Application Bulletin 125/3 e

Simultaneous determination of calcium, magnesium, and alkalinity by complexometric titration with potentiometric or photometric indication in water and beverage samples

Branch

General analytical laboratories; water analysis; beverages

Keywords

Titration; potentiometric titration; photometric titration; complexometric titration; water; beverages; water hardness; calcium; calcium hardness; magnesium; magnesium hardness; alkalinity; total hardness; EDTA; branch 1; branch 2; branch 7; 6.0510.100; 6.0750.100; 6.1115.000

Summary

This bulletin describes the determination of calcium, magnesium, and alkalinity in water by complexometric titration with EDTA as titrant. It is grouped into two parts, the potentiometric determination and the photometric determination.

There are multiple definitions of the different types of water hardness. In this Application Bulletin, the following definitions are used: alkalinity, calcium hardness, magnesium hardness, total hardness, and permanent hardness. The explanation of these definitions and further expressions are mentioned in the appendix.

In the potentiometric part, the determination of the alkalinity is done in a separate acid-base titration before the complexometric titration of calcium and magnesium in water. From these values, the permanent hardness can be calculated. Furthermore, the determination of calcium and magnesium in beverages (fruit and vegetable juices, wine) is described.

The photometric part includes the determinations of the total and calcium hardness and thereby indirectly the magnesium hardness using Eriochrome Black T and calconcarboxylic acid as indicators (according to DIN 38406-3).

Potentiometric determination

Instruments

- Titrator with DET mode
- Burette, cylinder volume 20 mL
- Stirrer

Electrodes

Combined Ca^{2+} selective electrode	6.0510.100
iEcotrode Plus with 845 iConnect or Ecotrode gel with NTC	6.0280.300 2.854.0010 6.0221.600

Reagents

- Hydrochloric acid, c(HCl) = 0.1 mol/L and 5 mol/L volumetric solutions.
- Disodium ethylendiaminetetraacetate dihydrate, c(EDTA) = 0.05 mol/L volumetric solution
- Acetylacetone, purum
- Calcium carbonate, $CaCO_3$, p.a.
- Tris(hydroxymethyl)aminomethane, TRIS, p.a.
- Ammonium chloride, NH_4Cl, purum
- Ammonia, w(NH_3) = 25%, purum

Solutions

Titrant 1	HCl, c(HCl) = 0.1 mol/L; titrant for the alkalinity.
Titrant 2	EDTA, c(EDTA) = 0.05 mol/L; titrant for the determination of Ca^{2+} and Mg^{2+}
Auxiliary solution	Acetylactone and TRIS in dist. water; c(acetylacetone) = 0.1 mol/L and c(TRIS) = 0.2 mol/L For this solution TRIS has not to

	be dried. 24.2 g TRIS are weighed into a 1000 mL volumetric flask and dissolved in approx. 500 mL dist. H_2O. 12 mL acetylacetone are added and the solution is made up to the mark with dist. H_2O. This solution has to be used within a few days. The auxiliary solution enhances the separation Ca^{2+} and Mg^{2+} and masks Fe^{3+} and Al^{3+}.
Buffer pH 10	54 g NH_4Cl and 350 mL $w(NH_3)$ = 25% are dissolved in dist. H_2O and made up to 1 liter with dist. H_2O.

Standards

TRIS	TRIS is dried over night in a drying oven at 105 °C and allowed to cool down in a desiccator for at least 1 h.
$CaCO_3$	$CaCO_3$ is dried over night in a drying oven at 140 °C and allowed to cool down in a desiccator for at least 2 h.

Sample preparation

Water samples

No sample preparation required.

Beverages (fruit and vegetable juices, wine)

25.0 mL sample are pipetted into an evaporating dish and evaporated in a drying cabinet at 140 °C. The residue is grinded as fine as possible and then heated to a red glow in a muffle furnace at 600 °C, until a white ash remains. After cooling down, 2 mL c(HCl) = 5 mol/L, are added. The mixture is heated to dissolve the ash and the resulting solution rinsed into a titration vessel with dist. H_2O.

Analysis

Titer HCl

80 – 150 mg TRIS are weighed out into the titration beaker with an accuracy of 0.1 mg, dissolved in 50 mL dist. H_2O and immediately titrated with c(HCl) = 0.1 mol/L to the first endpoint.

