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Techniques of Water-Resources Investigations
of the United States Geological Survey

Chapter A1

METHODS FOR DETERMINATION OF INORGANIC SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

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First Edition 1970
Second Edition 1979
Third Edition 1989

Book 5
LABORATORY ANALYSIS

Nitrogen, titrimetric, digestion-distillation

Parameter and Code:

Nitrogen, total-in-bottom-material, dry wt, I-5554-85 (mg/kg as N): 00603

1. Application

This method may be used to determine the total nitrogen concentration of any sample of bottom material containing at least 20 mg/kg. Only that portion of bottom material that passes a 2-mm sieve is taken for analysis.

2. Summary of method

Salicylic acid in concentrated sulfuric acid is added to the sample of bottom material. The sample is then subjected to a digestion whereby all nitrogen-containing compounds are converted to ammonium salts. The resulting mixture is then made strongly alkaline, and the ammonia so formed is distilled from the mixture into a solution of boric acid and subsequently determined by titration with standard sulfuric acid solution.

3. Interferences

There are no known interferences with this method.

4. Apparatus

Kjeldahl distillation apparatus, 500-mL flasks.

5. Reagents

5.1 *Ammonium chloride*, crystals.

5.2 *Boric acid solution*, 20 g/L: Dissolve 20 g H_3BO_3 crystals in 800 mL ammonia-free water and dilute to 1 L.

5.3 *Digestion catalyst*: Tablets containing 3.5 g K_2SO_4 and 0.175 g HgO (Scientific Chemical Sales Inc., Kel-catalyst No. KC-M3 or equivalent).

5.4 *Mixed indicator solution*: Dissolve 20 mg methyl red and 100 mg bromocresol green in 100 mL 95-percent ethanol. Store in a well-sealed bottle.

5.5 *Salicylic acid*, crystals.

5.6 *Sodium carbonate solution*, 0.0357*N*: Dissolve 1.892 g primary standard Na_2CO_3 in carbon dioxide-free water and dilute to 1,000 mL.

5.7 *Sodium hydroxide-thiosulfate solution*: With care, dissolve 500 g NaOH in 600 mL ammonia-free water. Add 80 g $Na_2S_2O_3 \cdot 5H_2O$ and dilute to 1 L.

5.8 *Sodium thiosulfate*, crystals $Na_2S_2O_3 \cdot 5H_2O$.

5.9 *Sucrose*.

5.10 *Sulfuric acid*, concentrated, sp gr 1.84.

5.11 *Sulfuric acid standard solution*, approx 0.036*N*: *Cautiously* add 1.0 mL concentrated H_2SO_4 (sp gr 1.84) to 800 mL ammonia-free water and dilute to 1 L. Standardize by titrating 25.0 mL 0.035*N* Na_2CO_3 to pH 4.5. Compute normality of sulfuric acid standard solution to four decimal places.

6. Procedure

6.1 Free the distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace using nessler reagent—**CAUTION: deadly poison.** (See nitrogen, ammonia, colorimetric, distillation-nesslerization method.)

6.2 Weigh, to the nearest milligram, 3 g of bottom-material sample, prepared as directed in method P-0810 (subsampling, bottom-material, coring), and transfer to the digestion flask.

6.3 Prepare a blank and standard, using 2.0 g sucrose for the blank and 0.1000 g NH_4Cl plus 2.0 sucrose for the standard.

6.4 *Cautiously*, add 25 mL concentrated H_2SO_4 (sp gr 1.84), and then add 1.0 g salicylic acid. Under a hood, swirl the contents of each flask until thoroughly mixed. Allow to stand for at least 30 min.

6.5 Under a hood, add 5 g $Na_2S_2O_3 \cdot 5H_2O$ and heat gently over a Bunsen burner. Let stand for about 5 min or until any frothing ceases.

6.6 Add three digestion-catalyst tablets and mix well. Add a few glass beads and begin the digestion. Continue the digestion until a clear solution is obtained, and then continue fuming 1 h.

6.7 Cool the flask until crystals appear. (Do not cool completely). Add 150 mL ammonia-free water; mix and allow to cool.

6.8 To avoid bumping during the subsequent distillation, transfer the entire solution from the digestion flask to a clean Kjeldahl flask. Rinse the digestion flask with a minimum of ammonia-free water and add to the contents of the clean flask.

6.9 Add 100 mL NaOH-$Na_2S_2O_3$ solution. Immediately connect the flask to the distillation apparatus and *cautiously* mix the contents by swirling.

6.10 Distill at a rate of not more than 10 mL/min or less than 6 mL/min; collect the distillate in a 250-mL volumetric flask containing 25 mL boric acid solution. The tip of the delivery tube must be below the surface of the boric acid solution in the receiving flask.

6.11 Collect approx 200 mL of distillate, dilute to 250 mL with ammonia-free water, and mix.

6.12 Add 3 drops mixed indicator solution to the distillate and titrate with standard H_2SO_4 until the solution changes from yellow to red.

7. Calculations

$$\text{Nitrogen, total, mg/kg} = \frac{V_a \times N_a \times 14{,}000}{Wt_s}$$

where

V_a = volume of standard H_2SO_4 used to titrate sample, milliliters, minus volume used to titrate blank, milliliters,

N_a = normality of standard H_2SO_4 solution, and

Wt_s = weight of sample, grams.

8. Report

Report nitrogen, total in bottom material (00603), as follows: less than 100 mg/kg, nearest 10 mg/kg; 100 mg/kg and above, two significant figures.

9. Precision

Precision data are not available for this method.

Nitrogen, ammonia, colorimetric, distillation-nesslerization

Parameters and Codes:

Nitrogen, ammonia, dissolved, I-1520-85 (mg/L as N): 00608
Nitrogen, ammonia, total, I-3520-85 (mg/L as N): 00610

1. Application

This method may be used to analyze water and water-suspended sediment containing from 0.01 to 2 mg/L of ammonia-nitrogen. Samples containing more than 2 mg/L need either to be diluted or to be analyzed by an alternative titration procedure.

2. Summary of method

2.1 The sample is buffered to a pH of 9.5 to minimize hydrolysis of organic nitrogen compounds. Ammonia is distilled from the buffered solution, and an aliquot of the distillate then is nesslerized. Essentially, nesslerization is the reaction between potassium mercuric iodide and ammonia to form a red-brown colloidal complex of mercuric ammono-basic iodide:

$$2(HgI_2 \cdot 2KI) + 2NH_3 \rightarrow$$

$$NH_2Hg_2I_3 + 4KI + NH_4I$$

Concentrations of ammonia are then determined by standard spectrometric measurements. Alternatively, the distillate may be titrated with standard sulfuric acid solution.

2.2 Additional information on the principle of the determination was given by Blaedel and Meloche (1963).

3. Interferences

3.1 Calcium, magnesium, iron, and sulfide interfere with the nesslerization, but the interference of the metals is eliminated by the distillation, and sulfide can be precipitated in the distillation flask by lead carbonate.

3.2 Some organic compounds may distill with the ammonia and form colors with nessler reagent, which cannot satisfactorily be read with the spectrophotometer. Under such conditions, the sample should be titrated with standard sulfuric acid solution.

4. Apparatus

4.1 *Cylinder, graduated, with ground-glass stopper*, 50-mL capacity (Corning No. 3002 or equivalent).

4.2 *Kjeldahl distillation apparatus*, 500-mL flasks.

4.3 *Spectrophotometer*, for use at 425 nm.

4.4 Refer to the manufacturer's manual to optimize instrument.

5. Reagents

5.1 *Ammonia standard solution I*, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL.

5.2 *Ammonia standard solution II*, 1.00 mL = 0.010 mg NH_3-N: Dilute 10.0 mL ammonia standard solution I to 1,000 mL with ammonia-free water. Prepare fresh daily.

5.3 *Borate buffer solution*: Dissolve 9.54 g $Na_2B_4O_7 \cdot 10H_2O$ in ammonia-free water. Adjust the pH to 9.5 with 1*M* NaOH (approx 15 mL) and dilute to 1 L with ammonia-free water.

5.4 *Boric acid solution*, 20 g/L: Dissolve 20 g H_3BO_3 in 800 mL ammonia-free water and dilute to 1 L.

5.5 *Nessler reagent*—**CAUTION: HgI_2 is a deadly poison, and the reagent must be so marked:** Dissolve 100 g HgI_2 and 70 g KI in a small volume of ammonia-free water. Add this mixture slowly, with stirring, to a cooled solution of 160 g NaOH in 500 mL ammonia- free water and dilute to 1 L. Allow the reagent to stand at least overnight and filter through a fritted-glass crucible.

5.6 *Sodium hydroxide solution*, 1*M*: Dissolve 40 g NaOH in ammonia-free water and dilute to 1 L.

6. Procedure

6.1 Rinse all glassware with ammonia-free water before beginning this determination.

6.2 Free the distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace using nessler reagent—**CAUTION: deadly poison.**

6.3 Pipet a volume of well-mixed sample containing less than 1.0 mg ammonia-nitrogen (250 mL max) into a 500-mL distillation flask, and adjust the volume to approx 250 mL with ammonia-free water (NOTE 1).

NOTE 1. For water-suspended sediment mixtures, rinse the pipet with ammonia-free water to remove adhering particles and combine with sample.

6.4 Add 12.5 mL borate buffer solution, and adjust the pH to 9.5 with 1*M* NaOH, if necessary.

6.5 Immediately distill at a rate of not more than 10 mL or less than 6 mL per min; collect the distillate in a 250-mL volumetric flask containing 25 mL boric acid solution. The tip of the delivery tube must be below the surface of the boric acid solution in the receiving flask.

6.6 Collect approx 200 mL of distillate, dilute to 250 mL with ammonia-free water, and mix.

6.7 Pipet an aliquot of distillate containing less than 0.1 mg ammonia-nitrogen (50.0 mL maximum) into a glass-stoppered, graduated mixing cylinder, and adjust the volume to 50.0 mL with ammonia-free water.

6.8 Prepare a blank of ammonia-free water and a series of standards in glass-stoppered, graduated mixing cylinders. Add 5 mL boric acid solution to each, and adjust the volume of each to 50.0 mL.

6.9 Add 1.0 mL nessler reagent—**CAUTION: deadly poison**—to each blank, standard, and sample. Stopper and invert several times to mix thoroughly.

6.10 Allow the solutions to stand at least 10 min, but not more than 30 min.

6.11 Determine the absorbance of each test sample and standard against the blank.

7. Calculations

7.1 Determine milligrams of ammonia-nitrogen in each sample from a plot of absorbances of standards.

7.2 Determine the ammonia-nitrogen concentration in milligrams per liter as follows:

$$\text{Ammonia-nitrogen as N, (mg/L)} = \frac{1{,}000}{\text{mL sample}} \times \frac{250}{\text{mL aliquot}} \times \text{mg N in aliquot}$$

8. Report

Report nitrogen, ammonia, dissolved (00608), and total (00610), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved ammonia-nitrogen for nine samples within the range of 0.10 to 2.0 mg/L may be expressed as follows:

$$S_T = 0.465X + 0.0001$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of ammonia-nitrogen, milligrams per liter.

The correlation coefficient is 0.8140.

9.2 Precision for dissolved ammonia-nitrogen for four of the nine samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
11	0.104	73
4	.600	33
8	1.51	44
7	2.04	63

9.3 It is estimated that the percent relative standard deviation for total ammonia- nitrogen will be greater than that reported for dissolved ammonia-nitrogen.

Reference

Blaedel, W. J., and Meloche, V. W., 1963, Elementary quantitative analysis: theory and practice (2d ed.): New York, Harper and Row, 826 p.

Nitrogen, ammonia, colorimetric, salicylate-hypochlorite, automated-segmented flow

Parameters and Codes:

Nitrogen, ammonia, dissolved, I-2522-85 (mg/L as N): 00608
Nitrogen, ammonia, total, I-4522-85 (mg/L as N): 00610
Nitrogen, ammonia, total-in-bottom-material, I-6522-85 (mg/kg as N): 00611

1. Application

1.1 This method may be used to analyze surface, domestic, and industrial water, brines, and water-suspended sediment containing from 0.01 to 1.5 mg/L of ammonia-nitrogen. Concentrations greater than 1.5 mg/L need to be diluted.

1.2 This method may also be used to determine concentrations of ammonia-nitrogen in bottom material containing at least 0.2 mg/kg NH_3-N. Prepared sample solutions containing more than 1.5 mg/L NH_3-N must first be diluted.

1.3 Sodium ion is a good replacement ion for ammonium in the slow-exchange positions of soil minerals (Jackson, 1958). The water-suspended sediment is treated and preserved in the field with mercury chloride and sodium chloride. The resulting mixture, prior to analysis in the laboratory, is either centrifuged or decanted to obtain a clear supernatent solution. Similarly, bottom material is treated with an acidified sodium chloride solution and the resulting mixture centrifuged to obtain a clear supernatant solution for analysis.

2. Summary of method

Ammonia reacts with sodium salicylate, sodium nitroprusside, and sodium hypochlorite, in an alkaline medium, to form an intensely colored compound. The resulting color is directly proportional to the concentration of ammonia present.

3. Interferences

3.1 No substance found in natural waters appears to interfere with this method.

3.2 The samples are easily contaminated by ammonia in the laboratory atmosphere; therefore, sample handling and analysis should be performed where there is no possibility of ammonia contamination.

