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SM 4500-NH_3-G -Ammonia in Water and Wastewater

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1 Scope and Application

1.1 This method covers the determination of ammonia in drinking, surface, saline waters and industrial wastes. Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color is intensified with sodium nitroprusside and read colorimetrically at 630 nm. Procedure is modified by using the Quickchem Method 10-107-06-1-B for use with the Lachat Quickchem Flow Injection Analysis (FIA) System instrument. 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. The EPD lab has a comparability study on file in manager's office. Used SM4500-NH_3-B for distillation study.

1.2 Restricted Procedure

This procedure is restricted to use by an analyst experienced in the operation of a Lachat Quickchem Flow Injection Analysis (FIA) System. Additionally, the analyst must complete the requirements of the GAEPD Initial Demonstration of Analyst Proficiency prior to the analysis of actual samples. Analysts are further warned that performance of this analysis involves the use of potentially hazardous chemicals; refer to the GAEPD Chemical Hygiene Plan for additional information regarding chemicals required by this method.

2 Definitions

2.1 Refer to Section 3 and Section 4 of the Georgia EPD Laboratory Quality Assurance Plan (see SOP reference 13.3) for Quality Control Definitions.

2.2 Primary Source (PS) – A standard that is used to make up the calibration points of a curve.

2.3 Second Source (SS) – A standard made from a manufacturer other than that of the primary source.

2.4 Initial Calibration Verification (ICV) – An ICV is a second source standard that is used to verify the correctness of the primary source calibration curve. The ICV is run at a level equal to that of a Laboratory Control Sample (LCS) or the midpoint on the calibration curve.

2.5 Continuing Calibration Check (CCC) or Continuing Calibration Verification (CCV) – A standard used to verify that the response of the instrument has not changed since initial calibration. The CCC is run at a level equal to that of a Laboratory Control Sample (LCS) or the midpoint on the calibration curve.

2.6 Calibration Blank (CB), Initial Calibration Verification Blank (ICB), Method Blank (MBLK), MDLB or Continuing Calibration Blank (CCB) – A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes.

2.7 MDLS (Method Detection Limit Spike) – MDLB spiked with analytes at the lowest calibration level to be used for the determination of MDL.

2.8 LCS (Laboratory Control Sample) and LCSD (Laboratory Control Sample Duplicate) are prepared by spiking laboratory reagent water, Ottawa sand or air sampling device with the target analyte or compound. They are used to validate the analytical batch with respect to accuracy and precision.

3 Interferences

3.1 Calcium and magnesium ions may precipitate if present in sufficient concentration. Tartrate or EDTA is added to the sample in-line in order to prevent this problem.

3.2 Color, turbidity and certain organic species may interfere. Turbidity is removed by manual filtration. Color in the samples that absorbs in the photometric range used for analysis interferes.

4 Safety

4.1 Refer to the EPD Laboratory Safety / Chemical Hygiene Plan & Fire Safety Plan, online revision.

5 Apparatus and Equipment

5.1 Sample Container: 250 ml Nalgene bottle

5.2 Plastic culture tubes, O.D. x L: 13mm x 100mm, Fisher Scientific part # 14-956-8E or equivalent or glass culture tubes 12mm x 75 mm VWR part # 60825-502 or equivalent.

