DETERMINATION OF NITRATE AND NITRITE IN WATER USING THE LACHAT QUICKCHEM 8500 AUTOANALYZER

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1. SCOPE AND APPLICATION

This method is applicable to the determination of nitrate (NO_3) and nitrite/nitrate (NO_2NO_3) in ground, surface, saline waters and wastes.

The calibration range for NO_2NO_3 is from the method detection limit (MDL) 0.004 mg N/L, to 0.80 mg N/L. The range may be extended by dilution. Tests covered by this SOP are W-NO2NO3, W-NO2NO3-F, and W-NO3. The practical quantitation limit (PQL) is 0.010 mg N/L.

Nitrate concentration may be determined by calculation using the NO_2NO_3 concentration (analysis method described in this SOP) and the nitrite concentration (see DEP SOP NU-087 and DEP SOP NU-96). The MDL and PQL for calculated nitrate are 0.004 mg N/L and 0.010 mg N/L, respectively.

2. SUMMARY OF THE METHOD

2.1. This method is based on EPA method 353.2, Rev 2.0 (1993) and Lachat method 10-107-04-1-C. Diethylenetriaminepentaacetic acid (DTPA) is used as complexing agent instead of ethylenediamine tetraacetic acid (EDTA).

2.2. A sample is passed through a column containing granular copper-cadmium, which reduces nitrate to nitrite. The nitrite originally present plus the reduced nitrate can then be determined by colorimetry. The nitrite is diazotized with sulfanilamide and coupled with N-(1-naphthyl)ethylenediamine dihydrochloride to form a highly colored azo dye, which is measured at a wavelength of 520 nm.

2.3. Interferences:

2.3.1. Build-up of suspended matter in the reduction column will restrict sample flow. Samples may be filtered prior to analysis.

2.3.2. Low results may be obtained for samples containing high concentrations of iron, copper and other metals. Diethylenetriaminepentaacetic acid (DTPA) is added to the buffer solution to eliminate these interferences.

2.3.3. Samples with background absorbance at the analytical wavelength may interfere. Color correction is used to eliminate this interference on a per sample basis.

3. EQUIPMENT AND SUPPLIES

3.1. Instrument 1:

Lachat QuickChem Series 2 FIA+ 8500 Series Flow Injection Analyzer; Unique ID: “Lachat 1”

Omnion 4.0 Software.

3.2. Instrument 2:

Lachat QuickChem Series 2 FIA+ 8500 Series Flow Injection Analyzer;

Unique ID: “Lachat 2”

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Omnion 4.0 Software.

3.3. Pump Tubing:

Orange = Carrier (0.2 % H_2SO_4) (4.2.3.)

Black = Sulfanilamide Color Reagent (4.2.2.)

Blue/Yellow = Buffer Solution (4.2.1.)

Green = Sample Intake

Purple = Probe Rinse

3.4. Glassware and pipettes: Class A type volumetric glassware and analytical pipettes:

Variable Eppendorf pipettes

15 mL Centrifuge Tubes

Glass sample tubes

50 mL, 250 mL, 1 L and 2 L volumetric flasks

2 L Beaker

3.5. Chlorine test strips e.g., Hach Aquachek Water Quality Test Strips for Total Chlorine and Free Chlorine, range = 0-10 ppm (cat. #27450-50), or SenSafe Free Chlorine Water Check test strips, range = 0-4 ppm (part #481026)

3.6. Disposable 10 mL syringes and 0.45 µm syringe filters (Whatman Puradisc PP cat. # 05-713-404A).

4. REAGENTS AND STANDARDS (SEE DEP SOPS NU-041 and NU-042)

Note: Before preparing reagents or standards, or running samples, please read the safety notes in the safety/hazardous waste section of this SOP and the MSDS for the chemicals used in this analysis.

