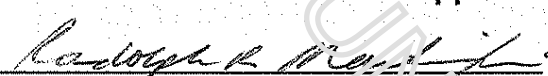
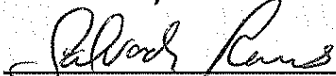
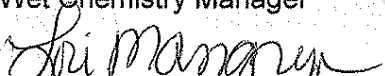
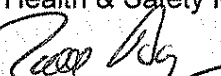
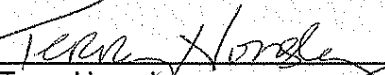



NITRITE, NITRATE PLUS NITRITE (NO_x) AND NITRATE (Calculated)

EPA 353.2

(Lachat QuikChem Method 10-107-04-1-C)

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1.0 Scope and Application

1.1 Analytes, Matrix(s), and Reporting Limits

This automated method for Nitrite plus Nitrate (NO_x), Nitrite and calculated Nitrate is applicable to ground water, surface water, domestic and industrial wastes, sediments and soils.

The routine target analyte lists, current Reporting Limit (RL), Method Detection Limit (MDL) and precision and accuracy limits associated with this procedure are given in the Method Limit Group (MLG) in LIMS.

On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 25 of the Tampa Quality Assurance Manual.

If for any reason a part of this SOP cannot be followed, seek the guidance of the Department Manager or the Laboratory Technical Director. All abnormalities must be noted on the data or the benchsheet, in the Non-conformance database in LIMS. See the corrective action procedures and Appendix 4 in the QA Manual.

2.0 Summary of Method

2.1 Nitrate is quantitatively reduced to nitrite by passage of the sample through a cadmium-copper reduction column. The nitrite (reduced nitrate plus original nitrite) is then determined by reacting with sulfanilamide followed by coupling with N-(1-naphthyl) ethylenediamine dihydrochloride. The resulting water-soluble dye has a pinkish violet color, which is read at 520 nm. Nitrite can also be determined as a single analyte by removing the cadmium reduction column.

2.2 This SOP is based on methods EPA 353.2, SM4500-NO₃ F and Lachat QuikChem Method 10-107-04-1-C.

3.0 Definitions

Definitions – Refer to SOP TP-AN-005: *Definitions, Terms, and Acronyms* and the most current revision of Tampa's *Quality Assurance Manual (QAM)* for a complete listing of applicable definitions.

4.0 Interferences

4.1 Residual chlorine can interfere by oxidizing the cadmium column.

4.2 Low results would be obtained for samples that contain high concentrations of iron, copper or other metals. In this method, EDTA is added to the buffer to reduce this interference.

4.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.

- 4.4 Sample turbidity may interfere with recoveries. Turbidity can be removed by filtration through a 0.45µm pore diameter syringe filter prior to analysis.
- 4.5 The build-up of matter suspended in the samples may restrict the flow through the cadmium reduction column. If this situation occurs, filter the samples through a 0.45µm pore diameter syringe filter prior to re-analysis.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

None

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material ¹	Hazards	Exposure Limit ²	Signs and symptoms of exposure
Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3- TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Phosphoric Acid	Corrosive	1 Mg/M3- TWA	Inhalation is not an expected hazard unless misted or heated to high temperatures. May cause redness, pain, and severe skin burns. May cause redness, pain, blurred vision, eye burns, and permanent eye damage.
Potassium Nitrate	Oxidizer	None	Causes irritation to the respiratory tract, skin and eyes. Symptoms may include coughing, shortness of breath. Symptoms include redness, itching, and pain.
Potassium Nitrite	Oxidizer	None	Causes irritation to the respiratory tract, skin and eyes. Symptoms may include coughing, shortness of breath. Symptoms include redness, itching, and pain.

¹Always add acid to water to prevent violent reactions.

²Exposure limit refers to the OSHA regulatory exposure limit.

6.0 Equipment and Supplies

6.1 Instrumentation

- QuikChem 8000 auto-analyzer with appropriate accessories for the determination of NO_x and nitrite.
- Auto-sampler
- Multichannel peristaltic proportioning pump
- Analysis manifold (see Attachment 1)
- Colorimetric detector
- 80µL glass flow cell with 10mm path length
- Cadmium-Copper reduction column
- 520nm optical filter
- **Omnion 3.0** software for instrument operation and data collection (see Attachment 1 for system parameter settings)
- Analytical Balance, capable of accurately weighing to the nearest 0.0001g
- Calibrated pH meter with electrode
- Stir plate with magnetic stir bars

6.2 Supplies

- Glassware - Class A volumetric flasks, graduated cylinders and pipettes or plastic containers as required
- 10mL disposable syringes
- 0.45µm pore diameter syringe filter
- 50mL centrifuge tubes
- 13X100mm disposable culture tubes

7.0 Reagents and Standards

Reagents and standards must be tracked in accordance with TestAmerica Tampa's SOP TP-AN-004: *Standard Materials and Reagent Traceability*.