5.3 Glassware – Class A volumetric flasks, graduated cylinders and pipettes

5.4 Lachat Quikchem flow injection analysis instrument
5.4.1 Lachat XYZ Auto-sampler
5.4.2 Auto-sampler rack (90 position)
5.4.3 Reagent pump
5.4.4 Reaction unit or manifold
5.4.5 Colorimetric detector with 630 nm interference filter
5.4.6 Computer with Microsoft Windows operating system with Lachat Omnion software or equivalent
5.5 Flow cell: 10 mm path length, 80 µl, glass
5.6 Air displacement pipettes of various volumes, auto-pipettor, pipette tips in various sizes. Air displacement pipettes and auto-pipettors may also be described as mechanical pipettes.
5.6.1 Each day of use, the volume dispensed by each mechanical pipette must be verified for the specific volume for which the pipette is being used.
5.6.1.1 Mechanical pipette volumes are verified by measuring the weight of a volume of water dispensed by the unit. At room temperature, 1 ml of water is equal to 1 g. Mechanical pipettes must be verified to be within ± 2.5% of the expected weight.
5.6.1.2 Auto-pipettors may be verified by measuring the volume dispensed with a graduated cylinder. The volume dispensed must be within ± 2.5 percent of the nominal volume.
5.6.1.3 Mechanical pipettes must be professionally calibrated every 6 months.
5.6.1.4 Balance: analytical, capable of accurately weighing to the nearest 0.0001g.
5.7 Disposable transfer pipettes:
5.7.1 Plastic - VWR® Disposable Transfer Pipets PN # 16001-190 or Fisherbrand™ Standard Disposable Transfer Pipettes PN # 13-711-7 M
5.8 Glass bottles, dark amber in color, for storage of reagents and standards.
5.9 HDPE bottles, various sizes, for storage of reagents
5.10 Sonicator
5.11 Vacuum source for degassing

6 Reagents

6.1 Reagent Water:
6.1.2 Purified water which does not contain any measurable quantities of target analytes or interfering compounds for each compound of interest (Deionized, HPLC, Milli-Q water, or equivalent. Milli-Q water has a resistivity of 18.2[MΩ.cm] @ 25ºC and a TOC of 50 ug/L or less).
6.2 10% Sulfuric Acid Solution:
6.2.1 Purchased from VWR, Part # BDH3358-4 or equivalent.
6.2.2 This solution is used for preservation of standards and blanks.
6.2.3 This purchased chemical is stable until expiration date on bottle or within 1 year of opening date, whichever is sooner. Store at room temperature.
6.3 Carrier and Diluent:
6.3.1 Use a 1L volumetric flask, dilute to the mark with reagent water and add 10 ml of 10% Sulfuric Acid Solution. Invert to mix.

6.3.2 This reagent has been modified from the Lachat method so that the matrix will be the same as the standards.
6.3.3 Prepare fresh daily.
6.4 Sodium Phenolate:
6.4.1 Purchased from Fisher, Aqua Solutions (PN 8710500ML) Fisher PN NC9451714 or equivalent.
6.4.2 Reagent is stable for up to 7 days after opening or the manufacturer's expiration date, whichever is sooner.
6.4.2.1 Experience with this method shows that QC passes when using this reagent up to 7 days after opening.
6.4.3 Due to the short shelf life, order approximately 4 bottles per month.
6.4.4 Keep under refrigeration at 0-6° C (not frozen).
6.5 Sodium Hypochlorite Solution (2.75%):
6.5.1 In a 500 ml volumetric flask, dilute 159 ml of Aqua Solutions Sodium Hypochlorite 8.25% or equivalent to the mark with reagent water. Invert to mix.
6.5.1.1 If the concentrated Sodium Hypochlorite solution contains 6.0% sodium hypochlorite (NaOCl), then in a 500 ml volumetric flask, dilute 219 ml of the 6.0 % sodium hypochlorite solution to the mark with reagent water.
6.5.1.2 If the concentrated Sodium Hypochlorite solution contains 5.25% sodium hypochlorite (NaOCl), then in a 500 ml volumetric flask, dilute 250 ml of the 5.25% sodium hypochlorite solution to the mark with reagent water.
6.5.2 May use another commercial vendor for sodium hypochlorite solution.
6.5.3 Prepare fresh daily.
6.6 Sodium Nitroprusside Solution:
6.6.1 To a 1L volumetric flask, dissolve 3.50 grams of sodium nitroprusside (Sodium Nitroferricyanide [Na_2Fe (CN) $5NO{\cdot}2H_2O$]) into 800 ml of reagent water. Dilute to the mark and invert to mix. Caution: Wear gloves when handling this chemical.
6.6.2 Reagent has been modified from Standard Methods per Lachat methodology.
6.6.3 Prepare fresh every two weeks.
6.7 Buffer:
6.7.1 In a 1L volumetric flask, dissolve 50.0 grams of disodium ethylenediamine tetraacetate dihydrate ($Na_2EDTA{\cdot}2H_2O$) and 9.0 g of sodium hydroxide (NaOH) in approximately 900 mL of reagent water. Dilute to the mark and mix with a magnetic stirrer until dissolved.
6.7.2 Reagent has been modified from Standard Methods per Lachat methodology.
6.7.3 Prepare fresh monthly
6.8 Primary Source(PS) Stock standard Ammonium Chloride Stock Standard (1000 mg NH_3/L):
Weigh out 3.819 g of ACS grade Ammonium Chloride, NH_4Cl, that has been dried for 2 hours at 110°C and place in a 1L volumetric flask and dissolve in reagent water then bring to volume.
6.8.1 Prepare fresh every 6 months.
6.8.2 Keep under refrigeration at 0-6° C (not frozen).
6.9 Primary Source(PS) Intermediate Stock A (10 mg NH_3/L):

