

Ammonia, SM 4500-NH₃ D, 22nd edition (1997) – Ammonia-Selective Electrode Method

40 CFR 136 Table 1B says the approved methodology is manual distillation⁶ or gas diffusion (pH>11) followed by any of the following: Nesslerization, titration, electrode, manual phenate or automated phenate. Footnote 6 states: “Manual distillation is not required if comparability data on representative effluent samples are on file to show that this preliminary distillation step is not necessary: however, manual distillation will be required to resolve any controversies. **In general, the analytical method should be consulted regarding the need for distillation.** If the method is not clear, the laboratory may compare a minimum of 9 different sample matrices to evaluate the need for distillation. For each matrix, a matrix spike and matrix spike duplicate are analyzed both with and without the distillation step. (A total of 36 samples, assuming 9 matrices). If results are comparable, the laboratory may dispense with the distillation step for future analysis. Comparable is defined as < 20% RPD for all tested matrices). Alternatively the two populations of spike recovery percentages may be compared using a recognized statistical test.”

Standard Methods

- 4500-NH₃ A.1 – In general, direct manual determination of low concentrations of ammonia is confined to drinking waters, clean surface or groundwater and good-quality nitrified wastewater effluent.
- 4500-NH₃ D.1.b. – Sample distillation is unnecessary.

Tennessee recommends that one sample is run yearly to compare the distilled and undistilled results and that the results are within 20% of each other.

- Note – if distilled sample and undistilled sample are below detection limit, you cannot calculate the percent difference.

Initial Demonstration of Capability (DOC)

- 1020 B. 1 – As a minimum, include a reagent blank and at least 4 LFBs at a concentration between 10 times the MDL and the midpoint of a calibration curve.
- 4020 B.1.a. - each analyst must run a known standard concentration at least four times and compare limits listed in the method.
- **Real people language – each operator running this test needs to calibrate the probe and analyze 4 samples of an NH₃ Standard at a concentration around 1.0 mg/L**
 - **Keep a folder for each analyst, keep a copy here**
 - **Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods.**
 - **Recommend backup analyst do this once a year.**

Method Detection Limit (MDL)

- 1020 B. 4 – As a starting point for selecting the concentration to use when determining the MDL, use an estimate of five times the estimated true detection level (5 x 0.03 mg/L = 0.15 mg/L).
 - Ideally, prepare and analyze at least seven (7) portions of this solution over a 3-day period to ensure that the MDL determination is more representative of routine measurements as performed in the laboratory.
 - The replicate measurements should be in the range of one to five times the estimated MDL, and recoveries of the known addition should be between 50 and 150%, with %RSD (relative standard deviation) values ≤ 20%.

- 4020 B.1.b. – Verify MDL at least **annually**.
 - Ideally use pooled data from several analysts rather than data from one analyst.
- **Real people language – have several operators, who run this test, analyze an NH₃ Standard at a concentration of 0.15 mg/L over several days with a total of at least 7 samples**
 - **Joe analyzes 3 samples on Monday**
 - **Bob analyzes 3 samples on Tuesday**
 - **Mary analyzes 3 samples on Wednesday**
- **Run this once a year**

Initial Calibration Verification (ICV)

- 1020 B.11.b. – Perform initial calibration using at least three concentrations of standards for linear curves.
- 4020 B.2.a. – Calibrate initially with at least one blank and three calibration standards.
 - The appropriate linear correlation coefficient for standard concentration-to-instrument response should be greater than or equal to 0.995.
 - The back-calculated and true concentrations should agree within $\pm 10\%$.
- 4500-NH₃ D.4.a. – Prepare a series of standard solutions covering the concentrations of 1000, 100, 10, 1 and 0.1 mg NH₃-N/L
- 4500-NH₃ D.4.b. – calibrate from lowest to highest concentration. Wait until the reading has stabilized (at least 2-3 min) before recording millivolts for standards and samples containing ≤ 1 mg NH₃-N/L.
- 4500-NH₃ D.4.c. – If the electrode is functioning properly, a tenfold change of NH₃-N concentration produces a potential change of about 59 mV.
- **Real people language – calibrate according to manufacturer's instructions with at least 3 standards that will bracket your sample range daily (day of).**
- **Analyze a 10 mg/L standard as a sample after calibration and before samples to verify initial calibration (ICV)**

