

UNCONTROLLED

WEST VALLEY NUCLEAR SERVICES CO., INC.

ANALYTICAL CHEMISTRY METHOD
ANALYTICAL AND PROCESS CHEMISTRY

ACM-NH3-3301 Rev. 0
Effective Date: 01/06/88

AMMONIA - SELECTIVE ELECTRODE METHOD

Approved by:

C. W. McVay

C. W. McVay, Manager
Analytical and Process Chemistry

Part I

1.0 PURPOSE

- 1.1 This establishes the method to be used in assaying the amount of ammonia in water samples.

2.0 APPLICATION

- 2.1 This method covers the determination of ammonia nitrogen exclusive of organic nitrogen in water.

3.0 DISCUSSION

- 3.1 The sample is made alkaline with sodium hydroxide to convert ammonium ion to ammonia. The ammonia thus formed diffuses through a gas-permeable membrane of a selective ion electrode and alters the pH of its internal solution which in turn is sensed by a pH electrode. The potential is measured by means of a pH meter or ion analyzer. The ammonia content can be determined from a calibration curve, from the formula that can be found in the calculations section (11.1.2), or read directly from the microprocessor.

3.2 Interferences

- 3.2.1 Volatile amines are positive interferences.
- 3.2.2 Mercury, if present, forms ammonia complexes thus causing negative interference.
- 3.2.3 Organic compounds that form ammonia readily (within 5 minutes) under alkaline conditions are a positive interference.

- 3.2.4 If interference is found in the sample, refer to procedure for distillation. Standard Methods, 16th Edition.

4.0 REFERENCES

Standard Methods - for the examination of water and wastewater, 16th Edition, 419E.

Annual Book of ASTM Standards - Water and Environmental Technology, Volume 11.01 Water (1).

Orion Selective Ammonia Electrode Manual

PART II

5.0 EQUIPMENT

NOTE: All calibrated equipment is controlled per ACP 7.1.

- 5.1 Gas-sensing, ammonia electrode, incorporating an internal reference electrode, and a diffusion-type membrane.
- 5.2 Microprocessor ionalyzer or equivalent accurate to ± 0.1 mV.
- 5.3 Electrode holder for mounting the electrode at 20° to the vertical.
- 5.4 Stirrer - magnetic with TFE-fluorocarbon-coated stirring bar.
- 5.5 Heat barrier - A 6 mm insulating material placed underneath the beaker to insulate the sample solution from heat generated by the magnetic stirrer.

6.0 REAGENTS

NOTE: All reagents and solutions are prepared per ACP 8.1 and have a shelf life of one year unless otherwise stated.

6.1 Ammonia Stock Standard Solution

- 6.1.1 Ammonia - stock standard solution (1,000 mg NH_3 as N/litre).
- 6.1.2 Dry reagent-grade ammonia sulfate $[(\text{NH}_4)_2\text{SO}_4]$ for one hour at 100°C . Accurately weigh 4.718 g and dissolve in ammonia-free water in a one-litre volumetric flask. Dilute to the mark with NH_3 -free water. This solution is stable for at least three months.

6.1.3 Ammonia - intermediate standard solution (100 mg NH₃ as N/litre). Pipet 100 mL of the 1,000 gm/litre standard solution to a one-litre volumetric flask and dilute to the mark with NH₃-free water. This solution is stable for one month.

6.1.4 Ammonia - standard working solutions (10, 1, 0.1, and 0.01 mg NH₃ as N/litre). Quantitatively transfer 100, 10, 1, and 0.1 mL of the 100 mg/litre standard solution into separate one-litre volumetric flasks. Dilute each to the mark with NH₃-free water. Prepare these solutions daily before use.

6.2 Ammonia chloride solution (5.4 g/litre) - Dissolve 5.4 g of ammonia chloride (NH₄ Cl) in ammonia-free water and dilute to 1 litre. This solution is used only for soaking the electrode.

6.3 Sodium hydroxide solution (400 g/litre). Dissolve 400 g of sodium hydroxide (NaOH) in NH₃-free water. Cool and dilute to one litre.

7.0 SAFETY PRECAUTIONS

7.1 Follow standard laboratory safety procedures ACP 7.2.

8.0 RECORDS

All measurement data and sample identification shall be recorded on the worksheet (Attachment A). The final result shall be recorded on the analytical request sheet (ACP 5.1).

