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STANDARD METHODS

FOR THE EXAMINATION OF WATER AND WASTEWATER

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4500-NO₃⁻ NITROGEN (NITRATE)*4500-NO₃⁻ A. Introduction

1. Selection of Method

Determination of nitrate (NO₃⁻) 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 NO₃⁻ 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 (C). Applicable ranges for other methods are: nitrate electrode method (D), 0.14 to 1400 mg NO₃⁻-N/L; cadmium reduction method (E), 0.01 to 1.0

mg NO₃⁻-N/L; titanous chloride method (G), 0.01 to 10 mg NO₃⁻-N/L; hydrazine reduction method (H), 0.01 to 10 mg NO₃⁻-N/L; automated cadmium reduction method (F), 0.5 to 10 mg NO₃⁻-N/L. For higher NO₃⁻-N concentrations, dilute into the range of the selected method.

Colorimetric methods require an optically clear sample. Filter turbid sample through 0.45- μ m-pore-diam membrane filter. Test filters for nitrate contamination.

2. Storage of Samples

Start NO₃⁻ determinations promptly after sampling. If storage is necessary, store for up to 24 h at 4°C; for longer storage, preserve with 2 mL conc H₂SO₄/L and store at 4°C. NOTE: When sample is preserved with acid, NO₃⁻ and NO₂⁻ cannot be determined as individual species.

* Approved by Standard Methods Committee, 1988.

4500-NO₃⁻ 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 NO₃⁻ calibration curve follows Beer's law up to 11 mg N/L.

Measurement of UV absorption at 220 nm enables rapid determination of NO₃⁻. Because dissolved organic matter also may absorb at 220 nm and NO₃⁻ does not absorb at 275 nm, a second measurement made at 275 nm may be used to correct the NO₃⁻ 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.

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 mL = 100 μg NO_3^- -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 mL = 10.0 μg NO_3^- -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 NO_3^- -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 NO_3^- -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

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4500- NO_3^- C. Ion Chromatographic Method

See Section 4110.

4500- NO_3^- D. Nitrate Electrode Method

1. General Discussion

a. Principle: The NO_3^- ion electrode is a selective sensor that develops a potential across a thin, porous, inert membrane that holds in place a water-immiscible liquid ion exchanger. The electrode responds to NO_3^- ion activity between about 10^{-5} and 10^{-1} M (0.14 to 1400 mg NO_3^- -N/L). The lower limit of detection is determined by the small but finite solubility of the liquid ion exchanger.

b. Interferences: Chloride and bicarbonate ions interfere when their weight ratios to NO_3^- -N are >10 or >5, respectively. Ions that are potential interferences but do not normally occur at

significant levels in potable waters are NO_2^- , CN^- , S^{2-} , Br^- , I^- , ClO_3^- , and ClO_4^- . Although the electrodes function satisfactorily in buffers over the range pH 3 to 9, erratic responses have been noted where pH is not held constant. Because the electrode responds to NO_3^- activity rather than concentration, ionic strength must be constant in all samples and standards. Minimize these problems by using a buffer solution containing Ag_2SO_4 to remove Cl^- , Br^- , I^- , S^{2-} , and CN^- , sulfamic acid to remove NO_2^- , a buffer at pH 3 to eliminate HCO_3^- and to maintain a constant pH and ionic strength, and $\text{Al}_2(\text{SO}_4)_3$ to complex organic acids.

2. Apparatus

- pH meter, expanded-scale or digital*, capable of 0.1 mV resolution.
- Double-junction reference electrode*.^{*} Fill outer chamber with (NH₄)₂SO₄ solution.
- Nitrate ion electrode*.[†] Carefully follow manufacturer's instructions regarding care and storage.
- Magnetic stirrer*: TFE-coated stirring bar.

