NC DENR/DWQ LABORATORY CERTIFICATION

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| LABORATORY NAME: | | CERT #: | |
| PRIMARY ANALYST: | | DATE: | |
| NAME OF PERSON COMPLETING CHECKLIST (PRINT): | | | |
| SIGNATURE OF PERSON COMPLETING CHECKLIST: | | | |

Parameter: **Ammonia Nitrogen ($NH_3$-N)**
Method: **Ion Selective Electrode (ISE)**

| METHOD OF ANALYSIS: | | | PREP METHOD: |
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| | Standard Methods 18th Edition: 4500-$NH_3$ F ☐ | | Standard Methods 18th Edition: 4500-$NH_3$ B ☐ |
| | Standard Methods 19th Edition: 4500-$NH_3$ D ☐ | | Standard Methods 19th Edition: 4500-$NH_3$ B ☐ |
| | Standard Methods 20th Edition: 4500-$NH_3$ D ☐ | | Standard Methods 20th Edition: 4500-$NH_3$ B ☐ |
| | Standard Methods 21st Edition: 4500-$NH_3$ D ☐ | | Standard Methods 21st Edition: 4500-$NH_3$ B ☐ |
| | Standard Methods Online 4500-$NH_3$ D-97 ☐ | | Standard Methods Online 4500-$NH_3$ B-97 ☐ |

SM Editions 20th and 21st are equivalent to the online versions (4500-$NH_3$ D-97 and 4500-$NH_3$ B-97)

Equipment:

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| | Specific Ion Meter (Model): | | Distillation Apparatus |
| | Ammonia-selective electrode (Model): | | Magnetic stirrer with TFE-coated stirring bar |

| | **PLEASE COMPLETE CHECKLIST IN INDELIBLE INK** | Y | N | EXPLANATION |
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| | PRESERVATION and STORAGE | | | |
| 1 | Are samples preserved at the time of collection with $H_2SO_4$ to pH of <2? [40 CFR 136 Table II.] | | | |
| 2 | What action is taken if not properly preserved? [15A NCAC 2H .0805 (a) (7) (N).] | | | Preserve sample, qualify data, and notify their NC WW/GW LC inspector |
| 3 | Is the pH of Ammonia samples checked to document pH <2? [40 CFR 136 Table II.] | | | pH must be checked and recorded – dechlorination must be performed prior to pH adjustment. Both chemicals cannot be placed in the bottle prior to sample collection. |
| 4 | Are samples checked for residual chlorine? [SM 4500-$NH_3$ A. (2).] | | | Remove residual chlorine by sample pretreatment. |
| 5 | What action is taken if chlorine is present? [15A NCAC 2H .0805 (a) (7) (N).] | | | Neutralize residual chlorine, qualify data, and notify their NC WW/GW LC inspector. |
| 6 | Are samples iced to above freezing but ≤ 6 ºC during shipment? [40 CFR 136 Table II.] | | | Sample temperatures must be checked and documented. Downward trend must be documented for short transport samples. |
| 7 | Are samples refrigerated above freezing but ≤ 6 ºC during storage? [40 CFR 136 Table II.] | | | |
| 8 | Are Ammonia samples analyzed within 28 days of collection? [40 CFR 136 Table II.] | | | Maximum hold time is 28 days (This includes both the distillation and potentiometric portions of the procedure). |
| | PROCEDURE | | | |
| 9 | Are Ammonia samples distilled before analysis? [40 CFR 136 Table IB.] | | | Distillation is required unless acceptable distillation comparison data on representative samples are on file. |
| 10 | If distillation is not performed, is an annual distillation comparison study on file? [NC WW/GW LC Policy February 2006.] | | | Municipal and Industrial Laboratories shall analyze initially four samples distilled and undistilled from each discharge and, thereafter, analyze two samples a year from each effluent.<br><br>Commercial Laboratories shall analyze initially at least six samples distilled and undistilled, but at least two samples from all waste types. Analyze one sample distilled and undistilled yearly from all waste types.<br><br>Samples may need to be spiked when performing the comparison if the ammonia concentration in the sample is low (< 1 mg/L).<br><br>It is recommended that both the distilled and |

