Metrohm

Application Bulletin 235/3 e

Potentiometric titration of calcium and magnesium in dairy products

Branch

General analytical chemistry; food, stimulants, beverages, flavours

Keywords

Titration; calcium; magnesium; dairy products; milk, cheese; yoghurt; food; Cu ISE; branch 1; branch 7; 6.0502.140

Summary

This bulletin describes a simple method for the determination of the calcium content in dairy products. The use of EGTA as titrant, CuEGTA as indicator and the ion-selective copper electrode (Cu ISE) as indicator electrode allows the determination without time-consuming sample preparation. If the complexing agent EDTA is used as titrant instead of EGTA, the sum of calcium and magnesium is obtained.

Ca in milk is only partly in an ionogenic state. The majority is present in bound form, but can be complexed by EGTA in alkaline solution. CuEGTA is added to the sample solution and reacts with the Ca^{2+} ions as follows:

$CuEGTA + Ca^{2+} \leftrightarrows CaEGTA + Cu^{2+}$

$Cu^{2+} + EGTA \rightarrow CuEGTA$

After the substitution, the free Cu is titrated with EGTA using the Cu-ISE.

Instruments

- Titrator with MET Mode
- 20 mL buret
- Stirrer

Electrodes

Cu ISE	6.0502.140
LL ISE Reference	6.0750.100

Reagents

- Ethylene glycol-bis-(2-aminoethyl)-tetraacetic acid, EGTA
- Ethylenediammoniumtetraacetic acid, EDTA
- Ammonium chloride, NH_4Cl
- Ammonia, $w(NH_3) = 25\%$
- Copper sulfate, $c(CuSO_4) = 0.1$ mol/L
- Sulfuric acid, $c(H_2SO_4) = 0.05$ mol/L
- Sodium hydroxide, c(NaOH) = 1 mol/L and 0.1 mol/L
- Copper diammonium EDTA, CuEDTA

Solutions

Titrant Ca	c(EGTA) = 0.1 mol/L Dissolve 38.04 g EGTA in 250 mL c(NaOH) = 1 mol/L and, after cooling down, make up to 1 L with dist. water.
Titrant Ca + Mg	c(EDTA) = 0.1 mol/L If possible this solution should be bought from a supplier.
Buffer solution pH 10	Dissolve 54 g NH_4Cl in approx. 400 mL dist. water, add 300 mL $w(NH_3) = 25\%$ and make up to 1 L with dist. water.
CuEGTA	Mix 100 mL c(EGTA) = 0.1 mol/L with 100 mL of a solution containing $c(NH_4Cl) = 0.2$ mol/L and exactly $c(CuSO_4) = 0.1$ mol/L. Titration can be used to check if this solution contains no excess Cu(II) or EGTA.
CuEDTA	c(CuEDTA) = 0.1 mol/L If possible this solution should be bought from a supplier.

Standard solution

Ca standard	$c(Ca^{2+}) = 0.1$ mol/L Metrohm 6.2301.070

Sample preparation

Milk, milk drinks, yogurt, brine bath, etc.

Approx. 10 g sample is weighed exactly into a titration vessel and diluted to approx. 50 mL with dist. water.

Cheese

Approx. 1 g finely grated cheese (calcium content approx. 1%) or an equivalent quantity of cheese with differing calcium content is weighed into a titration vessel. Add 10 mL $c(H_2SO_4)$ = 0.05 mol/L and approx. 50 mL dist. water, then heat the mixture to 40 °C and stir at this temperature for 10 min. After cooling down, neutralize to pH = 7 with c(NaOH) = 0.1 mol/L.

Analysis

Titer EGTA

2 to 18 mL Ca standard is pipetted into a titration vessel. 50 mL dist. H_2O, 1 mL CuEGTA and 10 mL buffer solution are added. After a pause of 30 s, the solution is titrated with c(EGTA) = 0.1 mol/L until after the equivalence point.

Titer EDTA

2 to 18 mL Ca standard is pipetted into a titration vessel. 50 mL dist. H_2O, 1 mL CuEDTA and 10 mL buffer solution are added. After a pause of 30 s, the solution is titrated with c(EDTA) = 0.1 mol/L until after the equivalence point.

Calcium determination

To the prepared sample solution 1 mL CuEGTA and 5 mL buffer solution are added. After a pause of 30 s, the solution is titrated with c(EGTA) = 0.1 mol/L until after the equivalence point.

Calcium and magnesium determination

To the prepared sample solution 1 mL CuEDTA and 5 mL buffer solution are added. After a pause of 30 s, the solution is titrated with c(EDTA) = 0.1 mol/L until after the equivalence point.