6.9.1 10 ml of stock standard is pipetted into a 1000 mL volumetric flask and diluted to volume with reagent water. Add 10 ml of 10% Sulfuric Acid Solution. Invert to mix.
6.9.2 This standard has been modified from the Lachat method.
6.9.3 Prepare fresh every 3 months.
6.10 Calibration standards:
6.10.1 Using the Primary Source(PS) Intermediate Stock A (10 mg NH_3/L), prepare calibration standards at six concentrations in reagent water. The calibration standards range from 0.00 mg/L-NH_3 – 3.00 mg/L-NH_3. After the standards are brought to volume, 1 ml of 10% Sulfuric Acid Solution per 100 ml of standard is added.
6.10.2 Keep under refrigeration at 0-6° C (not frozen).
6.10.3 Prepare weekly.
6.10.4 The acid concentration has been modified from the Lachat method.
6.10.5 Refer to Table 6.10.1.1 for working standard preparation.

Table 6.10.1.1 Working Standards

Ammonium Chloride Stock Standard (10 mg NH_3/L)	**ml of Reagent water**	**Concentration (NH_3/L)**
0.6 ml	200 ml	0.03
0.6 ml	100 ml	0.06
1 ml	100 ml	0.10
6 ml	100 ml	0.60
20 ml	200 ml	1.00
30 ml	100 ml	3.00

6.11 100 mg NH_3/L Primary Source(PS) Spiking solution:
Pipette 10 ml of Ammonium Chloride Stock standard into a 100 ml volumetric flask and bring to volume with reagent water.
6.11.1 Prepare every three months.
6.12 0.00 mg/L Standard, ICB, CCB, MBLK, MDLB and Dilution water):
To prepare an ICB/CCB, Pipette 10ml of 10% Sulfuric Acid Solution into a 1L flask that already contains 1L of reagent water.
6.12.1 Prepare fresh every 28 days.
6.13 Ammonium Chloride ICV Stock Solution or Second Source (SS)
6.13.1 The ICV stock standard is used as a second source standard.
6.13.2 This stock standard must be from a different source than the stock standard used to make the calibration standards.
6.13.3 It is prepared commercially and purchased.
6.13.4 The prepared standard is stable until expiration date on bottle or within 6 months of opening date, whichever is sooner.
6.13.5 Keep under refrigeration at 0-6° C (not frozen).
6.14 Ammonium Chloride ICV Second Source Solution (SS)
6.14.1 Prepare the ICV to a concentration as close to 1.0 mg/L NH_3-N as possible.