- 7.1 Reagent water, de-ionized, Type II
- 7.2 5N Sulfuric Acid
 - 7.2.1 Commercially purchased from a vendor or prepared as in step 7.2.2.
 - 7.2.2 Measure 140mL of 12N H₂SO₄ (concentrated sulfuric acid) using a graduated cylinder and **slowly** add it to 125mL of reagent water (250mL total volume) in a 1L beaker. **Caution: The solution will get very hot!** Cool the solution, and store it in a labeled plastic bottle.
- 7.3 10N Sodium Hydroxide
 - 7.3.1 Commercially purchased from a vendor or prepared as in step 7.3.2.
 - 7.3.2 Weigh out 100g of NaOH pellets (ACS grade) and **slowly** add them to 250mL of reagent water in a 1L beaker. **Caution: The solution will get very hot!** Cool the solution, and store it in a labeled plastic bottle.
- 7.4 2% Copper Sulfate solution
 - 7.4.1 Weigh out 2g of copper sulfate (CuSO₄•5H₂O).
 - 7.4.2 Dissolve the copper sulfate in 100mL of reagent water.
 - 7.4.3 When completely dissolved, store the solution in a labeled amber bottle. This solution is stable for one year.
- 7.5 Ammonium Chloride buffer solution (adjusted to pH 8.5).
 - 7.5.1 Weigh out 170g of ammonium chloride (NH₄Cl) and 2.0g of disodium ethylenediamine tetraacetic acid dihydrate (Na₂EDTA•2H₂O)
 - 7.5.2 Dissolve the 2 chemicals from 7.5.1 in a 2L volumetric flask containing approximately 1600mL of reagent water.
 - 7.5.3 Adjust the pH of this solution to 8.5 using the 10N NaOH solution.
 - 7.5.4 Bring the solution to a 2L final volume using reagent water. This solution is stable for one year.
- 7.6 Sulfanilamide color reagent
 - 7.6.1 Weigh out 40g of sulfanilamide and 1g of N-(1-naphthyl) ethylenediamine dihydrochloride (NED)
 - 7.6.2 Add approximately 600mL of reagent water to a 1L volumetric flask.
 - 7.6.3 Add 100mL of 85% phosphoric acid to the 600mL of water.

- 7.6.4** Add the dry chemicals to the phosphoric acid.
- 7.6.5** Stir the solution in the flask on a stir plate for 30 minutes.
- 7.6.6** Bring the solution to a 1L final volume using reagent water.
- 7.6.7** Store the solution in an amber bottle. **This solution is stable for one month.**
- 7.7** Primary and Secondary Source Stock Nitrate Standard (1000mg/L Nitrogen as NO_3)
- 7.7.1** Commercially purchased from two different vendors or prepared as in steps 7.7.2 to 7.7.4 (the steps for preparation are the same for both standards but dry chemical sources from two different vendors must be used).
- 7.7.2** Weigh out 7.218g of potassium nitrate (KNO_3).
- 7.7.3** Add approximately 600mL of reagent water to a 1L volumetric flask and dissolve the KNO_3 in it.
- 7.7.4** Bring the solution to a 1L final volume using reagent water. Stopper the flask and invert it to mix. **Both solutions are stable for 6 months.**
- 7.8** Primary Intermediate Stock Standard for NO_3 (20 mg/L Nitrogen as NO_3)
- 7.8.1** Add approximately 150mL of reagent water to a 200mL volumetric flask.
- 7.8.2** Using a Class A pipette, transfer 40mL of the Primary Source Stock Nitrate Standard (1000mg/L) to the 200mL volumetric.
- 7.8.3** Bring the solution to a 200mL final volume using reagent water. Stopper the flask and invert it to mix. **This intermediate standard must be made weekly and kept refrigerated.**
- 7.9** Primary Working Standards for NO_3 (Prepare Daily)

Primary Working Standards (mg/L Nitrogen as NO_3)	2.00	1.00	0.50	0.20	0.10	0.050	0.00
μL of Primary Intermediate NO_3 Standard diluted to 50mL with reagent water	10000	2500	1250	500	250	125	0.0

- 7.10** Primary and Secondary Source Stock Nitrite Standard (1000 mg/L Nitrogen as NO_2)
- 7.10.1** Commercially purchased from two different vendors or prepared as in steps 7.10.2 to 7.10.4 (the steps for preparation are the same for both standards but dry chemical sources from two different vendors must be used)
- 7.10.2** Weigh out 6.072g of potassium nitrite (KNO_2)

7.10.3 Add approximately 600mL of reagent water to a 1L volumetric flask and dissolve the KNO_2 in it.

7.10.4 Bring the solution to a 1L final volume using reagent water. Stopper the flask and invert it to mix. **Both solutions are stable for 6 months.**

7.11 Primary Intermediate Stock Standard for NO_2 (20 mg/L Nitrogen as NO_2)

7.11.1 Add approximately 150mL of reagent water to a 200mL volumetric flask

7.11.2 Using a Class A pipette, transfer 4.0mL of the Primary Source Stock Nitrite Standard (1000mg/L) to the 200ml volumetric

7.11.3 Bring the solution to a 200mL final volume using reagent water. Stopper the flask and invert it to mix. **This intermediate standard must be made weekly and kept refrigerated.**

7.12 Primary Working Standards for NO_2 (Prepare Daily)

Primary Working Standards (mg/L Nitrogen as NO_2)	2.00	1.00	0.50	0.20	0.10	0.050	0.00
μL of Primary Intermediate NO_2 Standard diluted to 50mL with reagent water	1000	2500	1250	500	250	125	0.0

