pH Alkalinity of Water

DOC316.52.93085

Based on ISO standard 9963-1:1994

pH-metric Titration
0.4 to 20 mmol/L of Total Alkalinity

1. Introduction

The alkalinity of water is its acid-neutralizing capacity. It is the sum of all the titratable bases. For many surface waters, alkalinity values are primarily a function of carbonate, bicarbonate, and hydroxide content. The measured values also may include contributions from borates, phosphates, silicates or other bases if these are present.

Alkalinity is determined by end point titration with a strong acid solution. Phenolphthalein alkalinity abbreviated by "**p**" is also known as composite alkalinity which corresponds to titratable alkalinity at pH 8.3. Total alkalinity is also known as methyl red (methyl orange) endpoint alkalinity which corresponds to titratable alkalinity at pH 4.5.

This application note is based on ISO standard 9963-1:1994 (Water quality – Determination of alkalinity – Part 1: Determination of total and composite alkalinity).

2. Principle

The phenolphthalein end point alkalinity or composite alkalinity abbreviated by "**p**" is the measurement by titration to the phenolphthalein end point (pH 8.3) of that portion of alkalinity arbitrarily attributed to all the hydroxyl $c(OH^-)$ and half the carbonate ($CaCO_3$) content of water.

$$p \approx c(CO_3^{2-}) - c(CO_{2aq}) + c(OH^-) - c(H^+) + c(*)$$

The methyl red (methyl orange) end point alkalinity is an arbitrary measurement of the total alkalinity of water, abbreviated "TA", and is obtained by titration to the methyl red (methyl orange) indicator endpoint (pH 4.5) to assess the equivalent hydrogen carbonate (HCO_3^-), carbonate ($CaCO_3$) and hydroxide (OH^-) concentration of water.

$$TA \approx 2\, c(CO_3^{2-}) + c(HCO_3^-) + c(OH^-) - c(H^+) + c(*)$$

Note: *In both cases, other buffering substances (*) such as ammonia, borate, phosphate silicate and organic anions may be included in the determination.*

The number of detected equivalent points depends on the initial pH of the solution. By definition, "**p**" is zero for water which has a pH value of 8.3 or less.

The current standard uses HCl 0.1 eq/L as a titrant, but another strong acid such as H_2SO_4 0.1 eq/L can also be used. Results are normally expressed as mmol/L (or meq/L) of "alkalinity" but other units can be used (see section **7 Results**). Using an appropriate combined pH electrode with temperature sensor, the alkalinity determination can be linked with a pH and temperature measurement of the sample.

3. Electrode and reagents

Electrode: PHC805, Intellical combined pH electrode with temperature sensor

Titrant: HCl or H_2SO_4 0.1 eq/L solution in deionized water

Solvent: Deionized water

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4. Working ranges

In accordance with the norm ISO 9963-1, the previous configuration with 0.1 eq/L of titrant HCl or H_2SO_4, 10 mL syringe is done for a Total Alkalinity between 0.4 mmol/L (20 mg/L $CaCO_3$) corresponding to 0.4 mL of titrant 0.1 eq/L and 20 mmol/L (1000 mg/L $CaCO_3$) corresponding to 20 mL of titrant 0.1 eq/L.

For **the best accuracy and reproducibility**, the result range is between 3.5 meq/L or 175 mg/L $CaCO_3$ for 35% of the cylinder 10 mL syringe capacity and 10 meq/L or 500 mg/L $CaCO_3$ for the cylinder 10 mL syringe capacity. With the same conditions, the "experimental" limit corresponding to a titrant volume of 0.5 mL is 0.5 meq/L or 25 mg/L $CaCO_3$.

For **low alkalinity,** below 0.5 mmol/L or 25 mg/L $CaCO_3$ (corresponding to 0.5 mL of titrant 0.1 eq/L), it is recommended to use a low alkalinity method with 0.02 eq/L titrant and 200 mL for sample volume, using the calculation above.

For **high alkalinity**, between 10 mmol/L (500 mg/L $CaCO_3$) and 20 mmol/L (1000 mg/L $CaCO_3$) it is recommended to use smaller sample volumes (less than 50 mL) with the same titrant 0.1 eq/L.