4. Apparatus

4.1 *Centrifuge.*

4.2 *Shaker*, wrist-action.

4.3 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.4 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 1.5 mg/L ammonia-nitrogen:

Absorption cell	50 mm
Wavelength	660 nm
Cam	50/h (2/1)
Heating-bath temperature	37 °C

5. Reagents

5.1 *Ammonia standard solution I*, 1.00 mL = 0.50 mg NH_3-N: Dissolve 1.9095 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1000 mL. Refrigerate.

5.2 *Ammonia standard solution II*, 1.00 mL = 0.0025 mg NH_3-N: Dilute 5.0 mL ammonia standard solution I to 1000 mL with ammonia-free water. Prepare fresh weekly and refrigerate.

5.2.1 *Ammonia working standards*, bottom materials: Prepare an ammonia-free blank and

at least 250 mL each of a series of ammonia working standards by appropriate quantitative dilution of ammonia standard solution II with acidified sodium chloride solution (5.8) as follows:

Ammonia standard solution II (mL)	Ammonia-nitrogen concentration (mg/L)
0.0	0.0
2.0	.02
10	.10
25	.25
50	.50
100	1.0
125	1.5

Prepare fresh weekly and refrigerate.

5.2.2 *Ammonia working standards*, water and water suspended-sediment: Prepare an ammonia-free blank and at least 250 mL each of a series of ammonia working standards by dilution of ammonia standard solution II with diluent solution (5.5) as follows:

Ammonia standard solution II (mL)	Ammonia-nitrogen concentration (mg/L)
0.0	0.0
2.0	.02
10	.10
25	.25
50	.50
100	1.0
125	1.5

Prepare fresh weekly and refrigerate.

5.3 *Buffer stock solution*, 71 g/L: Dissolve 134 g $Na_2HPO_4 \cdot 7H_2O$ in 800 mL ammonia-free water. Add 100 mL 5*M* NaOH, dilute to 1 L with ammonia-free water, and mix thoroughly.

5.4 *Buffer working solution*: Add, with stirring, 250 mL stock potassium sodium tartrate solution to 200 mL stock buffer solution. Slowly, with stirring, add 120 mL 5*M* NaOH. Dilute to 1 L with ammonia-free water, add 1 mL Brij-35 solution, and mix thoroughly.

5.5 *Diluent solution*: Dissolve 52 mg mercuric chloride ($HgCl_2$) and 600 mg sodium chloride (NaCl) in approximately 800 mL ammonia-free water, mix thoroughly, and dilute to 1 L with ammonia-free water.

5.6 *Hydrochloric acid*, concentrated (sp gr 1.19).

5.7 *Potassium sodium tartrate solution*, 149 g/L: Dissolve 200 g $NaKC_4H_4O_6 \cdot 4H_2O$ in approximately 600 mL ammonia-free water. Dilute to 1 L.

5.8 *Sodium chloride solution*, 100 g/L: Dissolve 100 g NaCl in 800 mL ammonia-free water, mix thoroughly, and dilute to 1 L. Adjust the pH to 2.5 using concentrated HCl (sp gr 1.19).

5.9 *Sodium hydroxide solution*, 5*M*: Add, with cooling and stirring, 200 g NaOH to approximately 800 mL ammonia-free water. Cool and dilute to 1 L.

5.10 *Sodium hypochlorite solution*: Dilute 50 mL sodium hypochlorite solution (a commercial bleach solution containing 5.25-percent available chlorine is satisfactory) to 500 mL with ammonia-free water. Add 1.0 mL Brij-35 solution. Prepare fresh daily.

5.11 *Sodium salicylate-sodium nitroprusside solution*: Dissolve 150 g sodium salicylate and 0.30 g sodium nitroprusside, $(Na_2Fe(CN)_5NO \cdot 2H_2O)$, in approximately 600 mL ammonia-free water. Filter through Whatman 41 filter paper or equivalent, and dilute to 1 L. Add 1.0 mL Brij-35 solution and store in a light-resistant container.

5.12 *Sulfuric acid*, concentrated (sp gr 1.84).

5.13 *Sulfuric acid*, 2.5*M*: *Cautiously* add 138 mL concentrated H_2SO_4 (sp gr 1.84) to approximately 700 mL ammonia-free water. Cool and dilute to 1 L with ammonia-free water.

6. Procedure

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

6.1.1 Weigh, to the nearest milligram, approximately 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 of the acidic sodium chloride solution (5.8) 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 acidic sodium chloride solution (5.8), recentrifuge, and transfer the clear wash solution

to the volumetric flask. Adjust to volume with acidic sodium chloride solution (5.8). Proceed to paragraph 6.2.

6.2 Set up the manifold (fig. 32). If the laboratory air is contaminated with ammonia, the air must be passed through a scrubber containing 2.5*M* H_2SO_4 before the air enters the air-manifold tube.

6.3 Allow the colorimeter, recorder, and heating bath to warm for at least 30 min, or until the temperature of the heating bath reaches 37 °C.

6.4 Adjust the baseline to read zero scale divisions on the recorder with all reagents (NOTE 1), but with either the acidic sodium chloride (paragraph 5.8, for bottom material analysis) or the diluent (paragraph 5.5, for water or water-suspended sediment analysis) in the sample line. The solution remaining in the wash reservoir from previous determinations may have become contaminated; therefore, this reservoir should be emptied and rinsed, and then refilled with fresh solution before proceeding.

NOTE 1. Place each reagent line except salicylate into its respective container; allow at least 5 min for the introduction of these reagents, and then place the salicylate line into its reagent container. If a precipitate forms after the addition of the salicylate, the pH of the solution stream is too low; check for contaminated reagents and (or) remake them, and start again using the procedure outlined above.

6.5 Place a complete set of standards and a blank (NOTE 2) in the first positions of the first sample tray, beginning with the most concentrated standard (NOTE 3). Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill the remainder of each tray with unknown samples.

NOTE 2. For analysis of bottom materials use blank and working standards prepared in paragraph 5.2.1. For analysis of waters and water-suspended-sediment mixtures, use blank and working standards prepared in paragraph 5.2.2.

NOTE 3. To avoid possible contamination of the sample cups, keep them sealed in their packages until just prior to use. Rinse each sample cup with sample prior to filling.

6.6 Begin analysis. When the peak from the most concentrated working standard appears on

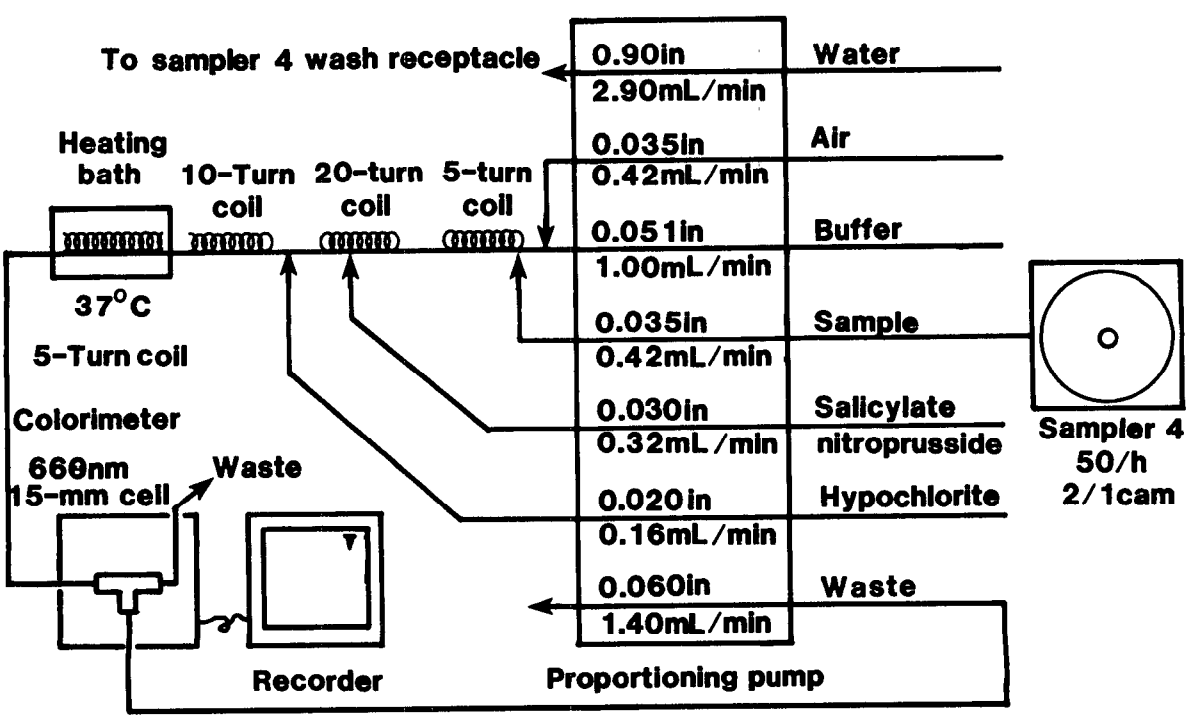

Figure 32.—Nitrogen, ammonia, salicylate-hypochlorite manifold

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 ammonia-nitrogen concentration.

7.2 Compute the concentration of dissolved or total ammonia-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 ammonia-nitrogen in each bottom-material sample as follows:

$$NH_3N\ (mg/kg) = \frac{C_N \times 100}{\text{wt of sample (g)}}$$

where

C_N = NH_3–N concentration in sample, milligrams per liter.

8. Report

8.1 Report nitrogen, ammonia, dissolved (00608), and total (00610), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

8.2 Report nitrogen, ammonia, total in bottom material (00611), concentrations as follows: less than 10 mg/kg, one decimal; 10 mg/kg and above, two significant figures.

9. Precision

9.1 Single-operator precision for dissolved ammonia-nitrogen, as determined on synthetic, deionized water-matrix samples, expressed in terms of the percent relative standard deviation, is as follows:

Number of determinations	Mean (mg/L)	Relative standard deviation (percent)
77	0.20	13
77	1.25	3
77	2.00	2

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

Reference

Jackson, M. L., 1958, Soil chemical analysis: Englewood Cliffs, N.J., Prentice-Hall, p. 193.

Nitrogen, ammonia, colorimetric, salicylate-hypochlorite, automated-discrete

Parameters and Codes:
Nitrogen, ammonia, dissolved, I-2521-85 (mg/L as N): 00608
Nitrogen, ammonia, total, I-4521-85 (mg/L as N): 00610

1. Application

This method may be used to analyze water, wastewater, water-suspended sediment, and brines containing 0.05 to 5.0 mg/L ammonia-nitrogen. Samples containing concentrations greater than 5.0 mg/L need to be diluted.

2. Summary of method

Ammonia reacts with sodium salicylate, sodium nitroprusside, and sodium hypochlorite to form an intensely colored compound in an alkaline medium. The resulting color is directly proportional to the concentration of the ammonia present.

3. Interferences

3.1 A comparison study of the results obtained by this method and those from the colorimetric, salicylate-hypochlorite, automated-segmented flow method (methods I-2522 and 4522) indicate the absence of interferences.

3.2 Samples are easily contaminated by ammonia in the laboratory atmosphere; therefore, sample handling and analysis should be performed where there is no possibility of ammonia contamination.

4. Apparatus

4.1 *Discrete chemical and analyzer system*, American Monitor IQAS or equivalent.

4.2 With this equipment, the following operating conditions have been found satisfactory for the range 0.01 to 5.00 mg/L.

Wavelength	620 nm
Absorption cell	1 cm square, temperature-controlled, flow-through, quartz cuvette
Reaction temperature	37°C
Sample volume	0.150 mL with 0.100 mL diluent (NOTE 1)
Reagent volumes	0.5 mL buffer solution, 0.50 mL sodium salicylate-sodium nitroprusside solution, 0.2 mL sodium hypochlorite solution, and 0.80 mL demineralized water (NOTE 1)

NOTE 1. Sample-to-diluent ratio and reagent volumes must be optimized for each individual instrument according to manufacturer's specifications.

5. Reagents

5.1 *Ammonia standard solution I*, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over concentrated sulfuric acid (sp gr 1.84), in ammonia-free water and dilute to 1,000 mL.

5.2 *Ammonia standard solution II*, 1.00 mL = 0.100 mg NH_3-N: Dilute 100.0 mL ammonia standard solution I to 1,000 mL with ammonia-free water.

5.3 *Ammonia working standards*: Prepare a blank and 1,000 mL each of a series of working standards by dilution of ammonia standard solution II. Dissolve 52 mg mercuric chloride and 600 mg sodium chloride in each working standard. For example:

Standard solution II (mL)	Ammonia-nitrogen concentration (mg/L)
0.0	0.00
2.5	.25
5.0	.50
10.0	1.00
50.0	5.00

5.4 *Buffer solution*: Add, with stirring, 250 mL potassium sodium tartrate solution to 200 mL sodium phosphate solution. Slowly, with stirring, add 120 mL 5*M* NaOH. Dilute to 1 L with ammonia-free water.

5.5 *Sodium hydroxide solution, 5M*: Add, with cooling and stirring, 200 g NaOH to approx 800 mL ammonia-free water. Cool and dilute to 1 L.