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| | | | | undistilled portions of the sample be analyzed by the same laboratory using the same methodology.<br><br>**Note:** A blank, second source standard (LCS) and MS must be distilled for the study. |
| 11 | **Date of distillation study:** | | | |
| 12 | Is the distillation apparatus steamed out until there are no traces of ammonia prior to use? [SM 4500-$NH_3$ B. (4) (a).] | | | Distilled blank shows that apparatus is steamed out adequately. |
| 13 | How is the distillation apparatus steamed out? [SM 4500-$NH_3$ B. (4) (a).] | | | 500 mL of DI water, 20 mL borate buffer, adjust pH to 9.5 with 6N NaOH. May vary depending on distillation apparatus. Maintain sample to borate buffer ratio of 25 mL to 500 mL. |
| 14 | What sample volume is distilled? [SM 4500-$NH_3$ B. (4) (b).] | | | Use 500 mL dechlorinated sample or a known portion diluted to 500 mL. May vary depending on distillation apparatus. Maintain sample to borate buffer ratio of 25 mL to 500 mL. |
| 15 | How is the sample prepared for distillation? [SM 4500-$NH_3$ B. (4) (b).] | | | Add 25 mL of borate buffer solution and adjust pH to 9.5 with 6N NaOH. |
| 16 | How is the distillate collected? [SM 4500-$NH_3$ B. (4) (c).] | | | Collect at a rate of 6 to 10 mL/min in 50 mL of 0.04N $H_2SO_4$ with the tip of the delivery tube below the surface. |
| 17 | How much distillate is collected? [SM 4500-$NH_3$ B. (4) (c).] | | | Collect at least 200 mL of distillate and dilute to 500 mL. Maintain ratio of volume distilled to volume collected. |
| 18 | What sample volume is analyzed? [SM 18th 4500-$NH_3$ F. (4) (e). SM 19th, 20th, 21st 4500-$NH_3$ D. (4) (e).] | | | 100 mL - if necessary, dilute sample to bring into the range of the calibration curve. |
| 19 | Are samples allowed to come to room temperature before analysis? [SM 18th 4500-$NH_3$ F. (4) e. SM 19th, 20th, 21st 4500-$NH_3$ D. (4) (e).] | | | Use standard solutions and samples that have the same temperature (about 25°C). |
| 20 | Are all readings made with constant stirring limited in speed to minimize possible loss of ammonia from the solution? [SM 18th 4500-$NH_3$ F. (4) (e). SM 19th, 20th, 21st 4500-$NH_3$ D. (4) (e).] | | | Maintain the stirring rate and a temperature of about 25°C throughout calibration and sample testing procedures. May also recommend keeping electrode at an angle to minimize air bubbles and insulating between the beaker and stir plate to prevent heating of sample by stir plate. |
| 21 | Is 10N NaOH added to all blanks, standards, and samples to raise the pH above 11 **after** immersing the electrode? [SM 18th 4500-$NH_3$ F. (4) (e). SM 19th, 20th, 21st 4500-$NH_3$ D. (4) (e).] | | | Add NaOH after immersing the electrode because ammonia may be lost from a basic solution. $NH_3$ is in a gaseous state at pH>11. |
| 22 | Is 10N NaOH/EDTA used in place of the NaOH if the presence of silver or mercury is possible? [NC WW/GW LC Policy based upon SM 19th, 20th, 21st 4500-$NH_3$ D. (4) (b).] | | | If historical data shows the presence of silver or mercury is possible, NaOH/EDTA must be used to elevate the pH. However, compilation of this data is not required. |
| 23 | Is the volume of 10N NaOH added to the blanks, standards, and samples documented? [SM 18th 4500-$NH_3$ F. (4) (e). SM 19th, 20th, 21st 4500-$NH_3$ D. (4) (e).] | | | 1 mL is usually sufficient. Orion's ISA solution (Ionic Strength Adjuster) states to use 2 mL. |
| 24 | If a different volume of NaOH is added to the sample than to the calibration standards, is a correction made to the result? [NC WW/GW LC Policy based upon SM 19th, 20th, 21st 4500-$NH_3$ D. (5).] | | | If a different volume of pH adjuster is needed for the sample, the following formula is used:<br><br>$Mg\ NH3 – N/L = A \times B \times \frac{(100 + D)}{(100 + C)}$<br><br>A= Dilution Factor<br>B= Concentration of NH3-N/L, mg/L, from calibration curve<br>C= Volume of 10N NaOH added to the calibration standards, mL<br>D= Volume of 10 N NaOH added to sample, mL |
| 25 | Is the adjusted pH verified and documented? [SM 18th 4500-$NH_3$ F. (4) (e). SM 19th, 20th, 21st 4500-$NH_3$ D. (4) (e).] | | | The pH must be raised above 11. If the purchased ISA is used, the sample will turn blue when the pH is greater than 11. No further verification is required, but the pH > 11 must be documented. If the lab uses 10 N NaOH (made or bought) without color indicator, the pH must be verified to be greater |