Note: Reagent and standard preparations must be documented in the Laboratory Information Management System (LIMS) 'Standard Preparation Tracker' module. Unique ID numbers for each standard and reagent are generated in the module and documented in the Reagent and Standard Logsheet NU-RGTSTD_W-NO2NO3 located on the network at: \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\worksheets_NO2NO3\Templates This sheet needs to be updated, printed, and submitted as part of the analysis folder. If available, a Certificate of Analysis for each purchased standard and reagent is maintained in the following folder\\FLDEP1\DEAR\Labs\Lab3\Chem Data\Inorganic\Nutrients\REAGENT_PREP\NO2NO3\Certificates of Analysis : All containers holding standards or reagents must be labeled with their unique ID and expiration date.

Note: The volumes prepared for the reagents and standards may be altered by the analyst as necessary. The final concentrations of the constituents of a standard or reagent must not be changed.

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4.1. Chemicals:

4.1.1. Granular copper-cadmium column (Hach cat. # 50237A)

4.1.2. Hydrochloric acid, concentrated (HCl)

4.1.3. Ammonium hydroxide (NH_4OH)

4.1.4. Diethylenetriaminepentaacetic acid (DTPA)

4.1.5. Phosphoric acid, concentrated (H_3PO_4)

4.1.6. Sulfanilamide

4.1.7. N-(1-naphthyl)ethylenediamine dihydrochloride (NED)

4.1.8. Sulfuric acid, concentrated (H_2SO_4)

4.1.9. Sodium chloride, reagent grade (NaCl)

4.1.10. Potassium nitrate (KNO_3)

4.1.11. Chloroform ($CHCl_3$)

4.1.12. Nitrite standard (NO_2)

4.1.13. Standard Reference Material (ALTQC) for nitrate (from Environmental Resource Associates, ERA)

4.1.14. Standard Reference Material (CATCHCK) for nitrite (from Ricca Chemical Company)

4.1.15. Sodium thiosulfate ($Na_2S_2O_35H_2O$), 0.025 N, ACS grade

4.2. Reagents:

4.2.1. Buffer solution:

4.2.1.1. In a laboratory hood, slowly add 210 mL of concentrated hydrochloric acid (4.1.2.) to 1 L deionized (DI) water in a 2 L volumetric flask while stirring. Slowly add 190 mL ammonium hydroxide (4.1.3.) and 2.0 g of DTPA (4.1.4.). Stir for five minutes and allow to cool. Dilute to the mark. Holding time, 30 days.

Note: This acid base reaction is exothermic and generates enough heat to cause burns through the flask. Use caution. Use a hood to prepare the solution to minimize exposure to fumes from the reagents. This solution should be prepared in a room that is separate from Ammonia and TKN analysis due to the possibility of contamination.

4.2.1.2. After cooling is complete check the pH of the solution using pH paper. The pH should be ≈ 8.5. Buffer solution should be made as needed. Record each new batch in the reagent log. Holding time, 30 days.

4.2.2. Sulfanilamide color reagent (COLOR REAGENT):

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4.2.2.1. Add 200 mL of 85 % phosphoric acid (4.1.5.) to 1.2 L of DI water in a 2 L volumetric flask. Mix and add 80 g of sulfanilamide (4.1.6.) and 4.0 g of N-(1-naphthyl)ethylenediamine dihydrochloride (NED, 4.1.7.).

4.2.2.2. Stir for twenty minutes and dilute to the mark. Filter reagent using an aspirator with a 0.45 μm filter. Transfer solution to a dark container. Holding time, 30 days.

4.2.3. Carrier solution (CAR, 0.2 % H_2SO_4):

This solution is used for the MDL, MBLKs, and Continuing Calibration Blanks (CCBs), and as the diluent for preparation of calibrants (4.3.2. and 4.3.3.), the ALTQC working solution (4.3.4.2), and for sample dilutions when necessary.

4.2.3.1. Add 4 mL of conc. sulfuric acid (4.1.8.) to approx. 200 mL of DI water in a 2 L volumetric flask. Dilute to mark and invert to mix. Prepare fresh daily.

