Hardness in Water

DOC316.52.93086

ISE method
Based on ISO standard 6059:1984

Total hardness: 0.1 to 3.8 mmol/L

1. 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 NH_4Cl/NH_4OH buffer and 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 NH_4Cl/NH_4OH 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.

2. Principle

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

$$Me^{2+} + H_2Y_2 \Rightarrow MeY_2 + 2H^+$$

Where:

Me^{2+} represents Ca^{2+} or Mg^{2+}
$H_2Y_2^-$ the di-sodium salt of EDTA

- 1 mole of EDTA corresponds to 1 mole of Ca^{2+} or Mg^{2+}
- The EDTA concentration is 0.01 mol/L

3. Electrode and reagents

Electrode: Calcium specific combined electrode, Ca^{2+} I.S. Electrode 9660C[1]
Legacy adapter

Titrant: Na_2EDTA 0.01 mol/L. The molecular weight of Na_2EDTA is 372.24 g/mol.

- Dissolve 3.723 g of Na_2EDTA in 1000 mL of water using a volumetric flask
- This titrant is also commercially available

Complexing 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(hydroxymethyl)-aminomethane) in 1000 mL of water using a volumetric flask
- Do not use this buffer for longer than one month

4. Titration default settings

4.1. Default settings

The settings have been defined with:

- Sample volume: 50 mL (or 100 mL)
- Titrant concentration: 0.01 mol/L
- Syringe volume: 10 mL

Name	Default parameter	Unit
Application		
Application name	Hardness in Water	
Advisable syringe	10 mL	

[1] Prepare and use the Calcium ion-selective electrode according to the operating instructions. During experiments, store the electrode in a 0.1 mol/L Ca^{2+} solution. For long-term storage, store it with its protective cap.

Name	Default parameter	Unit
Sample		
Name	Water ?[2]	
Amount	50.0	[mL]
QC		
Name	QC Sample	
Electrode		
Recommended electrode	ISECa9660C	
Titrant: Na_2EDTA 0.01 M		
Name	Na_2EDTA	
Real concentration	0.01000	[mol/L]
Leveling		
Active	No	
Manual buffer addition		
Active[3]	No	
Automatic buffer addition		
Active[3]	Yes	
Reagent	Buffer addition – 20 mL	
Pump ID	Pump 1	
Time	7	[s]
Stirring speed	25	[%]
Hardness		
Active	Yes	
Stirring speed	25	[%]
Predose type	Ordinate	
Predose ordinate	300	[mV]
Predose speed	20	[mL/min]
Delay	5	[s]
Max. vol. stop point	20	[mL]
Ordinate stop point	150	[mV]
Stop on last EQP	Yes	
IP1 min. ordinate	220	[mV]
IP1 max. ordinate	300	[mV]
IP2 min. ordinate	150	[mV]
IP2 max. ordinate	320	[mV]
Result 1 (R1) name	Calcium	
R1 hide	Yes	
R1 min.	0	[mmol/L]
R1 max.	4.2	[mmol/L]
R1 QC min.	0	[mmol/L]
R1 QC max.	4.2	[mmol/L]
Result 2 (R2) name	Magnesium	
R2 hide	Yes	
R2 min.	0	[mmol/L]
R2 max.	4.2	[mmol/L]
R2 QC min.	0	[mmol/L]
R2 QC max.	4.2	[mmol/L]
Result 3 (R3) name	Calcium	
R3 hide	No	
R3 min.	0	[mg/L]
R3 max.	170	[mg/L]
R3 QC min.	0	[mg/L]
R3 QC max.	170	[mg/L]
R3 molar weight	40.08	[g/mol]

[2] "?" in the name, indicates that the sample name will be automatically incremented with a number for each analysis

[3] Only one of these two fields must be set to "Yes"

Name	Default parameter	Unit
Result 4 (R4) name	Magnesium	
R4 hide	No	
R4 min.	0	[mg/L]
R4 max.	102	[mg/L]
R4 QC min.	0	[mg/L]
R4 QC max.	102	[mg/L]
R4 molar weight	24.31	[g/mol]
Result 5 (R5) name (=G1)	Total Hardness	
R5 hide	Yes	
R5 min.	0	[mmol/L]
R5 max.	4.2	[mmol/L]
R5 QC min.	0	[mmol/L]
R5 QC max.	4.2	[mmol/L]
R5 equation	R1+R2	
R5 unit	mmol/L	
Result 6 (R6) name	Total Hardness	
R6 hide	No	
R6 min.	0	[mg/L as $CaCO_3$]
R6 max.	420	[mg/L as $CaCO_3$]
R6 QC min.	0	[mg/L as $CaCO_3$]
R6 QC max.	420	[mg/L as $CaCO_3$]
R6 equation	FX*G1	
R6 unit	mg/L as $CaCO_3$	
R6 user value	100	

4.2. Recommendations for modification of settings

The predose in ordinate is defined by default up to 300 mV at 20 mL/min. It may be necessary to adjust the ordinate of this predose depending on the electrode and its ageing. If it is not correctly set, either the titration will be too slow or the equivalent point will not be found.

