Nitrogen, nitrite plus nitrate, colorimetric, cadmium reduction-diazotization, automated-segmented flow

Parameters and Codes:

Nitrogen, nitrite plus nitrate, dissolved, I-2545-85 (mg/L as N): 00631
Nitrogen, nitrite plus nitrate, total, I-4545-85 (mg/L as N): 00630
Nitrogen, nitrite plus nitrate, total-in-bottom-material, dry wt, I-6545-85 (mg/kg as N): 00633

1. Application

1.1 This method may be used to analyze surface, domestic, and industrial water, and brines and water-suspended sediment containing from 0.1 to 5.0 mg/L of nitrite- plus nitrate-nitrogen. Samples containing greater concentrations need to be diluted.

1.2 Water-suspended sediment may be analyzed by this procedure by decanting a suitable portion from a well-settled sample.

1.3 This method may be used to determine the sum of nitrite- plus nitrate-nitrogen concentrations in bottom material containing at least 2 mg/kg.

2. Summary of method

2.1 An acidified sodium chloride extraction procedure is used to extract nitrate and nitrite from bottom material for this determination (Jackson, 1958).

2.2 Nitrate is reduced to nitrite by a copper-cadmium column. The sample stream is then treated with sulfanilamide under acidic conditions to yield a diazo compound, which couples with N-1-naphthylethylenediamine dihydrochloride to form a red compound, the absorbance of which is measured colorimetrically. The final result is the sum of the nitrite originally present plus that formed by the reduction of the nitrate (Brewer and Riley, 1965; Kamphake and others, 1967; Morris and Riley, 1963; Strickland and Parsons, 1972; U.S. Environmental Protection Agency, 1979, p. 207-214; and Ehrlich and MacDonald, written commun., 1969).

2.3 Interferences from Hg^{+2} added to the samples as a preservative are overcome by adjusting the pH of the ammonium chloride buffer to 6.3.

3. Interferences

3.1 The concentrations of potentially interfering substances are seldom high enough to introduce error. High concentrations of oxidizing agents, reducing agents, and some metals, such as Cu^{+2}, interfere. See American Society for Testing and Materials (1984) for details on potential interferences.

3.2 Acids destroy the cadmium column; therefore, acid-treated samples cannot be analyzed by this method.

3.3 Repeated analysis of waters containing concentrations of sulfide more than 2 mg/L will rapidly deactivate the cadmium column by formation of cadmium sulfide (Strickland and Parsons, 1972).

4. Apparatus

4.1 *Centrifuge.*

4.2 *Shaker*, wrist-action.

4.3 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold (including copper-cadmium reduction column), proportioning pump, colorimeter, voltage stabilizer, recorder, and printer.

4.4 With this equipment the following operating conditions have been found satisfactory for the range from 0.1 to 5.0 mg/L (NO_2 + NO_3) as N:

Absorption cell -----	15 mm
Wavelength --------	520 nm
Cam --------------	40/h (4/1)

5. Reagents

5.1 *Ammonium chloride solution*, 10 g/L: Dissolve 10 g NH_4Cl in demineralized water and dilute to approx 950 mL. Adjust pH to 6.3 ± 0.2 with dilute NH_4OH solution and dilute to 1 L. Add 0.5 mL Brij-35 solution.

5.2 *Brij-35 solution*, 30-percent aqueous solution (Baker No. C706 or equivalent).

5.3 *Cadmium powder*, coarse, 99 percent pure (Technicon No. T11-5063, or equivalent): Wash cadmium powder with diethyl ether or 1*M* HCl followed by demineralized water. Allow to air-dry. Shake the dry powder with copper sulfate solution (20 g/L). The weight of the solution should be approx 10 times that of the cadmium. Wash thoroughly with demineralized water to remove colloidal copper, which is visible as a blue color in the wash solution. A minimum of 10 washings is usually required to eliminate perceptible blue color.

5.4 *Color reagent*: Add 200 mL concentrated phosphoric acid (sp gr 1.69) and 20 g sulfanilamide to approx 1,500 mL demineralized water. Dissolve completely (warm if necessary). Add 1.0 g N-1-naphthylethylenediamine dihydrochloride and dissolve completely. Dilute to 2 L with demineralized water. Add 1.0 mL Brij-35 solution. Store in a refrigerator. This reagent is stable for approx 1 month.

5.5 *Copper sulfate solution*, 20 g/L: Dissolve 20 g $CuSO_4$ (anhydrous) in demineralized water and dilute to 1 L.

