Timberline Ammonia-001

Determination of Inorganic Ammonia by Continuous Flow Gas Diffusion and Conductivity Cell Analysis

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1. SCOPE and APPLICATION

1.1. Ammonia gas permeation through a hydrophobic membrane is used to determine ammonia concentration in aqueous solutions.

1.2. For the determination of total ammonia from solutions that contain organic nitrogen (Kjeldahl nitrogen) and inorganic ammonia in aqueous and solid samples, a Kjeldahl digestion is required prior to analysis.

1.3. Detection limits and linear ranges for organic and inorganic ammonia will vary with the matrices. Tables B and C in Section 16 provide pooled results for method detection limit (MDL) and minimum level (ML) determined from the inter-laboratory method validation study for 4 inch or 10 inch membranes. However, actual method detection limits and linear working ranges will be dependent on the sample matrix, instrumentation, and selected operating conditions.

1.4. Users of the method data should state the data-quality objectives prior to analysis. Users of the method must document and have on file the required initial demonstration of capability data described in Section 9.2 prior to using the method for analysis.

2. SUMMARY

2.1. An aqueous sample is combined with 1-15% sodium hydroxide to attain a pH above 11 producing ammonia in a non-ionized form in solution.

$$NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \rightarrow NH_{3(g)} + H_2O_{(aq)}$$

2.2. This solution is conveyed to a membrane assembly and the gaseous ammonia in the aqueous sample migrates through the hydrophobic membrane into the borate buffer absorption solution, which is transported to a conductivity cell.

2.3. The measured changes in conductivity are used to quantitate ammonia in the sample using an external calibration.

3. DEFINITIONS

3.1. Ammonia Stock Standard Solution: A concentrated solution containing method analyte prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.2. Calibration Blank: A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the ammonia analyzer.

3.3. Calibration Standard: A solution prepared from the dilution of stock standard solutions. These solutions are used to calibrate the instrument response with respect to analyte concentration.

3.4. Continuing Calibration Verification (CCV): Ammonia standard that has a concentration between the lower calibration standard and upper calibration standard. A CCV will be run at least once per batch.

3.5. Control Charts: Graphical charts that contain the expected value (the central line) and the acceptable range of occurrence. The acceptable range is determined from the control limits and warning limits. Refer to Part 1000 of Standard Methods for the Examination of Water and Wastewater for further explanation and guidance.

3.6. Dynamic Range (DR): The concentration range over which the instrument response to an analyte is second order quadratic. This range is defined by the concentration range between the lowest concentration standard and the highest concentration standard.

3.7. Instrument Detection Limit (IDL): The concentration equivalent to the analyte signal which is equal to replicate measurements of the calibration blank.

3.8. Initial Demonstration of Capability (IDC) also called a Initial Precision and Recovery (IPR): IDC/IPR are run by analysts with no experience with this method before they run any samples to verify their capability with the method or when significant maintenance or modifications are performed on the instrument. A laboratory fortified blank (LFB) is analyzed four times, the mean recovery and standard deviation are calculated and compared to the limits listed in this method for IDC/IPR.

3.9. Instrument Performance Check (IPC) Solution: A solution of method analyte, used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.10. Laboratory Fortified Blank (LFB): An aliquot of ammonia free reagent water to which known quantities of ammonia is added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.11. Laboratory Fortified Sample Matrix/Duplicate (LFM/LFMD) also called a Matrix Spike/Duplicate (MS/MSD): An aliquot of an environmental sample to which known quantities of ammonia is added in the laboratory. The LFM/LFMD are analyzed exactly like a sample, and there purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM/LFMD corrected for background concentrations.

3.12. Laboratory Reagent Blank (LRB): An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents or apparatus.

3.13. Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero. Full requirements are listed in 40 CFR Part 136 Appendix B.

