

5. Calculation

Prepare a standard curve by plotting absorbance of standards against NO₂⁻-N concentration. Compute the 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/L NO₃⁻ + NO₂⁻-N, 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/L

NO₃⁻ + NO₂⁻-N, the recoveries were 100%, 102%, and 100%, respectively.¹

Reference

1. U.S. Environmental Protection Agency. Methods for chemical analysis of water and wastes; Method 353.3. Washington DC: 1979.

Bibliography

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4500-N_{org}

NITROGEN (ORGANIC)

Approved by Standard Methods Committee, 1997. Editorial revisions, 2021. Joint Task Group: Scott Stieg (chair), Bradford R. Fisher, Owen B. Mathre, Theresa M. Wright.

4500-N_{org}

A. INTRODUCTION

1. Selection of Method

The Kjeldahl methods (4500-N_{org} B and C) determine nitrogen in the trinegative state. They fail to account for nitrogen in the form of azide, azine, azo, hydrazone, nitrate, nitrite, nitrile, nitro, nitroso, oxime, and semi-carbazone. *Kjeldahl nitrogen* is the sum of organic nitrogen and ammonia nitrogen.

The major factor that influences the selection of a macro- or semi-micro-Kjeldahl method to determine organic nitrogen is its concentration. The macro-Kjeldahl method applies to samples containing either low or high concentrations of organic nitrogen but requires a relatively large sample volume for low concentrations. In the semi-micro-Kjeldahl method, which applies to samples containing high concentrations of organic nitrogen, choose a sample volume that contains organic plus ammonia nitrogen in the range of 0.2 to 2 mg.

The block digestion method (4500-N_{org} D) is a micro method with an automated analysis step capable of measuring organic nitrogen as low as 0.1 mg/L when blanks are carefully controlled.

2. Storage of Samples

The most reliable results are obtained on fresh samples. If an immediate analysis is not possible, preserve samples for Kjeldahl digestion by acidifying to pH 1.5 to 2.0 with concentrated H₂SO₄ and storing at 4 °C. Do not use HgCl₂ because it interferes with ammonia removal.

3. Interferences

a. Nitrate: During Kjeldahl digestion, nitrate in excess of 10 mg/L can oxidize a portion of the ammonia released from the

digested organic nitrogen, producing N₂O and resulting in a negative interference. When sufficient organic matter in a low state of oxidation is present, nitrate can be reduced to ammonia, resulting in a positive interference. The conditions under which significant interferences occur are not well defined and there is no proven way to eliminate the interference with the Kjeldahl methods described herein.

b. Inorganic salts and solids: The acid and salt content of the Kjeldahl digestion reagent is intended to produce a digestion temperature of about 380 °C. If the sample contains a very large quantity of salt or inorganic solids that dissolve during digestion, the temperature may rise above 400 °C, at which point pyrolytic loss of nitrogen begins to occur. To prevent an excessive digestion temperature, add more H₂SO₄ to maintain the acid-salt balance. Not all salts cause precisely the same temperature rise, but adding 1 mL H₂SO₄ per gram of salt in the sample gives reasonable results. Add the extra acid and the digestion reagent to both sample and reagent blank. Too much acid lowers the digestion temperature below 380 °C and results in incomplete digestion and recovery. If necessary, add sodium hydroxide-sodium thiosulfate before the final distillation step to neutralize the excess acid.

Large amounts of salt or solids also may cause bumping during distillation. If this occurs, add more dilution water after digestion.

c. Organic matter: During Kjeldahl digestion, H₂SO₄ oxidizes organic matter to CO₂ and H₂O. If a large amount of organic matter is present, a large amount of acid will be consumed, the ratio of salt to acid will increase, and the digestion temperature will increase. If enough organic matter is present, the temperature will rise above 400 °C, resulting in pyrolytic loss of nitrogen.

To prevent this, add to the digestion flask 10 mL conc H₂SO₄ for every 3 g of COD. Alternately, add 50 mL more digestion reagent per gram of COD. Additional sodium hydroxide-sodium thiosulfate reagent may be necessary to keep the distillation pH high. Because reagents may contain traces of ammonia, treat the reagent blank identically with the samples.

4. Use of a Catalyst

Mercury has been the catalyst of choice for Kjeldahl digestion. Because of its toxicity and problems associated with legal disposal of mercury residues, a less toxic catalyst is recommended.

