Total Hardness of Water by Photocolorimetry

DOC316.52.93111

Based on ISO standard 6059-1984(F) & Standard Methods 2340C Hardness

Titrimetric Titration
0.05 to 4 mmol/L (Max. 8 mmol/L) of $CaCO_3$

1. Introduction

Total hardness of water is a colorimetric titration of water hardness, i.e. the sum of concentrations of calcium and magnesium ions, using disodium ethylenediamine tetraacetate (Na_2EDTA) titrant. This method applies to drinking, surface and industrial waste waters with the smallest level at 0.05 mmol/L (5 mg/L as $CaCO_3$) and up to 8 mmol/L (800 mg/L as $CaCO_3$). The method is not applicable to waters and effluent with high salt concentration like seawater.

2. Principle

Calcium and magnesium ions are sequestered upon addition of disodium ethylenediamine tetraacetate (Na_2EDTA).

The equivalence point of the reaction is detected using the Eriochrome Black T or Calmagite indicator, which turns red when in contact with calcium and magnesium in an alkaline medium at pH of 10.1 ± 0.1 and blue when cations are sequestered by EDTA.

After the sample is buffered to pH 10.1 (± 0.1), the indicator is added and forms a red complex with a portion of the calcium and magnesium in the sample. EDTA titrant reacts first with the free calcium and magnesium ions, then with those bound to the indicator, causing it to change to a blue color at the end point.

The sharpness of the end point increases with pH. However the pH cannot be increased indefinitely because of the danger of precipitating calcium carbonate $CaCO_3$ or magnesium hydroxide $Mg(OH)_2$ and because the dye changes color at high pH values. The specified pH 10.1 ± 0.1 is a satisfactory compromise.

The titration can be performed using either inflection point based determination titration or end point based determination titration (after optimization of the sample specific end point value by inflection point).

3. Electrode and reagents

Electrode: OPT300 Photocolorimetric probe
PTM450 Photocolorimetric module
Legacy adapter configured with the parameters that follow:

Parameter	Select Metal/RedOx/Color
Sensor Name	Enter the name of the sensor (e.g., OPT300)
Default Temperature	Enter the ambient temperature (e.g., 25°C or 77°F)

Titrant: Standard disodium ethylenediamine tetraacetate solution, Na_2EDTA, 0.01 M titrant. This product is commercially available from Hach

Buffer 10.1 ± 0.1 pH:

Solution preparation:

1. Dissolve 16.9 g of ammonium chloride in 143 mL of concentrated ammonium hydroxide (28-30% w/w; d_{20} = 0.910 g/mL). Commercially available from Hach
2. Add 1.25 g magnesium salt of EDTA. Commercially available from Hach
3. Dilute to 250 mL with distilled water. Commercially available from Hach

***Note**: The presence of magnesium salt with EDTA ($EDTANa_2Mg$) in the buffer increases symmetry of the titration curve and is mandatory for low magnesium concentration samples*

Storage: Store the solution in a polyethylene bottle for no longer than one month

Validation of the solution: Dilute 10 mL of the solution to 100 mL with water and control the pH. If the pH solution is not 10.1 ± 0.1 reject the initial solution

Note: *A pre-prepared buffer solution "Buffer Solution Hardness 1" is commercially available from Hach.*

Indicator: The ISO standard 6059-1984 recommends the use of **Eriochrome Black T** (Sodium salt of 1-(1-hydroxy-2-naphthylazo)-5-nitro-2-naphtolo-4-sulfuric acid, Number 203 in the Color index). This product is commercially available from Hach.

1. Dissolve 0.5 g of dye in 100 g 2,2'2''-nitrilotriethanol (triethanolamine) or 2-methoxymethanol (ethylene glycol monoethyl ether).

The alternative indicator **Calmagite Indicator** can be used. It is stable in aqueous solution and produces the same color change as Eriochrome Black T, with a sharper end point.