Titer EDTA

50 – 90 mg $CaCO_3$ are weighed out into a titration beaker with an accuracy of 0.1 mg and suspended in 20 mL dist. H_2O. Under stirring, c(HCl) = 5.0 mol/L is added dropwise until the $CaCO_3$ has dissolved completely. After the addition of 30 mL dist. H_2O and 5 mL buffer pH 10, the solution is titrated with c(EDTA) = 0.05 mol/L to the first endpoint.

Water sample

100 mL sample are placed in the titration vessel and titrated in a first titration with c(HCl) = 0.1 mol/L to the first or second equivalence point, using the combined pH electrode in order to determine the alkalinity.

Afterwards, 15 mL auxiliary solution are added and after a short waiting time the calcium and magnesium ions are titrated in a second titration using c(EDTA) = 0.05 mol/L. The first equivalence point corresponds to the Ca^{2+} content, the difference between the second and first equivalence point to the Mg^{2+} content.

Beverages

To the prepared sample solution 20 mL auxiliary solution and 10 mL buffer pH 10 are added. The titration is performed using c(EDTA) = 0.05 mol/L.

Parameters

Water samples

Parameters for the determination of the alkalinity

Mode	DET pH
Drift	20 mV/min
Max. waiting time	38 s
Meas. point density	4
Min. increment	10 µL
EP criterion	5
EP regonition	all

Parameters for the determination of Ca^{2+} and Mg^{2+}

Mode	DET U
Pause	30 s
Drift	50 mV/min
Max. waiting time	26
Meas. point density	4
Min. increment	10 µL
EP criterion	5
EP regonition	all

Beverages

Mode	DET U
Drift	10 mV/min
Max. waiting time	52 s
Meas. point density	1
Min. increment	10 µL
EP criterion	5
EP recognition	all

Calculation

Titer

$$\text{Titer} = \frac{m_s}{V_{EP1} \times c(\text{Titrant}) \times M_A}$$

Titer:	Titer of the selected titrant
m_s:	Mass of standard in mg
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c(Titrant):	Concentration of the selected titrant in mol/L; here either c(HCl) = 0.1 mol/L or c(EDTA) = 0.05 mol/L
M_A:	Molecular weight of the analyte; here either 100.09 g/mol ($CaCO_3$) or 121.14 g/mol (TRIS).

1 mL c(HCl) = 0.1 mol/L corresponds to 12.114 mg TRIS.

1 mL c(EDTA) = 0.05 mol/L corresponds to 5.005 mg $CaCO_3$.

Water sample

$$\text{Alkalinity} = \frac{V_{EP1} \times c(\text{HCl}) \times f \times 1000}{V_S}$$

Alkalinity:	Alkalinity in mmol/L
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c(HCl):	Concentration of titrant in mol/L; here c(HCl) = 0.1 mol/L
f:	Correction factor («titer») without unit
1000:	Conversion factor to obtain result in mmol/L
V_S:	Sample size in mL

$$\text{Ca hardness} = \frac{V_{EP1} \times c(\text{EDTA}) \times f \times 1000}{V_s}$$

$$\text{Mg hardness} = \frac{(V_{EP2} - V_{EP1}) \times c(\text{EDTA}) \times f \times 1000}{V_s}$$

$$\text{total hardness} = \frac{V_{EP2} \times c(\text{EDTA}) \times f \times 1000}{V_s}$$

Ca hardness:	Amount of calcium in the sample in mmol/L
Mg hardness:	Amount of magnesium in the sample in mmol/L
Total hardness:	Total hardness of the sample in mmol/L
V_{EP1}:	Titrant consumption until the first equivalence point in mL
V_{EP2}:	Titrant consumption until the second equivalence point in mL
c(EDTA):	Concentration of titrant in mol/L; here c(EDTA) = 0.05 mol/L
f:	Correction factor («titer») without unit
1000:	Conversion factor to obtain result in mmol/L
V_s:	Sample size in mL

The permanent hardness can be calculated by subtracting the alkalinity from the total hardness.

If a higher value is obtained for the alkalinity than for the total hardness, the alkalinity is given as being the total hardness.