9.0 CALIBRATION AND CONTROL

9.1 Microprocessor ionanalyzer or pH meter - Refer to the manufacturer's instruction manual for proper operation of the microprocessor ionanalyzer. Prepare calibration curves using a minimum of three standard solutions (6.1.3) bracketing the expected concentration of the sample.

9.1.1 Treat the standards as directed in 8.1 and measure the potential of each standard and record in millivolts or in parts per million read directly from the instrument. The standards and the sample must be at the same temperature preferably about 25°C.

9.1.2 Using semilogarithmic graph paper, plot the concentration of ammonia nitrogen in milligrams per litre on the log axis against the corresponding electrode potential, in millivolts on the linear axis when reading in millivolts.

9.1.3 Check the calibration curve every three hours when analyzing a series of samples.

- 9.2 A 0.1 mg/L spike shall be added to a duplicate sample to assure proper calibration and recovery of spike.
- 9.3 A log book will contain the results of all spike samples per ACP 8.2; a divergence of greater than two standard deviations will require a retest of the spike. Two successive results greater than two standard deviations will require a review of the spike and/or the procedure by the Analytical Chemistry Manager.

10.0 PROCEDURE

10.1 Sample Treatment

- 10.1.1 Transfer 100 mL of the sample (or an aliquot diluted to 100 mL) to a 150 mL beaker. The sample temperature must be the same as that of the standards used in calibration.
- 10.1.2 Add the stirring bar and mix on the magnetic stirrer. Do not mix so rapidly that air bubbles are drawn into the solution.
- 10.1.3 Immerse the electrode into the sample, positioning it at an angle of approximately 20° to the vertical, making sure that no air bubbles are trapped on the membrane of the electrode. All precautions recommended by the manufacturer should be observed to ensure accurate measurements.
- 10.1.4 Add 1.0 mL of NaOH solution (6.3) to the sample. The NaOH solution should be added just prior to measurement, because ammonia may be lost to the atmosphere from a stirred alkaline solution.
- 10.1.5 Check the pH of the sample with pH paper. The pH must be greater than 11. Add additional NaOH solution (6.3) in 0.1/mL increments until the pH of the solution exceeds 11.
- 10.1.6 When the electrode comes to equilibrium, measure the electrode potential of the ammonia nitrogen concentration in millivolts.

10.2 Sample Measurement

- 10.2.1 Determine the ammonia nitrogen concentration by means of an ionanalyzer.
- 10.2.2 Record the observed potential in millivolts and convert to milligrams per litre of ammonia nitrogen by means of the calibration curve or the formula found in 9.1.2 or record results directly in parts per million (milligrams per litre) if instrument is equipped for automatic calibration.

11.0 CALCULATIONS

11.1 If instrument has no automatic calibration, report the ammonia nitrogen content in milligrams per litre by extrapolating the mg/litre by the calibration curve or calculate by the following method.

$$\text{Log Concentration of Sample} = \text{Log Concentration Standard}_1 + \frac{(\text{Log Conc. Standard}_1 - \text{Log Conc. Standard}_2) (\text{mV Sample} - \text{mV Standard}_1)}{(\text{mV Standard}_1 - \text{mV Standard}_2)}$$

The concentration of the sample will be in mg/litre; for example, the higher and lower standard are 10 mg/L and 0.1 mg/L; the middle standard should be 1.0 mg/L - mV were 0.10 mg/L - 163.3 mV; 1.0 mg/L - 105.3 mV; and 10.0 mg/L - 47.5 mV..

$$\text{Log concentration of middle standard} = \log 0.1 \text{ mg/L} + \frac{(\log 0.1 \text{ mg/L} - \log 10.0 \text{ mg/L}) (105.3 \text{ mV} - 163.3 \text{ mV})}{(163.3 \text{ mV} - 47.5 \text{ mV})}$$

Concentration of middle standard = 1.00 mg/L

12.0 ATTACHMENT

Attachment A - Nitrogen Ammonia (Electrode Method) Worksheet

ATTACHMENT A

AMMONIA WORKSHEET

SAMPLE NAME _____ LOG NUMBER _____

SPECIAL INSTRUCTIONS _____

SAMPLE ID				
STANDARD #1				
STANDARD #2				
STANDARD #3				
STANDARD #4				
SAMPLE				
SAMPLE + SPK				

ANALYST _____ DATE _____

APPROVED _____ DATE _____