1. Dissolve 0.10 g in 100 mL of distilled water.

Note 1: *The potential of the colorimetric titration curve may drift due to the aging of the dye reagent solution.*

Note 2: *A pre-prepared indicator solution "ManVer® Hardness Indicator – Hardness 2" is commercially available from Hach.*

Deionized water

4. Working ranges

This application can be used with total hardness samples from 0.05 mmol/L to 4 mmol/L of $CaCO_3$ (maximum 8 mmol/L with one syringe refill).

As described in the standards, the best results with EDTA 0.01 mol/L are obtained when the total hardness of the sample needs a delivery of titrant inferior to the volume of one syringe. With the 10 mL syringe, select a volume of sample that requires less than 8.5 mL of EDTA titrant.

For **low hardness samples - less than 0.05 mmol/L (5 mg/L as $CaCO_3$)**: Take a larger sample of up to 150 mL and select the most appropriate beaker size for titration. Add a proportionately larger amount of buffer, inhibitor and indicator. For low hardness samples, may be necessary to do a blank titration using the same volume of distilled water as the sample. Subtract the volume of EDTA used for the blank from the volume of EDTA used for the sample by completing a titration with "Sample with blank" option.

For **high hardness samples – more than 2 mmol/L (200 mg/L as $CaCO_3$)**: Dilute the sample until the concentration is below 2 mmol/L for an initial volume of 50 mL of sample, and note the dilution factor.

5. Settings

The total hardness application has been developed and optimized using a 10 mL syringe, a solution of EDTA at 0.01 mol/L as titrant, an incremental addition mode and with a 610 nm wavelength with a decreasing curve.

Two applications are available with two different detection modes:

Name of application	Detection mode
IP Total Hardness	Inflexion point
EP Total Hardness	End point

All parameters are identical for both applications, except those specific to the inflection and end point detection (refer to section **5.2.8 Equivalent point**).

5.1. Total hardness determination

Name	Default parameters	Units
Application		
Application name	IP Total Hardness **or** EP Total Hardness	
Advisable syringe	10 mL (Hamilton)	
Sample		

Name	Water ? [1]	
Amount	25	[mL]
QC		
Name	QC Sample	
Electrode		
Type	mV	
Recommended electrode	OPT300	
Titrant: Na2EDTA 0.01 M		
Name	Na2EDTA	
Real concentration	0.01000	[mol/L]
Method: Leveling		
Active	No	
Method: Manual buffer addition		
Active	No	
Method: Automatic buffer addition		
Active	Yes	
Reagent	Buffer solution (pH 10.1)	
Pump ID	Pump 1	
Time	0.5	[s]
Stirring speed	25	[%]
Method: Manual indicator addition		
Active	Yes	
Time	180	[s]
Message	Add indicator (< 1200 mV) and press Skip	
Stirring speed	25	[%]
Method: Automatic indicator addition		
Active	No	
Method: IP Titration *or* ***Method: EP Titration***		
Active	Yes	
Stirring speed	25	[%]
Predose type	Volume	
Predose volume	0	[mL]
Delay	45	[s]
Max. vol. stop point	20	[mL]
Ordinate stop point	0	[mV]
Stop on last EQP	Yes	
Result 1 (R1) name	Total Hardness	
R1 hide	No	
R1 min.	0	[mmol/L]
R1 max.	10	[mmol/L]
R1 QC min.	0	[mmol/L]
R1 QC max.	10	[mmol/L]
Result 2 (R2) name	Total Hardness	
R2 hide	No	
R2 min.	0	[mg/L]
R2 max.	1000	[mg/L]
R2 QC min.	0	[mg/L]
R2 QC max.	1000	[mg/L]
Result 3 (R3) name	Total Hardness	
R3 hide	No	
R3 min.	0	[German degree]
R3 max.	1000	[German degree]
R3 QC min.	0	[German degree]

[1] "?" in the name, indicates that the instrument automatically increments the sample name with a number for each analysis

R3 QC max.	1000	[German degree]
R3 equation	R3 = R1*FX	
R3 unit	German degree	
R3 user value	5.61	

5.2. Recommendations for modifications of the settings

5.2.1. Sample amount

Select a sample volume that requires less than 8 mL of EDTA titrant. Typically, dilute 25.0 mL of sample to about 50 mL with distilled water. Refer to section **6.1.1 Sampling** for additional sampling recommendations.