5. Settings

pH alkalinity applications have been developed and optimized using a 10 mL syringe, an acidic solution at 0.1 eq/L (HCl: 0.1 mol/L or H_2SO_4 0.05 mol/L) as titrant, with an incremental addition mode and end point detections.

Three applications are available with different titrants and standard for the titrant calibration

Name of application	Titrant	Standard for calibrations
pH Alkalinity HCl(Borax)	HCl	Borax
pH Alkalinity HCl(NaOH)	HCl	NaOH
pH Alkalinity H2SO4(NaOH)	H_2SO_4	NaOH

All parameters in the table below are identical for the three applications. Specifics for titration results are described in section **5.2.8 Result** and specifics on titrant calibration are described in section **10 Appendix: Electrode, titrant and autoleveling calibrations**.

5.1. pH Alkalinity determination

Name	Default parameters	Units
Application		
Application name	pH Alkalinity HCl(Borax)	
Advisable syringe	10 mL (Hamilton)	
Sample		
Name	Water ? [1]	
Amount	100	[mL]
QC		
Name	QC Sample	
Electrode		
Type	pH	
Recommended electrode	PHC805	
Titrant: HCl 0.1 N		
Name	HCl	
Real concentration	0.1000	[eq/L]
Method: Leveling		
Active	No	
Method: Sample homogenization		
Active	Yes	
Time	15	[s]
Stirring speed	25	[%]
Message	Sample homogenization. Please wait…	
Method: pHi		
Active	Yes	

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

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Max. stability time	120	[s]
Stability criterion	0.050	[pH/min]
Stirring speed	0	[%]
Result 1 (R1) name	pHi	
R1 hide	No	
R1 min.	0	[pH]
R1 max.	14	[pH]
R1 QC min.	0	[pH]
R1 QC max.	14	[pH]
Method: Alkalinity		
Active	Yes	
Measured parameter	pH	
Predose type	Volume	
Predose	0	[mL]
Max. vol. stop point	20	[mL]
Ordinate stop point	3.4	[pH]
Stop on last EQP	Yes	
Delay	0	[s]
Stability criterion	17000	[mpH/min]
Min. increment size	0.1	[mL]
Max. increment size	1.0	[mL]
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]
R1 EQP index	1	
Result 2 (R2) name	Total Alkalinity	
R2 hide	Yes	
R2 min.	0.4	[mmol/L]
R2 max.	20	[mmol/L]
R2 QC min.	0.4	[mmol/L]
R2 QC max.	20	[mmol/L]
R2 EQP index	2	
Result 3 (R3) name	p	
R3 hide	No	
R3 min.	0	[mg/L as $CaCO_3$]
R3 max.	500	[mg/L as $CaCO_3$]
R3 QC min.	0	[mg/L as $CaCO_3$]
R3 QC max.	500	[mg/L as $CaCO_3$]
R3 equation	R1*FX	
R3 unit	mg/L as $CaCO_3$	
R3 user value	50	
Result 4 (R4) name	Total Alkalinity	
R4 hide	No	
R4 min.	20	[mg/L as $CaCO_3$]
R4 max.	1000	[mg/L as $CaCO_3$]
R4 QC min.	20	[mg/L as $CaCO_3$]
R4 QC max.	1000	[mg/L as $CaCO_3$]
R4 equation	R2*FX	
R4 unit	mg/L as $CaCO_3$	
R4 user value	50	

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5.2. Recommendations for modifications of the settings

5.2.1. Sample amount

The sample amount and titrant concentration depends on the quality of the water; see section **4 Working ranges** for additional information.

5.2.2. Sample homogenization and initial pH measurement

This application follows the standard ISO 10523: 2008 which recommends stirring the sample for a few seconds and then measuring the pH of the sample without stirring (in *Method: pHi*, **Stirring speed = 0%**). This initial method of stirring can be deactivated (*Method: Stirring,* **Active: No**) and the stirring speed during the pH measurement set to 25% as the advised stirring speed (in *Method: pHi*, **Stirring speed = 25%**).

