1.0 TITLE

Nitrogen and Nitrate/Nitrite in Water, Sludge, and Soil Extracts by Automated Colorimetry

2.0 LOCATION

Wet Chemistry Instrument Lab

3.0 SCOPE & APPLICATION

3.1 $N\text{-}NO_3NO_2$ and $N\text{-}NO_2$ are determined in drinking water; ground water; surface water; and domestic and industrial wastewaters. The analytical ranges are 0.02 – 4.0 mg/L for $N\text{-}NO_3NO_2$ and 0.01 – 2.0 mg/L for $N\text{-}NO_2$. These ranges may be extended with sample dilution. To obtain the concentration of Nitrogen in the form of Nitrate ($N\text{-}NO_3$) subtract the Nitrite ($N\text{-}NO_2$) concentration from the $N\text{-}NO_3NO_2$ concentration.

3.2 $N\text{-}NO_3NO_2$ and $N\text{-}NO_2$ are determined in sludge and soil extracts. The Soils Department prepares the soil extracts; sludge extractions are prepared by the WC Instrument analyst. The analytical ranges of the extracts are 0.02 – 4.0 mg/L for $N\text{-}NO_3NO_2$ and 0.01 – 2.0 mg/L for $N\text{-}NO_2$. These ranges may be extended with sample dilution.

NOTE: ACZ has extended this procedure to the analysis of soils and sludge. Although ACZ believes this procedure to be technically sound, it should not be used for regulatory compliance monitoring of such matrices in lieu of an EPA approved method.

4.0 SUMMARY

4.1 **For $N\text{-}NO_3NO_2$** determination, a filtered unpreserved sample is passed through a Cadmium-Copper Reduction Column. This reduces the nitrate ion (NO_3^-) to the nitrite ion (NO_2^-). The nitrite in the sample plus the nitrite from the nitrate reduction step reacts with a color reagent in the stream of the automated analytical setup. The nitrite is diazotized with sulfanilamide and coupled with *N*-(1-naphthyl)-ethylenediamine dihydrochloride to form a substantially colored azo dye. The colored solution is measured colorimetrically at 540 nm using flow injection analysis on the Lachat 8500. Samples are stored at 0 – 6.0˚C.

NOTE: Raw samples may be used for analysis. Inspect the raw sample for suspended matter. If the sample contains suspended matter then filter/centrifuge small amount of sample before analysis.

4.2 **For $N\text{-}NO_2$** determination, a filtered unpreserved sample reacts with the color reagent in the stream of the automated analytical setup (no reduction step). The nitrite is diazotized with sulfanilamide and coupled with *N*-(1-naphthyl)-ethylenediamine dihyrdrochloride to form a substantially colored azo dye. The colored solution is measured colorimetrically at 540 nm using flow injection analysis on the Lachat 8500. Samples are stored at 0 – 6.0˚C.

NOTE: Raw samples may be used for analysis. Inspect the raw sample for suspended matter. If the sample contains suspended matter then filter/centrifuge small amount of sample before analysis.

4.3 **For N-NO_3NO_2 "Yellow"** determination an unfiltered, preserved sample is neutralized with NH_4OH prior to the reduction and colorimetric steps outlined in §4.1.

4.4 **Sludge Samples are prepared for N-NO_3NO_2 and N-NO_2** determination by diluting 1.0 g of the sludge to 50 mL of Type I H_2O. The sample is mixed and centrifuged prior to analysis.

4.5 **N-NO_3NO_2 and N-NO_2 water extracts of soil/solids** are prepared first by the Soils Department, and the N-NO_3NO_2 and N-NO_2 in the extractions are determined as outlined in §4.1 and §4.2. Extracted samples are stored at 0 – 6.0˚C.

4.6 Method 353.2 has been modified within the flexibility allowed in 40 CFR §136.6. EPA Method 353.2 instructs the use of 0.2% H_2SO_4 wash solution and the 9.1 pH ammonium chloride-EDTA solution for preserved samples. This SOP does not use these reagents per instrument manufacturer's instructions.

5.0 REFERENCES

5.1 "Determination of Nitrate-Nitrite by Automated Colorimetry, Method 353.2". EPA-600/R-93/100. United States Environmental Protection Agency, August 1993.

