

# 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  $\text{NH}_3\text{-N}$ . Prepared sample solutions containing more than 5.0 mg/L  $\text{NH}_3\text{-N}$  must first be diluted. The range may be extended to 10.0 mg/L  $\text{NH}_3\text{-N}$  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 5M 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  $\text{NH}_3\text{-N}$ : Dissolve 3.819 g  $\text{NH}_4\text{Cl}$ , 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  $\text{NH}_3\text{-N}$ : 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  $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$  and 24 g sodium citrate in 950 mL ammonia-free water. Adjust the pH of this solution to 5.0 with concentrated  $\text{H}_2\text{SO}_4$  (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  $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$  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 2.5M  $\text{H}_2\text{SO}_4$  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,

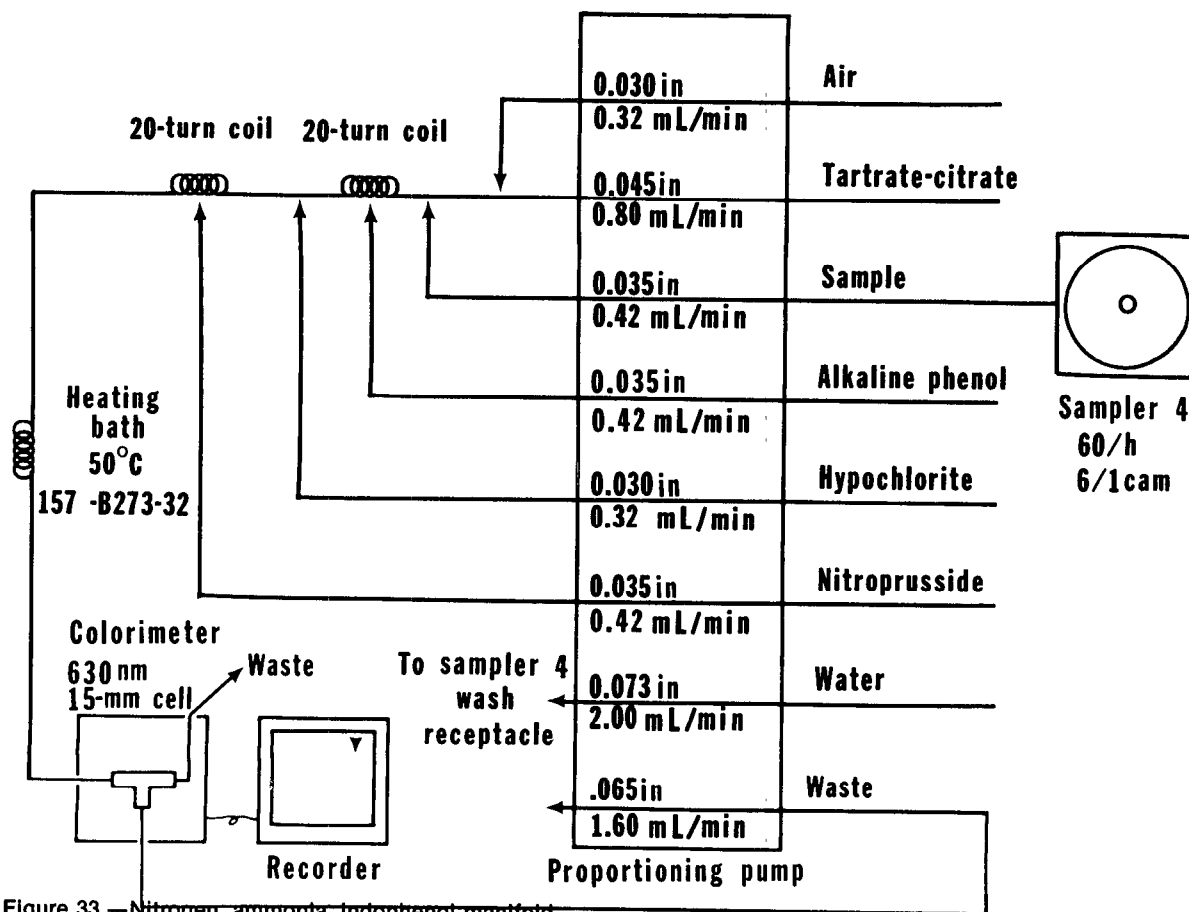


Figure 33.—Nitrogen, ammonia, indophenol manifold

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:

$$\text{NH}_3\text{-N (mg/kg)} = \frac{C_N \times 100}{\text{wt of sample (g)}}$$

where

$C_N$  =  $\text{NH}_3\text{-N}$  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

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