Method Blank – goes through distillation if you distill

- 1020 B.5.– A reagent blank (method blank) consists of reagent water and all reagents that normally are in contact with a sample during the entire analytical procedure.
- 4020 B.2.d. – Include at least one method blank daily or with each **batch of 20** or fewer samples, whichever is more frequent.
 - If any method blank measurements are at or above the reporting level, take immediate corrective action.
- **Real people language – analyze distilled water as a sample by going through distillation (if you still distill samples) and using ISA (ion strength adjuster).**
 - **Target value is less than reporting limit**
 - **Reporting limit will be equal to your Method Detection Limit (MDL)**
 - **Run on a 5% basis (see batch size for more information).**

Laboratory Fortified Blank (LFB) – goes through distillation if you distill

- 1020 B.6.– A laboratory-fortified blank is a reagent water sample to which a known concentration of the analyte of interest has been added.

- Sample batch = 5% basis = 1 every 20 samples
- Use an added concentration of at least 10 times the MDL, less than or equal to the midpoint of the calibration curve.
- 4020 B.2.e. – Calculate percent recovery, plot control charts and determine control limits (see Control Charts below)
- **Real people language – analyze an NH₃ standard at a concentration of 5.0 mg/L**
 - **Run on a 5% basis (see batch size for more information).**

Duplicate

- NONE

Laboratory Fortified Matrix (LFM)/Laboratory Fortified Matrix Duplicate (LFMD) – goes through distillation if you distill

- 1020 B.7.– A laboratory fortified matrix (LFM) is an additional portion of a sample to which a known amount of the analyte of interest is added before sample preparation
 - The LFM is used to evaluate analyte recovery in a sample
 - Sample batch = 5% basis
 - Add a concentration that is at least 10 times the MRL (minimum reporting level), less than or equal to the midpoint of the calibration curve.
 - Preferably use the same concentration as the LFB
- 4020 B.2.g. – When appropriate for the analyte, include at least one LFM/LFMD daily or with each batch of 20 or fewer samples
 - Add a known concentration of analyte to a randomly selected routine sample
 - Calculate percent recovery and relative percent difference, plot control charts and determine control limits for spikes at different concentrations (see Control Charts below)
- **Real people language – add a known amount of ammonia to a sample and expect that amount to be added to your sample concentration and repeat process for LFMD.**
 - **Run on a 5% basis (see batch size for more information).**
 - **Calculate RPD between spiked sample and spiked duplicate, target value should be close to the first value and have a small RPD (less than 20%).**
 - **Spike volume should be less than 1% of the volume.**
 - **Example: spike with 1 mL of 1000 mg/L into 100 mL sample will equal a 10 mg/L increase in ammonia concentration.**

Continuing Calibration Verification (CCV)

- 1020 B.11.c. – Analysts periodically use a calibration standard to confirm that the instrument performance has not changed significantly since initial calibration.
 - Verify calibration by analyzing one standard at a concentration near or at the mid-point of the calibration range.
- 4020.B.2.b. – Verify calibration by periodically analyzing a calibration standard and calibration blank during a run – typically after each batch of 10 samples and at the end of the run.
 - For the calibration verification to be valid, check standards must be within 10% of its true value
- **Real people language – analyze 10 mg/L at the end of all samples daily (day of).**

Control Charts – 1020 B.13.

- **Real people language**
 - **Create and maintain control charts if you have 20-30 data points within 90 days.**
 - **If you do not meet the above criteria, follow QC Acceptance Criteria below.**

Corrective Action - 1020 B.5., B.8., & B.15.

QC Acceptance Criteria

- Blanks < MDL
- LFB \pm 15%
- ICV/CCV \pm 10%
- LFM/LFMD \pm 20%
- RPD < 20%
- Reporting limit = MDL

Batch Size

- For samples that need to be analyzed on a 5% basis (1 for every 20 samples or once per month, whichever is more frequent) follow these criteria:
 - If a permit stated that 3 analyses per week, we would allow for a duplicate to be analyzed at least once per month.
 - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
 - If a permit stated 5 analyses per week, we would allow twice a month.
 - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!
 - If sampling only once a month, need to run QC once a month.

Calculations

- % Recovery for LFB
 - = $\frac{\text{LFB Result}}{\text{Expected Concentration}} \times 100\%$
- RPD – relative percent differences for duplicates and LFM/LFMD
 - = $\frac{\text{Difference between sample and duplicate}}{\text{Average of the sample and duplicate}} \times 100\%$
- % Recovery for LFM – when using less than or equal to 1% spike volume compared to sample volume
 - = $\frac{\text{LFM Result} - \text{Sample Result}}{\text{Actual Concentration of spike}} \times 100\%$