Applied Microbiology
&
Biotechnology Laboratory

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Standard Operating Procedure

AMBL-103-B

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Revised:	
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Alkalinity and Endpoint pH Determination by Acid Titration Curve

METHOD SUMMARY

This SOP describes the procedure for using a titration curve to determine alkalinity and the endpoint (potentiometric method) that is specific to a particular sample. This method is based on Method 2320 B of *Standard Methods for the Examination of Water and Wastewater*, 22nd Edition.

ENVIRONMENTAL HEALTH AND SAFETY

Hazards Assessment: This method involves the use of small volumes of concentrated and dilute sulfuric acid. Sulfuric acid is a clear, colorless and corrosive liquid that can burn skin, eyes and clothing. Concentrated acid is highly reactive with water and you should never add water into concentrated acid, but rather always slowly add the acid into a larger volume of water while stirring to dissipate the heat. Some of the potential health hazards considered specific to this method are as follows.

Skin Contact: The severity of the effect will depend on the strength of the acid. A strong, concentrated acid will result in burns, pain, redness and blistering. A more dilute acid, typical of that used during titration, will cause dry, red, and cracked skin with repeated exposure. Dry, cracked skin provides openings that can become more easily infected.

Eye Contact: Contact can cause severe burns, pain, redness, swelling and blurred vision. Permanent blindness can result if the exposure is severe enough.

Ingestion: Although, unlikely to occur during the performance of this method, ingestion can cause burns to the lips, tongue, throat and stomach. Nausea, stomach cramps, diarrhea and vomiting are all systems of an exposure by ingestion.

Inhalation: Exposure by inhalation is not expected unless the acid is heated or misted. This exposure pathway is very hazardous and will cause irritation to the nose and throat, and cause significant damage to respiratory system tissue leading to production and accumulation of fluid in the lungs. Coughing, shortness of breath, breathing difficulty and tightness in the chest are all symptoms of acid vapor or mist exposure by inhalation.

Severe exposures can lead to death.

Safety Equipment and Engineering Controls: This method requires that the handling of concentrated acids to be done in a fume hood and that an eye wash station and a shower be located nearby.

Personal Protective Equipment (PPE): This method requires the use of the following PPE.

When handling concentrated acid (in fume hood):

Gloves (nitrile, PVC or neoprene)

Safety goggles or face shield

Acid-resistant apron worn over a laboratory coat

When handling dilute acid titrants during performance of this method:

Gloves (nitrile, PVC or neoprene)

Safety goggles or glasses

Laboratory coat

Analysis-derived Wastes and Disposal:

Waste Generated	Hazardous (Y / N)	Disposal
This procedure neutralizes the mineral acid titrant in the sample resulting in a final pH of approximately 4.5.	N	May be disposed in sink.
More sodium carbonate solution is prepared than what can generally be used within the recommended self-life.	N	May be disposed in sink.

METHOD DESCRIPTION

1.0 Introduction and Applicability

Alkalinity is a measure of a water's acid neutralizing capacity and is considered an aggregate property of water. While bicarbonate, carbonate and hydroxide ions are the primary contributors, other constituents such as borate, phosphates or silicates may also contribute to alkalinity. The variability of these constituents in any given sample can result in the actual equivalence point reached during titration with acid to vary. While alkalinity of most environmental water samples may be routinely measured using the equivalence bicarbonate endpoint of 4.5, this may not be the case for certain individual samples. Routine measurement of alkalinity may be conducted by titrating a sample with a volume of standard acid a designated endpoint pH value, and reported as an equivalent concentration of calcium carbonate.

This method is applicable for determining the sample-specific endpoint for total alkalinity and the measurement of alkalinity in natural waters, including groundwater, municipal and industrial wastewaters.

2.0 Apparatus

a. pH meter and electrode
b. Magnetic stirrer and stir bar
c. Beaker, 100 or 150-mL, for titration vessel
d. Buret, 50-mL, for standard sulfuric acid titrant
e. Pipets, volumetric
f. Flasks, volumetric

3.0 Reagents

a. 0.05N (approximately) sodium carbonate, primary standard prepared according to procedure given in Method 2320 B.3.a (*Standard Methods*).
b. 0.1N standardized sulfuric acid stock solution prepared according to procedure given in Method 2320 B.3.b (*Standard Methods*).
c. 0.02N standardized sulfuric acid titrant prepared according to procedure given in Method 2320 B.3.c (*Standard Methods*).

