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**
Method: **Standard Method 4500-$NH_3$ D – 2011 (Aqueous)**

EQUIPMENT:

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| | Ammonia Selective Electrode **Model:** | | pH Meter/or Specific Ion Meter |
| | Magnetic stirrer, thermally insulated, with TFE-coated stirring bar | | |

ANALYSIS REAGENTS:

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| | Ammonia-free water |
| | Sodium hydroxide (NaOH), 10*N* |
| | NaOH/EDTA solution, 10*N* |
| | Stock ammonium chloride solution |
| | Standard ammonium chloride solutions |
| | ISA – Color indicator |

**PLEASE COMPLETE CHECKLIST IN INDELIBLE INK**
**Please mark Y, N or NA in the column labeled LAB to indicate the common lab practice and in the column labeled SOP to indicate whether it is addressed in the SOP.**

| | GENERAL | LAB | SOP | EXPLANATION |
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| 1 | Is the SOP reviewed at least every 2 years? What is the most recent review/revision date of the SOP? [15A NCAC 2H .0805 (a) (7)]<br><br>ANSWER: | | | Quality assurance, quality control, and Standard Operating Procedure documentation shall indicate the effective date of the document and be reviewed every two years and updated if changes in procedures are made.<br>Verify proper method reference. During review notate deviations from the approved method and SOP. |
| 2 | Are all revision dates and actions tracked and documented? [15A NCAC 2H .0805 (a) (7)] | | | Each laboratory shall have a formal process to track and document review dates and any revisions made in all quality assurance, quality control and SOP documents. |
| 3 | Is there North Carolina data available for review? | | | If not, review PT data |
| | **PRESERVATION and STORAGE** | **LAB** | **SOP** | **EXPLANATION** |
| 4 | Are samples preserved at time of collection with $H_2SO_4$ to pH of <2? [40 CFR 136.3 Table II] | | | Preservation not required if analyzed within 15 minutes. |
| 5 | Are samples checked for total residual chlorine at the time of collection? [SM 4500-$NH_3$ B-2011 (3) (d)] | | | TRC strips or DPD powder may be used |
| 6 | Is total residual chlorine neutralized at time of sample collection? [SM 4500-$NH_3$ B-2011 (3) (d)] | | | 3.5 g Sodium thiosulfate ($Na_2S_2O_3$ • $5H_2O$) per L. 1ml will neutralize 1 mg/L residual chlorine in 500 ml sample. |
| 7 | Are samples checked for total residual chlorine upon receipt in the lab? [40 CFR 136.3 Table II] | | | |
| 8 | What action is taken if chlorine is present?<br><br>ANSWER: | | | If another sample cannot be collected, dechlorinate the sample and notify NC WW/GW Certification group that a non-compliant sample was received. |

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| 9 | Are samples iced to above freezing but ≤ 6 º C during shipment? [40 CFR 136.3 Table II and footnote 18] | | | 40 CFR footnote 2 allows 15 minutes for sample preservation, including thermal. This means that if a sample is received in the lab within 15 minutes it is not required to be on ice. Document temperature downward trend for short transport samples. |
| 10 | Is pH checked to document pH <2 upon receipt? [40 CFR 136.3 Table II] | | | pH paper may be used |
| 11 | What action is taken if pH is >2?<br><br>ANSWER: | | | If another sample cannot be collected, analyze immediately or adjust pH to <2 and notify NC WW/GW Certification group that a non-compliant sample was received. |
| 12 | Are samples refrigerated above freezing to 6°C during storage? [40 CFR 136.3 Table II and footnote 18] | | | |
| 13 | Are samples analyzed within 28 days of collection? [40 CFR 136.3 Table II] | | | |
| | **PROCEDURE – Meter Calibration** | **LAB** | **SOP** | **EXPLANATION** |
| 14 | What is your laboratory's reporting limit? [15A NCAC 2H .0805 (a) (7) (I)]<br><br>ANSWER: | | | Lowest calibration standard. Generally, electrode methods are not accurate below 0.1 mg/L. |
| 15 | **List the values of standards used for the <u>daily</u> calibration:** [15A NCAC 2H .0805 (a) (7) (H) (iii)]<br><br>ANSWER: | | | Remember we certify for Ammonia as Nitrogen not Ammonia. Be sure to check the standards to be sure they are using the correct $NH_3$–N concentration not the $NH_3$ concentration.<br>Preparation of standards in Standard Methods: all the methods refer back to SM 4500 $NH_3$ D section (3)(d) which states: stock ammonium chloride solution: Dissolve 3.819 g anhydrous $NH_4Cl$ (dried at 100° C) in water, and dilute to 1000 mL. **1.00 mL = 1.00 mg N = 1.22 mg $NH_3$**<br><br>That solution equals a 1000 mg/L concentration of Ammonia as Nitrogen. The difference between the 1000 and 1220 can be calculated from the molecular weights, N = 14 and $NH_3$ = 17. So 17÷14 = 1.22. That is where you get a concentration of 1.0 mg/L for Ammonia as Nitrogen (N) and 1.22 mg/L for Ammonia ($NH_3$)<br><br>Calibration must be performed each day samples are analyzed. Method lists 5 standards. Calibration standards do not have to be distilled.<br>Based on method flexibility allowances 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.<br><br>Rules: For electrode analyses, a series of two or more non-zero standards shall be used. |

