
Application Bulletin

Of interest to: General analytical laboratories; Water analysis
Beverages

A 1, 2, 4, 7, 8

Simultaneous determination of calcium and magnesium in water samples and beverages and the different types of water hardness by complexometric titration with potentiometric indication

Summary

This bulletin describes a potentiometric titration method for the simultaneous complexometric determination of the calcium and magnesium ions in a sample using Na₂EDTA as titrant. The ion-selective calcium electrode is used as indicator electrode. To achieve a better differentiation between the Ca and Mg potential jumps an auxiliary complexing agent is added that additionally masks Fe³⁺ and Al³⁺. Fixing the pH value at pH = 8.5 prevents interferences that might be caused by the precipitation of CaCO₃.

The method described is suitable for the automatic determination of the different types of water hardness (carbonate, calcium, magnesium, total and permanent hardness). The determination of calcium and magnesium in beverages (fruit and vegetable juices, wine) is also dealt with.

Instruments and accessories

- 702 SET/MET Titrino, 716 DMS Titrino, 736 GP Titrino, 751 GPD Titrino or 785 DMP Titrino or 726 or 796 Titroprocessor
 - 700 Dosino, 765 Dosimat or 776 Dosimat as titration or auxiliary buret with corresponding 6.3031.220 Dosing Units or 6.3014.223 Exchange Units
 - 2.728.0040 Magnetic Stirrer
 - 6.0504.100 ion-selective calcium electrode (Ca ISE) with 6.2104.020 electrode cable
 - 6.0733.100 LL Ag/AgCl reference electrode with 6.2106.020 electrode cable
 - 6.0239.100 combined LL pH glass electrode with 6.2104.020 electrode cable
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Reagents

- Titrant for the determination of the carbonate hardness:
 $c(\text{HCl}) = 0.1 \text{ mol/L}$
- Titrant for the Ca and Mg determination:
 $c(\text{Na}_2\text{EDTA}) = 0.05 \text{ mol/L} + c(\text{KOH}) = 0.1 \text{ mol/L}$

- Auxiliary complexing solution:
 $c(\text{acetylacetonone}) = 0.1 \text{ mol/L} + c(\text{TRIS}) = 0.2 \text{ mol/L}$ [TRIS = tris(hydroxymethyl)-aminomethane]
- Hydrochloric acid $w(\text{HCl}) = 20\%$ and sodium hydroxide $w(\text{NaOH}) = 20\%$

Analysis

Water samples: determination of the water hardness

100 mL sample is placed in the titration vessel and titrated in a first titration with $c(\text{HCl}) = 0.1 \text{ mol/L}$ (combined pH glass electrode).

Using the auxiliary Dosimat, 15 mL of the auxiliary complexing solution is added and, after a short waiting time, the calcium and magnesium ions are titrated in a second titration with Na_2EDTA (Ca ISE). The first equivalence point corresponds to the Ca^{2+} content, the difference between the second and the first equivalence point to the Mg^{2+} content.

Calculations

1st titration:

Acid neutralizing capacity in mmol/L = $\text{EP1} * 0.1 * 1000 / \text{C00}$

Carbonate hardness (temporary hardness) in mmol/L
= $\text{EP1} * 0.1 * 0.5 * 1000 / \text{C00}$

EP1 = titrant consumption in mL

C00 = 100 (sample volume in mL)

2nd titration:

Calcium hardness in mmol/L = $\text{EP1} * 0.05 * 1000 / \text{C00}$

Magnesium hardness in mmol/L = $(\text{EP2} - \text{EP1}) * 0.05 * 1000 / \text{C00}$

Total hardness in mmol/L = $\text{EP2} * 0.05 * 1000 / \text{C00}$

Remaining hardness (permanent hardness) in mmol/L
= total hardness – carbonate hardness

EP1 = titrant consumption to reach the first EP in mL

EP2 = titrant consumption to reach the second EP in mL

C00 = 100 (sample volume in mL)

The results are given with two decimal places.