4.3. Leveling

With this application, the leveling option is available as the sample amount is between 50 mL and 100 mL. It is deactivated by default.

To use this method, an external pump is required. All elements (probes, tubes from the titrator and the tube from the external pump) have to be well installed on the probe holder. The beaker has to contain a level of sample higher than the position of the tube of the external pump. When the beaker is attached to the probe holder, this method allows the system to automatically remove the excess sample by a defined pump working time, and always keep the same sample volume before launching the analysis.

In order to define this volume, autoleveling calibration sequence has to be previously executed (see section **9.4 Autoleveling calibration**).

When this option is active, the working time of the external pump must be set (default 30 s). The minimum working time must allow the pump to be removing air during the last few seconds of the external pump activation.

Note: *Do not forget to re-edit the sample amount with the expected value when deactivating the leveling method.*

5. Procedure

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

1. Store the Ca Ion-Selective Electrode as indicated in the operating instructions in $CaCl_2$ 0.1 M for one hour prior to the first use.
2. Pipette 50 mL of water (or 100 mL if less than 100 mg/L $CaCO_3$ content).
3. Dip the electrode and delivery tips in the beaker.
4. Run the titration.

6. 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 (Ca^{2+} + Mg^{2+}) or Ca^{2+} if there is no Mg^{2+} in the water or if the ratio Ca^{2+}/ Mg^{2+} between relative concentrations of these 2 elements is too high.

For two inflection points:

- The first 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 (Ca^{2+} + Mg^{2+})

6.1. Calculated results

- R1: Calcium (mmol/L) $Ca = \frac{V1_{Na2EDTA} \times C_{Na2EDTA}}{V_{smp}} \times 1000$
- R2: Magnesium (mmol/L) $Mg = \frac{V2_{Na2EDTA} \times C_{Na2EDTA}}{V_{smp}} \times 1000$
- R3: Calcium (mg/L) $Ca = \frac{V1_{Na2EDTA} \times C_{Na2EDTA}}{V_{smp}} \times 40080$
- R4: Magnesium (mg/L) $Mg = \frac{V2_{Na2EDTA} \times C_{Na2EDTA}}{V_{smp}} \times 24310$
- R5 = G1: Total Hardness (mmol/L) TH = R1 + R2
- R6: Total Hardness (mg/L as $CaCO_3$) TH = G1 x FX

Where:

$V1_{Na2EDTA}$:	Volume of titrant to reach the first equivalent point (mL)
$V2_{Na2EDTA}$:	Volume of titrant to reach the second equivalent point (mL)
$C_{Na2EDTA}$:	Concentration of titrant (mol/L)
V_{smp}:	Volume of sample (mL)
FX:	User value

The total hardness unit can be converted using the user factor (FX) and multiplying the total hardness in mmol/L according to the table below. When the user factor is modified, the content of the unit field has also to be changed depending on the user value.

Total Hardness unit	User value (FX)
°DH	5.61
°Clark	7.02
°f	10
ppm or mg/L as $CaCO_3$	100

6.2. Displayed results

The three results displayed at the end of the analysis are:

- Calcium (mg/L)
- Magnesium (mg/L)
- Total Hardness (mg/L as $CaCO_3$)

The three other results are not displayed but are stored in the data log.

7. Examples of hardness determination

Example 1: For 5 determinations on Geneva tap water

- Mean: 1.37 mmol/L or 137 mg/L $CaCO_3$
- Relative standard deviation: 0.6%

Example 2: 50 mL mineral water (manufacturer data: 80 mg/L Ca^{2+} and 26 mg/L Mg^{2+})

