

NC DEQ/DWR WASTEWATER/GROUNDWATER LABORATORY CERTIFICATION BRANCH

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

**Parameter: Nitrate Nitrogen**  
**Method: Hach 10206 (Aqueous), Rev. 2.1, January 2013**  
**Also known as the Hach TNTplus 835/836 Method 10206**

**EQUIPMENT:**

|                            |  |
|----------------------------|--|
| Spectrophotometer (Model): |  |
|----------------------------|--|

**REAGENTS:**

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|---|---|
| Reagent water – Water in which nitrate is not detected at or above the method level of this method. Bottled distilled water, or water prepared by passage of tap water through ion exchange and activated carbon have been shown to be acceptable sources of reagent water. | Hach Company TNTplus Nitrate Reagent, Cat. No. TNT835 or TNT836.  |
| Sulfuric Acid   | Hach Company Nitrate Standard Solutions: 100 mg/L as NO <sub>3</sub> -N (Cat. No. 194749) and 1000 mg/L as NO <sub>3</sub> -N (Cat. No.1279249), or equivalent. |
| Sulfamic Acid (if needed for interference mitigation)   |   |

**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   | L<br>A<br>B | S<br>O<br>P | EXPLANATION   |
|----|---|-------------|-------------|---|
| 1. | Is the SOP reviewed at least every 2 years? What is the most recent review/revision date of the SOP? [15A NCAC 02H .0805 (a) (7)]<br><br><b>Date:</b> |             |             | 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. Verify proper method reference. During review notate deviations from the approved method and SOP. |
| 2. | Are all revision dates and procedural edits tracked and documented? [15A NCAC 02H .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  | L<br>A<br>B | S<br>O<br>P | EXPLANATION   |
| 4. | Are samples collected and stored in polyethylene, Teflon®, or glass containers? [40 CFR 136 Table II]   |             |             |   |
| 5. | Are samples iced to above freezing but ≤ 6 ° C during shipment? [40 CFR 136 Table II]   |             |             |   |
| 6. | Are samples refrigerated above freezing but ≤ 6 ° C during storage? [40 CFR 136 Table II]   |             |             |   |
| 7. | Are samples analyzed within 48 hours of collection? [40 CFR 136 Table II]   |             |             |   |
|    | INTERFERENCES   | L<br>A<br>B | S<br>O<br>P | EXPLANATION   |
| 8. | Is this method only used for samples with a Chemical Oxygen Demand (COD) less than 500 mg/L? [Hach 10206 Section 3.1]                                 |             |             | High loads of oxidizable organic substances cause the reagent to change color and to give high-bias results. The test can thus only be used for wastewater analyses if the chemical oxygen demand (COD) is less than 500 mg/L. Measurement results can be verified using sample dilutions or standard additions.      |