4500-N_{org} B. MACRO-KJELDAHL METHOD

1. General Discussion

a. Principle: In the presence of H₂SO₄, potassium sulfate (K₂SO₄), and cupric sulfate (CuSO₄) catalyst, amino nitrogen of many organic materials is converted to ammonium. Free ammonia also is converted to ammonium. After the addition of base, the ammonia is distilled from an alkaline medium and absorbed in boric or sulfuric acid. The ammonia may be determined colorimetrically, by ammonia-selective electrode, or by titration with a standard mineral acid.

b. Selection of ammonia measurement method: The sensitivity of colorimetric methods makes them particularly useful for determining organic nitrogen levels below 5 mg/L. The titrimetric and selective electrode methods of measuring ammonia in the distillate are suitable for determining a wide range of organic nitrogen concentrations. Selective electrode methods and automated colorimetric methods may be used for measurement of ammonia in digestate without distillation. Follow equipment manufacturer's instructions.

c. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:1.

2. Apparatus

a. Digestion apparatus: Kjeldahl flasks with a total capacity of 800 mL yield the best results. Digest over a heating device adjusted so 250 mL water at an initial temperature of 25 °C can be heated to a roiling boil in approximately 5 min. For testing, preheat heaters for 10 min if gas-operated or 30 min if electric. A heating device meeting this specification should provide the temperature range of 375 to 385 °C for effective digestion.

b. Distillation apparatus: See Section 4500-NH₃ B.2a.

c. Apparatus for ammonia determination: See Section 4500-NH₃ C.2, D.2, F.2, or G.2.

3. Reagents

Prepare all reagents and dilutions in ammonia-free water. All of the reagents listed for the determination of Nitrogen (Ammonia), Section 4500-NH₃ C.3, D.3, F.3, or G.3, are required, plus the following:

a. Digestion reagent: Dissolve 134 g K₂SO₄ and 7.3 g CuSO₄ in about 800 mL water. Carefully add 134 mL conc H₂SO₄. When

Digestion of some samples may be complete or nearly complete without the use of a catalyst. Effective digestion results from the use of a reagent having a salt:acid ratio of 1 g/mL with copper as catalyst (4500-N_{org} B.3a), and a specified temperature (4500-N_{org} B.2a) and time (4500-N_{org} B.4c). If a change is made in the reagent formula, report the change and indicate the percentage recovery relative to the results for similar samples analyzed using the previous formula.

Before results are considered acceptable, determine nitrogen recovery from samples with known additions of nicotinic acid to test the completeness of digestion and with ammonium chloride to test for loss of nitrogen.

it has cooled to room temperature, dilute the solution to 1 L with water. Mix well. Keep at a temperature close to 20 °C to prevent crystallization.

b. Sodium hydroxide-sodium thiosulfate reagent: Dissolve 500 g NaOH and 25 g Na₂S₂O₃ · 5H₂O in water and dilute to 1 L.

c. Borate buffer solution: See Section 4500-NH₃ B.3b.

d. Sodium hydroxide (NaOH), 6 N.

4. Procedure

a. Selection of sample volume and sample preparation: Place a measured volume of sample in an 800-mL Kjeldahl flask. Select sample size from the following tabulation:

Organic Nitrogen in Sample (mg/L)	Sample Size (mL)
0-1	500
2-10	250
11-20	100
21-50	50.0
51-100	25.0

If necessary, dilute sample to 300 mL, neutralize to pH 7, and dechlorinate as described in Section 4500-NH₃ B.4b.

b. Ammonia removal: Add 25 mL borate buffer and then 6 N NaOH until pH 9.5 is reached. Add a few glass beads or boiling chips, such as Hengar Granules #12, and boil off 300 mL. If desired, distill this fraction and determine ammonia nitrogen. Alternately, if ammonia has been determined by the distillation method, use the residue in the distilling flask for organic nitrogen determination.