4.2.3.2. High conductivity samples (≥ 5000 μmho/cm or salinity > 3 PPTh) are analyzed separately from fresh water samples. For high conductivity runs, a saline carrier solution is prepared by adding 70 g reagent grade sodium chloride (4.1.9.) and 4 mL of conc. sulfuric acid (4.1.8.) to approximately 1 L of DI water in a 2 L volumetric flask. Dilute to the mark with DI water and mix well. Prepare fresh daily.

4.2.4. Color Correction Reagent (COLOR CORR RGT):

Add 100 mL of 85 % phosphoric acid (4.1.5.) to 600 mL of DI water in a 1 L volumetric flask. Mix well and add 2.0 g of N-(1-naphthyl)ethylenediamine dihydrochloride (NED, 4.1.7.). Dilute to the mark with DI water and invert to mix. Filter reagent using an aspirator with a 0.45 μm filter. Transfer solution to a dark container. Holding time, 30 days.

4.2.5 Granular copper-cadmium column (4.1.1.):

The supplier for the granular copper-cadmium columns (Hach cat. # 50237A) gives an expiration date of 6 month from the manufacture date. The holding time of the columns can be extended an additional 180 days past the expiration date, based on a passing column efficiency check (CATCHCK Standard 4.3.5.) and a passing ALTQC standard (ERA 4.3.4.2.). The column will be reentered in LIMS and a new Reagent ID will be generated with an expiration 180 days after the manufacture's expiration.

4.3. Standards and spiking solutions

Note: For runs with high conductivity samples (≥ 5000 μmho/cm), the calibration standards (4.3.3.) including the PQL-level check standard (PQCK1, 4.3.3.) and the Continuing Calibration Verification standard (CHCK, 4.3.3.), the laboratory fortified blanks (LFBs,

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5.3.), and ALTQC (4.3.4.2.) solutions described below are prepared using the salt carrier solution (4.2.3.2.).

4.3.1. Nitrate Stock Standard (1000 mg N/L as NO_3):

4.3.1.1. Dissolve 7.218 g potassium nitrate (KNO_3, 4.1.10.) in a 1 L volumetric flask containing ≈ 800 mL DI water.

4.3.1.2. Add 2 mL chloroform (4.1.11.) and dilute to the mark with DI water. Invert flask 12 times to mix thoroughly and store in the refrigerator. Holding time, 180 days.

4.3.2. Nitrate Intermediate /Spiking Standard (20 mg N/L as NO_3):

Pipette 20 mL of 1000 mg N/L nitrate stock standard (4.3.1.) into a 1 L volumetric flask containing 500 mL of 0.2 % H_2SO_4 (4.2.3.). Dilute to the mark with carrier solution (4.2.3) and invert 12 times. Store the standard in the refrigerator. This working standard is used to prepare the calibration standards including the PQCK and the CHCK standards, LFBs, and the matrix spikes. Holding time, 90 days.

4.3.3. Calibration Standard Preparation:

The method uses a five point calibration. The calibration standard levels are shown in the table below. Six cups are loaded in the standards rack, the 6th cup having carrier (4.2.3.) for the calibration blank. Holding time, 30 days.

Concentration (mg N/L)	Volume added (mL) (20 mg/L Standard, 4.3.2.)	Final Volume (mL) (made up using carrier, 4.2.3*.)
0.800 (CHCK2)	20	500
0.200 (CHCK)	5	1000
0.050	1.25	500
0.020	0.500	500
0.010 (PQCK1)	0.250	500

* For runs containing samples with conductivities < 5,000 µmho/cm, use carrier solution prepared as described in 4.2.3.1. For runs containing high conductivity samples (≥ 5000 µmho/cm), use salt carrier solution prepared as described in 4.2.3.2.

