Determination of Alkalinity by Titration
(Short Method)

1. Scope and Application

   1.1. Alkalinity determination by titration is used when analysis by an auto analyzer is not possible due to the color or turbidity of a given sample. MMSD routinely uses the alkalinity titration in order to determine the alkalinity of the digesters (sludge matrix). MMSD uses a two end- point (5.75 and 4.0) and follows a proposed method adaptation found in a paper in the *"Journal WPCF"* in May 1983, which proposed an alkalinity titration end pH 5.75 instead of pH 4.3. The paper concluded that the alkalinity found from pH 5.75 to pH 4.3 was due to the unusable volatile acids buffering capacity.

2. Summary of Method

   2.1. Alkalinity of water is its acid-neutralizing capacity. It is the sum of all the titratable bases. The measured value may vary significantly with the end-point pH used. Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.

   2.2. For digester samples, there are two end-points, 5.75 and 4.0.

3. Interferences

   3.1. Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response. Allow additional time between titrant additions to let electrode come to equilibrium or clean the electrodes occasionally. Do not filter, dilute, concentrate or alter sample.

4. Equipment and Supplies

   4.1. pH meter

   4.2. Magnetic stirrer and stir bars

   4.3. Wide bore glass volumetric pipets: 20 mL and 25 mL

   4.4. 100 mL glass beakers

   4.5. Volumetric flasks

   4.6. 50 mL buret

   4.7. Centrifuge and centrifuging tubes

5. Reagents and Standards

   5.1. Reagent grade methanol, absolute

   5.2. pH 4 buffer and pH 7 buffer

5.3. Standard hydrochloric acid, 0.1N: To a 1 L volumetric flask, pipet 8.33 mL of concentrated HCl. Bring up to volume with DI water.

5.4. Standard sodium hydroxide, 0.1N: To a 1 L volumetric flask, add 4.0g of NaOH pellets. Dissolve and bring up to volume with DI water.

5.5. Potassium hydrogen phthalate solution (KHP), ~0.05N: After drying (KHP) at 120°C for 2 hours, weigh approximately 10.0g (recording the exact weight) and transfer to a 1 L volumetric flask, and dilute to 1000 mL with DI water. Given that 10.2115g of KHP gives a 0.05N solution, use the calculation in 7.1 to determine the exact normality of the KHP solution as prepared.

5.6. Phenolphthalein solution, alcoholic: Dissolve 0.08g phenolphthalein in 100 mL absolute methanol.

5.7. Standardization of ~0.1N HCl (5.3)

5.7.1. Pipet 20 mL of 0.1N NaOH (5.4). Add a few drops of the phenolphthalein solution. Using a buret, titrate from pink to clear with 0.05N KHP (5.5).

5.7.2. Pipet 20 mL of 0.1N NaOH (5.4). Add a few drops of the phenolphthalein solution. Using a buret, titrate from pink to clear with 0.1N HCl (5.3).

6. Procedure

6.1. Alkalinity determination for sludges.

6.1.1. Using a centrifuge, spin down the digester samples for 30-45 minutes.

6.1.2. While sample is stirring take the pH of the un-spun digester sample. Record this pH.

6.1.3. Take 25 mL of the supernatant and determine the pH. (The pH of the supernatant is typically greater than the pH recorded in 6.1.2.) Using the HCl solution in the buret, adjust the pH to match the pH recorded in 6.1.2. This is the start point for the total alkalinity titration. Note the volume contained in the buret at this point.

6.1.4. Titrate the supernatant until a pH of 5.75 is reached. This is the first end-point. Record the volume of HCl in the buret.

6.1.5. Continue to titrate the sample until a pH of 4.00 is reached. This is the final end-point. Record the volume of HCl in the buret.

6.1.6. Using the volumes recorded in 6.1.4 and 6.1.5, calculate the alkalinity at pH 5.75 and pH 4.00 as outlined in 7.4.

7. Data Analysis and Calculations

7.1. Determining the exact normality of the KHP solution:

$$\text{Normality of KHP:} \quad \frac{10.2115\ \text{g}}{W} = \frac{0.05\ \text{N}}{X}$$

W = exact weight of KHP in g (from 5.5)

X = exact normality of KHP

7.2. Determine the normality of the NaOH solution:

$$\text{Normality of NaOH} = \frac{A \times B}{20 \text{ ml NaOH}}$$

A = Normality of KHP (determined in 7.1)

B = Average mL of KHP used (from 5.7.1)

7.3. Determine the normality of the HCl solution:

$$\text{Normality of HCl} = \frac{(20 \text{ ml of NaOH}) \times C}{D}$$

C = Normality of NaOH solution (determined in 7.2)

D = Average mL of HCl used (from 5.7.2)

7.4. Alkalinity, mg $CaCO_3$/mL:

$$\text{Alkalinity, mg } CaCO_3\text{/mL} = \frac{A \times N \times 50{,}000}{\text{mL supernatant (6.1.3)}}$$

A = mL standard HCl (from 6.1.4 or 6.1.5)

N = Normality of standard HCl (determined in 7.3)

8. Waste Management

8.1. All samples and reagents used in this method are rinsed down the drain with copious amounts of water.

9. References

9.1. "Measuring Anaerobic Sludge Digestion and Growth by a Simple Alkalimetric Titration," *Journal WPCF,* Volume 55, Number 5. May 1983. p 448.

9.2. Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998. American Public Health Association, Washington, DC. Method 2310B and Method 2320, pp 2-24 to 2-28.

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