



Determination of Hardness in Water

(ISO 6059 & Standard methods for water 18th edition 2.36 2340C)

Introduction

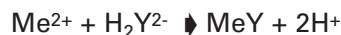
Hardness of water measures the sum of calcium and magnesium ions present in the water. The above-mentioned standard lays down a titration with EDTA at pH 10.00, using a $\text{NH}_4\text{Cl} / \text{NH}_4\text{OH}$ buffer and a colorimetric detection of the equivalent point.

This application note also uses EDTA titration with a potentiometric determination of the equivalent point by means of a Calcium ion-selective electrode.

Instead of the $\text{NH}_4\text{Cl} / \text{NH}_4\text{OH}$ buffer, we use a mixture of TRIS and acetylacetone. This buffer solution allows separation between Calcium and Magnesium when a Calcium selective electrode is used as measuring electrode.

Principle

The titrant EDTA reacts with Ca^{2+} according to the reaction



Where Me^{2+} represents Ca^{2+} or Mg^{2+} and H_2Y^{2-} the disodium salt of EDTA

1 mole of EDTA corresponds to 1 mole of Ca^{2+} or Mg^{2+}

The EDTA concentration is 0.02 mol/l. The results are generally expressed as mg/l of CaCO_3 or mmol/l but some other units can be used (see notes).

Electrode and reagents

ISE25Ca Calcium Ion-Selective Electrode (part no. E41M002) with a CL114 cable (part no. A94L114)

REF201 Reference Electrode (part no. E21M009)

EDTA titrant 0.02 mol/l (or 20 mmol/l)

The molecular weight of Na_2EDTA is 372.24 g/mol
Dissolve 7.445 of Na_2EDTA in 1000 ml of water using a volumetric flask

This titrant is also commercially available

Complexing and buffer solution

0.035 mol/l TRIS and 0.055 mol/l acetylacetone

Dissolve 3.50 g of acetylacetone and 6.65 g of TRIS (tri(hydroxy)-aminomethane) in 1000 ml of water using a volumetric flask.

Do not use this buffer for longer than one month.
 Ca^{2+} 0.01 mol/l and 0.1 mol/l solutions

Prepare the 0.01 mol/l solution by dilution of the 0.1 mol/l solution commercially available as standard solution

Inflection Detection settings

CONTINUOUS ADDITION MODE

| | |
|--------------------------|---------------|
| Stirring speed: | 450 rpm |
| Stirring delay: | 20 s |
| Burette volume: | 25 ml |
| Maximum volume: | 25 ml |
| Stop point: | -80 mV |
| Smoothing parameter: | 6 |
| Inflection point number: | 2 |
| Minimum speed: | 0.3 ml/min |
| Maximum speed: | 4 ml/min |
| Direction: | Decreasing mV |

| | |
|----------------|-----------------------|
| Inflection1 | |
| Min. ordinate: | -40 mV (see notes) |
| Max. ordinate: | 120 mV |

| | |
|----------------|--------|
| Inflection2 | |
| Min. ordinate: | -40 mV |
| Max. ordinate: | 120 mV |

| | |
|----------------|-----------|
| Sample unit: | ml |
| Sample amount: | 50 or 100 |

| | |
|--------------------|-------------|
| Results: | (see notes) |
| Results by: | cumulate |
| Number of results: | 2 |

| | |
|--------------------|----------------|
| Result 1 | |
| Result unit: | mmol/l |
| Reaction: | 1 smp + 1 titr |
| Calculate with IP: | 1 |

| | |
|--------------------|----------------|
| Result 2 | |
| Result unit: | mmol/l |
| Reaction: | 1 smp + 1 titr |
| Calculate with IP: | 2 |

Procedure

This procedure is suitable for surface waters, tap water and drinking waters.

Prepare and fill the ISE25Ca Ion- Selective Electrode as indicated in the operating instructions and store it in CaCl_2 for one hour prior to the first use.

Install electrodes and titrant

Pipette the necessary amount of water (generally 50 or 100 ml)

Add 20 ml of the buffer solution

Dip electrodes and delivery tip in the beaker

Run the titration.

