

Standard Methods for the Examination of Water and Wastewater**4500-NO₂⁻ NITROGEN (NITRITE)*#(1)****4500-NO₂⁻ A. Introduction****1. Occurrence and Significance**

For a discussion of the chemical characteristics, sources, and effects of nitrite nitrogen, see Section 4500-N.

2. Selection of Method

The colorimetric method (B) is suitable for concentrations of 5 to 1000 µg NO₂⁻-N/L (See ¶ B.1a). Nitrite values can be obtained by the automated method given in Section 4500-NO₃⁻.E with the Cu-Cd reduction step omitted. Additionally, nitrite nitrogen can be determined by ion chromatography (Section 4110), and by flow injection analysis (see Section 4130 and Section 4500-NO₃⁻.I).

4500-NO₂⁻ B. Colorimetric Method**1. General Discussion**

a. Principle: Nitrite (NO₂⁻) is determined through formation of a reddish purple azo dye produced at pH 2.0 to 2.5 by coupling diazotized sulfanilamide with *N*-(1-naphthyl)-ethylenediamine dihydrochloride (NED dihydrochloride). The applicable range of the method for spectrophotometric measurements is 10 to 1000 µg NO₂⁻-N/L. Photometric measurements can be made in the range 5 to 50 µg N/L if a 5-cm light path and a green color filter are used. The color system obeys Beer's law up to 180 µg N/L with a 1-cm light path at 543 nm. Higher NO₂⁻ concentrations can be determined by diluting a sample.

b. Interferences: Chemical incompatibility makes it unlikely that NO₂⁻, free chlorine, and nitrogen trichloride (NCl₃) will coexist. NCl₃ imparts a false red color when color reagent is added. The following ions interfere because of precipitation under test conditions and should be absent: Sb³⁺, Au³⁺, Bi³⁺, Fe³⁺, Pb²⁺, Hg²⁺, Ag⁺, chloroplatinate (PtCl₆²⁻), and metavanadate (VO₃²⁻). Cupric ion may cause low results by catalyzing decomposition of the diazonium salt. Colored ions that alter the color system also should be absent. Remove suspended solids by filtration.

c. Storage of sample: Never use acid preservation for samples to be analyzed for NO₂⁻. Make the determination promptly on fresh samples to prevent bacterial conversion of NO₂⁻

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to NO_3^- or NH_3 . For short-term preservation for 1 to 2 d, freeze at -20°C or store at 4°C .

2. Apparatus

Colorimetric equipment: One of the following is required:

- Spectrophotometer*, for use at 543 nm, providing a light path of 1 cm or longer.
- Filter photometer*, providing a light path of 1 cm or longer and equipped with a green filter having maximum transmittance near 540 nm.

3. Reagents

a. Nitrite-free water: If it is not known that the distilled or demineralized water is free from NO_2^- , use either of the following procedures to prepare nitrite-free water:

1) Add to 1 L distilled water one small crystal each of KMnO_4 and either $\text{Ba}(\text{OH})_2$ or $\text{Ca}(\text{OH})_2$. Redistill in an all-borosilicate-glass apparatus and discard the initial 50 mL of distillate. Collect the distillate fraction that is free of permanganate; a red color with DPD reagent (Section 4500-Cl.F.2b) indicates the presence of permanganate.

2) Add 1 mL conc H_2SO_4 and 0.2 mL MnSO_4 solution (36.4 g $\text{MnSO}_4 \cdot \text{H}_2\text{O}/100$ mL distilled water) to each 1 L distilled water, and make pink with 1 to 3 mL KMnO_4 solution (400 mg KMnO_4/L distilled water). Redistill as described in the preceding paragraph.

Use nitrite-free water in making all reagents and dilutions.

b. Color reagent: To 800 mL water add 100 mL 85% phosphoric acid and 10 g sulfanilamide. After dissolving sulfanilamide completely, add 1 g *N*-(1-naphthyl)-ethylenediamine dihydrochloride. Mix to dissolve, then dilute to 1 L with water. Solution is stable for about a month when stored in a dark bottle in refrigerator.

c. Sodium oxalate, 0.025M (0.05N): Dissolve 3.350 g $\text{Na}_2\text{C}_2\text{O}_4$, primary standard grade, in water and dilute to 1000 mL.

d. Ferrous ammonium sulfate, 0.05M (0.05N): Dissolve 19.607 g $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ plus 20 mL conc H_2SO_4 in water and dilute to 1000 mL. Standardize as in Section 5220B.3d.

e. Stock nitrite solution: Commercial reagent-grade NaNO_2 assays at less than 99%. Because NO_2^- is oxidized readily in the presence of moisture, use a fresh bottle of reagent for preparing the stock solution and keep bottles tightly stoppered against the free access of air when not in use. To determine NaNO_2 content, add a known excess of standard 0.01M (0.05N) KMnO_4 solution (see ¶ h below), discharge permanganate color with a known quantity of standard reductant such as 0.025M $\text{Na}_2\text{C}_2\text{O}_4$ or 0.05M $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$, and back-titrate with standard permanganate solution.