5.6 *Sodium hypochlorite solution*: Dilute 6.0 mL sodium hypochlorite solution (a commercial bleach solution containing 5.25-percent available chlorine is satisfactory) to 100 mL with ammonia-free water.

5.7 *Sodium phosphate, diabasic solution*, 71 g/L: Dissolve 71 g anhydrous Na_2HPO_4 in approx 800 mL ammonia-free water. Add 100 mL 5*M* NaOH, dilute to 1 L with ammonia-free water, and mix thoroughly.

5.8 *Sodium potassium tartrate solution*, 149 g/L: Dissolve 200 g $NaKC_4H_4O_6 \cdot 4H_2O$ in approx 600 mL ammonia-free water. Dilute to 1 L.

5.9 *Sodium salicylate-sodium nitroprusside solution*: Dissolve 150 g sodium salicylate and 0.30 g sodium nitroprusside in approx 600 mL ammonia-free water. Filter through Whatman 41 filter paper or equivalent, and dilute to 1 L. Store in a light-resistant container.

6. Procedure

6.1 Rinse all glassware with ammonia-free water before each use.

6.2 Set up analyzer and computer-card assignments according to manufacturer's instructions.

6.3 Place standards, beginning with the lowest concentrations, in ascending order (computer-calibration curve) in the first five positions on the sample turntable. Place samples and quality-control standards in the remainder of the sample turntable.

6.4 Begin analysis. The cathode-ray tube (CRT) will acknowledge the parameter and concentration range listing each sample-cup number and corresponding concentrations calculated from the working curve. During each run, the CRT display will provide a plot of standards, samples, and list blank and slope calculations. Retain copy of all information obtained from the printer.

7. Calculations

Determine the concentration in milligrams per liter of dissolved or total ammonia-nitrogen in each sample from either the CRT display or the printer output.

8. Report

Report nitrogen, ammonia, dissolved (00608), and total (00610), concentrations as follows: less than 1.00 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the standard deviation and percent relative standard deviation for replicate analysis of reference materials by a single operator is as follows:

Mean (mg/L)	Number of replicates	Standard deviation (mg/L)	Relative standard deviation (percent)
0.014	39	0.002	14.3
.030	39	.003	10.0
.186	30	.012	6.4
.651	22	.010	1.5
1.27	30	.020	1.6
2.48	22	.018	.7
3.36	22	.093	2.8
4.99	30	.027	.5

Nitrogen, ammonia, colorimetric, indophenol, automated-segmented flow

Parameters and Codes:

Nitrogen, ammonia, dissolved, I-2523-85 (mg/L as N): 00608
Nitrogen, ammonia, total, I-4523-85 (mg/L as N): 00610
Nitrogen, ammonia, total-in-bottom-material, I-6523-85 (mg/kg as N): 00611

1. Application

1.1 This method may be used to analyze surface, domestic, and industrial water, and brines and water-suspended sediment containing from 0.01 to 5.0 mg/L of ammonia-nitrogen. The range may be extended if the nitroprusside is omitted.

1.2 This method may be used to determine concentrations of ammonia-nitrogen in bottom material containing at least 0.2 mg/kg NH_3-N. Prepared sample solutions containing more than 5.0 mg/L NH_3-N must first be diluted. The range may be extended to 10.0 mg/L NH_3-N if the nitroprusside is omitted.

1.3 Sodium ion is a good replacement ion for ammonium in the slow-exchange positions of soil minerals (Jackson, 1958). Water-suspended sediment is treated and preserved in the field with mercury chloride and sodium chloride. The resulting mixture, prior to analysis in the laboratory, is either centrifuged or decanted to obtain clear supernatant solution. Similarly, bottom material is treated with an acidified sodium chloride solution, and the resulting mixture centrifuged to obtain a clear supernatant solution for analysis.

2. Summary of method

Ammonia reacts with hypochlorite and alkaline phenol to form an intensely colored indophenol compound, the absorbance of which is directly proportional to the ammonia concentration. Sodium nitroprusside may be added to improve the sensitivity of this determination (Bolleter and others, 1961; O'Brien and Fiore, 1962; Tetlow and Wilson, 1964; Van Slyke and Hiller, 1933).

3. Interferences

A complexing reagent consisting of sodium potassium tartrate and sodium citrate is added to remove interferences from several metal ions, including calcium, magnesium, and iron. The color development is pH dependent; therefore, samples whose pH values lie outside of the range from 4 to 10 must be analyzed with standards and a wash solution of approximately the same pH. Aromatic amines may interfere.

4. Apparatus

4.1 *Centrifuge.*

4.2 *Shaker*, wrist-action.

4.3 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.4 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 5.0 mg/L ammonia-nitrogen.

Absorption cell -----	15 mm
Wavelength --------	630 nm
Cam ----------	60/h (6/1)
Heating-bath temperature ----------	50 °C

5. Reagents

5.1 *Alkaline phenol solution*: Mix 89 mL liquid phenol (approx 90 percent) in 50 mL ammonia-free water. *Cautiously* add, while cooling, in small increments with agitation, 180 mL 5*M* NaOH. Dilute to 1 L with ammonia-free water (NOTE 1). Keep refrigerated in an amber bottle.

5.2 *Ammonia standard solution I*, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL. Refrigerate.

5.3 *Ammonia standard solution II*, 1.00 mL = 0.025 mg NH_3-N: Dilute 25.0 mL ammonia standard solution I to 1,000 mL with diluent solution (paragraph 5.6). Prepare fresh weekly and refrigerate.

5.4 *Ammonia working standards*: Prepare a blank and 250 mL each of a series of ammonia working standards by appropriate quantitative dilution of ammonia standard solution II with diluent solution (paragraph 5.6) as follows (NOTE 1):

Ammonia standard solution II (mL)	Ammonia-nitrogen concentration (mg/L)
0.0	0.0
10	1.0
20	2.0
30	3.0
40	4.0
50	5.0

Prepare fresh weekly and refrigerate.

NOTE 1. If ammonia-nitrogen in bottom material is being determined, the working standards are diluted with sodium chloride solution (paragraph 5.9).

5.5 *Brij-35 solution*: 30-percent aqueous solution (Baker Cat. No. C706 or equivalent).

5.6 *Diluent solution*: Dissolve 52 mg mercuric chloride and 600 mg sodium chloride in 800 mL ammonia-free water, mix thoroughly, and dilute to 1 L with ammonia-free water.

5.7 *Hydrochloric acid*, concentrated (sp gr 1.19).

5.8 *Potassium sodium tartrate-sodium citrate solution*: Dissolve 33 g $KNaC_4H_4O_6 \cdot 4H_2O$ and 24 g sodium citrate in 950 mL ammonia-free water. Adjust the pH of this solution to 5.0 with concentrated H_2SO_4 (sp gr 1.84) and dilute to 1 L with ammonia-free water. Add 0.5 mL Brij-35 solution.

5.9 *Sodium chloride solution*, 100 g/L: Dissolve 100 g NaCl in 800 mL ammonia-free water, mix thoroughly, and dilute to 1 L. Adjust the pH to 2.5 using concentrated HCl (sp gr 1.19).

5.10 *Sodium hydroxide solution, 5M: Cautiously*, dissolve 200 g NaOH in ammonia-free water. Cool and dilute to 1 L. Store in a plastic container.

5.11 *Sodium hypochlorite stock solution*: Clorox or any other good commercial household bleach having approx 5-percent available chlorine.

5.12 *Sodium hypochlorite working solution*: Dilute 200 mL of stock sodium hypochlorite to 1 L with ammonia-free water.

5.13 *Sodium nitroprusside solution*, 0.44 g/L: Dissolve 0.5 g $Na_2Fe(CN)_5NO \cdot 2H_2O$ in ammonia-free water and dilute to 1 L.

5.14 *Sulfuric acid*, concentrated (sp gr 1.84).

5.15 *Sulfuric acid, 2.5M: Cautiously*, add 138 mL concentrated (sp gr 1.84) to 500 mL ammonia-free water, cool, and dilute to 1 L.

6. Procedure

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

6.1.1 Weigh, to the nearest milligram, 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 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 NaCl solution, recentrifuge, and transfer the clear wash solution to the volumetric flask. Adjust to volume with NaCl solution. Proceed to paragraph 6.2.

6.2 Set up manifold (fig. 33). If the laboratory air is contaminated with ammonia, the air must be passed through a scrubber containing 2.5*M* H_2SO_4 before the air enters the air-manifold tube.

6.3 Allow the colorimeter, recorder, and heating bath to warm for at least 30 min, or until the temperature of the heating bath reaches 50 °C.

6.4 Adjust the baseline to read zero scale divisions on the recorder with all reagents,

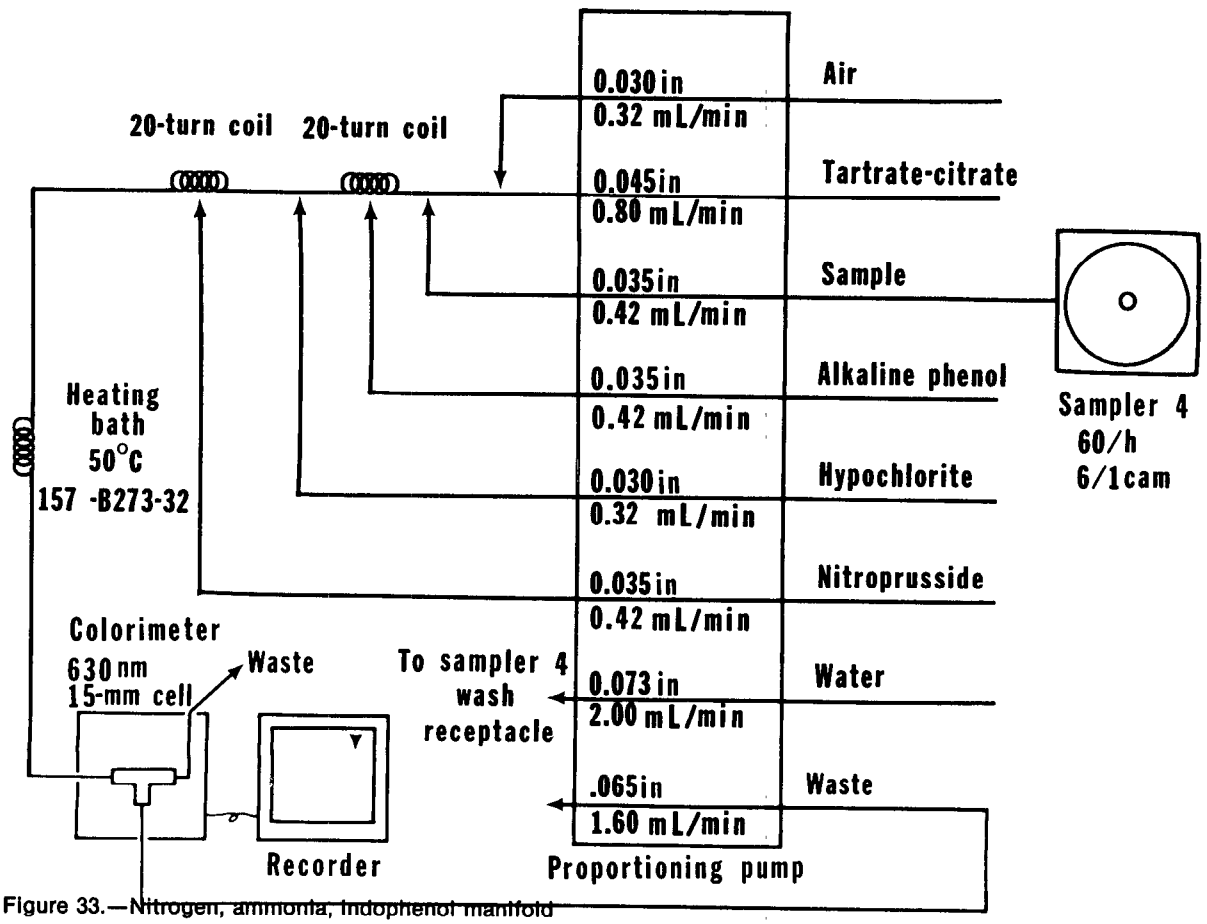

Figure 33.—Nitrogen, ammonia, indophenol manifold

but with ammonia-free water in the sample line.

6.5 Place a complete set of standards and a blank in the first positions of the first sample tray, beginning with the most concentrated standard (NOTE 2). Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

NOTE 2. To avoid possible contamination of the sample cups, keep them sealed in their packages until just prior to use. Rinse each sample cup with sample prior to filling.

6.6 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 ammonia-nitrogen concentration.

7.2 Compute the concentration of dissolved or total ammonia-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 ammonia-nitrogen concentrations in each bottom material sample as follows:

$$NH_3\text{-N (mg/kg)} = \frac{C_N \times 100}{\text{wt of sample (g)}}$$

where

C_N = NH_3-N concentration in sample, milligrams per liter.

8. Report

8.1 Report nitrogen, ammonia, dissolved (00608), and total (00610), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

8.2 Report nitrogen, ammonia, total-in-bottom-material (00611), 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 ammonia-nitrogen for nine samples within the range of 0.126 to 3.25 mg/L may be expressed as follows:

$$S_T = 0.098X + 0.079$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of ammonia-nitrogen, milligrams per liter.

