

VOLATILE ACIDS
and
ALKALINITY

VOLATILE ACIDS and ALKALINITY

Background

The volatile acids/alkalinity test is an important digester control test, much better than pH monitoring alone. Volatile acids/alkalinity tests will give more warning of impending digester problems, while pH testing may not indicate a problem until it is too late.

In a well-functioning digester, two groups of bacteria are working in harmony to break down organic matter. Saprophytic bacteria hydrolyze and convert complex organic compounds to low molecular weight (simple) compounds. These are essentially the waste products of the saprophytes. Among these waste products are short-chain fatty acids such as acetic, propionic and butyric acids. These are called volatile acids because they can be distilled at atmospheric pressure. Also working in the digester are the methane-formers. These bacteria convert the saprophytes' wastes to methane and carbon dioxide. In a stabilized system, the methane formers use the volatile acids as fast as the saprophytes produce them.

The alkalinity, or buffering capacity, of the system is the ability of the solution to resist massive changes in pH as acids are added and helps to stabilize the pH in the optimum range for the methane formers. As the saprophytes work on the wastes in the digester, volatile acids are produced. When these acids dissociate, hydrogen ions are released. The free hydrogen ions would gradually force the pH of the digester downward but the alkalinity of the system will pick up these ions and allow the methane-formers to "catch-up." If the system becomes out of balance, the alkalinity will gradually be exhausted and the pH in the digester will begin to fall. When the pH slips to below 6.5, the methane formers are inhibited and the digester goes "out of control," that is, the pH goes down faster because the methane formers are no longer effectively using the volatile acids. When the pH reaches 5, the saprophytes are inhibited and the digester has gone sour and no digestion is taking place.

Methane formers have a much narrower optimum range for pH and temperature and are slower in reproducing than the saprophytes. While the two groups of organisms do not compete with each other, any conditions which are favorable to the saprophytes and not to the methane formers result in a shift toward a sour digester. By monitoring the volatile acids/alkalinity relationship, this shift can be seen in an increase in volatile acids and a decrease in alkalinity.

The traditional method of digester control is monitoring pH. This method is not sufficient because a shift downward in pH has been preceded by the loss of the system's alkalinity. At this point, it may be too late to bring the digester back. A shift in the volatile acids/alkalinity relationship may occur days before the pH shift.

Strive to maintain a ratio between volatile acids and alkalinity of between 0.05 and 0.15. A shift over 0.15 warns of impending trouble and liming is indicated to bring the digester back into control.

Sampling

Samples for volatile acids/alkalinity analysis are taken from the primary digester. You can either sample from a tap off the recirculation line or from the sample taps at each level of the primary. The mixers should be on. Remember to let the sampling taps run a sufficient time to clear the lines. Samples should be run immediately.

Method

The following method is a combination of the potentiometric titration methods for acidity (Method 2310B) and alkalinity (Method 2320B), page 2-25 and 2-26 18th Edition of Standard Methods for the Examination of Water and Wastewater with sludge sample preparation techniques from the laboratory section of the EPA Operations Manual: Anaerobic Sludge Digestion.

Equipment

pH meter with ATC
50 ml buret
100 ml beaker
magnetic stirrer (sample may be agitated by hand but this is undesirable)
50 ml graduated cylinder
hot plate

Reagents

1.0N STANDARD SULFURIC ACID SOLUTION ("STOCK")

1.0 n H₂SO₄ - Partially fill a one-liter volumetric flask with approximately 500 mls distilled water. Carefully, while stirring, add 28.0 mls concentrated (36N) H₂SO₄. Cool, then dilute to the one-liter mark with distilled water.

0.10N STANDARD SULFURIC ACID SOLUTION ("WORKING")

For expected alkalinities of greater than 20 mg/L:

0.10N H₂SO₄ - Partially fill a one-liter volumetric flask with approximately 500 mls distilled water. Carefully add 100 mls of the 1.0N H₂SO₄. Dilute to the one-liter mark with distilled water.

0.02N STANDARD SULFURIC ACID SOLUTION

For expected alkalinities of less than 20 mg/L:

0.02N H₂SO₄ - Partially fill a one-liter volumetric flask with approximately 500 mls distilled water. Carefully pipet 20 mls of the 1.0N H₂SO₄. Dilute to the one-liter mark with distilled water. This solution would be used in situations where the alkalinity is expected to be less than 20 mg/L.