3.14. Minimum Level (ML): Minimum level is determined by multiplying the MDL by 3.18 and rounding the product to the number nearest to 1 or 2 or 5 x 10^n, where n is a positive or negative integer. The minimum level is used to determine the lowest standard concentration that can be used for the instrument.

3.15. Ongoing Demonstration of Capability (ODC) also called Ongoing Precision and Recovery (OPR): ODC/OPR are performed at least once per sample batch to demonstrate proficiency with the method. Reagent water is spiked with known quantities of ammonia. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

3.16. Sample Batch: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch. A batch cannot span between laboratory work days (24 hrs). New batches must be started each laboratory work day.

3.17. Solid Sample: For the purpose of this method, a sample taken from material classified as soil, sediment or sludge that is digested by the Total Kjeldahl Nitrogen method.

3.18. Total Kjeldahl Nitrogen: Digestion method of water or solid samples by methods currently approved in 40 CFR 136, Table IB.

3.19. Water Sample: For the purpose of this method, a sample taken from one of the following sources: surface, ground, storm runoff, industrial or domestic wastewater.

4. INTERFERENCES

4.1. Volatile amines can diffuse through the hydrophobic membrane to produce a conductivity response. Generally, interference from low molecular weight amines is not a practical problem because their natural occurrence is so limited.

4.2. Chloramines can decompose to produce ammonia.

4.3. Deionized water used in reagents and standards must be high quality and ammonia-free to avoid interference.

5. SAFETY

5.1. This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of any chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6. EQUIPMENT AND SUPPLIES

6.1. Sample Containers: As per current 40 CFR Part 136 Table II, polyethylene, fluoropolymer or glass..

6.2. Class A Volumetric Flasks: various sizes used for preparation of standards.

6.3. Test Tubes: 15 x 85 mm; used in autosampler.

6.4. Analytical Balance: analytical, capable of accurately weighing to 0.0001 ± 0.00005 g.

6.5. pH METER: double junction electrode; used when adjusting the pH of the boric acid solution.

6.6. Ammonia Analyzer with gas permeation cell and conductivity detector: Timberline Instruments TL-2800 Ammonia Analyzer or an equivalent instrument that uses the same chemistry/determinative techniques and can meet the QC performance criteria set in the method.

7. REAGENTS AND STANDARDS

7.1. Reagent Water – Deionized water that does not contain measurable quantities of ammonia above the detection level of the dynamic range or any interfering volatile conductive compounds. This water will be used for all standards, calibration zero, LRB, LFB, and sample dilutions preparation.

(Note: Prolonged storage of reagent water will expose it to ammonia absorption from the laboratory environment. Prepare fresh as needed.)

7.2. Caustic Solution: Sodium Hydroxide (NaOH) or Potassium Hydroxide- 50% (w/v) solution. Prepare by weighing a known amount of ACS or better grade sodium hydroxide or potassium hydroxide to the nearest gram and add slowly to a known volume of reagent water in mL with the ratio of 1 gram sodium hydroxide or potassium hydroxide to 1 mL of reagent water. Mix thoroughly in a beaker with a magnetic stirrer.

(Caution: Reaction produces excessive heat and is caustic to unprotected skin. Prolonged storage of reagent water will expose it to ammonia absorption from the laboratory environment. Prepare fresh as needed.)

7.3. Caustic Working Solutions – 1-15% (w/v). Select caustic solution as needed per sample characteristics. Selection is based on the caustic solutions ability to raise the pH of the sample to a point that free ammonia is formed to diffuse through the membrane. Typically, with most ammonia concentrations, the 5% caustic solution is utilized. Other caustic solution concentrations may be needed based on higher ammonia concentrations, lower ammonia concentration or water matrix. Final caustic solution concentration will be based on ammonia concentration in the sample, the water matrix and QC performance requirements.

7.3.1. 1 %: Dilute 20 ml of 50% (w/w) sodium hydroxide or potassium hydroxide solution to 1 L with reagent water. Mix well by inversion. Prepare fresh weekly

7.3.2. 5 %: Dilute 100 ml of 50% (w/w) sodium hydroxide or potassium hydroxide solution to 1 L with reagent water. Mix well by inversion. Prepare fresh weekly.