4.3.4. ALTQC standard:

4.3.4.1. The supplier for the standard reference material (currently Environmental Resource Associates) differs from the supplier of the calibration standards. This quality control standard (4.1.13) is prepared from the ampule according to the manufacturer's instructions. For the concentration and expiration date of the

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ampule, see the manufacturer's certificate. The holding time of the prepared stock standard is 180 days, and this solution should be stored refrigerated.

4.3.4.2. The stock ALTQC standard is diluted appropriately with the carrier solution (4.2.3.) so that the concentration falls within the calibration range. This sample is called ERAALTQCNOX# on the run, where '#' indicates the stock standard increment. Holding time of the working solution, 30 days.

4.3.5. CATCHCK standard solution - The CATCHCK solution is prepared by diluting the stock standard solution (1000 mg N/L NO_2) purchased from Ricca Chemical Company (4.1.14.) to 0.20 mg N/L using DI water. For runs with high conductivity samples, dilute the stock standard solution using a solution of DI water with 35 g/L NaCl added. **Do not dilute with carrier solution or acidify the nitrite standard. The presence of acid will oxidize the nitrite to nitrate.** Holding time, 2 days.

The following formula can be used to determine the correct dilution:

$$M_1V_1 = M_2V_2$$

Where; M_1 = Concentration of stock solution used (4.1.14.),
V_1 = Volume of stock required,
M_2 = Concentration of working standard and
V_2 = Volume being prepared.

5. SAMPLE PREPARATION (SEE DEP SOP NU-033)

5.1. Samples are preserved at the time of collection with sulfuric acid to a concentration of 0.2 % to achieve a pH of less than 2 units. They are stored at ≤ 6°C (not frozen) in the Nutrients refrigerator located in receiving room C301. The samples must be analyzed within 28-days of the collection date to be reported unqualified.

5.2. Remove the samples from the refrigerator following the proper protocols to preserve the samples' chain of custody. Allow the samples to come to room temperature before pouring them into the tubes for analysis.

5.3. For each batch prepare two low-level 0.20 mg N/L matrix spikes by adding 100 µL of the Nitrate Working Intermediate/Spiking Standard (4.3.2.) into 10 mL of a selected sample (spike code N1). Also prepare a single high-level 0.40 mg N/L matrix spike by adding 200 µL of the Nitrate Working Intermediate/Spiking Standard (4.3.2.) into 10 mL of the selected sample (spike code N2). This high-level spike allows for reporting a spike recovery in case the low level matrix spikes are buried due to high background levels of nitrate in the sample. Prepare one LFB at 0.20 mg N/L following the same procedure substituting carrier solution (4.2.3.) for the sample.

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5.4. All ground water samples that feed residential and commercial wells and samples from wastewater treatment facilities where the field sheets indicate the presence of a residual chlorine content are tested for chlorine. If residual chlorine is detected it is removed according to the following procedure:

5.4.1. Use chlorine test strips (3.5) to determine if chlorine is present and its approximate concentration. Pour about 15 ml of sample in a small plastic cup and swirl the test strip in the sample for 30 seconds. Compare the color of the test strip against the color templates on the test strip container to determine total residual chlorine concentration in ppm. Record the result on the bench sheet and the run report.

If chlorine is detected, use the following formula to determine the amount of 0.025 N sodium thiosulfate solution to add to the sample:

$$X = [(A) \times (\text{total sample volume}) / 886.3]$$

Where; X = Volume (mL) of 0.025 N sodium thiosulfate solution to be added to the total sample volume (mL) for dechlorination

A = Concentration (mg/L) of total residual chlorine in the sample.

Note: A 0.0250 N thiosulfate solution is equivalent to 886.3 µg Cl as Cl_2 /1.00 mL.

5.4.2. Record the volume of sodium thiosulfate solution used to dechlorinate the sample in the Excel spreadsheet template NU-CHLORINE found at: \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\worksheets_NO2NO3\Templates. After adding the sodium thiosulfate, take a small aliquot of the sample and reanalyze with a chlorine test strip (see 5.4.1.) to ensure that all the chlorine in the sample has been treated. This procedure is consistent with DEP SOP TA-09.18. Save the completed worksheet as YYMMDDM#CL (Lachat 1), or YYMMDDN#CL (Lachat 2) in \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\worksheets_NO2NO3\Chlorine.

