

# pH / Alkalinity / Hardness in Water

DOC316.52.93110

Based on the Determination of Langelier Index in Water settings

ISO 10523: 2008

ISO 6059: 1984

ISO 9963: 1994

Total Alkalinity and Ca Hardness: 10 - 1000 mg/L CaCO<sub>3</sub>

## 1. Introduction

This application is a combination of the determination of three different parameters on the same sample, in the same beaker: pH, alkalinity and hardness.

The aim of this application note is to describe how this application works, based on the description of the Langelier Index application note. The main difference between these two applications is in the results supplied after an analysis because two inflections are expected for both titrations, contrary to the Langelier Index determination.

## 2. Principle

In the same beaker, after a pH measurement, alkalinity of the sample is determined by a two end point titration by HCl 0.02 M up to 8.3 pH and 4.5 pH. Then a complexing buffer is automatically added through a pump and the hardness (Ca<sup>2+</sup> + Mg<sup>2+</sup>) is titrated by Na<sub>2</sub>EDTA 0.01 M.

## 3. Electrodes and reagents

**Electrodes:** Combined pH electrode with temperature sensor, IntelliCAL PHC805  
Calcium specific combined electrode, Ca<sup>2+</sup> I.S. Electrode 9660C  
Legacy adapter configured with the parameters that follow:

<b>Parameter</b>	Select ISE
<b>Sensor Name</b>	Enter the exact name of the sensor as programmed in the application (e.g., ISECa9660C). <i>Note: the sensor name is case sensitive.</i>
<b>Default Temperature</b>	Enter the ambient temperature (e.g., 25 °C or 77 °F)

**Titants:** Hydrochloric acid, HCl 0.02 mol/L solution in deionized water  
Disodic EDTA, Na<sub>2</sub>EDTA 0.01 mol/L solution in deionized water

**Hardness buffer:** TRIS (Tris(hydroxymethyl)aminomethane) 0.275 mol/L+ Acetylacetone 0.035 mol/L  
For 1 L of solution, in a 1 L volumetric flask, dissolve 33.3 g of TRIS in deionized water and add 3.5 g of acetylacetone. Complete up to 1 L with deionized water. Do not use this buffer for longer than one month

**Storage:** Calcium solution 0.1 mol/L (CaCl<sub>2</sub>) for ISE Ca electrode storage or activation if needed

**pH buffers:** Refer to [9.1 pH electrode calibration](#)

**Standards:** Refer to [9.2 HCl 0.02 mol/L calibration](#) and [9.3 Na<sub>2</sub>EDTA 0.01 mol/L calibration](#) for titrant solution calibrations

**Solvent:** Deionized water

## 4. Settings

### 4.1. pH / Alkalinity / Hardness determination

From the stirring part before the pH measurement, all parameters are the same as those used for the determination of the Langelier Index. The settings below about equivalence point detection and results replace existing ones of the Langelier Index application.

They have been defined with:

- Sample volume: 50 mL
- Titrant concentrations: 0.02 mol/L for HCl and 0.01 mol/L for Na<sub>2</sub>EDTA
- Syringe volumes: 10 mL for both titrants

Name	Default parameter	Unit
<b>Application</b>		
Application name	pH Alkalinity Hardness	
Advisable syringe	10 mL	
<b>Total Alkalinity</b>		
Predose type	None	
EP1 ordinate	8.3	pH
EP2 ordinate	4.5	pH
Result 1 (R1) name	p	
R1 hide	Yes	
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 Alkalinity	
R2 hide	Yes	
R2 min	0	mmol/L
R2 max	20	mmol/L
R2 QC min	0	mmol/L
R2 QC max	20	mmol/L
Result 3 (R3) name	p	
R3 hide	No	
R3 min	0	mg/L as CaCO <sub>3</sub>
R3 max	500	mg/L as CaCO <sub>3</sub>
R3 QC min	0	mg/L as CaCO <sub>3</sub>
R3 QC max	500	mg/L as CaCO <sub>3</sub>
R3 equation	R1*FX	
R3 unit	mg/L as CaCO <sub>3</sub>	
R3 user value	50	
Result 4 (R4) name	Total Alkalinity	
R4 hide	No	
R4 min	10	mg/L as CaCO <sub>3</sub>
R4 max	1000	mg/L as CaCO <sub>3</sub>
R4 QC min	10	mg/L as CaCO <sub>3</sub>
R4 QC max	1000	mg/L as CaCO <sub>3</sub>
R4 equation	R2*FX	
R4 unit	mg/L as CaCO <sub>3</sub>	
R4 user value	50	
<b>Hardness Ca</b>		
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.	10	mmol/L