7.3.3. 10%: Dilute 200 ml of 50% (w/w) sodium hydroxide or potassium hydroxide solution to 1 L with reagent water. Mix well by inversion. Prepare fresh weekly.

7.3.4. 15%: Dilute 300 ml of 50% (w/w) sodium hydroxide or potassium hydroxide solution to 1 L with reagent water. Mix well by inversion. Prepare fresh weekly.

7.4. Boric Acid Solution 10,000 ppm boric acid (H_3BO_3). Add 10 ± 0.001 g of ACS grade or better boric acid in a 1 L volumetric flask and dilute to volume with reagent water. Mix until the boric acid has completely dissolved in the solution.

(Note: Prolonged storage of Boric Acid will expose it to ammonia absorption from the laboratory environment. Prepare fresh as needed.)

7.5. Ammonium Hydroxide (NH_4OH) - 1.0 N. Transfer 135 mL of 28% ACS grade or better ammonium hydroxide to ~ 100 mL of reagent water in a 1 L volumetric flask. Dilute to the mark with reagent water and mix well. Make fresh monthly.

7.5.1. Ammonium Hydroxide Working Solutions - 0.01 N Ammonium hydroxide. Transfer 1 mL of 1 N ammonium hydroxide to 100 mL volumetric flask. Dilute to volume with reagent water. Mix well by inversion. Prepare fresh weekly.

7.6. Buffer Solutions – pH adjusted Boric acid, Select boric acid solution as needed per sample characteristics. Typically, with most ammonia concentrations, the 250 ppm Buffer Solution is utilized. Other Buffer Solution concentrations may be needed based on higher ammonia concentrations (100 ppm ammonia or greater) or lower ammonia concentration (0.1 ppm or lower).Final Buffer Solution concentration will be based on ammonia concentration in the sample and QC performance requirements.

7.6.1. 100 ppm. Transfer 10 mL of the 10,000 ppm boric acid solution to a 2 L beaker. Add ~ 975 mL of reagent water. While stirring adjust the pH to 6.5-7 using 0.01 or 0.02 N ammonium hydroxide solution. Prepare fresh weekly

7.6.2. 250 ppm. Transfer 25 mL of the 10,000 ppm boric acid solution to a 2 L beaker. Add ~ 930 mL of reagent water. While stirring adjust the pH to 6.5-7 using 0.01 or 0.02 N ammonium hydroxide solution. Prepare fresh weekly.

7.6.3. 400 ppm. Transfer 40 mL of the 10,000 ppm boric acid solution to a 2 L beaker. Add ~ 875 mL of reagent water. While stirring adjust the pH to 6.5-7 using 0.01 or 0.02 N ammonium hydroxide solution. Prepare fresh weekly.

7.7. Ammonia Standard Solutions

7.7.1. Calibration Blank: Reagent water. Replace daily or per analytical batch.

7.7.2. Ammonia Stock Solution: Accurately weigh out, to the nearest 0.001 ± 0.0005 g, dried (at 100º C) ACS grade ammonium sulfate $(NH_4)_2SO_4$ or ammonium chloride (NH_4Cl) to make the desired ammonia concentration in Table 1, below. Transfer the reagent to a 1L volumetric flask and dilute to volume with reagent water. Mix well by inversion. Prepare fresh monthly.

Table 1: Ammonia Stock Standards

Ammonium Salt	**Ammonium Chloride**	**Ammonium Sulfate**
Molecular Weight	53.49	132.14
Ammonia-N Concentration	**Ammonia Salt Weight (g)**	
2000 mg/L	7.641	18.877
500 mg/L	1.910	4.719
100 mg/L	0.382	0.944
10 mg/L	0.038	0.094

7.7.3. Calibration Standards –A minimum of 5 calibration concentrations along with a calibration blank will be required to prepare the initial calibration curve and

ongoing calibration curve. The calibration curve fit can be either linear or quadratic, but must have a R value of 0.995 or higher. Prepare the calibration standards over the dynamic range of interest as defined in Table 2 from dilutions of the ammonia stock solution. The calibration standards must be prepared using regent grade water and prepared fresh weekly.

