Nitrogen, nitrite plus nitrate, low ionic-strength water, colorimetry, cadmium reduction-diazotization, automated-segmented flow

Parameter and Code:
Nitrogen, nitrite plus nitrate, dissolved, I-2546-91
(mg/L as N): 00631

1. Application

This method is used to analyze samples of precipitation or natural water, containing from 0.005 to 1.0 mg/L of nitrite- plus nitrate-nitrogen. Concentrations greater than 1.0 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

Nitrate is reduced to nitrite by cadmium metal. The sample stream then is treated with sulfanilamide under acidic conditions to yield a diazo compound, which couples with N-1-naphthylethylenediamine dihydrochloride to form an azo dye, the absorbance of which is measured colorimetrically. The result is the sum of the nitrite originally present plus that formed by the reduction of the nitrate (Morris and Riley, 1963; Brewer and Riley, 1965; Wood and others, 1967; Strickland and Parsons, 1972; Nydahl, 1976; Sherwood and Johnson, 1981; Patton, 1982; U.S. Environmental Protection Agency, 1983).

3. Interferences

3.1 Concentrations of potentially interfering substances generally are negligible in unpolluted surface and ground water. For specific details of inorganic and organic compounds that interfere, see Norwitz and Keliher (1985, 1986) as well as more general information from the American Society for Testing and Materials (1991).

3.2 Sulfides, often present in anoxic water, rapidly deactivate cadmium reactors by forming an insoluble layer of cadmium sulfide on the active metal surface (Strickland and Parsons, 1972).

3.3 The buffer capacity of the imidazole solution and the approximate 10:1 volume ratio of buffer to sample eliminate the possibility of erroneous results for moderately acidic (pH >_ 1) samples.

4. Apparatus

4.1 *Alpkem rapid flow analyzer (RFA),* consisting of sampler, peristaltic pump, analytical cartridge (including copper-cadmium reduction column), colorimeter, data station, and printer.

4.2 With this equipment, the following operating conditions are satisfactory for the range from 0.005 to 1.0 mg/L (NO_2 + NO_3) as N:

Flow cell	10 mm
Wavelength	540 nm
Sample time	24 seconds
Sampling rate	64 per hour
Wash time	32 seconds
Pecking	OFF
Damp (RC)	l second

5. Reagents

5.1 *Brij-35 solution,* 30-percent aqueous solution.

5.2 *Cadmium powder,* 100 mesh: Weigh 10 g cadmium powder into a 50-mL Griffin beaker and wash with 1*M* HCl. Stir vigorously to break clumps of cadmium formed by the addition of HC1. Rinse with copper sulfate solution (20 g/L). Wash thoroughly with imidazole solution to remove colloidal copper which is visible as a blue color in the wash solution. A minimum of five washings usually is required to eliminate perceptible blue color. Store in imidazole solution.

5.3 *Cadmium reduction column:* The reduction column is 4 cm long, 1/8-in. OD standard Teflon tubing (about 3.0-mm OD x 1.5-mm ID). Plugs to retain the cadmium in the column are cut from a sheet of hydrophilic, porous plastic with an average pore size of 40 gm. The cadmium column is plugged at the bottom with a plastic frit and attached to a syringe filled with imidazole solution. A custom-made funnel is attached to the top of the cadmium column, and the column and part of the funnel are filled with imidazole solution. The cadmium is added slowly to prevent air bubbles and pockets. Decant the solution in the funnel to facilitate the insertion of the top frit without introducing air to the column. The reduction efficiency of the column needs to 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 to less than 90 percent.

5.4 *Color reagent:* Add 200 mL concentrated phosphoric acid (sp gr 1.69) and 20 g sulfanilamide to about 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 mL Brij-35 solution. Store in an amber bottle and refrigerate. This reagent is stable for about 1 month.

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

5.6 *Hydrochloric acid,* 1*M*: Add 83 mL concentrated HCl (sp gr 1.19) to demineralized water and dilute to 1 L.

5.7 *Imidazole solution:* Dissolve 6.8 g of imidazole in demineralized water. Stir and dilute to about 950 mL. Adjust pH to 7.5 ± 0.1 with concentrated HCl (about 4 mL). Add 0.5 mL copper sulfate solution and dilute to 1 L. Add 1 mL Brij-35 solution.

5.8 *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 L.

5.9 *Nitrate-nitrogen standard solution II*, 1.00 mL = 0.005 mg NO_3-N: Dilute 10.0 mL nitrate-nitrogen standard solution I to 1,000 mL with demineralized water.

5.10 *Nitrate-nitrogen working solutions:* Prepare a blank and 200 mL of a series of working solutions by appropriate dilution of nitrate-nitrogen standard solution II or working solution No. 3 as listed in the following table. If the samples to be analyzed are preserved, the nitrate-nitrogen working solutions need to contain an equivalent concentration of the same preservative.

Working solution No.	Solution added mL	Solution used	Nitrate nitrogen concentration (mg/L)
1	40	Standard solution II	1.000
2	20	Standard solution II	.500
3	10	Standard solution II	.250
4	2	Standard solution II	.050
5	20	Working solution No. 3	.025
6	8	Working solution No. 3	.010
7	4	Working solution No. 3	.005

6. Procedure

6.1 Set up manifold (fig. 1).

6.2 Allow colorimeter recorder to warm for at least 10 minutes.

6.3 Allow the color reagent to come to room temperature.

6.4 Begin pumping reagents but do not connect the reduction column to the analytical cartridge until all air has been removed from the reagent and sample tubes (NOTE 1).