4.0 Procedure

a. Read Method 2320 Alkalinity (*Standard Methods*) and AMBL SOP 205A for measuring pH.

b. Prepare fresh or standardized 0.1N sulfuric acid stock and 0.02N sulfuric acid titrant solutions as needed.

c. Fill a clean buret with 0.02N titrant, making sure that there is no air space in the stopcock or the tip of the buret.

d. Equilibrate the sample's temperature with the room's temperature and volumetrically transfer enough sample to a 100- or 150-mL beaker so that the titrant used will provide good volumetric precision. Generally, a sample volume of 25- to 50-mL is considered appropriate for most waters. Adjust sample volume or prepare and standardize new titrant with a different normality.

e. Place a stir bar in the beaker (avoid splashing), place the beaker on the magnetic stirrer and insert the pH electrode into the beaker so that it is adequately immersed in the sample and off-center enough to allow room for the buret tip.

f. Adjust the magnetic stirring speed to provide a well-mixed condition without splashing or aerating the sample.

g. Measure and record the sample pH.

h. Record the initial buret reading; read at the bottom of the meniscus.

i. Add standard acid titrant in increments of 0.5 mL or less to cause a pH change of about 0.2 pH units with each increment.

j. After each increment when the pH has stabilized, record the pH and the buret reading.

k. Continue this addition of acid titrant until pH 4.0 or lower has been reached.

l Construct the titration curve by plotting the pH readings on the ordinate (*y*-axis) against the titrant volume added on the abscissa (*x*-axis).

m. Find and report the total alkalinity endpoint as the pH of the bicarbonate equivalence point (the inflection point).

5.0 Calculation and Reporting

a. Calculate phenolphthalein alkalinity

$$\text{Alkalinity } (P_{Alk}), \text{ as mg/L } CaCO_3 = \frac{A \times N \times 50{,}000}{S}$$

where A = mL of sulfuric acid titrant used to reach pH 8.3

N = normality of the standardized acid titrant

S = mL of sample volume

b. Report as "phenolphthalein alkalinity to pH 8.3 = _____ mg/L as $CaCO_3$"

c. Calculate total alkalinity

$$\text{Alkalinity } (T_{Alk}), \text{ as mg/L } CaCO_3 = \frac{B \times N \times 50{,}000}{S}$$

where B = mL of sulfuric acid titrant used to reach pH endpoint as determined by this procedure

N = normality of the standardized acid titrant

S = mL of sample volume

d. Report as "total alkalinity to pH (as determined) = _____ mg/L as $CaCO_3$"

e. Calculate alkalinity relationships according to the following table.

Titration Results	Bicarbonate Alkalinity	Carbonate Alkalinity	Hydroxide Alkalinity
If $P_{Alk} = 0$	T_{Alk}	0	0
If $P_{Alk} < ½ T_{Alk}$	$T_{Alk} – 2P_{Alk}$	$2P_{Alk}$	0
If $P_{Alk} = ½ T_{Alk}$	0	$2P_{Alk}$	0
If $P_{Alk} > ½ T_{Alk}$	0	$2(T_{Alk} – P_{Alk})$	$2P_{Alk} - T_{Alk}$
If $P_{Alk} = T_{Alk}$	0	0	T_{Alk}

Key: P_{Alk} = phenolphthalein alkalinity, T_{Alk} = total alkalinity, all alkalinity values are expressed in mg/L as $CaCO_3$.

6.0 Quality Control

Standardize the stock 0.1 N acid titrant monthly. Prepare new 0.02N acid titrant and any other acid titrant used, monthly, or standardize. Perform one duplicate sample measurement for every 20 or fewer samples analyzed.

7.0 Bibliography

1. Eugene W. Rice, Rodger B. Baird, Andrew D. Eaton, and Lenore S. Clesceri (2012) *Standard Methods for the Examination of Water and Wastewater*. APHA, Washington, DC, 22nd Edition.