5.2.3. Predose

To reduce the titration time, a predose (by default, the predose in volume is set at 0 mL) followed by a delay of at least 5 seconds can be set after preliminary tests. Settings have to be adjusted depending on the sample and the sample preparation. Ensure that the predose does not overshoot the end point by completely titrating the sample.

5.2.4. Delay

Depending of the sample, the delay prior to the titration can be adapted. This delay guarantees the homogeneity of the solution after buffer and dye additions. By default, this is set at 0 seconds.

5.2.5. Leveling

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 **10.4 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.*

5.2.6. Max. vol. stop point

“Max. vol. stop point” set at 20 mL allows one refill of the syringe and a total volume delivered of up to 20 mL to reach 20 mmol/L of total alkalinity with the appropriate sample volume and titrant concentration.

5.2.7. End point values

The values of phenolphthalein alkalinity (p) at pH 8.3 and total alkalinity at pH 4.5 can be modified in the titration program depending on the sample.

Test condition	End point pH	
	Total Alkalinity	Phenolphthalein Alkalinity
Alkalinity, 30 mg $CaCO_3$/L	4.9	8.3
Alkalinity, 150 mg $CaCO_3$/L	4.6	8.3
Alkalinity, 500 mg $CaCO_3$/L	4.3	8.3
Silicates, phosphates known or suspected	4.5	8.3
Routine or automated analyses	4.5	8.3
Industrial waste or complex system	4.5	8.3

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5.2.8. Result

Four results are calculated at the end of the titration.

- **Result 1 (R1)** corresponds to the phenolphthalein alkalinity (abbreviated to p), and uses the coordinates of the end point with EQP index at 1 corresponding to 8.3 pH
- **Result 2 (R2)** corresponds to the total alkalinity, and uses the coordinates of the end point with EQP index at 2 corresponding to 4.5 pH

For results R1 and R2, only the ***Name*** and the ***R1*** *or* ***R2 max. resolution*** fields can be modified. R1 and R2 have to be expressed in mmol/L in order to have the correct results for R3 and R4 as results of the equation.

- **Result 3 (R3)** corresponds to the phenolphthalein alkalinity abbreviate p expressed by default in mg/L as $CaCO_3$ with the User Value set at 50
- **Result 4 (R4)** corresponds to the Total Alkalinity expressed by default in mg/L as $CaCO_3$ with the User Value set at 50

For results R3 and R4, the ***R3*** *or* ***R4 max. resolution, R3*** *or* ***R4 min, R3*** *or* ***R4 max, R3*** *or* ***R4 unit*** and ***R3*** *or* ***R4 user value*** fields can be modified to express the results in alternative units using the ***R3*** *or* ***R4 user value*** from mmol/L following the table in section **7.1.2 Alternative units**.

The three applications have been developed taking account of the exchanged equivalents by the titrant as summarized in the table below:

Name of application	Titrant	Sample equivalents	Titrant equivalents
pH Alkalinity HCl(Borax)	HCl	1	1
pH Alkalinity HCl(NaOH)	HCl	1	1
pH Alkalinity H2SO4(NaOH)	H_2SO_4	1	2

6. Procedure

6.1. Sample analysis

6.1.1. Sampling

This standard can be used with natural, drinking and waste waters with TA between 0.4 and 20 mmol/L. The sample must not be filtered, diluted, concentrated or altered in any way. Avoid excessive agitation and prolonged exposure to air. Samples should be analyzed as soon as possible after collection but can be stored at least 24 hours by cooling to 4 °C or below. Warm the sample to room temperature before analyzing.

6.1.2. Sample preparation

Pipette 100 mL of water into the 150 mL plastic beaker.

6.1.3. Analysis step

Dip the electrode and delivery tip in the sample. Press **Start**.