5.6 *Hydrochloric acid*, 1.0*M*: Add 83.3 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 L.

5.7 *Nitrate-nitrogen standard solution I*, 1.00 mL = 0.50 mg NO_3-N: Dissolve 3.609 g KNO_3, dried overnight over concentrated H_2SO_4, in demineralized water and dilute to 1,000 mL.

5.8 *Nitrate-nitrogen standard solution II*, 1.00 mL = 0.025 mg NO_3-N: Dilute 50.0 mL nitrate-nitrogen standard solution I to 1,000 mL with demineralized water.

5.9 *Nitrate-nitrogen working standards*: Prepare a blank and 500 mL each of a series of nitrate-nitrogen working standards by appropriate quantitative dilution of nitrate standard solution II (NOTE 1). Dissolve 26 mg mercuric chloride and 300 mg sodium chloride in each working standard. For example:

Nitrite-nitrogen standard solution II (mL)	Nitrite-nitrogen concentration (mg/L)
0.0	0.00
2.0	.10
5.0	.25
10.0	.5
20.0	1.0
30.0	1.5
40.0	2.0
60.0	3.0
80.0	4.0
100.0	5.0

NOTE 1. If nitrate-nitrogen in bottom material is being determined, the working standards are diluted with sodium chloride solution (5.10). Mercuric chloride is not added.

5.10 *Sodium chloride solution*, 100 g/L, acidified: Dissolve 100 g NaCl in 950 mL ammonia-free water. Acidify with concentrated HCl (sp gr 1.19) to a pH of 2.5. Dilute to 1 L.

6. Procedure

6.1 Proceed to paragraph 6.2 for waters or water-suspended sediment mixtures. For bottom materials begin with paragraph 6.1.1.

6.1.1 Weigh approx 5 g of sample, prepared as directed in either method P-0520 or P-0810, and transfer to a 250-mL Erlenmeyer flask.

6.1.2 Add 50 mL NaCl solution (5.10) and shake on the wrist-action shaker for 30 min.

6.1.3 Carefully transfer the entire sample, including all sediment particles, to a centrifuge tube. Centrifuge for 5 min; if the sample does not flocculate, add a drop of concentrated HCl (sp gr 1.19) and recentrifuge.

6.1.4 Transfer the supernatant solution to a 100-mL volumetric flask, taking care not to disturb the residue in the bottom of the centrifuge tube.

6.1.5 Wash the sediment in the centrifuge tube with 20 mL sodium chloride solution, recentrifuge, and transfer the clear wash solution to the volumetric flask. Adjust to volume with sodium chloride solution (5.10). Proceed to paragraph 6.2.