5.2.2. Manual or automatic addition of buffer

By default, the pH 10.0 buffer is delivered by pump 1. Automatic addition of the buffer can be deactivated (**Active: No**) and manual addition of the buffer can be activated (**Active: Yes**). A message is then displayed to follow for manual addition: **Add pH 10.1 buffer solution and press OK** with stirring set at 25% by default.

5.2.3. Manual or automatic addition of indicator

By default, the indicator is added manually under stirring. Automatic addition of the indicator can be activated using Pump 2. The automatic mode is not recommended because of the quantity of dye to be added (a few drops).

5.2.4. Predose

To reduce the titration time, a predose followed by a delay can be set after preliminary tests. By default, the predose in volume is set at 0 mL. Settings have to be adjusted depending on the sample and the sample preparation. Make sure that the predose does not overshoot the end point by titrating the sample completely.

5.2.5. Delay

Depending on the sample, the delay before the titration can be adjusted. This delay guarantees the homogeneity of the solution after buffer and dye additions (by default 45 seconds).

5.2.6. Leveling

For a sample volume of 50 mL only, it is possible to use a leveling method. 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.

To define this volume, the autoleveling calibration sequence has to be previously executed (refer to section **11.2 Autoleveling calibration** and the User Manual).

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. Add the buffer and dye afterward.

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

5.2.7. Max. vol. stop point

Max. vol. stop point is set at 20 mL allowing one refill of the syringe and a total volume delivered of up to 20 mL to reach total hardness of up to 8 mmol/L (800 mg/L as Ca_2CO_3) with the appropriate sample volume.

5.2.8. Equivalent point

For applications based on inflexion detection (application **IP Total Hardness**):

	Setting	Unit
IP1 min. ordinate	0	[mV]
IP1 max. ordinate	950	[mV]

For applications based on end point detection (application **EP Total Hardness**):

	Setting	Unit
EP1 ordinate	450	[mV]

By default, a value is set at 450 mV but this value has to be adjusted by first performing a series of titrations based on the inflection point, to precisely determine the end point of the water being used.

The amount of dye (and buffer) used can drastically impact the electrode mV potential reading of the titration curve and can be responsible for the large up or down shift of the curve. In this case, the value of the end point has to be corrected.

5.2.9. Result

Result 1 (R1) gives the result of the total hardness in mmol/L. This result can be hidden (**Hide: Yes**) but must not be modified. The result is used in the equation for the calculation of result R3.

Result 2 (R2) returns the volume in mg/L as $CaCO_3$.

Result 3 (R3) allows the customer to automatically display the result in his working unit by adjusting **R3 min**, **R3 max**, **R3 unit** and **R3 user value**. Refer to the User Manual for additional information on settings and the table in section **7.1.2 Results calculation of total hardness in mg/L as CaCO3** for alternative units and the R3 user value list.

These results can be selectively hidden (**Hide: Yes**), refer to the User Manual for additional information.

6. Procedure

6.1. Sample analysis

6.1.1. Sampling

Indicative table for sample amount vs expected range of concentration:

Range mmol/L	Range mg/L as $CaCO_3$	Sampled Volume in mL	Added deionized water in mL
0.05 – 2	5 – 200	50	0
1.6 - 4	160 - 400	25	25
4 - 8	400 - 800	10	40

Note: *When necessary, modify the initial volume of sample (by default 25 mL) in the application settings (refer to the User Manual). The titrator will do the calculations automatically.*

6.1.2. Sample preparation

- **Buffer 10 pH addition:**

Standards provide the following recommendations for the buffer solution: add 1 to 2 mL of buffer solution per 50 ml of solution to be titrated. Usually, 1 mL is sufficient to give a pH of 10.0 to 10.1. Discard the buffer when 1 or 2 mL added to the sample fails to produce a pH of 10.1 ± 0.1 at the titration end point.