6.14.2 The ICV solution must be prepared fresh every 3 months.
6.14.3 Keep under refrigeration at 0-6° C (not frozen).
6.14.4 Prepare the ICV per manufacturer's instructions.
6.14.5 Once ICV is diluted with reagent water, make sure to preserve ICV using appropriate amount of 10% Sulfuric Acid Solution. Use 10 ml of 10% Sulfuric Acid Solution per 1 L of ICV solution.
6.15 Volumes and amounts of reagents, chemicals and standards may be altered as long as final concentrations remain the same. Sample volumes and injection amounts may be altered as long as required detection limits can be met and sample/reagent ratios remain the same.
6.16 LCS/LCD 1.0 mg/L NH_3-N concentration:
6.16.1 Prepare the LCS and LCSD by pipetting 0.25 mL of the 100 mg NH_3/L Primary Source (PS) Spiking solution into a 25mL volumetric flask and bring to volume with dilution water that was stored in a 250 ml sample collection bottle (See Section 6.12).
6.17 MS/MSD 1.0 mg/L NH_3-N concentration:
6.17.1 Prepare the MS and MSD by pipetting 0.25 mL of the 100 mg NH_3/L Primary Source (PS) Spiking solution into a 25mL volumetric flask and bring to volume with sample chosen as the spike.
6.18 Continuing Calibration Check (CCC) 1.0 mg/L NH_3-N Standard:
To prepare the CCC, pipette 20.0 ml of the Primary Source (PS) Intermediate Stock A (10 mg NH_3/L) into a 200 ml volumetric flask. Once the standard is diluted to volume with reagent water, preserve the solution with 2 ml of 10% Sulfuric Acid Solution.
6.18.1 Prepare weekly. Keep under refrigeration.
6.19 Method Detection Limit Spike/Low level Standard (MDLS) 0.03 mg/L NH_3-N Standard:
To prepare the MDLS, pipette 0.6 ml of the Primary Source (PS) Intermediate Stock A (10 mg NH_3/L) into a 200 ml volumetric flask. Once the standard is diluted to volume with reagent water, preserve the solution with 2.00 mL of 10% Sulfuric Acid Solution.
6.19.1 Prepare fresh weekly.

7 Sample Collection

7.1 Samples are collected in 250 mL HDPE bottles.
7.2 The sample bottles are pre-preserved with 2.5mL of 10% Sulfuric Acid to a pH of < 2 in the field.
7.3 Sample preservation is checked in the receiving lab at time of receipt.
7.4 Samples are cooled and stored at 0-6° C (not frozen).
7.5 Sample holding time is 28 days.

8 Calibration

8.1 Calibration Standards

The calibration curve consists of the calibration standards at the following concentrations: 0.00 mg NH_3/L, 0.03 mg NH_3/L, 0.06 mg NH_3/L, 0.10 mg NH_3/L, 0.60 mg NH_3/L, 1.00 mg NH_3/L, 3.00 mg NH_3/L

8.2 Calibration Curve

The Lachat Quickchem 8000 is calibrated daily. Seven standards are used to construct the NH_3-N calibration curve for ammonia samples. Minimum acceptable correlation coefficient is 0.995 using a linear regression. The Lachat Quikchem is calibrated daily. Dilute all samples with a response greater the high standard 3.00 mg/L.

8.3 Calibration Verification

8.3.1 An Initial Calibration Verification standard (ICV), a Continuing Calibration Check (CCC) and an Initial Calibration Blank (ICB) must be analyzed immediately after the calibration standards.

8.3.1.1 The %Drift (see calculation 11.1.) of the ICV from the true value must be within ±10%. Repeat once if it fails. If it fails the second attempt, determine the source of the problem, correct and recalibrate.

8.3.1.2 The ICB, CCB and MBLK values must be less than the method RL or the run will have to be repeated.

8.3.1.3 A CCC and a Continuing Calibration Blank (CCB) must be analyzed every 10 samples and at the end of the sample run and must meet the same criteria as the ICV and ICB respectively.

8.3.1.3.1 The CCC may be from the same source as the calibration standards.

8.3.1.4 If the CCC or CCB do not meet acceptance criteria, then all samples affected by the out of control CCC or CCB are to be rerun.

8.3.2 A low level calibration check standard at a concentration of 0.03 mg/L must be analyzed prior to sample analysis for each analytical run. Recovery of the standard must be ±50%.

8.3.3 A MDLS (low level spike) at the concentration of 0.03 mg/L must be analyzed with each batch to perform ongoing MDL study. All batch QC must be valid to report this result.

8.4 A MDLB (MDLB) must be analyzed once per analytical batch to perform an ongoing MDL study. All batch QC must be valid to report this result.

9 Quality Control

9.1 Refer to Table 14.1 for Reporting Limits (RL's), Table 14.2 for Quality Control Acceptance Criteria. Table 14.3 for Quality Control Procedures associated with this method and the Standard Operating Procedures for Control Charts and Control Limits.