3. Reagents

- Nitrate-free water*: Prepare as described in ¶ B.3a. Use for all solutions and dilutions.
- Stock nitrate solution*: Prepare as described in ¶ B.3b.
- Standard nitrate solutions*: Dilute 1.0, 10, and 50 mL stock nitrate solution to 100 mL with water to obtain standard solutions of 1.0, 10, and 50 mg NO₃⁻-N/L, respectively.
- Buffer solution*: Dissolve 17.32 g Al₂(SO₄)₃·18H₂O, 3.43 g Ag₂SO₄, 1.28 g H₃BO₃, and 2.52 g sulfamic acid (H₂NSO₃H), in about 800 mL water. Adjust to pH 3.0 by slowly adding 0.10N NaOH. Dilute to 1000 mL and store in a dark glass bottle.
- Sodium hydroxide*, NaOH, 0.1N.
- Reference electrode filling solution*: Dissolve 0.53 g (NH₄)₂SO₄ in water and dilute to 100 mL.

4. Procedure

- Preparation of calibration curve*: Transfer 10 mL of 1 mg NO₃⁻-N/L standard to a 50-mL beaker, add 10 mL buffer, and stir with a magnetic stirrer. Immerse tips of electrodes and record millivolt reading when stable (after about 1 min). Remove elec-

^{*} Orion Model 90-02, or equivalent.

[†] Orion Model 93-07, Corning Model 476134, or equivalent.

trodes, rinse, and blot dry. Repeat for 10-mg NO₃⁻-N/L and 50-mg NO₃⁻-N/L standards. Plot potential measurements against NO₃⁻-N concentration on semilogarithmic graph paper, with NO₃⁻-N concentration on the logarithmic axis (abscissa) and potential (in millivolts) on the linear axis (ordinate). A straight line with a slope of +57 ± 3 mV/decade at 25°C should result. Recalibrate electrodes several times daily by checking potential reading of the 10 mg NO₃⁻-N standard and adjusting the calibration control until the reading plotted on the calibration curve is displayed again.

- Measurement of sample*: Transfer 10 mL sample to a 50-mL beaker, add 10 mL buffer solution, and stir (for about 1 min) with a magnetic stirrer. Measure standards and samples at about the same temperature. Immerse electrode tips in sample and record potential reading when stable (after about 1 min). Read concentration from calibration curve.

5. Precision

Over the range of the method, precision of ±0.4 mV, corresponding to 2.5% in concentration, is expected.

6. Bibliography

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4500-NO₃⁻ E. Cadmium Reduction Method

1. General Discussion

- Principle*: NO₃⁻ is reduced almost quantitatively to nitrite (NO₂⁻) in the presence of cadmium (Cd). This method uses commercially available Cd granules treated with copper sulfate (CuSO₄) and packed in a glass column.

The NO₂⁻ produced thus is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye that is measured colorimetrically. A correction may be made for any NO₂⁻ present in the sample by analyzing without the reduction step. The applicable range of this method is 0.01 to 1.0 mg NO₃⁻-N/L. The method is recommended especially for NO₃⁻ levels below 0.1 mg N/L where other methods lack adequate sensitivity.

- Interferences*: Suspended matter in the column will restrict sample flow. For turbid samples, see ¶ A.1. Concentrations of iron, copper, or other metals above several milligrams per liter lower reduction efficiency. Add EDTA to samples to eliminate

this interference. Oil and grease will coat the Cd surface. Remove by pre-extraction with an organic solvent (see Section 5520). Residual chlorine can interfere by oxidizing the Cd column, reducing its efficiency. Check samples for residual chlorine (see DPD methods in Section 4500-Cl). Remove residual chlorine by adding sodium thiosulfate (Na₂S₂O₃) solution [Section 4500-NH₃.B.3d1]. Sample color that absorbs at about 540 nm interferes.

2. Apparatus

- Reduction column*: Purchase or construct the column^{*} (Figure 4500-NO₃⁻:1) from a 100-mL volumetric pipet by removing the top portion. The column also can be constructed from two pieces of tubing joined end to end: join a 10-cm length of 3-cm-

^{*} Tudor Scientific Glass Co., 555 Edgefield Road, Belvedere, S.C. 29841, Cat. TP-1730, or equivalent.