5.2 "Determination of Nitrate\Nitrite in Surface and Waste Waters by Flow Injection Analysis," Diane Prizlaff, Lachat Instruments, August 28, 2000.

5.3 "Determination of Nitrite in Surface and Waste Waters by Flow Injection Analysis Colorimetry," Ninglan Liao, Lachat Instruments, December 11, 2000.

5.4 "QuickChem QC8500 Automated Ion Analyzer User Manual", Lachat Instruments, Hach Company 2004

6.0 SAMPLE COLLECTION, HANDLING & PRESERVATION

NOTE: If samples have visible sediment, they may be filtered and /or centrifuged before analysis.

6.1 For N-NO_3NO_2 and N-NO_2 parameters samples are collected in plastic bottles.

6.1.1 The hold time is 48 hours from sampling for aqueous samples. Analysis must be completed within the hold time.

6.1.2 Use a **filtered**, **unpreserved** sample (white dot) and store at 0 – 6.0˚C. If no white-dot sample is available, a raw sample may be used. Inspect the raw sample for suspended matter. If the sample contains suspended matter, filter/centrifuge only what is necessary for the test and document the event in the WG package.

6.2 For the "Yellow" N-NO_3NO_2 parameter samples are collected in plastic or glass bottles.

6.2.1 The hold time is 28 days from the sampling date. Analysis must be completed within the hold time.

6.2.2 Samples are preserved with H_2SO_4 to a pH < 2 at the time of collection.

6.2.3 Use a **preserved**, **unfiltered** sample (yellow dot) and store at 0 – 6.0˚C.

6.3 Soil and sludge samples are collected in plastic or glass bottles or jars.

6.3.1 There is no established hold time for sludge / semi-solid samples. Perform analyses within 48 hours from sampling time if sample is mostly water and can be analyzed as described in §11.3.

6.3.2 For samples with high solid content, determine if the sample should first be prepared into an aqueous matrix by the Soils Department. No hold time is specified for soils extract from date of sampling to start of extraction. Post extraction hold time for unpreserved samples is 48 hours from extraction completion. For preserved extracted samples the hold time is 28 days from extraction completion. Extracted samples must be stored at 0 – 6.0˚C.

6.3.3 Soil extracts first prepared by the Soils Department and are analyzed in the same manner as aqueous samples.

6.4 Hold Times

Table 6.1: N-NO3NO2 Hold Times

Product	Matrix	Department #	Hold Time (In Days)	Hold Time Starts - Ends With
N-NO3NO2/-T	Liquid	37	2	Collect Date to D37 Measure Date
N-NO3NO2-Y			28	
N-NO3NO2-1312*/ -MWMT	Solid with extraction	20	N/A	No pre-extraction hold time
		37	2	D20 Time Out to D37 Measure Date
N-NO3NO2-KCL		20	N/A	No pre-extraction hold time
		37	2	D20 Measure Date to D37 Measure Date
N-NO3NO2-WE		20	N/A	No pre-extraction hold time
		37	2	D20 Filter Date to D37 Measure Date
N-NO3NO2-WET-DI		20	N/A	No pre-extraction hold time
		37	2	Collect Date to D37 Measure Date

Table 6.2: N-NO2 Hold Times

Product	Matrix	Department #	Hold Time (In Days)	Hold Time Starts - Ends With
N-NO2/-T/-IC	Liquid	37	2	Collect Date to D37 Measure Date
N-NO2-1312*/ -MWMT	Solid with extraction	20	N/A	No pre-extraction hold time
		37	2	D20 Time Out to D37 Measure Date
N-NO2-KCL		20	N/A	No pre-extraction hold time
		37	2	D20 Measure Date to D37 Measure Date

N-NO2-WE		20	N/A	No pre-extraction hold time
		37	2	D20 Filter Date to D37 Measure Date
N-NO2-WET-DI		20	N/A	No pre-extraction hold time
		37	2	Collect Date to D37 Measure Date