Name	Default parameter	Unit
R1 QC min.	0	mmol/L
R1 QC max.	10	mmol/L
Result 2 (R2) name	Magnesium	
R2 hide	Yes	
R2 min.	0	mmol/L
R2 max.	10	mmol/L
R2 QC min.	0	mmol/L
R2 QC max.	10	mmol/L
Result 3 (R3) name	Calcium	
R3 hide	Yes	
R3 min.	0	mg/L
R3 max.	450	mg/L
R3 QC min.	0	mg/L
R3 QC max.	450	mg/L
R3 molar weight	40.08	g/mol
Result 4 (R4) name	Magnesium	
R4 hide	Yes	
R4 min.	0	mg/L
R4 max.	300	mg/L
R4 QC min.	0	mg/L
R4 QC max.	300	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.	10	mmol/L
R5 QC min.	0	mmol/L
R5 QC max.	10	mmol/L
R5 equation	R1 + R2	
R5 unit	mmol/L	
Result 6 (R6) name	Total Hardness	
R6 hide	No	
R6 min.	10	mg/L as CaCO <sub>3</sub>
R6 max.	1000	mg/L as CaCO <sub>3</sub>
R6 QC min.	10	mg/L as CaCO <sub>3</sub>
R6 QC max.	1000	mg/L as CaCO <sub>3</sub>
R6 equation	G1 * FX	
R6 unit	mg/L as CaCO <sub>3</sub>	
R6 user value	100	

#### 4.2. Recommendations for modification of settings

Mainly for analysis time reduction, some parameters can be adjusted. It must be noted, however, that the impact can be a loss of precision on the results.

##### 4.2.1. Sample amount

The sample amount is set at 50 mL by default. It has to be adjusted and changed in the editor, depending on the expected sample concentrations according to the following table:

<b>Sample volume / Titrant added (mg/L CaCO<sub>3</sub> of total alkalinity or Ca hardness)</b>	<b>0.50 mL</b>	<b>10 mL</b>	<b>20 mL</b>
<b>20 mL (qs 50 mL deionized water)</b>	25.0	500	1000
<b>25 mL (qs 50 mL deionized water)</b>	20.0	400	800
<b>50 mL</b>	10.0	200	400

##### 4.2.2. Predose

Predoses are defined in both titrations up to a certain ordinate with a titrant addition speed of 20 mL/min. For low equivalent volume for total alkalinity titration, the predose can be stopped over the fixed ordinate and lead

to a 0 mg/L result. That is why, in this case, it is recommended to deactivate the predose in ordinate for expected volumes lower than 5 mL. If in the analyzed sample, the equivalent volume is always lower than 5 mL, it is possible to set a predose in volume to reduce the analysis time.

#### 4.2.3. Leveling

It is possible to use a leveling method only for a sample volume of 50 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 (refer to [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.

#### 4.2.4. pH measurement

This application follows the ISO 10523: 2008 standard which recommends stirring the sample a few seconds and then measuring the pH without sample stirring. To perform the pH measurement with stirring, deactivate the method named **Sample homogenization** and set the required stirrer speed in the pH measurement section.

### 5. Procedure

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#### 5.1. Electrode / Titrant calibration

If the pH electrode, and/or titrants calibration, and/or autoleveling calibration is required, refer to [9 Appendix: pH electrode, titrants and autoleveling calibrations](#).

#### 5.2. Sample analysis

Pour the required sample amount (refer to table in section [4.2.1 Sample amount](#)) into a beaker. Complete to 50 mL with deionized water if needed. Add a stir bar and fix the beaker on the probe holder.

Start the application. The pH measurement is done according to ISO 10523: 2008. The sample is stirred for 15 s, and then the pH value is measured without stirring. The total alkalinity of the sample is determined by titration with HCl 0.02 mol/L up to pH 8.3 and pH 4.5. After addition of the buffer, the hardness ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) is finally measured in the same beaker.