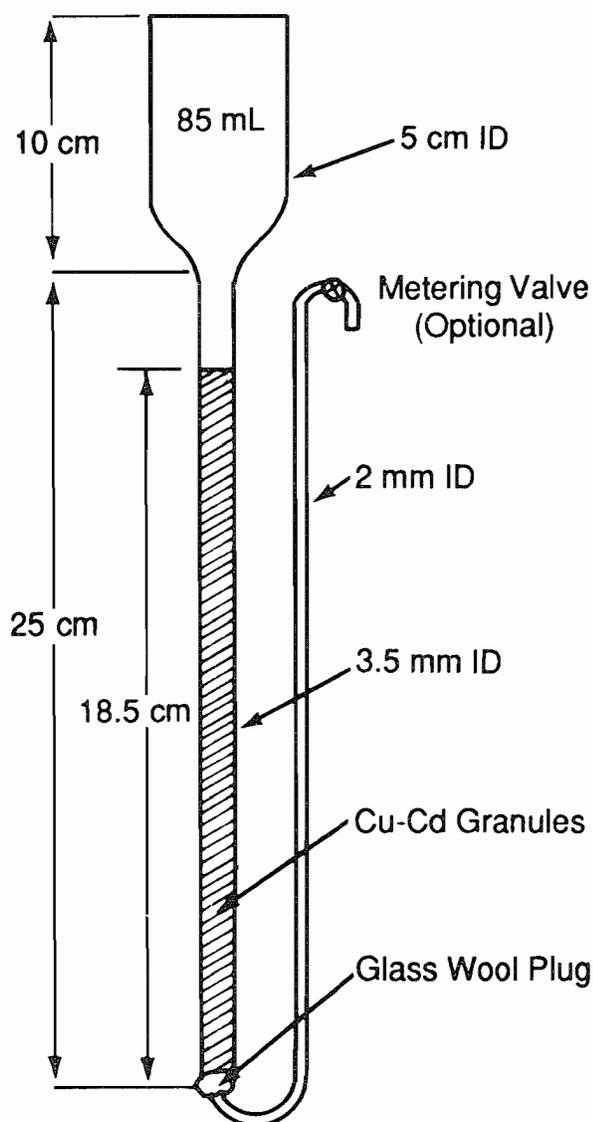


Figure 4500-NO₃⁻:1. Reduction column.

ID tubing to a 25-cm length of 3.5-mm-ID tubing. Add a TFE stopcock with metering valve¹ to control flow rate.

b. *Colorimetric equipment:* One of the following is required:

1) *Spectrophotometer*, for use at 543 nm, providing a light path of 1 cm or longer.

2) *Filter photometer*, with light path of 1 cm or longer and equipped with a filter having maximum transmittance near 540 nm.

3. Reagents

a. *Nitrate-free water:* See ¶ B.3a. The absorbance of a reagent blank prepared with this water should not exceed 0.01. Use for all solutions and dilutions.

b. *Copper-cadmium granules:* Wash 25 g new or used 40- to 60-mesh Cd granules† with 6N HCl and rinse with water. Swirl

Cd with 100 mL 2% CuSO₄ solution for 5 min or until blue color partially fades. Decant and repeat with fresh CuSO₄ until a brown colloidal precipitate begins to develop. Gently flush with water to remove all precipitated Cu.

c. *Color reagent:* Prepare as directed in Section 4500-NO₂⁻.B.3b.

d. *Ammonium chloride-EDTA solution:* Dissolve 13 g NH₄Cl and 1.7 g disodium ethylenediamine tetraacetate in 900 mL water. Adjust to pH 8.5 with conc NH₄OH and dilute to 1 L.

e. *Dilute ammonium chloride-EDTA solution:* Dilute 300 mL NH₄Cl-EDTA solution to 500 mL with water.

f. *Hydrochloric acid, HCl, 6N.*

g. *Copper sulfate solution, 2%:* Dissolve 20 g CuSO₄·5H₂O in 500 mL water and dilute to 1 L.

h. *Stock nitrate solution:* Prepare as directed in ¶ B.3b.

i. *Intermediate nitrate solution:* Prepare as directed in ¶ B.3c.

j. *Stock nitrite solution:* See Section 4500-NO₂⁻.B.3e.

k. *Intermediate nitrite solution:* See Section 4500-NO₂⁻.B.3f.

l. *Working nitrite solution:* Dilute 50.0 mL intermediate nitrite solution to 500 mL with nitrite-free water; 1.00 mL = 5 µg NO₂⁻-N.

