Alkalinity

For water, wastewater and seawater | **Titration Method**

Introduction

Alkalinity is a measure of the capacity of water to neutralize acids. Alkalinity of water is due primarily to the presence of bicarbonate, carbonate, and hydroxide ions. Salts of weak acids, such as borates, silicates and phosphates, may also contribute. Salts of certain organic acids may contribute to alkalinity in polluted or anaerobic water, but their contribution usually is negligible. Bicarbonate is the major form of alkalinity. Carbonates and hydroxide may be significant when algal activity is high and in certain industrial water and wastewater, such as boiler water.

Alkalinity is significant in the treatment processes for potable water and wastewater. The alkalinity acts as a pH buffer in coagulation and lime-soda softening of water. In wastewater treatment, alkalinity is an important parameter in determining the amenability of wastes to the treatment process and control of processes such as anaerobic digestion, where bicarbonate alkalinity, total alkalinity and any fraction contributed by volatile acid salts become considerations.

Alkalinity is expressed as phenolphthalein alkalinity or total alkalinity. Both types can be determined by titration with a standard sulfuric acid solution to an end point pH, evidenced by the color change of a standard indicator solution. The pH also can be determined with a pH meter.

Phenolphthalein alkalinity is determined by titration to a pH of 8.3 (the phenolphthalein end point) and registers the total hydroxide and one half the carbonate present. Total alkalinity is determined by titration to a pH of 4.9, 4.6, 4.5, or 4.3, depending on the amount of carbon dioxide present. The total alkalinity includes all carbonate, bicarbonate and hydroxide alkalinity.

The following end points are recommended for determining total alkalinity in water samples of various compositions and alkalinity concentrations.

Table 1 Determine total alkalinity

Sample Trait	End Point
Alkalinity approximately 30 mg/L	pH 4.9
Alkalinity approximately 150 mg/L	pH 4.6
Alkalinity approximately 500 mg/L	pH 4.3
Silicates or phosphates known present or suspected	pH 4.5
Industrial waste or complex system	pH 4.5
Routine or automated analyses	pH 4.5

Chemical reactions

Sulfuric acid (hydrochloric acid may be used) reacts with the three forms of alkalinity, converting them to water or carbonic acid. If hydroxide is present, it reacts to form water:

$$2OH^{-} + H_2SO_4 \rightarrow 2H_2O + SO_4^{2-}$$

This conversion usually is complete at a pH of about 10. Phenolphthalein alkalinity is determined by titration to an end point pH of 8.3, which corresponds to the conversion of carbonate to bicarbonate.

$$2CO_3^{2-} + H_2SO_4 \rightarrow 2HCO_3^{-} + SO_4^{2-}$$

If hydroxide is present, titration to pH 8.3 will indicate the alkalinity due to all of the hydroxide plus one-half of the carbonate. Continued titration to pH 4.5 completes the conversion of carbonate plus any bicarbonate present to carbonic acid. This value is termed Total Alkalinity.

$2HCO_3^- + H_2SO_4$ ç $2H_2CO_3 + SO_4^{2-}$

Methyl red

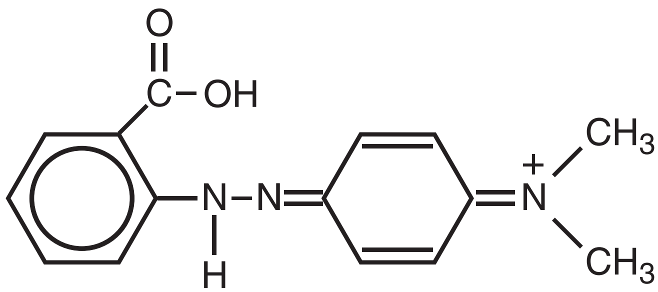

Figure 1 Red=pH 4.8

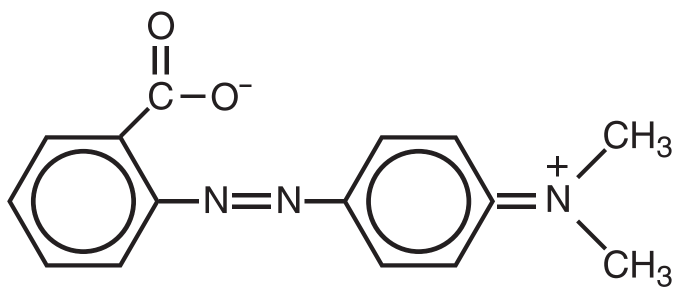

Figure 2 Yellow=pH 6.0

Bromcresol green

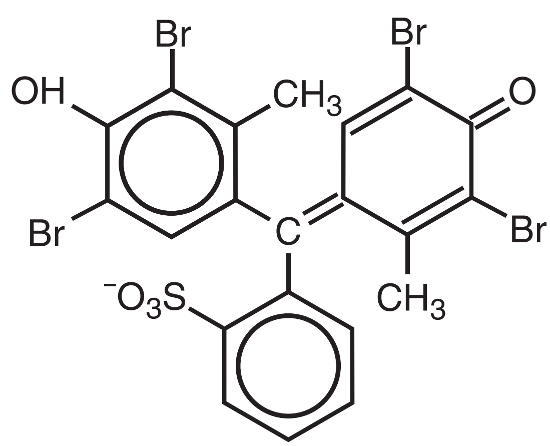

Figure 3 Blue=pH 5.5

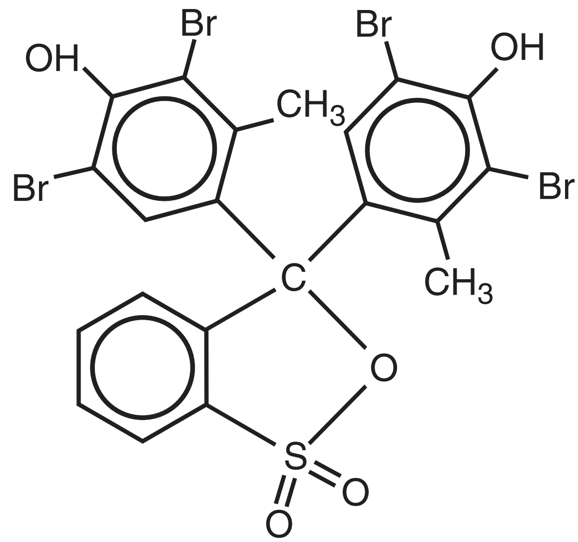

Figure 4 Yellow=pH 3.8