Analytical methods

Acidity, electrometric titration

Parameters and Codes:

Acidity, I-1020-85 (mg/L as H^{+1}): 71825 (mg/L as $CaCO_3$): 00435

1. Application

This method is applicable to many acidic samples. When the sample is suspected or known to contain mostly weak acids, however, the construction of a neutralization curve is imperative, and the acidity value is reported and interpreted in terms of the character of the curve obtained.

2. Summary of method

2.1 Acidity is determined by titrating the sample with a standard solution of a strong base to an electrometrically observed end point pH of 8.3. The titration is carried out at room temperature, except that the sample is heated briefly near the end of the titration to increase the rate of hydrolysis of metal ions present.

2.2 For additional information concerning the determination of acidity and for instructions for constructing an electrometric titration curve, see ASTM Method D 1067-82, "Standard Methods of Test for Acidity or Alkalinity of Water," (American Society for Testing and Materials, 1984).

3. Interferences

Dissolved gases that are acidic, such as CO_2 and H_2S, may easily be lost from the sample. If any substantial part of the acidity is due to gaseous solutes, special care must be taken to prevent their escape prior to and during the titration. Gases are less soluble in warm water than in cold; hence, the sample must be kept chilled until analyzed, and even then the analysis must be performed as soon as possible. Stirring and agitation of the sample cause expulsion of dissolved gases; care must be taken to avoid unnecessary agitation of the sample. A tightly capped bottle is essential for storing and transporting samples. The determination should be performed at the time of sampling for greatest accuracy.

4. Apparatus

4.1 *Buret*, 50-mL capacity.

4.2 *Hotplate.*

4.3 *pH meter.*

4.4 *Stirrer*, magnetic.

5. Reagents

5.1 *Sodium hydroxide stock solution*, approx. 2*N*: Dissolve 80 g NaOH in carbon dioxide-free water and dilute to 1 L with carbon dioxide-free water. Store in a tightly capped polyethylene bottle.

5.2 *Sodium hydroxide standard solution*, approx. 0.025*N*: Dilute 12.5 mL 2*N* NaOH with carbon dioxide-free water to approx 1 L. Standardize the solution against primary standard potassium hydrogen phthalate ($KHC_8H_4O_4$) as follows: Lightly crush 3 g of the salt to a fineness of approx 100 mesh and dry for at least 1 h at 110°C. Dissolve about 2 g, accurately weighed to the nearest milligram, in carbon dioxide-free water and dilute to 500.0 mL. Titrate 50.0 mL of the solution with the NaOH standard solution to pH 8.6:

$$\text{Normality of NaOH} = \frac{\text{g } KHC_8H_4O_4 \text{ in 50.0 mL} \times 4.896}{\text{mL NaOH}}$$

6. Procedure

6.1 Samples should be collected in tightly capped polyethylene bottles, with as little agitation as possible, particularly if it is suspected or known that any significant part of the acidity is due to dissolved gases. Chill or otherwise keep the sample cool during transportation to the laboratory and perform the determination as soon as possible. Do not open the sample bottle until ready to determine the acidity, and then perform the determination without delay once the bottle has been opened.

6.2 Carefully pipet an aliquot of sample containing less than 1.0 mg H^{+1} (50.0 mL max) into a 150-mL beaker. Avoid disturbing any sediment in the sample bottle. Do not filter.

6.3 Insert the beaker in the titration assembly and record the pH.

6.4 Titrate the sample with standard NaOH solution to pH 8.3.

6.5 Heat the solution to about 90 °C (do not boil), and maintain this temperature for 2 min.

6.6 Cool to room temperature and resume the titration, titrating again to a final pH of 8.3. Record the total volume of titrant used (mL_b).

7. Calculations

7.1 Determine acidity as me/L as follows:

$$\text{Acidity, me/L} = \frac{mL_b}{mL_s} \times N_b \times 10^3$$

7.2 Determine acidity as hydrogen ion in mg/L as follows:

$$\text{Acidity, mg/L as } H^{+1} = \frac{mL_b}{mL_s} \times N_b \times 1.008 \times 10^3$$

7.3 Determine acidity as $CaCO_3$ in mg/L as follows:

$$\text{Acidity, mg/L as } CaCO_3 = \frac{mL_b}{mL_s} \times N_b \times 10^3 \times 50.05$$

where

mL_b and mL_s = volumes of standard NaOH solution and sample, respectively,

and

N_b = normality of standard NaOH solution.

8. Report

8.1 Report acidity values in milliequivalents per liter or milligrams per liter as hydrogen ion as follows: less than 10 me/L (mg/L), one decimal; 10 me/L (mg/L) and above, two significant figures.

8.2 Report acidity, hydrogen ion (71825), concentrations as milligrams per liter.

8.3 Report acidity, calcium carbonate (00435), concentrations in milligrams per liter as follows: less than 100 mg/L, whole numbers; 100 mg/L and above, two significant figures.

9. Precision

The precision for one sample expressed in both standard deviation and percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L as H^{+1})	Standard deviation (mg/L as H^{+1})	Relative standard deviation (percent)
21	26.0	0.9	3.5

Reference

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 125–133.