7.0 APPARATUS & SUPPLIES

7.1 50 mL plastic centrifuge tubes with caps

7.2 Analytical balance, accurate to 0.0001 g. Verify calibration as required by §SOPAD013.

7.3 Class A volumetric flasks

7.4 Fixed or adjustable mechanical pipettes. Verify accurate delivery as required by §SOPAD013.

7.5 Erlenmeyer flasks

7.6 Disposable culture tubes

7.7 Flow injection analysis instrument and manifold designed to deliver/react sample and reagents.

7.8 Sampler

7.6.1 Multi-channel proportioning pump
7.6.2 Reaction unit or manifold
7.6.3 Colorimetric detector
7.6.4 Data system

7.9 Centrifuge

7.10 15 mL plastic centrifuge tubes.

7.11 250 µL syringe for pH adjustment with NH_4OH.

7.12 pH test strips.

7.13 Potassium iodide-starch test strips.

7.14 Transfer pipettes.

7.15 45 µm, 25 mm syringe filters.

7.16 20 mL Syringe Luer-Lok Tip.

7.17 0.45 µm filter verified by lot to be free of contamination from NO_3NO_2/NO_2.

8.0 REAGENTS & STANDARDS

NOTE: Wash all glassware with Type II H_2O, if necessary wash glassware with 20% HCl and rinse with Type II H_2O.

NOTE: If necessary, all reagents except standards may be degassed with He to prevent bubble formation during analysis. Bubble He through a degassing tube for about one minute.

8.1 **$N\text{-}NO_3NO_2$/ $N\text{-}NO_2$**

8.1.1 10N NaOH: In a 1 L flask dissolve 400 g NaOH in ~ 600 mL Type I H_2O. QS to 1 L and stir. Shelf life is one year. Store at room temperature.

8.1.2 5N NaOH: In a 1 L flask dissolve 200 g NaOH in ~ 600 mL Type I H_2O. QS to 1 L and stir. Shelf life is one year. Store at room temperature.

8.1.3 Ammonium chloride-EDTA Stock Buffer: In a 4 L beaker add ~ 3000 mL Type I H_2O. Add 680 g of ammonium chloride (NH_4Cl) [FW = 53.50 g mol^{-1}] and 0.8 g of disodium EDTA [FW = 373.25 g mol^{-1}]. Transfer solution to 10 L carboy and dilute to the 8 L mark on the carboy with Type I H_2O and mix well. Adjust the pH to 8.5 with NaOH (use approximately 90 mL of 10N NaOH, or 180 mL 5N NaOH) and store in 10 L plastic carboy at 0 – 6.0˚C. Shelf life = 1 year.

8.1.4 Color Reagent: In a 2 L flask add ~ 1500 mL Type I H_2O. While stirring, carefully add 200mL H_3PO_4 [FW = 98.00 g mol^{-1}]. Dissolve 80 g sulfanilamide ($H_2NC_6H_5SO_2NH_2$) and 4.0 g N-1 NED (*N*-1-Naphthyethylendiamine Dihydrochloride ($C_{10}H_7HCH_2CH_2NH_2 \bullet 2HCl$)) in the phosphoric acid solution. Dilute to 2 L and mix well. Store in brown glass bottles at 0 – 6.0˚C. Shelf life = 90 days.

8.2 **Cadmium-Copper Reduction Column Regeneration reagents:**

8.2.1 **Stock NH_4Cl / EDTA buffer** (prepared in §8.1.3).

8.2.2 **2% Cupric Sulfate Solution:** In a 1 L flask dissolve 20.0 g of cupric sulfate ($CuSO_4 \cdot 5H_2O$) [FW = 249.69 g mol^{-1}] in ~ 900 mL of Type I H_2O. Dilute to the mark with Type I H_2O and mix well. Store in plastic at room temperature. Shelf life = 1 year.

8.2.3 **1M Hydrochloric Acid (HCl):** In a 1 L Erlenmeyer flask add 82.5 mL of concentrated HCl [FW = 36.46 g mol^{-1}] to ~ 750 mL of Type I H_2O in a 1 L container. QS with Type I H_2O and mix well. Store in plastic at room temperature. Manufacturer's expiration applies.