Table 2: Membrane Dynamic Range		
Membrane Type	**Membrane Length (Inches)**	**Concentration Calibration Dynamic Range (Ammonia-N mg/L)**
High Sensitivity	10	2-0.020
Standard	4	500-0.0500

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT, DIGESTION and STORAGE

8.1. Sample Collection

8.1.1. Collect and store ammonia or Kjeldahl samples in glass or high density polyethylene bottles. Most reliable results are obtained on fresh samples.. For preservation for up to 28 d, preserve samples by acidifying to pH <2 with sulfuric acid upon collection and store at 6°C to just above 0°C, without freezing

8.2. Total Kjeldahl Nitrogen Digestion

8.2.1. Digest Kjeldahl sample as per approved method in 40 CFR Part 136 Table IB (e.g. 4500-N_{org} -1997). Digested sample is stored in a covered borosilicate container at room temperature until analyzed. Analyze within 4 hours of digestion completion.

9. QUALITY CONTROL

9.1. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. Control charts of each QC check will be kept and appropriate control limits calculated. Any QC result that fails to meet control criteria must be documented and corrective action, including a root cause analysis, must be performed.

9.2. Initial Demonstration of Capability: A laboratory fortified blank whose concentration is between the 10% and 50% of the dynamic range is analyzed four times. The mean recovery and standard deviation are calculated and evaluated for acceptance.

9.2.1. Acceptance Criteria: IDC control limit for the laboratory is based on the limits determined in this method and shall not exceed 82%-110 % with a percent Relative Standard Deviation less than 8%.

9.2.2. Corrective Action: If the IDC recovery falls outside of these limits, the analyst or instrument is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the IDC repeated until passed.

9.3. Continuing Calibration Verification: At least one CCV standard will be prepared so as to have a concentration in the dynamic range of the instrument. The CCV will be run at least once per each batch. The CCV percent recovery is calculated and evaluated for acceptance.

9.3.1. Acceptance Criteria: CCV control limit for the laboratory is based on the limits determined in this method and shall not exceed 90%-110 %.

9.3.2. Corrective Action: If the CCV recovery falls outside of these limits, the batch is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the sample batch repeated.

9.4. Laboratory Reagent Blank: A LRB is analyzed as a sample at least once per batch. The LRB concentration result will be evaluate for acceptance.

9.4.1. Acceptance Criteria: The LRB concentration result will be below the lowest calibration standard in the dynamic range.

9.4.2. Corrective Action: If the LRB falls outside of the acceptance limit, the batch is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the sample batch repeated.

9.5. Laboratory Fortified Blank: A LFB with a concentration of ammonia between 10% and 50% of the dynamic range is analyzed at least once per batch. The LFB concentration result will be evaluate for acceptance.

9.5.1. Acceptance Criteria: LFB percent recovery is based on the limits determined in this method and shall not exceed 87%-104 %.

9.5.2. Corrective Action: If the LFB recovery falls outside of these limits, the batch is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the sample batch repeated.

9.6. Laboratory Fortified Sample Matrix Spikes (LFM/LFMD): A duplicate set of ammonia or Kjeldahl samples are spiked with a known amount of ammonia with a concentration that is between 10% and 50% of the dynamic range

9.6.1. Acceptance Criteria: The LFM/LFMD percent recovery is based on the limits determined in this method and shall not exceed 84%-115 %. The relative percent difference (RPD) shall not exceed 20%.

9.6.2. Corrective Action: If the LFM and LFMD percent recovery or the RPD fall outside of these limits, the batch is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the sample batch repeated.