6. SAMPLE ANALYSIS/QUANTITATION

Note: High conductivity samples (≥ 5000 µmho/cm) are run with a salt calibration (4.3.3.) and a salt carrier solution (4.2.3.2.) is used for sample dilutions.

6.1. Instrument Setup:

6.1.1. Turn on all four instrument components and computer.

6.1.2. Locate manifold for NO2NO3, and check the condition of the tubing and column. Make sure all connections are made as shown in the Lachat method manual located in the drawer under the instrument.

6.1.3. Lock down all tubing in the peristaltic pump and flush with reagents for at least 15 minutes prior to start of run.

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6.1.4. While tubing is flushing select the Omnion icon on the computer desktop to open the instrument software.

6.1.5. Select *New* icon on the Omnion toolbar.

6.1.6. Modify the sample run sequence of the template to reflect the new run. To print the sequence worksheet select *Run → Export Worksheet Data.*

An example run sequence includes:

CalStd A-F (Calibration Standards from 4.3.3. plus a blank (4.2.3.))
PQCK1 (4.3.3.)
MDL (4.2.3.)
CATCHCK (4.3.5.)
ERAALTQCNOX# (ALTQC, 4.3.4.)
CHCK2 (0.800 mg N/L standard (4.3.3.), to check for carryover)
CAR (Carrier solution, 4.2.3.)
CHCK (4.3.3.)
CCB (4.2.3.)
Batched samples, with an **MBLK_F, LFB,** and **spikes** (5.3.) for each batch (the notation "**_F**" indicates the sample was filtered)
CAR
CHCK
CCB

6.1.7. Load samples.

6.1.8. Select *Start* button on the tool bar to begin analysis. If the analysis needs to be paused or stopped select the *Stop* button on the tool bar. If you want to resume analysis select *Resume* or select *Stop Now* to end current sequence.

6.1.9. After completing the run save the data by selecting Run → *Save As* → *FileName.* Use the notation YYMMDD**M**# for files run on Lachat 1 and YYMMDD**N**# for files run on Lachat 2 (where YY is for the year, MM is for the month, DD is for the day, and # is for the 1st, 2nd, etc run of the day).

6.2. Color Correction:

6.2.1. Manual color correction - Any sample with a concentration at or above the MDL and a noticeable color should be run for color correction. At the end of the run remove the intake line from the sulfanilamide (color reagent), and put it in another beaker containing Color Correction Reagent (4.2.4.). Wait approximately 5 minutes until system equilibrates. Meanwhile set up the new sequence beginning with five blanks followed by the samples to be corrected followed by another five blanks at the end.

6.2.2. Repeat steps 6.1.6. – 6.1.9.

6.2.3. Color correction calculations - In the Excel spreadsheet template NU-COLORCORR), found at:

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\\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\worksheets_NO2NO3\Templates, enter all blank concentrations from the color correction run (Sample ID: MBLK), sample ID of samples that required color correction, their respective raw result (A) and color correction value (B). An average blank concentration (Avg. Blank) is calculated from the 10 blanks run before and after the samples (6.2.1.) and the color correction is calculated as follows:

Color correction = A – (B – Avg. Blank)

6.2.4. Save the worksheet as YYMMDDM# (Lachat 1), or YYMMDDN# (Lachat 2) in \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\worksheets_NO2NO3. .

6.3 Quantitation/Calculations:

6.3.1 The instrument will give the analysis results for NO_2NO_3 in mg N/L.

6.3.2 The QC Manager calculates recoveries for spikes and QC standards as well as relative percent differences (RPD) for duplicate samples and spikes. For general calculations including RPDs and spike recoveries see Section 5.9 of the FDEP Quality Manual.