Beverages

$$\text{Ca content} = \frac{V_{EP1} \times c(\text{EDTA}) \times f \times M_A \times 1000}{V_s}$$

$$\text{Mg content} = \frac{(V_{EP2} - V_{EP1}) \times c(\text{EDTA}) \times f \times M_A \times 1000}{V_s}$$

Ca content:	Amount of calcium in the sample in mg/L
Mg content:	Amount of magnesium in the sample in mg/L
V_{EP1}:	Titrant consumption until the first equivalence point in mL
V_{EP2}:	Titrant consumption until the second equivalence point in mL
c(EDTA):	Concentration of titrant in mol/L; here c(EDTA) = 0.05 mol/L
f:	Correction factor («titer») without unit
M_A:	Molar mass of analyst; here 24.31 g/mol (Mg^{2+}) respectively 40.08 g/mol (Ca^{2+}).
1000:	Conversion factor to obtain result in mg/L
V_s:	Sample size in mL

1 mL c(EDTA) = 0.05 mol/L corresponds to 2.004 mg Ca^{2+} or 1.216 mg Mg^{2+}

Example determination

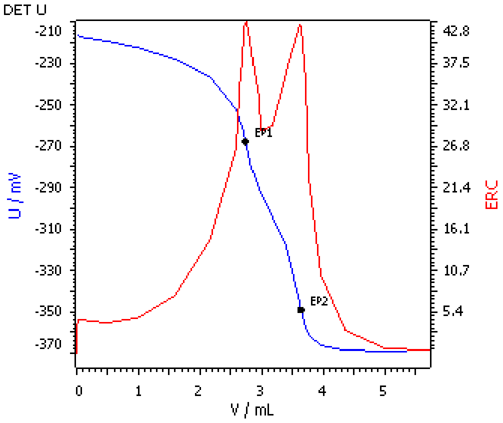

Fig. 1: Determination of Ca^{2+} (109.8 mg/L) and Mg^{2+} (21.89 mg/L) in tap water from Herisau using a combined Ca ISE.

Comments

- Before starting the titration of the alkalinity, the pH value of the water sample is measured. This value can be printed out as pH(init).
- The added volume of the auxiliary solution can be optimized according to the magnesium content. As a rule of thumb, the molar ratio Mg/acetylacetone should be approximately 0.05.
- Ca^{2+} electrodes, that have been stored dry, are conditioned in c($CaCl_2$) = 0.01 mol/L for approx. 10 min prior to the titration. Alternatively, the first three determinations are discarded.
- The alkalinity is defined by the m value (pH 4.3) and p value (pH 8.2). Not for every water sample a p value can be determined, therefore one does not necessarily get two equivalence points in the alkalinity titration. These values can be determined using a fixed endpoint; for more information concerning their determination see Metrohm Application Bulletin No. AB-178.
- 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 solution has to be used, to which a defined quantity of Mg^{2+} standard has been added. This addition of Mg^{2+} ions must, of course, be taken into account in the calculations.
- In 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.
- For fully automated determinations of further parameters of water samples see Metrohm Application Bulletin No. 178.
- Ca^{2+} selective electrodes should be stored dry.
- To prolong the lifetime of the titrant KOH can be added. The concentration of KOH should be c(KOH) = 0.1 mol/L

Photometric determination

Instruments

- Titrator with MET mode
- 20 mL burette
- Stirrer

Electrodes

Optrode	6.1115.000

Reagents

- Disodium ethylendiaminetetraacetate dihydrate, c(EDTA) = 0.1 mol/L volumetric solution
- Magnesium disodium ethylendiaminetetraacetate monohydrate, Mg complexonate, MgEDTA, puriss
- Sodium hydroxide, c(NaOH) = 0.1 mol/L volumetric solution and = 2 mol/L volumetric solution
- Ammonium chloride, NH_4Cl, purum
- Ammonia, w(NH_3) = 25%, purum
- Eriochrome Black T, Reag. Ph. Eur.
- Ascorbic acid, purum
- Calconcarboxylic acid, analytical grade
- $CaCl_2$ anhydrous, p.a. or certified $CaCl_2$ standard (e.g. Metrohm ion standard 6.2301.070)

Solutions

Eriochrome Black T indicator	100 mg Eriochrome Black T are dissolved in 100 mL dist. H_2O and 100 mg ascorbic acid are added to stabilize the solution.
Calconcarboxylic acid indicator	50 mg calconcarboxylic acid are dissolved in 100 mL of c(NaOH) = 0.1 mol/L.
Buffer pH 10	54 g NH_4Cl and 350 mL w(NH_3) = 25% are dissolved in dist. H_2O and made up to 1 liter with dist. H_2O.