9.7. Ongoing Demonstration of Capability (ODC): A LFB with a concentration of ammonia between 10% and 50% of the dynamic range is analyzed at least once per batch. The LFB percent recovery will be charted by control charts and be evaluated for acceptance.

9.7.1. Acceptance Criteria: LFB percent recovery must stay within the control limits calculated for the control chats.

9.7.2. Corrective Action: If the LFB percent recovery falls outside of these control

limits, the batch is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the sample batch repeated.

10. PROCEDURE

10.1. Sample Analysis Sequence: Typical sample analysis sequence .

10.1.1. Instrument Start Up

10.1.2. Calibration zero

10.1.3. Calibration standards, 1-5

10.1.4. LRB

10.1.5. LFB

10.1.6. Sample used for LFM/LFMD

10.1.7. LFM

10.1.8. LFMD

10.1.9. Samples (First half of batch)

10.1.10. CCV

10.1.11. Samples (Second half of batch)

10.1.12. Repeat CCV (Optional)

10.2. Instrument Preparation

10.2.1. Start the instrument as per the Timberline TL2800 instrument manual (or an equivalent instrument that uses the same chemistry/determinative techniques and can meet the QC performance criteria set in the method.).

10.2.2. Prepare quality control samples.

10.3. Sample Preparation

10.3.1. Remove refrigerated samples from the refrigerator and warm to room temperature.

10.3.2. Kjeldahl digested samples are diluted 10:1 with the reagent water to achieve a nominal 10% (wt) sulfuric acid.

10.3.3. Spike the LFB and LFM/LFMD per QC spiking requirement.

10.3.4. Prepare CCV standard.

10.3.5. Prepare LRB water.

10.3.6. Prepare a calibration zero that is ammonia free water.

10.3.7. Prepare five (5) calibration standards that bracket the dynamic range of the analysis. The lowest concentration standard must be at or above the ML.

10.3.8. Transfer aliquots of all samples to autosampler tubes.

10.4. Initial Calibration:

10.4.1. Initial calibration is performed at the beginning of each batch.

10.4.2. Calibrate instrument with calibration zero and five calibration standards of ammonia.

10.4.3. Apply linear or polynomial curve-fitting statistics, as appropriate, to analyze the concentration–instrument response relationship.

10.4.3.1. Acceptance Criteria: The linear or nonlinear correlation coefficient for standard concentration-to-instrument response shall be greater than or equal to 0.995.

10.4.3.2. Corrective Action: If the correlation coefficient falls outside of the limit, the initial calibration is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the initial calibration repeated.

10.4.4. Back calculate the standard concentration of each calibration point using the calibration equation determined by the curve fitting statistics.

10.4.4.1. Acceptance Criteria: The back-calculated and true concentrations should agree within ± 10% and cannot exceed ± 15%.

10.4.4.2. Corrective Action: If the standard back calculations fall outside of the limits, the initial calibration is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the initial calibration repeated.

10.5. Continuing Calibration Verification:

10.5.1. A CCV is analyzed at the midpoint of the batch sample set. The CCV is prepared from a different source (chemical lot) than that used for the calibration standards.

10.5.1.1. Acceptance Criteria: CCV control limit for the laboratory is based on the limits determined in this method and shall not exceed 90%-110 %.

10.5.1.2. Corrective Action: If the CCV recovery falls outside of these limits, the batch is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the sample batch repeated.

10.6. Sample Analysis

10.6.1. Operate the instrument as per manual instructions.

10.6.2. Report the values of all samples and QC samples analyzed.

10.6.3. Determine the appropriate timing parameters and integration times for the peaks.

10.6.4. Load the filled autosampler tubes into the autosampler and start the injection sequence.

10.6.5. Calibrate the system by generating a calibration curve with 5 standards and an instrument blank.

Note: (For Kjeldahl samples) The samples need to be run with a 10-15% (w/v) NaOH solution to neutralize the acid (22.5% molar excess).

