

Standard Methods for the Examination of Water and Wastewater

1.04 mg $\text{NO}_3^- + \text{NO}_2^-$ -N/L, the standard deviations were ± 0.005 , ± 0.004 , ± 0.005 , and ± 0.01 , respectively. In a single laboratory using wastewater samples at concentrations of 0.24, 0.55, and 1.05 mg $\text{NO}_3^- + \text{NO}_2^-$ -N/L, the recoveries were 100%, 102%, and 100%, respectively.¹

7. Reference

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1979. Methods for Chemical Analysis of Water and Wastes. Method 353. 3. U.S. Environmental Protection Agency, Washington, D.C.

8. Bibliography

- BOLTZ, D.F., ed. 1958. Colorimetric Determination of Nonmetals. Interscience Publishers, New York, N.Y.
- NYDAHL, F. 1976. On the optimum conditions for the reduction of nitrate by cadmium. *Talanta* 23:349.

4500- NO_2^- C. (Reserved)

4500- NO_3^- NITROGEN (NITRATE)*#(60)

4500- NO_3^- A. Introduction

1. Selection of Method

Determination of nitrate (NO_3^-) is difficult because of the relatively complex procedures required, the high probability that interfering constituents will be present, and the limited concentration ranges of the various techniques.

An ultraviolet (UV) technique (Method B) that measures the absorbance of NO_3^- at 220 nm is suitable for screening uncontaminated water (low in organic matter).

Screen a sample; if necessary, then select a method suitable for its concentration range and probable interferences. Nitrate may be determined by ion chromatography (Section 4110) or capillary ion electrophoresis (Section 4140). Applicable ranges for other methods are: nitrate electrode method (D), 0.14 to 1400 mg NO_3^- -N/L; cadmium reduction method (E), 0.01 to 1.0 mg NO_3^- -N/L; automated cadmium reduction methods (F and I), 0.001 to 10 mg NO_3^- -N/L. For higher NO_3^- -N concentrations, dilute into the range of the selected method.

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Colorimetric methods (B, E) require an optically clear sample. Filter turbid sample through 0.45- μm -pore-diam membrane filter. Test filters for nitrate contamination.

2. Storage of Samples

Start NO_3^- determinations promptly after sampling. If storage is necessary, store for up to 2 d at 4°C; disinfected samples are stable much longer without acid preservation. For longer storage of unchlorinated samples, preserve with 2 mL conc $\text{H}_2\text{SO}_4/\text{L}$ and store at 4°C. NOTE: When sample is preserved with acid, NO_3^- and NO_2^- cannot be determined as individual species.

4500- NO_3^- B. Ultraviolet Spectrophotometric Screening Method

1. General Discussion

a. Principle: Use this technique only for screening samples that have low organic matter contents, i.e., uncontaminated natural waters and potable water supplies. The NO_3^- calibration curve follows Beer's law up to 11 mg N/L.

Measurement of UV absorption at 220 nm enables rapid determination of NO_3^- . Because dissolved organic matter also may absorb at 220 nm and NO_3^- does not absorb at 275 nm, a second measurement made at 275 nm may be used to correct the NO_3^- value. The extent of this empirical correction is related to the nature and concentration of organic matter and may vary from one water to another. Consequently, this method is not recommended if a significant correction for organic matter absorbance is required, although it may be useful in monitoring NO_3^- levels within a water body with a constant type of organic matter. Correction factors for organic matter absorbance can be established by the method of additions in combination with analysis of the original NO_3^- content by another method. Sample filtration is intended to remove possible interference from suspended particles. Acidification with 1N HCl is designed to prevent interference from hydroxide or carbonate concentrations up to 1000 mg CaCO_3/L . Chloride has no effect on the determination.

b. Interference: Dissolved organic matter, surfactants, NO_2^- , and Cr^{6+} interfere. Various inorganic ions not normally found in natural water, such as chlorite and chlorate, may interfere. Inorganic substances can be compensated for by independent analysis of their concentrations and preparation of individual correction curves. For turbid samples, see ¶ A.1.

2. Apparatus

Spectrophotometer, for use at 220 nm and 275 nm with matched silica cells of 1-cm or longer light path.

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3. Reagents

a. *Nitrate-free water*: Use redistilled or distilled, deionized water of highest purity to prepare all solutions and dilutions.

b. *Stock nitrate solution*: Dry potassium nitrate (KNO_3) in an oven at 105°C for 24 h. Dissolve 0.7218 g in water and dilute to 1000 mL; $1.00\text{ mL} = 100\ \mu\text{g NO}_3^- \text{-N}$. Preserve with 2 mL CHCl_3/L . This solution is stable for at least 6 months.

c. *Intermediate nitrate solution*: Dilute 100 mL stock nitrate solution to 1000 mL with water; $1.00\text{ mL} = 10.0\ \mu\text{g NO}_3^- \text{-N}$. Preserve with 2 mL CHCl_3/L . This solution is stable for 6 months.

d. *Hydrochloric acid solution*, HCl, 1N.

4. Procedure

a. *Treatment of sample*: To 50 mL clear sample, filtered if necessary, add 1 mL HCl solution and mix thoroughly.

b. *Preparation of standard curve*: Prepare NO_3^- calibration standards in the range 0 to 7 mg $\text{NO}_3^- \text{-N/L}$ by diluting to 50 mL the following volumes of intermediate nitrate solution: 0, 1.00, 2.00, 4.00, 7.00 . . . 35.0 mL. Treat NO_3^- standards in same manner as samples.

c. *Spectrophotometric measurement*: Read absorbance or transmittance against redistilled water set at zero absorbance or 100% transmittance. Use a wavelength of 220 nm to obtain NO_3^- reading and a wavelength of 275 nm to determine interference due to dissolved organic matter.

5. Calculation

For samples and standards, subtract two times the absorbance reading at 275 nm from the reading at 220 nm to obtain absorbance due to NO_3^- . Construct a standard curve by plotting absorbance due to NO_3^- against $\text{NO}_3^- \text{-N}$ concentration of standard. Using corrected sample absorbances, obtain sample concentrations directly from standard curve. NOTE: If correction value is more than 10% of the reading at 220 nm, do not use this method.

6. Bibliography

HOATHER, R.C. & R.F. RACKMAN. 1959. Oxidized nitrogen and sewage effluents observed by ultraviolet spectrophotometry. *Analyst* 84:549. GOLDMAN, E. & R. JACOBS. 1961.

Determination of nitrates by ultraviolet absorption. *J. Amer. Water Works Assoc.* 53:187.

ARMSTRONG, F.A.J. 1963. Determination of nitrate in water by ultraviolet spectrophotometry. *Anal. Chem.* 35:1292.

NAVONE, R. 1964. Proposed method for nitrate in potable waters. *J. Amer. Water Works Assoc.* 56:781.