- **Indicator addition:**

The amount of dye added into the sample is critical for the analysis with a photocolorimetric sensor. The color of the resulting solution must not be too transparent or too opaque.

Standards also provide recommendations for the two common indicators: for Eriochrome Black T the addition of 2 drops per 50 mL of solution to be titrated, and for Calmagite indicator the addition of 1 mL per 50 mL of

solution to be titrated. However, this amount has to be carefully adapted to fit with the use of a photometric probe for the detection of the equivalent point (**Inflection point** or **End point**).

When the amount of dye is determined, always use the same quantity of dye for all the analysis. If the OPT300 or PTM450 setting changes, make sure that the amount of dye is correct for the new setting.

For optimal results, it is recommended to add an indicator to obtain an initial potential of around 1200 mV. This initial condition allows a titration curve with a large jump of potential, avoids saturation at the beginning, prevents a flattened curve at the end and limits wrong inflection point detection as described below.

Initial potential	Symptom	Cause	Risk	Possible solution
Ei > 1250 mV	The signal is saturated at 1250 mV	The concentration of dye in the sample is too low. The color of the sample is pale to very pale	As a part of the curve is missing, the EQP position can be wrong	Increase the amount of dye or increase sample dilution
1200 mV < Ei < 1250 mV	Warning message: “Measure out of range”	Potential is between the limit of the saturation at 1250 mV and the maximum potential allowed	None	Slightly increase the amount of dye
Ei < 300 mV	The curve is flattened	The concentration of dye is too high	EQP wrong or not detected	Decrease the amount of dye or adjust your sample volume before dilution
	A portion of the curve is missing => saturation of the lower part			
	No EQP is detected			

Note: *The complete titration has to be done within 5 minutes measured from the time of the buffer addition. This will minimize any tendency towards a $CaCO_3$ precipitation.*

6.1.3. Interferences

Some transition and heavy metals complex the indicator and prevent the color change at the end point.

Interfering substance	Interference levels and treatments
Acidity	Does not interfere at 10,000 mg/L (as $CaCO_3$)
Alkalinity	Does not interfere at 10,000 mg/L (as $CaCO_3$)
Aluminum	A 0.5 gram scoop of potassium cyanide* (commercially available from Hach) raises the permissible aluminum level to 1 mg/L.
Barium	Titrates directly
Cobalt	Interferes at all levels and must be absent or masked. A 0.5 gram scoop of potassium cyanide* (commercially available from Hach) removes interference from up to 100 mg/L cobalt
Copper	Interferes at levels of 0.10 and 0.20 mg/L. A 0.5 gram scoop of potassium cyanide* (commercially available from Hach) removes interference from up to 100 mg/L copper
Iron	Does not interfere up to 15 mg/L. Above this level it causes a red-orange to green end point which is sharp and usable up to 30 mg/L iron. Substitute a 0.0800 M CDTA (commercially available from Hach) or 0.800 M CDTA (commercially available from Hach) titration cartridge for the 0.0800 M Na_2EDTA or 0.800 M Na_2EDTA titration cartridges, respectively, if iron interference is probable
Manganese	Titrates directly up to 20 mg/L but masks the end point above this level. Adding a 0.1 gram scoop of hydroxylamine hydrochloride monohydrate (commercially available from Hach) raises this level to 200 mg/L manganese
Nickel	Interferes at all levels and must be absent or masked. A 0.5 gram scoop of potassium cyanide* (commercially available from Hach) removes interference from up to 100 mg/L nickel

Orthophosphate	Causes a slow end point
Polyphosphate	Polyphosphate must be absent for accurate results
Polyvalent metal ions	Although less common than calcium and magnesium, other polyvalent metal ions cause the same hardness effects and will be included in the results
Sodium chloride	Saturated sodium chloride solutions do not give a distinct end point, but the titration can be run directly on seawater
Strontium	Titrates directly
Zinc	Titrates directly. A 0.5 gram scoop of potassium cyanide* (commercially available from Hach) removes interference from up to 100 mg/L zinc
Highly buffered samples or extreme sample pH	May exceed the buffering capacity of the reagents and require sample pretreatment

*Metals masked with cyanide will not be included in the hardness result.