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| 16 | Are curves plotted using Ammonia concentration versus potential (mV) developed? [SM 4500-$NH_3$ D-2011 (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] |
| 17 | Is the slope documented? [15A NCAC 2H .0805 (a) (7)] | | | Slope of tenfold 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.<br><br>SM 4020 B. (2) (a) states:<br>Apply linear or polynomial curve-fitting statistics, as appropriate, to analyze the concentration-instrument response relationship. The appropriate linear or nonlinear correlation coefficient for standard concentration-to-instrument should be greater than or equal to 0.995. Back calculate the concentration of each calibration point.<br><br>For Ammonia, a true curve is not created. Instead, it creates a point to point straight line between the calibration standards. And **since it is not a true curve, calculation of the correlation coefficient is not required because there isn't one**. This is another indicator that the section of the QC is not applicable. Instead, we require calculation and documentation of the slope because it is a straight line rather than a curve. |
| 18 | What is the acceptable slope range? [Manufacturer's instruction manual]<br><br>**ANSWER:** | | | **Slope generally obtained:**<br>See previous explanation |
| | **PROCEDURE – Sample Analysis** | **LAB** | **SOP** | **EXPLANATION** |
| 19 | **Distillation is not required except to resolve any controversies** | | | . |
| 20 | What sample volume is analyzed? [SM 4500-$NH_3$ D-2011 (4) (e)]<br><br>ANSWER: | | | 100 mL - if necessary, dilute sample to bring into the range of the calibration curve. Use same low speed stirring rate for standard solutions and samples. |
| 21 | Are samples allowed to come to room temperature before analysis? [SM 4500-$NH_3$ D-2011 (4) (b)] | | | Use standard solutions and samples that have the same temperature (about 25°C). |
| 22 | Is 10*N* NaOH added to all blanks, standards, and samples to raise the pH above 11 **after** immersing the electrode? [SM 4500-$NH_3$ D-2011 (4) (b)] | | | 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. |
| 23 | Is 10*N* NaOH/EDTA used in place of the NaOH if the presence of silver or mercury is possible? [SM 4500-$NH_3$ D-2011 (4) (b)] | | | If historical data shows the presence of silver or mercury is possible, NaOH/EDTA must be |