7. Results

7.1. Displayed Results

At the end of the titration the following results are available:

1. Value of pHi
2. Value of p in mg/L as $CaCO_3$ (volume of titrant in mL to reach defined pH, 8.3 pH by default)
3. Value of total alkalinity in mg/L as $CaCO_3$ (volume in mL to reach defined pH, 4.5 pH by default)

Note: *Results in mmol/L are calculated, but by default they are hidden in the result screen. However, they are available in the Data Log (refer to the User Manual for additional information).*

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7.1.1. Results calculation of alkalinity in mmol/L

The results are normally expressed in **mmol/L** of alkalinity as described by the following relations with the default settings:

$$\textbf{R1 or p}_{[mmol/L]} = \frac{V_{titrant} \times C_{titrant} \times 1000}{V_{sample}}$$

$V_{titrant}$: Total volume of titrant in mL, delivered to reach the end point at 8.3 pH
$C_{titrant}$: Titrant concentration in eq/L (currently 0.1 eq/L)
V_{sample}: Volume of the sample (currently 100 mL)

$$\textbf{R2 or Total Alkalinity}_{[mmol/L]} = \frac{V_{titrant} \times C_{titrant} \times 1000}{V_{sample}}$$

$V_{titrant}$: Total volume of titrant in mL, delivered to reach the end point at 4.5 pH
$C_{titrant}$: Titrant concentration in eq/L (currently 0.1 eq/L)
V_{sample}: Volume of the sample (currently 100 mL)

Note: *With these parameters, 1 mL of 0.1 eq/L of strong acid represents 0.1 meq or mmol of alkalinity.*

7.1.2. Alternative units

Depending on the country, many other units can be used for the results. Factors for the conversion from **millimoles per liter** are given in the table with the formula below:

$$\textbf{R3 or p}_{[user\ unit]} = \textbf{FX} \times \textbf{p}_{[mmol/L]}$$

$$\textbf{R4 or Total Alkalinity}_{[user\ unit]} = \textbf{FX} \times \textbf{Total Alkalinity}_{[mmol/L]}$$

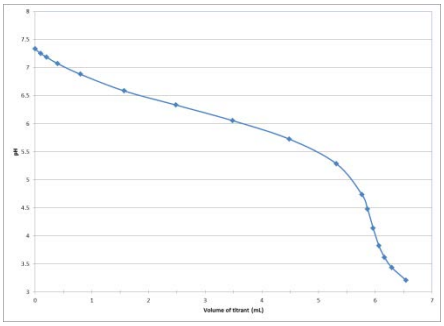
Unit	R3 and R4 user value (FX)	Comments
mmol/L $CaCO_3$	0.5	CO_3^{2-} has 2 alkalinity functions per molecule
mg/L $CaCO_3$	50	MW of $CaCO_3$ is 100.09 g/mol with 2alkaline functions per molecule
mg/L HCO_3	61	MW of HCO_3^- is 61 g/mol with 1 alkaline function per molecule
Clark degree	3.50	
German degree	2.80	
French degree	5.0	
U.S. degree	2.90	

8. Examples of pH-alkalinity 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.

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

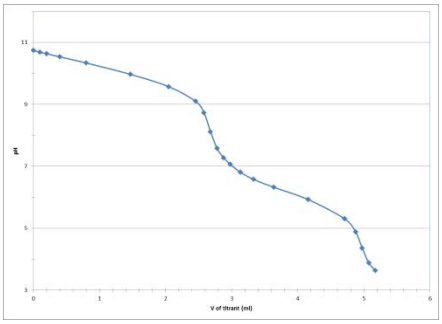
- **Sample**: 100 mL of mineral water. Nominal concentration: 296 mg/L as $CaCO_3$
- **Settings:** see values by default
- **Number of determinations**: 10
- **Temperature of analysis**: room temperature
- **Mean value of total alkalinity**: 5.940 mmol/L
- **Standard deviation:** 0.001 mmol/L
- **Relative standard deviation:** 0.02%
- **Curve pH versus volume of titrant:**



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

- **Sample**: 100 mL of Na_2CO_3 solution Nominal concentration: 250 mg/L as $CaCO_3$
- **Settings:** see values by default
- **Number of determinations**: 10
- **Temperature of analysis**: room temperature
- **Mean value of total alkalinity**: 5.00 mmol/L
- **Standard deviation:** 0.01 mmol/L
- **Relative standard deviation:** 0.26%
- **Curve pH versus volume of titrant:**