6.2 Set up manifold (fig. 36).

6.3 Allow the color reagent to come to room temperature.

6.4 Allow colorimeter and recorder to warm for at least 30 min.

6.5 Fill the reduction column, which is a U-shaped, 36-cm length of 2.0-mm ID glass tubing

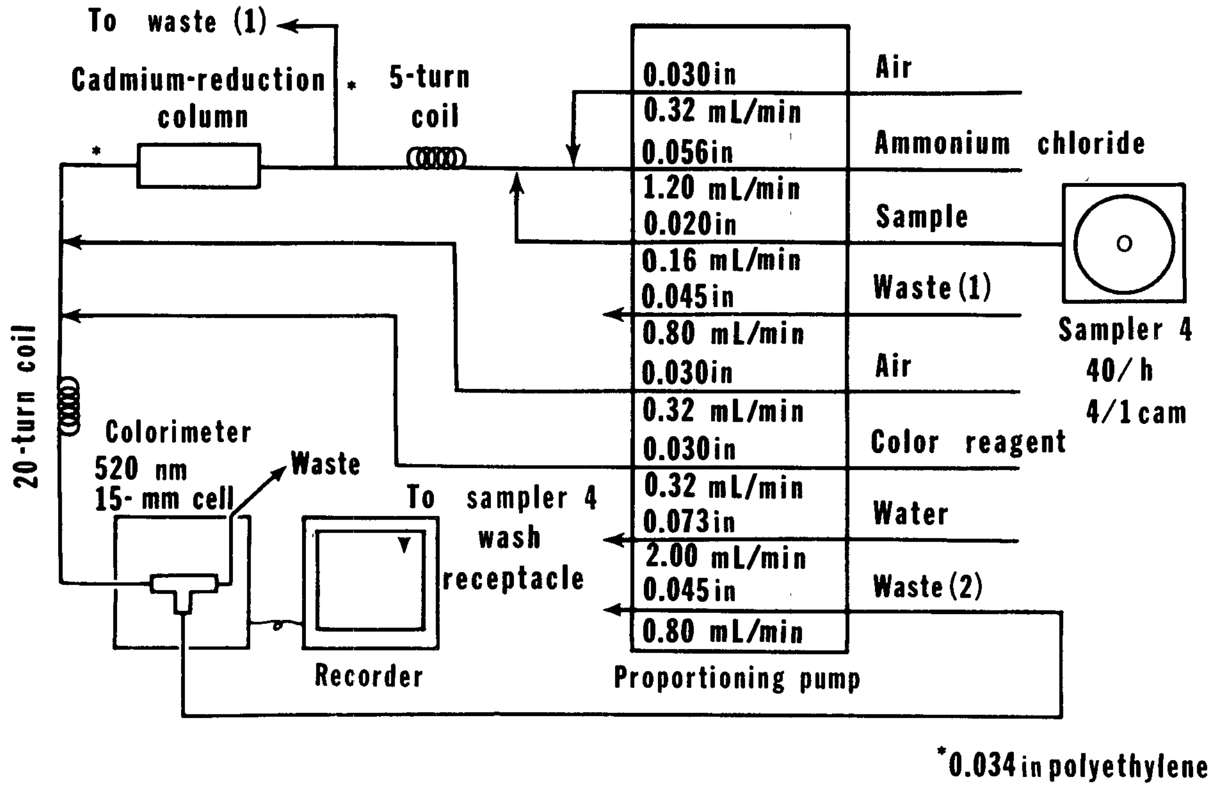

Figure 36.—Nitrogen, nitrite plus nitrate, cadmium reduction-diazotization, manifold

(Technicon No. 189-0000 or equivalent), with water. This prevents entrapment of air bubbles when filling the tube with cadmium. Transfer the prepared cadmium granules to the reduction column. After filling is completed, insert borosilicate glass wool in the exit end of the tube. This column should function for several hundred samples before it needs to be refilled (NOTE 2).

NOTE 2. The reduction efficiency of the column should be checked regularly by comparing the peak heights of nitrite and nitrate standards. Equal concentration standards should give equal heights. Replace the column if the efficiency falls below 90 percent.

6.6 Begin pumping reagents, but do not connect the reduction column to the manifold system until air has been pumped from the reagent and sample tubes (NOTE 3).

NOTE 3. It is important to avoid introduction of air bubbles into the reduction column, because they adversely affect sample contact with the cadmium powder and decrease the reduction efficiency. Column must be replaced if air bubbles are introduced.

6.7 Activate and stabilize the reduction column by pumping a 3.0 mg/L NO_3-N standard through the sample line until a steady state is attained.

6.8 Switch to demineralized water in the sample line and adjust the baseline to read zero scale divisions on the recorder.

6.9 Place a complete set of standards and two blanks in the first positions of the first sample tray, beginning with the most concentrated standard. Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.10 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective nitrite- plus nitrate-nitrogen concentration.

7.2 Compute the concentration of dissolved or total nitrite- plus nitrate-nitrogen in milligrams per liter in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

7.3 Compute the concentration of nitrite- plus nitrate-nitrogen in bottom material samples in milligrams per liter in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

$$NO_3\text{-N} + NO_2\text{-N (mg/kg)} = \frac{C_N \times 100}{\text{wt of sample (g)}}$$

where

C_N = NO_3-N + NO_2-N concentration in sample, milligrams per liter.

8. Report

8.1 Report nitrogen, nitrite plus nitrate, dissolved (00631), and total (00630), concentrations as follows: 0.1 to 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

8.2 Report nitrogen, nitrite plus nitrate, total-in-bottom-material (00633), concentrations as follows: less than 10 mg/kg, one decimal; 10 mg/kg and above, two significant figures.

9. Precision

9.1 Precision for dissolved nitrite- plus nitrate-nitrogen for 18 samples within the range of 0.62 to 5.0 mg/L may be expressed as follows:

$$S_T = 0.120X + 0.009$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of nitrogen, milligrams per liter.

The correlation coefficient is 0.6826.

9.2 Precision for dissolved nitrite- plus nitrate-nitrogen for five of the 18 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
24	0.62	8
4	1.05	4
9	1.27	16
16	2.38	16
24	5.05	8

9.3 It is estimated that the percent relative standard deviation for total nitrite- plus nitrate-nitrogen and for total nitrite- plus nitrate-nitrogen in bottom material will be greater than that reported for dissolved nitrite- plus nitrate-nitrogen.

References

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