The correlation coefficient is 0.9085.

9.2 Precision for dissolved ammonia-nitrogen for four of the nine samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
8	0.126	17
21	.665	13
20	1.20	17
23	3.25	12

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

References

Bolleter, W. T., Bushman, C. J., and Tidwell, P. W., 1961, Spectrophotometric determination of ammonia as indophenol: Analytical Chemistry, v. 33, p. 592–3.

Jackson, M. L., 1958, Soil chemical analysis: Englewood Cliffs, N.J., Prentice-Hall, p. 193.

O'Brien, J. E., and Fiore, J., 1962, Ammonia determination by automatic analysis: Wastes Engineering, v. 33, p. 352.

Tetlow, J. A., and Wilson, A. L., 1964, An absorptiometric method for determining ammonia in boiler-feed water: Analyst, v. 89, p. 453–65.

Van Slyke, D. D., and Hiller, A. J., 1933, Determination of ammonia in blood: Biological Chemistry Journal, v. 102, p. 499.

Nitrogen, ammonia, electrometric, ion-selective electrode

Parameters and Codes:

Nitrogen, ammonia, dissolved, I-1524-85 (mg/L as N): 00608
Nitrogen, ammonia, total, I-3524-85 (mg/L as N): 00610

1. Application

This method may be used to analyze water, brines, and water-suspended sediment containing at least 0.10 mg/L ammonia-nitrogen. Samples containing less than 0.10 mg/L need to be analyzed by the single standard addition technique (paragraph 6.6).

2. Summary of method

Ammonia is determined potentiometrically in an alkaline medium by using an ammonia gas-detecting electrode. The internal solution of the electrode is separated from the sample solution by a gas-permeable membrane. Dissolved ammonia in the sample diffuses through the membrane until the partial pressure of ammonia is the same on both sides. The change in partial pressure is proportional to the ammonia concentration and is measured as a potential with an internal chloride-sensing reference electrode and a glass electrode.

3. Interferences

3.1 Color and turbidity do not affect the measurements. Significant quantities of inorganic cations and anions cannot penetrate the nonwettable, gas-permeable membrane and do not interfere directly. However, as the salinity of the sample increases, there is an increase in the observed ammonia concentration. Samples containing dissolved substances at a total concentration greater than 1*M* should be analyzed by standard addition or, if the ammonia concentration is sufficiently high, be analyzed after appropriate dilution.

3.2 Certain gases do present a potential interference; however, common gases such as CO_2, HCN, SO_2, and Cl_2 do not interfere (Orion Research Inc., 1971).

4. Apparatus

4.1 *Ammonia electrode*, Orion Model No. 95-10 or equivalent.

4.2 *pH/millivolt meter*, with expanded scale.

4.3 *Stirrer*, magnetic, battery-operated, with Teflon-coated stirring bar.

5. Reagents

5.1 *Ammonia standard solution I*, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g ammonium chloride (NH_4Cl), dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL.

5.2 *Ammonia standard solution II*, 1.00 mL = 0.010 mg N: Dilute 10.0 mL of ammonia standard solution I to 1,000 mL with ammonia-free water. Prepare fresh daily.

5.3 *Ammonia working standards*: Prepare a series of three standard solutions containing 0.1, 1.0, and 5.0 mg/L NH_3-N by appropriate dilution of either ammonia standard solution I or II with ammonia-free water.

5.4 *Sodium hydroxide solution*, 10*M*. Dissolve *with caution* 400 g NaOH in ammonia-free water and dilute to 1 L.

6. Procedure

6.1 Rinse all glassware with ammonia-free water before beginning this determination.

6.2 Adjust the pH/millivolt meter according to the manufacturer's instructions.

6.3 Pipet 50.0 mL of each ammonia chloride working standard (0.1, 1.0, and 5.0 mg/L NH_3-N, respectively) into 100-mL beakers.

6.4 Pipet 50.0 mL of well-mixed sample into a 100-mL beaker.

6.5 Place each standard and sample consecutively on a magnetic stirrer (NOTE 1), immerse the electrode, and then add 0.5 mL 10*M*

NaOH solution. Start the stirrer and record the potential (mV) reading after it has stabilized (2 to 5 min). Rinse the electrode thoroughly with distilled water between samples and blot with a damp tissue.

NOTE 1. Insulate the top of the stirrer with an asbestos sheet and an air space to avoid raising the temperature of the solution.

6.6 If the millivolt reading from the analytical curve (paragraph 7) indicates a concentration of less than 0.10 mg/L, determine NH_3-N in the sample by single standard addition (paragraph 6.7).

6.7 Add 0.5 mL ammonia chloride standard solution II to the sample (paragraph 6.5), equivalent to an increase in concentration of 0.10 mg/L NH_3-N, and record the new potential. Approx 5 min is required for the potential to stabilize.

7. Calculations

Construct an analytical curve of potential (mV) versus concentration of standards on semilog paper, with concentrations plotted on the logarithmic axis. Determine the milligrams per liter ammonia-nitrogen in each sample from the analytical curve. When standard addition is used to determine NH_3-N (paragraph 6.7), subtract 0.10 mg/L NH_3-N from the concentration obtained from the analytical curve.

8. Report

Report nitrogen, ammonia, dissolved (00608), and total (00610), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved ammonia-nitrogen for seven samples within the range of 0.339 to 3.48 mg/L may be expressed as follows:

$$S_T = 0.140X + 0.083$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of ammonia-nitrogen, milligrams per liter.

The correlation coefficient is 0.8331.

9.2 Precision for dissolved ammonia-nitrogen for four of the seven samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
7	0.339	45
4	.620	13
7	1.01	29
6	3.48	17

9.3 It is estimated that the percent relative standard deviation for total ammonia-nitrogen will be greater than that reported for dissolved ammonia-nitrogen.

Reference

Orion Research, Inc., 1971, Instruction manual, ammonia ammonia electrode, Model 95-10: Cambridge, Mass.

Nitrogen, ammonia plus organic, colorimetric, block digestor-salicylate-hypochlorite, automated-segmented flow

Parameters and Codes:

Nitrogen, ammonia plus organic, dissolved, I-2552-85 (mg/L as N): 00623
Nitrogen, ammonia plus organic, total, I-4552-85 (mg/L as N): 00625
Nitrogen, ammonia plus organic, suspended-total, I-7552-85 (mg/L as N): 00624
Nitrogen, ammonia plus organic, total-in-bottom-material, dry wt, I-6552-85 (mg/kg as N): 00626

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing 0.2 to 10 mg/L total ammonia plus organic nitrogen. Samples containing concentrations greater than 10 mg/L need to be diluted.

1.2 Suspended total ammonia plus organic nitrogen is calculated by subtracting dissolved ammonia plus organic nitrogen from total ammonia plus organic nitrogen.

1.3 This method may be used to analyze samples of bottom material containing at least 10 mg/kg total ammonia plus organic nitrogen. Concentration ranges for determining 10 to 120 mg/kg and 80 to 400 mg/kg of nitrogen are used.

2. Summary of method

Organic nitrogen compounds are reduced to the ammonium ion by digestion with sulfuric acid in the presence of mercuric sulfate, which acts as a catalyst, and potassium sulfate. The ammonium ion produced by this digestion, as well as the ammonium ion originally present, is determined by reaction with sodium salicylate, sodium nitroprusside, and sodium hypochlorite in an alkaline medium. The resulting color is directly proportional to the concentration of ammonia present.

3. Interferences

3.1 A comparison study of results obtained by this method with those from the colorimetric, digestion-distillation-nesslerization method, and the colorimetric, digestion-distillation-indophenol, automated method (methods I-1550 and I-2551, respectively) indicated the absence of interferences.

3.2 The samples are easily contaminated by ammonia in the laboratory atmosphere. The digestion process should be performed in a fume hood that is operating properly and that is located in an ammonia-free area of the laboratory. Other laboratory procedures may be performed outside or near this hood only if there is no possibility of ammonia contamination.

4. Apparatus

4.1 *Technicon block digestor*, Model BD-40 with 75-mL digestion tubes or equivalent.

4.2 With this equipment, the following operating conditions have been found satisfactory:

Modeswitch	Automatic
Low-temperature regulator	160°C
High-temperature regulator	370°C
Low-temperature timer	1.5 h
Total cycle time	3.5 h

4.3 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer.

4.4 With this equipment, the following operating conditions have been found satisfactory (NOTE 1):

Absorption cell	15 mm
Wavelength	660 nm
Cam	60/h (6/1)
Water-bath temperature	37°C

NOTE 1. Two concentration ranges—0.2 to 3 mg/L and 2 to 10 mg/L N—are obtained by using different STD CAL settings.

5. Reagents

5.1 *Ammonia standard solution I*, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL.

5.2 *Ammonia standard solution II*, 1.00 mL = 0.010 mg NH_3-N: Dilute 10.0 mL ammonia standard solution I to 1,000 mL with ammonia-free water. Prepare fresh daily.

5.3 *Buffer stock solution*, 71 g/L: Dissolve 71 g anhydrous Na_2HPO_4 in approx 800 mL ammonia-free water. Add 100 mL 5*M* NaOH, dilute to 1 L with ammonia-free water, and mix thoroughly.

5.4 *Buffer working solution*: Add, with stirring, 250 mL stock potassium sodium tartrate solution to 200 mL stock buffer solution. Slowly, with stirring, add 120 mL 5*M* NaOH. Dilute to 1 L with ammonia-free water, add 1 mL Brij-35 solution, and mix thoroughly.

5.5 *Mercuric sulfate solution*, 11 g/100 mL: Dissolve 8 g red HgO in 50 mL 3.6*M* H_2SO_4 and dilute to 100 mL with ammonia-free water.

5.6 *Potassium sodium tartrate solution*, 149 g/L: Dissolve 200 g $NaKC_4H_4O_6 \cdot 4H_2O$ in approx 600 mL ammonia-free water. Dilute to 1 L.

5.7 *Sodium hydroxide solution*, 5*M*: Add, with cooling and stirring, 200 g NaOH to approx 800 mL ammonia-free water. Cool and dilute to 1 L.

5.8 *Sodium hypochlorite solution*: Dilute 6.0 mL sodium hypochlorite solution (a commercial bleach solution containing 5.25-percent available chlorine is satisfactory) to 100 mL with ammonia-free water. Add 0.1 mL Brij-35 solution. Prepare fresh daily.

5.9 *Sodium salicylate-sodium nitroprusside solution*: Dissolve 150 g sodium salicylate and 0.30 g sodium nitroprusside, $(Na_2Fe(CN)_5NO \cdot 2H_2O)$, in approx 600 mL ammonia-free water. Filter through Whatman 41 filter paper or equivalent, and dilute to 1 L. Add 1.0 mL Brij-35 solution and store in a light-resistant container.

5.10 *Sulfuric acid*, concentrated (sp gr 1.84).

5.11 *Sulfuric acid*, 0.20*M*: *Cautiously*, add 11 mL concentrated H_2SO_4 (sp gr 1.84) to ammonia-free water and dilute to 1 L.

5.12 *Sulfuric acid*, 3.6*M*: *Cautiously*, add 200 mL concentrated H_2SO_4 (sp gr 1.84) to approx 700 mL ammonia-free water. Cool and dilute to 1 L with ammonia-free water.

5.13 *Sulfuric acid-mercuric sulfate-potassium sulfate solution*: Dissolve 267 g K_2SO_4 in approx 1,300 mL ammonia-free water. *Cautiously*, add 400 mL concentrated H_2SO_4 (sp gr 1.84) and 50 mL mercuric sulfate solution. Cool and dilute to 2 L with ammonia-free water.

6. Procedure

6.1 Rinse all glassware with ammonia-free water before each use.

6.2 Follow instructions in paragraph 6.2.1 for waters or water-suspended sediments and in paragraph 6.2.2 for bottom materials.

6.2.1 Pipet a volume (20.0 mL max) of well-mixed sample (NOTE 2) containing less than 0.2 mg ammonia plus organic nitrogen (as N) into a digestion tube and adjust the volume to 20 mL with ammonia-free water.

NOTE 2. For water-suspended sediment, rinse the pipet with a small amount of ammonia-free water to remove adhering particles, and combine with sample.

6.2.2 Weigh, to the nearest milligram, an amount of wet sample (500 mg max) containing less than 0.2 mg total ammonia plus organic nitrogen. Transfer the weighed sample to a digestion tube, rinsing the weighing container with ammonia-free water as needed. Add additional ammonia-free water as necessary to bring the liquid volume in the digestion tube to approximately 20 mL.

6.3 Prepare an ammonia-free water blank and at least five standards containing either from 0.004 to 0.06 mg or from 0.04 to 0.20 mg ammonia-nitrogen, depending upon use of 0.2- to 3-mg/L or 2- to 10-mg/L concentration range of interest (NOTE 3). The standards and blank must also undergo the digestion process.

NOTE 3. The blank and standards must contain mercuric chloride fortified with sodium chloride. For example, if 250 mL is prepared, dissolve 13 mg $HgCl_2$ and 150 mg NaCl in each standard.

6.4 Add 4.0 mL sulfuric acid-mercuric sulfate-potassium sulfate solution and two boiling chips. CAUTION: Hazardous. Mix well before placing in digestor (NOTES 4 and 5).