10.6.6. Analyze the samples and QC checks. The sample concentration should not exceed the range of the initial calibration curve. If the sample does fall outside the range of the calibration, a new calibration curve should be run to include the range of the sample or the sample should be diluted with reagent water to a concentration within the dynamic range.

11. CALCULATIONS / DATA REDUCTION

11.1. Calculate the ammonia concentrations using the initial calibration curve generated. The batch should be reviewed for any incorrect peak identification or poor integration.

11.2. Samples and QC sample final concentrations are calculated as follow :

11.2.1. $$(s \text{ x Diluted Sample Concentration}) = \text{Sample Concentration}$$

$$s = \text{Dilution Correction}$$

11.3. Laboratory Reagent Blank (LRB); The LRB will be run at a minimum of once per sample batch. Results are reported as sample concentration and should be at or below the ML. Laboratory Fortified Blank (LFB): The LFB percent recovery is calculated as follows:

11.3.1. Percent Recovery for LFB

$$\left(\frac{\text{Experimental Value}}{\text{Expected Value}}\right)*100 = \text{Percent Recovery LFB}$$

Experimental Value = LFB Concentration determined experimentally

Expected Value = Known LFB concentration

11.4. Initial Demonstration of Capability (IDC) is determined by calculating for four LFBs, the mean percent recovery and standard deviation.

11.4.1. $$\overline{X}_{(\text{Mean})} = \left(\sum_i X_i\right) \Big/ n$$

11.4.2. $$S_{(\text{Standard Deviation})} = \left[\frac{\sum_{i=1}^{n} (X_i - \overline{X})^2}{n-1}\right]^{\frac{1}{2}}$$

11.4.3. $$\% \text{ Relative Standard Deviation} = \left(S/\overline{x}\right) \times 100$$

11.5. Laboratory Fortified Sample Matrix -Laboratory Fortified Sample Matrix Duplicate (LFM-LFMD): The LFM/LFMD percent recoveries and RPD are calculated as follows:

11.5.1. Percent Recovery for LFM

$$\left(\frac{\text{Spiked Value} - (s \times \text{Unspiked Value})}{\text{Concentration of Spike}}\right) * 100 = \text{Percent Recovery LFM}$$

Spiked Value = LFM concentration determined experimentally
Unspiked Value = Concentration of sample before spiking
s=Dilution Correction

11.5.2. Relative Percent Difference (RPD)

$$\left(\frac{(\text{LFM-LFMD})}{\left(\frac{\text{LFM+LFMD}}{2}\right)}\right) * 100 = \text{RPD}$$

LFM = Concentration determined for LFM
LFMD = Concentration determined for LFM duplicate

11.6. Continuing Calibration Verification (CCV): Check standards will be prepared so as to have a concentration between the lower and upper calibration of the dynamic range.

11.6.1. $$\left|\frac{\text{CCV Value - Initial Standard Value}}{\text{Initial Standard Value}}\right| * 100 = \text{Percent Difference}$$

11.7. Control Charts: Control charts will be kept for LFB and LFM percent recovery per sample batch, LFM and LFMD RPD per sample batch, and LRB concentration. Trends will be calculated to show whether the values determined go outside the control limits. If these trends exceed control limits of this method, then corrective action (Root Cause Analysis) must be performed.

11.8. Corrective Action (Root Cause Analysis): The laboratory analyst(s) and laboratory management will perform a root cause analysis for any QC failures. The analysis will have at a minimum the following areas described in detail:

11.8.1. Identify the problem: Identify the QC failure. Include instrument, reagent, sampling, personnel and any other problems.

11.8.2. Investigate to identify the root cause: Determine how each problem identified interacted with each other to create the QC problem.

11.8.3. Come up with the solution: Develop an encompassing solution to address all problems that created the QC failure.

11.8.4. Implement the solution: Develop an implementation plan that includes all components of the developed solution and have laboratory management implement it.