9.1.1 The default control limits, as set by the EPD Laboratory, are 90 -110% recovery for SM4500-NH3-G, Ammonia for LCS recoveries. The EPD Laboratory applies LCS recovery limits to LCSDs. Note, unless specified by method, the EPD Laboratory does not validate batch quality based on LCSD recoveries.

9.1.2 By default, the EPD Laboratory sets LCS/LCSD precision control limits for this

method to be 0 – 15% RPD.

9.1.3 10% of all routine samples must be spiked. The EPD Laboratory requires recovery control limits of 90 – 110% for matrix spikes. The EPD Laboratory applies MS recovery limits to MSDs. These limits are static by EPD lab default.

9.1.4 By default, the EPD Laboratory sets default MS/MSD precision control limits to be 0 – 15% RPD. These limits are static by EPD lab default.

9.1.5 See Administrative SOP for Control Charting and Control Limits for further details.

9.2 Batch samples in groups of 20. For each batch, analyze a Matrix Spike (MS) and a Matrix Spike Duplicate (MSD) for a minimum of 10% of routine samples.

9.2.1 For batches of 1 to 10 routine samples, one MS/MSD pair must be spiked. For batches of 11 to 20 routine samples, two MS/MSD pairs must be spiked using different samples for each pair.

9.3 MDL (method detection limit) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.

9.3.1 The actual MDL varies depending on instrument and matrix.

9.3.2 The MDL must be determined annually for each instrument prior to results being reported for that instrument. The MDL determined for each compound must be less than the reporting limit for that compound.

9.3.3 The Method Detection Limit Study for all analytes must be performed initially on a new instrument and performed after major instrument repairs or changes to procedures. There are two ways to perform the MDL. The first is with 7 samples and 7 blanks over 3 separate days. The second preferred way the MDL is run as a continuous format.

9.3.4 The 7 MDL samples study is performed by preparing 7 spiked vials, MDLSpike, spiked at the lowest calibration point of the curve, and preparing 7 clean blank vials filled with DI water, MDLBlank. These 7 sets of spiked and blank vial "pairs" are analyzed over 3 separate days, there may or may not be a non-analysis day between each of the 3 days. A total of 14 vials are prepared, 7 spiked and 7 blank.

9.3.5 A continuous format MDL study is performed where one vial is spiked as an MDLSpike, at the lowest point of the calibration curve and analyzed with every batch of samples along with the method blank vial as an MDLBlank.

9.3.6 The results of the MDLBlank will be entered into Labworks using the Method Blank test code, B_NH-3. The MDLSpike result will be entered using the MLNH-3. The MDL Spiked Amount will be entered into the test code MANH-3. The instrument used for the MDL and Blank analysis will be selected using the test code INSTR-NH-3.

9.3.7 MDL study must be performed twice yearly basis and before the MDL for the instrument expires.

10 Procedure

10.1 Sample Preparation

10.1.1 Remove sample bottles, standards, and reagents from cold storage and allow them to equilibrate to room temperature prior to sample preparation and/or analysis.

10.1.2 From Labworks, print a backlog of pending samples. Samples are batched in groups of 20 field samples. Select QC samples for MS/MSD. MS/MSD pairs are to be analyzed at a frequency of 10% of samples over time.

10.1.2.1 For batches of 1-10 field samples, 1 MS/MSD pair is required. For batches of 11-20 field samples, 2 MS/MSD pairs are required.

10.1.3 Prepare the LCS and LCSD pairs at the 1.00 mg/L level by pipetting 0.25 mL of the 100 mg NH_3/L Primary Source (PS) Spiking solution into a 25mL volumetric flask and bringing to volume with dilution water that was stored in a 250 ml sample collection bottle. (See Section 6.16). Prepare one LCS/LCSD pair per batch. Record lot # of bottle used.

10.1.4 Prepare the MS and MSD at the 1.00 mg/L level by pipetting 0.25 mL of the 100 mg NH_3/L Primary Source (PS) Spiking solution into a 25mL volumetric flask and bring to volume with sample chosen as the spike. Prepare one MS/MSD pair per 10% of samples.