NOTE 4. Protective eyeglasses and clothing are mandatory for this procedure because sulfuric acid and high-temperature solutions are very hazardous.

NOTE 5. Teflon boiling chips, available from Cole-Parmer Instrument Co., are preferable. Before use they should be soaked in dilute HCl (approx 6*M*), rinsed several times in ammonia-free water, and dried at 180 °C. In order to avoid contamination by laboratory fumes, store them in a tightly stoppered container in an ammonia-free area of the laboratory.

6.5 Digest under a hood for 3½ h using the listed conditions. It is imperative that the heating block cool to 150 °C before subsequent batches of samples are placed in the digestor or extreme spattering will occur.

6.6 *Cautiously* remove tubes from the digestor and allow to cool for approx 15 min in a hood. Quickly add approx 50 mL ammonia-free water to each tube with vigorous agitation and *extreme caution* (NOTE 6). Allow to cool briefly before making the final dilution to the calibration mark. Stopper the tubes and invert several times until well mixed (NOTE 7). If a portion of this solution must be diluted to remain within the designated concentration range, this dilution must be made with 0.20*M* H_2SO_4.

NOTE 6. The precipitation of salts is minimized by this procedure. A vortex mixer is useful for agitating the water-acid mixture.

NOTE 7. Allow any precipitate that has formed or any boiling chip flakes to settle before filling the sample cups as described in paragraph 6.10.

6.7 Set up manifold (fig. 34). If the laboratory air is contaminated with ammonia, the air must be passed through a scrubber containing 2.5*M* H_2SO_4 before the air enters the air-manifold tube.

6.8 Allow the colorimeter, recorder, and heating bath to warm for at least 30 min.

6.9 Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with 0.20*M* H_2SO_4 in the sample line. The solution remaining in the wash reservoir from previous analyses may have become contaminated; therefore, this reservoir should be emptied and rinsed, and filled with fresh wash solution before proceeding. Place each reagent line except salicylate into its respective container; allow at least 5 min for the introduction of these reagents, and then place the salicylate

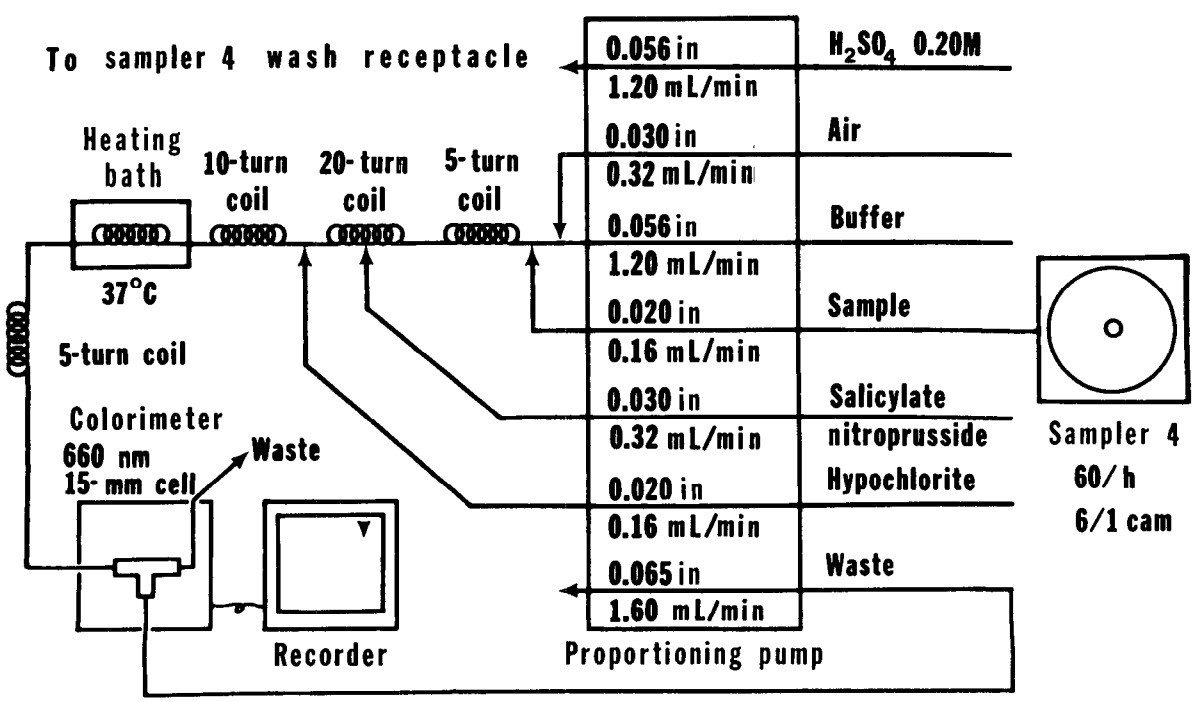

Figure 34.—Nitrogen, ammonia plus organic, salicylate-hypochlorite manifold

line into its reagent container. If a precipitate forms after the addition of the salicylate, the pH of the solution stream is too low.

6.10 Place a complete set of standards and a blank in the first positions of the first sample tray, beginning with the most concentrated standard (NOTE 8). Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

NOTE 8. To avoid possible contamination of the sample cups, keep them sealed in their packages until just prior to use. Rinse each sample cup with sample prior to filling.

6.11 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 Determine the milligrams of ammonia-nitrogen in each sample from a plot of peak heights of standards. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak. Likewise, the amount of NH_3–N present from the addition of H_2SO_4, as indicated by the concentration of NH_3–N in the blank, must be subtracted from the total milligrams of NH_3–N in each sample.

7.2 Determine the concentration of dissolved or total ammonia plus organic nitrogen as follows:

$$\text{Nitrogen, ammonia plus organic (mg/L)} = \frac{1{,}000}{\text{mL sample}} \times \text{mg } NH_3\text{–N in sample}$$

7.3 To determine the concentration of suspended total ammonia plus organic nitrogen, subtract dissolved ammonia-plus-organic nitrogen concentration from total ammonia-plus-organic nitrogen concentration.

7.4 Determine the concentration of total ammonia plus organic nitrogen in bottom material as follows:

$$\text{Nitrogen, ammonia plus organic (mg/kg)} = \frac{\text{mg } NH_3\text{–N in sample}}{\text{ample dry wt (g)}} \times 1000$$

8. Report

8.1 Report nitrogen, ammonia plus organic, dissolved (00623), total (00625), suspended-total (00624), concentrations as follows: 0.2 to 1.0 mg/L, one decimal; 1.0 mg/L and above, two significant figures.

8.2 Report nitrogen, ammonia plus organic, total-in-bottom-material (00626), in milligrams per kilogram of dry-weight sample, concentrations as follows: less than 1,000 mg/kg, nearest 10 mg/kg; 1,000 mg/kg and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved ammonia plus organic nitrogen within the range of 0.68 to 1.41 mg/L for seven samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 0.577 mg/L ranged from 0.486 to 0.750 mg/L.

9.2 Precision for dissolved ammonia plus organic nitrogen for three of the seven samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
8	0.675	63
8	1.14	54
8	1.41	54

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

Nitrogen, ammonia plus organic, colorimetric, block digestor–salicylate-hypochlorite, automated-discrete

Parameters and Codes:

Nitrogen, ammonia plus organic, dissolved, I-2558-85 (mg/L as N): 00623
Nitrogen, ammonia plus organic, total, I-4558-85 (mg/L as N): 00625
Nitrogen, ammonia plus organic, suspended total, I-7558-85 (mg/L as N): 00624

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 0.2 to 5.0 mg/L ammonia plus organic nitrogen. Samples containing concentrations greater than 5.0 mg/L need to be diluted.

1.2 Suspended total ammonia plus organic nitrogen is calculated by subtracting dissolved ammonia plus organic nitrogen from total ammonia plus organic nitrogen.

2. Summary of method

Organic nitrogen compounds are reduced to the ammonium ion by digestion with sulfuric acid in the presence of mercuric sulfate, which acts as a catalyst, and potassium sulfate. The ammonium ion produced by this digestion, as well as the ammonium ion originally present, is determined by reaction with sodium salicylate, sodium nitroprusside, and sodium hypochlorite in an alkaline medium. The resulting color is directly proportional to the concentration of ammonia present.

3. Interferences

3.1 A comparision study of results obtained by this method with those from the colorimetric, block-digestor salicylate-hypochlorite, automated-segmented-flow method (method I-2552) indicates the absence of interferences.

3.2 The samples are easily contaminated by ammonia in the laboratory atmosphere. The digestion process should be performed in a fume hood that is operating properly and that is located in an ammonia-free area of the laboratory. Other laboratory procedures may be performed outside or near this hood only if there is no possibility of ammonia contamination.

4. Apparatus

4.1 *Block digestor*, Technicon Model BD-40 with 75-mL digestion tubes or equivalent.

4.2 With this equipment, the following operating conditions have been found satisfactory:

Modeswitch ---	Automatic
Low-temperature regulator ---	160°C
High-temperature regulator	370°C
Low-temperature timer ------	1.5 h
Total cycle time	3.5 h

4.3 *Discrete analyzer system*, American Monitor IQAS or equivalent.

4.4 With this equipment, the following operating conditions have been found satisfactory:

Wavelength ---	620 nm
Absorption cell	1 cm square, temperature-controlled, flow-through quartz cuvette
Reaction temperature ---------	40°C
Sample volume	0.375 mL with 0.075 mL diluent
Reagent volumes	1.0 mL buffer solution, 0.45 mL sodium salicylate-sodium nitroprusside solution, and 0.25 mL sodium hypochlorite solution

NOTE 1. Sample-to-diluent ratio and reagent volumes must be optimized for each instrument according to manufacturer's specifications.

5. Reagents

5.1 *Ammonia standard solution I*, 1.00 mL = 1.00 mg NH_3-N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL.

5.2 *Ammonia standard solution II*, 1.00 mL = 0.10 mg NH_3-N: Dilute 100.0 mL ammonia standard solution I to 1,000 mL with ammonia-free water.

5.3 *Ammonia working standards*: Prepare a blank and 1,000 mL each of a series of working standards by dilution of ammonia standard solution II. Dissolve 52 mg mercuric chloride and 600 mg sodium chloride in each working standard.

Standard solution II (mL)	Nitrogen concentration (mg/L)
2.0	0.2
5.0	0.5
10	1
30	3
50	5

5.4 *Buffer solution*: Add, with stirring, 250 mL potassium sodium tartrate solution to 200 mL sodium phosphate solution. Slowly, with stirring, add 120 mL 5 *M* NaOH. Dilute to 1 L with ammonia-free water.

5.5 *Mercuric sulfate solution*, 11 g/100 mL: Dissolve 40 g red HgO in 250 mL 3.6 *M* H_2SO_4 and dilute to 500 mL with ammonia-free water.

5.6 *Sodium hydroxide solution*, 5 *M*: Add, with cooling and stirring, 200 g NaOH to approx 800 mL ammonia-free water. Cool and dilute to 1 L.

5.7 *Sodium hypochlorite solution*: Dilute 6.0 mL sodium hypochlorite solution (a commercial bleach solution containing 5.25-percent available chlorine is satisfactory) to 100 mL with ammonia-free water.

5.8 *Sodium phosphate, dibasic, solution*, 71 g/L: Dissolve 134 g $Na_2HPO_4 \cdot 7H_2O$ in approx 800 mL ammonia-free water. Add 100 mL 5 *M* NaOH, dilute to 1 L with ammonia-free water, and mix thoroughly.

5.9 *Sodium potassium tartrate solution*, 149 g/L: Dissolve 200 g $NaKC_4H_4O_6 \cdot 4H_2O$ in approx 600 mL ammonia-free water. Dilute to 1 L.

5.10 *Sodium salicylate-sodium nitroprusside solution*: Dissolve 150 g sodium salicylate and 0.50 g sodium nitroprusside in approx 600 mL ammonia-free water. Dilute to 1 L with ammonia-free water, and store in a light-resistant container.

5.11 *Sulfuric acid*, concentrated (sp gr 1.84).

5.12 *Sulfuric acid*, 0.20 *M*: *Cautiously*, add 11 mL concentrated H_2SO_4 (sp gr 1.84) to ammonia-free water and dilute to 1 L with ammonia-free water.

5.13 *Sulfuric acid*, 3.6 *M*: *Cautiously*, add 200 mL concentrated H_2SO_4 (sp gr 1.84) to approx 700 mL ammonia-free water. Cool and dilute to 1 L with ammonia-free water.

5.14 *Sulfuric acid-mercuric sulfate-potassium sulfate solution*: Dissolve 267 g K_2SO_4 in approx 1,300 mL ammonia-free water. *Cautiously*, add 400 mL concentrated H_2SO_4 (sp gr 1.84) and 50 mL mercuric sulfate solution. Cool and dilute to 2 L with ammonia-free water.

6. Procedure

Rinse all glassware with ammonia-free water before each use.

6.1 Pipet a volume (20.0 mL max) of well-mixed sample containing less than 0.1 mg ammonia plus organic nitrogen (as N) into a digestion tube and adjust the volume to 20 mL with ammonia-free water. For water-suspended sediment mixtures, rinse the pipet with a small amount of ammonia-free water to remove adhering particles, and combine with sample.

6.2 Prepare a blank and four standards in a similar manner. The blank and standards must also undergo the digestion process.