### 6. Results

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#### 6.1. Displayed results

At the end of the sequence, the following results are displayed:

1. pH (pH)
2. Phenolphthalein alkalinity: p (mg/L as  $\text{CaCO}_3$ )
3. Total Alkalinity (mg/L as  $\text{CaCO}_3$ )
4. Total Hardness (mg/L as  $\text{CaCO}_3$ )

#### 6.2. Results calculation

Other results are calculated and stored:

##### 6.2.1. Alkalinity titration

- R1: p (mmol/L)

$$p = \frac{V_{1\text{eq}} \times C_{\text{HCl}}}{V_{\text{smp}}} \times 1000$$

- R2: Total Alkalinity (mmol/L)

$$\text{Total Alkalinity} = \frac{V_{2\text{eq}} \times C_{\text{HCl}}}{V_{\text{smp}}} \times 1000$$

- R3: p (mg/L as CaCO<sub>3</sub>)  $p = R1 \times FX$
- R4: Total Alkalinity (mg/L as CaCO<sub>3</sub>)  $Total\ Alkalinity = R2 \times FX$

Where:

- $C_{HCl}$ : Titrant concentration (mol/L)
- $V_{smp}$ : Sample volume (mL)
- $V_{1_{eq}}$ : Volume of titrant to reach 8.3 pH (mL)
- $V_{2_{eq}}$ : Volume of titrant to reach 4.5 pH (mL)
- FX: User value used for alkalinity unit conversion

Alkalinity unit	User value (FX)
mmol/L CaCO <sub>3</sub>	0.50
mg/L CaCO <sub>3</sub>	50
mg/L HCO <sub>3</sub> <sup>-</sup>	61
Parts/100 000	5
Clark degree	3.5
German degree	2.8
French degree	5
U.S. degree	2.9

When the user value is changed, the result unit has also to be manually modified to fit with the calculation.

### 6.2.2. Hardness titration

- R1: Calcium (mmol/L)  $Ca = \frac{V_{1_{Na2EDTA}} \times C_{Na2EDTA}}{V_{smp}} \times 1000$
- R2: Magnesium (mmol/L)  $Mg = \frac{(V_{2_{Na2EDTA}} - V_{1_{Na2EDTA}}) \times C_{Na2EDTA}}{V_{smp}} \times 1000$
- R3: Calcium (mg/L)  $Ca = \frac{V_{1_{Na2EDTA}} \times C_{Na2EDTA}}{V_{smp}} \times 40080$
- R4: Magnesium (mg/L)  $Mg = \frac{(V_{2_{Na2EDTA}} - V_{1_{Na2EDTA}}) \times C_{Na2EDTA}}{V_{smp}} \times 24310$
- R5 = G1: Total Hardness (mmol/L)  $TH = R1 + R2$
- R6: Total Hardness (mg/L as CaCO<sub>3</sub>)  $TH = G1 \times FX$

Where:

- $C_{Na2EDTA}$ : Titrant concentration (mol/L)
- $V_{smp}$ : Sample volume (mL)
- $V_{1_{Na2EDTA}}$ : Volume of titrant to reach the first equivalent point (mL)
- $V_{2_{Na2EDTA}}$ : Volume of titrant to reach the second equivalent point (mL)
- FX: User value used for total hardness unit conversion

Total hardness unit	User value (FX)
°DH	5.61
°Clark	7.02
°f	10
ppm or mg/L as CaCO <sub>3</sub>	100

When the user value is changed, the result unit has also to be manually modified to fit with the calculation.

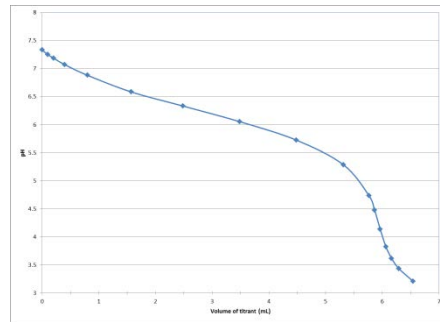
## 7. Examples of pH alkalinity and hardness determinations

The results described below are indicative and obtained for a given water type in optimized conditions respecting Good Laboratory Practices. These indicative values are sample-dependent, electrode-dependent and operating cell-dependent.