4. Procedure

a. *Preparation of reduction column:* Insert a glass wool plug into bottom of reduction column and fill with water. Add sufficient Cu-Cd granules to produce a column 18.5 cm long. Maintain water level above Cu-Cd granules to prevent entrapment of air. Wash column with 200 mL dilute NH₄Cl-EDTA solution. Activate column by passing through it, at 7 to 10 mL/min, at least 100 mL of a solution composed of 25% 1.0 mg NO₃⁻-N/L standard and 75% NH₄Cl-EDTA solution.

b. *Treatment of sample:*

1) *Turbidity removal*—For turbid samples, see ¶ A.1.

2) *pH adjustment*—Adjust pH to between 7 and 9, as necessary, using a pH meter and dilute HCl or NaOH. This insures a pH of 8.5 after adding NH₄Cl-EDTA solution.

3) *Sample reduction*—To 25.0 mL sample or a portion diluted to 25.0 mL, add 75 mL NH₄Cl-EDTA solution and mix. Pour mixed sample into column and collect at a rate of 7 to 10 mL/min. Discard first 25 mL. Collect the rest in original sample flask. There is no need to wash columns between samples, but if columns are not to be reused for several hours or longer, pour 50 mL dilute NH₄Cl-EDTA solution on to the top and let it pass through the system. Store Cu-Cd column in this solution and never let it dry.

4) *Color development and measurement*—As soon as possible, and not more than 15 min after reduction, add 2.0 mL color reagent to 50 mL sample and mix. Between 10 min and 2 h afterward, measure absorbance at 543 nm against a distilled water-reagent blank. NOTE: If NO₃⁻ concentration exceeds the standard curve range (about 1 mg N/L), use remainder of reduced sample to make an appropriate dilution and analyze again.

c. *Standards:* Using the intermediate NO₃⁻-N solution, prepare standards in the range 0.05 to 1.0 mg NO₃⁻-N/L by diluting the following volumes to 100 mL in volumetric flasks: 0.5, 1.0, 2.0, 5.0, and 10.0 mL. Carry out reduction of standards exactly as described for samples. Compare at least one NO₂⁻ standard to a reduced NO₃⁻ standard at the same concentration to verify reduction column efficiency. Reactivate Cu-Cd granules as described in ¶ 3b above when efficiency of reduction falls below about 75%.

† EM Laboratories, Inc., 500 Exec. Blvd., Elmsford, N.Y., Cat. 2001, or equivalent.

5. Calculation

Obtain a standard curve by plotting absorbance of standards against NO₃⁻-N concentration. Compute sample concentrations directly from standard curve. Report as milligrams oxidized N per liter (the sum of NO₃⁻-N plus NO₂⁻-N) unless the concentration of NO₂⁻-N is separately determined and subtracted.

6. Precision and Bias

In a single laboratory using wastewater samples at concentrations of 0.04, 0.24, 0.55, and 1.04 mg NO₃⁻ + NO₂⁻-N/L, the standard deviations were ±0.005, ±0.004, ±0.005, and ±0.01, respectively. In a single laboratory using wastewater with additions of 0.24, 0.55, and 1.05 mg NO₃⁻ + NO₂⁻-N/L, the recoveries were 100%, 102%, and 100%, respectively.²

7. References

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4500-NO₃⁻ F. Automated Cadmium Reduction Method

1. General Discussion

a. *Principle:* See ¶ E.1a.

b. *Interferences:* Sample turbidity may interfere. Remove by filtration before analysis. Sample color that absorbs in the photometric range used for analysis also will interfere.

c. *Application:* Nitrate and nitrite, singly or together in potable, surface, and saline waters and domestic and industrial wastewaters, can be determined over a range of 0.5 to 10 mg N/L.

