



Parameter

Total Kjeldahl Nitrogen (as N)

Sample Type

Digested and Distilled 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. Distill before analysis if necessary for reporting purposes. Ammonia in the distilled sample 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. See Electrode Log #40 for direct analysis of the digestate.

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	28.0 mg/L	2.5%

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 and distillation.

Required Solutions

Ammonia Standard 1000 ppm as N (Orion 951007); pH adjustor/ISA for Ammonia (Orion 951211); Filling Solution (Orion 951209); 0.04N H₂SO₄; deionized water (DI). Note: See Reference 1 for solutions required for digestion and distillation.

Solutions Preparation

1. Prepare 0.04N H₂SO₄ by pipetting 1.11mL concentrated H₂SO₄ in 1000mL volumetric flask and diluting to the mark with deionized water.
2. Prepare 1.0 mg/L ammonia standard by pipetting 0.250mL of 1000 ppm (mg/L) standard into a 250mL volumetric flask and diluting to the mark with 0.04N H₂SO₄.
3. Prepare 10.0 mg/L ammonia standard by pipetting 2.5mL of 1000 ppm standard into a 250mL volumetric flask and diluting to the mark with 0.04N H₂SO₄.
4. Prepare 100.0 mg/L ammonia standard by pipetting 25mL of 1000 ppm standard into a 250mL volumetric flask and diluting to the mark with 0.04N H₂SO₄.

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

Before testing, condition electrode for 15 min. in 1mg/L ammonia standard with ISA. Between measurements, rinse the electrode by immersing in two beakers of DI water in sequence. See electrode manual for long term storage. Store electrode overnight in 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 method)

For precise measurements, allow all the standards and the samples to reach the same temperature before analysis. Digest and distill the samples according to the procedure in SM 4500-N_{org} B. Distill into 0.04N H₂SO₄ as is instructed for measurement of ammonia by ISE. Measure 50mL of distilled sample into a beaker. Just prior to analysis, add 1 mL of ISA to the sample. If the sample pH is not between 11 – 13, add ISA drop wise until sample turns blue (indicating the necessary pH is achieved). Analyze immediately to avoid loss of ammonia from the alkaline solution.

Calibration

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 the reading is stable, the icon will stop flashing, the stirrer will stop and the results will be displayed and printed. Multiply the results the dilution factor to obtain sample concentration.

Quality Control (See page 2)



Ammonia in Wastewater	mg/L as Nitrogen
Sample 1	27.3
Sample 2	28.0
Sample 3	28.7
Mean	28.0
Standard Deviation	0.7
%CV	2.5%

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 gently tapping the electrode. If the electrode performance is not improved, change membrane and filling solution, condition in 1mg/L standard (w/ISA) for 15 minutes and re-calibrate the electrode.

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

Sample Preparation

For precise measurements, allow all the standards and the samples to reach the same temperature before analysis. Digest and distill the samples according to the procedure in SM 4500-N_{org} C. Starting with 10mL of 0.04N H₂SO₄ in the receiver, distill the digestate and collect 40mL distillate as is instructed for measurement of ammonia by ISE. Just prior to analysis, add 1 mL of ISA to the sample. If the sample pH is not 11 – 13, add ISA drop wise until sample turns blue (indicating the necessary pH is achieved). Analyze immediately to avoid loss of ammonia from the alkaline solution.