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# Application Bulletin

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Of interest to: General analytical laboratories; Water analysis

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## Determination of the total, calcium and magnesium hardness of water samples by photometric titration

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### Summary

This bulletin describes the determination of the total, calcium and magnesium hardness of water samples using the photometer with light guide and/or the Spectrode.

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### Instruments and accessories

- 702 SET/MET Titrino, 716 DMS Titrino, 736 GP Titrino, 751 GPD Titrino or 785 DMP Titrino or 726 Titroprocessor with 685 Dosimat or 700 Dosino
  - 2.728.0040 Magnetic Stirrer
  - 662 Photometer including 6.1108.010 light guide or 6.5501.01X Spectrode 610 nm
  - 6.3014.223 Exchange Unit 20 mL (with flat PCTFE/PTFE stopcock)
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### Reagents

- Titrant c(EDTA) = 0.1 mol/L:  
Dissolve 37.224 g Na<sub>2</sub>EDTA \* 2 H<sub>2</sub>O in dist. water, add 10 mL c(NaOH) = 1 mol/L and make up to 1 L with dist. water.
- Buffer solution pH = 10:  
Dissolve 54 g NH<sub>4</sub>Cl and 300 mL w(NH<sub>3</sub>) = 25% in dist. water and make up to 1 L.
- Alkaline borate buffer (as an alternative to the above-mentioned buffer solution pH = 10):  
Dissolve 40 g NaOH in ca. 500 mL dist. water. Also dissolve 65 g H<sub>3</sub>BO<sub>3</sub> in this solution, allow to cool and make up to 1 L with dist. water.
- Sodium hydroxide c(NaOH) = 2 mol/L
- Eriochrome black indicator:  
w(Eriochrome black) = 0.1% in dist. water. Add 100 mg vitamin C per 100 mL solution to stabilize.
- Murexide indicator:  
Dissolve 50 mg murexide in 100 mL dist. water.
- Magnesium complexonate MgEDTA

## Analysis

### Determination of the total hardness

Add ca. 0.1 g MgEDTA as well as 10 mL buffer solution to 100 mL water sample. After addition of 0.25 mL Eriochrome black indicator titrate with  $c(\text{EDTA}) = 0.1$  mol/L using the MET mode of the titrator (wavelength  $\lambda = 610$  nm).

### Determination of the calcium hardness

Add 2.5 mL murexide indicator to 100 mL water sample. Adjust the pH value to 12 with  $c(\text{NaOH}) = 2$  mol/L and titrate immediately with  $c(\text{EDTA}) = 0.1$  mol/L using the MET mode of the titrator (wavelength  $\lambda = 610$  nm).

### Determination of the magnesium hardness

The magnesium hardness is obtained from the difference between the total hardness and the calcium hardness.

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## Calculation

1 mL  $c(\text{EDTA}) = 0.1$  mol/L corresponds to 0.1 mmol Ca/Mg or 4.008 mg Ca or 2.4305 mg Mg

**Total hardness TH:**

TH in mmol/L	=	EP1
TH in °dH	=	EP1 * 5.6
TH in °fH	=	EP1 * 10
with EP1	=	titrant consumption in mL

**Calcium hardness CaH:** Same calculations as for the total hardness.

**Magnesium hardness MgH:**  $\text{MgH} = \text{TH} - \text{CaH}$

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## Remarks

- The buffer solution pH = 10 smells strongly of ammonia. When working with a sample changer, the evaporating  $\text{NH}_3$  can cause alteration of the pH value of the following samples. In this case it is therefore advisable to use the alkaline borate buffer.
- When performing photometric titrations, attention has to be paid to the fact that no air bubbles are incorporated through stirring nor adhere to the mirror of the light guide.

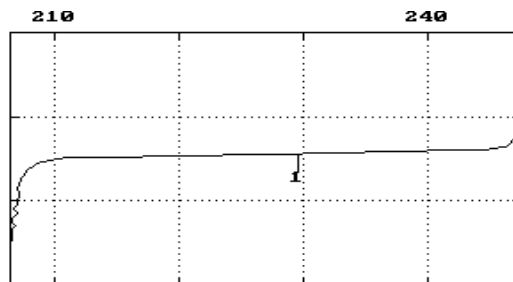
**Figures**

```
'pa
785 DMP Titrino      02287  785.0010
user                MEIER
date 1999-06-24    time 09:34      7
MET U              *****
parameters
>titration parameters
  V step            0.10 ml
  dos.rate          max. ml/min
  signal drift      50 mV/min
  equilibr.time     26 s
  start V:          OFF
  pause             0 s
  meas.input:       1
  temperature       25.0 °C
>stop conditions
  stop V:           abs.
  stop V            5 ml
  stop U            OFF mV
  stop EP           9
  filling rate      max. ml/min
>statistics
  status:           OFF
>evaluation
  EPC               30 mV
  EP recognition:   all
  fix EP1 at U     OFF mV
  pK/HNP:           OFF
>preselections
  req.ident:        OFF
  req.smpl size:    OFF
  limit smpl size: OFF
  activate pulse:   OFF
-----
```

**Fig. 1:** Parameter settings on the 785 DMP Titrino.

```
'fr
785 DMP Titrino      02287  785.0010
user                MEIER
date 1999-06-23    time 12:01      2
U(init)            247 mV MET U     *****
EP1                2.901 ml         230 mV
GH/mmoll           2.90
GH/°dH              16.25
GH/°fH              29.01
manual stop
=====

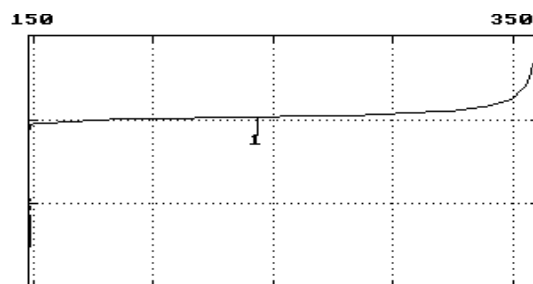
'cu
785 DMP Titrino      02287  785.0010
user                MEIER
date 1999-06-23    time 12:01      2
start V            0.000 ml MET U   *****
2.0 ml/div         dU=10.0 mV/div
```



**Fig. 2:** Result block and titration curve for the determination of the total hardness of tap water.

```
'fr
785 DMP Titrino      02287  785.0010
user                MEIER
date 1999-06-24    time 08:44    5
U(init)            361 mV MET U  *****
EP1                 1.941 ml      243 mV
CaH/mmol           1.94
CaH°dH             10.87
CaH°fH             19.41
MgHmmolL          0.95
MgH/°dH            5.36
MgH/°fH            9.56
stop V reached
=====
```

```
'cu
785 DMP Titrino      02287  785.0010
user                MEIER
date 1999-06-24    time 08:44    5
start V            0.000 ml MET U *****
2.0 ml/div         dU=50.0 mV/div
```



**Fig. 3:** Result block and titration curve for the determination of the calcium and magnesium hardness of tap water (Spectrode).

## Literature

- ASTM D 511-93 (1998)  
Standard Test Methods for Calcium and Magnesium in Water.
- DIN 38406, part 3 (1982)  
Kationen (Gruppe E). Bestimmung von Calcium und Magnesium.
- EPA 130.2 (1983)  
Hardness, total (mg/L as CaCO<sub>3</sub>). Titrimetric, EDTA.
- ISO 6058: 1984  
Water quality – Determination of calcium content – EDTA titrimetric method.
- ISO 6059: 1984  
Water quality – Determination of the sum of calcium and magnesium – EDTA titrimetric method.