9. Bibliography

- *Water quality - Determination of total and composite alkalinity*, International standard **ISO 9963-1 (1994)**
- EPA method number 310.1
- *Standard Methods For the Examination of Water and Wastewater,* 22nd edition, **2012**, 2-34 part 2320

10. Appendix: Electrode, titrant and autoleveling calibrations

To increase the accuracy of the measurement of pH-alkalinity of the sample, it is recommended to perform a calibration of the electrode and titrant every 7 days. Always perform a calibration for a new electrode and/or titrant.

10.1. Calibration of the electrode

10.1.1. Electrode and reagents

Electrode: PHC805, Intellical combined pH Electrode with Temperature sensor
Titrant: HCl or H_2SO_4 0.1 eq/L solution in deionized water
Buffers: IUPAC Series pH standards: pH 4.005, pH 7.000 and pH 10.012
Solvent: Deionized water

10.1.2. Electrode calibration

Calibrate the electrode with pH 4.005, 7.000 and pH 10.012 IUPAC Series pH standards. It is possible to change the buffer set according to your SOP, see *User Manual* for further details.

10.1.3. Settings

Name	Default parameters	Units
Application		
Application name	pH Alkalinity HCl(Borax) **or** pH Alkalinity HCl(NaOH) **or** pH Alkalinity H2SO4(NaOH)	
Electrode		
Type	pH	
Recommended electrode	PHC805	
Calibration frequency	7	[days]
Stability criterion	0.050	[pH/min]
Max. stability time	300	[s]
Stirring speed	25	[%]
Stirring duration	15	[s]
Buffer set	IUPAC 1.68, 4.01, 7.00, 10.01, 12.45	

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10.1.4. Recommendations for modifications of the settings

By default the electrode calibration follows the standard ISO 10523: 2008 which recommends to stir the sample for a few seconds (by default *Stirring duration: 15 s*) and then to measure the pH of the sample without stirring. It is possible to stir the buffer solution only during the measurement by setting the ***Stirring duration*** **to 0 seconds**.

10.1.5. Results of electrode calibration

At the end of the series of buffers, the results are displayed. The values given below are indicative results, obtained in optimized conditions and respecting good laboratory practices. These indicative values are sample-dependent, electrode-dependent and operating cell–dependent.

Electrode: PHC 805
Slope at 25°C: 99.2%
Slope: -58.69 mV/pH
Offset: 10.5 mV

10.2. Calibration of the titrant by a primary standard: Borax

10.2.1. Principle

The strong acid (HCl or H_2SO_4) used as the titrant has to be calibrated with Borax which reacts with H^+ ions according to:

$$B_4O_7^{2-} + 2H^+ + H_2O \rightarrow 4HBO_2.$$

10.2.2. Specific reagents

Standard: 95 mg of Borax ($Na_2B_4O_7.10H_2O$), purity 99.5% diluted to 100 mL with deionized water

10.2.3. Settings

The calibration of the titrant HCl at 0.1 eq/L (0.1 mol/L) of application "pH Alkalinity HCl(Borax)" has been developed and optimized using a 10 mL syringe and with a dynamic incremental addition mode and inflexion point detection.

Name	Default parameters	Units
Application		
Application name	pH Alkalinity HCl(Borax)	
Advisable syringe	10 mL (Hamilton)	
Electrode		
Type	pH	
Recommended electrode	PHC805	
Titrant: HCl 0.1 N		
Name	HCl	
Real concentration	0.1000	[eq/L]
HCl 0.1 N method: Titrant calibration		
Active	Yes	
Calibration frequency	0	[Day(s)]
Stirring speed	25	[%]
Predose type	Volume	
Predose volume	2	[mL]
Delay	5	[s]
Max. vol. stop point	8	[mL]
Ordinate stop point	2	[pH]
Stop on last EQP	Yes	
IP1 min. ordinate	4.5	[pH]
IP1 max. ordinate	6.5	[pH]
Min. titrant conc.	0.09	[eq/L]
Max. titrant conc.	0.11	[eq/L]
Standard name	Borax	
Standard amount	95	[mg]

