Alkalinity of Natural Waters and How It Is Measured

Alkalinity of Natural Waters

The alkalinity of water is a measurement of its buffering capacity, which is its ability to neutralize acid or to resist acidification. In contrast, pH is a logarithmic scale for expressing Hydrogen (H^+) ion concentration. A solution of pH 7.0 is considered to be neutral, whereas a solution above pH 4.5 is considered to have alkalinity.

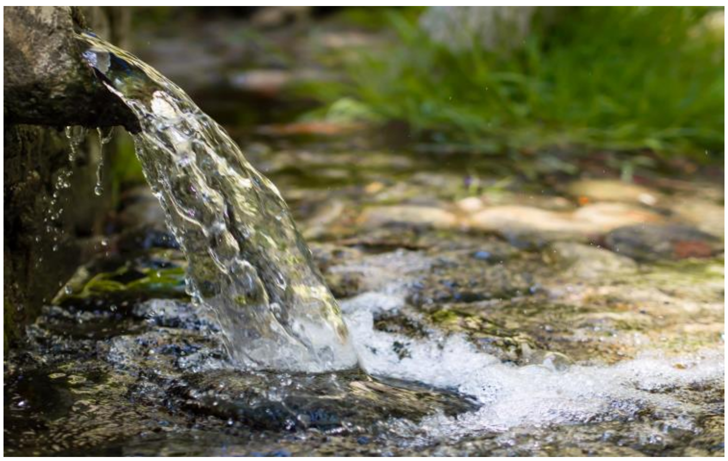

Figure 1: The geology around natural waters will affect alkalinity

Alkalinity of natural waters is comprised of a combination of bicarbonate, carbonate, and hydroxide ions, the proportions of which vary depending on pH. Bedrock (typically limestone), soil type, weathering processes, and precipitation will influence the predominant form of alkalinity. For example, waters flowing through limestone regions ~~tends~~ to have a higher alkalinity than waters flowing through granite, conglomerate, and sandstone regions.

As pH rises, more bicarbonate will change to carbonate. Sewage and wastewaters usually exhibit higher alkalinities due to the presence of silicates and phosphates. Bicarbonate and hydroxide alkalinity cannot coexist in general terms and occur at different pHs. At pH 7, the proportion of carbonate is very small.

pH	Composition
1.0 - 4.5	Free mineral acidity, CO_2 escapes (i.e. no HCO_3^-, $CO_3^=$)
4.5 - 9.6	Bicarbonate alkalinity (HCO_3^-)
8.3 - 14.0	Carbonate alkalinity ($CO_3^=$)
9.5 - 14.0	Hydroxide alkalinity (OH^-)

At or below pH 4.5, all bases have been reduced to water and carbon dioxide. Waters between pH 4.5 and 8.3 contain weak acids such as carbonic acid, and below pH 4.5 contain mineral acids. Carbon dioxide and carbonic acid exist in a chemical equilibrium in solution.

Phenolphthalein alkalinity is the sum of all carbonate ($CO_3^{=}$), bicarbonate (HCO_3^-) and hydroxide (OH^-) alkalinity above pH 8.3. Hydrate Alkalinity, on the other hand, is simply the hydroxide (OH^-) component of alkalinity above pH 8.3.

Alkalinity Measurement

Alkalinity is measured by titrating a water sample with a strong acid to a designated titration end point. The endpoint is commonly determined using pH (visual) indicators. Alternatively, a pH meter may be used.

Both bromocresol green / methyl red and phenolphthalein indicators are specified in the American Public Health Association (APHA)'s Standard Methods, Method 2320 B for the determination of total alkalinity and phenolphthalein alkalinity, respectively.

Alkalinity is expressed in terms of its base concentration, usually as equivalent mg/L $CaCO_3$. There are three main forms of alkalinity that are distinguished by their endpoints:

Type	pH Indicator	Definition
Total Alkalinity (T or M)	Bromocresol Green / Methyl Red	Alkalinity above pH 4.5
Phenolphthalein Alkalinity (P)	Phenolphthalein	Alkalinity above pH 8.3
Hydrate Alkalinity (OH)	Phenolphthalein	Hydroxide Alkalinity above pH 8.3

Below pH 4.5 there is said to be no total alkalinity; below pH 8.3 there is said to be no phenolphthalein or hydrate alkalinity.

