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| **TITLE:** | **Ammonia-Nitrogen – Ion Selective Electrode Method** |
| **ANALYTE:** | **Ammonia Nitrogen (NH3-N)** |
| **FACILITY:** | **Acme WWTP** |
| **REFERENCE METHOD:** | **Standard Methods 4500-NH3 D – 1997** |
| **DATE OF ISSUE:** | **7/18/18** |

1. Applicable Matrices
   1. This method is applicable to the determination of ammonia in drinking water, surface water, and domestic and industrial waste matrices.
2. Summary of the Test Method
   1. The ammonia-selective electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an electrode internal solution of ammonium chloride. Dissolved ammonia (NH3(aq) and NH4+(g)) is converted to NH3(aq) by raising the pH to above 11 with a strong base. NH3(aq) diffuses through the membrane and changes the internal solution pH that is sensed by a pH electrode. Potentiometric measurements are made with a pH meter having an expanded millivolt scale.
   2. Data are on file that shows distillation is not required prior to analysis of domestic wastewater effluents using this method. See references for details. All industry samples and influent samples must be distilled before analyzing. If the laboratory has performed a study demonstrating distillation is unnecessary, maintain that data. THIS SOP IS ONLY FOR SAMPLES NOT REQUIRING DISTILLATION.
3. Safety
   1. Proper personal protection equipment, such as a lab coat, safety glasses, and nitrile gloves should be worn when performing any laboratory test.
   2. When using acid solutions, wear appropriate protective clothing: rubber apron, protective sleeves, gloves, and safety goggles or glasses.
   3. Always have adequate ventilation when working with acids, bases, and solvents to minimize exposure to vapors.
   4. Refer to the Safety Data Sheet for information on a specific chemical.
4. Equipment and Supplies
   1. Specific ion meter with a direct concentration readout or a pH meter with an expanded millivolts scale, ABC Company Model 123
   2. High performance probe, ABC Company Model XYZ
   3. Class A pipets or verified mechanical pipettors
   4. Acid-rinsed glassware: graduated cylinders, volumetric flasks, beakers
   5. Magnetic stirrer
   6. Magnetic stir bars
   7. Residual chlorine test strips with a minimum detection capability of 0.1 mg/L
   8. pH paper, narrow range (0 – 6.0); used to confirm pH of <2 for preservation
   9. pH paper, narrow range (9 – 13); used to confirm samples are >11 pH after buffer addition
5. Reagents and Standards
   1. Distilled water, ammonia-free
   2. Buffer solution options:
      1. NaOH, 10 N
      2. NaOH/EDTA solution, 10 N. Dissolve 400 g NaOH in 800 mL distilled water. Add 45.2 g ethylenediaminetetraacetic acid, tetrasodium salt, tetrahydrate (Na4EDTA • 4H2O) and stir to dissolve. Cool and dilute to 1000 mL. This solution may also be commercially purchased. This solution expires according to manufacturer’s expiration date. Use this buffer if the samples are suspected to have mercury or silver interferences.
      3. Color indicating buffer; must be compatible with probe. Use this buffer in place of using a pH meter or pH strips to verify the pH is >11 after buffer addition.
   3. Ammonia stock standards, 20 mg/L, 2.0 mg/L, and 0.2 mg/L NH3-N. Store at ≤ 6ºC but above freezing. These solutions expire according to manufacturer’s expiration date.
      1. Alternatively, these can be prepared. Dry anhydrous ammonium chloride (NH4Cl) at 100°C for at least 1 hour. Dissolve 0.3819 g NH4Cl in water, and dilute to 1000 mL. This is a 100 mg/L NH3 as N stock solution. Prepare the 20, 2.0, and 0.2 mg/L standards from this 100 mg/L solution.
   4. ICV (initial calibration verification standard)/LCS (lab control standard), second source ammonia stock standard, 5 mg/L NH3-N. Must be a lot # different from 5.3. above. This solution expires according to manufacturer’s expiration date.
   5. CCV (continuing calibration verification standard) ammonia solution, 2.0 mg/L NH3-N. May be the same source as the calibration standards.
   6. Sulfuric acid solution, 5 N (for preserving samples)
   7. Dechlorinating reagent; used to remove residual chlorine. Dissolve 0.35 g sodium thiosulfate (Na2S2O3 • 5H2O) in water and dilute to 100 mL. Prepare fresh weekly.
   8. Proficiency Testing samples from an approved provider
6. Interferences
   1. Residual chlorine reacts with ammonia; remove by sample pretreatment. If a sample is likely to contain residual chlorine, immediately upon collection, treat with dechlorinating agent. Refer to Standard Methods 4500-NH3.B.3*d*.