11.8.5. Document the solution: Document all corrective action steps taken under laboratory management implementation of the corrective action.

11.8.6. Communicate the solution: Develop training and management programs to communicate and evaluate all personnel included in the corrective action solution.

11.8.7. Evaluate the effectiveness of the solution: Document QC results in trend charts and laboratory staff performance to validate corrective action solution.

12. METHOD PERFORMANCE

12.1. Method Detection Limit and Method Limit Study(MDL-ML):

12.1.1. MDL and ML are determined for the initial start-up of the instrument prior to any sample analysis and when the instrument has had maintenance or repairs of the membrane, detector or any other internal analytical components. These requirements do not include consumable supplies or reagents. Analytical procedures for the MDL and ML are listed in the current promulgated 40 CFR 136 Appendix B.

12.1.2. Prepare seven samples at three to five times the estimated MDL concentration. The MDL samples are prepared in the Synthetic

12.1.3. Prepare and analyze the MDL standards as described in Section 10.

12.1.4. Calculate the average concentration found in µg/L or mg/L, and the standard deviation of the concentration(s) for each analyte .

12.1.5. The MDL is calculated as Students t for the 99th percentile times the standard deviation of the MDL replicate results, following the procedure at 40 CFR 136, Appendix B.

12.1.6. The ML is calculated as per “Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; National Primary Drinking Water Regulations; and National Secondary Drinking Water Regulations: Analysis and Sampling Procedures”.

12.1.7. $(\text{MDL} \times 3.18) = \text{ML}$

12.2. Instrument Detection Limit Study:

12.2.1. Prepare three laboratory reagent blanks.

12.2.2. Analyze the IDL blanks as per Section 10.

12.2.3. The IDL is calculated as per Standard Methods for the Examination of Water and Wastewater Part 1000.

12.2.4. Instrument Detection Limit = $(3 \times S_{LRB})$

S_{LRB} = Standard Deviation of Laboratory Reagent Blanks

12.3. Demonstration of Capabilities

12.3.1. All laboratory personnel are required to perform an initial demonstration of capability (IDC) on the instrument they will be using for analysis prior to testing samples. Ongoing demonstration of capability must be demonstrated by

control charts with LFBs being analyzed at least once per sample batch. Initial and ongoing demonstrations of capabilities are conducted as follows.

12.3.2. Initial Demonstration of Capability Analyst Proficiency - Four LFBs are analyzed using the same instrumental conditions and procedures used to analyze samples. Using these four LFBs demonstrates the analyst's ability to optimize and calibrate the instrument and to prepare analytical solutions. Calculate the average percent recovery and standard deviation of the recovery.

12.3.2.1. Acceptance Criteria: IDC control limit for the laboratory is based on the limits determined in this method and shall not exceed 82%-110 % with a percent Relative Standard Deviation less than 8%.

12.3.2.2. Corrective Action: If the IDC recovery falls outside of these limits, the analyst or instrument is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the IDC repeated until passed.

12.3.3. Ongoing Demonstration of Capability Analyst Proficiency: A LFB is analyzed using the same instrumental conditions and procedures used to analyze samples at least once per batch. The LFB percent recovery will be charted by control charts and be evaluated for acceptance.

12.3.3.1. Acceptance Criteria: LFB percent recovery must stay within the control limits calculated for the control chats.

12.3.3.2. Corrective Action: If the LFB percent recovery falls outside of these control limits, the batch is judged to be out of control. A root cause analysis must be performed, corrective action taken, all findings recorded and the sample batch repeated.

13. POLLUTION CONTROL

13.1. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect air, water, and land by minimizing and control all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

14. WASTE MANAGEMENT

14.1. There are no standards or reagents used in this method at the concentrations required that pose a threat to the environment. Refer to Local, State or Federal for correct disposal of all chemicals.

15. REFERENCES / BIBLIOGRAPHY

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