For sludge and sediment samples, weigh a wet sample in a crucible or weighing bottle, transfer contents to a Kjeldahl flask, and determine Kjeldahl nitrogen. Follow a similar procedure for ammonia nitrogen and organic nitrogen determined by difference. Determinations of organic and Kjeldahl nitrogen on dried sludge and sediment samples are not accurate because drying results in a loss of ammonium salts. Measure the dry weight of the sample on a separate portion.

c. Digestion: Cool and add carefully 50 mL digestion reagent (or substitute 6.7 mL conc H₂SO₄, 6.7 g K₂SO₄, and 0.365 g CuSO₄) to the distillation flask. Add a few glass beads and, after

mixing, heat under a hood or with suitable ejection equipment to remove acid fumes. Boil briskly until the volume is greatly reduced (to about 25 to 50 mL) and copious white fumes are observed (fumes may be dark for samples high in organic matter). Then continue to digest for an additional 30 min. As digestion continues, colored or turbid samples become transparent and pale green. After digestion, let cool, dilute to 300 mL with water, and mix. Tilt flask away from personnel and carefully add 50 mL sodium hydroxide-thiosulfate reagent to form an alkaline layer at the flask bottom. Connect the flask to a steamed-out distillation apparatus and swirl the flask to ensure complete mixing. The pH of the solution should exceed 11.0.

d. Distillation: Distill and collect 200 mL distillate. Use 50 mL indicating boric acid as absorbent solution when ammonia is to be determined by titration. Use 50 mL 0.04 N H₂SO₄ solution as absorbent for manual phenate or electrode methods. Extend the tip of the condenser well below the level of the absorbent solution and do not let the temperature in the condenser rise above 29 °C. Lower the collected distillate free of contact with the condenser tip and continue the distillation during the last 1 or 2 min to cleanse the condenser.

e. Final ammonia measurement: Use the titration, ammonia-selective electrode, manual phenate, or automated phenate method, in Sections 4500-NH₃ C, D, F, and G, respectively.

f. Standards: Carry a reagent blank and standards through all steps of the procedure.

5. Calculation

See Section 4500-NH₃ C.5, D.5, F.5, or G.5.

6. Precision and Bias

Two analysts in one laboratory prepared reagent water solutions of nicotinic acid and digested them by the macro-Kjeldahl method. Ammonia in the distillate was determined by titration. Results are summarized in Table 4500-N_{org}:1.

Bibliography

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4500-N_{org} C. SEMI-MICRO-KJELDAHL METHOD

1. General Discussion

See 4500-N_{org} B.1.

2. Apparatus

a. Digestion apparatus: Use Kjeldahl flasks with a capacity of 100 mL in a semi-micro-Kjeldahl digestion apparatus equipped with heating elements to accommodate Kjeldahl flasks and a suction outlet to vent fumes. The heating elements should provide the temperature range of 375 to 385 °C for effective digestion.

b. Distillation apparatus: Use an all-glass unit equipped with a steam-generating vessel containing an immersion heater (Figure 4500-N_{org}:1).

c. pH meter.

d. Apparatus for ammonia determination: See Section 4500-NH₃ C.2, D.2, F.2, or G.2.

3. Reagents

All of the reagents listed for the determination of NH₃-N (Section 4500-NH₃ B.3) and N_{org} macro-Kjeldahl (4500-N_{org} B.3) are required. Prepare all reagents and dilutions with ammonia-free water.

4. Procedure

a. Selection of sample volume: Determine the sample size from the following tabulation:

For sludge and sediment samples, weigh a portion of a wet sample containing between 0.2 and 2 mg organic nitrogen in a crucible or weighing bottle. Transfer the sample quantitatively to a 100-mL beaker by diluting it and rinsing the weighing dish several times with small quantities of water. Make the transfer using as small a quantity of water as possible and do not exceed a total volume of 50 mL. Measure the dry weight of the sample on a separate portion.

b. Ammonia removal: Pipet 50 mL sample or an appropriate volume diluted to 50 mL with water into a 100-mL beaker. Add 3 mL borate buffer and adjust to a pH of 9.5 with 6 N NaOH, using a pH meter. Quantitatively transfer sample to a 100-mL Kjeldahl flask and boil off 30 mL. Alternatively, if ammonia removal is not required, digest samples directly as described in paragraph *c* below. Distillation following this direct digestion yields Kjeldahl nitrogen concentration rather than organic nitrogen.