6.3.3 The individual calibration standards are prepared according to section 4.3.3. The linear calibration is calculated by the instrument software and is presented in Table 1 and Figure 1 of the analysis report. It includes the correlation coefficient and % residuals that are used to evaluate the linear fit.

6.4 Post-Run Procedure:

6.4.1. Printing Data:

6.4.1.1. Select the *Tools -> Custom Report*

6.4.1.2. Select *Print* button. (Font size may be changed.)

6.4.1.3. Calibration info will print along with data.

6.5. Exporting Files:

6.5.1. Select Run tab in the Run Properties window.

6.5.2. Select *Export Data to File* button.

6.5.3. Save raw omnion data file to the Nutrients drive under the appropriate instrument in the current year's subfolder by clicking *Open* in the Omnion Software→ right click on the current day's saved file →select copy →paste the data file in: \\FLDEP1\DEAR\Labs\lab3\Chem Data\Inorganic\Nutrients\FIA\Raw Omnion Data Files and selecting the appropriate subfolders for the instrument and current year.

6.5.4. Convert file in QC Manager, and save as raw file.

6.5.5. Format data file, select uploadable samples, and prepare folder for further

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review by supervisor.

7. DATA ARCHIVAL

7.1. The raw data is archived in paper format. A report folder is created for each analytical run. Occasionally more than one run may be in one folder. The folder is labeled with the test (W-NO2NO3), filename/s (NOYYMMDDM# (Lachat 1), or NOYYMMDDN# (Lachat 2)), and initials of the analyst. If nitrate by calculation was performed as well the test W-NO3 is added to the label.

7.2. Each report folder should contain the following items - the run report(s), the color correction calculations spreadsheet (if color correction was necessary), bench sheet(s), reagents and standard logsheet, the backlog containing the batching documentation, the thiosulfate log sheet (see section 5.4.2.) if applicable, and a copy of the data and QC assessments uploaded from QC Manager to LIMS at the time of test authorization. If nitrate by calculation was performed a copy of the nitrate by calculation excel sheet (see section 9) should be included.

7.3. The report folders are on file with the nutrients and general chemistry supervisory personnel. Periodically, the files are moved to the State Records Center for long time storage according to DEP SOP LB-006.

7.4. Lachat instrument data excel transfer files for upload to QC manager are stored in electronic format in the current year's subfolder located in: \\FLDEP1\DEAR\Labs\lab3\Chem_Data\Inorganic \Nutrients\FIA.

7.5. Lachat raw instrument files are stored in electronic format in the current year's subfolder located in: \\FLDEP1\DEAR\Labs\lab3\Chem Data\Inorganic\Nutrients\FIA\Raw Omnion Data Files

7.6. Current worksheet templates are located in subfolder:
For nitrate and nitrite:
\\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\worksheets_NO2NO3\Templates .
For nitrate by calculation:
\\Fldep1\dear\Labs\Lab3\Chem_Data\Inorganic\Nutrients\Nitrate-by-calculation .

7.7. Method validation data is on file with the supervisor. Digital copy is also stored on the network :

\\Fldep1\dear\Labs\Lab5\Chemistry\Inorganic\Nutrient\Validations\Lachat .

8. QUALITY CONTROL/DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES (SEE DEP SOPS NU-038 AND NU-043)

8.1. For method performance and acceptance criteria for QC measures and contingencies for handling out-of-control or unacceptable data refer to the following DEP SOP's: NU-038 and NU-043.

8.2. One practical quantitation limit level standard, PQCK1 (4.3.3.), and one certified standard reference material, ALTQC for nitrate (4.3.4.), are analyzed on every

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analytical run. Acceptance limits for recovery for the PQCK standard are 70 - 130 %. Acceptance limits for recovery for the ALTQC are 90 - 110 %.