7.13 Continuing Calibration Verification (CCV) Standard for NO_3 or NO_2 (1.0mg/L)

Add 100 μL of the Primary Source Stock Nitrate or Nitrite Standard (1000 mg/L) to a 100mL volumetric flask containing about 50mL of reagent water and bring it to final volume. **Prepare Daily.**

7.14 Initial Calibration Verification (ICV) Standard for NO_3 (0.90mg/L)

Add 0.90mL of the Secondary Stock Nitrate Standard (1000 mg/L) to a 100mL volumetric flask containing about 50mL of reagent water and bring it to final volume. **Prepare Daily.**

7.15 Initial Calibration Verification (ICV) Standard for NO_2 (0.45mg/L)

Add 0.45mL of the Secondary Stock Nitrite Standard (1000 mg/L) to a 100mL volumetric flask containing about 50mL of reagent water and bring it to final volume. **Prepare Daily.**

7.16 Laboratory Control Standard (LCS) for NO_3 or NO_2 (1.0mg/L)

Add 0.50mL of the Secondary Stock Nitrate or Nitrite Standard (1000 mg/L) to a 50mL volumetric flask containing about 50mL of reagent water and bring it to final volume. **Prepare Daily.**

7.17 Matrix Spike/Matrix Spike Duplicate (MS/MSD) for NO_3 or NO_2 (1.0mg/L)

Add 0.5mL of the Secondary Stock Nitrate or Nitrite Standard (1000 mg/L) to a 50mL volumetric flask containing the sample to be spiked and bring it to final volume with the sample.

7.18 Column Efficiency Standards (0.90mg/L)

Add 90µL of Nitrate 1000ppm Standard to a 100mL volumetric flask containing about 50mL of reagent water and bring to volume. **Prepare Daily.**

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time ¹	Reference
Water (NO _x)	HDPE	100mLs	H ₂ SO ₄ , pH < 2; Cool ≤ 6°C	28 Days	40 CFR Part 136.3
Water (NO ₂)	HDPE	100mLs	Cool ≤ 6°C	48 Hours	40 CFR Part 136.3
Soil	Glass	10 grams	Cool ≤ 6°C	14 Days	N/A

¹ Soil matrix requires that the preparation of the leachate be completed within hold time.

Analysis must be started within 48 hours of completion of preparation.

9.0 Quality Control

9.1 Sample QC - The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency	Control Limit
Method Blank (MB)	1 in 20 or fewer samples	< MDL
Laboratory Control Sample (LCS)	1 in 20 or fewer samples	Statistical Limits ²
LCS Duplicate (LCSD)*	1 in 20 or fewer samples	Statistical Limits ²
Matrix Spike (MS) ¹	1 in 10 or fewer samples	Statistical Limits ²
MS Duplicate (MSD) ¹	1 in 10 or fewer samples	Statistical Limits ²

* LCS Duplicate (LCSD) is performed only when there are TMDL samples in the batch.

¹ The sample selection for MS/MSD is random, unless specifically requested by a client.

² Statistical control limits are updated annually and entered into the MLG in LIMS.

9.2 Instrument QC

9.2.1 Before any instrument is used as a measurement device, the instrument response to known reference materials must be determined. The manner in which various instruments are calibrated depends on the particular type of instrument and its intended use. All sample measurements must be made within the calibration range of the instrument.

- 9.2.2** A calibration curve is performed daily, followed by an Initial Calibration Verification (ICV) and Initial Calibration Blank (ICB).
- 9.2.3** A Continuing Calibration Verification (CCV) and Calibration Verification Blank (CCB) are analyzed every 10 or fewer samples.
- 9.2.4** The accuracy (% Recovery) and precision (% RPD) for the lab spike and matrix spikes should be checked against the limits listed in the method. The lab spikes must meet these accuracy and precision limits. If limits are not met, investigate the cause and either reanalyze or re-extract. The matrix spike recoveries are used to evaluate the matrix effect on the analysis and are advisory.
- 9.2.5** NO₂ efficiency standard is made fresh daily for each analysis. It is analyzed at the beginning of each analytical run.

9.2.5.1 The column efficiency can be determined as follows:

- Calibrate with NO₃ standards.
- Run a known concentration NO₂ standard
- Run a matching concentration NO₃ standard
- The column efficiency is determined by the equation:

$$E = \frac{[\text{NO}_3]}{[\text{NO}_2]} \times 100$$

where:

E = column efficiency

[NO₃] = concentration of nitrate standard

[NO₂] = concentration of nitrite standard

- The column efficiency acceptance range is 85 - 115%. The column should be replaced if the efficiency standard is not within this range.

9.2.6 Linear Calibration Range

9.2.6.1 After the calibration curve has been analyzed, the low, mid, and high points are analyzed as samples. They are then compared to the actual values, and must agree within 10%. If they are not within the 10%, the calibration curve must be analyzed again, followed by another linear calibration range set. This must be performed initially, and every six months thereafter. Since the initial calibration is performed almost every analytical run, and the initial calibration satisfies the requirements for the LCR, the ICAL will be considered to have fulfilled the LCR requirement.