c. Digestion: Carefully add 10 mL digestion reagent to the Kjeldahl flask containing the sample. Add 5 or 6 glass beads (3- to 4-mm size) to prevent bumping during digestion. Set each heating unit on the micro-Kjeldahl digestion apparatus to its medium setting and heat the flasks under a hood or with suitable ejection equipment to remove the fumes of SO₃. Continue to boil briskly until the solution becomes transparent and pale green and copious fumes are observed. Then turn each heating unit up to its maximum setting, and digest for an additional 30 min. Cool. Quantitatively transfer the digested sample by diluting and rinsing several times into the micro-Kjeldahl distillation apparatus

Table 4500-N_{org}:1. Precision Data for Kjeldahl Nitrogen Method Based on Mean of Triplicate Analyses of Nicotinic Acid

Laboratory/Analyst	Nicotinic Acid (mg/L N)	Recovery of N (%)	Standard Deviation (mg/L)	Relative Standard Deviation (%)
1/1	5	93.3	0.16	3.46
1/2	5	101	0.16	3.17
1/1	10	87.7	0.16	1.84
1/2	10	91.5	0.28	3.06
1/1	20	95.7	0.16	0.84
1/2	20	95.7	0.58	3.03
2/1	0.5	97.4	0.005	1.04
2/2	0.5	95.3	0.027	5.46
3/1	0.5	87.3	0.130	29.9
4/1	0.5	113	0.235	41.7
2/1	1.0	103	0.012	1.15
2/2	1.0	101	0.046	4.63
3/1	1.0	84.3	0.081	9.66
4/1	1.0	99.3	0.396	39.9
2/1	2.0	104	0	0
2/2	2.0	99.2	0.029	1.44
3/1	2.0	89.2	0.071	3.98
4/1	2.0	112	0.139	6.18

so the total volume in the distillation apparatus does not exceed 30 mL. Add 10 mL sodium hydroxide-thiosulfate reagent and turn on the steam.

d. Distillation: Control the rate of steam generation to boil the contents in the distillation unit so neither escape of steam from the tip of the condenser nor the bubbling of contents in the receiving flask occurs. Distill and collect 30 to 40 mL distillate through a delivery tube immersed below the surface of 10 mL of the absorbent solution contained in a 125-mL Erlenmeyer flask. Use indicating boric acid for a titrimetric finish. Use 10 mL 0.04 N H₂SO₄ solution for collecting the distillate for the phenate or electrode methods. Extend the tip of the condenser well below the level of the absorbent solution and do not let the temperature in the condenser rise above 29 °C. Lower the collected distillate free of contact with the condenser tip and continue the distillation during the last 1 or 2 min to cleanse the condenser.

e. Standards: Carry a reagent blank and standards through all steps of the procedure and apply necessary correction to results.

f. Final ammonia measurement: Use the titration, ammonia selective electrode, manual phenate, or automated phenate method from Sections 4500-NH₃ C, D, F, and G, respectively.

5. Calculation

See Section 4500-NH₃ C.5, D.5, F.5, or G.5.

6. Precision and Bias

No data on the precision and bias of the semi-micro-Kjeldahl method are available.

Bibliography

See 4500-N_{org} B.7.

4500-N_{org}

D. BLOCK DIGESTION AND FLOW INJECTION ANALYSIS

1. General Discussion

a. Principle: Samples of drinking, ground, and surface waters and of domestic and industrial wastes are digested in a block digester with sulfuric acid and copper sulfate as a catalyst. The digestion recovers nitrogen components of biological origin, such as amino acids, proteins, and peptides, as ammonia but may not recover the nitrogenous compounds of some industrial wastes, such as amines, nitro compounds, hydrazones, oximes, semicarbazones, and some refractory tertiary amines. Nitrate is not recovered. See Section 4500-N for a discussion of the various forms of nitrogen found in waters and wastewaters, 4500-N_{org} B and C for a discussion of Kjeldahl nitrogen methods, and Section 4130 Flow Injection Analysis (FIA).

The digested sample is injected onto the FIA manifold, where its pH is controlled by raising it to a known, basic pH by neutralization with a concentrated buffer. This in-line neutralization converts the ammonium cation to ammonia, and also prevents undue influence of the sulfuric acid matrix on the pH-sensitive color reaction that follows. The ammonia thus produced is heated with salicylate and hypochlorite to produce a blue color that is proportional to the ammonia concentration. The color is intensified by adding sodium nitroprusside. The presence of EDTA in the buffer prevents the precipitation of calcium and magnesium. The resulting peak's absorbance is measured at 660 nm. The peak area is proportional to the concentration of total Kjeldahl nitrogen in the original sample.

