

## **OLI Tips #35 Alkalinity and OLI**

What does OLI mean when it discusses Alkalinity? Alkalinity is a frequently measured and reported quality of many waters. Stumm and Morgan define alkalinity as:

***"Acidimetric or alkalimetric titrations of carbonate-bearing water to the appropriate end points represent operations procedures for determining alkalinity and acidity, that is, the equivalent sum of the bases that are titratable with strong acid and the equivalent sum of the acids that are titratable with strong base. Alkalinity and acidity are then the capacity factors that represent, respectively, the acid- and base-neutralizing capacities ... of an aqueous system. For solutions that contain no protolysis system other than that of aqueous carbonate, alkalinity is a measure of the quantity of strong acid per liter required to attain a pH equal to that of a total concentration (molar) solution of  $H_2CO_3$ . Alternatively, acidity is a measure of the quantity per liter of strong base required to attain a pH equal to that of a total concentration (molar) solution of  $Na_2CO_3$ ."***<sup>1</sup>

The key to this statement involves the fact that many users think that the alkalinity is the concentration of various forms of carbonate ion. This would be true of other acid or base systems were not present in solution. Even simple ions such as sodium and magnesium may affect the free carbonate in solution and have markedly different alkalinities.

OLI considers alkalinity to be the total base capacity of the brine. We will use a titration to determine the alkalinity exactly. We will now show some examples featuring the OLI/LabAnalyzer™ program.

We will consider a simple brine with the following concentration

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<sup>1</sup> "Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters". Werner Stumm and James J. Morgan. John-Wiley & Sons, New York. 1981 p 185

Variable	Value	Unit
<b>Analysis Parameters</b>		
Stream Amt - Total Inflow	1.00000	L
Temperature	25.000	°C
Pressure	1.0000	atm
<b>Recorded Properties</b>		
pH	0.0	pH
Density - Aqueous	0.0	g/ml
Total Dissolved Solids - Total Inflow	0.0	mg/L
Electrical Cond, specific	0.0	1K(ohm-cm)
<b>Calc Parameters</b>		
<b>Neutrals</b>		
Water		
<b>Cations</b>		
Sodium ion(+1)	23000	mg/L
Calcium ion(+2)	50.000	mg/L
<b>Anions</b>		
Chloride ion(-1)	35000	mg/L
Bicarbonate ion(-1)	375.00	mg/L

Figure 1 Brine composition.

The user would suspect that the alkalinity would be the same as the bicarbonate concentration of 375 mg/L. The electrically neutral pH of this brine is:

Unit Set: WaterAnalysis Concentration		
Automatic Chemistry Model		
Databases: Public		
Dominant Ion Charge Balance		
Cation Charge:	1.002931	eq/L
Anion Charge:	-0.993368	eq/L
Imbalance:	0.009563	eq/L
339.041 mg/L of Chloride ion(-1) is needed to balance.		
Isothermal Calculation		
Temperature	25.000	°C
Pressure	1.0000	atm
Phase Amounts		
Aqueous	56.303	mol
Vapor	0.0	mol
Solid	0.0	mol
2nd Liquid	0.0	mol
Aqueous Phase Properties		
pH	7.7014	pH
Ionic Strength	1.0247	molality
Density	1.0370	g/ml
Calc. elapsed time: 0.330 sec		

Figure 2 the pH is 7.7

We will use HCl to titrate the brine to the standard end point pH of 4.5.

The amount of HCl added to bring the pH down to 4.5 is:

Databanks:	
Public	
Dominant Ion Charge Balance	
Cation Charge:	1.002931 eq/L
Anion Charge:	-0.993368 eq/L
Imbalance:	0.009563 eq/L
339.041 mg/L of Chloride ion(-1) is needed to balance.	
Set pH Calculation	
Temperature:	25.000 °C
Pressure:	1.0000 atm
pH:	4.5000 pH
Acid Titrant:	Hydrogen chloride
Total:	215.43 mg/L
Base Titrant:	Sodium hydroxide
Phase Amounts	
Aqueous:	56.304 mol
Vapor:	0.0 mol
Solid:	0.0 mol
2nd Liquid:	0.0 mol
Aqueous Phase Properties	
pH:	4.5000 pH
Ionic Strength:	1.0266 molality
Density:	1.0370 g/ml
Calculation time: 0.240 sec	

Figure 3 215.4 mg/L of HCl required.