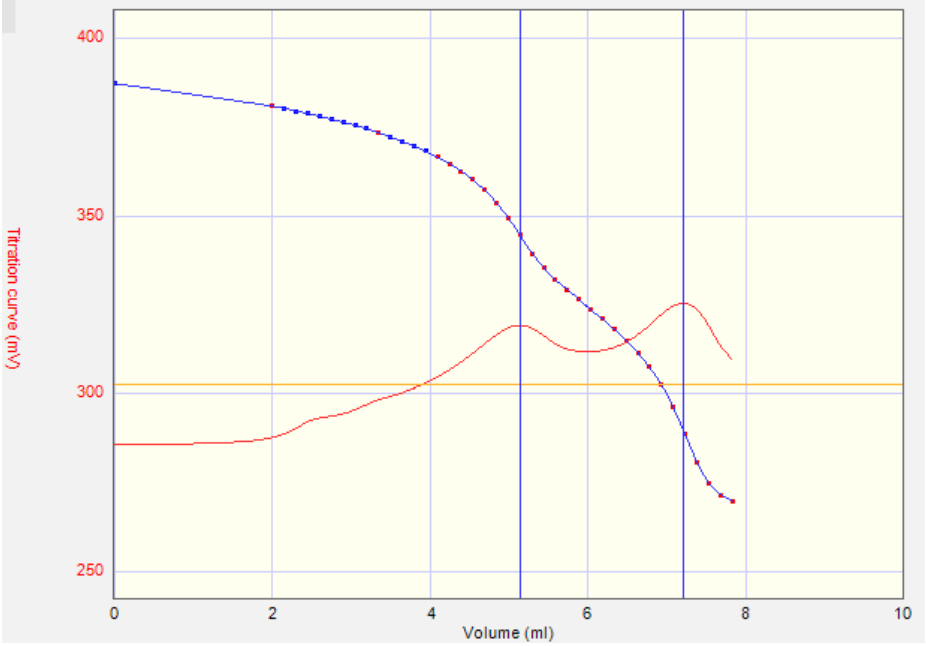
- Mean of 5 measurements: 83.4 mg/L Ca^{2+} and 25.8 mg/L Mg^{2+}
- Relative standard deviation: 1.9% on Ca^{2+} and 2.4 % on Mg^{2+} and 1 % on the total volume

Example 3: 50 mL of a Ca standard solution at 80.2 mg/L (0.002 M)

- Mean value of 10 measurements: 81.02 mg/L with a RSD of 0.65% (Accuracy = 1%)

For 50 to 100 mL of sample and a 10 mL syringe volume, a titrant volume between 1 and 19 mL corresponds to a working range between 0.1 and 3.8 mmol/L or 20 and 360 mg/L of $CaCO_3$ (see above formulae).

Curve example



8. Bibliography

- ISO 6059:1984 – Determination of Hardness in Water – and Standard methods for water 18th edition 2.36 2340C

9. Appendix: Titrant and autoleveling calibrations

9.1. Na_2EDTA 0.01 mol/L calibration

9.1.1. Principle

The Na_2EDTA used as titrant for hardness determination has to be calibrated with Ca^{2+} solution. The standard used is a solution of $CaCl_2$ at 1000 mg/L as $CaCO_3$.

$$Y^{2-} + Ca^{2+} \rightarrow CaY$$

9.1.2. Electrode and reagents

Electrode: Calcium specific combined electrode, Ca^{2+} I.S. Electrode 9660C and legacy adapter
Titrant: Disodic EDTA, Na_2EDTA 0.01 mol/L solution in deionized water
Standard: $CaCl_2$ solution at 1000 mg/L as $CaCO_3$
Deionized water

9.1.3. Settings

The following parameters have been set to use about 5 mL of titrant for the calibration.

Name	Default parameter	Unit
Application		
Application name	Langelier Index	
Advisable syringe	10 mL	
Electrode		
Recommended electrode	ISECa9660C	
Titrant: Na_2EDTA 0.01 M		
Name	Na_2EDTA	
Nominal concentration	0.01	[mol/L]
Na_2EDTA 0.01 M method: Manual buffer addition		
Active[4]	No	
Na_2EDTA 0.01 M method: Automatic buffer addition		
Active[4]	Yes	
Reagent	Buffer addition – 20 mL	
Pump ID	Pump 1	
Time	7	[s]
Stirring speed	0	[%]
Na_2EDTA 0.01 M method: Calibration		
Active	Yes	
Calibration frequency	0	[Day]
Stirring speed	25	[%]
Predose type	Ordinate	
Predose ordinate	300	[mV]
Predose speed	20	[mL/min]
Delay	5	[s]
Max. vol. stop point	8	[mL]
Ordinate stop point	150	[mV]
Stop on last EQP	Yes	
IP1 min. ordinate	150	[mV]
IP1 max. ordinate	300	[mV]
Min. titrant conc.	0.00900	[mol/L]
Max. titrant conc.	0.01100	[mol/L]
Standard name	$CaCl_2$	
Standard amount	5	[mL]
Min. amount	4	[mL]
Max. amount	6	[mL]
Concentration	1000	[mg/L]
Molar weight	100.09	[g/mol]

[4] Only one of these two fields must be set at "Yes"

9.1.4. Procedure

Accurately measure 5 mL of $CaCl_2$ 1000 mg/L as $CaCO_3$ standard solution in a beaker. Add a sufficient amount of deionized water to cover the electrode and the delivery tips with solution (qs 50 mL). Put in a magnetic stir bar and place the beaker on the titrator. Dip the electrode and delivery tips into the solution. Launch the titrant calibration sequence.