8.3 **Cadmium-Copper Reduction Column Efficiency Check Standards**

8.3.1 **2 mg/L $N\text{-}NO_3$ Standard:** In a 15 mL plastic graduated centrifuge tube add 0.2 mL of the 100 mg/L $N\text{-}NO_3$ stock standard. Dilute to 10 mL with Type I H_2O and mix well. Prepare standard daily. Store at room temperature.

8.3.2 **2 mg/L $N\text{-}NO_2$ Standard:** In a 15 mL plastic graduated centrifuge tube add 0.2 mL of the 100 mg/L $N\text{-}NO_2$ stock standard. Dilute to 10 mL with Type I H_2O and mix well. Prepare standard daily. Store at room temperature.

8.4 **Neutralizing Reagent**

8.4.1 **Concentrated Ammonium Hydroxide (NH_4OH).** Shelf life = manufacturer's date applies or one year, whichever expires first. Store at room temperature.

8.4.2 **Concentrated Hydrochloric acid (HCl) acid.** Shelf life = manufacturer's date applies or one year, whichever expires first. Store at room temperature.

8.5 **Residual Chlorine Treatment Solution:**

8.5.1 **Sodium thiosulfate:** Dissolve 3.5 g $Na_2S_2O_3 \bullet 5H_2O$ (CASRN 10102-17-7) in Type I H_2O and dilute to 1 L. One mL removes 1 mg/L of residual chlorine per 500 mL of sample. Store at room temperature. Shelf life = 1 year.

8.6 **Stock Solutions and Standards**[1]

NOTE: All standards are prepared using Class A glassware and Type I water. Store samples separate from standards and reagents.

8.6.1 **1000 mg/L NO_3 as N calibration stock:** a 1000 mg/L stock in the form of NO_3 as N is purchased pre-made from a vendor. Manufacturer's expiration date applies. Store at 0 – 6.0˚C in the standards cooler.

8.6.2 **1000 mg/L NO_2 as N calibration stock:** a 1000 mg/L stock in the form of NO_2 as N is purchased pre-made from a vendor. Manufacturer's expiration date applies. Store at 0 – 6.0˚C in the standards cooler.

8.6.3 **100mg/L N-NO_3 Stock:** Add 100 mL of 1000 mg/L NO_3 as N calibration stock to 1L volumetric flask. Dilute to volume. Alternatively, in a 1 L volumetric flask, add ~ 800 mL of Type I H_2O and then dissolve 0.7218 g of potassium nitrate (KNO_3). Dilute to the mark with Type I H_2O and mix well. Add 2 mL of chloroform to preserve. This solution is used to make calibration standards and spikes. Store in an amber bottle at 0 – 6.0˚C in standards cooler. Expires after 6 months.

8.6.4 **100mg/L N-NO_2 Stock:** Add 100 mL of 1000 mg/L NO_2 as N calibration stock to 1 L volumetric flask. Dilute to volume. Alternatively, in 1 L volumetric flask, add ~ 800 mL of Type I H_2O and then dissolve 0.4926 g of sodium nitrite ($NaNO_2$). Dilute to the mark with Type I H_2O and mix well. Add 2 mL of chloroform to preserve. This solution is used to make calibration standards and spikes. Store the solution in an amber bottle at 0 – 6.0˚C in standards cooler. Expires after 6 months.

8.6.5 **1000mg/L ICV stock:** Separate solutions are purchased from a vendor for each Nitrate and Nitrite. Manufacturer's expiration date applies. Store at 0 – 6.0˚C in standards cooler.

8.6.6 **Quality Control Standards:**

Table 8.1: QC Standards

QC STD	Source	mL of Stock used	Final Volume (mL)	Final Conc. (mg/L)
ICV*	1000 mg/L Stock	$NaNO_2$ = 2 $NaNO_3$ = 8	1000	NO_2 = 0.609 NO_3 = 1.807 NO_2NO_3 = 2.416

[1] ACZ has found inconsistency between different manufacturer's storage recommendations of standards and has decided that storing them at 0-6.0˚C in the reagent cooler is sound practice. Samples that are tested for these parameters are also stored at 0-6.0˚C. (CAR 1211)

