

Application Bulletin

Of interest to: Food, especially dairy products

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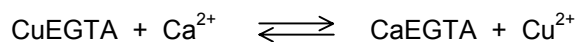
Potentiometric titration of calcium (magnesium) in dairy products

Summary

This bulletin describes a simple method for the determination of the calcium content in dairy products. Use of CuEGTA and the ion-selective copper electrode (Cu ISE) as indicator electrode allows the determination to be performed 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. The magnesium content can then be calculated from the difference between the results of the two titrations.

Theory

If the Cu ISE is used to indicate the complexometric titration of calcium, addition of copper ions is necessary. As the Cu^{2+} ions would also react with the titrant EGTA, they are already added to the sample in complexed form as CuEGTA. This complex reacts with the Ca^{2+} ions as follows:



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 with 700 Dosino or 685 Dosimat
- 2.728.0040 Magnetic Stirrer
- 6.3014.XX3 Exchange Unit(s)
- 6.0502.140 ion-selective copper electrode (Cu ISE) with 6.2104.020 electrode cable
- 6.0726.100 double-junction Ag/AgCl reference electrode (bridge electrolyte KNO_3 sat.) with 6.2106.020 electrode cable

Reagents

- Titrant: $c(\text{EGTA}) = 0.1 \text{ mol/L}$:
Dissolve 38.04 g ethylene glycol-bis-(2-aminoethyl)-tetraacetic acid in 250 mL $c(\text{NaOH}) = 1 \text{ mol/L}$ and, after cooling down, make up to 1 L with dist. water.
- Buffer solution $\text{pH} = 10$:
Dissolve 54 g NH_4Cl in approx. 400 mL dist. water, add 300 mL $w(\text{NH}_3) = 25\%$ and make up to 1 L with dist. water.
- CuEGTA complex solution:
Mix 100 mL $c(\text{EGTA}) = 0.1 \text{ mol/L}$ with 100 mL of a solution containing 0.2 mol/L NH_4Cl and exactly 0.1 mol/L $\text{Cu}(\text{NO}_3)_2$. Titration can be used to check if this solution contains no excess Cu(II) or EGTA.
- Sulfuric acid, $c(\text{H}_2\text{SO}_4) = 0.05 \text{ mol/L}$
- Sodium hydroxide solution, $c(\text{NaOH}) = 0.1 \text{ mol/L}$

Sample preparation

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

Approx. 10 g sample is weighed exactly into a glass beaker and diluted with approx. 90 mL 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 glass beaker. Add 10 mL $c(\text{H}_2\text{SO}_4) = 0.05 \text{ mol/L}$ 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 $\text{pH} = 7$ with $c(\text{NaOH}) = 0.1 \text{ mol/L}$.

Analysis

Add 1 mL CuEGTA solution and 10 mL buffer solution $\text{pH} = 10$ to the prepared sample solution. Allow to react for 10 ... 30 s under stirring, then titrate with $c(\text{EGTA}) = 0.1 \text{ mol/L}$, using, e.g., the MET mode.

Calculation

1 mL $c(\text{EGTA}) = 0.1 \text{ mol/L}$ corresponds to 4.008 mg Ca^{2+}

$$\% \text{Ca}^{2+} = \text{EP1} * \text{C01} * \text{C02} / \text{C00}$$

EP1 = titrant consumption in mL

C00 = sample weight in g

C01 = 4.008

C02 = 0.1 (conversion factor for %)

Remarks

- If the magnesium content is also required, a second titration is carried out with $c(\text{EDTA}) = 0.1 \text{ mol/L}$ and addition of CuEDTA. This determines the sum of calcium and magnesium. The magnesium content can then be calculated from the difference between the titrant consumption of the two titrations:

$$\text{EP1(Mg)} = \text{EP1(Ca + Mg)} - \text{EP1(Ca)} \quad \text{Use the same sample weight for both titrations!}$$

1 mL $c(\text{EDTA}) = 0.1 \text{ mol/L}$ corresponds to $2.4305 \text{ mg Mg}^{2+}$

- If for cheese, work is done without heating and without addition of H_2SO_4 (as for milk), it is not possible to determine the total calcium concentration (results found too low).

Figures

```
'pa
736 GP Titrimo      03222  736.0012
date 1999-05-25    time 17:14    6
DET U              *****
parameters
>titration parameters
  meas.pt.density      1
  min.incr.           10.0 µl
  titr.rate            max. ml/min
  signal drift        OFF mV/min
  equilibr.time       5 s
  start V:            OFF
  pause               0 s
  dos.element:       internal D0
  meas.input:         1
  temperature         25.0 °C
>stop conditions
  stop V:             abs.
  stop V              6 ml
  stop U              OFF mV
  stop EP             9
  filling rate        max. ml/min
>statistics
  status:            OFF
>evaluation
  EPC                5
  EP recognition:    all
  fix EP1 at U       OFF mV
  pK/HNP:           OFF
>preselections
  req.ident:         OFF
  req.smpl size:     all
  activate pulse:    OFF
  =====
```

Fig. 1: Parameter settings on the 736 GP Titrimo.

```
'fr
736 GP Titrino          03222  736.0012
date 1999-05-25      time 16:44      6
card label:Appl.736
U(init)              -52 mV  DET U    *****
smpl size 10.00914 g
EP1                 3.057 ml          -126 mV
Ca %                 0.122 %
stop V reached
=====
```

```
'cu
736 GP Titrino          03222  736.0012
date 1999-05-25      time 16:44      6
start V              0.000 ml  DET U    *****
1.0 ml/div           dU=50.0 mV/div
```

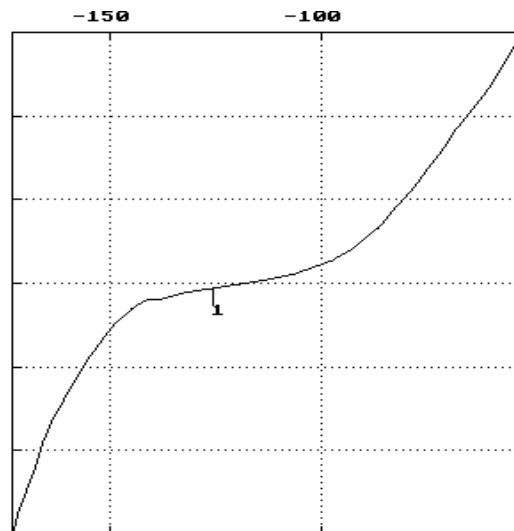


Fig. 2: Result block and titration curve for the determination of calcium in milk.

Literature

- Metrohm Application Bulletin No. 101
Complexometric titrations with the Cu ISE
Metrohm Ltd., Herisau.
- E. Tschager, H. Jager
Milchwirtschaftliche Berichte 87 (1986) 91–95.