ESS Method 220.3: Ammonia Nitrogen and Nitrate + Nitrite Nitrogen, Automated Flow Injection Analysis Method

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1.0 Scope and Application

1.1 This method pertains to the simultaneous determination of ammonia and nitrate in surface, drinking and ground waters, and domestic and industrial wastes samples which have been preserved with H_2SO_4.

1.2 The applicable range of the ammonia channel is 0.02-10.0 mg NH_3-N/L. The applicable range of the nitrate channel is 0.02-35.0 mg NO_3+NO_2-N/L. The ranges may be extended with the digital diluter.

2.0 Summary of Method

2.1 NH_3-N: Alkaline phenol and sodium hypochlorite react with ammonia to form a blue indophenol compound which is proportional to the ammonia concentration. The presence of EDTA in the buffer prevents precipitation of calcium and magnesium. The color is intensified by adding sodium nitroprusside. The resulting water soluble colored dye is measured colorimetrically at 630 nm.

2.2 NO_3+NO_2-N: The same sample is passed through a copperized cadmium column which reduces nitrate quantitatively to nitrite. The total nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl) ethylenediamine dihydrochloride. The resulting water soluble magenta colored dye is measured colorimetrically at 520 nm. Nitrite alone can also be determined by removing the cadmium column.

3.0 Sample Handling and Preservation

3.1 The samples are collected in 250 mL high density polyethylene containers.

3.2 Samples are preserved in the field with 2 mL of 12.5% H_2SO_4/250 mL (1 mL of conc. H_2SO_4/L, pH <2) and stored at 4°C.

4.0 Interferences

4.1 Calcium, magnesium, iron and copper ions, or other metals may precipitate if present in sufficient concentration. EDTA is added to the sample in-line in order to prevent this problem.

4.2 Color, turbidity, and certain organic species may interfere.

4.2.1 Sample color may be corrected for by running the samples through the manifold with all reagents pumping except hypochlorite, which is replaced by Milli-Q water. The resulting absorbance readings are then subtracted from those obtained for samples determined with color formation in addition to sample color.

4.2.2 Turbidity is removed by manual filtration. Build up of suspended matter in the reduction column will restrict sample flow.

4.2.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent, such as Freon.

5.0 Apparatus

Lachat QuikChem AE Automated Flow Injection Ion Analyzer consisting of:

5.1 XYZ Sampler.

5.2 Peristaltic Pump.

5.3 Two QuikChem AE Sample Processing modules with Alpha and Beta detectors.

5.3.1 Interference filters: two 520 nm for NO_3-N and two 630 nm filters for NH_3-N.

5.3.2 Flow cells: 2 Alpha 0.1 cm, 8.0 µL and 2 Beta 1.0 cm., 80 µL.

5.3.3 Sample Loops: Ammonia - 180 cm loop, Nitrate - 59 cm loop.

5.4 Reaction Module 10-107-06-1-Z with heating unit.

5.5 Reaction Module 10-107-04-1-Z with cadmium column.

5.6 Automated Digital Diluter.

5.7 IBM Personal System 12 Computer.

5.8 QuikChem AE System Unit.

6.0 Reagents

Ammonia

6.1 Milli-Q water: Millipore Corp., Bedford, MA. All reagents must be made with NH_3-free Milli-Q water.

6.2 Dilution water: Add 1 mL H_2SO_4 to 1 L Milli-Q water.

6.3 Alkaline phenol: Dissolve 83 g phenol in a 1 L Erlenmeyer flask containing about 500 mL Milli-Q water. While stirring, slowly add 32 gm NaOH. Cool, dilute to 1 L, and filter through a glass fiber filter if necessary. Two liters can be made at one time. Store in a dark bottle.

6.4 Sodium hypochlorite solution: Dilute 500 mL of commercial bleach containing 5.25% available chlorine (e.g. Clorox) to 1 L with Milli-Q water, and filter through a 0.45 µm membrane filter, if necessary. Store at 4°C.

6.5 Buffer: Dissolve 50 g disodium ethylenediamine-tetraacetate (Na_2 EDTA) and 12.5 g NaOH in 900 mL of Milli-Q water. Dilute to 1 L.

6.6 Sodium nitroprusside: Dissolve 7 g of $Na_2Fe(CN)_5NO{\cdot}2H_2O$ (alternate name: sodium nitroferricyanide) in 900 mL of Milli-Q water and dilute to 1 L. Reagent is light sensitive, store in dark container.

Nitrate

6.7 Ammonium chloride buffer, pH 8.5: In a hood, to a 1 L volumetric flask, add 500 mL Milli-Q water, 105 mL concentrated HCl, 95 mL concentrated ammonium hydroxide (NH_4OH) and 1.0 g disodium EDTA. Dissolve and dilute almost to volume. Allow to cool overnight. Adjust the pH to 8.5 ± 0.1 with either conc. HCl or conc. NH_4OH. Dilute to volume. 2 L can be made at one time.

6.8 Sulfanilamide color reagent: To approximately 1500 mL of Milli-Q water, add 200 mL 85% phosphoric acid (H_3PO_4), 80 g sulfanilamide ($C_6H_8N_2O_2S$), and 2.0 g N-(1-naphthyl) ethylenediamine dihydrochloride ($C_{12}H_{14}N_2{\cdot}2HCl$). Dissolve and dilute to 2 L. Store in brown bottle and keep in a cool, dark place. This solution is stable for several months.

