# Nitrogen, ammonia, colorimetry, salicylate-hypochlorite, automated-segmented flow

Parameters and Codes:
Nitrogen, ammonia, dissolved, I-2522-90 (mg/L as N): 00608
Nitrogen, ammonia, total-in-bottom-material, I-6522-90 (mg/L as N): 00611

## 1. Application

1.1 This method is used to analyze samples of surface, domestic, and industrial water, and brines containing from 0.01 to 1.5 mg/L of ammonia-nitrogen. Concentrations greater than 1.50 mg/L must be diluted. This modified method was implemented in the National Water Quality Laboratory in March 1988.

1.2 This method also is used to determine concentrations of ammonia-nitrogen in samples of 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 need to be diluted.

1.3 Sodium ion is a good replacement for ammonium ion in the slow-exchange positions of soil minerals (Jackson, 1958). Bottom material is treated with an acidified sodium chloride solution, and the resulting mixture is allowed to settle and then decanted to obtain a clear supernatant solution for analysis.

## 2. Summary of method

Ammonia reacts with salicylate and hypochlorite ions in the presence of ferricyanide ions to form the salicylic acid analog of indophenol blue (Reardon and others, 1966; Patton and Crouch, 1977; Harfmann and Crouch, 1989). The resulting color is directly proportional to the concentration of ammonia present.

## 3. Interferences

3.1 Sulfide interferes. Bromide and nitrite can interfere. Calcium and magnesium in highly alkaline waters (pH greater than 13.6) can exceed the ability of the tartrate to complex both ions.

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

## 4. Apparatus

4.1 *Shaker,* wrist action.

4.2 *Alpkem rapid flow analyzer (RFA),* consisting of sampler, peristaltic pump, analytical cartridge, heating bath, colorimeter, data station, and printer.

With this equipment, the following operating conditions are satisfactory for the range from 0.01 to 1.50 mg/L of ammonia-nitrogen:

| | |
|---|---|
| Flow cell | 15 mm |
| Wavelength | 660 nm |
| Sample time | 24 seconds |
| Wash time | 16 seconds |
| Sampling rate | 90 per hour |
| Heating Bath (2mL) | 37°C |
| Pecking | ON |
| Damp (RC) | *1* second |

## 5. Reagents

*5.1 Ammonia standard solution 1,* 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 1,000 mL. Refrigerate.

5.2 Ammonia standard solution II, 1.00 mL = 0.0015 mg $NH_3$-N:
Dilute 3.0 mL ammonia standard solution I to 1,000 mL with ammonia-free water. Prepare fresh weekly and refrigerate.

*5.2.1 Ammonia working solutions,* bottom materials: Prepare an ammonia-free blank and 250 mL each of a series of ammonia working solutions by appropriate quantitative dilution of ammonia standard solution II or working solutions with acidified sodium chloride solution (paragraph 5.7), as follows:

| Working solution No. | Solution added (mL) | Solution used | Ammonia concentration (mg/L) |
|---|---|---|---|
| 1 | 250 | Standard solution II | 1.50 |
| 2 | 125 | Standard solution II | .75 |
| 3 | 50 | Standard solution II | .30 |
| 4 | 25 | Standard solution II | .15 |
| 5 | 25 | Working solution No. 2 | .075 |
| 6 | 25 | Working solution No. 4 | .015 |

*Ammonia working solutions,* water: Prepare an ammonia-free blank and *250* mL each of a series of ammonia working solutions by dilution of ammonia standard solution II or working solutions with ammonia-free water as listed in the following table. If the samples to be analyzed are preserved, the ammonia working solutions need to contain an equivalent concentration of the same preservative.

| Working solution No. | Solution added (mL) | Solution used | Ammonia concentration (mg/L) |
|---|---|---|---|
| 1 | 250 | Standard solution II | 1.50 |
| 2 | 125 | Standard solution II | .75 |
| 3 | 50 | Standard solution II | .30 |
| 4 | 25 | Standard solution II | .15 |
| 5 | 25 | Working solution No. 2 | .075 |
| 6 | 25 | Working solution No. 4 | .015 |

Prepare weekly and refrigerate.

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

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

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

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

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

5.8 *Sodium hydroxide solution, 5M:* CAUTION: Add, while cooling and stirring, 200 g NaOH to about 800 mL ammonia-free water. Cool and dilute to 1 L.

*5.9 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. Prepare fresh daily.