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| | | | | used to elevate the pH. However, compilation of this data is not required. |
| 24 | Is the volume of 10*N* NaOH or NaOH/EDTA solution added to the blanks, standards, and samples documented? [SM 4500-$NH_3$ D-2011 (4) (e)] | | | 1 mL is usually sufficient. Orion's ISA solution (Ionic Strength Adjuster) states to use 2 mL. |
| 25 | If a different volume of NaOH is added to the sample than to the calibration standards, is a correction made to the result? [SM 4500-$NH_3$ D-2011 (5)] | | | If a different volume of pH adjuster is needed for the sample, the following formula is used:<br><br>Mg $NH_3$–N/L = A x B x $\frac{(100 + D)}{(100 + C)}$<br><br>A = Dilution Factor<br>B = Concentration of $NH_3$-N/L, mg/L, from calibration curve<br>C = Volume of 10*N* NaOH added to the calibration standards, mL<br>D = Volume of 10*N* NaOH added to sample, mL |
| 26 | Is the adjusted pH verified and documented? [SM 4500-$NH_3$ D (4) (b) -1997 and 15A NCAC 2H .0805 (a) (7)] | | | 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 than 11 with either a pH meter or pH strips. This must also be documented. A check box indicating the pH is > 11 may be used. |
| 27 | How is the adjusted pH verified?<br><br>ANSWER: | | | Color indicator, pH meter (calibrated with buffer >11), pH strips. |
| | **QUALITY ASSURANCE** | **LAB** | **SOP** | **EXPLANATION** |
| 28 | Is a reagent/method blank analyzed with each batch of 20 or fewer samples? [SM 4020 B-2001 (2) (d)] | | | The reagent/method blank contains the same acid used to preserve samples and is carried through all sample preparatory steps (this would include the distillation step when applicable). A calibration blank is not carried through the distillation step nor does it include preservation acid.<br>**SM states:** Include at least one MB daily or with each batch of 20 or fewer samples, whichever is more frequent. |
| 29 | Is the reagent/method blank concentration less than or equal to ½ the concentration of the lowest calibration standard? [15A NCAC 2H .0805 (a) (7) (H) (i)] | | | Rule: The concentration of reagent, method, and calibration blanks shall not exceed 50 percent of the lowest reporting concentration or as otherwise specified by the reference method.<br><br>**Note:** Often you will see the blank reported as less than the PQL value. This is because the meter is so slow in the low end of the calibration that analysts do not wait for meter to stabilize. Instead of a specific reading and they just document less than the lowest standard. They need to allow meter to stabilize until the reading is less than ½ the PQL and then document that value.<br>**SM states:** Any constituent(s) recovered must generally be less than or equal to one-half the reporting level (unless the method specified otherwise). |
| 30 | What corrective action is taken if the reagent/method blank is not acceptable? [15A NCAC 2H .0805 (a) (7) (B)] | | | Our Rule requires corrective action any time quality control results indicate a problem.<br>**SM states:** If any MB measurements are at |

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| | ANSWER: | | | or above the reporting level, take immediate corrective action as outlined in Section 1020 B.5. This may include re-analyzing the sample batch. |
| 31 | Is the calibration verified by analyzing a **calibration standard** after each batch of ten samples and at the end of the run? [SM 4020 B-2011 (2) (b)] **List value(s) of standard used.** | | | The calibration verification standard (CVS) is a same source calibration standard. SM uses the word "typically" to provide more flexibility so that calibration verification standards are not required after exactly every ten samples as long as all samples are bracketed by acceptable quality control.<br>**SM states:** Verify calibration by periodically analyzing a calibration standard and calibration blank during a run – **typically**, after each batch of ten samples and at the end of the run. The calibration verification standard's analyte concentration **should** be varied over the calibration range to determine detector response. **Results must not exceed ±10% of its true value and calibration blank results must not be > one-half the reporting level** (unless the method specifies otherwise). |
| 32 | Does the laboratory take appropriate corrective action if the calibration verification standard result exceeds ±10% of the true value? [SM 4020 B-2011 (2) (b)] | | | **SM states:** If the calibration verification fails, immediately cease analyzing samples and initiate corrective action. Then, re-analyze the calibration verification. If the calibration verification passes continue the analysis. Otherwise, repeat initial calibration and reanalyze samples run since the last acceptable calibration verification. |
| 33 | Is the calibration verified by analyzing a **calibration blank** after each batch of ten samples and at the end of the run? [SM 4020 B-2011 (2) (b)] | | | For the electrode method, when distillation is not employed, the calibration blank may be equivalent to the reagent/method blank (refer to question #26).<br><br>SM uses the word "typically" to provide more flexibility so that calibration verification standards are not required after exactly every ten samples as long as all samples are bracketed by acceptable quality control.<br><br>**SM states:** Verify calibration by periodically analyzing a calibration standard and calibration blank during a run – **typically**, after each batch of ten samples and at the end of the run. The calibration verification standard's analyte concentration **should** be varied over the calibration range to determine detector response. **Results must not exceed ±10% of its true value and calibration blank results must not be > one-half the reporting level** (unless the method specifies otherwise). |
| 34 | Does the laboratory take appropriate corrective action if the calibration blank results are greater than one-half the reporting level? [SM 4020 B-2011 (2) (b)] | | | **SM states:** If the calibration verification fails, immediately cease analyzing samples and initiate corrective action. Then, re-analyze the calibration verification. If the calibration verification passes continue the analysis. Otherwise, repeat initial calibration and reanalyze samples run since the last acceptable calibration verification. |
| 35 | Does the laboratory analyze a second source standard to verify standard preparation? [SM 4020 B-2011 (2) (b) and (2) (e)] **List value and acceptance criterion of standard used for second** | | | A second source standard must be analyzed at least initially to confirm the accuracy of the standard preparation. The required Laboratory Fortified Blank (LFB) may serve |

