

Application Bulletin

Of interest for: General, Water, beverages

A 1, 2, 4, 7, 8

Complexometric simultaneous determination of calcium and magnesium in waters and beverages, as well as water hardnesses by means of potentiometric titrations

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 for the automatic determination of all hardnesses (carbonate, Ca, Mg, total and permanent hardness) is suitable. The determination of Ca and Mg in beverages (fruit and vegetable juices, wine) is also described.

Apparatus and accessories

- 702 or 716 or 736 or 751 or 785 Titrino or 726 Titroprocessor
- 700 Dosino or 765 or 776 Dosimat as titrating or auxiliary burette with corresponding dosing units 6.3031.220 or exchange units 6.3014.223
- 2.728.0040 magnetic stirrer
- 6.0504.100 Ca-ISE with 6.2104.020 electrode cable
- 6.0733.100 reference electrode with 6.2106.020 electrode cable
- (6.0239.100 comb. pH glass electrode with 6.2104.020 electrode cable)

Reagents

- c(HCl) = 0.1 mol/L, for carbonate hardness
- c(Na₂EDTA) = 0.05 mol/L + c(KOH) = 0.1 mol/L, for Ca and Mg
- Auxiliary complexing solution; c(acetyl acetone) = 0.1 mol/L + c(TRIS) = 0.2 mol/L (TRIS = trishydroxymethylaminomethane)
- w(HCl) = 20 % and w(NaOH) = 20 %

Analyse

Water samples: Titration of water hardness

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

An auxiliary complexing solution (15 mL) is added with the auxiliary Dosimat and after a short waiting time the Ca and Mg titrated in a second titration with Na₂EDTA (Ca-ISE). The first potential jump represents Ca, the difference between the second and the first potential jump Mg.

Calculations

1. Titration:

Acid-binding capability (ABC) / acid capacity in mmol/L = EP1 * 1000 / C00

Carbonate hardness in mmol/L = EP1 * 0.1 * 1000 / C00

2. Titration:

Calcium hardness in mmol/L = EP1 * 0.05 * 1000 / C00

Magnesium hardness in mmol/L = (EP2 - EP1) * 0.05 * 1000 / C00

Total hardness in mmol/L = EP2 * 0.05 * 1000 / C00

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

The results are given with 2 decimal places.

C00 = sample size in mL (normally 100)

1 mmol Ca²⁺ = 40.08 mg

1 mmol Mg²⁺ = 24.31 mg

Remarks

- Before starting the carbonate hardness determination, the pH value of the sample solution is measured and can be printed out as pH init.
- The volume of the added auxiliary complexing solution can be optimised for the magnesium content. The rule of thumb is that the ratio Mg/acetyl acetone should be approx. 0.05.
- Dried-stored calcium electrodes are conditioned before the determination for ca. 10 min. in c(CaCl₂) = 0.01 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 pH value is measured with modern titrators, this parameter can also be used for the assessment of the water sample.
- Samples containing a large amount of Ca and only a small amount of Mg, 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 this is then added to the sample. Naturally, the addition must be deducted in the calculations.

Beverages (fruit and vegetable juices, wines): Calcium and magnesium

A sample (25.0 mL) is pipetted into an evaporating dish and evaporated in a drying cupboard 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(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 the titration performed with Na₂EDTA using the Ca-ISE.

Calculations

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

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

The results are given with 2 decimal places.

C00 = sample size in mL (normally 25)

Remarks

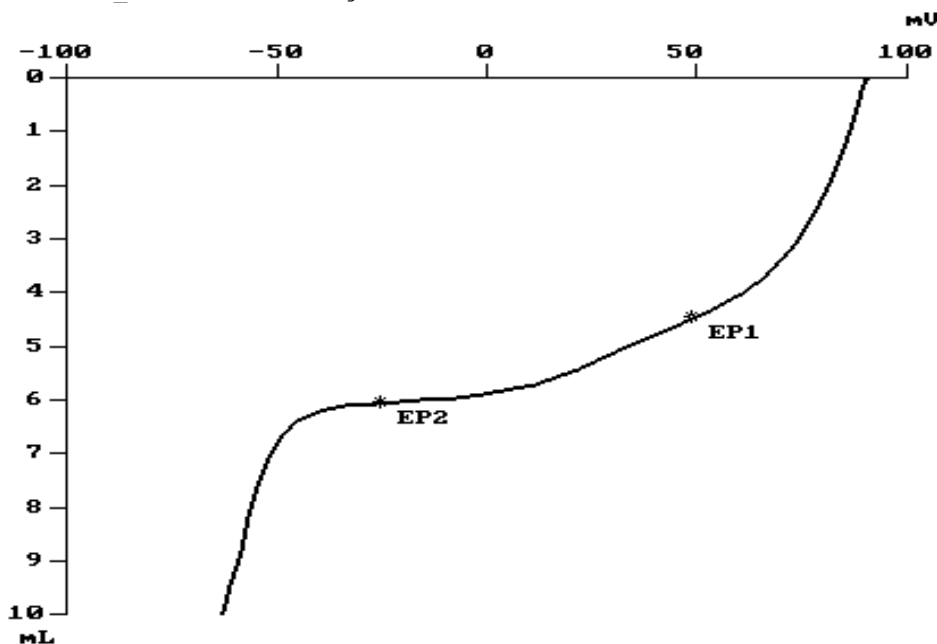
In these beverages calcium and magnesium ions are only partially in a free form. The rest is combined, in a complex manner, to organic components. This is the reason why an ashing process is necessary for the determination the total concentration.

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 curves 726 Titroprocessor Ca and Mg-hardness, in tap water

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'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
  =====
    
```

Fig. 2 Parameters Titrino for Ca and Mg in grape fruit juice

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'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
    
```

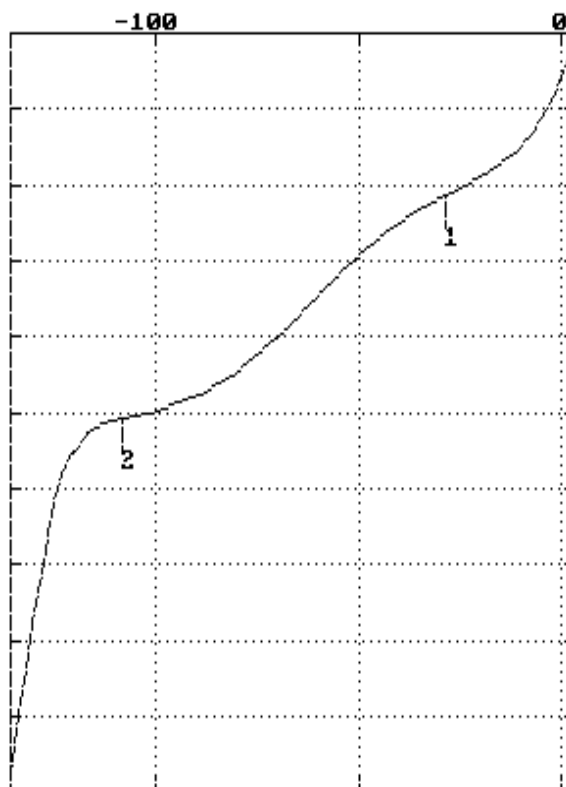


Fig. 3 Result and titration curve Titrino Ca and Mg in grape fruit juice

Literature

- EN ISO 9963-1: 1995
- DIN 38406 Teil 3: 1982
- EPA Methods 130.2 and 310.1
- 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 (2976) 1051 - 1056