5.10 *Sodium salicylate—sodium nitroferricyanide solution:* Dissolve 150 g sodium salicylate and 0.30 g sodium nitroferricyanide $[Na_2Fe(CN)_5NO \cdot 2H_2O]$ in about 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.

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

5.12 *Sulfuric acid, 2.5M:* Cautiously add 138 mL concentrated $H_2SO_4$ (sp gr 1.84) to about 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 water. For bottom materials, begin with paragraph 6.1.1.

6.1.1 Weigh, to the nearest milligram, about 5 g of sample prepared as directed in method P-0520, and transfer to a 250-mL Erlenmeyer flask.

6.1.2 Add 50 mL of the acidic sodium chloride solution (paragraph 5.7), shake on the wrist-action shaker for 30 minutes, and allow to settle.

6.1.3 Transfer the supenatant solution to a 200-mL volumetric flask, taking care not to disturb the residue in the bottom of the Erlenmeyer flask.

6.1.4 Wash the sediment in the Erlenmeyer flask with 20 mL acidic sodium chloride solution (paragraph 5.7), let settle, and transfer the clear wash solution to the volumetric flask. Adjust to volume with acidic sodium chloride solution (paragraph 5.7). Proceed to paragraph 6.2.

6.2 Set up manifold (fig. 4). If the laboratory air is contaminated with ammonia, the air needs to be passed through a scrubber containing 2.5*M* $H_2SO_4$ before it enters the air manifold tube.

6.3 Allow the colorimeter, recorder, and heating bath to warm for at least 10 minutes or until the temperature of the heating bath reaches 37°C.

6.4 After all reagents are on line (NOTE 1), adjust the sample output of the photometer to 5 V. Then switch the photometer to "absorbance" mode and use the reference detector "fine gain" control to adjust the baseline absorbance to about 0.2 V. See operation manuals for complete details (Alpkem Corp., 1986). The solution remaining in the wash reservoir from previous determinations might be contaminated; therefore, this reservoir needs to 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 minutes 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 remake them, and start again using the aforementioned procedure.

6.5 Place the most concentrated working solution in two cups before analysis. As the peaks appear on the recorder, adjust the STD CAL control until the peak obtains 95 percent of full scale.

6.6 When the system is clear of all working solutions, determine a dwell time using the most concentrated working solution.

6.7 Place a complete set of working solutions and a blank in the first positions of the sample tray beginning with the most concentrated working solution (NOTES 2 and 3). Place individual working solutions of differing concentrations in approximately every tenth position on the tray following the accepted protocol. Fill the remainder of each tray with unknown samples.

