



Parameter

Total Kjeldahl Nitrogen (as N)

Sample Type

Digested Sample

Introduction

Total Kjeldahl Nitrogen is the sum of organic nitrogen and ammonia in a sample, which are converted to ammonium by digestion in sulfuric acid, potassium sulfate and cupric sulfate solution. Ammonia in the digestate is measured directly by adding base and using the 9512HP electrode with an Orion Star meter to obtain the Total Kjeldahl Nitrogen in the sample. Note: per Standard Methods 4500-N_{org} B & C, the selective electrode method may be used for measurement of ammonia without distillation. Check with local regulators when testing for reporting purposes.

References

1. Method 4500-N_{org} B & C. Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005. APHA, AWWA, & WEF, Washington, D.C. www.standardmethods.org
2. Method 4500-NH₃ D. Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005. APHA, AWWA, & WEF, Washington, D.C. www.standardmethods.org

Result Statistics

# Trials	Average	%CV
3	31.1 mg/L	4.6%

Recommended Equipment

Orion Star Benchtop Meter (Orion 1115000 or Orion 1119000); Ammonia electrode (Orion 9512HPBNWP); Stirrer (Orion 096019); Optional: printer (Orion 1010006); Star Navigator Software (Orion 1010007). Note: See Reference 1 for equipment required for digestion.

Required Solutions

Ammonia Standard 1000 ppm as N (Orion 951007); pH adjustor/ISA for Ammonia (Orion 951211); Adjusted Filling Solution (Orion 951209 + NaNO₃); Digestion Solution; deionized water (DI).

Solutions Preparation (see page 2 for semi-micro analysis)

1. Digestion Solution: 134g K₂SO₄, 7.3g CuSO₄, 134mL conc. H₂SO₄ to 1L volumetric flask. Cool then bring to mark with DI water.
2. Adjusted Filling Solution: Add 2.55g NaNO₃ to 60mL of Filling Solution (Orion 951209).
3. Prepare 1.0 mg/L ammonia standard by pipetting 1mL of 1000 ppm (mg/L) standard into a 1L volumetric flask and diluting to the mark with DI water.
4. Prepare 10.0 mg/L ammonia standard by pipetting 10mL of 1000 ppm standard into a 1L volumetric flask and diluting to the mark with DI water.
5. Prepare 100.0 mg/L ammonia standard by pipetting 100mL of 1000 ppm standard into a 1L volumetric flask and diluting to the mark with DI Water.

Meter Setup

Connect the electrode and stirrer to the meter. Set measurement mode to ISE. Set stir speed to 4 and read type to AUTO. In ISE Setup mode, set resolution to 3, units to mg/L, range to high; enable a blank correction by setting "nLIn" option to AUtO. If all steps were followed correctly, the meter display will show three digits in the top line and "ISE: mg/L" to the right of the top line.

Electrode Performance Check

Check if slope is between 54-60 mV at least daily according to the procedure in the electrode manual. Check electrode drift by comparing a 2 and 3 minute reading of 1 mg/L standard w/ISA. The difference in readings should be less than or equal to 0.5mV. See notes on page 2 or troubleshooting section of manual if experiencing slope or drift problems.

Electrode Storage, Soaking, and Rinsing

Use adjusted fill solution. Before testing, condition electrode for 15 min. in 1mg/L ammonia standard in Digestion Solution (see Calibration for prep.). Between measurements, rinse the electrode by immersing in two beakers of DI water in sequence. Store electrode overnight in adjusted electrode filling solution.

Sample Preservation

Analyze immediately (w/in 15 min.) after collection or acidify to pH<2 with sulfuric acid and store at ≤ 6°C for up to 28 days. Refer to reference and/or EPA 40 CFR Part 136.3 for details.

Sample Preparation (see page 2 for semi-micro analysis)

Digest the samples according to the procedure in SM 4500-N_{org} B. After digestion, dilute the sample to 300mL, but do not add base or distill. Measure 50mL of sample into a beaker. Just prior to analysis, add **9 mL of ISA** to the sample. If the sample pH is not between 11 – 13, add ISA drop wise until necessary pH is achieved. Analyze immediately to avoid loss of ammonia from the alkaline solution. For more precise measurements, allow all standards and samples to reach the same temperature before analysis

Calibration (see page 2 for semi-micro analysis)

If nitrogen recovery from a digested standard has been confirmed, the standards do not need to be digested. Prepare non-digested standards by adding the same volume of standard as sample which was digested (See SM 4500-N_{org} B Section 4.), 50mL Digestion Solution and DI water to the mark of 300mL volumetric flask. Use 50mL aliquots of this standard for calibration and calibration verification (adding 9mL ISA to each aliquot as with the samples). Perform a three point calibration using 1.0mg/L, 10.0mg/L, and 100 mg/L ammonia standards. The electrode slope will be displayed and should be above 54 mV/decade. Verify the calibration by analyzing a fresh portion of a mid-range standard. If reading is not acceptable, see troubleshooting section of electrode manual.