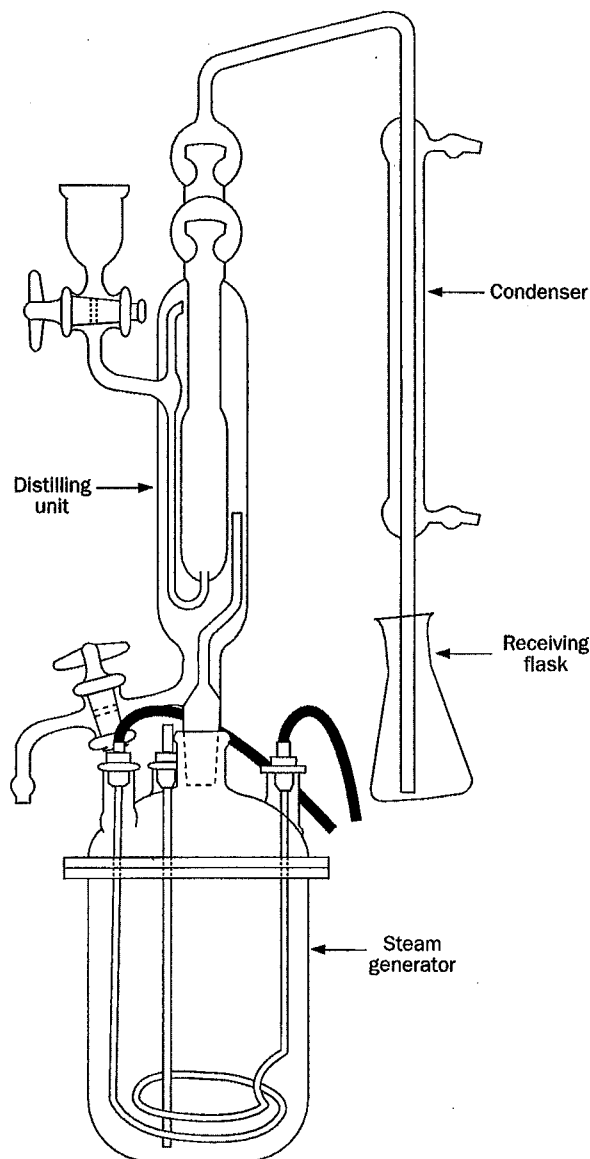


Figure 4500-N_{org}:1. Micro-Kjeldahl distillation apparatus.

b. Interferences: Remove large or fibrous particulates by filtering the sample through glass wool.

The main source of interference is ammonia. Ammonia is an airborne contaminant that is removed rapidly from ambient air by the digestion solution. Guard against ammonia contamination in reagents, water, glassware, and the sample preservation process. It is particularly important to prevent ammonia contamination in the sulfuric acid used for the digestion. Open sulfuric acid bottles away from laboratories in which ammonia or ammonium chloride have been used as reagents and store sulfuric acid away from such reagents. Ensure that the open ends of the block digester's tubes can be covered to prevent ammonia from being scrubbed from the fume hood make-up air during the digestion.

If a sample consumes more than 10% of the sulfuric acid during digestion, the pH-dependent color reaction will show a matrix effect. The color reaction buffer accommodates a range of $5.4 \pm 0.4\%$ H₂SO₄ (v/v) in the diluted digested sample. Sample

matrices with a high concentration of carbohydrates or other organic material may consume more than 10% of the acid during digestion. If this effect is suspected, titrate the digested sample with standardized sodium hydroxide to determine whether more than 10% of the sulfuric acid has been consumed during digestion. Avoid loss of sulfuric acid from the digestion tubes during the digestion period.

Also see 4500-N_{org} A and B.

c. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:1.

2. Apparatus

Digestion and flow injection analysis equipment consisting of:

a. Block digester capable of maintaining a temperature of 380 °C for 2 h.

b. Digestion tubes capable of being heated to 380 °C for 2 h and having a cover to prevent ammonia contamination and loss of sulfuric acid.

c. FIA injection valve with sample loop or equivalent.

d. Multichannel proportioning pump.

e. FIA manifold (Figure 4500-N_{org}:2) with tubing heater and flow cell. Relative flow rates only are shown in Figure 4500-N_{org}:2. Tubing volumes are given as an example only; they may be scaled down proportionally. Use manifold tubing of an inert material, such as PTFE.

f. Absorbance detector, 660 nm, 10-nm bandpass.

g. Injection valve control and data acquisition system.