### 7.1. pH alkalinity determination of mineral water (pHi < 8.3)

Results for 5 determinations in milliequivalents/L:

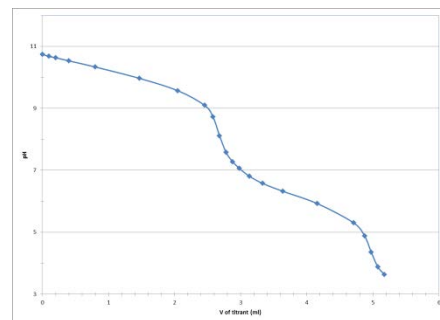
- **Sample:** 100 mL of mineral water. Nominal concentration: 296 mg/L as CaCO<sub>3</sub>
- **Settings:** see values by default
- **Number of determinations:** 10
- **Temperature of analysis:** room temperature
- **Mean value of Total Alkalinity:** 5.940 mmol/L
- **Standard deviation:** 0.001 mmol/L
- **Relative standard deviation:** 0.02%
- **Curve pH versus volume of titrant:**



### 7.2. pH alkalinity determination of water with pHi > 8.3 and high alkalinity

Results for 10 determinations in milliequivalents/L:

- **Sample:** 100 mL of Na<sub>2</sub>CO<sub>3</sub> solution Nominal concentration: 250 mg/L as CaCO<sub>3</sub>
- **Settings:** see values by default
- **Number of determinations:** 10
- **Temperature of analysis:** room temperature
- **Mean value of Total Alkalinity:** 5.001 mmol/L
- **Standard deviation:** 0.013 mmol/L
- **Relative standard deviation:** 0.26%
- **Curve pH versus volume of titrant:**



### 7.3. Examples of hardness determination

**Example 1:** For 5 determinations on Geneva tap water

- Mean: 1.37 mmol/L or 137 mg/L CaCO<sub>3</sub>
- Relative standard deviation: 0.6%

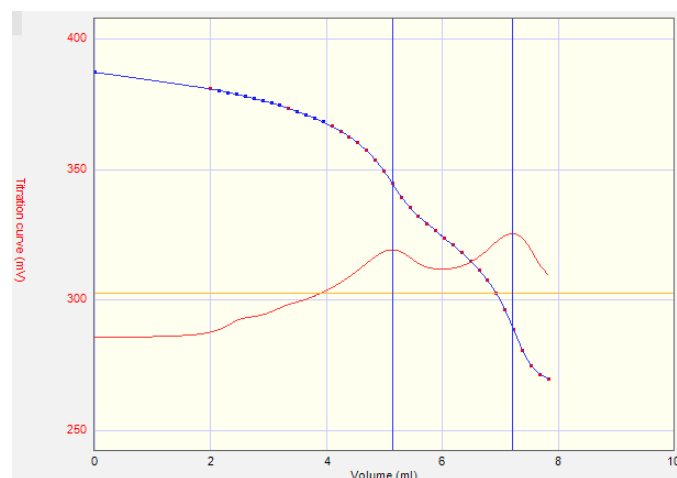
**Example 2:** For 5 determinations on 50 mL mineral water (manufacturer data: 80 mg/L Ca<sup>2+</sup> and 26 mg/L Mg<sup>2+</sup>)

- Mean: 83.4 mg/L Ca<sup>2+</sup> and 25.8 mg/L Mg<sup>2+</sup>
- Relative standard deviation: 1.9% on Ca<sup>2+</sup> and 2.4 % on Mg<sup>2+</sup> and 1 % on the total volume

**Example 3:** For 10 determinations on 50 mL of a Ca standard solution at 80.2 mg/L (0.002 M)

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

**Curve example of hardness determination**



## 8. Bibliography

- ISO 10523:2008 *Water quality – Determination of pH*
- ISO 9963:1994 *Water quality – Determination of alkalinity*

- ISO 6059:1984 *Water quality – Determination of the sum of calcium and magnesium – EDTA titrimetric method*

## 9. Appendix: pH electrode, titrants and autoleveling calibrations

To increase the accuracy of the Langelier Index determination, it is recommended to perform a pH electrode calibration every week. For the titrants, it is recommended to calibrate them after a bottle change or after a long storage time.