6.1.4. Analysis steps

1. Accurately take 25.0 mL of sample and dilute to approximately 50 mL by adding distilled water.
2. Dip the electrode and delivery tip in the sample. Press **Start**.
3. The embedded peristaltic pump automatically adds the appropriate amount of buffer.
4. Manually add the indicator by setting the measured potential to about 1200 mV. Press **Skip.**

The titration starts. The equivalent point is reached when the last shade of red has disappeared. The titrator monitors the evolution of potential linked to the color of the solution.

7. Results

7.1. Displayed Results

At the end of the titration the following results are automatically calculated:

1. Value of Total Hardness in mmol/L
2. Value of Total Hardness in mg/L as $CaCO_3$
3. Free unit for the customer (by default in German degree or °DH)

***Note**: These results can be selectively hidden, refer to the User Manual for additional information.*

7.1.1. Results calculation of total hardness in mmol/L

Based on ISO standard 6059-1984, the results are expressed in mmol/L following the equation:

$$\textbf{Total Hardness}_{\text{[mmol/L]}} = \frac{V_{titrant} \times C_{titrant} \times 1000}{V_{sample}}$$

$V_{titrant}$: Total volume of titrant in mL, delivered to reach the inflexion point of the end point
$C_{titrant}$: Titrant concentration in mol/L (currently 0.01 mol/L)
1000: Conversion factor from mol/L to mmol/L
V_{sample}: Sample volume taken (by default 25 mL)

7.1.2. Results calculation of total hardness in mg/L as $CaCO_3$

Total hardness is usually expressed in mg/L as $CaCO_3$. The result is expressed in this unit following the equation above. In this case, 1 equivalent of Na_2EDTA reacts with 1 equivalent of calcium or magnesium:

$$\textbf{Total Hardness}_{\text{[mg/L as CaCO3]}} = \frac{V_{titrant} \times C_{titrant}}{V_{sample}} \times 100.09 \times 1000$$

$V_{titrant}$: Total volume of titrant in mL, delivered to reach the inflexion point of the end point
$C_{titrant}$: Titrant concentration in mol/L (currently 0.01 mol/L)
V_{sample}: Sample volume taken (by default 25 mL)
100.09: Molecular weight of $CaCO_3$ in g/mol
1000: Conversion factor from g/L to mg/L

7.1.3. Alternative units

Depending on the country, many other units can be used to express the total hardness. Factors for the conversion from millimoles per liter are given in the table below (column R3 user value):

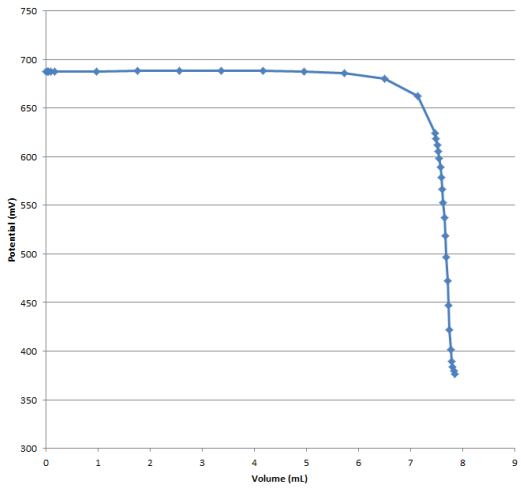
Total Hardness $_{[user\ unit]}$ **= FX x Total Hardness** $_{[mmol/L]}$