10.1.5 The MDLS/0.03 mg NH_3/L standard must be poured into a 250 ml sample collection bottle before it is poured into the appropriate instrument sample cup. Record lot # of bottle used.

10.1.6 The ICB/CCB/MBLK/MDLB must be poured into a 250 ml sample collection bottle before it is pipetted into the appropriate tubes. Record lot # of bottle used.

10.2 Instrument Setup/Data Analysis

10.2.1 Turn on computer, monitor, auto-sampler, pump and colorimetric detector.

10.2.2 Prepare fresh reagent water, sodium hypochlorite solution, and buffer. De-gas sodium hypochlorite solution, buffer, carrier and nitroprusside solution using sonicator and laboratory house vacuum system.

10.2.3 Click on Omnion icon, then click OK.

10.2.4 Click Open, and navigate to the Methods/Ammonia folder. Open the NH-3 template file. Alternately, open a previous run's worksheet and edit.

10.2.5 Type in all samples, standard numbers and reagent numbers according to the template format. Save as "NH-3(Date): with the date in the MM-DD-YY format.

10.2.6 Print tray worksheet by clicking Export Worksheet Data from the file menu.

10.2.7 Inspect pump tubes for wear and replace if necessary. Snap pump tube cartridges down into cartridge holders and adjust tension levers to tensioned position. Place instrument waste lines into a properly labeled NH-3 waste container.

10.2.8 Place lines in fresh reagent water and turn pump on. Set pump speed to 35 and press Manual run. Pump reagent water through all reagent lines for approximately 5 minutes to check for leaks or back flow problems.

10.2.9 Next place all lines in the appropriate reagent containers and allow to run for a least 5 minutes.

10.2.10 Verify that heating unit has reached 60°C and then click Preview to monitor baseline.
10.2.11 Load standards, samples and QC samples according to tray worksheet.
10.2.12 When baseline is stable, record baseline reading in maintenance log along with any maintenance that was performed on instrument.
10.2.13 Select the Run icon to begin run.
10.2.14 After the run is finished, click Custom Report icon to generate a report that includes the run's results and calibration curve. Click Format icon to rename headers to include the date, analyst, and instrument name.
10.2.15 Print the report.

10.3 Dilutions
10.3.1 If the response of any sample or QC is greater than the high standard of 3.0 mg NH_3/L, those samples must be diluted and rerun in a valid sequence or at the end of the run, followed by an ending CCC or CCB. Dilution ratios should be determined, as nearly as possible, so that the response is near the mid-point of the calibration range.
10.3.2 To prepare dilutions, use Dilution water (See 6.12) to dilute the samples.

10.4 Shutdown Procedure
10.4.1 When the run is finished, exit all windows.
10.4.2 Turn off colorimeter detector by hitting the power switch. Allow heater to begin cooling.
10.4.3 Next place lines in reagent water for 5 minutes, then take lines out of reagent water and lay on paper towel and run air through system until tubing is completely dry.
10.4.4 Finally, turn off pump, auto-sampler and computer and computer monitor.
10.4.5 Loosen pump tube cartridges by releasing tensioners and then disconnecting cartridges from the pump rollers.
10.4.6 Cap reagent waste container.

11 Calculations

11.1 The weighted external standard calibration is calculated by the instrument software and is documented in the instrument software.

11.2 Mean ($\overline{X}$):

$$\overline{X} = \frac{X_1 + X_2 + \cdots X_n}{n}$$

11.2.1 Where:

$X_1 + X_2 + \cdots X_n$ = The sum of a set of values X_i, i = 1 to n

n = The number of values in the set

11.3 Standard Deviation (n – 1) (σ_{n-1}):

$$\sigma_{n-1} = \sqrt{\sum_{i=1}^{n} \frac{(X_i - \bar{X})^2}{n-1}}$$

11.3.1 Where:

$\bar{X}$ = Mean of the values

X_i = Individual values 1 through i

n = Number of values

11.4 Percent Relative Standard Deviation (%RSD):

$$\%RSD = \frac{\sigma_{n-1}}{\bar{X}} * 100$$

11.4.1 Where:

σ_{n-1} = Sample Standard Deviation

$\bar{X}$ = Mean of the values

11.5 Relative Percent Difference (%RPD or RPD):

$$\%RPD = \frac{|X_1 - X_2|}{\frac{(X_1 + X_2)}{2}} * 100$$

11.6 Percent Drift, %Drift:

$$\%Drift = \frac{(Concentration_{Calculated} - Concentration_{Expected})}{Concentration_{Expected}} * 100$$

11.6.1 Where:

$Concentration_{Calculated}$ = Concentration calculated from result

$Concentration_{Expected}$ = Theoretical concentration of the standard

11.7 Extract Concentration:

The extract concentration is calculated relative to the calibration curve by the instrument software.