6.3 Add 4.0 mL sulfuric acid-mercuric sulfate-potassium sulfate solution and two boiling chips. **CAUTION: Hazardous.** Mix well before placing in digestor (NOTES 2 and 3).

NOTE 2. Protective eyeglasses and clothing are mandatory for this procedure because sulfuric acid and high-temperature solutions are very hazardous. The addition of the above mixture must be carried out in a hood.

NOTE 3. Teflon boiling chips, available from Cole-Parmer Instrument Co., are preferable. Before use they should be soaked in dilute HCl

(approx 6*M*), rinsed several times in ammonia-free water, and dried at 180 °C. In order to avoid contamination by laboratory fumes, store them in a tightly stoppered container in an ammonia-free area of the laboratory.

6.4 Digest under a hood for 3½ h using the listed conditions. It is imperative that the heating block cool to 150 °C before subsequent batches of samples are placed in the digestor or extreme spattering will occur.

6.5 *Cautiously*, remove tubes from the digestor and allow to cool for approx 15 min in a hood. Quickly add approx 50 mL ammonia-free water to each tube with vigorous agitation and *extreme caution* (NOTE 4). Allow to cool briefly before making the final dilution to the calibration mark. Stopper the tubes and invert several times until well mixed (NOTE 5). If a portion of this solution must be diluted to remain within the designated concentration range, this dilution must be made with 0.20*M* H_2SO_4.

NOTE 4. The precipitation of salts is minimized by this procedure. A vortex mixer is useful for agitating the water-acid mixture.

NOTE 5. Allow any precipitate that has formed or any boiling chip flakes to settle before filling the sample cups as described in paragraph 6.8.

6.6 Set up analyzer and computer-card assignments according to the manufacturer's instructions.

6.7 Place standards, beginning with the lowest concentration, in ascending order (computer-calibration curve) in the first five positions on the sample turntable. These standards should be 0.2, 0.5, 1.0, 3.0, and 5.0 mg/L NH_3-N. Place samples and quality-control standards in the remainder of the sample turntable.

6.8 Begin analysis. The cathode-ray tube (CRT) will acknowledge the parameters and concentration range, listing each sample-cup number and corresponding concentrations calculated from the working curve. During each run, the CRT display will provide a plot of standards, samples, and list blank and slope calculations. Retain copy of all information obtained from printer.

7. Calculations

Determine the concentration in milligrams per liter of dissolved or total ammonia plus organic nitrogen in each sample from either the CRT display or the printer output.

7.2 To determine concentration of suspended total ammonia plus organic nitrogen, subtract dissolved-ammonia-plus-organic nitrogen concentration from total ammonia-plus-organic nitrogen concentration.

8. Report

Report nitrogen, ammonia plus organic, dissolved (00623), total (00625), and suspended-total (00624), concentrations as follows: 0.2 to 1.0 mg/L, one decimal; 1.0 mg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the standard deviation and percent relative standard deviation for replicate analysis of reference materials by a single operator is as follows:

Mean (mg/L)	Number of replicates	Standard deviation (mg/L)	Relative standard deviation (percent)
0.11	10	0.04	36.4
.42	34	.09	21.4
4.2	35	.08	1.9
5.0	26	.08	1.6

Nitrogen, ammonia plus organic, colorimetric, digestion-distillation-nesslerization

Parameter and Code:
Nitrogen, ammonia plus organic, dissolved, I-1550-85 (mg/L as N): 00623

1. Application

This method, is recommended for analysis of water containing from 0.01 to 2.0 mg/L of dissolved ammonia plus organic nitrogen. Samples with greater concentrations need either to be diluted or to be analyzed by a titrimetric procedure.

2. Summary of method

2.1 Organic nitrogen-containing compounds are degraded to ammonium salts by digestion with sulfuric acid in the presence of copper sulfate, which acts as a catalyst. The solution is then made alkaline with sodium hydroxide, and the resulting free ammonia is distilled and nesslerized. The color developed is proportional to the ammonia-plus-organic nitrogen content of the sample.

2.2 Additional information on the principle of the determination is given in Kolthoff and others (1969).

3. Interferences

3.1 Nitrate and nitrite do not interfere.

3.2 Calcium, magnesium, iron, and sulfide interfere with the nesslerization, but the distillation eliminates interference of the metals, and sulfides are completely destroyed during the digestion.

4. Apparatus

4.1 *Cylinder*, graduated, with ground-glass stopper, 50-mL capacity (Corning No. 3002 or equivalent).

4.2 *Kjeldahl distillation apparatus*, 800-mL flasks.

4.3 *Spectrometer*, for use at 425 nm.

5. Reagents

5.1 *Ammonia standard solution I*, 1.00 mL = 1.00 mg N: Dissolve 3.819 g NH_4Cl, dried overnight over sulfuric acid, in ammonia-free water and dilute to 1,000 mL.

5.2 *Ammonia standard solution II*, 1.00 mL = 0.010 mg N: Dilute 10.00 mL ammonia standard solution I to 1,000 mL with ammonia-free water. Prepare fresh daily.

5.3 *Borate buffer solution*: Dissolve 9.54 g $Na_2B_4O_7 \cdot 10H_2O$ in ammonia-free water. Adjust the pH to 9.5 with 1*M* NaOH (approx 15 mL), and dilute to 1 L with ammonia-free water.

5.4 *Boric acid solution*, 20 g/L: Dissolve 20 g H_3BO_3 in ammonia-free water and dilute to 1 L.

5.5 *Copper sulfate solution*, 6.5 g/100 mL: Dissolve 6.5 g $CuSO_4$ (anhydrous) in ammonia-free water and dilute to 100 mL.

5.6 *Methyl red indicator solution*, 0.1 g/100 mL: Dissolve 0.1 g methyl red indicator in 100 mL 95-percent ethanol.

5.7 *Nessler reagent*— **CAUTION: HgI_2 is a deadly poison, and the reagent must be so marked:** Dissolve 100 g HgI_2 and 70 g KI in a small volume of ammonia-free water. Add this mixture slowly, with stirring, to a cooled solution of 160 g NaOH in 500 mL ammonia-free water and dilute to 1 L. Allow the reagent to stand at least overnight and filter through a fritted-glass crucible.

5.8 *Sodium hydroxide solution*, 10*M*: Dissolve 400 g NaOH in ammonia-free water and dilute to 1 L.

5.9 *Sulfuric acid*, concentrated (sp gr 1.84).

6. Procedure

6.1 Rinse all glassware with ammonia-free water before use.

6.2 Free the Kjeldahl distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace using nessler reagent—**CAUTION: deadly poison.**

6.3 Pipet a volume of sample containing less than 1.0 mg ammonia plus organic nitrogen (250 mL max) into a 800-mL Kjeldahl digestion flask.

6.4 Add 5.0 mL concentrated H_2SO_4 and 0.5 mL $CuSO_4$ solution, and mix.

6.5 Digest under a hood until copious fumes are given off. Continue heating until the fumes have subsided and the liquid becomes colorless or pale yellow. Continue digestion an additional 30 min.

6.6 Cool and dilute to approx 150 mL with ammonia-free water.

6.7 Add 25 mL 10*M* NaOH *cautiously* down the side of the flask.

6.8 Immediately connect the flask to the distillation apparatus, and *cautiously* mix the contents by gentle swirling.

6.9 Distill at a rate of no more than 10 and no less than 6 mL/min: collect the distillate in a 250-mL volumetric flask containing 25 mL boric acid solution. The tip of the delivery tube must be below the surface of the boric acid solution in the receiving flask.

6.10 Collect approx 150 mL distillate, dilute to the mark with ammonia-free water, and mix.

6.11 Pipet an aliquot of distillate containing less than 0.1 mg ammonia-nitrogen (50.0 mL max) into a glass-stoppered, graduated mixing cylinder, and adjust the volume to 50.0 mL with ammonia-free water.

6.12 Prepare a blank of ammonia-free water and a series of standards in glass-stoppered, graduated mixing cylinders. Add 5 mL boric acid solution to each, and adjust the volume of each to 50.0 mL.

6.13 Add 1.0 mL nessler reagent—**CAUTION: deadly poison**—to each blank, standard, and sample. Stopper and invert several times to mix thoroughly.

6.14 Allow the solutions to stand at least 10 min, but not more than 30 min.

6.15 Determine the absorbance of each test sample and standard against that of the blank.

7. Calculations

7.1 Determine a reagent blank for each new batch of H_2SO_4 by taking 250 mL ammonia-free water through the entire procedure:

$$\text{mg reagent blank} = \left(\begin{array}{c}\text{mg ammonia}\\ \text{plus organic N}\\ \text{per 5.0 mL } H_2SO_4\end{array}\right) \times \frac{\text{mL aliquot}}{\text{mL distillate}}$$

7.2 Determine the milligrams of ammonia plus organic nitrogen in each sample aliquot from a plot of absorbances of standards.

7.3 Determine the ammonia-plus-organic nitrogen concentration in milligrams per liter as follows:

$$\text{Ammonia plus organic nitrogen, mg/L} = \frac{1{,}000}{\text{mL sample}} \times \frac{250}{\text{mL aliquot}} \times$$

[(mg ammonia plus organic N in aliquot)–(mg reagent blank)].

8. Report

Report nitrogen, ammonia plus organic, dissolved (00623), concentrations as follows: less than 1.0 mg/L, two decimals; 1 mg/L and above, two signifcant figures.

9. Precision

9.1 The standard deviation for dissolved ammonia plus organic nitrogen within the range of 0.43 to 1.81 mg/L for nine samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 0.682 mg/L ranged from 0.603 to 0.786 mg/L.

9.2 Precision for dissolved ammonia plus organic nitrogen for four of the nine samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
11	0.434	58
13	.957	79
15	1.003	53
8	1.807	72

Reference

Kolthoff, I. M., Sandell, E. B., Meehen, E. J., and Bruckenstein, S., 1969, Quantitative chemical analysis (4th ed.): New York, Macmillan, 1199 p.

Nitrogen, ammonia plus organic, titrimetric, digestion-distillation

Parameter and Code:

Nitrogen, ammonia plus organic, total-in-bottom-material, dry wt, I-5553-85 (mg/kg as N): 00626

1. Application

This method may be used for analysis of bottom material containing at least 10 mg/kg of total ammonia plus organic nitrogen. Only that portion of bottom material that passes a 2-mm sieve is taken for analysis (method P-0810, subsampling, bottom material, coring).

2. Summary of method

The sample is subjected to a digestion whereby all organic nitrogen-containing compounds are converted to ammonium salts. The resulting mixture is then made strongly alkaline, and the ammonia so formed is distilled from the mixture into a solution of boric acid and subsequently determined by titration with standard sulfuric acid solution.

3. Interferences

There are no known interferences with this method.

4. Apparatus

Kjeldahl distillation apparatus, 500-mL flasks.

5. Reagents

5.1 *Ammonium chloride*, crystals.

5.2 *Boric acid solution*, 20 g/L: Dissolve 20 g H_3BO_3 crystals in 800 mL ammonia-free water and dilute to 1 L.

5.3 *Digestion catalyst*: Tablets containing 3.5 g K_2SO_4 and 0.175 g HgO (Scientific Chemical Technical Sales Inc., SCT Kel-catalyst No. KC-M3, or equivalent).

5.4 *Mixed indicator solution*: Dissolve 20 mg methyl red and 100 mg bromocresol green in 100 mL 95-percent ethanol. Store in a well-sealed bottle.

5.5 *Sodium carbonate solution*, 0.0357*N*: Dissolve 1.892 g primary standard Na_2CO_3 in carbon dioxide-free water and dilute to 1,000 mL.

5.6 *Sodium hydroxide-thiosulfate solution*: *Cautiously*, dissolve 500 g NaOH in 600 mL ammonia-free water. Add 80 g $Na_2S_2O_3 \cdot 5H_2O$ and dilute to 1 L.

5.7 *Sodium thiosulfate*, crystals, $Na_2S_2O_3 \cdot 5H_2O$.

5.8 *Sucrose*.

5.9 *Sulfuric acid*, concentrated, sp gr 1.84.

5.10 *Sulfuric acid standard solution*, approx 0.036*N*: *Cautiously*, add 1.0 mL concentrated H_2SO_4 (sp gr 1.84) to 800 mL ammonia-free water and dilute to 1 L. Standardize by titrating 25.0 mL 0.0357*N* Na_2CO_3 to pH 4.5. Compute normality of sulfuric acid standard solution to four decimal places.

6. Procedure

6.1 Free the distillation apparatus of ammonia by boiling ammonia-free water until the distillate shows no trace using nessler reagent—**CAUTION: deadly poison.**

6.2 Weigh to the nearest milligram, 3 g of bottom-material sample, prepared as directed in method P-0810, and transfer to the digestion flask.

6.3 In the same manner prepare a blank, using 2.0 g sucrose. Analyze the blank and each sample as directed in paragraphs 6.4 to 6.10.

6.4 *Cautiously*, add 25 mL concentrated H_2SO_4 (sp gr 1.84), and under a hood, swirl the contents of the flask until thoroughly mixed.

6.5 Add three digestion-catalyst tablets and mix well. Add a few glass beads and begin the digestion. Continue the digestion until a clear solution is obtained, and then continue fuming 1 h.