1 mmol Ca^{2+} = 40.08 mg Ca^{2+}

1 mmol Mg^{2+} = 24.31 mg Mg^{2+}

Remarks

- Before starting the titration of the carbonate hardness the pH value of the water sample is measured. This value can be printed out as pH(init).
- The volume of the added auxiliary complexing solution can be optimized according to the magnesium content. As a rule of thumb the molar ratio Mg/acetylacetonone should be ca. 0.05.
- Ca electrodes that have been stored dry are conditioned in $c(\text{CaCl}_2) = 0.01 \text{ mol/L}$ for ca. 10 min prior to the titration.

- Using the fixed endpoint A of the first titration, it is also possible to calculate the m value of the water sample (titrant consumption up to pH = 4.5).
- Since the initial pH value is measured with modern titrators, this parameter can also be used for the assessment of the water sample.
- Samples containing only small amounts of magnesium besides high calcium concentrations yield only one single potential jump for the sum of both ions. In such cases an auxiliary complexing solution has to be used, to which a defined quantity of Mg standard has been added. This addition of Mg²⁺ ions must then, of course, be taken into account in the calculations.

Beverages (fruit and vegetable juices, wine): determination of calcium and magnesium

25.0 mL sample is pipetted into an evaporating dish and evaporated in a drying cabinet at 140 °C. The residue is then heated to redness in a muffle furnace at 600 °C, until a white ash remains. After cooling down, 2 mL w(HCl) = 20% is added, the mixture heated to dissolve the ash and the resulting solution rinsed into a glass beaker with dist. water. The pH value of this sample solution is then adjusted to 8.5 with w(NaOH) = 20%. 20 mL of the auxiliary complexing solution is added and titration is performed with c(Na₂EDTA) = 0.05 using the Ca ISE.

Calculations

1 mL c(Na₂EDTA) = 0.05 mol/L corresponds to 2.004 mg Ca²⁺ or 1.216 mg Mg²⁺

$$\text{mg/L Ca}^{2+} = \text{EP1} * 2.004 * 1000 / \text{C00}$$

$$\text{mg/L Mg}^{2+} = (\text{EP2} - \text{EP1}) * 1.216 * 1000 / \text{C00}$$

EP1 = titrant consumption to reach the first EP in mL

EP2 = titrant consumption to reach the second EP in mL

C00 = 25.0 (sample volume in mL)

The results are given with two decimal places.

Remark

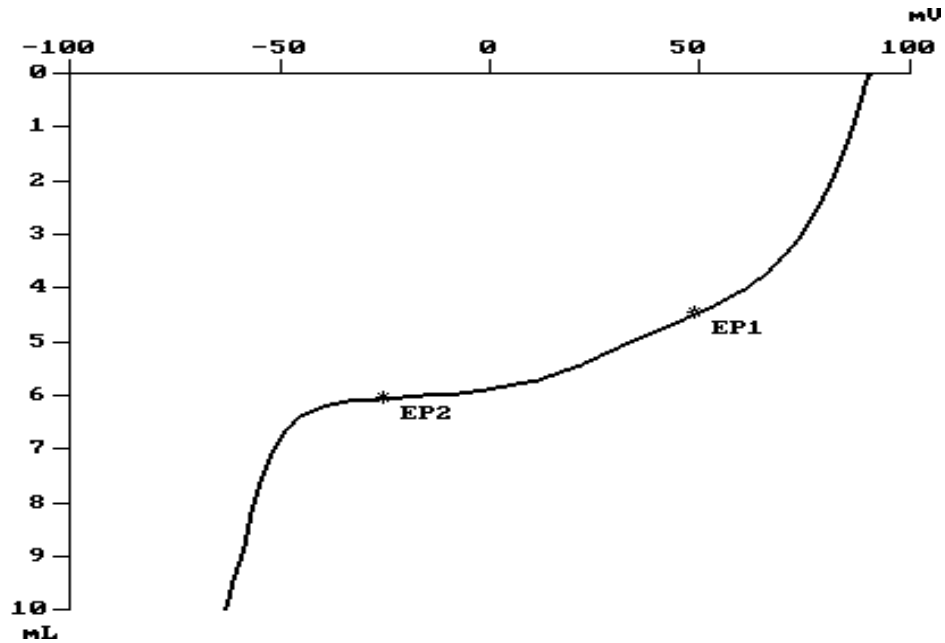
In the beverages analyzed calcium and magnesium are only partially present as free ions. The rest is bound in complexes with organic components. In order to determine the total metal contents it is therefore necessary to ash the samples.

