrodes stored dry are conditioned before the determination for approx. 10 min in $c(\text{CaCl}_2) = 0.01 \text{ mol/L}$.

With the aid of the fixed-end point A in the first titration the M-value could also be calculated (titrant consumption up to pH 4.5).

Since the initial pH value is measured with both Titrators this parameter can also be used for the assessment of the water sample.

Samples that contain only a small amount of Mg in the presence of a large amount of Ca produce only one potential jump for the total of the two ions. In such cases, Mg standard is added to the auxiliary complexing solution and added with this to the sample. Naturally this added amount must be deducted in the calculations.

Beverages (fruit and vegetable juices, wine)

The sample (25.0 mL) is pipetted into an evaporating dish and evaporated in a drying oven at 140°C. The residue is then heated to redness in a muffle furnace at 600°C until a white ash remains. After cooling, 2 mL $w(\text{HCl}) = 0.2$ are added, the mixture warmed to dissolve the ash and the resulting solution rinsed into a beaker with dist. water. The pH value of this sample solution is adjusted to 8.5 with NaOH. The auxiliary complexing solution (20 mL) is added and titration performed with Na_2EDTA using the Ca-ISE.

Calculation

R1 ppm Ca:	$F1 = EP1 * C01 * C02 / C00; 2; \text{ppm}$
R2 ppm Mg:	$F2 = (EP2 - EP1) * C03 * C02 / C00; 2; \text{ppm}$
	C01 = 2.004 (Equivalent weight Ca)
	C02 = 1000 (Conversion factor to 1 litre sample)
	C03 = 1.216 (Equivalent weight Mg)
	C00 = 25 (Sample size in mL)

Literature

Christiansen, T.F. / Busch, J.E. / Krogh, S.C.
Successive determination of calcium and magnesium in drinking water by complexometric, potentiometric digital titration to two equivalence points.
Anal. Chem. **48** (1976) 1051-1056