METHOD #: 350.3   Approved for NPDES (Issued 1974)

TITLE: Nitrogen, Ammonia (Potentiometric, Ion Selective
                                        Electrode)

ANALYTE: CAS #   Nitrogen, N   7727-37-9
                                        CAS #   Ammonia, NH_3 7664-41-7

INSTRUMENTATION: ISE

STORET No.   Total   00610
                                        Dissolved   00608

1.0   Scope and Application

    1.1   This method is applicable to the measurement of ammonia-nitrogen in drinking,
           surface and saline waters, domestic and industrial wastes.
    1.2   This method covers the range from 0.03 to 1400 mg NH_3-N/L. Color and turbidity
           have no effect on the measurements, thus, distillation may not be necessary.

2.0   Summary of Method

    2.1   The ammonia is determined potentiometrically using an ion selective ammonia
           electrode and a pH meter having an expanded millivolt scale or a specific ion
           meter.
    2.2   The ammonia electrode uses a hydrophobic gas-permeable membrane to separate
           the sample solution from an ammonium chloride internal solution. Ammonia in
           the sample diffuses through the membrane and alters the pH of the internal
           solution, which is sensed by a pH electrode. The constant level of chloride in the
           internal solution is sensed by a chloride selective ion electrode which acts as the
           reference electrode.

3.0   Sample Handling and Preservation

    3.1   Samples may be preserved with 2 mL of conc. H_2SO_4 per liter and stored at 4°C.

4.0   Interferences

    4.1   Volatile amines act as a positive interference.
    4.2   Mercury interferes by forming a strong complex with ammonia. Thus the samples
           cannot be preserved with mercuric chloride.

5.0   Apparatus

    5.1   Electrometer (pH meter) with expanded mV scale or a specific ion meter.
    5.2   Ammonia selective electrode, such as Orion Model 95-10 or EIL Model 8002-2.
    5.3   Magnetic stirrer, thermally insulated, and Teflon-Coated stirring bar.

6.0   Reagents

6.1 Distilled water: Special precautions must be taken to insure that the distilled water is free of ammonia. This is accomplished by passing distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin.

6.2 Sodium hydroxide, 10N: Dissolve 400 g of sodium hydroxide in 800 mL of distilled water. Cool and dilute to 1 liter with distilled water (6.1).

6.3 Ammonium chloride, stock solution: 1.0 mL = 1.0 mg NH_3-N. Dissolve 3.819 g NH_4Cl in water and bring to volume in a 1 liter volumetric flask using distilled water (6.1).

6.4 Ammonium chloride, standard solution: 1.0 mL = 0.01 mg NH_3-N. Dilute 10.0 mL of the stock solution (6. 3) to 1 liter with distilled water (6.1) in a volumetric flask. **NOTE 1:** When analyzing saline waters, standards must be made up in synthetic ocean water (SOW); found in Nitrogen, Ammonia: Colorimetric, Automated Phenate Method (350. 1).

7.0 Procedure

7.1 Preparation of standards: Prepare a series of standard solutions covering the concentration range of the samples by diluting either the stock or standard solutions of ammonium chloride.

7.2 Calibration of electrometer: Place 100 mL of each standard solution in clean 150 mL beakers. Immerse electrode into standard of lowest concentration and add 1 mL of 10N sodium hydroxide solution while mixing. Keep electrode in the solution until a stable reading is obtained.
NOTE 2: The pH of the solution after the addition of NaOH must be above 11. Caution: Sodium hydroxide must not be added prior to electrode immersion, for ammonia may be lost from a basic solution.

7.3 Repeat this procedure with the remaining standards, going from lowest to highest concentration. Using semilogarithmic graph paper, plot the concentration of ammonia in mg NH3-N/L on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

7.4 Calibration of a specific ion meter: Follow the directions of the manufacturer for the operation of the instrument.

7.5 Sample measurement: Follow the procedure in (7.2) for 100 mL of sample in 150 mL beakers. Record the stabilized potential of each unknown sample and convert the potential reading to the ammonia concentration using the standard curve. If a specific ion meter is used, read the ammonia level directly in mg NH_3-N/L.

8.0 Precision and Accuracy

8.1 In a single laboratory (EMSL), using surface water samples at concentrations of 1.00, 0.77, 0.19, and 0.13 mg NH_3-N/L, standard deviations were ± 0.038, ± 0.017, ± 0.007, and ± 0.003, respectively.

8.2 In a single laboratory (EMSL), using surface water samples at concentrations of 0.19 and 0.13 mg NH_3-N/L, recoveries were 96% and 91%, respectively.

Bibliography

1. Booth, R. L., and Thomas, R. F., "Selective Electrode Determination of Ammonia in Water and Wastes", Envir. Sci. Technology, 7, p 523-526 (1973).
2. Banwart, W. L., Bremner, J. M., and Tabatabai, M. A., "Determination of Ammonium in Soil Extracts and Water Samples by an Ammonia Electrode", Comm. Soil Sci. Plant.,3,p 449 (1952).
3. Midgley, D., and Torrance, K., "The Determination of Ammonia in Condensed Steam and Boiler Feed-Water with a Potentiometric Ammonia Probe", Analyst, 97 p 626-633 (1972).