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| | **source.**<br><br>ANSWER: | | | as the second source standard (refer to question #35). If the LFB is second source, use control charts to establish limits. (see question 41 Bottom Line)<br>If a purchased quality control standard is used, the manufacturer's limits may be used.<br><br>**SM states:** If the LFB is **not** prepared from a second source to confirm method accuracy, the lab must also verify the accuracy of its standard preparation by analyzing a mid-level second-source calibration standard **whenever a new initial calibration curve is prepared**. Results must agree within 15%, unless otherwise specified in a method.<br>LFBs (and LFMs) do not have to be made from a second source (unless the method specifies otherwise) as long as each initial calibration solution is verified via a second source.<br><br>**Bottom line:** For a held calibration curve, a second source standard is not required each day samples are analyzed – only with the intial making or verification of the standard curve. **Since a held curve is not acceptable for this method the second source standard must be analyzed daily.** |
| 36 | What corrective action is taken if the second source standard recovery is outside of established control limits? [15A NCAC 2H .0805 (a) (7) (B)]<br><br>ANSWER: | | | If quality control results fall outside established limits or show an analytical problem, the laboratory shall identify the Root Cause of the failure. The problem shall be resolved through corrective action, the corrective action process documented, and any samples involved shall be reanalyzed, if possible. |
| 37 | Does the laboratory analyze a laboratory-fortified blank (LFB) at least daily or per batch of 20 or fewer samples? [SM 4020 B-2011 (2) (e)] **List value(s) and acceptance criterion of standard used.**<br><br>ANSWER: | | | The LFB may be either a primary or secondary source standard so it may serve dual roles.<br><br>The LFB is a reagent blank (i.e., treated just like a sample including addition of the preservation acid) fortified with the analyte.<br><br>If the LFB is **primary source**, it may be equivalent to the CVS (refer to question #29). Analyze at least one daily or per batch of 20 or fewer samples. Use control charts to establish limits or default to the CVS acceptance criterion of ±10%.<br><br>If the LFB is **secondary source**, it may be equivalent to the second source standard (refer to question #33). Analyze one daily or per batch of 20 or fewer samples. Use control charts to establish limits.<br><br>**SM states:** LFBs (and LFMs) do not have to be made from a second source (unless the method specifies otherwise) as long as each initial calibration solution is verified via a second source. Ideally, vary LFB concentrations to cover the range from the midpoint to the lower part of calibration curve, including the reporting limit. Include one LFB daily or per each batch of 20 or fewer samples. Calculate %recovery, plot control charts and determine control limits for the |