Results

Depending on the ratio between concentration of Ca^{2+} and Mg^{2+} , the titration curve can show one or two inflection points.

For one inflection point

It corresponds to the cumulate ($\text{Ca}^{2+} + \text{Mg}^{2+}$) or Ca^{2+} if there is no Mg^{2+} in the water or if the ratio $\text{Ca}^{2+}/\text{Mg}^{2+}$ between relative concentrations of these 2 elements is too high.

For two inflection points

The first one corresponds to Ca^{2+} . The difference between the first and the second corresponds to Mg^{2+}

The total volume delivered to the second equivalent point corresponds to the cumulate ($\text{Ca}^{2+} + \text{Mg}^{2+}$)

Results are generally expressed in mmol/l or mg/l of CaCO_3 for the cumulate ($\text{Ca}^{2+} + \text{Mg}^{2+}$)

$$R \text{ (mmol/l)} = V(\text{titr}) * C(\text{titr}) / V(\text{smp})$$

$$R \text{ (mg/l CaCO}_3) = V(\text{titr}) * C(\text{titr}) * 100 / V(\text{smp})$$

- $V(\text{titr})$ = Total volume of titrant used in ml

- $C(\text{titr})$ = Concentration of titrant in mmol/l

- $V(\text{smp})$ = Sample volume in ml

- 100 = molecular weight of CaCO_3

For 5 determinations on a mineral water

Mean: 3.25 mmol/l
or 325 mg/l CaCO_3

Standard deviation: 0.03 mmol/l

Rel standard deviation: 0.9%

Working range

For 100 ml of sample and a 20 ml burette volume, a titrant volume between 1 and 18 ml corresponds to a working range between 0.2 and 3.6 mmol/l or 20 and 360 mg/l of CaCO_3 (see above formulas).

Notes

Note regarding the inflection points ordinates

The above-mentioned values correspond to the curve ordinates Determination of Hardness in Water (ISO 6059 and Standard methods for water 18th edition 2.36 2340C) generally observed for normal tap water

For the first inflection point (Calcium determination), the inflection point is often close to 80/90 mV and for the second (Magnesium determination), it is close to 15/30 mV

Refer to the electrode operating instructions.

Note regarding the result

Result expressed in mg/l of CaCO_3

The above-mentioned settings allow a result in line with the standard (total hardness expressed in mmol/l) whether the titration curve presents one or two inflection points.

If a result expressed in mg/l of CaCO_3 is needed, use the following settings.

Result unit: mg/l
Molar weight: 100
Reaction: 1 smp + 1 titr

Results expressed separately in mg/l of Ca^{2+} and Mg^{2+} and total hardness

If the titration curve presents 2 inflection points, the first point corresponds to the Calcium and the second to Magnesium.

The results can then be modified as follows:

Results by: Difference

Result 1
Result unit: mg/l
Molar weight: 40.1
(molar weight of Ca)
Reaction: 1 smp + 1 titr
Calculate with IP: 1

Result 2
Result unit: mg/l
Molar weight: 24.31
(molar weight of Mg)
Reaction: 1 smp + 1 titr
Calculate with IP: 2

Equation 1
Title: Hardness mmol/l
Equation: $(R1/40.1) + (R2/24.31)$

OR/AND

Equation 1 (or 2)

Title: Hardness mg/l
Equation: $(R1 * 100 / 40.1) + (R2 * 100 / 24.31)$

Note regarding titrant calibration

If necessary, the EDTA solution can be calibrated using 0.01 mol/l Ca^{2+} solution. To calculate the titrant concentration, enter the Ca^{2+} standard concentration in mol/l and ask for a result in mol/l with a reaction corresponding to 1 smp +1 Titr.

Note regarding Calcium ionselective electrode maintenance

Prepare and use the Calcium ionselective electrode according to the operating instructions.

During experiments, store the electrode in a 0.01 mol/l Ca^{2+} solution.

For long-term storage, empty the electrode and store it in its box.

Curve