Type	Concentration(mg/L)	Frequency	Control Limits
Initial Calibration Curve (Linear/Quadratic)	See Section 7.9(NO ₃) or 7.12(NO ₂) for values	Daily or more frequently if needed	$r \geq 0.990$, $r^2 \geq 0.995$
Initial Calibration Verification (ICV) ¹	NO ₃ = 0.90 NO ₂ = 0.45	After Initial Calibration	90% - 110 %
Continuing Calibration Verification (CCV)	1.0	1 in 10 or fewer samples	90% - 110 %
Continuing Calibration Blank (CCB)	0.0	1 in 10 or fewer samples	< MDL
Efficiency Standard	0.90	Everyday after calibration	85% - 115%

¹ICV has to be a different source than the calibration standards.

NOTE: ICV, LCS, and MS/MSD are required to be from a different source standard than the calibration and CCV standards.

10.0 Procedure

10.1 Sample Preparation

10.1.1 Using a calibrated pH meter and probe, check the pH of any unpreserved sample that has been marked by the login personnel as having an abnormal pH.

10.1.2 If the pH of the unpreserved sample is below 5 or above 9, adjust the pH with either 5N H₂SO₄ (to lower the pH) or 10N NaOH (to raise the pH) so that it reads between 5 and 9.

10.1.3 Samples for NO_x only will be preserved with H₂SO₄ to pH <2 and adjust the pH prior to the analysis.

10.1.4 Soils for this analysis are to be leached with reagent water.

10.1.4.1 Homogenize the sample and then weigh 5.0g of it into a 125mL plastic bottle. Record the weight of the sample to the nearest 0.10g. A percent solids analysis must be done on any soil samples that are leached by this procedure.

10.1.4.2 Add 50mL of reagent water to the plastic bottle containing the sample.

10.1.4.3 Shake or rotate the sample for 2 hours.

10.1.4.4 Allow the sediment to settle and filter 25mL of the sample through a 0.45µm syringe filter.

10.1.4.5 The sample can now be treated as an aqueous sample and must be run within 48 hours for NO₂ analysis. If the sample is to be run for NO_x, then aliquot a portion of the leachate into a separate bottle and preserve it with H₂SO₄ to a pH < 2.

10.2 Calibration

Before any instrument is used as a measurement device, the instrument response to known reference materials must be determined. The manner in which various instruments are calibrated depends on the particular type of instrument and its intended use. All sample measurements must be made within the calibration range of the instrument. Preparation of all reference materials used for calibration must be documented.

10.2.1 Prepare reagents, standards and matrix spikes as described in Section 7.0.

10.2.2 Make sure that the analysis manifold is set up properly and that the data system parameters are configured correctly (see Attachment 1 for the manifold diagram and the specified instrument settings for each analyte).

10.2.3 Secure the pump platens in place and turn on the auto-sampler and the peristaltic pump.

10.2.4 When the auto-sampler completes its system check, turn on the power to the instrument.

10.2.5 Click on the Omnic 3.0 icon to start the data system software.

10.2.6 Pump reagent water through all the reagent lines to check for leaks or plugs. Make sure that the switching valve for the cadmium-copper reduction column is in the correct position for the analyte of interest.

10.2.7 Switch the reagent lines to the reagents for the chemistry being run and allow the system to equilibrate until a stable baseline is present on the software display.

10.2.8 Aliquot the standards for the analysis being run and put them in the proper places in the auto-sampler tray.

10.2.9 Open the appropriate sequence template based on the analyte of interest and the quantity of samples.

10.2.10 Calibrate the instrument by injecting the standards. The data system software will produce a calibration curve that correlates the peak area for each standard with its concentration.

10.2.11 Check the correlation coefficient for the curve as soon as the injection of the standards has finished. If the value is acceptable, continue with sample analysis.

NOTE: If the Cadmium-Copper reduction column is being used, a nitrite (NO_2) standard **MUST** be compared to a nitrate (NO_3) standard of the same concentration. The two are divided to verify complete reduction of the NO_3 . If the recovery does not fall between 85-115%, the column must be regenerated or replaced. The efficiency must be verified after every curve.

10.3 Sample Analysis

10.3.1 Make sure to verify that the curve is in control by running an initial calibration verification (ICV) standard from a secondary source. Following the ICV, run an initial calibration blank (ICB) to verify that there is no system contamination and that the curve is not skewed.

10.3.2 Enter the sample numbers and required quality control samples into the sequence template (see below for a sequence example). Make sure to properly bracket every 10 analytical samples with a CCV and a CCB. Save the completed sequence template under its own unique filename. The sequence is ready to be started but can still be edited if needed.

Calibration Standards
Efficiency Standard
Initial Calibration Verification (ICV)
Initial Calibration Blank (ICB)
MB, LCS, LCS-D (if necessary)
10 Samples & MS/MSD
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)
10 Samples & MS/MSD
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)

10.3.3 Aliquot the samples, the check standards and the matrix spikes and place them in the appropriate positions in the auto-sampler rack.

10.3.4 Start the sequence. Monitor the ICV and ICB to insure that they meet acceptance criteria. If either one fails, the instrument must be recalibrated. If the failure is repeated after recalibration, check the system for contamination and/or try remaking the standards (both primary and secondary from freshly made stock) before trying again.

