METHOD #: 305.1	Approved for NPDES (Technical Revision 1974)
TITLE:	Acidity (Titrimetric)
ANALYTE:	Acidity
INSTRUMENTATION:	Titration
STORET No.	70508

- 1.0 Scope and Application
 - 1.1 This method is applicable to surface waters, sewages and industrial wastes, particularly mine drainage and receiving streams, and other waters containing ferrous iron or other polyvalent cations in a reduced state.
 - 1.2 The method covers the range from approximately 10 mg/L acidity to approximately 1000 mg/L as $CaCO_3$, using a 50 mL sample.
- 2.0 Summary of Method
 - 2.1 The pH of the sample is determined and a measured amount of standard acid is added, as needed, to lower the pH to 4 or less. Hydrogen peroxide is added, the solution boiled for several minutes, cooled, and titrated electrometrically with standard alkali to pH 8.2.
- 3.0 Definitions
 - 3.1 This method measures the mineral acidity of a sample plus the acidity resulting from oxidation and hydrolysis of polyvalent cations, including salts of iron and aluminum.
- 4.0 Interferences
 - 4.1 Suspended matter present in the sample, or precipitates formed during the titration may cause a sluggish electrode response. This may be offset by allowing a 15-20 second pause between additions of titrant or by slow dropwise addition of titrant as the endpoint pH is approached.
- 5.0 Apparatus
 - 5.1 pH meter, suitable for electrometric titrations.
- 6.0 Reagents
 - 6.1 Hydrogen peroxide (H_2O_2 , 30% solution).
 - 6.2 Standard sodium hydroxide, 0.02 N.
 - 6.3 Standard sulfuric acid, 0.02 N.

7.0 Procedure

- 7.1 Pipet 50 mL of the sample into a 250 mL beaker.
- 7.2 Measure the pH of the sample. If the pH is above 4.0, add standard sulfuric acid (6.3) in 5.0 mL increments to lower the pH to 4.0 or less. If the initial pH of the sample is less than 4.0, the incremental addition of sulfuric acid is not required.
- 7.3 Add 5 drops of hydrogen peroxide (6.1).
- 7.4 Heat the sample to boiling and continue boiling for 2 to 4 minutes. In some instances, the concentration of ferrous iron in a sample is such that an additional amount of hydrogen peroxide and a slightly longer boiling time may be required.
- 7.5 Cool the sample to room temperature and titrate electrometrically with standard sodium hydroxide (6.2) to pH 8.2.
- 8.0 Calculations

8.1 Acidity, as mg/ L CaCo₃ =
$$\frac{[(A \times B) - (C \times D)] \times 50,000}{mL \text{ of sample}}$$

where:

- A = vol. of standard sodium hydroxide used in titration
- B = normality of standard sodium hydroxide
- C = volume of standard sulfuric acid used to reduce pH to 4 or less
- D = normality of standard sulfuric acid
- 8.2 If it is desired to report acidity in milliequivalents per liter, the reported values as $CaCO_3$ are divided by 50, as follows:

Acidity, as meq/L =
$$\frac{\text{mg/L CaCo}_3}{50}$$

9.0 Precision

9.1 On a round robin conducted by ASTM on 4 acid mine waters, including concentrations up to 2000 mg/ L , the precision was found to be \pm 10 mg/L.

Bibliography

- 1. Annual Book of ASTM Standards, Part 31, "Water", p 116, D 1067, Method E (1976).
- 2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 277, Method 402(4d) (1975).