Standards

$CaCl_2$	It is recommended to use a calibrated standard solution (e.g. Metrohm ion standard 6.2301.070). Otherwise $CaCl_2$ is dried over night in a drying oven at 140 °C and allowed to cool down in a desiccator for at least 2 h.

Sample preparation

No sample preparation required.

Analysis

Titer of EDTA

10 mL $CaCl_2$ standard are pipetted into a titration vessel or 80 – 150 mg of dried standard are weighed into a titration vessel. 90 mL dist. H_2O, 1.5 mL calconcarboxylic acid indicator as well as 4 mL c(NaOH) = 2 mol/L are added. The solution is then titrated immediately with c(EDTA) = 0.1 mol/L until after the first equivalence point.

Total hardness

To 100 mL sample, about 0.1 g MgEDTA and 10 mL buffer pH 10 are added. After the addition of 0.25 mL Eriochrome Black T indicator the solution is titrated using c(EDTA) = 0.1 mol/L, to the first equivalence point.

Calcium hardness

To 100 mL sample, 1.5 mL calconcarboxylic acid indicator and 4 mL c(NaOH) = 2 mol/L are added. The solution is titrated using c(EDTA) = 0.1 mol/L, to the first equivalence point.

Parameters

Titer

Mode	MET U
λ	610 nm
Start volume	9.5 mL
Drift	50 mV/min
Max. waiting time	26 s
Volume increment	0.1 mL
EP criterion	30 mV
EP recognition	all

Total hardness

Mode	MET U
λ	610 nm
Pause	30 s
Drift	50 mV/min
Max. waiting time	26
Volume increment	0.1 mL

EP criterion	30 mV
EP regonition	greatest

Calcium hardness

Mode	MET U
λ	610 nm
Pause	10 s
Drift	50 mV/min
Max. waiting time	26
Volume increment	0.1 mL
EP criterion	30 mV
EP regonition	all

Calculation

Titer

$$\text{Titer} = \frac{V_s \times c(\text{CaCl}_2)}{V_{EP1} \times c(\text{EDTA})}$$

or

$$\text{Titer} = \frac{m_s}{V_{EP1} \times c(\text{EDTA}) \times M_A}$$

Titer:	Titer of the titrant
V_s:	Added volume standard solution in mL
m_s:	Mass of standard in mg
$c(\text{CaCl}_2)$:	Exact concentration of standard solution in mol/L
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c(Titrant):	Concentration of the selected titrant in mol/L; here c(EDTA) = 0.1 mol/L
M_A:	Molecular weight of the analyte; here 110.98 g/mol (CaCl_2)

Total hardness

$$\text{Total hardness} = \frac{V_{EP1} \times c(\text{EDTA}) \times f \times 1000}{V_S}$$

Total hardness:	Total hardness in mmol/L
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c(EDTA):	Concentration of titrant in mol/L; here c(EDTA) = 0.1 mol/L
f:	Correction factor («titer») without unit
1000:	Conversion factor to obtain result in mmol/L
V_S:	Sample size in mL

Calcium hardness

$$\text{Ca hardness} = \frac{V_{EP1} \times c(\text{EDTA}) \times f \times 1000}{V_s}$$

Mg hardness = Total hardness - Ca hardness

Ca hardness:	Amount of calcium in the sample in mmol/L
Mg hardness:	Amount of magnesium in the sample in mmol/L
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c(EDTA):	Concentration of titrant in mol/L; here c(EDTA) = 0.1 mol/L
f:	Correction factor («titer») without unit
1000:	Conversion factor to obtain result in mg/L
V_s:	Sample size in mL

The total hardness can be saved as a common variable and used for the Mg hardness later on.

Example determination

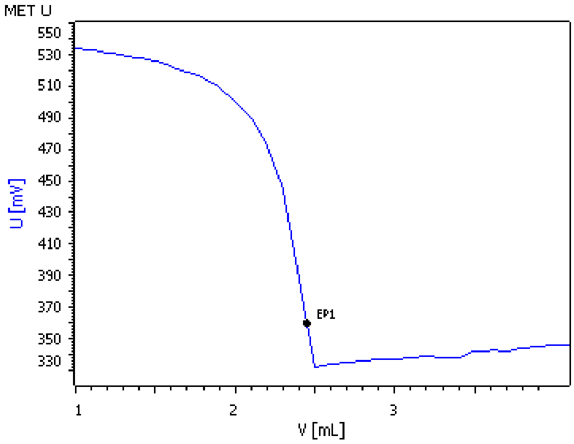

Fig. 2: Determination of the total hardness.