The term 'alkalinity' is usually used to refer to total alkalinity (T alkalinity) or methyl orange alkalinity, otherwise known as M alkalinity. Phenolphthalein alkalinity is usually abbreviated to P alkalinity. Hydrate alkalinity is also known as hydroxide alkalinity, OH alkalinity, or just O alkalinity.

CHEMetrics offers three Total Alkalinity Titrets® Test Kits employing bromocresol green/methyl red pH indicators to deliver sensitivity and accuracy within minutes, covering the ranges 10-100 ppm (K-9810), 50-500 ppm (K-9815), and 100-1000 ppm $CaCO_3$ (K-9820).

Titrets ampoules use a reverse titration technique to measure analyte concentration levels. This means that the titrant volume inside the ampoule is fixed while the sample volume is varied. After snapping the ampoule tip, sample is drawn into the test ampoule in small doses until a color change signals that the endpoint has been reached. The titration is stopped at the end point, and the liquid level in the ampoule corresponds to the concentration printed on a scale on the ampoule's outer surface.

The endpoint of the titration for CHEMetrics Total Alkalinity Titrets Test Kits is signaled by a color change from pink to bright green. If the test ampoule is filled with sample but remains pink, the total alkalinity is below the test range. If the solution changes to bright green immediately upon introduction of the first small dose of sample, the total alkalinity is above the test range. If the sample itself turns pink immediately upon addition of the indicator (activator) solution (prior to introduction of the sample into the test ampoule), the sample pH is less than or equal to 4.5, which indicates that the alkalinity of the sample is 0 ppm.

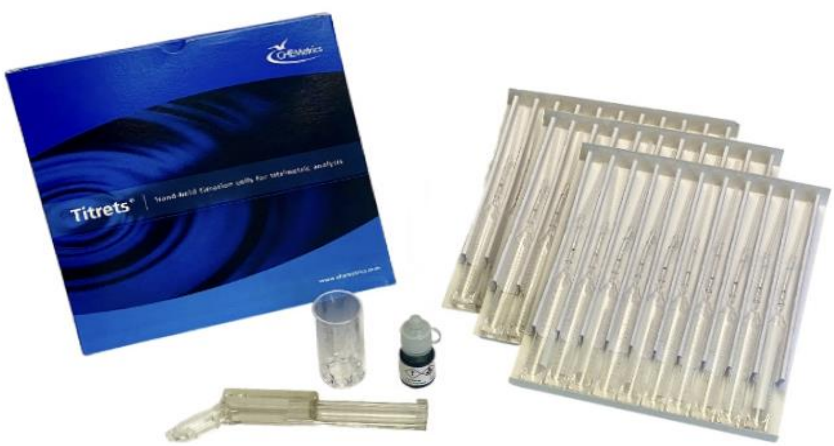

Figure 2: CHEMetrics Alkalinity Titrets Test Kit

Alkalinity Calculations

By determining both the T and P alkalinity values of a sample, an analyst can calculate the individual concentrations of $CO_3^{=}$, HCO_3^- and OH^-, which are the components that are typically attributed to a sample's alkalinity using the table below. This table presupposes incompatibility of OH^- and HCO_3^- alkalinities, which is essentially correct, although there is actually a slight overlap in pH transition between the two.

T Alkalinity ≈ 2 [$CO_3^{=}$] + [HCO_3^-] + [OH^-]

Titration Result	OH^- Alkalinity as $CaCO_3$	$CO_3^{=}$ Alkalinity as $CaCO_3$	HCO_3^- Alkalinity as $CaCO_3$
P=0	0	0	T
P<0.5T	0	2P	T-2P
P=0.5T	0	2P	0
P>0.5T	2P-T	2(T-P)	0
P=T	T	0	0

Source: APHA Standard Methods, 22nd ed., Method 2320 B: Table 2320:II (1997).

Patrik Askert, Galgo, May 2019
Edited by CHEMetrics, August 2021

References:

1. APHA (1997). *Standard Methods*, 22nd ed., Method 2320 B. Washington DC: APHA.
2. CHEMetrics (2018). *Total Alkalinity Titrets Kit Instructions.* Rev.11. Midland, VA: CHEMetrics, Inc.