Parameters

Titer

Mode	MET U
Stirring rate	8
Signal drift	50 mV/min
Min. waiting time	5 s
Max. waiting time	26 s
Volume increment	0.1 mL
EP criterion	30 mV
EP recognition	Greatest

Sample

The same parameters are used for both titrations.

Mode	MET U
Stirring rate	8
Signal drift	50 mV/min
Min. waiting time	5 s
Max. waiting time	26 s
Volume increment	0.1 mL
EP criterion	30 mV
EP recognition	Greatest

Calculation

Titer

$$f = \frac{V_{Std} \times c_{Std}}{V_{EP1} \times c_{EGTA}}$$

f:	Titer of EGTA
V_{Std}:	Added volume of standard solution in mL
c_{Std}:	Concentration of the standard solution in mol/L
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c_{EGTA}:	Concentration of EGTA in mol/L

Sample

Calcium

$$w_{Ca} = \frac{V_{EP1} \times c_{EGTA} \times f \times M_{Ca} \times 0.1}{m_S}$$

w_{Ca}:	Calcium content in %
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c_{EGTA}:	Concentration of EGTA in mol/L
f:	Titer of EGTA
M_{Ca}:	Molecular weight of calcium, 40.078 g/mol
m_S:	Sample size in g
0.1	Conversion factor

Titrant consumption

$$n_{Ca} = \frac{V_{EP1} \times c_{EGTA} \times f}{m_S}$$

n_{Ca}:	Titrant consumption for the calcium in mmol/g (saved as common variable)
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c_{EGTA}:	Concentration of EGTA in mol/L
f:	Titer of EGTA
m_S:	Sample size in g

Magnesium

$$w_{Mg} = \left(\frac{V_{EP1} \times c_{EDTA} \times f}{m_S} - n_{Ca} \right) \times M_{Mg} \times 0.1$$

W_{Mg}:	Magnesium content in %
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c_{EDTA}:	Concentration of EDTA in mol/L
f:	Titer of EDTA
m_S:	Sample size in g
n_{Ca}:	Titrant consumption for the calcium in mmol/g
M_{Mg}:	Molecular weight of magnesium, 24.305 g/mol
0.1	Conversion factor

Example determination

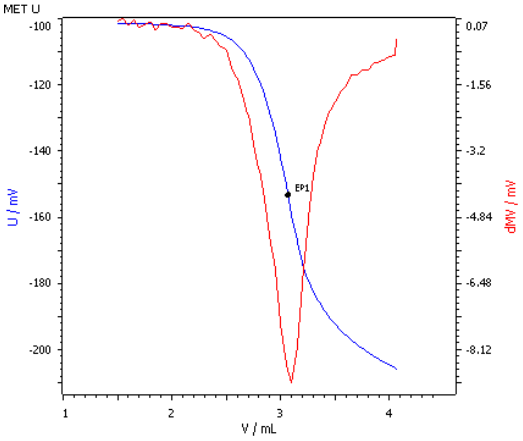

Fig. 1: Titration curve of the calcium determination in milk with c(EGTA) = 0.1 mol/L as titrant

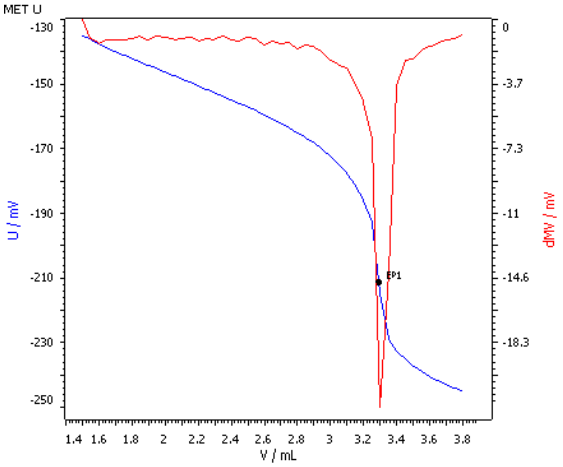

Fig. 1: Titration curve of the magnesium determination in milk with c(EDTA) = 0.1 mol/L as titrant

Comments

- It is not possible to determine the total calcium concentration in cheese, without the described sample preparation. The found values are too low.
- The Cu ISE instead of the Ca ISE is used because most of the calcium in dairy products is present in a bound form.
- For the thermometric determination of calcium and magnesium in milk, see Metrohm Application Bulletin 342.

References

- Metrohm Application Bulletin 101
Complexometric titrations with the Cu ISE

Author

Competence Center Titration

Metrohm International Headquarters