Analysis (see page 2 for semi-micro analysis)

Rinse electrode and stirrer by immersing in two beakers of DI water in sequence and place in the prepared sample. Press the MEASURE key. The stirrer should turn on. The "ISE:mg/L" icon will flash until the reading is stable. Once reading is stable, the icon will stop flashing, the stirrer will stop and the results will be displayed and printed.



Ammonia in Wastewater	mg/L as Nitrogen
Sample 1	30.4
Sample 2	32.7
Sample 3	30.1
Mean	31.1
Standard Deviation	1.42
%CV	4.6%

Quality Control (QC)

Recommended QC procedures include: calibration and calibration verification, initial demonstration of laboratory capability and method detection limit determination, laboratory control samples (LCS), method blanks, matrix spikes (MS), sample duplicates, and independent reference materials. See references above for details.

Note:

1). With Auto-blank correction activated, slope on the meter's display can be higher than the expected range of -54 and -60mV/decade due to auto-blank calculation.

2). If sample concentration is outside the calibrated concentration range, dilute the sample into range and rerun or run higher calibration standards which bracket the sample concentration.

3). If the electrode does not give reproducible results or demonstrates a slow response, do the following: Remove any bubbles on the membrane surface by tapping the electrode. If the electrode performance is not improved, change membrane and filling solution, condition in 1mg/L standard in digestion solution for 15 minutes and re-calibrate the electrode.

For Semi-Micro Analysis, make the following changes to the procedure on page 1:

Solutions Preparation

1. Digestion Solution: 134g K₂SO₄, 7.3g CuSO₄, 134mL conc. H₂SO₄ to 1L volumetric flask. Cool then bring to mark with DI water.
2. Adjusted Filling Solution: Add 2.55g NaNO₃ to 60mL of Filling Solution (Orion 951209).
3. Prepare 1.0 mg/L ammonia standard by pipetting 0.5mL of 1000 ppm (mg/L) standard into 83mL of digestion solution in a 500mL volumetric flask and diluting to the mark with DI water.
4. Prepare 10.0 mg/L ammonia standard by pipetting 5mL of 1000 ppm (mg/L) standard into 83mL of digestion solution in a 500mL volumetric flask and diluting to the mark with DI water.
5. Prepare 100.0 mg/L ammonia standard by pipetting 50mL of 1000 ppm (mg/L) standard into 83mL of digestion solution in a 500mL volumetric flask and diluting to the mark with DI water.

Sample Preparation

Digest the samples according to the procedure in SM 4500-N_{org} C. After digestion, dilute the sample to 30mL, but do not add base or distill. Just prior to analysis, add **5.4 mL of ISA** to the sample. If the sample pH is not between 11 and 13, add ISA drop wise until necessary pH is achieved. Analyze immediately to avoid loss of ammonia from the alkaline solution. For more precise measurements, allow all standards and samples to reach the same temperature before analysis

Calibration

If nitrogen recovery from a digested standard has been confirmed, the standards do not need to be digested. Use 30mL aliquots of standards for calibration and calibration verification (adding 5.4mL ISA to each aliquot as with the samples). Perform a three point calibration using 1.0mg/L, 10.0mg/L, and 100 mg/L ammonia standards. The electrode slope will be displayed and should be above 54 mV/decade. Verify the calibration by analyzing a fresh portion of a mid-range standard. If reading is not acceptable, see troubleshooting section of electrode manual.

Analysis

Rinse electrode and stirrer by immersing in two beakers of DI water in sequence and place in the prepared sample. Press the MEASURE key. The stirrer should turn on. The "ISE:mg/L" icon will flash until the reading is stable. Once reading is stable, the icon will stop flashing, the stirrer will stop and the results will be displayed and printed. Multiply the results by the dilution factor to get concentration of sample.