   2. High concentrations of dissolved ions affect the measurement, but color and turbidity do not.
   3. Amines are a positive interference. This may be enhanced by acidification. Mercury and silver interfere by complexing with ammonia, unless the NaOH/EDTA solution is used.
7. Sample Collection, Preservation, and Storage
   1. Collect samples in clean plastic or glass bottles.
   2. If samples cannot be analyzed within 15 minutes of collection, samples must be preserved by acidifying with sulfuric acid (H2SO4) to a pH <2 immediately after collecting.
      1. Generally, 0.5 mL of 5 N H2SO4 per 200 mL of sample is sufficient to reduce the pH to <2.
      2. Samples must be tested periodically (at least quarterly) with narrow range pH paper (0-6 pH) to confirm the pH is <2 and documented on the bench sheet or on a separate log.
   3. If a sample is likely to contain residual chlorine, immediately upon collection, treat with dechlorinating agent. Use 1 mL dechlorinating agent to remove 1 mg/L residual chlorine in a 500 mL sample. Record this on the bench sheet.
   4. Store the preserved samples at ≤6°C but above freezing.
   5. Hold times may not exceed 28 days from the time of collection.
8. Quality Control
   1. Initial Quality Control
      1. All analysts shall perform an IDC once for each lab technician. An IDC is required of all new lab technicians.
   2. Initial and On-going Quality Control
      1. Method Detection Limit (MDL): every thirteen months, calculate and verify the MDL. See the “Method Detection Limits and Reporting” section.
      2. Calibrate the meter with each use or whenever the calibration check verification (ICV/LCS or CCV) standard fails (see “Calibration and Standardization” section).
      3. Verify the calibration immediately following calibration by analyzing an initial calibration verification (ICV/LCS) standard. The ICV/LCS must be from a second source standard. (If the calibration standards are processed the same as the samples and the ICV, the LCS will be the same as the ICV; in this case, a separate LCS does not need to be analyzed.)
      4. Annually a Performance Test (PT) sample must be obtained and analyzed from one of the Wisconsin DNR approved providers.
   3. On-going Quality Control
      1. Analyze a method blank (MB) every run of 20 samples after the ICV/LCS or CCV.
      2. If more than 20 samples are analyzed, analyze a continuing calibration verification standard (CCV) with every run of 20 samples.
9. Calibration and Standardization
   1. The ABC Company Model 123 ion selective meter and XYZ probe is used. Refer to the User Manual for additional information.
   2. Calibration must be performed each day of use or whenever the ICV/LCS or CCV fails. If the temperature has changed or the meter is being used for more than 2 hours, repeat the calibration.
   3. The calibration curve must be generated with at least 3 standards.
   4. Be sure the standards are at room temperature.
   5. Place a piece of cardboard or other insulating material between the stirrer and the beaker to prevent heating of the solutions.
   6. Add 100 mL of the 0.2, 2.0, and 20.0 mg/L standards into separate beakers using a graduated cylinder.
   7. Turn on the meter, press “mode” until the indicator displays “CON.” Press “calibrate,” enter in 3 for the number of standards, and press “yes.”
   8. Enter 0.2 for the calibration value, and press “yes.”
   9. Rinse off the electrode, dab dry, and place it in the 0.2 mg/L standard.
   10. Turn on the magnetic stirrer making sure the probe is above the stir bar. Keep the stirrer at the same slow speed for all standards and samples.
   11. Add 1 mL of buffer solution. **Do not add buffer before immersing the electrode because ammonia may be lost from the basic solution.**
   12. When the reading on the meter is stable (at least 4 minutes), record the millivolts (mV). When the prompt appears, press “yes.”
   13. Enter 2.0 for the calibration value, and press “yes.” Rinse off the electrode, dab dry, and place it in the 2.0 mg/L standard. While stirring, add 1 mL of buffer solution. When the reading is stable, record the mV, and when the prompt appears, press “yes.”
   14. Enter 20 for the calibration value, and press “yes.” Rinse off the electrode, dab dry, and place it in the 20.0 mg/L standard. While stirring, add 1 mL of buffer solution. When the reading is stable, record the mV, and when the prompt appears, press “yes.”
   15. The meter will display the calibration slope. Record the slope on the bench sheet. The slope must be between -54 and -60 (or according to the probe manual’s slope criteria). If not, recalibrate.
   16. Document all of the calibration results and information on the bench sheet.
10. Procedure
    1. Warm all samples, standards, and reagents to room temperature.
    2. Using a graduated cylinder, add 100 mL of the ICV/LCS standard to a clean beaker.
    3. Rinse off the electrode from the calibrated meter, dab dry, and place it in the ICV/LCS standard.
    4. Turn on the magnetic stirrer making sure the probe is above the stir bar. Keep the stirrer at the same slow speed for all standards and samples.
