Ammonia, SM 4500-NH_3 D-2011, (SM 22nd edition) – Ammonia-Selective Electrode Method

40 CFR 136 Table 1B says the approved methodology is manual distillation[6] 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-NH_3 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-NH_3 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

- 1020 B. 1 – At 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.
    - Upper Control Limit = Mean + 3(Standard deviation)
    - Lower Control Limit = Mean - 3(Standard deviation)
- 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 analyze 4 samples of an NH3 Standard at a concentration around 1.0 mg/L**
    - **Keep a copy of the analyst's DOC in his personal folder.**

Method Detection Limit

- 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).
    - 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.
- **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**
- Annual (every 13 months) verification required using data collected within the past 24 months. Include all data from the On-going Data Collections and the initial MDL determination where appropriate (<24 months old). A minimum of 7 data points are required for ***both spiked samples (MDL_s) and method blanks (MDL_b)***.
- Refer to the MDL Examples and EPA Guidance for complete requirements.
- Refer to document titled "Method Update Rule – Method Detection Limit Math 2019" on Fleming Training Center website for MDL Calculator.

Initial Calibration Verification

- 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 ± 10%.
- 4500-NH_3 D.4.a. – Prepare a series of standard solutions covering the concentrations of 1000, 100, 10, 1 and 0.1 mg NH_3-N/L
- 4500-NH_3 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 NH_3-N/L.
- 4500-NH_3 D.4.c. – If the electrode is functioning properly, a tenfold change of NH_3-N concentration produces a potential change of about 59 mV.
- **Real people language – calibrate with at least 3 standards *daily*.**

Method Blank

- 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 MDL**
    - **Run on a 5% basis, see batch size for more information**

Laboratory Fortified Blank

- 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
- **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)

- 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 = 1 every 20 samples
  - 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 (ideally from a second source) to a randomly selected routine sample without increasing its volume by more than 5%
  - Calculate percent recovery and relative percent difference, plot control charts and determine control limits for spikes at different concentrations
- **Real people language – add a known amount of ammonia to a sample and expect that amount to double your sample concentration and repeat process for LFMD.**

- **Results from 90-110% recovery are acceptable.**
  - **If your sample value is 1 mg/L, you want to add 1 mg/L to double your sample concentration**
    - **Pour up 100 mL sample**
    - **Insert probe**
    - **Add ion strength adjuster**
    - **Take reading, this is your unspiked sample value**
    - **Add 1 mL of 100 mg/L to sample**
    - **Take another reading, this is your spiked sample value**
  - **Example from Hach's Nitrogen, Ammonia Method for ISE Electrode(Method 10001):**

Standard additions method (sample spike)
To verify measurement accuracy, perform a standard addition spike on the sample. The spike should roughly double the measured concentration without significantly diluting the sample.

To perform a standard addition sample:

1. Use the *Spike volumes for standard additions* table to determine the concentration and volume of standard to spike the sample. The volume of sample transferred must be accurate.
2. Add the amount and concentration specified in the *Spike volumes for standard additions* table to the 100 mL of sample.
3. After adding the standard, proceed with the calculations. Results from 90-110% recovery are typically considered acceptable. Calculate percent recovery as follows:

$$\% \text{ Recovery} = \frac{100(X_s - X_u)}{K}$$

Where:
X_s = measured value for spiked sample in mg/L

X_u = measured value for unspiked sample adjusted for dilution by the spike, in mg/L

K = known value of the spike in the sample in mg/L

Continuing Calibration Verification

- 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, and calibration blank results must not be greater than one-half the reporting level
- **Real people language – analyze 10 mg/L at the end of all samples daily.**

Control Charts – 1020 B.13.

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

Batch Size –

- For samples that need to be analyzed on a 5% basis or once for every 20 samples 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 suggest 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!!

Calculations –

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