6.6 Cool the flask until crystals appear (do not cool completely). Add 150 mL ammonia-free water; mix and allow to cool.

6.7 Add 100 mL NaOH-$Na_2S_2O_3$ solution. Immediately connect the flask to the distillation apparatus and *cautiously* mix the contents by swirling.

6.8 Distill at a rate of not more than 10 mL/min and no less than 6 mL/min; collect the distillate in a 250-mL volumetric flask containing 25 mL boric acid solution. The tip of the delivery tube must be below the surface of the boric acid solution in the receiving flask.

6.9 Collect approx 200 mL of distillate, dilute to 250 mL with ammonia-free water, and mix.

6.10 To the distillate, add 3 drops mixed indicator solution, and titrate with sulfuric acid standard solution until the color of the solution changes from yellow to red.

7. Calculations

Nitrogen, ammonia plus organic (mg/kg) =

$$\frac{V_a \times N_a \times 14{,}000}{Wt_s}$$

where

V_a = volume of standard H_2SO_4 used to titrate sample, milliliters, minus volume used to titrate blank, milliliters,

N_a = normality of standard H_2SO_4 solution, and

Wt_s = weight of sample, grams.

8. Report

Report nitrogen, ammonia plus organic, total-in-bottom-material (00626), concentrations as follows: 10 to 100 mg/kg, nearest 1 mg/kg; 100 mg/kg and above, two significant figures.

9. Precision

Precision data are not available for this method.

Nitrogen, nitrate, ion-exchange chromatographic, automated

Parameters and Codes:

Nitrogen, nitrate, dissolved, I-2057-85 (mg/L as N): 00618
Nitrogen, nitrate, dissolved, I-2058-85 (mg/L as N): 00618

2. Summary of method

Nitrate is determined sequentially with six other anions by ion-exchange chromatography. Ions are separated based on their affinity for the exchange sites of the resin. The separated anions in their acid form are measured using an electrical-conductivity cell. See method I-2057, anions, ion-exchange chromatographic, automated, and method I-2058, anions, ion-exchange chromatographic, precipitation, automated.

Nitrogen, nitrite, colorimetric, diazotization

Parameter and Code:

Nitrogen, nitrite, dissolved, I-1540-85 (mg/L as N): 00613

1. Application

This method may be used to analyze water containing between 0.01 and 0.6 mg/L of nitrite-nitrogen; samples containing greater concentrations need to be diluted.

2. Summary of method

Nitrite is diazotized with sulfanilamide, and the resulting diazo compound is coupled with N-1-naphthylethylenediamine dihydrochloride to form an intensely colored red compound, which is determined spectrometrically at 540 nm. Sulfanilamide and N-1-naphthylethylenediamine dihydrochloride are combined with a sodium acetate buffer to form a single reagent solution.

3. Interferences

Oxidizing agents interfere by oxidizing nitrite to nitrate. Sulfide also interferes. No other substance commonly occurring in natural water interferes with this method.

4. Apparatus

4.1 Spectrometer for use at 540 nm.

4.2 Refer to manufacturer's manual to optimize instrument.

5. Reagents

5.1 *Color-buffer solution*: Add 105 mL concentrated HCl (sp gr 1.19), 5.0 g sulfanilamide, and 0.5 g N-1-naphthylethylenediamine dihydrochloride to 250 mL demineralized water. Stir until dissolved. Add 136 g $CH_3COONa \cdot 3H_2O$ or 82 g CH_3COONa and stir until dissolved. Dilute to 500 mL with demineralized water. When 2 mL of this solution is added to 50 mL demineralized water, the resultant solution should have a pH of 1.8. Store the color-buffer solution in the dark and protect from nitrogen oxides that may be in the atmosphere. The solution is stable for several months.

5.2 *Nitrite-nitrogen standard solution I*, 1.00 mL = 0.50 mg NO_2-N: Dissolve 3.038 g KNO_2 in demineralized water and dilute to 1,000 mL. This and the following nitrite standard solution are not stable indefinitely; their concentrations must be checked frequently.

5.3 *Nitrite-nitrogen standard solution II*, 1.00 mL = 0.05 mg NO_2-N: Dilute 100.0 mL nitrite-nitrogen standard solution I to 1,000 mL with demineralized water.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.03 mg NO_2-N (50.0 mL max) into a 100-mL beaker and adjust the volume to 50.0 mL with demineralized water (NOTE 1).

NOTE 1. If the sample has a pH greater than 10 or less than 4 (or greater than 600 mg/L alkalinity or acidity), adjust to approx pH 6 with 3*M* HCl or 2.5*M* NaOH.

6.2 Prepare a blank and sufficient standards, and adjust the volume of each to 50.0 mL (NOTE 2).

NOTE 2. If the samples were preserved with mercuric chloride fortified with sodium chloride, add an equivalent amount to the blank and standards.

6.3 Add 2.0 mL color-buffer solution and mix.

6.4 Allow the color to develop for at least 15 min and measure the absorbances of the sample and standards against that of the blank.

7. Calculations

7.1 Determine milligrams of nitrite-nitrogen in each test sample from a plot of absorbances of standards.

7.2 Determine the nitrite-nitrogen concentration in milligrams per liter as follows:

$$NO_2\text{-N (mg/L)} = \frac{1{,}000}{\text{mL aliquot}} \times \text{mg } NO_2\text{-N in sample}$$

8. Report

Report nitrogen, nitrite dissolved (00613), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved nitrite-nitrogen for 19 samples within the range of 0.005 to 2.17 mg/L may be expressed as follows:

$$S_T = 0.096X + 0.006$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of nitrite-nitrogen, milligrams per liter.

The correlation coefficient is 0.9094.

9.2 Precision for dissolved nitrite-nitrogen for five of the 19 samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
11	0.005	100
11	.050	20
14	.556	9
17	1.48	8
10	2.17	12

Nitrogen, nitrite, colorimetric, diazotization, automated-segmented flow

Parameters and Codes:
Nitrogen, nitrite, dissolved, I-2540-85 (mg/L as N): 00613
Nitrogen, nitrite, total, I-4540-85 (mg/L as N): 00615

1. Application

1.1 This method may be used to analyze surface, domestic and industrial water, and brines and water-suspended sediment containing from 0.01 to 1.0 mg/L of nitrite-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.

2. Summary of method

Nitrite ion reacts with sulfanilamide under acidic conditions to form a diazo compound, which then couples with N-1-naphthylethylenediamine dihydrochloride to form a red compound, the absorbance of which is measured colorimetrically (Kamphake and others, 1967).

3. Interferences

Oxidizing agents interfere by oxidizing nitrite to nitrate. Sulfide also interferes. No other substance commonly occurring in natural water interferes with this method.

4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold, proportioning pump, colorimeter, voltage stabilizer, recorder, and printer.

4.2 With this equipment the following operating conditions have been found satisfactory:

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

5. Reagents

5.1 *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. Store in an amber bottle and refrigerate; however, the reagent must be at room temperature when it is used. The reagent is stable for approx 1 month.

5.2 *Nitrite-nitrogen standard solution I*, 1.00 mL = 0.100 mg NO_2-N: Dissolve 0.6076 g KNO_2 in demineralized water and dilute to 1,000 mL. This and the following nitrite standard solutions are not stable indefinitely; their concentrations must be checked frequently.

5.3 *Nitrite-nitrogen standard solution II*, 1.00 mL = 0.010 mg NO_2-N: Quantitatively dilute 100.0 mL nitrite-nitrogen standard solution I to 1,000 mL with demineralized water.

5.4 *Nitrite-nitrogen working standards*: Prepare a blank and 100 mL each of a series of nitrite-nitrogen working standards by appropriate quantitative dilution of nitrite-nitrogen standard solution II. Dissolve 5.2 mg mercuric chloride and 60 mg sodium chloride in each working standard. For example:

Nitrite-nitrogen standard solution II (mL)	Nitrite-nitrogen concentration (mg/L)
0.0	0.00
.5	.05
2.0	.2
5.0	.5
10.0	1.0

6. Procedure

6.1 Set up manifold (fig. 35).

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

6.3 Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample tube.

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

6.5 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-nitrogen concentration.

7.2 Compute the concentration of dissolved or total nitrite-nitrogen in each sample by comparing its 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.

8. Report

Report nitrogen, nitrite, dissolved (00613), and total (00615), concentrations as follows: less than 1 mg/L, two decimals; 1 mg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved nitrite-nitrogen for 19 samples within the range of 0.006 to 2.22 mg/L may be expressed as follows:

$$S_T = 0.093X + 0.004$$

where

S_T = overall precision, milligrams per liter, and

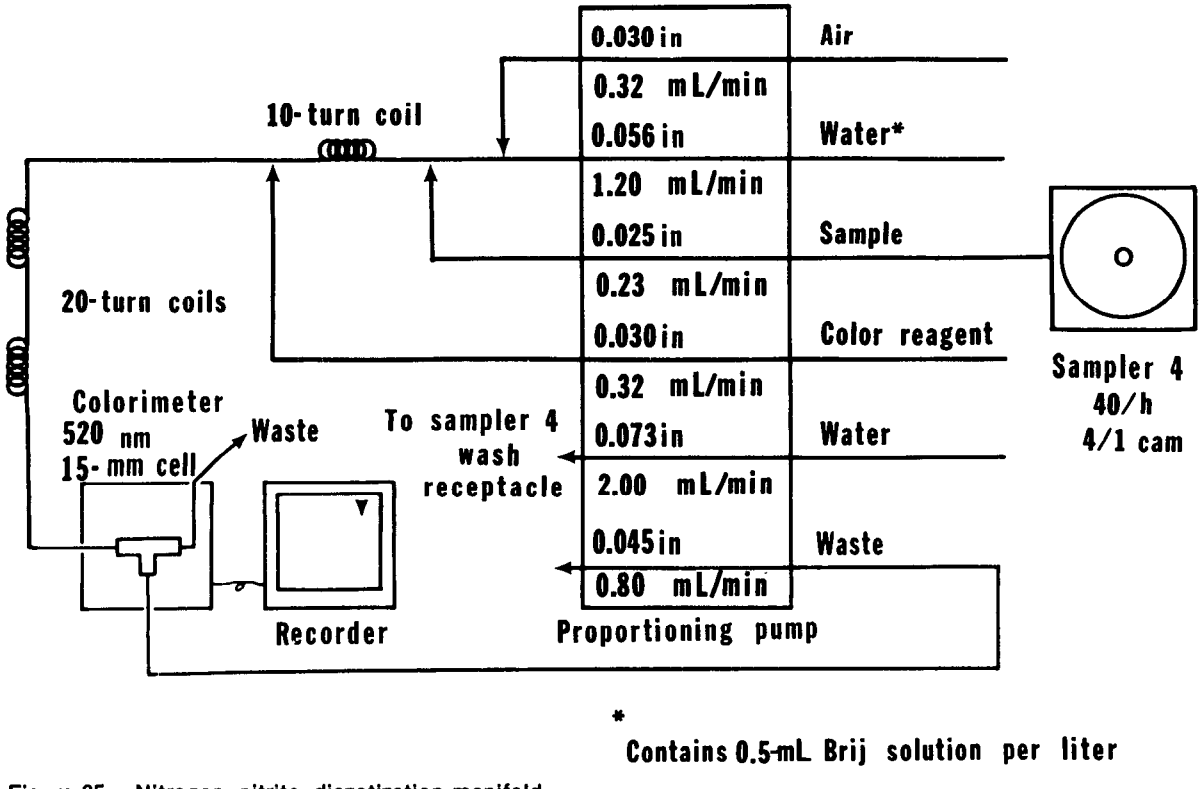

Figure 35.—Nitrogen, nitrite, diazotization manifold

X = concentration of nitrite-nitrogen, milligrams per liter.

The correlation coefficient is 0.9445.

9.2 Precision for dissolved nitrite-nitrogen for six of the 19 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
13	0.006	133
14	.010	60
20	.050	16
20	.540	6
21	1.40	13
19	2.22	9

9.3 It is estimated that the percent relative standard deviation for total nitrite-nitrogen will be greater than that reported for dissolved nitrite-nitrogen.

Reference

Kamphake, L., Hannah, S., and Cohen, J., 1967, Automated analysis for nitrite by hydrazine reduction: Water Research, v. 1, p. 205–16.

Nitrogen, nitrite, colorimetric, diazotization, automated-discrete

Parameters and Codes:

Nitrogen, nitrite, dissolved, I-2539-85 (mg/L as N): 00613
Nitrogen, nitrite, total, I-4539-85 (mg/L as N): 00615

1. Application

1.1 This method may be used to analyze surface, domestic, and industrial water, and water-suspended sediment containing from 0.01 to 1.00 mg/L of nitrite-nitrogen. Samples containing concentrations greater than 1.0 mg/L 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.

2. Summary of method

Nitrite ion reacts with sulfanilamide under acidic conditions to form a diazo compound, which then couples with N-1-naphthylethylenediamine dihydrochloride to form a red-colored compound, the absorbance of which is measured colorimetrically (Kamphake and others, 1967).

3. Interferences

3.1 Oxidizing agents interfere by oxidizing nitrite to nitrate. Sulfide also interferes. No other substance commonly occurring in natural water interferes.

4. Apparatus

4.1 *Discrete chemical analyzer system*, American Monitor IQAS or equivalent.