    5. Add 1 mL of buffer solution. **Do not add buffer before immersing the electrode because ammonia may be lost from the basic solution.**
    6. Test the pH to make sure the pH is above 11, and record on the bench sheet.
       1. If it is not above 11, add more buffer solution in 1 mL increments. Record how much is added and include this volume in calculating the final result.
       2. If using a color indicating buffer, testing the pH is not necessary. Ensure the color change is observed indicating the pH is above 11.
    7. When the reading on the meter is stable (at least 4 minutes), record the mV and concentration on the bench sheet.
    8. Rinse off the electrode, dab dry, and continue reading the method blank and all samples.
    9. If any sample has a result higher than the highest standard in the calibration curve, the sample must be diluted and reanalyzed.
11. Calculations
    1. Results are calculated from the linear calibration curve based on the Nerst equation, and concentrations are read from the meter. Include any applicable dilution factors.
    2. Report results as mg/L NH3-N.
12. Method Detection Limits and Reporting
    1. This method has an applicable range from the LOD (about 0.03) to 1400 mg/L NH3-N. All samples above the highest calibration standard must be diluted. The lowest value that can be reported is no lower than the MDL: report as less than (<) the MDL.
    2. The MDL must be less than the permit limit.
    3. The MDL is calculated annually by following the EPA 40 CFR Part 136 Appendix B protocol.
       1. All method blanks associated with reported results are entered into the WDNR supplied spreadsheet.
       2. Two spiked blanks are analyzed each quarter and entered into the WDNR supplied spreadsheet.
13. QC Data Assessment, Acceptance Criteria, and Corrective Actions and Contingencies for Out-of-Control QC Measures
    1. Quality control samples summary:

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| QC Test | Criteria |
| Calibration curve | Slope between -54 and -60 |
| ICV/LCS | 90 – 110% true value |
| Method Blank | ≤ Highest of:  LOD,  5% permit limit, or  10% sample conc’n |
| CCV (if more than 20 samples are run) | 90 – 110% true value |

* 1. If the calibration slope is not between -54 and -60, recalibrate. The slope between each standard should also be between -54 and -60. Corrective actions may also include preparing new calibration standards or replacing the probe membrane.
  2. If the ICV/LCS is not 90-110% of the true value, re-make the ICV/LCS solution and reanalyze. If the ICV/LCS still does not pass, re-calibrate.
  3. If the method blank is not ≤LOD (or 5% of the permit limit or 10% sample concentration), reanalyze. If it is still out of range, qualify the data.
  4. If the CCV is not 90-110% of the true value, take corrective action such as re-make the CCV solution and reanalyze. If the CCV still does not pass, re-calibrate.
  5. Qualify all sample results with method blank or CCV exceedances on the bench sheet and the eDMR.
     1. Samples that fail the Quality Control will have to be qualified back to the last date that the quality control met the above conditions. Include a lab comment on the DMR.
  6. The Proficiency Testing (PT) sample must be within the criteria of the provider. If the criteria limits are not met, the technician must immediately order another sample to be analyzed.
  7. For any of the above items or if there are any other obvious errors or deviations from the standard operating conditions, complete the Corrective Actions Log and resolve the problem. Notify the Supervisor.
     1. If results are unacceptable, take appropriate corrective action. This may include changing the probe membrane, acid washing all containers, checking the water source, checking expiration dates, and documenting any changes or adjustments made.
     2. Complete the Corrective Actions in the log sheets. Enter in all information as completely as possible, even if the short-term reasons for failures are not clear.
     3. Seek help from an outside source if specific QC issues cannot be resolved. These sources may be another lab, the Wisconsin Rural Water Association wastewater trainer, or the facility’s lab auditor.

1. Pollution Prevention
   1. Consider environmental impact when purchasing materials, handling chemicals, and disposing of wastes.
   2. Prevent pollution at the source whenever possible.
2. Waste Management
   1. All laboratory waste, excess reagents, and samples must be disposed of in a manner that is consistent with applicable rules and regulations.
3. References
   1. Standard Methods for the Examination of Water and Wastewater, Method 4500-NH3, 1997.
   2. Evaluation of Preliminary Distillation Prior to Ion Selective Electrode Determination of Ammonia in Municipal Wastewater Effluent, Wisconsin State Laboratory of Hygiene, University of Wisconsin-Madison. March 1986.
4. Disclaimer
   1. The mentioning of company or product names does not constitute endorsement by the Wisconsin Department of Natural Resources or the authors.