

# Application Bulletin

Of interest to: Food analysis, Special milk products

A 1, 7

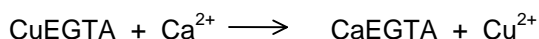
## Potentiometric titration of Ca (Mg) in milk products

### Summary

A simple method to determine the calcium content in milk products is described. Use of Cu-EGTA and the ion selective Cu electrode (Cu-ISE) allows the determination to be performed without time-consuming sample preparation. If EDTA is employed as a complexing agent in place of EGTA, the sum of the Ca and Mg contents can be determined. The amount of magnesium can then be calculated as the difference between the two titrations.

### Theory

If the Cu-ISE is used to indicate the complexometric determination of calcium, addition of Cu-ions is necessary. As these Cu ions would also react with the complexing agent (titrant), they are added to the sample in the form of a Cu complex. The complex reacts with Ca-ions as follows:



### Apparatus and accessories

- Titrimo 702 or 716 or 736 or 751 or 785 or Titroprocessor 726 with Dosino 700 or Dosimat 685
- Magnetic Swing-out stirrer 2.728.0040
- Exchange unit(s) 6.3014.XX3
- Cu-ISE 6.0502.140 and electrode cable 6.2104.020
- Ag/AgCl - reference electrode 6.0726.107 (sat. KNO<sub>3</sub> external electrolyte) with electrode cable 6.2106.020

### Reagents

- Titrant: c(EGTA) = 0.1 mol/L  
Dissolve 38.04 g ethylene glycol-0,0'-bis-(2-aminoethyl)-N,N,N',N'-tetraacetic acid in 250 mL c(NaOH) = 1 mol/L and, after cooling, fill up to 1 L with dist. H<sub>2</sub>O.
- Buffer solution pH = 10  
Dissolve 54 g NH<sub>4</sub>Cl in ca. 400 mL dist. H<sub>2</sub>O. Add 300 mL w(NH<sub>3</sub>) = 25% and fill up to 1 L with dist. H<sub>2</sub>O.

- Cu complex  
Mix 100 mL  $c(\text{EGTA}) = 0.1 \text{ mol/L}$  with 100 mL of a solution containing  $0.2 \text{ mol/L}$   $\text{NH}_4\text{Cl}$  and exactly  $0.1 \text{ mol/L}$   $\text{Cu}(\text{NO}_3)_2$ . Titration can be used to check that this solution contains no excess  $\text{Cu}(\text{II})$  or EGTA.
- Sulphuric acid:  $c(\text{H}_2\text{SO}_4) = 0.05 \text{ mol/L}$
- Sodium hydroxide:  $c(\text{NaOH}) = 0.1 \text{ mol/L}$

---

### Sample preparation

#### **Milk, milk drinks, yoghurt, brine bath, etc.**

Weigh ca. 10 g of sample exactly into a beaker and dilute with ca. 90 mL dist.  $\text{H}_2\text{O}$ .

#### **Cheese**

Weigh approx. 1 g finely grated cheese (ca. 1% Ca) or an equivalent amount of a different type of cheese into a beaker. Add 10 mL sulphuric acid and ca. 50 mL dist.  $\text{H}_2\text{O}$ . Heat at  $40^\circ\text{C}$  and stir at this temperature for 10 min. After cooling, neutralise to  $\text{pH} = 7$  with NaOH.

---

### Analysis

Add 1 mL Cu-EGTA and 10 mL buffer solution  $\text{pH} = 10$  to the prepared sample solution. Stirring, allow between 10 - 30 s time for reaction, then titrate with EGTA in the MET-mode of the Titrator.

#### **Calculation:**

1 mL  $c(\text{EGTA}) = 0.1 \text{ mol/L} = 4.008 \text{ mg Ca}$

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

C00 = Sample weight in g

C01 = 4.008

C02 = 0.1 (for %)

---

### Remarks

- If the magnesium content is also required, a second titration has to be performed with  $c(\text{EDTA}) = 0.1 \text{ mol/L}$  and Cu-EDTA. This determines the sum of Ca and Mg. The Mg content can then be determined by calculation:  
mL EDTA - mL EGTA (use the same sample quantity!)  
1 mL  $c(\text{EDTA}) = 0.1 \text{ mol/L} = 2.4305 \text{ mg Mg}$
- If for cheese, work is done without heating and without addition of  $\text{H}_2\text{SO}_4$  (similar to the milk procedure), the Ca can not be completely determined (results found too low).

---

### Literature

- Metrohm Application Bulletin No. 101
- Tschager, E. / Jager, H.  
Milchwirtschaftliche Berichte 87, (1986) 91 - 95

**Figures**

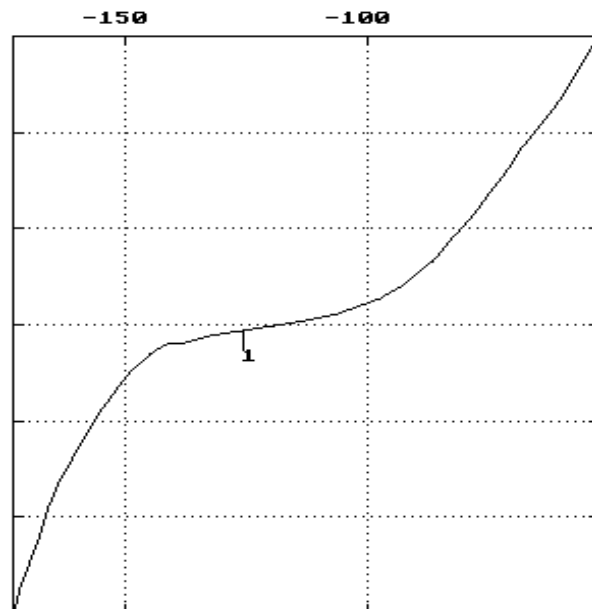
```
'pa
736 GP Titrino          03222  736.0012
date 1999-05-25      time 17:14      6
DET U          *****
parameters
>titration parameters
  meas.pt.density      1
  min.incr.            10.0 µl
  titr.rate            max. ml/min
  signal drift         OFF mV/min
  equilibr.time        5 s
  start 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 report Titrino

```
'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
```

```
'BMP-File: C:\DATASCAN\AQT4Q6.bmp
=====
```



**Fig.2** Results report and titration curve; Ca in milk