This amount of HCl needs to be converted to equivalents of bicarbonate ion for reporting purposes.

$$215.43 \frac{\text{mgHCl}}{\text{L}} \frac{1 \text{mmoleHCL}}{36.461 \text{mgHCL}} \frac{1 \text{meq}}{1 \text{mmoleHCL}} \frac{1 \text{mmoleHCO}_3^{-1}}{1 \text{meq}} 61.017 \frac{\text{mgHCO}_3^{-1}}{\text{mmoleHCO}_3^{-1}} = 360.5 \frac{\text{mgHCO}_3^{-1}}{\text{L}}$$

So there is actually less alkalinity than the input concentration of bicarbonate ion would indicate. The reason for this is that some of the bicarbonate ion is tied up in the form of a complex,  $\text{NaHCO}_3^0$  and is not available to the alkalinity titration.

What would happen if organics acids were present in the brine? The following brine concentration has 150 mg/L of acetic acid added:

Variable	Value	Unit
<b>Analysis Parameters</b>		
Stream Amt - Total Inflow	1.00000	L
Temperature	25.000	°C
Pressure	1.0000	atm
<b>Recorded Properties</b>		
pH	4.5000	pH
Density - Aqueous	0.0	g/ml
Total Dissolved Solids - Total Inflow	0.0	mg/L
Electrical Cond, specific	0.0	1K(ohm-cm)
<b>Calc Parameters</b>		
Target: pH	4.5000	pH
Acid: Hydrogen chloride		
Base: Sodium hydroxide		
<b>Neutrals</b>		
Water		
Acetic acid	150.00	mg/L
<b>Cations</b>		
Sodium ion(+1)	23000	mg/L
Calcium ion(+2)	50.000	mg/L
<b>Anions</b>		
Chloride ion(-1)	35000	mg/L
Bicarbonate ion(-1)	375.00	mg/L

Figure 4 Added acetic acid

The alkalinity was determined as before to an end point pH of 4.5.

Unit Set: WaterAnalysis Concentration	
Automatic Chemistry Model	
Databanks: Public	
Dominant Ion Charge Balance	
Cation Charge:	1.002931 eq/L
Anion Charge:	-0.993368 eq/L
Imbalance:	0.009563 eq/L
339.041 mg/L of Chloride ion(-1) is needed to balance.	
Set pH Calculation	
Temperature	25.000 °C
Pressure	1.0000 atm
pH	4.5000 pH
Acid Titrant:	Hydrogen chloride
Total	164.82 mg/L
Base Titrant:	Sodium hydroxide
Phase Amounts	
Aqueous	56.302 mol
Vapor	0.0 mol
Solid	0.0 mol
2nd Liquid	0.0 mol
Aqueous Phase Properties	
pH	4.5000 pH

Figure 5 164.8 mg/L of HCl required.

This corresponds to an alkalinity of 275.8 mg/L as  $\text{HCO}_3^-$ . This is considerably less than the original bicarbonate ion concentration of 375 mg/L. The problem occurs in that the acetic acid is also reacting with the HCl. At a pH of 4.5 (the titration end point) not all of the acetic acid has reacted. The reason is that the dissociation constant for acetic acid is near the end point pH.



Most procedures state that if organic acids are present the pH end point must be lowered to react both the carbonate and the acid. We used a lower pH end point of 3.0 and obtained this result:

Unit Set: WaterAnalysis Concentration	
Automatic Chemistry Model	
Databanks: Public	
Dominant Ion Charge Balance	
Cation Charge:	1.002931 eq/L
Anion Charge:	-0.993368 eq/L
Imbalance:	0.009563 eq/L
339.041 mg/L of Chloride ion(-1) is needed to balance.	
Set pH Calculation	
Temperature	25.000 °C
Pressure	1.0000 atm
pH	3.0000 pH
Acid Titrant: Hydrogen chloride	
Total	263.63 mg/L
Base Titrant: Sodium hydroxide	
Phase Amounts	
Aqueous	56.305 mol
Vapor	0.0 mol
Solid	0.0 mol
2nd Liquid	0.0 mol
Aqueous Phase Properties	
pH	3.0000 pH

Figure 6 263.6 mg/L of HCl to reach the end point pH of 3.0

This corresponds to an alkalinity of 441 mg/L as  $\text{HCO}_3^{-1}$ . This value is greater than the bicarbonate ion concentration that was entered. This means that the organic acid is also a source of alkalinity.

It is true that any organic or inorganic species that has significant acid/base chemistry near the end point of the alkalinity titration will contribute the alkalinity. Species such as acetic acid (as just seen) and formic acid contribute to alkalinity. Inorganic species such as hydrofluoric acid ( $\text{pKa} = 4.3$ ) also contribute. Some boric acids also contribute.

The OLI code does not make any direct calculation of alkalinity since we do not know a priori what ions may appear in solution. We calculate the alkalinity via a titration. The OLI/ScaleChem program also uses this philosophy. When ions exist in the brine (e.g., acetate, formate, fluoride, borate, etc.) it is left to the user to determine what end point pH is appropriate for the alkalinity titrations.