9.1.5. Result

The result is expressed as mol/L concentration of the titrant and based on the following formula:

$$C_{Na2EDTA} = \frac{V_{std} \times C_{std}}{V_{Na2EDTA} \times 100090}$$

Where:

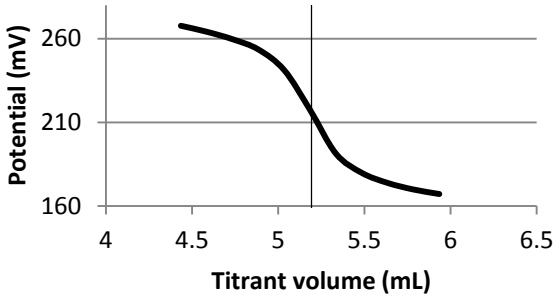
$C_{Na2EDTA}$:	Titrant concentration in mol/L
V_{std} :	Volume of calcium standard solution in mL
C_{std} :	Concentration of calcium standard solution in mg/L or ppm as $CaCO_3$
$V_{Na2EDTA}$:	Volume of Na_2EDTA at the equivalence point in mL

The calibration result can be accepted if five determinations give a result with a relative standard deviation of less than 1 %.

9.1.6. Example of titrant calibration

The results described below are indicative and obtained for a given titrant in optimized conditions respecting good laboratory practices. These indicative values are sample-dependent, electrode-dependent and operating cell-dependent.

Standard: 5 mL of $CaCl_2$ standard solution at 1000 mg/L as $CaCO_3$.
Temperature of analysis: Room temperature
Concentration of titrant: 0.00966 mol/L
SD: 0.00003 mol/L
RSD: 0.3 %
Titration curve:



9.2. Autoleveling calibration

This option is **ONLY** available from the calibration menu if **Method Leveling** is set to Active (**Yes**). Refer to the documentation delivered with the external pump for a correct installation, paying particular attention to the suction tube from the pump.

9.2.1. Example of titrant calibration

Name	Default parameter	Unit
Application		
Application name	Hardness in water	
Sample		
Min. amount	45	[mg/L]
Max. amount	110	[mg/L]
Leveling		
Active	Yes	
Time	30	[s]
Autoleveling calibration		
Solution name	$CaCl_2$	
Concentration	100	[mg/L]

At the end of the titration, the result is compared to the minimum and maximum sample amounts defined in the **Sample** section of the application editor.

- If the targeted sample volume is 50 mL, set **Max. amount** to 55 mL
- If the targeted sample volume is 100 mL, set **Min. amount** to 90 mL

The goal is to work with a sample volume between ± 10% of the recommended volume.

9.2.2. Standard preparation

For the determination of the remaining sample volume in the beaker after leveling, a titration of a standard with a known concentration is required. For this application, the determination is done with a $CaCl_2$ standard solution at 100 mg/L as $CaCO_3$.

For 1 L of standard solution, in a 1 L volumetric flask, accurately pour 100 mL of $CaCl_2$ standard solution at 1000 mg/L as $CaCO_3$ and complete to 1 L with deionized water.

For this standard concentration, the target is to consume about 5 mL of titrant for a sample volume of around 50 mL. For samples of 100 mL, it is recommended to prepare a solution at 50 mg/L as $CaCO_3$ (50 mL of $CaCl_2$ standard solution at 1000 mg/L as $CaCO_3$ in 1L of deionized water) to avoid the equivalence point detection on the top of the syringe.

Note: *It is important to set the standard concentration used in the* ***Concentration*** *field.*

9.2.3. Procedure

Pour a sufficient amount of the standard solution in a beaker that allows the external pump tube to be immersed in the liquid. In the calibration menu select **Autoleveling calibration** and then the application being used. For this application, the titration settings are the same as those used for Na_2EDTA calibration.

When the sequence is launched, the sample leveling is done and then the same titration as Na_2EDTA calibration is performed.

9.2.4. Result

At the end of the sequence, the result obtained is the volume remaining in the beaker after leveling. It is automatically written in the **Sample amount** field in the application editor and will be used in next titration calculations of the application.

$$V_{smp} = \frac{V_{titrant} \times C_{titrant}}{C_{Standard}} \times 100090$$

With:

V_{smp}:	Sample volume in mL
$C_{Standard}$:	Concentration of standard solution in mg/L as $CaCO_3$ (currently 100 mg/L or 50 mg/L depending on the targeted sample volume)
$C_{titrant}$:	Concentration of titrant in mol/L (currently Na_2EDTA 0.01 mol/L)
$V_{titrant}$:	Volume of titrant added for the titration in mL