11.8 Percent Recovery:

11.8.1 *LCS/LCSD*:

$$\%\text{Recovery} = \frac{\text{Conc}_{\text{spiked}}}{\text{Conc}_{\text{expected}}} * 100$$

11.8.1.1 Where:

$\text{Conc}_{\text{spiked}}$ = Concentration found in the spiked sample

$\text{Conc}_{\text{expected}}$ = Expected concentration

11.8.2 *MS/MSD*:

$$\%\text{Recovery} = \frac{\text{Conc}_{\text{spiked}} - \text{Conc}_{\text{unspiked}}}{\text{Conc}_{\text{expected}}} * 100$$

11.8.2.1 **Where:**

$\text{Conc}_{\text{spiked}}$ = Concentration found in the spiked sample

$\text{Conc}_{\text{unspiked}}$ = Concentration found in unspiked sample

$\text{Conc}_{\text{expected}}$ = Expected concentration

11.9 Calculation of Dilution Factors

C x D = F

11.9.1 Where:

C = concentration from instrument in mg/L

D = dilution factor, if any

F = final concentration in mg/L

12 Waste Management

12.1 See GA EPD Laboratory SOP-EPD Laboratory Waste Management Standard Operating procedures, See SOP reference 13.6.

13 References

13.1 Standard Methods for the Examination of Water and Wastewater, 20th Edition, 4500-NH3-G, Automated Phenate Method, 1997, Editorial Revision 2011.

13.2 Determination of Ammonia (Phenolate) by Flow Injection Analysis Colorimetry, Lachat Instruments Quickchem Method 10-107-06-1-B. Written by William Prokopy. Revision March 13, 1998.

13.3 EPD Laboratory Quality Assurance Plan, online revision.

13.4 GA EPD Laboratory SOP's – Initial Demonstration of Capability SOP 6-001, online revision or Continuing Demonstration of Capability SOP 6-002, online revision.

13.5 GA EPD Laboratory SOP-EPD Laboratory Procedures for Control Charts and Control Limits SOP, SOP 6-025, online revision.

13.6 GA EPD Laboratory SOP-EPD Laboratory Waste Management SOP, SOP 6-015, Rev. 2 or later and Appendix A SOP 6-015, online revision.

13.7 GA EPD Laboratory SOP – Determination of Method Detection Limit, Method Detection Limit SOP 6-007, online revision.

13.8 GA EPD Laboratory Safety Plan – EPD Laboratory Safety / Chemical Hygiene Plan & Fire Safety Plan, online revision.

13.9 Standard Methods for the Examination of Water and Wastewater, 20th Edition. 4500-NH3-B, Preliminary Distillation Step, 1997, Editorial Revision 2011.

14 Reporting Limits (RLs), Precision and Accuracy Criteria, and Quality Control Approach

Table 14.1 RL's for SM 4500-NH_3-G

Parameter/Method	Analyte	Matrix (aqueous)	
		RL	Unit
SM 4500-NH_3-G	Ammonia Nitrogen	0.03	mg/L

Table 14.2 Acceptance Criteria for Method SM 4500-NH_3-G

Method	Analyte	Accuracy Water (%R)	Precision Water (RPD)
SM 4500-NH_3-G	Ammonia Nitrogen	90-110	15

Table 14.3 Summary of Calibration and QC Procedures for Method SM 4500-NH_3-G

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
SM 4500-NH_3-G	Ammonia Nitrogen	Seven point initial calibration for all analytes	Initial calibration prior to sample analysis	Correlation coefficient (r) ≥ 0.995 linear	Correct problem then repeat initial calibration	
		Second source calibration verification	Once per seven-point initial calibration	Ammonia value within 10% of expected value	Correct problem then repeat initial calibration	

