Nitrogen, ammonia, low ionic-strength water, colorimetry,
salicylate-hypochlorite, automated-segmented flow

Parameter and Code:
Nitrogen, ammonia, dissolved, I-2525-89 (mg/L as N): 00608

1. Application

This method is used to analyze samples of precipitation and natural water containing from 0.002 to 0.30 mg/L of ammonia-nitrogen. Concentrations greater than 0.30 mg/L must be diluted. This method was implemented in the National Water Quality Laboratory in March 1986 and modified in May 1989.

2. Summary of method

Ammonia reacts with hypochlorite and salicylate ions in the presence of ferricyanide ions to form the salicylic acid analog of indophenol (Reardon and others, 1966; Patton and Crouch, 1977; Harfmann and Crouch, 1989).

3. Interferences

3.1 No substance found in natural water seems to interfere with this method.

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

4.2 With this equipment, the following operating conditions are satisfactory for the range from 0.002 to 0.30 mg/L of ammonia-nitrogen:

Flow cell ..... ……20 mm
Wavelength . .....…...660 nm
Sample time . ……..….24 seconds
Wash time ... . ……...32 seconds
Sampling rate ……64 per hour
Heating bath (4 mL) …. 37°C
Pecking ..... ……OFF
Damp (RC) .... ……1 second

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 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.

5.3 *Ammonia working solutions*: Prepare an ammonia-free blank, 200 mL each of a series of ammonia working solutions by dilution of ammonia standard solution II or ammonia working solution No. 3 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	40	Standard solution II	0.3000
2	20	Standard solution II	0.1500
3	10	Standard solution II	0.0750
4	02	Standard solution II	0.0150
5	20	Working solution No. 3	0.0075
6	08	Working solution No. 3	0.0030
7	04	Working solution No. 3	0.0015

Prepare fresh weekly and refrigerate.

5.4 *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.

5.5 *Buffer working solution*: Add, with stirring, 250 mL stock potassium sodium tartrate solution to 200 mL buffer stock 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. Filter and degas for at least 30 minutes.

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 1L.

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

5.8 *Sodium hypochlorite solution*: Dilute 25 mL sodium hypochlorite solution (a commercial bleach solution containing 5.25-percent available chlorine is satisfactory) to 100 mL with ammonia-free water. Prepare fresh daily.

5.9 *Sodium salicylate-sodium nitroferricyanide solution*: Dissolve 83 g sodium salicylate and 0.17 g sodium nitroferricyanide $[Na_2Fe(CN)_2NO \cdot 2H_2O]$ in about 300 mL ammonia-free water. Filter through Whatman 41 filter paper or equivalent, and dilute to I L. Add 2.0 mL Brij-35 solution, degas for at least 30 minutes, and store in a light-resistant container.

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

5.11 *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 Set up manifold (fig. 1). If the laboratory air is contaminated with ammonia, it needs to be passed through a scrubber containing 2.5*M* H_2SO_4 before it enters the air-manifold tube.

6.2 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.

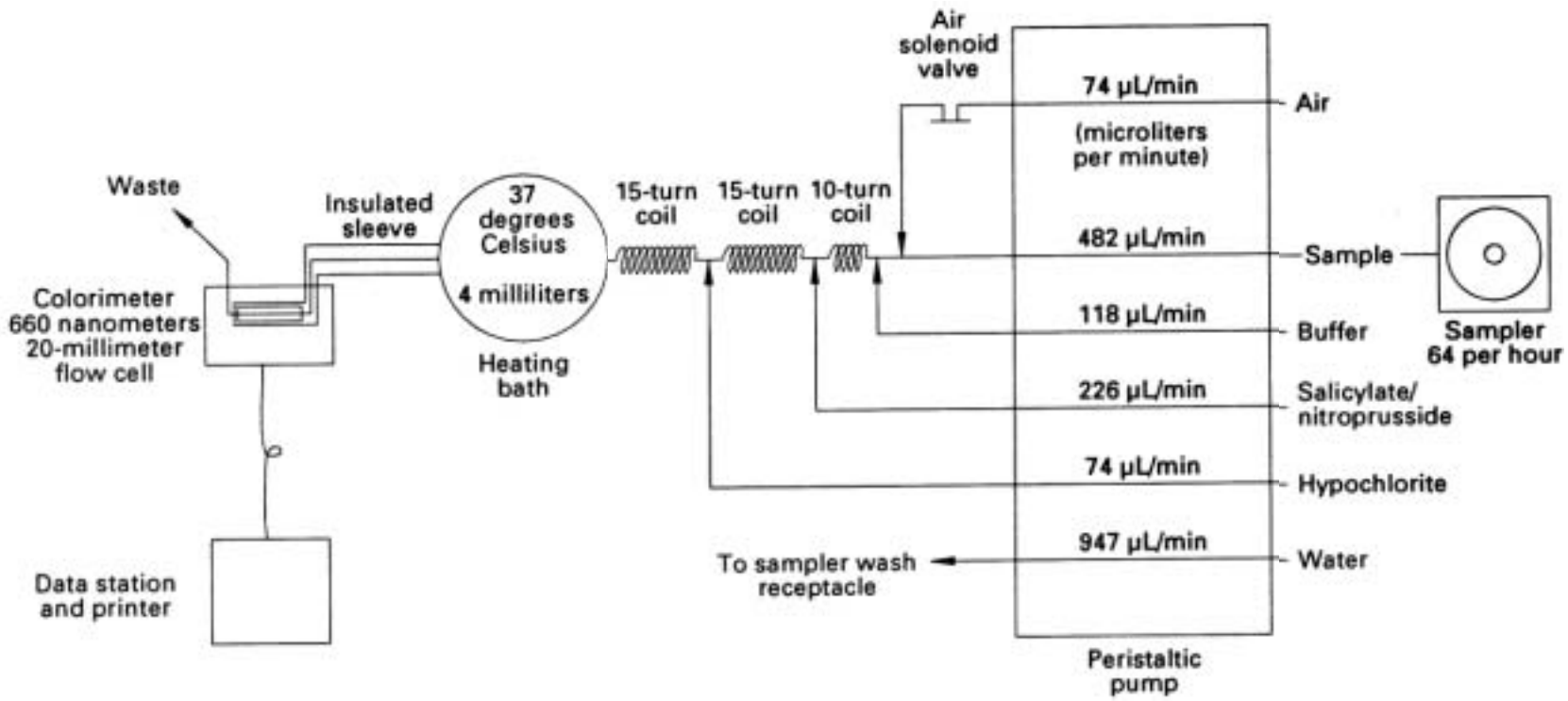

Figure 1. - Nitrogen, ammonia, low ionic-strength water, salicylate-hypochlorite manifold.

6.3 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 or remake them, and start again using the aforementioned procedure.

6.4 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.

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

6.6 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 (NOTE 2). Place individual working solutions of differing concentrations in approximately every eighth position on the tray following the accepted protocol. Fill the remainder of each tray with unknown samples.

NOTE 2. 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.

6.7 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 Softpac 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 working solution peak; the RFA software automatically corrects for baseline drift.

8. Report

Report concentrations of ammonia-nitrogen, dissolved (00608), as follows: less than 0.10 mg/L, three decimals; 0.10 mg/L 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)
22	0.030	0.004	14.0
22	0.168	0.004	2.3
34	0.197	0.005	2.4

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.

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.