6.9 Cadmium column: Use prepacked column from Lachat. The efficiency should be above 90%. To check this:

6.9.1 Have system running with all reagents, but *no* cadmium column.

6.9.2 Run calibration curve with nitrite standards: 20, 10, 5, 1.0 mg NO_2-N/L.

6.9.3 Attach cadmium column and run calibration curve with nitrate standards: 20, 10, 5, 1 mg NO_3-N/L.

6.9.4 Calculate percent recovery of standards.

7.0 Stock Standards

7.1 Ammonia standard solution A (1000 mg NH_3-N/L): Dissolve 3.819 g of anhydrous ammonium chloride (NH_4Cl), dried at 105°C for 1 hr, in 900 mL Milli-Q water. Add 1 mL conc. H_2SO_4 and dilute to 1 L (1.0 mL = 1.0 mg NH_3-N).

7.2 Ammonia standard solution B (100 mg NH_3-N/L): Dilute 100 mL standard solution A to 900 mL Milli-Q water. Add 1 mL conc. H_2SO_4 and dilute to 1 L (1.0 mL = 0.1 mg NH_3-N).

7.3 Ammonia standard solution C (10 mg NH_3-N/L): Dilute 25 mL standard solution B to 250 mL (1.0 mL = 0.01 mg NH_3-N).

7.4 Nitrate standard solution A (1000 mg NO_3-N/L): Dissolve 7.218 g potassium nitrate (KNO_3) in 900 mL Milli-Q water. Add 2 mL chloroform and dilute to 1 L (1.0 mL = 1.0 mg NO_3-N).

7.5 Nitrate standard solution B (100 mg NO_3-N/L): Dilute 100 mL standard solution A to 900 mL Milli-Q water. Add 2 mL chloroform and dilute to 1 L (1.0 mL = 0.1 mg NO_3-N).

7.6 Nitrate standard solution C (10 mg NH_3-N/L): Dilute 25 mL standard solution B to 250 mL (1.0 mL + 0.01 mg NO_3-N).

8.0 Mixed Working Standards

Prepare the following standards by adding appropriate amounts of stock standards to 500 mL Milli-Q water. Add 1 mL conc. H_2SO_4 and dilute to 1 L.

Std. ID	Conc.		mL Stock Standard A	
	mg NH_3-N/L	mg NO_3-N/L	mL(1000 mg NH_3-N/L)	mL(1000 mg NO_3-N/L)
C	5.0	10.0	5.0	10.0
B	7.5	20.0	7.5	20.0
A	10.0	35.0	10.0	35.0

Std. ID	Conc.		mL Stock Standard B	
	mg NH_3-N/L	mg NO_3-N/L	mL(100 mg NH_3-N/L)	mL(100 mg NO_3-N/L)
E	0.5	0.5	5.0	5.0
D	1.0	1.0	10.0	10.0
SP	2.0	5.0	20.0	50.0
CK	3.0	5.0	30.0	50.0

Std. ID	Conc.		mL Working Standard C	
	mg NH_3-N/L	mg NO_3-N/L	mL(10 mg/NH_3-N/L)	mL(10 mg NO_3N/L)
H	0.02	0.02	2.0	2.0
G	0.05	0.05	5.0	5.0
F	0.10	0.10	10.0	10.0
CK	0.30	0.30	30.0	30.0

9.0 Setup for Both Channels

9.1 Use alpha and beta detectors for optical dilution: Place the 0.1 cm flowcell in the alpha detector and the 1.0 cm flowcell in the beta detector for each channel.

9.2 Sample loops - ports 1 and 4.

a. Ammonia - 180 cm loop.
b. Nitrate - 59 cm loop.

9.3 Connect the sample line to port 6 of the NH_3-N channel.

9.4 Connect the port 5-6 tube from port 5 of the NH_3-N channel to port 6 of the NO_3-N channel.

9.5 Attach pump tubes according to flow diagram.

a. Sample line: Green, cut to 2 cm at each end.
b. Wash line: Green.
c. Nitroprusside: Orange.
d. Hypochlorite: Black.
e. Alkaline phenol: Orange.
f. EDTA buffer: Red.

g. NH_3 Carrier water: Blue.
h. NH_4Cl buffer: Yellow-blue.
i. Sulfanilamide: White.
j. NO_3 carrier water: Orange.

9.6 Degas all ammonia reagents, except phenol, with helium for 2 to 3 minutes just prior to attaching lines to system.

10.0 Start-up

10.1 Turn on and check diagnostics.

10.2 Attach reagent lines.

10.3 Attach cadmium column.

10.3.1 Turn pump down to 05.

10.3.2 First remove line from column.

10.3.3 Remove line from * connection (buffer + sample inlet).

10.3.4 Attach * line to column.

10.3.5 Attach column line to *.

10.3.6 To remove column, reverse procedure.

10.3.7 Turn pump speed to 35.

10.4 Pour standards.

11.0 Procedure

11.1 Follow directions in General Operating Procedures.

11.2 Clean both channels with 10% HCl during final shutdown.

12.0 Precision and Accuracy

Precision and accuracy data are available in the Inorganic Chemistry Unit Quality Assurance Manual.

13.0 References

13.1 U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Method 350.1, (1979).

13.2 U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Method 353.2, (1979).

13.3 Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, U.S. Geological Survey Techniques of Water Resources Inv., Book 5, Ch. A1, (1979).

13.4 Lachat Instruments, Method 10-107-06-1-Z, March 1990.

13.5 Lachat Instruments, Method 10-107-04-1-Z, March 1990.