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| 9.  | Are samples containing Nitrites in excess of 2.0 mg/L treated with 50 mg of sulfamic acid per 5.0 mL of sample, and allowed to sit for 10 minutes after the sulfamic acid has dissolved? [Hach 10206 Section 3.2]   |                      |                      | Nitrite concentrations of more than 2.0 mg/L interfere (high-bias results). Add 50 mg of sulfamic acid (amidosulfonic acid) to 5.0 mL of sample, dissolve and wait for 10 minutes. Analyze the prepared sample as described in the procedure.  |
|     | <b>ANALYTICAL PROCEDURE</b>   | <b>L<br/>A<br/>B</b> | <b>S<br/>O<br/>P</b> | <b>EXPLANATION</b>   |
| 10. | For Low Range TNT 835, is 1.0 mL of sample pipetted into the vial? [Hach 10206 Section 11.2.1]  |                      |                      | TNT 835 = 0.23-13.5 mg/L   |
| 11. | For Low Range TNT 835, is 0.2 mL of Solution A added to the vial? [Hach 10206 Section 11.3.1]   |                      |                      |  |
| 12. | For High Range TNT 836, is 0.2 mL of sample added to the vial? [Hach 10206 Section 11.2.1]  |                      |                      | TNT 836 = 5-35 mg/L  |
| 13. | For High Range TNT 836, is 1.0 mL of Solution A added to the vial? [Hach 10206 Section 11.3.1]  |                      |                      |  |
| 14. | Are the vials capped and inverted 2-3 times until no more streaks can be seen? [Hach 10206 Section 11.3.2]  |                      |                      | Cap and invert the reaction tube 2-3 times until no more streaks can be seen in the reaction tube solution.  |
| 15. | Are the vials allowed to react for 15 minutes? [Hach 10206 Section 11.3.3]  |                      |                      |  |
| 16. | Are the vials wiped and inserted into the spectrophotometer for analysis? [Hach 10206 Section 11.4.1]   |                      |                      | Wipe the vial and insert the prepared vial into the spectrophotometer. The instrument reads the barcode, then selects and performs the correct test. No zero is required. Results are in mg/L NO <sub>3</sub> -N   |
|     | <b>QUALITY ASSURANCE</b>  | <b>L<br/>A<br/>B</b> | <b>S<br/>O<br/>P</b> | <b>EXPLANATION</b>   |
| 17. | Has an initial MDL study been performed according to 40 CFR 136, Appendix B? [Hach 10206 Section 9.2.1]   |                      |                      | Method Detection Limit (MDL) - To establish the ability to detect nitrate the analyst shall determine the MDL per the procedure in 40 CFR 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method.   |
| 18. | Is ongoing MDL data being collected quarterly? [Procedure for the Determination of the Method Detection Limit, Rev. 2, (3) (a)]   |                      |                      | During any quarter in which samples are being analyzed, prepare and analyze a minimum of two spiked samples on each instrument, in separate batches, using the same spiking concentration used in Section 2.   |
| 19. | Are MDL values verified at least every 13 months according to the ongoing MDL determination requirements and updated if necessary? [Procedure for the Determination of the Method Detection Limit Procedure, Rev. 2, (4)]<br><br><b>List current MDL:</b> |                      |                      | The verified MDL is the greater of the MDL <sub>s</sub> or MDL <sub>b</sub> . If the verified MDL is within 0.5 to 2.0 times the existing MDL, and fewer than 3% of the method blank results (for the individual analyte) have numerical results above the existing MDL, then the existing MDL may optionally be left unchanged. Otherwise, adjust the MDL to the new verification MDL. (The range of 0.5 to 2.0 approximates the 95th percentile confidence interval for the initial MDL determination with six degrees of freedom.)                    |
| 20. | Is the Minimum Level calculated per Section 9.2.1 of the method? [Hach 10206 Sections 9.2.1 and 13.0]<br><br><b>List calculated Minimum Level:</b>  |                      |                      | The analyst also shall calculate the Minimum Level (ML) of quantitation by multiplying the MDL by 3.18 and rounding to the number nearest to (1, 2 or 5) x 10 <sup>n</sup> , where n is a positive or negative integer. The calculated MDL should be less than or equal to the MDL in Section 13.0 prior to the practice of this method. Similarly, the calculated ML should be less than or equal to the ML in Section 13.0<br><br>Note that the ML is not the reporting limit. The reporting limit is based upon the lowest calibration concentration. |
| 21. | Were 4 replicate Initial Precision and Recovery standards analyzed and the average percent recovery and RSD calculated per 9.3.2 prior to use of the method? [Hach 10206 Section 9.3 and 13.0]<br><br><b>IPR RSD:</b><br><b>IPR recovery:</b>             |                      |                      | The method acceptance criteria for the Initial Recovery Range is 90% - 110% and the Initial Precision (RPD) is ±10%.   |