1.0N STANDARD SODIUM HYDROXIDE SOLUTION ("STOCK")

1.0N NaOH - Partially fill a one-liter volumetric flask with approximately 500 mls distilled water. Carefully dissolve 40 grams of reagent grade sodium hydroxide in this. Dilute to the one-liter mark with distilled water.

0.1N SODIUM HYDROXIDE SOLUTION ("WORKING")

0.1N NaOH - Partially fill a one-liter volumetric flask with distilled water. Carefully add 100 mls of the 1.0N NaOH solution. Dilute to the one-liter mark with distilled water.

0.02N SODIUM HYDROXIDE SOLUTION

0.02N NaOH - Partially fill a one-liter volumetric flask with distilled water. Carefully pipet 20 mls of the 1.0N NaOH stock solution. Dilute to the one-liter mark with distilled water.

Procedure

- 1) Standardize the pH meter to buffer 7 and 4.
- 2) Filter, centrifuge, or decant off clear supernate from the sample.

NOTE: There is literature that suggest that 30% or more of the alkalinity in anaerobic digesters may be contained in the sludge solids, and that by using only supernate in the analysis, much of the alkalinity is overlooked. There may be some validity to this argument and, in fact, either method (supernate or "whole sludge") is acceptable as long as the same method is used consistently.

If you decide to change from one method to the other, keep in mind that the ratio of alkalinity to volatile acids may change.

- 3) Add 50 mls of clear supernate to a 100 ml beaker.
- 4) Immerse pH electrodes into sample and change sample pH.

5) With meter on, titrate sample with standard H_2SO_4 to pH 4.0*. Note amount of acid used.

NOTE: If only interested in alkalinity - **STOP HERE** and perform CALCULATIONS.

6) Continue adding acid until sample reaches pH 3.5 to 3.3. Remove electrodes.

7) Check sample temperature.

8) Turn on hot plate and lightly boil the sample for at least three (3) minutes.

9) Standardize the pH meter to buffer 4.

10) Cool sample in cold water bath to the original temperature in Step 7.

11) Titrate sample with standard NaOH back to pH 4 (note buret reading).

12) Continue titration to pH 7 (note buret reading).

Calculations

The total alkalinity is figured first, using the amount of acid needed to titrate the sample from the starting pH to pH 4.0.

$$\text{Total Alkalinity, in mg/l} = \frac{\text{mls of acid used} \times N(\text{normality}) \text{ of acid} \times 50,000}{\text{mls of sample used}}$$

$$\text{Total Alkalinity, in mg/l} = \frac{\text{mls of acid} \times 0.10 \times 50,000}{50 \text{ mls}}$$

$$= \text{mls of acid used} \times 100$$

The volatile acids alkalinity is next figured using the amount of hydroxide needed to titrate the sample from pH 4 back up to pH 7. From the volatile acids alkalinity is calculated the volatile acids.

$$\text{Volatile Acids, Alkalinity, in mg/l} = \frac{\text{mls of hydroxide used} \times N \text{ of hydroxide} \times 50,000}{\text{mls of sample used}}$$

$$= \frac{\text{mls of hydroxide} \times 0.10 \times 50,000}{50 \text{ mls}}$$

$$= \text{mls of hydroxide} \times 100$$

To calculate the volatile acids, multiply the volatile acids alkalinity by:

If the volatile acids alkalinity is less than 180 mg/l by 1.0

If the volatile acids alkalinity is greater than 180 mg/l by 1.5

Example:

Using a 50 ml sample of digester supernate:
starting pH 7.4, mls acid 0.0
at pH 4.0, mls acid 23.5
temperature = 21 °C

After boiling and cooling to 21 °C:
starting pH 3.7, mls hydroxide 0.0
at pH 4.0, mls hydroxide 1.05
at pH 7.0, mls hydroxide 3.30

Total alkalinity = $23.5 \times 100 = 2,350$ mg/l
Volatile acids alkalinity = $(3.30 - 1.05) \times 100 = 225$ mg/l
Volatile acids (alkalinity over 180 mg/l) = $225 \times 1.5 = 338$

The volatile acids/alkalinity ratio is now calculated:

$$\text{Volatile acids/alkalinity} = \frac{338}{2,350} = 0.14$$

Quality Control

Running samples in duplicate is the best means of checking your procedure. Run two 50 ml portions of the sample through the entire test. Question any tests that do not duplicate within a reasonable amount, say 10%.