2. Apparatus

Automated analytical equipment: The required continuous-flow analytical instrument* consists of the components shown in Figure 4500-NO₃⁻:2.

3. Reagents

a. *Deionized distilled water:* See ¶ B.3a.

b. *Copper sulfate solution:* Dissolve 20 g CuSO₄·5H₂O in 500 mL water and dilute to 1 L.

c. *Wash solution:* Use water for unpreserved samples. For samples preserved with H₂SO₄, add 2 mL conc H₂SO₄/L wash water.

d. *Copper-cadmium granules:* See ¶ E.3b.

e. *Hydrochloric acid, HCl, conc.*

f. *Ammonium hydroxide, NH₄OH, conc.*

g. *Color reagent:* To approximately 800 mL water, add, while stirring, 100 mL conc H₃PO₄, 40 g sulfanilamide, and 2 g N-(1-naphthyl)-ethylenediamine dihydrochloride. Stir until dissolved and dilute to 1 L. Store in brown bottle and keep in the dark when not in use. This solution is stable for several months.

h. *Ammonium chloride solution:* Dissolve 85 g NH₄Cl in water and dilute to 1 L. Add 0.5 mL polyoxyethylene 23 lauryl ether. †

* AutoAnalyzer™II: Technicon Instrument Corp., Tarrytown, N.Y., or equivalent.

† Brij-35, available from ICI Americas, Inc., Wilmington, Del., or Technicon Instruments Corp., Tarrytown, N.Y., or equivalent.

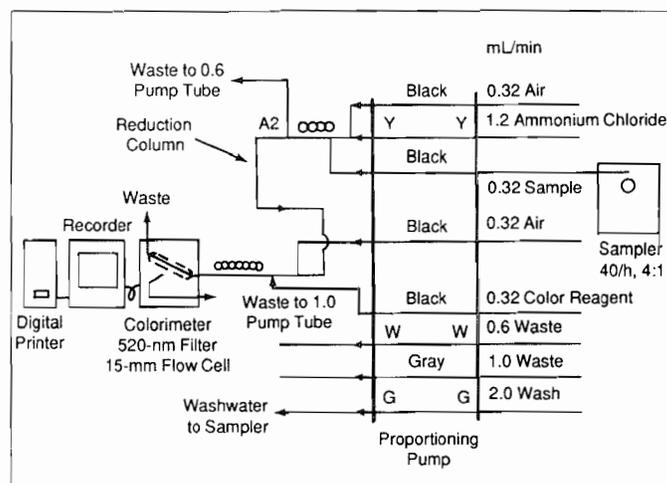


Figure 4500-NO₃⁻:2. Nitrate-nitrite manifold.

i. *Stock nitrate solution:* See ¶ B.3b.

j. *Intermediate nitrate solution:* See ¶ B.3c.

k. *Standard nitrate solutions:* Using intermediate NO₃⁻-N solution and water, prepare standards for calibration curve in appropriate nitrate range. Compare at least one NO₂⁻ standard to a NO₃⁻ standard at the same concentration to verify column reduction efficiency. To examine saline waters prepare standard solutions with the substitute ocean water described in Section 4500-NH₃.H.3g.

l. *Standard nitrite solution:* See 4500-NO₂⁻.B.3g.

4. Procedure

Set up manifold as shown in Figure 4500-NO₃⁻:2 and follow general procedure described by the manufacturer.

If sample pH is below 5 or above 9, adjust to between 5 and 9 with either conc HCl or conc NH₄OH.

5. Calculation

Prepare standard curves by plotting peak heights of standards processed through the manifold against NO_3^- -N concentration in standards. Compute sample NO_3^- -N concentration by comparing sample peak height with standard curve.

6. Precision and Bias

Data obtained in three laboratories with an automated system based on identical chemical principles but having slightly different configurations[‡] are given in the table below. Analyses were conducted on four natural water samples containing exact increments of inorganic nitrate:

Increment as NO_3^- -N $\mu\text{g/L}$	Standard Deviation $\mu\text{g N/L}$	Bias %	Bias $\mu\text{g N/L}$
290	12	+5.75	+17
350	92	+18.10	+63
2310	318	+4.47	+103
2480	176	-2.69	-67

[‡] Automated System I, described in the 16th edition of this publication, Section 418F.