8.3. A standard, CATCHCK for nitrite (4.3.5.), is analyzed on every analytical run to check the column efficiency. If the recovery is greater than 115 % the run is invalid and the column needs to be replaced. If the recovery falls between 110 and 115 % the column will need to be replaced as soon as possible. If recovery is less than 85 % then an analytical error has occurred and the analyst should discontinue analysis and report the failure to a supervisor.

8.4. A CHCK standard (4.3.3.) and CCB (4.2.3.) are run before samples are analyzed, every 10 samples and at the end of the run. Acceptance limits for recovery of the CHCK and CHCK2 standard are 90 - 110 %. Acceptance limits for the MBLKs, CCBs, and MDL are < 0.004 and > -0.004 mg N/L.

8.5. An MBLK (4.2.3.), an LFB (5.3), two low-level duplicate matrix spikes, and one high-level matrix spike (5.3) should be analyzed for every batch of 10 samples. Acceptance limits for the LFB and matrix spike recoveries are 90 - 110 %. The sample/matrix spike reproducibility should be less than 20 % RPD for results above the practical quantitation limit (PQL).

8.6. Calibration Range - See FDEP Quality Manual Appendix B, Section 7.0, 'Protocol for Determining the Test Method Range of Applicability'. The calibration standards (4.3.3.) are nitrate only. Every day samples are analyzed a new calibration is performed at the beginning of the analysis. Consecutive runs on one day may use the same calibration. The color correction runs use the calibration performed the same day for NO_2NO_3 analysis. To verify the linear calibration range (LCR) the % residual for each calibration standard above the PQL must be within 90 - 110 % and 70 - 130 % for the PQL-level standard. The analyst is responsible for checking the % residual for each of the calibrants and if any calibrant falls outside the acceptable limits, the run should be aborted, and calibration performed again. The correlation coefficient of the linear calibration must be equal to or larger than 0.995.

8.7. If the CAR solution analyzed after the CHCK2 standard in the analysis run sequence fails acceptance limits for a CCB (see section 8.4) this usually indicates carryover from the CHCK2 standard. If carryover is observed the analysis should be stopped and the instrument maintained.

8.8. Annual MDL (MBLK, 4.2.3; MDLSPK (PQCK1, 4.3.3)) and PQL verification is required, (see NU-043, 2.3.7 for details). Perform annual verifications using statistics tracker and save digital report on the drive.

9. NITRATE DETERMINATION BY CALCULATION

In order to calculate the nitrate content of a sample an acidified aliquot is analyzed for NO2NO3 as described herein, and an unacidified aliquot is analyzed for nitrite (see DEP SOPs NU-087 and NU-096). The nitrate concentration is then calculated from the raw data as follows:

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$$[NO_3]_{calculated} = ([NO_2NO_3]_{measured} \times D_f) - ([NO_2]_{measured} \times D_f)$$

Where; $[NO_3]_{calculated}$ = Calculated concentration of nitrate in mg N/L
$[NO_2NO_3]_{measured}$ = Raw NO2NO3 concentration in mg N/L as determined by NU-066.
$[NO_2]_{measured}$ = Raw nitrite concentration in mg N/L as determined by NU-087 or NU-096.
D_f = Dilution factor

The calculation is documented in the excel spreadsheet NU-NO3-CALC and the result is reported to the Laboratory Information Management System (LIMS) using the Results Editor module. The excel template is located on the nutrients drive: \\FLDEP1\DEAR\Labs\lab3\Chem_Data\Inorganic\Nutrients\Nitrate-by-calculation .

10. SAFETY/HAZARDOUS WASTE MANAGEMENT/POLLUTION PREVENTION

10.1 Review the Laboratory Health and Safety Plan (accessible on the intranet at https://www.fldepnet.org/content/dear/bureau-laboratories-safety-documents.

10.2. Safety glasses, gloves, and a lab coat should be worn at all times whilst handling samples and reagents.

10.3. Read the MSDS information for safe reagent and sample handling.

10.4 Used/expired cadmium columns are lab packed, labeled, and stored in the hazardous waste storage room until disposal.