10.3.5 Let the sequence run until all the samples have been analyzed.

10.3.6 Check the CCV and CCB after each set of ten samples while the run is in progress or at its completion. If either the CCV or CCB does not meet acceptance criteria, the block of ten samples before and after the failing check standard must be reanalyzed.

10.3.7 If the concentration of a sample exceeds the value of the highest standard, the sample must be diluted to reduce the value so that it falls within the calibration range (preferably a value in the midrange of the curve). The dilution must not result in a value that is below the lowest curve standard. The dilution factor is calculated by dividing the final volume of the dilution by the amount of sample actually used.

10.3.8 Additional samples or diluted samples may be added to the run sequence if the run is not complete. Make sure to bracket the additional samples with a CCV and CCB and to save the modified sequence table.

10.3.9 When the data is ready, it may be uploaded electronically or manually entered into TALS at the analyst's discretion.

10.4 Preventive Maintenance

10.4.1 The pump tubes on the manifold and peristaltic pump should be monitored daily for wear and stretching. If the tubes show excessive wear due to the frequency of use, they should be replaced immediately. Otherwise, the tubes should be replaced monthly.

10.4.2 The valve tubing and flares should be monitored daily for leaks and should be replaced if a leak is detected. Otherwise, replace the tubing and flares annually.

10.4.3 Negative peaks in the blanks or low level standards are indicative of carrier contamination. If these dips in the baseline are seen in the chromatograms, replace the contaminated carrier with fresh (make sure to thoroughly clean and rinse the container before refilling it with fresh carrier).

10.4.4 If the Cadmium-Copper reduction column efficiency is outside the acceptable range, the column must be regenerated (see Attachment 1 for procedure). If the regeneration is ineffective, then the column must be replaced.

11.0 Calculations / Data Reduction

11.1 Cadmium-Copper Reduction Column Percent Efficiency

$$\text{\% Efficiency} = \frac{\text{NO}_3 \text{ value of Efficiency Standard}}{\text{NO}_2 \text{ value of Standard}} \times 100$$

NOTE: The concentrations of the 2 standards being used must be the same.

11.2 Accuracy

11.2.1 ICV, CCV and LCS Percent Recovery

$$\text{\% Recovery} = \frac{\text{Observed concentration}}{\text{Known concentration}} \times 100$$

11.2.2 MS/MSD Percent Recovery

$$\text{MS \% Recovery} = \frac{(\text{spiked sample} - \text{unspiked sample})}{\text{Spiked concentration}} \times 100$$

11.3 Precision - MS/MSD Relative Percent Difference (RPD)

$$\% \text{ RPD} = \frac{|\text{Matrix Spike value} - \text{MS Duplicate value}|}{[(\text{MS value} + \text{MSD value})/2]} \times 100$$

11.4 Concentration**11.4.1 NO₂ or NO_x Sample (Liquid)**

$$\text{NO}_2 \text{ or NO}_x \text{ Concentration (mg (N)/L)} = C (\text{Curve}) \times DF$$

Where:

C (Curve) = Sample concentration of NO₂ or NO_x generated from the curve

DF = Dilution factor (for concentration above curve range)

11.4.2 NO₂ or NO_x Sample (Solid)

$$\text{NO}_2 \text{ or NO}_x \text{ Concentration (mg (N)/Kg)} = \frac{C (\text{Curve}) \times FV \times DF \times \% \text{ Solids}}{W \times 100}$$

Where:

C (Curve) = Sample concentration of NO₂ or NO_x generated from the curve

FV = Final volume of the leachate (mL)

DF = Dilution factor (for concentration above curve range)

% Solids = Percent dry residue by Percent Moisture or Total Solids analysis

W = Weight of sample that was leached (g)

NOTE: This manual calculation will yield a result that is already corrected for dry weight. However, this result should not be entered into LIMS because all dry weight calculations are normally performed by the LIMS software when the final report is prepared.

11.4.3 NO₃ by Calculation (Liquid)

$$\text{NO}_3 \text{ Concentration (mg (N)/L)} = \text{NO}_x \text{ value (mg (N)/L)} - \text{NO}_2 \text{ Value (mg(N)/L)}$$

11.4.4 NO₃ by Calculation (Solid)

$$\text{NO}_3 \text{ Concentration (mg (N)/Kg)} = \text{NO}_x \text{ value (mg (N)/Kg)} - \text{NO}_2 \text{ Value (mg (N)/Kg)}$$

12.0 Method Performance

12.1 Method Detection Limit Study (MDL) - The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined accordance with 40 CFR, Chapter 1, Part 136, Appendix B and with reference to the laboratory's MDL procedure in Section 20 of the Quality Assurance Manual. An MDL reflects a calculated (statistical) value determined under ideal laboratory conditions in

a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

- 12.2 Demonstration of Capabilities - Each analyst must perform an Initial Demonstration of Capability (IDOC) in accordance with the procedure outlined in Section 20 of the Quality Assurance Manual. The evaluation of the IDOC data should be completed prior to the analysis of samples. A Continuing Demonstration of Capability (CDOC) must be performed annually or whenever there is a significant change in the instrument parameters or the associated method.
- 12.3 Training Requirements – Each analyst's required employee training (such as orientation to the laboratory's policies and procedures and in-house method training) are outlined in Section 18 of the Quality Assurance Manual.
- 12.4 PT Studies - The laboratory participates in formal performance evaluation (PT) studies, where solutions of unknown concentrations are analyzed and the performances of all the participants are compared. The QA department maintains the records of the results of these studies.

