Alkalinity

What is alkalinity?

According to Standard Methods for the Examination of Water and Wastewater (SM 2320 Alkalinity), "Alkalinity of a water is its acid-neutralizing capacity. It is the sum of all the titratable bases." It can be also described as the water's capacity to resist changes in pH that would make the water more acidic (so called buffering capacity of water). The ions that contribute to alkalinity are carbonate, bicarbonate, and hydroxide. Alkalinity may also include contributions from borates, phosphates, silicates, or other bases.

Why measure alkalinity?

Alkalinity measurement is important in many environmental and industrial applications such as:

Water quality – The alkalinity level is important for fish and other freshwater aquatic life, because it protects against rapid pH changes that occur naturally or as a result of human activity. In order to identify the sensitivity of surface waters to acidification, US EPA has monitored regional surface water alkalinity and has published a Total Alkalinity of Surface Waters map (http://water.usgs.gov/owq/hardness-alkalinity.html). Conversely, excessive alkalinity can be damaging for aquatic life.

Wastewater treatment plants – Alkalinity plays a role in wastewater treatment. Raw wastewater alkalinity depends on many factors including the source of the water, the amount of suspended organic matter, the presence or absence of free hydroxyl alkalinity, the amount of bicarbonate and dissolved CO_2, etc. During wastewater treatment, different chemicals are used to provide the optimal alkalinity for treatment processes including: biological nitrification in aeration tanks, gas chlorination for effluent disinfection, neutralization of acids generated by the active biomass in anaerobic digester, and to inhibit corrosion.

Drinking water treatment plants – Alkalinity is important for drinking water treatment. Drinking water plants measure alkalinity at different stages of the treatment process: for example, on the raw water, in the sedimentation basin, and the finished water. Alkalinity is important for: the water softening process, for corrosion control, for disinfection, coagulation, and the oxidation process. Drinking water plants report source water alkalinity along with TOC to demonstrate compliance with the Disinfectants and Disinfection Byproducts Rules (DBPR).

Sampling and Storage for Alkalinity Samples

In general, sample collection should follow these guidelines: collect in polyethylene or borosilicate glass bottles and store at a low temperature. Record the sample pH at the source where the sample is collected. Bottles should be completely filled and capped tightly. Do not filter, dilute, concentrate, or alter the sample. Samples should be analyzed as soon as possible; holding time is generally up to 14 days at 4 ºC. Consult your local regulations for details.

Ways to Measure Alkalinity

Titration Method

The traditional, EPA-approved method to measure alkalinity is a titration at room temperature with a standard acid solution to a preselected end point. Results are expressed as mg/L as CaCO3 (calcium carbonate). The end point can be determined by using a pH electrode or observing a color change with color indicators. Alkalinity is calculated from the volume of standard sulfuric acid or hydrochloric acid required to reach the end point or to change the color.

The following forms of alkalinity can be determined and reported:

- **P-alkalinity** (also known as phenolphthalein alkalinity) – is determined by titration with acid to pH 8.3. It measures the amount of carbonate alkalinity, hydroxyl alkalinity, and a part of bicarbonate alkalinity in a sample. A certain level of the P-alkalinity (causticity) is necessary to protect from corrosion, while excessive P-alkalinity can result in a caustic attack (embrittlement) or caustic water, which causes a burning sensation when it is tasted.

  P-alkalinity is calculated using the equation below:

  $$\text{P-alkalinity, mg } CaCO_3/L = \frac{\text{((mL standard acid used to pH 8.3) * (normality of standard acid) * 50,000)}}{\text{mL sample}}$$

- **Total Alkalinity** also called M-alkalinity (M from methyl orange) is determined by titration with acid to pH 4.5. At this pH, all the hydroxyl, carbonate, and bicarbonate (as well as other basic anions) have been titrated.

  T-alkalinity (or M-alkalinity) can be calculated as follows:

  $$\text{M-alkalinity, mg } CaCO_3/L = \frac{\text{((mL standard acid used to pH 4.5) * (normality of standard acid) * 50,000)}}{\text{mL sample}}$$

The P- and T-alkalinity results allow users to determine the properties of water. For example, if P-alkalinity is greater than half the T-alkalinity, the water is caustic from contributions of hydroxide alkalinity and carbonate alkalinity. If P-alkalinity is zero, then the water is free of hydroxide and carbonate alkalinity. *See Standard Methods 2320 Alkalinity for more details.*

Thermo Scientific™ Orion™ pH electrodes are used for alkalinity titration using the preset end point technique. It is very important to calibrate the pH electrode before the analysis when using the preset end point titration method. Interferences for the titration method are soaps, oily matter, suspended solids, or precipitates, which may coat the glass electrode and cause a sluggish response. Clean the electrodes when needed and allow additional time between titrant additions to let the electrode come to equilibrium, if necessary.

Colorimetric Method

Colorimetric alkalinity measurement methods are based on a similar principle to the conventional titration, but the acid added is preset while the pH of the endpoint varies. In these methods, the reagent(s) is composed of several acids and a pH-sensitive color indicator. Acids react with the alkaline species in the sample and change sample pH; as a result, the color indicator changes its color. The change in pH and resulting increase in color is proportional to the alkalinity of the sample and is measured at a specific wavelength (e.g., T-alkalinity at 610 nm and P-alkalinity at 560 nm).

Orion Total Alkalinity Test Kit

The Orion total alkalinity test kit reagent is also composed of several acids, which react with the titratable bases in a sample. As a result, the pH of the sample changes. The resulting pH is measured with pH electrode. The pH reading after the addition of the reagent varies directly with the total alkalinity. For more information, read Technical Bulletin 517 “Total Alkalinity Measurement in Natural Waters”.

	Titration	Colorimetry	Kit
P-alkalinity	Yes	Yes	No
M-alkalinity	Yes	Yes	Yes
Sample Size	200 mL	10 mL	100 mL
Test Range	All concentration ranges of alkalinity	P-alk: 5 – 200 mg/L $CaCO_3$ M-alk: 5 – 500 mg/L $CaCO_3$	0 – 225 mg/L $CaCO_3$
Interferences	Substances that can coat the pH electrode	Turbidity or color in the sample	Substances that can coat the pH electrode
Advantages	Color and turbidity do not interfere. Titration may be automated. Wide test range.	Small sample size. Immediate results. Easy to use. Portable. P- and M-alkalinity tests available.	Color and turbidity do not interfere. Quicker than a titration. Wide test range.
Products for Alkalinity Testing	Orion pH electrode: 8172BNWP, 8156BNUWP, 9107APMD, 9156BNWP, or others. Orion pH meter	Orion Reagents: AC2002 (m-alk), AC3002P Orion Meters: AQ3700, AQ7000 or AQ8000	Orion 700010 Total Alkalinity Test Kit
EPA Approval	EPA-approved test method	Not EPA-approved.	Not EPA-approved

References

Standard Methods for the Examination of Water and Wastewater (SM 2320 Alkalinity), https://www.standardmethods.org/

Total Alkalinity of Surface Waters map, United States Environmental Protection Agency, http://water.usgs.gov/owq/hardness-alkalinity.html

Total Alkalinity Measurement in Natural Waters, Technical Bulletin 517, Thermo Fisher Scientific, http://tools.thermofisher.com/content/sfs/manuals/D16874~.pdf

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