### 9.1. pH electrode calibration

#### 9.1.1. Electrode and buffers

**Electrode:** Combined pH electrode with temperature sensor, IntelliCAL PHC805.

**pH standards:** IUPAC pH 1.68, pH 4.01, pH 7.00, pH 10.01 and pH 12.45 are set by default. It is possible to change these according to your SOP (refer to the full user manual for details).

#### 9.1.2. Electrode calibration settings

By default the electrode calibration is done with the parameters described below:

Name	Default parameter	Unit
<b>Application</b>		
Application name	Langelier Index	
<b>Electrode</b>		
Type	pH	
Recommended electrode	PHC805	
Calibration frequency	7	days
Stability criterion	0.050	pH/min
Max. stability time	300	seconds
Stirring speed	25	%
Stirring duration	15	seconds
Calibration mode	Auto	
Buffer set	IUPAC 1.68, 4.01, 7.00, 10.01, 12.45	

**Note:** The parameters are defined to calibrate the electrode following the ISO 10523:2008 standard which recommends stirring the buffer before the measurement, and to stop stirring during measurement. If your SOP requires stirring during the measurement process, set the **Stirring duration** to 0 s.

#### 9.1.3. Electrode calibration procedure

It is recommended to calibrate the electrode at a temperature close to the sample temperature.

Pour a sufficient amount of buffer into a beaker so that the electrode dips into the solution. Add a magnetic stir bar and launch the calibration sequence. Rinse the electrode between each buffer. The electrode can be calibrated with up to five different buffers.

#### 9.1.4. Calibration results

At the end of the series of buffers, the following results are displayed:

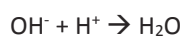
- Slope in mV/pH
- Slope in % compared with the theoretical slope (-59.16 mV/pH)
- Offset in mV

The acceptance limits for the PHC805 electrode for the slope are 97-102% and between -30 and +30 mV for the offset.

## 9.2. HCl 0.02 mol/L calibration

### 9.2.1. Principle

The strong acid used as titrant has to be calibrated with NaOH which reacts with H<sup>+</sup> ions according to:



### 9.2.2. Electrode and reagents

**Electrode:** Combined pH electrode with temperature sensor, IntelliCAL PHC805  
**Titrant:** Hydrochloric acid, HCl 0.02 mol/L solution in deionized water (commercially available)  
**Standard:** Sodium hydroxide, NaOH 0.02 mol/L solution in deionized water (commercially available)  
**Deionized water**

As the standard solution absorbs carbon dioxide from the atmosphere, carbonate species are formed and other inflection points can appear. This phenomenon leads to bad calibrations due to the presence of more than one inflection point on the titration curve (refer to the warning message at the end of the calibration). In these conditions, the sodium hydroxide solution should not be used for titrant calibration.

If commercially available standard is not used, NaOH solutions have to be prepared with freshly boiled deionized water and not exposed to ambient air. Freshly prepared solutions have to be used straight away for calibration and carefully stored in a polythene flask between calibrations. To limit the carbonation during storage, minimize the head space volume.

### 9.2.3. Settings

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

Name	Default parameter	Unit
<b>Application</b>		
Application name	Langelier Index	
<b>Electrode</b>		
Recommended electrode	PHC805	
<b>Titrant: HCl 0.02 M</b>		
Name	HCl	
Nominal concentration	0.02	mol/L
<b>HCl 0.02 M method: HCl Calibration</b>		
Active	Yes	
Calibration frequency	0	days
Stirring speed	25	%
Predose type	Volume	
Predose volume	3	mL
Delay	5	seconds
Max. vol. stop point	7	mL
Ordinate stop point	2.0	pH
Stop on last EQP	Yes	
IP1 min. ordinate	4.5	pH
IP1 max. ordinate	8.5	pH
Min. titrant conc.	0.0180	mol/L
Max. titrant conc.	0.0220	mol/L
Standard name	NaOH	
Standard amount	5	mL
Min. amount	4	mL
Max. amount	6	mL
Concentration	0.0200	mol/L



### Inflection points detection and result acceptance

The degradation of the standard solution of NaOH can easily and quickly appear and lead to bad results for calibrations. To prevent this situation, the detection range of the inflection point and stop conditions have been optimized to validate the status of the standard solution through a possible multiple IP detection. Therefore, it is not recommended to modify the settings described below.