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Min. amount	75	[mg]
Max. amount	115	[mg]
Concentration	99.5	[%]
Molar weight	381.372	[g/mol]

10.2.4. Remarks on settings

In this application, the settings have been adapted to the chemistry of the reaction between HCl and borax:

- The range of ordinate for the inflexion point detection is set between 4.5 and 6.5 pH
- The value of exchanged equivalents is adapted to the nature of the titrant HCl and standard Borax:

Name of application	Titrant	Standard	Standard equivalents	Titrant equivalents
pH Alkalinity HCl(Borax)	HCl	Borax	2	1

10.2.5. Procedure – analysis steps

To calibrate the acidic titrant with the 10 mL syringe:

1. Prepare a 100 mL sample of 0.1 eq/l Borax solution by accurately weighing about 95 mg of Borax.
2. Complete to 100 mL with deionized water.
3. Dip the electrode and delivery tip in the solution.
4. Press **Start**.

10.2.6. Results of the titrant calibration

At the end of the titrant calibration the real concentration is calculated and expressed in eq/L. The saved value will be used for the following alkalinity titrations.

$$\mathbf{C_{titrant}} = \frac{[2 \times m_{standard} \times \mathrm{P\%}\,]}{[M_{standard} \times V_{titrant}]}$$

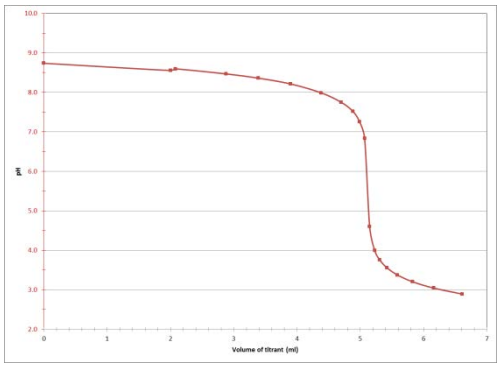
$m_{standard}$: Weighed mass of Borax in mg, about 95 mg weighed accurately
$M_{standard}$: Molar weight of Borax, 381.372 g/mol
P%: Purity of the weighed powder, 99.5%
$V_{titrant}$: Total volume of titrant delivered to reach the equivalent point, in mL

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

10.2.7. Examples of titrant calibration

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

- **Sample**: 95 mg of Borax with purity 99.5% completed to 100 mL of distilled water
- **Settings:** see values by default
- **Number of determinations**: 5
- **Temperature of analysis**: room temperature
- **Titer of titrant**: 0.0997 eq/L
- **SD**: 0.0001 eq/L
- **RSD**: 0.09 %
- **Calibration curve:**



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10.3. Calibration of the titrant by a secondary standard: NaOH

10.3.1. Principle

In some cases sodium hydroxide (NaOH) is used to calibrate HCl or H_2SO_4 titrant despite the fact that NaOH is not suitable as a primary standard because it readily absorbs moisture (H_2O) and carbon dioxide (CO_2) from the atmosphere. This classical reaction takes place:

$$NaOH + H^+ \text{ --> } H_2O + Na^+$$

10.3.2. Specific reagents

Standard: For both applications "pH Alkalinity HCl(NaOH)" and "pH Alkalinity H2SO4(NaOH)", the determination is done with a freshly prepared standard solution of NaOH at 0.005 eq/L.

Note: *A 0.005 eq/L NaOH solution contains 0.0050 mol/L.*

Quality of the standard solution:

As the solution absorbs carbon dioxide from the atmosphere, carbonate species are formed and other inflexion points appear. This phenomenon leads to bad calibrations due to the presence of more than one inflexion 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.

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.

10.3.3. Settings

The calibration of the titrant HCl or H_2SO_4 at 0.1 eq/L in applications "pH Alkalinity HCl(NaOH)" and "pH Alkalinity HCl(NaOH)" has been developed and optimized using a 10 mL syringe with a dynamic incremental addition mode and inflexion point detection.