Unit name	Unit abbreviation	R3 user value (FX)	Comments
English Hardness	°Clark	7.02	1 degree of English Hardness (1° Clark) is the hardness corresponding to a content in $CaCO_3$ of 1 grain per imperial gallon, 14.3 mg/L or in molar concentration 0.143 mmol/L
German Hardness	°DH	5.61	1 degree of German Hardness (1° DH) is the hardness corresponding to a content of $(CaOH)_2$ (calcium oxide) of 10 mg/L or in molar concentration 0.178 mmol/L
French Hardness	°f	10	1 degree of French Hardness correspond to a content of $CaCO_3$ of 10 mg/L or in molar concentration 0.1 mmol/L
U.S. Hardness	ppm $CaCO_3$	100	In the USA, the hardness is expressed as ppm of $CaCO_3$ or as mg of $CaCO_3$ per liter. 1 mg/L of $CaCO_3$ corresponds to a molar concentration of 0.01 mmol/L

8. Examples of total hardness determination

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

- **Sample**: 25 mL of EVIAN mineral water with nominal concentration 307 mg/L as $CaCO_3$ (with Ca^{2+}: 80 mg/L and Mg^{2+}: 26 mg/L)$^{(*)}$ diluted approximately to 50 mL by adding distilled water. The addition of indicator (ManVer® Hardness Indicator – Hardness 2) and buffer 10.1 pH (Buffer solution Hardness 1).
- **Settings:** see values by default
- **Number of determinations**: 7
- **Temperature of analysis**: room temperature
- **Average value of TH**: 3.15 mmol/L
- **Standard deviation:** 0.01 mmol/L
- **Relative standard deviation:** 0.3 %
- **Titration curve:**



(*) It is possible to determine hardness by computing it from the separate determinations of calcium and magnesium. The hardness is calculated based on the following formula:

Hardness $_{mg\ equivalent\ CaCO3/L}$ **= 2.497 x [Ca]** $_{mg/L}$ **+ 4.118 x [Mg]** $_{mg/L}$

9. Bibliography

- International ISO standard ISO 6059-1984; Water quality – Determination of calcium and Magnesium – EDTA titrimetric method
- AWWA, APHA, and WEF. 1998. Standard Methods for the Examination of Water and Wastewater, 20th ed. Washington, DC: American Public Health Association. (Standard Methods 2340C Hardness)

10. Troubleshooting list

Symptom	Possible cause	Risk	Possible solution(s)
Warning message: "Measure out of range" and E > 1250 mV	The signal is saturated at 1250 mV. The concentration of dye in the sample is too low. The color of the sample is pale to very pale	As a part of the curve is missing, EQP position may be wrong	Increase the amount of dye or increase sample dilution
Small potential jump A portion of the curve is missing	The concentration of dye is too high	Wrong EQP or EQP not detected	Decrease the amount of dye
Not well specified potential jump (square shape)	The concentration of dye is too small	Not well specified EQP	Increase the amount of dye
Measured potential set at 0 mV	No power to the Module PTM450	No potential detection => titration lost	Check the power to the PTM450 Check the ON/OFF switch of the 610 nm LED
The volume of titrant is in line with those accepted but the result is wrong	The sample volume in the application is wrong	Wrong result for total alkalinity	Modify the volume of the sample (25 mL by default) to be in line with the actual sample taken
Unexpected variations of potential during titration	Bubbles in the optical pathway of the optode	Wrong result	Correct the position of the optode, control the stirring, make sure that no bubbles appear

11. Appendix: Titrant and autoleveling calibration

11.1. Titrant calibration

Solutions of EDTA are known to be very stable. Hach proposes EDTA solutions already controlled. However both total hardness applications (**IP Total Hardness** and **EP Total Hardness**) proposed a calibration method of the titrant. Standards recommend the use of standard calcium solution for titrant standardization containing $CaCl_2$.

11.1.1. Specific reagents

The titrant calibration has been developed by accurately taking 5 mL of a standard solution of $CaCl_2$ at 1000 mg/L as $CaCO_3$ diluted to 50 mL with deionized water. This should guarantee 5 mL of titrant delivery.

Preparation of standard calcium solution: Weigh 1.000 g of anhydrous $CaCO_3$ powder (primary standards or special reagent low in heavy metals, alkalis, and magnesium) into a 500 mL Erlenmeyer flask. Place a funnel in the flask neck and add, a little at a time 1 + 1 HCl until all the $CaCO_3$ has dissolved. Add 200 mL of distilled water and boil for a few minutes to expel any CO_2. Cool, add a few drops of methyl red indicator, and adjust to the intermediate orange color by adding 3N NH_4OH or 1 + 1 HCl as required. Transfer quantitatively and dilute to 1000 mL with distilled water; 1 mL = 1.00mg $CaCO_3$.