13.0 Data Assessment And Acceptance Criteria For Quality Control Measures

- 13.1 The following represent data assessment for samples and acceptance criteria for QC measures. Corrective actions for any failure in QC measures are shown in Section 13.
- 13.2 QC sample acceptance criteria
 - 13.2.1 **Method Blank.** No target analytes may be present in the method blank above the reporting limit. RL > 0.1 mg/L.
 - 13.2.2 **Laboratory Control Sample (LCS).** 90 - 110% The analyte must be within established control limits for accuracy (%Recovery) and precision (RPD). Exceptions are allowed only with QA and project management approval.
 - 13.2.3 **Matrix Spike/Matrix Spike Suplicate (MS/MSD).** 90 - 110% The analyte should be within established control limits for accuracy (%Recovery) and precision (%RPD). Deviations from this may be the results of matrix effects, which are confirmed by passing LCS/LCSD. No specific corrective actions are required in the evaluation of the MS/MSD results provided that the batch LCS is in control. Analysts should use sound judgement in accepting MS/MSD results that are not within control limits, especially if the LCS results are borderline. Check with supervisor, Lab Manager and or Project Manager on reporting out of control limits QC.
- 13.3 Sample result evaluation

13.3.1 Dilutions: If the response for any compound exceeds the working range of the analytical system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit in the upper half of the calibration range. The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

14.0 Corrective Actions For Out Of Control Data

14.1 Method Blank. The samples in the batch associated to the defective method blank are evaluated. If the analyte found in the method blank is confirmed to not be present in one or more of the associated samples at any level, the contamination did not affect those samples. This represents a non-impact situation and no specific corrective action is taken. A nonconformance memo is written to notify project management of the situation for evaluation against project requirements. If the analyte found in the method blank is confirmed to be present in one or more of the associated samples, the concentrations are compared. If the concentration in the method blank exceeded 10% of concentration found in one or more samples, the prescribed corrective action is to re-analyze all affected samples. If the concentration in the method blank was less than 10% of the concentration found in one or more samples, the sample can be reported by qualifying the affected analytes. A nonconformance memo (NCM) is written and discussed with the laboratory supervisor and Project Management for evaluation against project requirements.

14.2 Laboratory control sample. If the analyte is out of control for accuracy (90 - 110%), the associated samples are evaluated. If the recovery is biased high and the associated samples have no positive results for that analyte, a non-impact situation ensues. A nonconformance memo (NCM) is written to notify project management of the situation for evaluation against project requirements. If the recovery is biased high and the associated samples have positive results for that analyte, the prescribed corrective action is reanalysis of the affected sample(s). If the recovery is biased low and the samples have no positive results for that analyte, the prescribed corrective action is reanalysis of the affected sample(s). If the analyte is out of control for precision (RPD), the associated samples are evaluated. All decisions about corrective action(s) are made in consultation with the project manager. If there are no positive results in one or more samples, a non-impact situation ensues for those samples. A nonconformance memo is written to notify project management of the situation for evaluation against project requirements.

14.2.1 If there are positive results for one or more analytes, the likelihood of poor reproducibility increases and corrective action must be evaluated. A nonconformance memo is written and discussed with the laboratory supervisor and Project Management of the situation for a project decision on whether the affected sample(s) should be reanalyzed.

15.0 Contingencies For Handling Out-Of-Control Or Unacceptable Data

- 15.1 Method blanks.** If there is insufficient sample to perform re-analysis; the analyst must notify the project manager for consultation with the client. In this situation, all associated samples are flagged with an "I" qualifier and appropriate comments in the narrative.
- 15.2 LCS/LCSD.** If the batch is not reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. Acceptable matrix spike recoveries are not sufficient justification to preclude re-extraction of the batch. If reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation. An NCM will have to be filled out stating this problem and or a solution.
- 15.3 Insufficient sample.** If there is insufficient sample to repeat the analysis, the situation is discussed with the project manager for consultation with the client and documentation is provided in an NCM.

16.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

17.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Tampa's current revision of SOP TP-HAZ-001 *Waste Management*). The following waste streams are produced when this method is carried out.

- 17.1** Unpreserved aqueous samples that are analyzed may be discharged into the local sewer system.
- 17.2** Unused acid solutions, reagents or acidified samples should be neutralized and then discharged into the local sewer system.
- 17.2** The acidic waste that is generated by the instrument is collected in a secondary container and transferred to the hazardous waste area to be neutralized and disposed of by the hazardous waste coordinator.