Be sure to properly standardize the pH meter before beginning the analysis.

**VOLATILE ACIDS and ALKALINITY
TROUBLESHOOTING GUIDE**

PROBLEM	MOST PROBABLE CAUSE	SOLUTION
Acidity, Results unreasonably high	<p>Over titration due to missing end point</p> <p>Improper calibration of pH meter</p> <p>Improper standardization of NaOH titrant</p>	<p>Add NaOH solution more slowly - allow time for sample to equilibrate before adding next drop.</p> <p>Recalibrate meter and rerun analysis</p> <p>Restandardize titrant and rerun analysis</p>
Acidity, Results unreasonably low	Using 0.1 or 0.2N NaOH as opposed to 0.02N	Dilute NaOH titrant to proper (0.02N) strength and rerun analysis
Alkalinity, Results unreasonably high	<p>Over titration due to missing the end point</p> <p>Improper standardization of H₂SO₄ titrant</p>	<p>Add the H₂SO₄ solution very slowly; allow time for sample to equilibrate before adding next drop</p> <p>Restandardize titrant and rerun analysis</p>
Alkalinity, Results unreasonably low	<p>Using higher concentration of H₂SO₄ than required</p> <p>pH electrode has become fouled</p>	<p>Restandardize H₂SO₄ titrant to 0.02N</p> <p>Follow manufacturer's instructions for cleaning electrodes. If the sample contains soaps, oily substances or excessive suspended matter; dilute the sample to reduce this problem before reanalyzing.</p>

Quality Control for Volatile Acids & Alkalinity

Document

Sample Collection

Grab - Exact time collected
Exact time analyzed
Location

Glassware Preparation - (Sampling Container)

Thoroughly rinse with distilled H₂O

Equipment

Meter

Range 0 to 14
Accuracy - 0.1 pH
Repeatability - 0.1 pH
Temperature Compensation
Capable of 2 Point Calibration

pH Probe

Document Age & Maintenance
(Gel filled - refillable)
Storage & Use Instruction
Stress Rinsing

Temperature Probe

Must Be Connected To Meter and In Analyte During Analysis
Calibration of Probe Against NIST Traceable Thermometer

Buret

Record all pertinent buret readings on bench sheets

Reagents

NIST Traceable (Fischer, etc.)
If using powder pillows or making your own buffers (from NIST Traceable materials)
Document quality of make up water
Preparation and Expiration Date
Standardization of Titrants Sulfuric Acid Sodium Hydroxide

Calibration

Document

Date and Time
Buffers Used & Order of Use
Exact Instrument Results
Analyst Performing Calibration
Buffer Temperature

Sample

Type
Temperature
Duplicate Results
Special Conditions
High Ionic Strength
Dilute - poorly buffered

REPORTING VOLATILE ACID/ALKALINITY DATA

Volatile Acid/Alkalinity Bench Sheet			
ANALYST:			
SAMPLE TIME and DATE:			
SAMPLE LOCATION:			
ANALYSIS TIME and DATE:			
METER STANDARDIZATION: (Date and Buffers Used)			
NORMALITY OF ACID (H ₂ SO ₄) TITRANT: (Date Standardized)			
NORMALITY OF BASE (NaOH) TITRANT: (Date Standardized)			

Volatile Acids	Volume (mls) of NaOH used to titrate sample from pH 4.0 to pH 7.0	Normality (concentration) of NaOH used	Sample Volume
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Alkalinity	Volume (mls) of H ₂ SO ₄ used to titrate sample from original sample pH to pH 4.0	Normality (concentration) of H ₂ SO ₄ used	Sample Volume
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References

A discussion of the volatile acid/alkalinity relationship can be found on page 163 of Operation of Wastewater Treatment Plants, 4th Edition, Volume 2. The actual analyses are described on pages 472 through 476 of that reference.

In the 18th Edition of Standard Methods for the Examination of Water and Wastewater, analytical methods for acidity (Method 2310B) and alkalinity (Method 2320B) can be found on pages 2-23 through 2-28.