10.5 All excess acid used for preparing reagents should be neutralized using the acid neutralizing station located in the lab. The pH should be tested and be between 6-8 before discarding contents down the lab sink.

11. REFERENCES/DEFINITIONS

For definitions see section 3 of the FDEP Quality Manual. All abbreviations used throughout the document are defined at least once in the document usually at the first time of use.

11.1. EPA Method 353.2, Revision 2(1993).

11.2. Lachat QuickChem Method 10-107-04-1-B.

11.3. Quality Manual, Bureau of Laboratories, DEP.

11.4. Laboratory Health and Safety Plan.

11.5. DEP SOP NU-033, Summary of Sample Analysis Procedures for the General Chemistry and Nutrients Workgroups.

11.6. DEP SOP NU-038, Nutrients and General Chemistry: Quality Assurance and Quality Control.

11.7. DEP SOP NU-041, Reagent Preparation Procedure.

11.8. DEP SOP NU-042, Standard Preparation Procedure.

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11.9. DEP SOP NU-043, Nutrients and General Chemistry Quality Assurance and Data Authorization Guidelines.

11.10 DEP SOP NU-087, Determination of Nitrite in Water Using the AQ2 Discrete Analyzer.

11.11 DEP SOP NU-096, Determination of Nitrite in Water Using the Lachat QuickChem 8500 Autoanalyzer.

11.12 DEP SOP TA-09.18 Dechlorination Procedure Using Sodium Thiosulfate.

11.13 Standard Methods for the Examination of Water and Wastewater

American Public Health Association, Washington, DC, 1995.

11.14 DEP SOP LB-006, Standard operating procedure for records maintenance and storage.

Appendix of Significant Changes

02/20/2008 Updated SOP to comply with latest revision of method: 353.2, Rev 2.0 (1993).

02/11/2008 Changes were made to sections 3.1 and 4.6 to reflect the use of a new instrument and auto-dilutor.

02/09/2010 Changes were made to sections 3 and 4 to reflect the use of two instruments, one equipped with an autodilutor and the other without.

02/02/2011 The autodilutor was removed from the setup of instrument 2 (4/21/10). The MDL for samples with a conductivity ≥ 5000 µmho/cm was elevated to 0.005 mg N/L.

03/14/2011 Amended the list of chemicals needed in section 4.

02/27/2012 A note was added to section 4.3 about the preparation of calibration and QC standards in salt carrier for high conductivity runs.
The preparation of the ALTQC standard was modified and described in section 4.3.4.
A section (6.2.4.) describing the use of the Excel spreadsheet template for color correction calculations was added.
A procedure for the determination of nitrate by calculation is described in Section 9.

05/16/2012 The MDL was changed to 0.004 mg N/L for samples with high conductivity (≥ 5000 µmho/cm).
Instrument 1 was upgraded and appropriate information changed in Section 3.1.

07/01/2013 Section 5.4 has been added detailing the detection and removal procedure for residual chlorine in samples, if necessary.

02/10/2014 Replaced ethylenediamine tetraacetic acid (EDTA) complexing agent with DTPA.

11/06/2014 Color correction reagent was modified to resemble the color reagent matrix as closely as possible by adding phosphoric acid and NED.

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01/30/2015 The concentration for the CHCK and CATCHCK standards were changed to 0.20 mg N/L. The source for the CHCK standard was changed from the ALTQC to the working stock standard (see section 4.3.2.). Data archival information was clarified in section 7.

01/21/2016 File paths were updated and Appendix A and B were added.

05/03/2017 Appendix A and B were removed. Location of worksheets and templates was updated. Assessment of the LCR was modified in section 8.

02/16/2018 Section 4.2.5. was added to address the cadmium columns expiration policy.

02/25/2019 Reference to the method validation data was updated to include the file path under data archival. A note was added to section 8.6 about checking % residuals for calibrants. A section was added under quality control detailing ongoing MDL verifications. Section 10 was updated to include neutralizing excess acid.

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