CCV (C2) 8.6.7 W	Both 100 mg/L Stocks	NO_2= 5 NO_3 = 5	500	NO_2 = 1.0 NO_3 = 1.0 NO_2NO_3 = 2.0
Spike/LFB for White samples	Both 100 mg/L Stocks	NO_2 = 0.1 NO_3 = 0.1	10	NO_2 = 1.0 NO_3 = 1.0 NO_2NO_3 = 2.0
Spike/LFB for Yellow samples	NO_3 100 mg/L stock only	NO_3 = 0.2	10	NO_3 = 2.0
PQV for DW samples only	C6 Calibration Standard	–	–	NO_3 = 0.1 NO_2 = 0.05

*Store working ICV at 0 – 6.0˚C for up to 3 months.

†For soil and sludge samples there are no LCSS available – prepare & analyze a LFB.

working calibration standards. **Prepare weekly**. Store at room temperature.

Table 8.2: Working Calibration Standards

STD	C1	C2	C3	C4	C5	C6**	C7
Final Volume (mL)	200	500	200	*	*	*	blank
mL added (both 100mg/L stocks)	4	5	1	*	*	*	blank
Final mg/L (NO_2NO_3)	4	2	1	0.4	0.2	0.1	blank
Final mg/L (NO_2)	2	1	0.5	0.2	0.1	0.05	blank

***C4**, **C5**, and **C6** may be prepared as dilutions. Dilutions must be performed manually with a Class A pipette or mechanical pipette. **C7** (calibration blank) is Type I H_2O.

** There must be a calibration standard with a concentration ≤ PQL.

9.0 SAFETY

9.1 HAZARDS

This procedure does not propose to address all 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.

9.2 SAFETY TECHNIQUE

9.2.1 Safety glasses are required and the use of gloves and lab coat is strongly recommended. Shorts and open-toed shoes are not allowed in the lab.

9.2.2 Use care when pouring and pipetting reagents. Always add acid to water. Use the proper method when washing glassware.

9.2.3 Do not use tobacco products in the lab and do eat or drink in unauthorized areas.

9.2.4 Wipe up ALL spills immediately. Implement Emergency Response Plan if necessary.

9.2.5 Do not wear gloves or lab coat outside of the laboratory. Remove gloves before using a computer, telephone, etc.

9.2.6 Do not conduct "experiments" unrelated to the analysis.

9.3 PROTECTIVE EQUIPMENT

9.3.1 Use a fume hood when there is a potential for strong fumes.

9.3.2 A fire extinguisher is located near each analytical laboratory.

9.3.3 The emergency shower and eye wash station are located in the metals prep lab.

10.0 INTERFERENCES

10.1 Any substance that alters the efficiency of the cadmium-copper reduction column will interfere with the analysis, including turbidity, high sulfide, pH < 5 or pH >10, oil and grease. Filter turbid samples prior to analysis. Dilute samples high in sulfide prior to analysis. Samples high in oil and/or grease may be pre-extracted with organic solvents. Samples high in dissolved bicarbonate and/or carbonate can bubble in the analytical flow stream causing air spikes. Dilute to neutralize these samples.

10.2 High concentrations of divalent metal ions such as Fe^{+2} and Cu^{+2} can also cause interference. The EDTA in the buffer solution should minimize these interferences.

10.3 Sample color that absorbs in the photometric range for Nitrite/Nitrate will give positive interference.

10.4 Residual chlorine can produce negative interference by limiting reduction efficiency. If the presence of chlorine is suspected, the samples may be screened with potassium starch iodide paper. If the sample is positive for chlorine, dechlorinate with sodium thiosulfate before proceeding with analysis.

11.0 PROCEDURES

NOTE: If samples have visible sediment, they may be filtered and /or centrifuged before analysis.

NOTE: For each client sample, verify that the sample Log-in number on the workgroup matches the sample number on the container. This ensures that samples are not inadvertently switched.

11.1 Check all samples (whites, yellows, and extracts) for residual chlorine using potassium iodide-starch paper. If residual chlorine is present add approximately 20.0 µL per 10.0 mL sample of the sodium thiosulfate solution and test again for residual chlorine. Document the test on the bench sheet. Retest treated sample to confirm that residual chlorine has been removed.

