What is alkalinity and how is it speciated into hydroxide, carbonate, bicarbonate fractions?

Alkalinity is the buffering capacity of a solution. It is a valuable water quality parameter used for many applications, including, but not limited to: drinking water treatment, domestic and industrial wastewater treatment, swimming pools, food and beverage, soil, agriculture, and other environmental testing.

The main compounds of alkalinity are: hydroxides (OH^-), carbonates (CO_3^{2-}), and bicarbonates (HCO_3^-). The buffering capacity of a solution depends on the absorption of positively charged hydrogen ions by negatively charged bicarbonate and carbonate molecules. When bicarbonate and carbonate molecules absorb hydrogen ions, there is a shift in equilibrium without a significant shift in pH. A sample with high buffering capacity will have high bicarbonate and/or carbonate content, and a greater resistance to changes in pH.

MANTECH complies with EPA Method 310.1, ASTM Method D 1067-92, and Standard Method 2320, for determining alkalinity, which calculates the concentrations of OH^-, CO_3^2, and HCO_3^-. Total alkalinity is calculated as the sum of these three species and is expressed in units of milligrams of calcium carbonate per litre (mg $CaCO_3$/L).

The alkalinity method involves titrating samples with a titrant of known concentration, commonly, 0.02N sulphuric acid (H_2SO_4), to pH endpoints of 8.3 and 4.5. The alkalinity calculated up to endpoint 8.3 is classified as phenolphthalein alkalinity (p_{alk}), whereas the alkalinity calculated up to endpoint 4.5 is classified as total alkalinity (t_{alk}). A titration curve is generated by plotting pH versus volume of dispensed titrant (Figure 1).

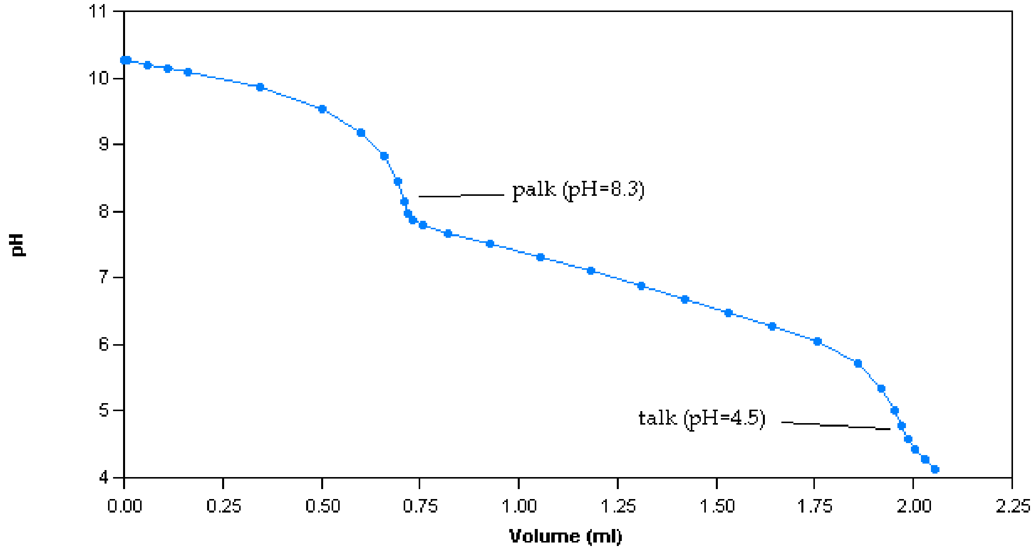

Figure 1: Sample titration curve for a 100ppm alkalinity sample

The titration curve is used to determine the volume of dispensed titrant at each endpoint. To calculate p_{alk}, the following equation is used:

$$p_{alk} = \frac{xvol(8.3) \times\ t_{con} \times 50\,000}{svol}$$

Where:
$xvol(8.3) = volume\ of\ titrant\ used\ to\ titrate\ to\ pH\ 8.3\ (mL)$
$t_{con} = normality\ of\ titrant (N)$
$50\,000 =\ equivalent\ weight\ of\ CaCO_3\ as\ defined\ in\ Standard\ Methods\ (mg/mol)$
$svol = volume\ of\ sample\ titrated\ (mL)$

t_{alk} is calculated using the following equation:

$$t_{alk} = \frac{xvol(4.5) \times\ t_{con} \times\ 50\,000}{svol}$$

Where:
$xvol(4.5) = volume\ of\ titrant\ used\ to\ titrate\ to\ pH\ 4.5\ (mL)$
$t_{con} = normality\ of\ titrant\ (N)$
$50\,000 =\ equivalent\ weight\ of\ CaCO_3\ as\ defined\ in\ Standard\ Methods\ (mg/mol)$
$svol = volume\ of\ sample\ titrated\ (mL)$

For samples with t_{alk} less than 20ppm, a low alkalinity titration procedure requires the sample to be titrated to a pH of 4.3, as per Standard Method 2320. To calculate t_{alk} of low alkalinity samples, the following equation is used:

$$t_{alk} = \frac{(2\ \times\ xvol(4.5) - xvol(4.2))\ \times\ t_{con} \times\ 50\,000}{svol}$$

Where:
$xvol(4.5) = volume\ of\ titrant\ used\ to\ titrate\ to\ pH\ 4.5\ (mL)$
$xvol(4.2) = volume\ of\ titrant\ used\ to\ titrate\ to\ pH\ 4.2\ (mL)$
$t_{con} = normality\ of\ titrant\ (N)$
$50\,000 = equivalent\ weight\ of\ CaCO_3\ as\ defined\ in\ Standard\ Methods\ (mg/mol)$
$svol = volume\ of\ sample\ titrated\ (mL)$

The values for t_{alk} and p_{alk} can be used to determine the concentrations of OH^-, CO_3^2, and HCO_3^-, and indicate the following conditions:

1. OH^- alkalinity is present if p_{alk} is greater than half of the t_{alk}
2. CO_3^{2-} alkalinity is present when p_{alk} is not zero, but is less than t_{alk}
3. HCO_3^- ions are present if p_{alk} is less then half the t_{alk}

Table 1 shows the calculations for determining the concentration of each species of alkalinity based on the results for p_{alk} and t_{alk}.

Table 1: Alkalinity species calculations

Result of Titration	Hydroxide (OH^-) Alkalinity as $CaCO_3$	Carbonate (CO_3^{2-}) Alkalinity as $CaCO_3$	Bicarbonate (HCO_3^-) Alkalinity as $CaCO_3$
$p_{alk} = 0$	0	0	t_{alk}
$p_{alk} < ½ t_{alk}$	0	$2*p_{alk}$	$t_{al} – 2*p_{alk}$
$p_{alk} = ½ t_{alk}$	0	$2*p_{alk}$	0
$p_{alk} > ½ t_{alk}$	$2*p_{alk} – t_{alk}$	$2*(t_{alk} – p_{alk})$	0
$p_{alk} = t_{alk}$	t_{alk}	0	0

MANTECH's MT Series automates alkalinity and low alkalinity measurements, following EPA, ASTM, ISO and Standard Methods. For more information on how MANTECH can simplify your alkalinity analysis, refer to the MT Series product info page or contact your local MANTECH distributor.