1) Preparation of stock solution—Dissolve 1.232 g NaNO_2 in water and dilute to 1000 mL; 1.00 mL = 250 μg N. Preserve with 1 mL CHCl_3 .

2) Standardization of stock nitrite solution—Pipet, in order, 50.00 mL standard 0.01M

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(0.05N) KMnO_4 , 5 mL conc H_2SO_4 , and 50.00 mL stock NO_2^- solution into a glass-stoppered flask or bottle. Submerge pipet tip well below surface of permanganate-acid solution while adding stock NO_2^- solution. Shake gently and warm to 70 to 80°C on a hot plate. Discharge permanganate color by adding sufficient 10-mL portions of standard 0.025M $\text{Na}_2\text{C}_2\text{O}_4$. Titrate excess $\text{Na}_2\text{C}_2\text{O}_4$ with 0.01M (0.05N) KMnO_4 to the faint pink end point. Carry a water blank through the entire procedure and make the necessary corrections in the final calculation as shown in the equation below.

If standard 0.05M ferrous ammonium sulfate solution is substituted for $\text{Na}_2\text{C}_2\text{O}_4$, omit heating and extend reaction period between KMnO_4 and Fe^{2+} to 5 min before making final KMnO_4 titration.

Calculate NO_2^- -N content of stock solution by the following equation:

$$A = \frac{[(B \times C) - (D \times E)] \times 7}{F}$$

where:

A = mg NO_2^- -N/mL in stock NaNO_2 solution,

B = total mL standard KMnO_4 used,

C = normality of standard KMnO_4 ,

D = total mL standard reductant added,

E = normality of standard reductant, and

F = mL stock NaNO_2 solution taken for titration.

Each 1.00 mL 0.01M (0.05N) KMnO_4 consumed by the NaNO_2 solution corresponds to 1750 μg NO_2^- -N.

f. Intermediate nitrite solution: Calculate the volume, G , of stock NO_2^- solution required for the intermediate NO_2^- solution from $G = 12.5/A$. Dilute the volume G (approximately 50 mL) to 250 mL with water; 1.00 mL = 50.0 μg N. Prepare daily.

g. Standard nitrite solution: Dilute 10.00 mL intermediate NO_2^- solution to 1000 mL with water; 1.00 mL = 0.500 μg N. Prepare daily.

h. Standard potassium permanganate titrant, 0.01M (0.05N): Dissolve 1.6 g KMnO_4 in 1 L distilled water. Keep in a brown glass-stoppered bottle and age for at least 1 week. Carefully decant or pipet supernate without stirring up any sediment. Standardize this solution frequently by the following procedure:

Weigh to the nearest 0.1 mg several 100- to 200-mg samples of anhydrous $\text{Na}_2\text{C}_2\text{O}_4$ into 400-mL beakers. To each beaker, in turn, add 100 mL distilled water and stir to dissolve. Add

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10 mL 1 + 1 H₂SO₄ and heat rapidly to 90 to 95°C. Titrate rapidly with permanganate solution to be standardized, while stirring, to a slight pink end-point color that persists for at least 1 min. Do not let temperature fall below 85°C. If necessary, warm beaker contents during titration; 100 mg will consume about 6 mL solution. Run a blank on distilled water and H₂SO₄.

$$\text{Normality of KMnO}_4 = \frac{\text{g Na}_2\text{C}_2\text{O}_4}{(A - B) \times 0.33505}$$

where:

A = mL titrant for sample and

B = mL titrant for blank.

Average the results of several titrations.

4. Procedure

a. Removal of suspended solids: If sample contains suspended solids, filter through a 0.45- μm -pore-diam membrane filter.

b. Color development: If sample pH is not between 5 and 9, adjust to that range with 1*N* HCl or NH₄OH as required. To 50.0 mL sample, or to a portion diluted to 50.0 mL, add 2 mL color reagent and mix.

c. Photometric measurement: Between 10 min and 2 h after adding color reagent to samples and standards, measure absorbance at 543 nm. As a guide use the following light paths for the indicated NO₂⁻-N concentrations:

Light Path Length <i>cm</i>	NO ₂ ⁻ -N $\mu\text{g/L}$
1	2–25
5	2–6
10	<2

5. Calculation

Prepare a standard curve by plotting absorbance of standards against NO₂⁻-N concentration. Compute sample concentration directly from curve.

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 \pm

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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

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Endnotes

1 (Popup - Footnote)

* APPROVED BY STANDARD METHODS COMMITTEE, 1993.