The **Stop after last EQP** field is selected as **No** to make sure that the titration will not be stopped at the first IP detection and will not hide the other(s) if they exist. The **Max. vol. stop point** being at 7 mL, the titration will always stop at this volume. For the same reason the **IP1 min. ordinate** and **IP1 max. ordinate** fields are set respectively at 4.5 pH and 8.5 pH.

With these settings, at the end of a standard titration, if an EQP has been found and if there is no warning regarding the number of IPs detected, the result is considered as reliable. Otherwise, if the message **More than one IP has been found for this expected IP** appears, it is recommended to reject the result and perform another titration. If it there is no improvement, it is better to prepare a fresh standard solution.

#### 9.2.4. Procedure

Accurately measure 5 mL of NaOH 0.02 mol/L solution, and put it in a beaker. Add a sufficient amount of deionized water to cover the electrode and the delivery tip with solution. Put in a magnetic stir bar and place the beaker on the titrator. Dip the electrode and delivery tip into the solution. Launch the titrant calibration sequence.

#### 9.2.5. Result

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

$$C_{\text{HCl}} = \frac{V_{\text{NaOH}} \times C_{\text{NaOH}}}{V_{\text{HCl}}}$$

Where:

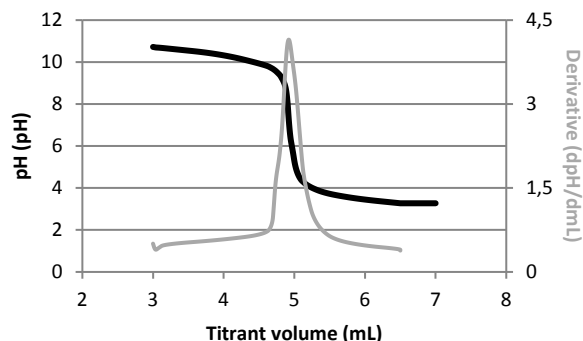
- $C_{\text{HCl}}$ : Titrant concentration in mol/L
- $V_{\text{NaOH}}$ : Volume of standard solution (NaOH) in mL
- $C_{\text{NaOH}}$ : Concentration of standard solution (NaOH) in mol/L
- $V_{\text{HCl}}$ : Volume of HCl at the equivalence point in mL

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

#### 9.2.6. Example of titrant calibration on five determinations

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.

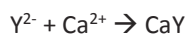
**Standard:** 5 mL of 0.0200 mol/L NaOH solution  
**Temperature of analysis:** Room temperature  
**Concentration of titrant:** 0.0204 mol/L  
**SD:** 0.0002 eq/L  
**RSD:** 0.89 %  
**Titration curve:**



### 9.3. Na<sub>2</sub>EDTA 0.01 mol/L calibration

#### 9.3.1. Principle

The Na<sub>2</sub>EDTA used as titrant for hardness determination has to be calibrated with Ca<sup>2+</sup> solution. The standard used is a solution of CaCl<sub>2</sub> at 1000 mg/L as CaCO<sub>3</sub>.