Name	Default parameters	Units
Application		
Application name	pH Alkalinity HCl(NaOH) **or** pH Alkalinity H2SO4(NaOH)	
Advisable syringe	10 mL (Hamilton)	
Electrode		
Type	pH	
Recommended electrode	PHC805	
Titrant: HCl 0.1 N		
Name	HCl **or** H2SO4	
Real concentration	0.1000	[eq/L]
HCl or H2SO4 0.1 N method: Titrant calibration		
Active	Yes	
Calibration frequency	0	[days]
Stirring speed	25	[%]
Predose type	Volume	
Predose volume	2	[mL]
Delay	5	[s]
Max. vol. stop point	8	[mL]
Ordinate stop point	2	[pH]
Stop on last EQP	No	
IP1 min. ordinate	4.5	[pH]
IP1 max. ordinate	8.5	[pH]
Min. titrant conc.	0.09	[eq/L]
Max. titrant conc.	0.11	[eq/L]
Standard name	NaOH	
Standard amount	100	[mL]
Min. amount	95	[mL]
Max. amount	105	[mL]
Concentration	0.0050	[eq/L]
Molar weight	39.997	[g/mol]

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10.3.4. Remarks on settings

Inflexion points detection and result acceptance

The degradation of the standard solution of NaOH can easily and quickly appear and lead to a bad result of the calibrations. To prevent this situation, the detection range of inflexion point and stop conditions have been optimized to validate the status of the standard solution through possible multiple IP detections. As such, 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 field **Max. vol. stop point** is set to 8 mL, so the titration will always stop at this volume. For the same reason the **IP1 min. ordinate** and **IP1 max. ordinate** fields are set respectively to 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 IP 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.

Exchanged equivalents

In this application, settings have been adapted to the chemistry of the reaction between HCl or H_2SO_4 and NaOH. The value of exchanged equivalents is adapted to the nature of the titrant HCl or H_2SO_4 and standard NaOH for each application:

Name of application	Titrant	Standard	Standard equivalents	Titrant equivalents
pH Alkalinity HCl(NaOH)	HCl	NaOH	1	1
pH Alkalinity H2SO4(NaOH)	H_2SO_4	NaOH	1	2

10.3.5. Procedure – analysis steps

To calibrate the titrant HCl or H_2SO_4 with the 10 mL syringe:

1. Accurately prepare a 100 mL sample of 0.005 eq/L NaOH freshly prepared solution.
2. Dip the electrode and delivery tip in the solution.
3. Press **Start**.

10.3.6. Results of the titrant calibration

At the end of the titrant calibration, the real concentration is calculated and expressed in **eq/L**. The saved value will be used for the following alkalinity titrations.

$$C_{titrant} = \frac{V_{standard} \times C_{standard}}{V_{titrant}}$$

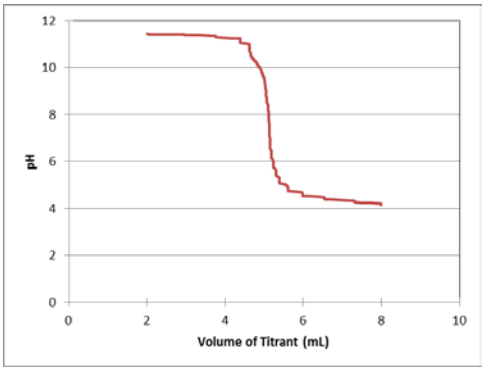
$V_{standard}$: Volume of NaOH solution in mL, 100.00 mL
$C_{standard}$: Concentration of NaOH solution in mL, 0.005 eq/L
$V_{titrant}$: Total volume of titrant delivered to reach the equivalent point, in mL

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

10.3.7. Examples of titrant calibration

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

- **Titrant**: H_2SO_4
- **Sample**: 100 mL of NaOH 0.0050 eq/L
- **Settings:** see values by default
- **Number of determinations**: 5
- **Temperature of analysis**: room temperature
- **Titer of titrant (Average)**: 0.1027 eq/L
- **SD**: 0.0001 eq/L
- **RSD**: 0.1135 %
- **Calibration curve:**



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10.4. Autoleveling calibration

10.4.1. 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.*

10.4.2. 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 the application **pH Alkalinity HCl(Borax),** the determination is done with a standard solution of Borax at 0.005 eq/L.