3. Reagents

Use reagent water (>10 megohm) for all solutions. To prevent bubble formation, degas the carrier and buffer with helium. Pass He at 140 kPa (20 psi) through a helium degassing tube. Bubble He through 1 L solution for 1 min. As an alternative to preparing reagents by w/w, use w/v.

a. Digestion solution: In a 1-L volumetric flask, dissolve 134.0 g potassium sulfate, K₂SO₄, and 7.3 g copper sulfate, CuSO₄, in 800 mL water. Then add slowly while swirling 134 mL conc sulfuric acid, H₂SO₄. Let cool, dilute to the mark, and invert to mix.

b. Carrier and diluent: To a tared 1-L container, add 496 g digestion solution (¶ a above) to 600 g water and mix thoroughly.

c. Sodium hydroxide (NaOH), 0.8 M: To a tared 1-L plastic container, add 32.0 g NaOH and 985.0 g water. Stir or shake until dissolved.

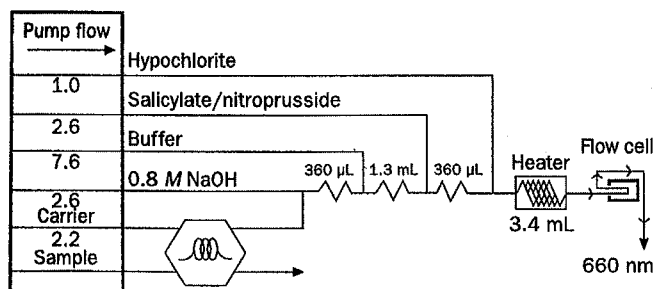


Figure 4500-N_{org}:2. FIA total Kjeldahl nitrogen manifold.

Table 4500-N_{org}:2. Results of Single-Laboratory Studies with Selected Matrices

Matrix	Sample/Blank Designation	Known Addition (mg/L N)	Recovery (%)	Relative Standard Deviation (%)
Wastewater treatment Plant Influent	Reference sample ^a	—	97	—
	Blank ^b	3.0	97	—
		6.0	99	—
		0	—	3.3
	Site A ^{c,d}	3.0	91	—
		6.0	95	—
		0	—	3.6
	Site B ^{c,d}	3.0	115	—
		6.0	93	—
		0	—	5.1
	Site C ^{c,d}	3.0	97	—
		6.0	107	—
		—	—	—
	Wastewater treatment Plant Effluent	Reference sample ^a	—	92
Blank ^b		3.0	97	—
		6.0	100	—
		0	—	5.4
Site A ^{c,e}		3.0	94	—
		6.0	100	—
		0	—	4.1
Site B ^{c,e}		3.0	119	—
		6.0	81	—
		0	—	7.3
Site C ^{c,e}		3.0	93	—
		6.0	105	—
		—	—	—
Landfill leachate		Reference sample ^a	—	96
	Blank ^b	3.0	101	—
		6.0	99	—
		0	—	3.3
	Site A ^{c,f}	3.0	95	—
		6.0	98	—
		0	—	4.4
	Site B ^{c,f}	3.0	134	—
		6.0	85	—
		0	—	3.8
	Site C ^{c,f}	3.0	98	—
		6.0	105	—
		—	—	—

^a U.S. EPA nutrient QC sample, 1.52 mg/L N.

^b Determined in duplicate.

^c Samples without known additions determined 4 times; samples with known additions determined in duplicate.

^d Sample dilutions: A – 5-fold; B – 10-fold; C – 5-fold. Typical relative difference between duplicates 3%.

^e Sample dilutions: A – none; B – 2-fold; C – none. Typical relative difference between duplicates 1%.