NOTE: Do not dip test strips in the sample. Use a pipette to apply sample to the strip.

11.2 Check the pH of all samples (whites, yellows, and extracts). If the pH is not between 5 and 9, adjust the pH so that it is within this window with concentrated HCl or concentrated NH_4OH. If the sample matrix makes this impossible, document the problem and qualify the sample data at review. Record adjusted sample pH on the workgroup bench sheet in the ph screen column to verify the pH adjustment.

NOTE: Analysts may find it easier to raise the pH of samples with diluted aliquots of concentrated NH_4OH for more precise adjustments. Prepare 10 – 20x dilutions of NH_4OH using Type I H_2O. Prepare fresh daily.

NOTE: Sample pH must be 5 – 9 to run through the reduction column

NOTE: Do not dip pH test strips in the sample bottle. Use a transfer pipette to apply sample to the strip.

11.3 **Sludge Sample Preparation**

11.3.1 Verify the balance calibration if necessary. Refer to §SOPAD013 for instructions.

11.3.2 Label 50 mL centrifuge tubes for all QC and client samples in the workgroup.

11.3.3 Place a beaker on the balance. Put the centrifuge tube in the beaker and tare the balance.

11.3.4 Inspect the sludge sample to make sure it is not too high in solid content for analysis. If it is, sample needs to be re-logged for extraction in the soils department. Notify supervisor, soils supervisor and PM that the sample must be extracted.

11.3.5 Weigh ~ 1.0 g of sludge into the centrifuge tube. Record the exact weight on the SAGE workgroup sheet.

11.3.6 Prepare a PBS (50 mL Type I H_2O).

11.3.7 Dilute each sample to the 50 mL mark with Type I H_2O. If the final volume is greater than 50 mL then start over with a new centrifuge tube and weigh a fresh sample.

11.3.8 Cap each tube tightly and shake the sample to mix and break apart the sludge mass. If the sample does not break up after centrifuging it must be extracted by the soils department.

11.3.9 Centrifuge the samples for 5 minutes at 3000 rpm.

11.3.10 Analyze the supernatant according to the procedure in §11.6.

11.4 **NO_3NO_2 & NO_2, "Yellow", and Soils Extracts Sample Preparation**

11.4.1 For "Yellow" samples only: To prevent possible sample contamination from the NH_4OH neutralizing pH solution, pour off sample into sample/centrifuge tubes and carefully re-cap sample bottle and place back into sample bin before adjusting the sample pH.

11.5 **Efficiency Check and Regeneration for Cadmium-copper Reduction Column**

11.5.1 An efficiency check is required each day that NO_3/NO_2 analysis is performed. In addition, an efficiency check is required each time a new calibration curve is generated, even if the check has already been performed that day. This is to determine if cadmium-copper reduction column is still functioning as it should.

11.5.2 The efficiency standard pair is run following the ICB. The measured concentration of the NO_3 standard must be ≥ 90 % of the NO_2 standard in order to continue.

11.5.3 If the efficiency is < 90% the cadmium column must be repacked with regenerated cadmium. For repacking and regenerating instructions refer to procedure outlined in Appendix A.

11.5.4 Record the efficiency check and/or regeneration or repacking of the column in the OTCR logbook.

11.6 **Instrument Set-Up Analysis**

11.6.1 Turn on the instrument and start the computer and then the Lachat software (Omnion) by clicking on the Omnion 3.0 icon.

11.6.2 Refer to Figure 18.1 to set up each reagent in the proper location. Connect NO_2 and/or NO_3/NO_2 sample loops to positions 1 and 4 in the six port valve on the FIA (Figure 18.1). Insert the 520 nm interference filter(s) in the FIA (refer to FIA 8500 series manual).

11.6.3 **Check the date the manifold was last inspected.** If more than one month has passed since the last inspection, then visually check and verify that all connectors and unions are clean; replace dirty o-rings, pump tube adaptors, and tee fittings; inspect reagent tubing for wear. If the reagent tubing appears flat when twisted then replace the reagent tubing with new tubing. Record inspection and replacements in the logbook. Write the date of inspection and initials on the manifold.