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| | | | | LFB unless otherwise specified in the method. |
| 38 | What corrective action is taken if the LFB recovery is outside established control limits? [15A NCAC 2H .0805 (a) (7) (B)]<br><br>ANSWER: | | | If quality control results fall outside established limits or show an analytical problem, the laboratory shall identify the Root Cause of the failure. The problem shall be resolved through corrective action, the corrective action process documented, and any samples involved shall be reanalyzed, if possible.**SM states**: Establish corrective actions to take if the LFB does not satisfy acceptance criteria. |
| 39 | Is a Laboratory Fortified Matrix (LFM)/Laboratory Fortified Matrix Duplicate (LFMD) analyzed with each batch of 20 or fewer samples? [SM 4020 B-2011 (2) (g)] | | | Laboratory fortified matrix is the same as a matrix spike; that is, a spiked sample. **Note: No option to perform an environmental sample duplicate and then spike separately – must perform MS/MSD for this method.**<br>**SM states:** Include at least one LFM/LFMD daily or with each batch of 20 or fewer samples. |
| 40 | How is the LFM (spike) prepared? [SM 4020 B-2011 (2) (g)]<br><br>ANSWER: | | | See Matrix Spike Technical Assistance document. Use the same solution as the LFB for the LFM to evaluate bias attributed to matrix and accuracy of the LFM.<br>**SM states:** To prepare an LFM, add a known concentration of analytes (**ideally** from a second source) to a randomly selected routine sample without increasing its volume by more than 5%. Ideally the new concentration **should be** at or below the midpoint of the calibration curve, and for maximum accuracy, the spike **should** approximately double the sample's original concentration. If necessary dilute the spiked sample to bring the measurement within the calibration curve. Also rotate the range of spike concentrations to verify performance at various levels .to rotate spike range. If the spike solution contribution to the fortified sample is kept to 1% or less, a spike dilution correction does not have to be calculated. |
| 41 | What is the acceptance criterion for LFM/LFMD recovery? [SM 4020 B-2011 (2) (g)]<br><br>ANSWER: | | | Will have two % recovery calculations for accuracy from spike recoveries and one RPD calculation for precision from duplicate calculation<br>**SM states:** Calculate recovery limits and RPD, and plot control charts to determine acceptance criteria. (see question 41 Bottom Line). |
| 42 | What corrective action does the laboratory take if the LFM/LFMD results are outside of established control limits for **accuracy**? [15A NCAC 2H .0805 (a) (7) (B)]<br><br>ANSWER: | | | If quality control results fall outside established limits or show an analytical problem, the laboratory shall identify the Root Cause of the failure. The problem shall be resolved through corrective action, the corrective action process documented, and any samples involved shall be reanalyzed, if possible. Compare to LFB result and other QC. Reanalyze LFM. If it still fails, qualify the spiked sample result.<br>**SM states**: Establish corrective actions to be taken if the LFM does not satisfy acceptance criteria. |
| 43 | What is the acceptance criterion for LFM/LFMD relative percent difference? [SM 4020 B-2011 (2) (g)]<br><br>ANSWER: | | | **SM states:** Calculate percent recovery and relative percent difference, plot control charts (unless method specifies acceptance criteria) and determine control limits for spikes at different concentrations. Ensure the method's |

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| | | | | performance criteria are satisfied.<br>**Bottom line:** We are not requiring control charts but will instead accept a system of trend analysis. That is, the lab's monitoring of the trends in the data. 40 CFR part 136.7 (viii) states: Control charts (or other trend analysis of quality control results). |
| 44 | What corrective action does the laboratory take if the LFM/LFMD results are outside of established control limits for **precision**? [15A NCAC 2H .0805 (a) (7) (B)]<br><br>ANSWER: | | | If quality control results fall outside established limits or show an analytical problem, the laboratory shall identify the Root Cause of the failure. The problem shall be resolved through corrective action, the corrective action process documented, and any samples involved shall be reanalyzed, if possible.**SM states:** Ensure the method's performance criteria are satisfied |
| 45 | Is the data qualified on the Discharge Monitoring Report (DMR) or client report if Quality Control (QC) requirements are not met? [15A NCAC 2H .0805 (a) (7) (B)] | | | If the sample cannot be reanalyzed, or if the quality control results continue to fall outside established limits or show an analytical problem, the results shall be qualified as such.<br>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<br>laboratory to provide the client or end-user of the data with sufficient information to determine the usability of the qualified data. |

Additional Comments:

Stock Standard – Dissolve 3.819 g anhydrous $NH_4CL$ (dried at 100 ºC) in ammonia-free water, and dilute to 1000 mL.
1.00mL = 1.00 mg N = 1.22 mg $NH_3$.

NOTE: Data is reported as $NH_3$–N, that is Ammonia as Nitrogen, so 1.00 mL of stock standard equals 1 mg of Ammonia nitrogen

Additional Comments:

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Inspector: _____Date: _____