Preparation: For 1 liter of standard solution, weigh exactly 0.958 g of analytical grade Borax decahydrate powder ($Na_2BO_4O_7.10H_2O$) with a purity of 99.5%, and dilute to 1000 mL with deionized water in a volumetric flask.

Note: *A 0.0050 eq/L Borax solution contains 0.0025 mol/L.*

For the applications **pH Alkalinity HCl(NaOH)** and **pH Alkalinity H2SO4(NaOH)**, the determination is done with a freshly prepared standard solution of NaOH at 0.005 eq/L.

Note: *A 0.005 eq/L NaOH solution contains 0.005 mol/L.*

10.4.3. Settings

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

	Setting	**Units**
Application		
Application name	pH Alkalinity HCl(Borax)	
Sample		
Min. amount	45	[mL]
Max. amount	110	[mL]
Method: Leveling		
Active	Yes	
Time	30	[s]
Autoleveling calibration		
Solution name	Borax	
Solution concentration	0.005	[eq/L]

For the application “pH Alkalinity HCl(Borax)” refer to sections **10.2.3** and **10.2.4** for specific information on the settings.

	Setting	**Units**
Application		
Application name	pH Alkalinity HCl(NaOH) **or** pH Alkalinity H2SO4(NaOH)	
Sample		
Min. amount	45	[mL]
Max. amount	110	[mL]
Method: Leveling		
Active	Yes	
Time	30	[s]
Autoleveling calibration		
Solution name	NaOH	
Solution concentration	0.005	[eq/L]

For the applications “pH Alkalinity HCl(NaOH)” and “pH Alkalinity H2SO4(NaOH)” refer to sections **10.3.3** and **10.3.4** for specific information on the settings.

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10.4.4. Recommendations for modifications of the settings

Min. sample and **Max. sample** amount:

The result of the autoleveling calibration is compared to **Min. sample** and **Max. sample** amount defined on the top of the application editor. By default, limits of acceptance for the volume of sample for all applications (pH Alkalinity HCl(Borax), pH Alkalinity HCl(NaOH) and pH Alkalinity H2SO4(NaOH)) are set respectively at 45 mL and 110 mL (see section **4 Working ranges**). Leveling has to be used for a sample volume without dilution and sample **Min. amount** has to be adapted if the "leveling" method is active.

For example, with a 100 mL sample volume set **Min. amount** to 90 mL. It is recommended to work with a sample volume of between ± 10% of the targeted sample amount.

Solution concentration:

Settings by default have been optimized (including **Predose volume** and **Max. vol. stop point**, see sections **10.2.3** for calibration with Borax as standard and **10.3.3** for calibration with NaOH as standard) to have a delivered volume of titrant of 5 mL at equivalence with a 10 mL syringe.

By default, with a titrant at 0.1 eq/L (HCl or H_2SO_4) and a targeted volume of 100 mL for levelling, a 0.005 eq/L standard solution (Borax or NaOH) is used.

If the targeted sample amount is 50 mL, use a 0.0025 eq/L standard solution (Borax or NaOH) and modify the **Solution concentration** in **Autoleveling calibration** settings.

10.4.5. Procedure - analysis steps

Pour a sufficient amount of the standard solution into 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. 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 of the titrant calibration described in section **10.2.5** with Borax as the standard and **10.3.5** with NaOH as the standard.

10.4.6. Results

At the end of the sequence, the result obtained is the volume (in mL) remaining in the beaker after leveling. It is automatically updated in the **Sample Amount** field in the application editor and will be used in the next titration calculations of the application being used.

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

V_{sample}: Sample volume in mL

$C_{standard}$: Concentration of the standard solution in eq/L (currently 0.005 eq/L for Borax or NaOH standard solution)

$C_{titrant}$: Concentration of the titrant in eq/L (currently HCl or H_2SO_4 at 0.1 eq/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)

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