Commercial standard calcium solution: Commercial calcium chloride standard solution (1000 mg/L as $CaCO_3$) is available from Hach and can be used directly as the reference.

11.1.2. Settings

Calibration of the titrant has been developed for 610 nm wavelengths with decreasing curve dynamic incremental addition mode and an inflection point detection method with the parameters described below:

Name	Default parameters	Units
Application		
Application name	IP Total Hardness **or** EP Total Hardness	
Advisable syringe	10 mL (Hamilton)	
Electrode		
Type	mV	
Recommended electrode	OPT300	
Titrant: Na2EDTA 0.01 M		
Name	Na2EDTA	
Real concentration	0.01000	[eq/L]
Na2EDTA 0.01 M method: Manual buffer addition		
Active	No	
Na2EDTA 0.01 M method: Automatic buffer addition		
Active	Yes	
Reagent	Buffer solution (pH 10.1)	
Pump ID	Pump 1	
Time	0.5	[s]
Stirring speed	25	[%]
Na2EDTA 0.01 M method: Manual indicator addition		
Active	Yes	
Time	180	[s]
Message	Add indicator (< 1200 mV) and press Skip	
Stirring speed	25	[%]
Na2EDTA 0.01 M method: Automatic indicator addition		
Active	No	
Na2EDTA 0.01 M method: Titrant calibration		
Active	Yes	
Calibration frequency	0	[days]
Stirring speed	25	[%]
Predose type	Volume	
Predose volume	0	[mL]
Delay	45	[s]
Max. vol. stop point	8	[mL]
Ordinate stop point	0	[mV]
Stop on last EQP	Yes	
IP1 min. ordinate	0	[mV]
IP1 max. ordinate	950	[mV]
Min. titrant conc.	0.008	[mol/L]
Max. titrant conc.	0.012	[mol/L]
Standard name	CaCl2	
Standard amount	5	[mL]
Min. amount	4	[mL]
Max. amount	6	[mL]
Concentration	1000	[mg/L]
Molar weight	100.09	[g/mol]

11.1.3. Analysis steps

1. Accurately take 5.0 mL of standard calcium solution and dilute to approximately 50 mL by adding distilled water.
2. Dip the electrode and delivery tip in the sample. Press **Start**.
3. The embedded peristaltic pump automatically adds the appropriate amount of buffer.
4. Manually add the indicator by setting the measured potential at about 1200 mV. Press **Skip.**

The calibration starts. The equivalent point is reached when the last shade of red disappears. The titrator monitors the evolution of potential linked to the color of the solution.

11.1.4. Results of the titrant calibration

At the end of the titrant calibration, the real concentration is calculated and expressed in mol/L. The saved value will be used for the following total hardness determinations.

$$C_{EDTA,[mol/L]} = \frac{V_{standard} \times C_{standard} \times 0.001}{V_{titrant} \times 100.09}$$

$V_{standard}$:	Volume of Standard in mL (currently 5 mL)
$C_{standard}$:	Standard concentration in mg/L as $CaCO_3$ (currently 1000 mg/L)
0.001:	Conversion factor from mg/L to g/L
$V_{titrant}$:	Total volume of titrant in mL, delivered to reach the inflection point
100.09:	Molecular weight of $CaCO_3$ in g/mol