11.6.4 Connect the manifold to the unit.

11.6.5 Remove the tube from the tee position marked “from valve” (the furthermost left connection on the manifold).

11.6.6 Connect this tube to position 2 on the six port valve.

11.6.7 Connect the tube from position 3 on the six port valve to the tee position marked “from valve.”

11.6.8 Fit the pump tubes carefully in the plantons, making sure that the tabs are placed in the slots on either side to prevent the tubes from twisting.

11.6.9 Place pump tubes in Type I H_2O and run H_2O through the manifold for several minutes.

11.6.10 Collect all reagents from storage location(s).

11.6.11 Place reagent tubing in the appropriate reagents and pump for several minutes before turning the switch valve for the cadmium column to the on-line position. Avoid pumping air or straight water through the Cadmium column.

11.6.12 **Importing Workgroup**

11.6.12.1 In the Omnion software under the file heading "Run" click on "Open." Choose "ACZ Methods" and then "NO_3/NO_2" and open appropriate template.

11.6.12.2 Open "NO3/NO2" or "NO3/NO2-Y" template.

11.6.12.3 The Auto Data Quality Management (DQM) should already be set up in the existing template. To modify, highlight the DQM rows and right click on the mouse. Select "Clear DQM Set," "yes." Modifications can then be made to the DQM in the "properties box" to the right. Once changed, set the DQM by highlighting the DQM rows, right click and select "Define DQM set." For ICV/ICB set choose "once" under "Scheduling Options." For CCV/CCB set choose "After every N samples" and type in "10" in Enter # box and "enter." Make sure "End of Run" box is checked to automatically insert a CCV and CCB after every 10 samples and at the end of the run.

11.6.12.4 To import workgroup into "Blank Template," go under "Run" and choose "Import Worksheet Data." Cut and paste samples into the other template. If running an efficiency check, prior to importing samples change the cup # of the first sample to 3. Then right click and select auto number cups.

11.6.12.5 The templates begin with a calibration followed by ICV and ICB (and efficiency check) measurement before analyzing the workgroup samples. A CCV and CCB are measured after every ten samples and at the end of each run. This procedure allows the use of a continuing calibration, whereby a calibration curve generated in a previous sample batch is used for subsequent batch analyses so long as instrument QC results remain acceptable. Two consecutive attempts are allowed for a continuing calibration before the instrument must be recalibrated.

NOTE: If the run uses a continuing calibration, the sequence must begin with a CCV. The data set containing the valid calibration curve must be identified by its workgroup # on the data review checklist. The DQM template can be modified by deleting the blue calibration section and the green ICV and ICB DQM sections. The raw data and workgroup bench sheet must indicate which verification standard was used.

11.6.12.6 Review the workgroup to check for any dilutions that need to be edited. Make sure that the proper dilution factors are typed into the "Dilution" space in the tray table (include dilution factors provided by Soils Dept). Changes must be reflected on the tray in the Lachat software. In the "Manual Dilution" column find the correct row where the sample is located and type in the correct dilution factor in the MDF column and press "enter."

NOTE: Dilution factors must be documented on the bench sheet, including reason for dilution.

11.6.12.7 Select the workgroup number to upload the correct QC and samples from the network in the correct order. Review what was uploaded to verify the correct workgroup and the correct order will be analyzed

11.6.13 **Sample Organization & Analysis Set-up**

11.6.13.1 For workgroups containing NO3NO2 & NO2 and "Yellow" drinking water samples a PQV must be analyzed. For the PQV standard, pour off an aliquot of C6 standard into a sample tube and place into sample rack. The PQV is measured immediately following the column efficiency check or after initial CCB in a continuing calibration workgroup.

11.6.13.2 Pour off the samples according to order on the workgroup bench sheet. To print a copy of the samples and their corresponding cup numbers, go to the "Run" heading and choose "export worksheet data."

NOTE: For each client sample, verify that the sample Log-in number on the workgroup matches the sample number on the container. This ensures that samples are not inadvertently switched when they are poured-off.

11.6.13.3 Set up the cup tray with the samples in their correct locations. Continually check the sample sheet to verify that samples are placed in the correct cup number.