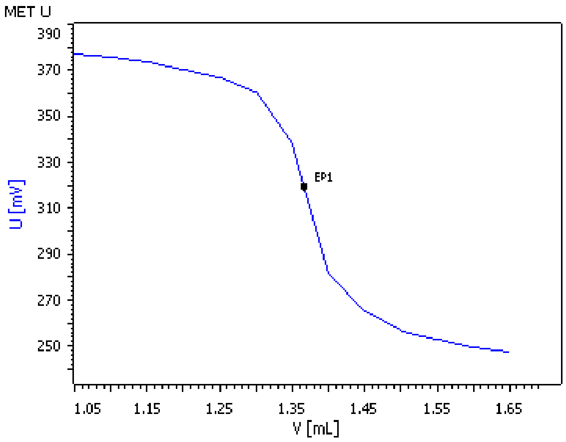

Fig. 3: Determination of the Ca hardness

Comments

- The light intensity must have stabilized sufficiently before use. Each time the optical electrode is switched on or the wavelength changed one should wait at least for five minutes before starting the first determination.
- It is not recommended to use $CaCO_3$ for titer determination, as the titration needs to be carried out at pH 12 to 13 and thereby $CaCO_3$ precipitates.
- If the expected amount of Ca^{2+} ions is too high (> 100 mg/L, 2.5 mmol/L respectively) $CaCO_3$ can precipitate. It is therefore recommended to dilute such samples.
- A concentration of more than 1 mg/L orthophosphate ions lead to a precipitation of calcium at the pH used for the titration.
- When working with a sample changer, the buffer pH 10 would release NH_3, what can cause alteration of the pH value of the following samples. In this case it is advisable to use alkaline borate buffer or to cover the samples.
- When performing photometric titrations, attention has to be paid to the fact that no air bubbles are incorporated through stirring.
- According to the norm DIN 38406-3 the photometric method is not suitable for sea water and waters with a similar salinity as well as waste water.

References

- DIN 38406-3
  German standard methods for the examination of water, waste water and sludge – Cations (group E) – Part 3; Determination of calcium and magnesium, complexometric method (E 3)
- EN ISO 9963-1
  Water quality – Determination of alkalinity – Part 1: Determination of total and composite alkalinity
- EPA 130.2
  Hardness, Total (mg/L as CaCO3) (Titrimetric, EDTA)
- EPA 310.1
  Alkalinity (Titrimetric, pH 4.5)
- ASTM D1126
  Standard Test Method for Hardness in Water
- Christiansen, T.F.; Busch, J. E.; 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.
- SCA, blue book 43
  Total hardness, calcium hardness, and magnesium hardness in raw and potable waters by EDTA titrimetry
- SCA, blue book 44
  The determination of alkalinity and acidity in water
- Metrohm Application Bulletin AB-206
  Titer determination in potentiometry
- Metrohm Application Bulletin AB-221
  Standard methods in water analysis

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Appendix

Table of the definitions for water hardness used in this Application Bulletin as well as further expressions.

Alkalinity	The alkalinity is defined as the acid neutralizing capacity, the result is given in mmol/L
Calcium hardness	The calcium hardness gives the amount of Calcium in mmol/L
Magnesium hardness	The magnesium hardness gives the amount of Magnesium in mmol/L
Total hardness	The total hardness is the sum of the calcium and magnesium hardness in mmol/L
Permanent hardness	The permanent hardness can be calculated from the total hardness and the alkalinity (see calculations in potentiometric part)
Carbonate hardness	The carbonate hardness is another expression for the alkalinity
Temporary hardness	The temporary hardness is another expression for the alkalinity
Remaining hardness	The remaining hardness is another expression for the permanent hardness

Table for the conversion of the different hardness units

	mmol/L	mg/L $CaCO_3$	°dH	°fH	°e
1 mmol/L =	1	100.0	5.6	10.00	7.02
1 mg/L $CaCO_3$ =	0.01	1	0.056	0.1	0.07
1 °dH =	0.1783	17.8	1	1.78	1.253
1 °fH =	0.1	10	0.560	1	0.702
1 °e =	0.142	14.3	0.798	1.43	1

mg/L $CaCO_3$	corresponds to the American degree.
°dH	German degrees
°fH	French degrees
°e	English degrees