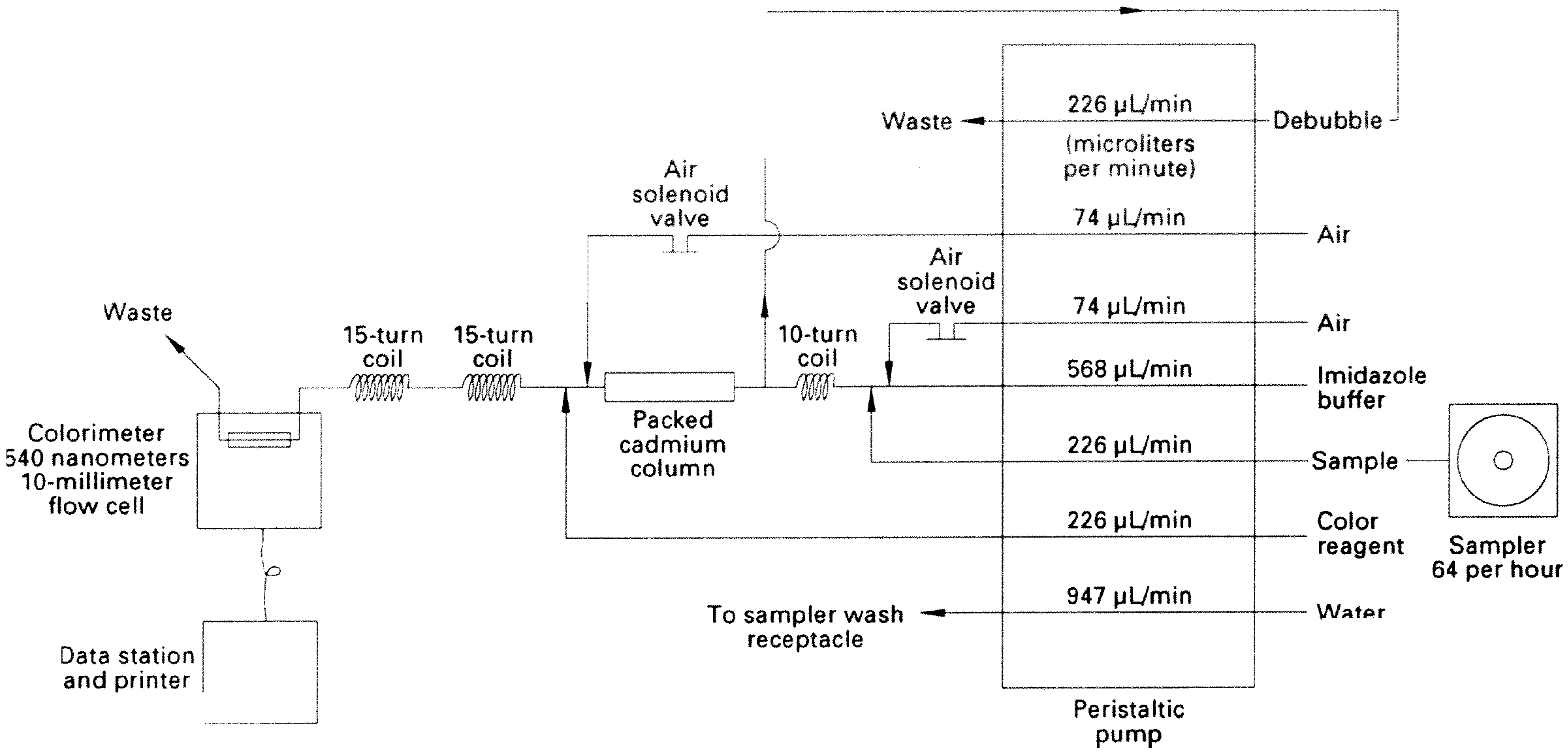
NOTE 1. It is important to avoid introduction of air bubbles into the reduction column because they adversely affect sample contact with the cadmium powder and decrease the reduction efficiency. Column needs to be replaced if air bubbles are introduced.

6.5 After all reagents are on line, 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).

6.6 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.

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

Figure 1.-Nitrogen, nitrite plus nitrate, tow ionic-strength water, cadmium reduction-diazotization manifold.



6.8 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. Place individual working solutions of differing concentrations in about every eighth position on the tray following the accepted protocol. Fill the remainder of each tray with unknown samples.

6.9 Begin analysis.

7. Calculations

7.1 Prepare an analytical curve by plotting the voltage of each working solution peak in relation to its respective nitrite- plus nitrate-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 nitrite- plus nitrate-nitrogen in milligrams per liter in each sample either 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 nitrogen, nitrite plus nitrate, dissolved (00631), as follows: 0.005 to 0.10 mg/L, three decimals; 0.10 mg/L and greater, two significant figures.

9. Precision

Single operator precision for nitrite- plus nitrate-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)
11	0.009	0.001	11.1
21	.105	.006	5.7
22	.465	.015	3.2
22	.717	.011	1.5

References

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