Figures

METROHM 726 Titroprocessor 01107 5.726.0012

Method CaMgTap.mth [o] Calcium / Magnesium in Tap Water

2 DET_U* Ca++ and Mg++ determination with Ca++ ISE Curve



*Standard report

Method	Ident1	Ident2	Ident3	Size	Unit
CaMgTap	Tap Water	Herisau		100	mL
Remark					

#	DET_U*	Ca++ and Mg++ determination with Ca++ ISE			
EP1	48.9 mV	4.482 mL	Ca++	2.24 mmol/L	
EP2	-25.3 mV	6.078 mL	Mg++	0.80 mmol/L	
			Total	3.04 mmol/L	
Stop condition		volume			

Original data Determination time: 1999-05-07 07:40:39
 Data file 99050707.002 Tap Water Herisau CaMgTap

printed: 1999-05-07 07:46:10

Fig. 1: Titration curve and result report for the determination of the calcium and magnesium hardness of tap water (726 Titroprocessor).

```
'pa
716 DMS Titrino      OE2/239  716.0020
date 99-05-06      time 14:25    8
DET U              *****
parameters
>titration parameters
  meas.pt.density    4
  min.incr.          10.0 µl
  titr.rate          max. ml/min
  signal drift       50 mV/min
  equilibr.time      26 s
  start V:           OFF
  pause              0 s
  meas.input:        1
  temperature        23.0 °C
>stop conditions
  stop V:            abs.
  stop V             10 ml
  stop U             OFF mV
  stop EP            9
  filling rate       max. ml/min
>statistics
  status:            OFF
>evaluation
  EPC                30
  EP recognition:    all
  fix EP1 at U      OFF mV
  pK/HNP:           OFF
>preselections
  req.ident:         OFF
  req.smpl size:     OFF
  activate pulse:    OFF
=====
```

```
'fr
716 DMS Titrino      OE2/239  716.0020
date 99-05-06      time 13:21    5
U(init)            112 mV DET U *****
smpl size          25 ml
EP1                2.156 ml      -28 mV
EP2                5.078 ml      108 mV
Ca                 166.568 ppm
Mg                 137.031 ppm
stop V reached
=====

'cu
716 DMS Titrino      OE2/239  716.0020
date 99-05-06      time 13:21    5
start V            0.0000 ml DET U *****
1.0 ml/div         dU=50.0 mV/div
```

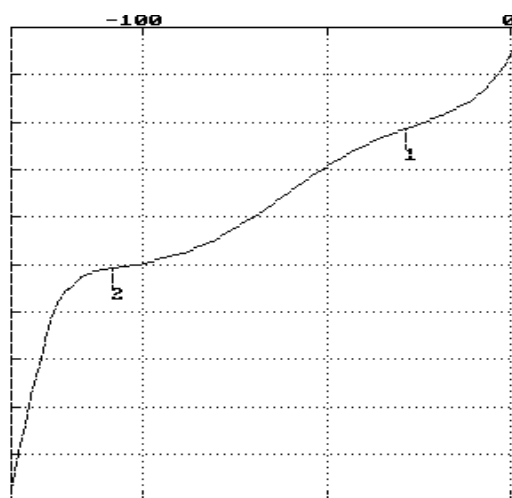


Fig. 2: Parameter settings on the 716 DMS Titrino for determining calcium and magnesium in grapefruit juice.

Fig. 3: Result block and titration curve.

Literature

- EN ISO 9963-1: 1995
- DIN 38406 part 3: 1982
- EPA Methods 130.2 and 310.1
- T. F. Christiansen, J. E. Busch, S. C. Krogh
Successive determination of calcium and magnesium in drinking water by complexometric, potentiometric digital titration to two equivalence points
Anal. Chem. 70 (1976) 1051–1056.