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| 22. | If the average percent recovery and RSD of the replicate IPR standards do not meet method acceptance criteria, is the problem corrected and the test repeated? [Hach 10206 Section 9.3.2.2]  |  |  | If, however, the RSD exceeds the precision limit or x falls outside the range for recovery, system performance is unacceptable. In this event correct the problem and repeat the test.  |
| 23. | Is the factory-set calibration curve verified with a series of three or more non-zero standards that bracket the range of sample concentrations each day? [15A NCAC 02H .0805 (a) (7) (H) (v)]<br><br><b>Lower Reporting Limit Std Conc:</b><br><b>Upper Reporting Limit Std Conc:</b> |  |  | The range of TNT 835 is 0.23-13.5 mg/L.<br>The range of TNT 836 is 5-35 mg/L<br><br>If using both TNT835 and TNT836 in one analysis, it is acceptable to verify three standards that bracket the range of both kits.  |
| 24. | Is a calibration blank and calibration verification standard analyzed prior to sample analysis, after every tenth sample, and at the end of each sample group? [15A NCAC 02H .0805 (a) (7) (H)]<br><br><b>Calibration Verification Std Conc:</b>                                       |  |  | A calibration blank and calibration verification standard shall be analyzed prior to sample analysis, after every tenth sample, and at the end of each sample group, unless otherwise specified by the method, to check for carryover and calibration drift.  |
| 25. | Is the recovery of the calibration verification standards within $\pm 10\%$ ? [15A NCAC 02H .0805 (a) (7) (H) and Factory-set Calibration Curve Verification Policy]<br><br><b>Answer:</b>   |  |  | These are the standards listed in #s 23 and 24.<br><br>Policy: Compare the measured concentration of each standard to the expected value. Each calibration verification standard must be within $\pm 10\%$ of its expected value unless different criteria are specified in an individual method.   |
| 26. | What corrective action is taken if daily calibration verification standards are unacceptable? [15A NCAC 02H .0805 (a) (7) (B)]<br><br><b>Answer:</b>   |  |  | 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.  |
| 27. | Is at least one LRB analyzed with each batch of samples? [Hach 10206 Section 9.4]  |  |  | The laboratory reagent blank (LRB) is an aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment and reagents that are used with other samples. The laboratory must analyze at least one LRB with each batch of samples.<br><br>If using both TNT835 and TNT836 vials in one analysis, an LRB is required for each kit. |
| 28. | Are the values of all blanks $\leq \frac{1}{2}$ the reporting limit? [15A NCAC 02H .0805 (a) (7) (H) (i)]  |  |  | 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.   |
| 29. | What corrective action is taken if the LRB or calibration blanks do not meet the established criteria? [15A NCAC 02H .0805 (a) (7) (B)]<br><br><b>Answer:</b>  |  |  | Check for contamination, check viability of low standard, re-analyze blank, re-digest and re-analyze entire batch or qualify the data.  |
| 30. | Are at least 5% of the samples from each analytical batch spiked in duplicate? [Hach 10206 Section 9.6]  |  |  | Matrix Spike and Matrix Spike Duplicate Precision and Recovery (MS/MSD) – The laboratory must, on an ongoing basis, spike at least 5% of the samples from each analytical batch as defined in Section 9.1.2.<br><br>An analytical batch is a set of samples processed during a contiguous 8-hour period, not to exceed 20 samples.  |

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| 31. | Are matrix spike recoveries within the limits of 90 – 110%? [Hach 10206 Sections 9.6.1 and 17.1, Table 3]  |  | Calculate each percent recovery (P) as 100 (A-B)%/T, where A is the concentration of Nitrate in the spiked samples and T is the known true value of the spike. Compare the percent recovery (P) with the corresponding QC acceptance criteria found in Section 17, Table 3.   |
| 32. | What corrective action does the laboratory take if the spike recoveries are outside of established acceptance limits? [15A NCAC 02H .0805 (a) (7) (B)]<br><b>Answer:</b> |  | 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. 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. |
| 33. | Is the RPD between the spike and spike duplicate within the limit of 20%? [Hach 10206 Sections 9.6 and 17.1, Table 3]  |  | Calculate the relative percent difference (RPD) between two sample results using the following equation:<br>$RPD = \frac{ D_1 - D_2 }{(D_1 + D_2) / 2} \times 100$ Where, D1 = Concentration of analyte in the MS, D2 = Concentration of analyte in the MSD. Compare the calculated RPD with the corresponding QC acceptance criteria found in Section 17, Table 3.   |
| 34. | What corrective action does the laboratory take if the RPD is outside of acceptance criterion? [15A NCAC 02H .0805 (a) (7) (B)]<br><b>Answer:</b>                        |  | 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. 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. |
| 35. | Are results qualified to indicate quality control failures or sample anomalies? [15A NCAC 02H .0805 (e) (5)]   |  | Reported data associated with Quality Control failures, improper sample collection, holding time exceedances, or improper preservation shall be qualified as such.  |

Additional Comments:

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