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| | | | | than 11 with either a pH meter or pH strips. This must also be documented. |
| 26 | How is the adjusted pH verified? [SM 18th 4500-$NH_3$ F. (4) (e). SM 19th, 20th, 21st 4500-$NH_3$ D. (4) (e).] | | | Color indicator, pH meter (calibrated with buffer >11), pH strips. A check box indicating the pH is > 11 may be used. |
| | QUALITY ASSURANCE | | | |
| 27 | What is your laboratory's reporting limit? [15A NCAC 2H .0805 (a) (7) (I).] | | | Lowest calibration standard. Generally, electrode methods are not accurate below 0.1 mg/L. |
| 28 | **List the values of standards used for the <u>daily</u> calibration:** [15A NCAC 2H .0805 (a) (7) (I).] | | | Calibration must be performed each day samples are analyzed. Method lists 5 standards. Calibration standards do not have to be distilled.<br>A two-point calibration bracketing the anticipated range of sample concentration is acceptable. Caution: If a two-point calibration is performed, the difference in concentration between the standards should not be greater than tenfold. A multipoint calibration is also acceptable. This can be either as a direct calibration, or the values obtained may be calculated in a linear regression formula to obtain the best fit straight line. (Correlation coefficient must be $\geq$0.995). See Calibration |
| 29 | Are curves plotted using Ammonia concentration versus potential (mV) developed? [SM 18th 4500-$NH_3$ F. (4) (c). and SM 19th, 20th, 21st 4500-$NH_3$ D. (4) (c).] | | | No is an acceptable answer - either plot a curve or **use a direct reading from the meter if available.** A millivolt vs. concentration plot is made on semi-logarithmic graph paper. It is more preferable to calculate a manual linear regression of the log of the standard conc. versus mV response to obtain the slope and intercept. Sample results are then converted to mg/L using the following equation:<br><br>Conc. = antilog of [sample mV x slope + intercept] |
| 30 | Is the slope documented? [15A NCAC 2H .0805 (a) (7).] | | | Slope of ten fold millivolt change (i.e., difference in millivolt readings between one standard and another with a concentration ten times greater than the first standard) should be within manufacturer's requirement (generally -54 to -60 mV) (SM ≈ 59). The millivolt change may vary from the given ranges depending on the concentration of the standards used. Harder to achieve with 0.1 and 1.0 mg/L standards, should be routine for 1 and 10 mg/L. If the calibration range is two decades (e.g., 0.1 to 10 mg/L), the difference in mV between the upper and lower standard should be 108 to 120 mV. |
| 31 | What is the acceptable slope range? [Manufacturer's instruction manual] | | | **Slope generally obtained:**<br>See previous explanation |
| 32 | Is a reagent blank analyzed after calibration, but before samples are analyzed? [SM 4500-$NH_3$ B. (3) (a).] | | | If samples are distilled, this blank must also be distilled. |
| 33 | Is the blank concentration less than or equal to ½ of the lowest calibration standard concentration? [NC WW/GW LC Policy] | | | |
| 34 | What corrective action is taken if the blank is not acceptable? [15A NCAC 2H .0805 (a) (7) (F).] | | | Reanalyze blank. If still not acceptable, repeat the initial calibration, etc. Once problem is resolved, repeat sample determinations since the last acceptable blank. |
| 35 | What is the concentration of the daily mid-range verification standard? [NC WW/GW LC Policy 01/28/08.] | | | |
| 36 | What corrective action is taken if the mid-range standard varies by more than 10%? [NC WW/GW LC Policy 01/28/08.] | | | Reanalyze standard. If still not acceptable, repeat the initial calibration, etc. Once problem is resolved, repeat sample determinations since the last acceptable standard. |