^f Sample dilutions: A, B, and C – 25-fold. Typical relative difference between duplicates 4%.

d. Buffer: To a tared 1-L container, add 941 g water. Add and completely dissolve 35.0 g sodium phosphate dibasic heptahydrate, Na₂HPO₄ · 7H₂O. Add 20.0 g disodium EDTA (ethylenediaminetetracetic acid disodium salt). The EDTA does not dissolve but forms a turbid solution. Finally, add 50 g NaOH. Stir or shake until dissolved.

e. Salicylate/nitroprusside: To a tared 1-L dark container, add 150.0 g sodium salicylate (salicylic acid sodium salt), C₆H₄(OH)(COO)Na, 1.00 g sodium nitroprusside (sodium nitro-ferricyanide dihydrate), Na₂Fe(CN)₅NO · 2H₂O, and 908 g water. Stir or shake until dissolved. Prepare fresh monthly.

f. Hypochlorite: To a tared 250-mL container, add 16 g commercial 5.25% sodium hypochlorite bleach solution and 234 g deionized water. Shake to mix.

g. Stock standard, 250 mg/L N: In a 1-L volumetric flask, dissolve 0.9540 g ammonium chloride, NH₄Cl (dried for 2 h at

110 °C), in about 800 mL water. Dilute to the mark and invert to mix.

h. Standard ammonia solutions: Prepare ammonia standards in the desired concentration range, using the stock standard (¶ g above) and diluting with water.

Organic Nitrogen in Sample (mg/L)	Sample Size (mL)
4–40	50
8–80	25
20–200	10
40–400	5

i. Simulated digested standards: To prepare calibration standards without having to digest the standards prepared in paragraph *h* above, proceed as follows:

j. Stock standard, 5.00 mg/L N: To a tared 250-mL container, add about 5.0 g stock standard (250 mg/L N). Divide the actual weight of the added solution by 0.02 and make up to this resulting total weight with diluent (¶ *b* above). Shake to mix. Prepare working standards from this stock standard, diluting with the diluent (¶ *b* above), not water.

4. Procedure

a. Digestion procedure: Carry both standards and samples through this procedure.

To a 75-mL block digester tube, add 25.0 mL sample or standard and then add 10 mL digestion solution (4500-N_{org} D.3a) and mix. Add 4 alundum granules to each tube for smooth boiling. Place tubes in preheated block digester for 1 h at 200 °C. After 1 h, increase the block temperature to 380 °C and continue to digest for 1 h at 380 °C. Remove tubes from the block and let cool for about 10 min. Dilute each tube to 25.0 mL with water and mix with a vortex mixer. Cover the tubes to prevent ammonia contamination.

b. FIA analysis: Set up a manifold equivalent to that in Figure 4500-N_{org}:2 and analyze digested standards and samples by the method supplied by the manufacturer or laboratory standard operating procedure. Follow the quality control protocols described in Section 4020.

5. Calculations

Prepare standard curves by plotting absorbance of standards processed through the manifold versus ammonia concentration. The calibration curve is linear.

6. Precision and Bias

a. Recovery and relative standard deviation: Table 4500-N_{org}:2 gives the results of single-laboratory studies.

b. MDL: A 130-µL sample loop was used in the method described above. Using a published MDL method,¹ analysts ran 21 replicates of a 0.1-mg/L N standard. These gave a mean of 0.103 mg/L N, a standard deviation of 0.014 mg/L N, and MDL of 0.034 mg/L N. A lower MDL may be obtained by increasing the sample loop volume and increasing the ratio of carrier flow rate to reagents flow rate.

Reference

1. U.S. Environmental Protection Agency. Definition and procedure for the determination of method detection limits. Appendix B to 40 CFR 136 rev. 1.11. Published 1984, amended June 30, 1986. 49 CFR 43430.

4500-O

OXYGEN (DISSOLVED)

Approved by Standard Methods Committee, 2016. Editorial revisions, 2021. Joint Task Group: Michael A. Michaud (chair), Gregg L. Oelker, Marc Oliver D. Quijano.

4500-O A. INTRODUCTION

1. Significance

The dissolved oxygen (DO) levels in natural and waste waters depend on the physical, chemical, and biochemical activities in a waterbody. The analysis of DO is a key test in water pollution and waste treatment process control.

2. Selection of Method

This section describes 3 methods for DO analysis:

- the iodometric (Winkler) method and its modifications (based on DO's oxidizing property),
- the membrane-electrode method (based on molecular oxygen's diffusion rate across a membrane),² and

- the optical-probe method (which uses luminescence-based oxygen sensors to measure light emissions that correlate to the DO concentration).³

The choice of procedure depends on the interferences present, the accuracy desired, and, in some cases, convenience or expedience.

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