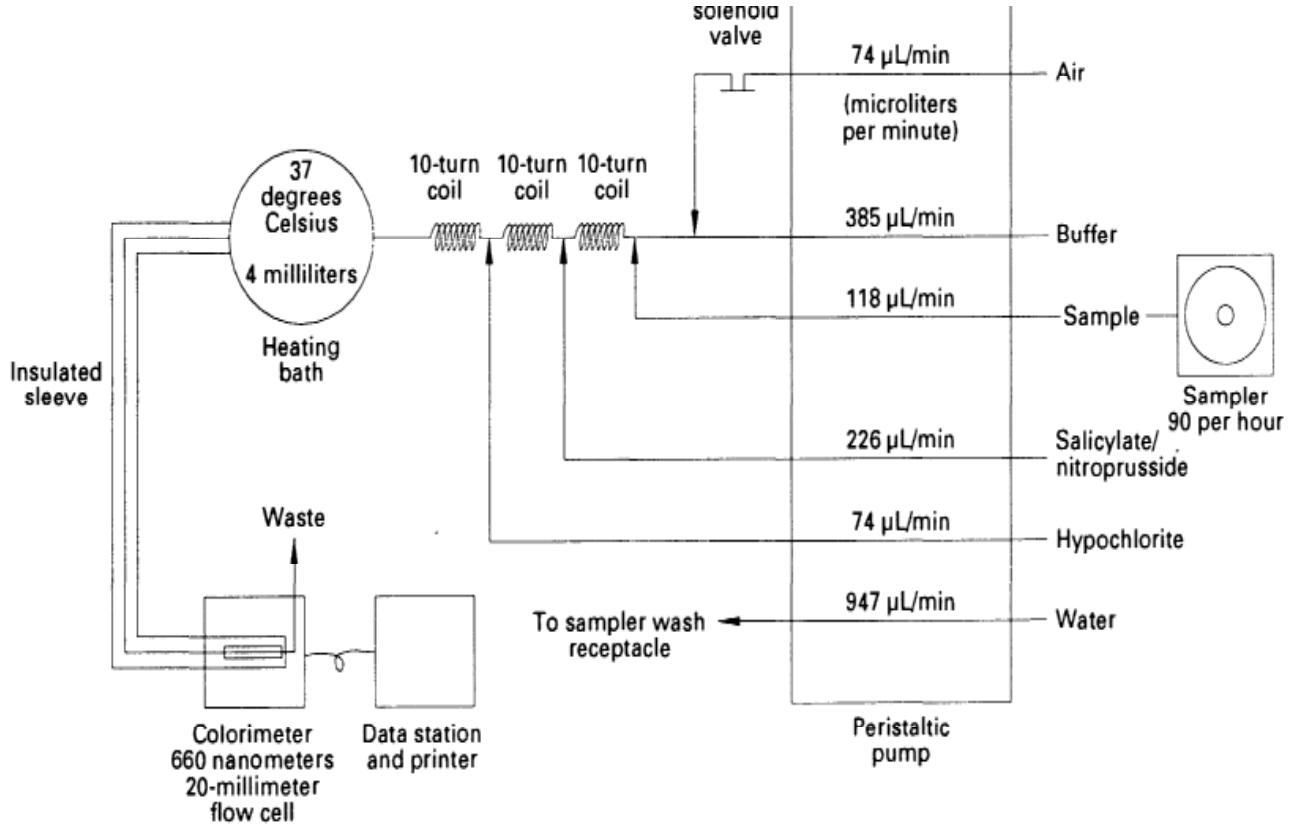


Figure 4.—Nitrogen, ammonia, salicylate-hypochlorite manifold.

NOTE 2. For analysis of bottom materials, use blank and working solutions as prepared in paragraph 5.2.1. For analysis of water, use blank and working solutions as prepared in paragraph 5.2.2.

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

6.8 Begin analysis.

## 7. Calculations

7.1 Prepare an analytical curve by plotting the voltage of each working solution peak in relation to its respective ammonia-nitrogen concentration, or by using the RFA Softpak data reduction package. See operation manuals for complete details (Alpkem Corp., 1986).

7.2 Compute the concentration of dissolved ammonia-nitrogen in each sample by comparing its voltage to the analytical curve or by using the software. Any baseline drift needs to be accounted for when computing the voltage of a sample or standard peak; the RFA software automatically corrects for baseline drift.

7.3 Compute the concentration of ammonia-nitrogen in each sample of bottom material, as follows:

$$\text{NH}_3\text{-N (mg/kg)} = \frac{C_N \times 200 \text{ (NOTE 4)}}{\text{wt of sample, in g}}$$

where CN = $NH_3$-N concentration in sample, in milligrams per liter.
NOTE 4. The factor 200 is used in converting to milligrams per kilogram.

## 8. Report

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

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

## 9. Precision

Single operator precision for ammonia-nitrogen, as determined for natural-water samples, expressed as standard deviation and percentage relative standard deviation, is as follows:

| Number of determinations | Mean (mg/L) | Standard deviation (mg/L) | Relative standard deviation (percent) |
|---|---|---|---|
| 180 | 1.23 | 0.011 | 0.89 |
| 193 | .17 | .001 | .59 |
| 147 | .28 | .004 | 1.4 |
| 252 | .71 | .005 | .70 |
| 240 | .54 | .006 | 1.1 |
| 209 | .06 | .001 | 1.7 |
| 240 | .12 | .002 | 1.7 |

## References


Alpkem Corp., 1986, Rapid flow analyzer operator's manual, ALPKEM, methodology section.

Harfmann, R.G., and Crouch, S.R., 1989, Kinetic study of Berthelot reaction steps in the absence and presence of coupling reagents: Talanta, v. 36, p. 261-269.

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

Patton, C.J., and Crouch, S.R., 1977, Spectrophotometric and kinetics investigation of the Berthelot reaction for the determination of ammonia: Analytical Chemistry, v. 49, p. 464-469.

Reardon, J., Foreman, J.A., and Searcy, R.L., 1966, New reactants for the colorimetric determination of ammonia: Clinical Chimica Acta, v. 14, p. 403-405.