18.0 References / Cross-References

- 18.1** *Determination of Nitrate/Nitrite in Surface and Wastewaters by Flow Injection Analysis*: QuikChem Method 10-107-04-1-C, Lachat Instruments, Milwaukee, Wisconsin, 28 August 2000.
- 18.2** *Standard Methods for the Examination of Water and Wastewater*, 21st Edition; American Public Health Association: Washington, DC, 2005.
- 18.3** *Methods for Chemical Analysis of Water and Wastes*: EPA-353.2; USEPA EMSL Office of Research and Development, Cincinnati, Ohio, August 1993.
- 18.4** TestAmerica's Environmental Health & Safety Manual CW-E-M-001, most current revision.
- 18.5** Tampa's *Quality Assurance Manual*, (TP-QAM), most current revision.
- 18.6** TestAmerica Tampa SOP's:
- 18.6.1** TP-HAZ-001 *Waste Management*
 - 18.6.2** TP-AN-005: *Definitions, Terms, and Acronym*
 - 18.6.3** TP-AN-016 *Glassware Cleaning Procedures*

19.0 Method Modifications

Item	Method xx	Modification
1	QuikChem Method 10-107-04-1-C, Section 7.1	Section 7.4.3: A 10N NaOH solution is substituted for the 15N NaOH solution that is used to adjust the pH of the NH_4Cl buffer solution. This change reduces the safety risk of using a more concentrated solution and the analysis cost by using the same reagent twice.
2	QuikChem Method 10-107-04-1-C, Section 11.8	Section 10.1.2: A 10N NaOH solution is substituted for the concentrated NH_4OH that is used to adjust the pH of the unpreserved samples. This change reduces the safety risk from the hazardous fumes released by NH_4OH and the analysis cost by using the same reagent twice.
3	QuikChem Method 10-107-04-1-C, Section 11.8	Section 10.1.2: A 6N HCl solution is substituted for the concentrated HCl that is used to adjust the pH of the unpreserved samples. This change reduces the safety risk of using a more concentrated solution and the analysis cost by using the same reagent twice.
4	ASTM D3987-06	Section 10.1.4: Addition of the ASTM method for the leaching of NO_2 and NO_3 from soils and solid wastes.

20.0 Attachments

- 20.1** Attachment 1: Procedure for Regeneration of Cadmium-Copper Reduction Column
- 20.2** Attachment 2: Nitrate/Nitrite Manifold Diagram

20.3 Attachment 3: Data System Parameters for QuikChem 8000 (NO₂/ NO₃)

20.0 Revision History

- Revision 6, dated 15 February 2009
 - Minor formatting changes
 - Clarified efficiency standard
 - Added sections 9.2.1. thru 9.2.6
 - Added Linear Calibration Range
- Revision 5, dated 15 November 2009
 - SOP updated to new format
 - Sections 13-15 added
 - Clarified efficiency standard preparation and frequency
- Revision 4, dated 30 November 2008
 - SOP rewritten and updated to TestAmerica format
- Revision 3, dated 1 June 2007
 - SOP updated to STL format with minor revisions

Attachment 1

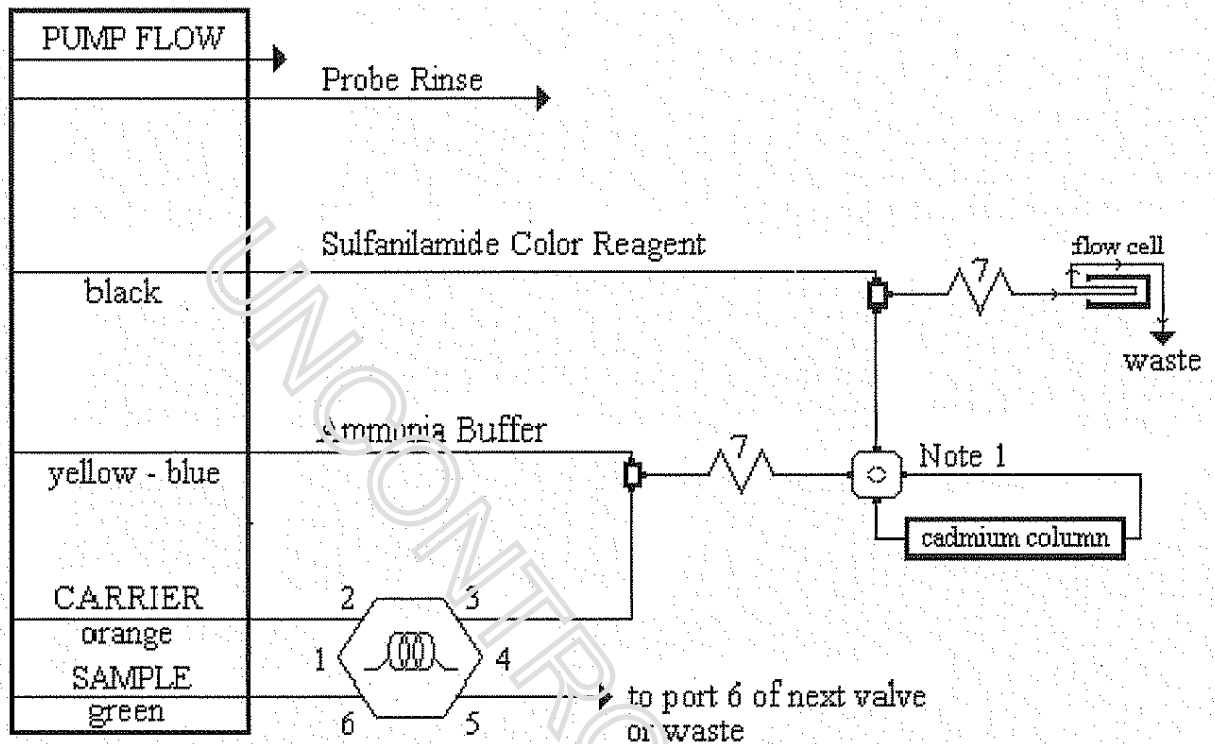
Procedure for Regeneration of Cadmium-Copper Reduction Column