#### 9.3.2. Electrode and reagents

**Electrode:** Calcium specific combined electrode, Ca<sup>2+</sup> I.S. Electrode 9660C

**Titrant:** Disodic EDTA, Na<sub>2</sub>EDTA 0.01 mol/L solution in deionized water

**Standard:** CaCl<sub>2</sub> solution at 1000 mg/L as CaCO<sub>3</sub>

**Deionized water**

#### 9.3.3. Settings

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

Name	Default parameter	Unit
<b>Application</b>		
Application name	Langelier Index	
Advisable syringe	10 mL	
<b>Electrode</b>		
Recommended electrode	ISECa9660C	
<b>Titrant: Na<sub>2</sub>EDTA 0.01 M</b>		
Name	Na <sub>2</sub> EDTA	
Nominal concentration	0.01	mol/L
<b>Na<sub>2</sub>EDTA 0.01 M method: Manual buffer addition</b>		
Active <sup>1</sup>	No	
<b>Na<sub>2</sub>EDTA 0.01 M method: Automatic buffer addition</b>		
Active <sup>1</sup>	Yes	
Reagent	Buffer addition – 20 mL	
Pump ID	Pump 1	
Time	7	seconds
Stirring speed	0	%
<b>Na<sub>2</sub>EDTA 0.01 M method: Calibration</b>		
Active	Yes	
Calibration frequency	0	days
Stirring speed	25	%
Predose type	Ordinate	
Predose ordinate	300	mV
Predose speed	20	mL/min
Delay	5	seconds
Max. vol. stop point	8	mL
Ordinate stop point	150	mV
Stop on last EQP	Yes	
Min. increment size	0.02	mL
Max. increment size	0.8	mL
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 <sub>2</sub>	
Standard amount	5	mL
Min. amount	4	mL
Max. amount	6	mL

<sup>1</sup> Only one of these two fields must be set to "Yes"

Name	Default parameter	Unit
Concentration	1000	mg/L
Molar weight	100.09	g/mol

#### 9.3.4. Procedure

Accurately measure 5 mL of CaCl<sub>2</sub> 1000 mg/L as CaCO<sub>3</sub> standard solution and put it 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.

#### 9.3.5. Result

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

$$C_{\text{Na}_2\text{EDTA}} = \frac{V_{\text{std}} \times C_{\text{std}}}{V_{\text{Na}_2\text{EDTA}} \times 100090}$$

Where:

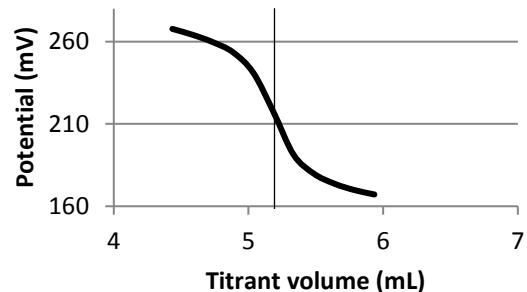
$C_{\text{Na}_2\text{EDTA}}$ :	Titrant concentration in mol/L
$V_{\text{std}}$ :	Volume of calcium standard solution in mL
$C_{\text{std}}$ :	Concentration of calcium standard solution in mg/L or ppm as CaCO <sub>3</sub>
$V_{\text{Na}_2\text{EDTA}}$ :	Volume of Na <sub>2</sub> EDTA at the equivalence point in mL

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

#### 9.3.6. 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<sub>2</sub> standard solution at 1000 mg/L as CaCO<sub>3</sub>.  
**Temperature of analysis:** Room temperature  
**Concentration of titrant:** 0.00966 mol/L  
**SD:** 0.00003 mol/L  
**RSD:** 0.3 %  
**Titration curve:**



### 9.4. 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.

#### 9.4.1. Settings

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.

For this application, leveling is usable only for a sample volume of 50 mL so **Sample min. amount** has to be set to **45 mL** instead of 20 mL if **Method Leveling** is set to Active (**Yes**). It is recommended to work with a sample volume between ± 10% of the targeted sample amount.

Name	Default parameter	Unit
<b>Application</b>		
Application name	Langelier Index	
Advisable syringe	10 mL	
<b>Sample</b>		
Min. amount	20	mL
Max. amount	55	mL
<b>Leveling</b>		
Active	Yes	
Time	30	seconds
<b>Autoleveling calibration</b>		
Solution name	NaOH	
Concentration	0.00200	mol/L

#### 9.4.2. 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 0.002 mol/L NaOH solution.

For 1 L of standard solution, in a 1 L volumetric flask, accurately pour 100 mL of 0.02 mol/L NaOH standard solution and complete to 1 L with freshly boiled deionized water.

#### 9.4.3. 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 HCl calibration.

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

#### 9.4.4. 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 the next titration calculations of the application.

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

Where:

$V_{\text{smp}}$ :	Sample volume in mL
$C_{\text{Standard}}$ :	Concentration of standard solution in mol/L (currently NaOH 0.002 mol/L)
$C_{\text{titrant}}$ :	Concentration of titrant in mol/L (currently HCl 0.02 mol/L)
$V_{\text{titrant}}$ :	Volume of titrant added for the titration in mL (for a targeted sample volume of 50 mL it should be close to 5 mL)

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