Table 14.3 Summary of Calibration and QC Procedures for Method SM 4500-NH_3-G

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
SM 4500-NH_3-G	Ammonia Nitrogen	Initial Calibration Blank (ICB)	Once per analytical run	Value mist be < RL.	Correct problem and repeat initial calibration	
		Initial Demonstration: Demonstrate ability to generate acceptable accuracy and precision using four analysis of a QC check sample, a method blank and a blind sample. In addition, the analyst must prepare one standard.	Once per analyst	QC Acceptance Criteria Table, SOP 3-029 Appendix A and Continuing Demonstration of Capability SOP (Reference 13.3)	Recalculate results: locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria	
		Continuing Demonstration: Demonstrate ability to generate acceptable accuracy and precision using a variety of analysis options of a QC sample(s)	Every 6 months	QC Acceptance Criteria Table, SOP 3-029 Appendix A and Continuing Demonstration of Capability SOP (Reference 13.3)	Recalculate results: locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria	
		Low level standard (0.03 mg/L)	Prior to sample analysis	Value must be ± 50% of expected value	Evaluate recovery exceedances, reanalyze or recalibrate	
		Method Blank (MBLK)	Once per analytical batch	Ammonia value must be < 0.03 mg/L	Correct problem then analyze method blank and all samples processed with the contaminated blank	If unable to reanalyze, flag with a "B"
		Laboratory Control Sample (LCS/ LCSD)	One LCS/LCSD per analytical batch	QC Acceptance Criteria Table, SOP 3-029 Appendix A	Correct problem then reanalyze the LCS/LCSD and all samples in the affected batch	If unable to reanalyze, flag with a "J"
		Matrix Spike (MS/MSD)	10% of samples	QC Acceptance Criteria Table, SOP 3-029 Appendix A	Evaluate out of control event, reanalyze or flag data	
		Continuing Calibration Check (CCC)	After every 10 samples and at the end of a sample run	Ammonia concentration within 10% of expected value	Correct problem then reanalyze CCC and all samples associated with out of control CCC.	

Table 14.3 Summary of Calibration and QC Procedures for Method SM 4500-NH_3-G

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
SM 4500-NH_3-G	Ammonia Nitrogen	Continuing Calibration Blank (CCB)	After every 10 samples and at the end of the sample run	Ammonia concentration must be < 0.03 mg/L	Correct problem then reanalyze all samples associated with out of control CCB.	
		MDL Low level Spike (MDLS) 0.03 mg/L	Once per analytical batch	All batch QC must be valid	Correct problem then reanalyze the affected batch	
		MDL Blank (MDLB)	Once per analytical batch	All batch QC must be valid	Correct problem then reanalyze the affected batch	
		MDL study	Twice yearly or after major maintenance of the instrument	All Spiked MDLs must have a value greater than 0. Minimum Detection Limits established shall be < the RLs in Table 14.1	Re-do MDL Study	None
		MDL analysis	Once per batch or as needed to acquire data points per SOP 6-007, online revision	All Spiked MDLs must have a value greater than 0. All other QC in the MDL blank and MDL sample (i.e. Surrogate Spike or Internal Standard, etc. if included) must meet established criteria	Correct problem and re-run the MDL sample or MDL blank once and initiate a corrective action. If the re-run fails a second time, do not use MDL data. Update corrective action, and use associated sample data	None

Appendix A – Quality Assurance Criteria for Method SM4500-NH-3-G

Table A.1 Quality Assurance Criteria for Method SM4500-NH-3-G					
QC Type	Analyte	Accuracy(%R) LCL		UCL	Precision (%RPD)
LCS/LCSD	Ammonia	90	-	110	15
MS/MSD	Ammonia	90*	-	110*	15
*MS/MSD Control limits are static by EPD Lab default. Control Chart data generated from 01/01/2019 - 01/01/2021					

Updates to Previous Version:
Section 2
Section 4
Section 6
Section 9
Section 13
Table 14.3
Appendix A