4.2 With this equipment, the following operating conditions have been found satisfactory for the range 0.01 to 1.00 mg/L:

Wavelength	547 nm
Absorption cell	1 cm square, temperature-controlled, flow-through quartz cuvette
Reaction temperature	37 °C
Sample volume	0.125 mL with 0.100 mL diluent (NOTE 1)
Reagent volume	1.0 mL color reagent (NOTE 1)

NOTE 1. Sample-to-diluent ratio and reagent volume must be optimized for each instrument according to manufacturer's specifications.

5. Reagents

5.1 *Color reagent*: Add 100 mL concentrated phosphoric acid (sp gr 1.69) and 10 g sulfanilamide to approx 750 mL demineralized water. Dissolve completely (warm if necessary). Add 0.5 g N-1-naphthylethylenediamine dihydrochloride and dissolve completely. Dilute to 1000 mL with demineralized water. Store in an amber bottle and refrigerate. Solution is stable for approx 1 month.

5.2 *Nitrite-nitrogen standard solution I*, 1.00 mL = 1.00 mg NO_2-N: Dissolve 6.076 g KNO_2 in demineralized water and dilute to 1000 mL. This and the following nitrite standard solutions are not stable indefinitely; their concentrations must be checked frequently.

5.3 *Nitrite-nitrogen standard solution II*, 1.00 mL = 0.01 mg NO_2-N: Quantitatively dilute 10.0 mL nitrite-nitrogen standard solution I to 1000 mL with demineralized water.

5.4 *Nitrite-nitrogen working standards*: Prepare a blank and 1000 mL each of a series of nitrite-nitrogen working standards by dilution of nitrite-nitrogen standard solution II. Dissolve 52 mg mercuric chloride and 600 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	.02
5.0	.05
30.0	.30
100.0	1.00

6. Procedure

6.1 Set up the analyzer and computer-card assignments according to manufacturer's instructions.

6.2 Place standards, beginning with the lowest concentrations, in ascending order (computer-calibration curve) in the first five positions on the sample turntable. Place samples and quality-control standards in the remainder of the sample turntable.

6.3 Begin analysis. The cathode-ray tube (CRT) will acknowledge the parameter and concentration range, listing each sample-cup number and corresponding concentrations calculated from the working curve. During each run, the CRT display will provide a plot of standards, samples, and list blank and slope calculations. Retain copy of all information obtained from printer.

7. Calculations

Determine the concentration in milligrams per liter of dissolved or total nitrite-nitrogen in each sample from either the CRT display or the printer output.

8. Report

Report nitrogen, nitrite, dissolved (00613), and total (00615), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 mg/L and above, two significant figures.

9. Precision

The precision expressed in terms of the standard deviation and percent relative standard deviation for replicate analysis of reference materials by a single operator is as follows:

Mean (mg/L)	Number of replicates	Standard deviation (mg/L)	Relative standard deviation (percent)
0.019	11	0.002	10.5
.051	14	.004	7.8
.156	14	.004	2.6
.243	14	.003	1.2
.470	14	.006	1.3
.822	14	.016	2.0

Nitrogen, nitrite, ion-exchange chromatographic, automated

Parameter and Code:

Nitrogen, nitrite, dissolved, I-2057-85 (mg/L as N): 00613

2. Summary of method

Nitrite is determined sequentially with six other anions by ion-exchange chromatography. Ions are separated based on their affinity for the exchange sites of the resin. The separated anions in their acid form are measured using an electrical-conductivity cell. See method I-2057, anions, ion-exchange chromatographic (IC), automated.

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

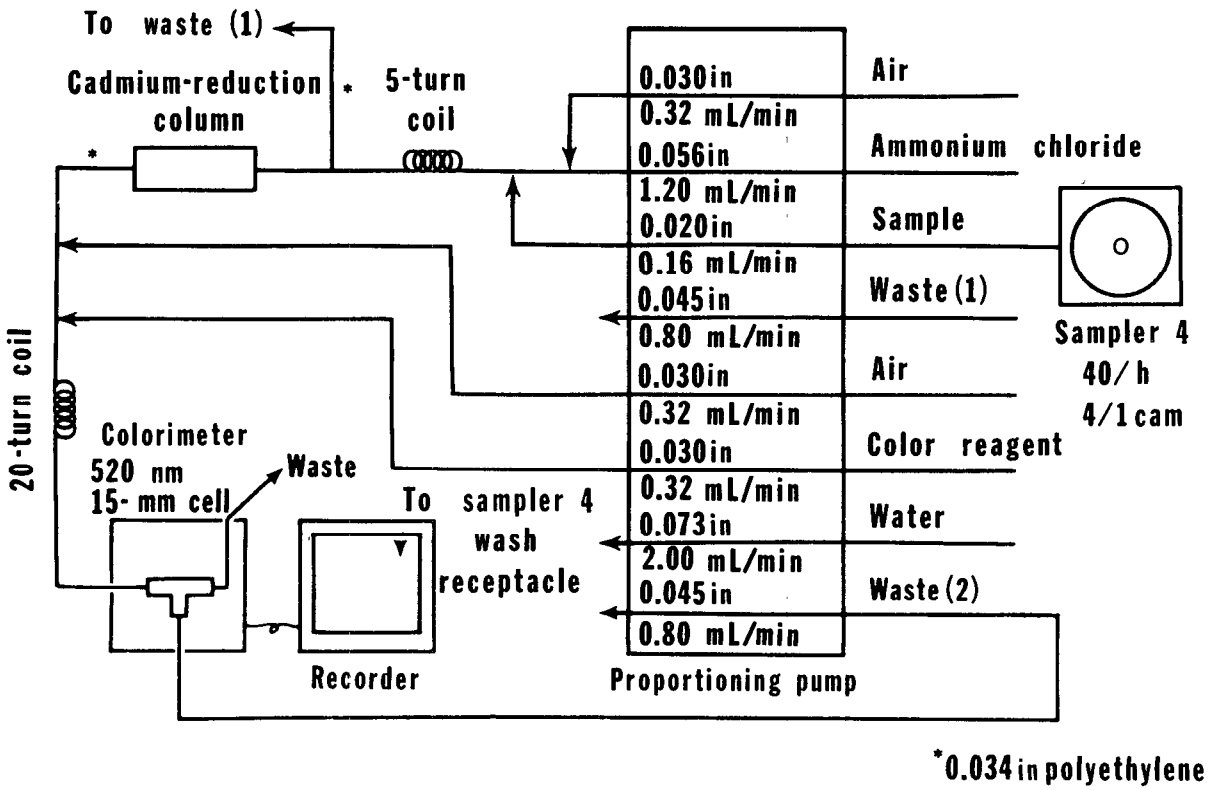

Figure 36.—Nitrogen, nitrite plus nitrate, cadmium reduction-diazotization, manifold

(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.

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

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

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 559–71.

Brewer, P. G., and Riley, J. P., 1965, The automatic determination of nitrate in sea water: Deep Sea Research, v. 12, p. 765–72.

Kamphake, L., Hannah, S., and Cohen, J., 1967, Automated analysis for nitrate by hydrazine reduction: Water Research, v. 1, p. 205–16.

Morris, A. W., and Riley, J. P., 1963, The determination of nitrate in sea water: Analytica Chimica Acta, v. 29, p. 272–9.

Strickland, J. D. H., and Parsons, T. R., 1972, A manual of sea water analysis: Canada Fisheries Research Board Bull. 167, 310 p.

U.S. Environmental Protection Agency, 1979, Methods for the chemical analysis of water and wastes: Washington, U.S. Government Printing Office, p. 353.2–1.

Nitrogen, nitrite plus nitrate, colorimetric, hydrazine reduction-diazotization, automated-discrete

Parameters and Codes:

Nitrogen, nitrite plus nitrate, dissolved, I-2543-85 (mg/L as N): 00631
Nitrogen, nitrite plus nitrate, total, I-4543-85 (mg/L as N): 00630

1. Application

1.1 This method may be used to determine the concentration of the sum of nitrite- plus nitrate-nitrogen in surface, ground, domestic, and industrial water, and water-suspended sediment in the range from 0.01 to 3.0 mg/L. 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.

2. Summary of method

Nitrate is reduced to nitrite with hydrazine sulfate in alkaline solution. The nitrite (that originally present plus reduced nitrate) is then treated with sulfanilamide under acidic conditions to yield a diazo compound, which is coupled with N-1-napthylethylenediamine dihydrochloride to form a red azo dye. The absorbance of this dye is measured colorimetrically at 520 nm (Kamphake and others, 1967; U.S. Environmental Protection Agency, 1979).

3. Interferences

3.1 Sample color that absorbs at the spectrophotometric wavelength used for analysis will interfere and must be corrected if the color exceeds 50 platinum cobalt units.

3.2 Samples containing concentrations greater than 5000 mg/L sulfate, 1000 mg/L calcium, sodium, potassium, or chloride, 150 mg/L magnesium, 30 mg/L phosphate, and 2 mg/L sulfide interfere.

4. Apparatus

4.1 *Discrete analyzer system*, American Monitor IQAS or equivalent.

4.2 With this equipment, the following operating conditions have been found satisfactory for the range 0.01 to 3.0 mg/L:

Wavelength ---	520 nm
Absorption cell	1 cm square, temperature-controlled, flow-through quartz cuvette
Reaction temperature ------	37 °C
Sample volume	0.13 mL with 0.27 mL of diluent (NOTE 1)
Reagent volumes	0.25 mL NaOH, 0.25 mL working reductant solution, and 0.80 mL color reagent (NOTE 1)

NOTE 1. Sample-to-diluent ratio and reagent volumes must be optimized for each instrument according to manufacturer's specifications.

5. Reagents

5.1 *Color reagent*: Add 100 mL concentrated H_3PO_4 (sp gr 1.69) and 10 g sulfanilamide to 750 mL demineralized water and warm if necessary for complete dissolution. Add 0.5 g N-1-napthylethylenediamine dihydrochloride and dissolve completely. Dilute to 1000 mL with demineralized water. Store in a dark bottle in a refrigerator. Solution must be at room temperature before use. Solution is stable for approximately one month.

5.2 *Copper sulfate solution*, 4 g/L: Dissolve 4 g $CuSO_4$ (anhydrous) in 500 mL demineralized water and dilute to 1000 mL.

5.3 *Hydrazine sulfate solution*, 27.5 g/L: Dissolve 13.75 g $N_2H_4 \cdot H_2SO_4$ in 400 mL demineralized water and dilute to 500 mL—**CAUTION: Poisonous.**

5.4 *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.

5.5 *Nitrate-nitrogen standard solution II*, 1.00 mL = 0.025 mg NO_3-N: Dilute 50.0 mL nitrate-nitrogen standard solution I to 1000 mL with demineralized water.

5.6 *Nitrate-nitrogen working standards*: Prepare a blank and 500 mL each of a series of nitrate-nitrogen working standards by appropriate dilution of the nitrate standard solution II. 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
1.0	.05
2.0	.10
10.0	.50
20.0	1.0
60.0	3.0

5.7 *Sodium hydroxide solution*, 0.3*M*: Dissolve 12 g NaOH in 500 mL demineralized water and dilute to 1000 mL.

5.8 *Working reductant solution*: Add 13.5 mL hydrazine sulfate solution plus 8 mL copper sulfate solution to 500 mL demineralized water and dilute to 1000 mL. Prepare fresh daily.

6. Procedure

6.1 Set up the analyzer and computer-card assignments according to the manufacturer's instructions. Add the 0.3*M* NaOH solution from the first available dispensing station and the working reductant solution from the last available dispensing station. The color reagent is added from a dispensing station during a second cycle of the turntable (NOTE 2).

NOTE 2. This second cycle of the turntable is necessary to ensure complete reduction of nitrate to nitrite prior to the formation of the red-colored azo dye.

6.2 Place four standards (0.1, 0.5, 1.0, and 3.0 mg/L NO_3-N, respectively) and blank, beginning with the lowest concentration in the first positions, on the sample turntable. Fill remainder of turntable with samples.

6.3 Begin analysis. The cathode-ray tube (CRT) will acknowledge the parameter and concentration range, listing each sample-cup number and corresponding concentrations calculated from the working curve. During each run the CRT display will provide a plot of standards, samples, and list blank and slope calculations. Retain copy of all information obtained from printer.

7. Calculations

Determine the concentration in milligrams per liter of dissolved or total nitrite plus nitrate-nitrogen in each sample from either the printer output or the CRT display.

8. Report

Report nitrogen, nitrite plus nitrate, dissolved (00631) and total (00630), concentrations as follows: less than 1.0 mg/L, nearest 0.01 mg/L; 1.0 mg/L and above, two significant figures.

9. Precision

Precision expressed in terms of the standard deviation and percent relative standard deviation for replicate analyses of reference materials by a single operator are as follows:

Number of replicates	Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)
40	0.10	0.01	10
40	.24	.02	8
17	.31	.03	10
40	.50	.02	4
40	1.01	.02	2
16	1.63	.08	5
57	3.05	.09	3

References

Kamphake, L., Hannah, S., and Cohen, J., 1967, Automated analysis for nitrate by hydrazine reduction: Water Research, v. 1, p. 205.

U.S. Environmental Protection Agency, 1979, Methods for chemical analyses of water and wastes: Cincinnati, p. 353.1–1.