1. Make sure the switching valve is turned to isolate the column, and remove the column tubing from both sides of the valve. Elevate the tubing at both ends so that no liquid escapes.
2. Remove the carrier tube flare fitting between the union and the sample valve.
3. Clamp the platen in place for the carrier line, and turn on the peristaltic pump.
4. Place the reagent straw in fresh reagent water, and pump the air from the tubing.
5. Immediately attach one end of the column to the union fitting for the carrier line. Let the tubing at the other end of the column drain into a waste container.
6. Rinse the column for 2 minutes with the reagent water, and turn off the pump.
7. Place the reagent straw in a beaker containing a 6N HCl solution, and continue pumping for 5 minutes before turning the pump off again.
8. Place the reagent straw in reagent water, and pump it through the column for 2 minutes. When the rinsing is complete, the cadmium should be silvery in color.
9. Turn off the pump, place the reagent straw in a beaker containing a 2% Copper Sulfate solution and resume pumping for 10 - 15 minutes or until a brown colloidal precipitate forms.
10. Turn off the pump, place the reagent straw in the Ammonium Chloride buffer solution and rinse the column with the solution for 5 minutes. At this point, the color of the cadmium should be black.
11. Stop the pump, and place the column so that the end attached to the pump is pointing at a downward angle and the waste end is held below the surface level of the container of buffer solution. This will prevent the buffer from running out of the column.
12. Uncap the waste end of the column, and remove the sponge covering over the cadmium. Be careful not to spill the cadmium.
13. Rinse the sponge with reagent water to remove any precipitate, and then restore the sponge and the cap to the column.
14. Pump buffer solution through the column for 2 more minutes to force any remaining precipitate into the sponge, and then repeat steps 11 to 13 to make sure that no precipitate is left in the sponge.
15. Pump buffer solution through the column for an additional minute to remove any air bubbles.

16. Place a waste container under the union connected to the column end to catch any excess solution, and, with the pump running, disconnect the column tubing from the union. Elevate the tubing at both ends of the column so that no liquid escapes.
17. Reconnect the flare end to the union, and allow the buffer solution to pump until all of the air bubbles are out of the tubing.
18. Place a paper towel under the switching valve, and open the valve to let the buffer flow.
19. Immediately attach one end of the column to the front side of the valve so that the buffer solution is flowing through the column. Check the column for any bubbles and tap the column to free any that are trapped inside.
20. Attach the other end of the column to the detector side of the switching valve, and let the buffer pump for 3 more minutes before turning off the pump.
21. Close the switching valve. The column is now ready to be tested for its efficiency.

Attachment 2

Nitrate/Nitrite Manifold Diagram



Carrier: Helium Degassed DI water

Manifold Tubing: 0.8mm (0.032in) i.d. This is 5 μ L/cm.

AE Sample Loop: 17cm x 0.8mm i.d.

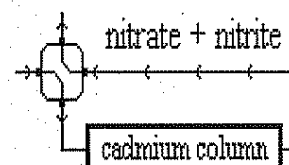
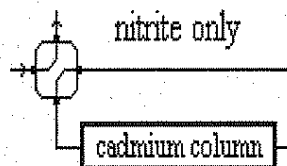
QC8000 Sample Loop: 22.5cm x 0.8mm i.d.

Interference Filter: 520nm

Apparatus: An injection valve, a 10mm path length flow cell, and a calorimetric detector module is required.

7: 135cm of tubing on a 7cm coil support

Note 1: This is a 2 state switching valve used to place the cadmium column in-line with the manifold



Attachment 3**Data System Parameters for QuikChem 8000 (NO₂/ NO₃)**

The timing values listed below are approximate and will need to be optimized using graphical events programming.

Sample throughput: 55 samples/hour, 65 sec/sample
Pump Speed: 35
Cycle Period: 65 sec (NO₂), 70 sec (NO₃)

Analyte Data:

Concentration Units: mg N/L
Peak Base Width: 25 sec
% Width Tolerance: 100
Threshold: 5000 (NO₂), 8000 (NO₃)
Inject to Peak Start: 22 sec (NO₂), 35 sec (NO₃)
Chemistry: Direct

Calibration Data:

Level	1	2	3	4	5	6	7
Concentration mg N/L	2.00	1.00	0.50	0.20	0.10	0.05	0.00

Calibration Rep Handling: Average
Calibration Fit Type: 2nd Order Polynomial
Weighting Method: None
Force through zero: No

Sampler Timing:

Min. Probe in Wash Period: 19 s
Probe in Sample Period: 32 s

Valve Timing:

Load Time: 0 s
Load Period: 25 s
Inject Period: 40 s