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| 37 | Is the blank and mid-range standard analyzed after every tenth sample and at the end of each sample group to check for carry-over and calibration drift? [NC WW/GW LC Policy 01/28/08.] | | | Do not have to be distilled. |
| 38 | Does the laboratory analyze a second source verification standard daily? [15A NCAC 2H .0805 (a) (7) (B).] | | | If samples are distilled, second source standard must also be distilled. |
| 39 | What is the acceptance criterion for the second source standard? [15A NCAC 2H .0805 (a) (7).] [NC WW/GW LC Policy based upon 15A NCAC 2H .0805 (a) (7) (B), (a) (7) (F), and SM 20th Edition - Method 1020 B. (2) and (5).] | | | |
| 40 | At what frequency is a Matrix Spike (MS) analyzed? [NC WW/GW Policy based upon SM 1020 B.] | | | Unless the referenced method states a greater frequency, spike 5% of samples on a monthly basis. Laboratories analyzing less than 20 samples per month must analyze at least one matrix spike (MS) each month samples are analyzed. If samples are distilled, the MS must also be distilled. |
| 41 | How is the MS prepared? [NC WW/GW LC Matrix Spike Technical Assistance.] | | | See Matrix Spike Technical Assistance document. |
| 42 | What is the acceptance criterion for MS recovery? [SM 1020 B.] | | | Establish laboratory control limits. |
| 43 | What corrective action does the laboratory take if the MS results are outside of established control limits? [NC WW/GW LC Matrix Spike Technical Assistance and 15A NCAC 2H .0805 (a) (7) (F).] | | | |
| 44 | At what frequency are duplicates and/or Matrix Spike Duplicates (MSD) analyzed? [15A NCAC 2H .0805 (a) (7) (C).] | | | If sufficient sample volume is not collected to analyze a MSD, use an additional portion of an alternate sample to obtain results for a duplicate sample to gather data on precision. Spike and duplicate 5% of samples on a monthly basis. Laboratories analyzing less than 20 samples per month must analyze at least one duplicate or MSD each month samples are analyzed. MSD are recommended when sample concentrations are so low that viable statistics cannot be calculated for precision. |
| 45 | What is the acceptance criterion for duplicates and/or MSD? [15A NCAC 2H .0805 (a) (7).] | | | Establish laboratory control limits. |
| 46 | What corrective action does the laboratory take if the duplicate and/or MSD results are outside of established control limits? [15A NCAC 2H .0805 (a) (7) (F).] | | | |
| 47 | Does the laboratory have a SOP procedure and associated QA manual? [15A NCAC 2H .0805 (a) (7).] | | | |
| 48 | What is the most recent review/revision date of the SOP? [15A NCAC 2H .0805 (a) (7).] | | | |
| 49 | Is the data qualified on the Discharge Monitoring Report (DMR) or client report if Quality Control (QC) requirements are not met? [NC WW/GW LC policy 6/26/2008 based upon 15A NCAC 2B .0506 (b) (3) (J).] | | | When quality control (QC) failures occur, the laboratory must determine the source of the problem and apply corrective action. Part of the corrective action is notification to the end user. If data qualifiers are used to qualify samples not meeting QC requirements, the data may not be useable for the intended purposes. It is the responsibility of the laboratory to provide the client or end-user of the data with sufficient information to determine the usability of the qualified data. |

Additional Comments: _____

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Inspector: _____ Date: _____