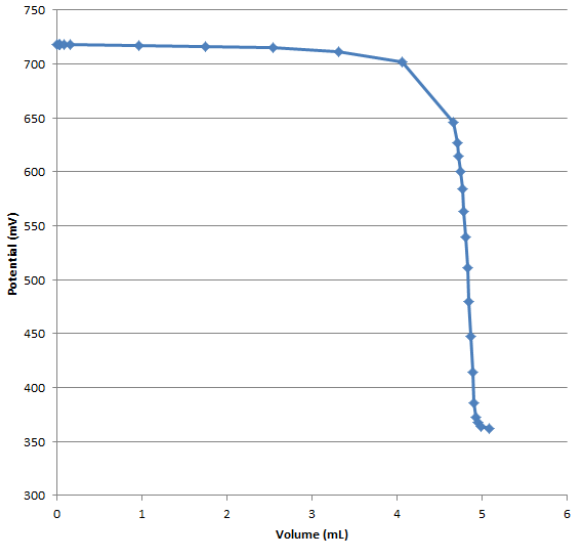
The calibration result can be accepted if 5 determinations give a result with a relative standard deviation of less than 0.5%.

11.1.5. Examples of titrant calibration

Results for 10 determinations in mol/L

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

- **Sample**: 5.0 mL of $CaCl_2$ solution at 1000 mg/L as $CaCO_3$ diluted to 50 mL. Addition of indicator ManVer® Hardness Indicator – Hardness 2) and buffer 10.1 pH (Buffer solution Hardness 1).
- **Settings:** see values by default
- **Number of determinations**: 5
- **Temperature of analysis**: room temperature
- **Average titer**: 0.01020 mol/L
- **Standard deviation:** 0.00002 mol/L
- **Relative standard deviation:** 0.2 %
- **Calibration curve:**



11.2. Autoleveling calibration

11.2.1. Principle

The aim of this method is to calibrate the volume of sample by leveling. The result of this calibration will be used as the sample volume for the following titrations.

Note: *This option is* ***only*** *available in the Calibration menu if* ***Method Leveling*** *is set as* ***Active*** *(=* ***Yes****) and requires an external pump commercially available from Hach.*

11.2.2. 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 $CaCO_3$ (commercially available from Hach) and complete to 1 L with deionized water.

11.2.3. Settings

Autoleveling calibration uses the same settings as those optimized for the titrant calibration described in section **11.1 Titrant calibration**, in particular the exchanged equivalent defined in the standard section of the titrant calibration and the same reagents. Specific settings used by default for leveling and autoleveling calibration are described below.

	Setting	**Units**
Application		
Application name	IP Total Hardness **or** EP Total Hardness	
Sample		
Min. amount	9	[mL]
Max. amount	55	[mL]
Method: Leveling		
Active	Yes	
Time	30	[s]
Autoleveling calibration		
Solution name	CaCl2	
Solution concentration	100	[mg/L]

11.2.4. Recommendations for modifications of the settings

The result of autoleveling calibration is compared to **Min. sample** and **Max. sample** amount defined in the application editor. By default, limits of acceptance for the volume of sample for both applications IP Total Hardness and EP Total Hardness are set respectively at 9 mL and 55 mL (refer to section: **6.1.1 Sampling**).

For both, leveling has to be used for a sample volume of 50 mL (without dilution) and “Sample Min. amount” has to be set at 45 mL if the “leveling” method is active. It is recommended to work with a sample volume of between ± 10% of the targeted sample amount.

11.2.5. Procedure

Pour a sufficient amount of the standard solution into a beaker allowing the external pump tube to be immersed in the liquid. In the calibration menu select **Autoleveling calibration** and then the application being used. Press **Start**.

The sample is leveled as a first step using the time set in the **Method: Leveling** section. For this application, the steps are the same as those in the titrant calibration described in section **11.1.3 Analysis steps**.

11.2.6. Results

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.

$$\mathbf{V_{sample}} = \frac{\mathbf{V_{titrant}} \times \mathbf{C_{titrant}}}{\mathbf{C_{Standard}}}$$

V_{sample}: Sample volume in mL
$C_{standard}$: Concentration of standard solution in mol/L (currently $CaCl_2$ at 100 mg/L as $CaCO_3$)
$C_{titrant}$: Concentration of titrant in mol/L (currently Na_2EDTA 0.01 mol/L)
$V_{titrant}$: Volume of titrant added for the titration in mL (for a targeted sample volume of 50 mL it should be close to 5 mL)