In a single laboratory using surface water samples at concentrations of 100, 200, 800, and 2100 $\mu\text{g N/L}$, the standard deviations were 0, ± 40 , ± 50 , and ± 50 $\mu\text{g/L}$, respectively, and at concentrations of 200 and 2200 $\mu\text{g N/L}$, recoveries were 100 and 96%, respectively.

Precision and bias for the system described herein are believed to be comparable.

7. Bibliography

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4500- NO_3^- G. Titanous Chloride Reduction Method (PROPOSED)

1. General Discussion

a. Principle: NO_3^- is determined potentiometrically using an NH_3 gas-sensing electrode after reduction of the NO_3^- to NH_3 . Reduction is accomplished by use of titanous chloride reagent. The electrode is calibrated with NO_3^- solutions and the concentrations of samples are determined in the same background solution containing sodium hydroxide and titanous chloride.

This method is applicable to the determination of NO_3^- in water containing 0.1 to 20 mg NO_3^- -N/L. The concentration range can be extended by appropriate sample dilution.

b. Interferences: NH_3 and NO_2^- , if present, are measured with NO_3^- . If either concentration is significant, relative to the NO_3^- concentration, measure separately and subtract.

2. Apparatus

- pH meter*, with 0.1 mV resolution, or a specific ion meter.
- NH_3 gas-sensing electrode*^{*}.
- Magnetic stirrer*, with a TFE-coated stirring bar.

3. Reagents

- Titanous chloride reagent solution*, TiCl_3 , practical grade, 20%.
- Sodium hydroxide solution*, NaOH, 10N: Dissolve 400 g reagent-grade NaOH pellets and dilute to 1000 mL with water.

* Orion Model 95-12, or equivalent.

c. Stock nitrate solution: See ¶ B.3b.

d. NH_3 electrode filling solution, NH_4Cl and NaNO_3 : Dissolve 0.535 g NH_4Cl and 8.500 g NaNO_3 and dilute to 100 mL with distilled water. Add 0.3 mL 0.1M AgNO_3 . Solution will be slightly cloudy.

4. Procedure

a. Preparation of calibration curve: Assemble and check NH_3 electrode according to manufacturer's instructions, but use the filling solution prepared in ¶ 3d. By serial dilution of the NO_3^- stock solution, prepare NO_3^- standards at 0.1, 1.0, and 10.0 mg/L. Transfer 100 mL 0.1 mg/L standard into a 150-mL beaker, add a stirring bar, and stir moderately. Add 10 mL 10N NaOH and 2 mL TiCl_3 reagent. Immerse electrode in stirring solution, let potential stabilize, and record the reading in millivolts. Plot as 0.1 mg NO_3^- -N/L and repeat for each remaining standard. Prepare a calibration curve by plotting smoothly, on semilogarithmic graph paper, the potential observed on the linear axis (ordinate) and the NO_3^- -N concentration on the logarithmic axis (abscissa). NOTE: Volume corrections are incorporated into calibration, so that readings can be made directly from the graph.

b. Measurement of samples: Transfer 100 mL sample to a 150-mL beaker, add a stirring bar, and stir moderately. Add 10 mL 10N NaOH and 2 mL TiCl_3 reagent. Immerse electrode in stirring solution, let potential stabilize, and use the voltage to read NO_3^- /L directly from the calibration curve. Rinse electrode with distilled water between samples.

6. Precision and Bias

In a single laboratory using drinking water, surface water, and industrial waste at concentrations of 0.39, 1.15, 1.76, and 4.75 mg NO₃⁻-N/L, the standard deviations were ±0.02, ±0.01, ±0.02, and ±0.03, respectively. In a single laboratory using drinking water at concentrations of 0.75 and 2.97 the recoveries were 99% and 101%.¹

7. Reference

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

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