11.6.13.4 Sample dilutions can be prepared manually by using a mechanical pipette and Type I H_2O. Mix sample and diluents well.

11.6.13.5 Review current settings in the "Run Properties Display" box click on "Analytes" tab, Analyte name under Channel #. This will display the analyze properties in the box on the right. Make sure "Calibration Fit Type" is first order (if not click then select "first order") this will apply a first order (linear) polynomial equation to fit the calibration curve generated. Make sure the weighting is set to "none" (if not then select "none").

11.6.13.6 Start the analysis by clicking the green **Start** button.

11.6.14 **Calibration Verification**

11.6.14.1 The instrument must be calibrated at least once daily using at least three standards and a blank. Analyze the standards in order of decreasing concentration, ending with the blank. Check the calibration under the calibration icon. "R" must be ≥ 0.995. Recalibrate if $R < 0.995$. The following factors can lead to a failing calibration. Refer also to §11.8 for additional information on troubleshooting.

- Are the standards prepared correctly?
- Are the correct standards in their corresponding cups?
- Is the autosampler sampling the correct cups?
- Is the tray setup properly for the calibration?

- Are the sample tubes flowing correctly?
- Is the heater set at the correct temperature and functioning properly?
- Reagent contamination

11.7 **Failing QC**

11.7.1 If QC fails during the analysis; steps must be taken to ensure the data is valid. If $R \geq 0.995$ for the calibration but the ICV or ICB fails (or first CCV or CCB for continuing calibration), the standard may be retested once. If the retest fails, then recalibrate before restarting the analysis. If succeeding CCVs or CCBs fail then decide whether to stop the analysis and run an "R" group or add the associated samples to the end of the tray (cut and paste the updated workgroup).

11.8 **Troubleshooting**

11.8.1 Indications of impaired analytical capability should be inspected immediately and resolved prior to continuing analysis. Effective troubleshooting employs a logical, systematic approach. Common problems encountered with this procedure include the following. If problems continue after going through these possible scenarios call LACHAT at (800) 247-7613. Any general maintenance, troubleshooting, repairs, calls to Lachat technical support, etc., **must** be documented in the instrument and/or maintenance logbook(s).

- Are the platens crimped down on the pump tubes? Or pump tubes need to be replaced?
- Is the peristaltic pump turned on?
- Is the sample tray sitting correctly on the auto sampler tray?
- Are the standards placed correctly on the auto sampler rack?
- Are leaks occurring on the manifold? Or cracks or breaks in the manifold tubing?
- Is there a sufficient amount of rinse water in the carboy for the auto sampler?
- Is the drain carboy for the auto sampler full and needing to be emptied?
- Is the correct manifold and filter being used for the analyte?
- Does the analyte method require a backpressure loop?
- If contamination shows up in non-prepped blanks, check the auto rinse carboy.
- If contamination in prepped blanks, check digestion glassware and reagents.
- Are the pump tubes in the correct reagents?
- Is the correct "Method, DQM, and Channel" defined in the software?
- Any clogs on the manifold or in pump tubes? Or are drain lines pinched or plugged?
- If the baseline is reading perfectly at "0," then the computer is not communicating with the instrument and it must be restarted.
- If the software is incorrectly marking peaks then valve timing, threshold and/or inject to peak start need to be changed in the Analyte table. The timing can be checked with green dye – make sure the sample loop being filled.
- If there is no reading, check the bulb and channel.
- If the baseline becomes jumpy (huge peaks or just very noisy), check for air bubbles passing through the manifold, check to see that the flow cell is properly set in the detector.
- Noisy baselines can also be attributed to a bad detector, bad fluidics, etc. If the detector is suspected, exchange with another on the instrument. Fluidics could be pinpointed to pump tubes, clogs, or a degenerating pump.

11.9 **"R" Group**

11.9.1 If any non-conformance occurs and the final CCV/CCB have been sampled then an "R" group must be run. An "R" group includes the samples to be retested and required instrument QC. Create an "R" group by editing the current tray. Delete the calibration, ICV/ICB DQM sets, and any samples and QC that don't need to be re-run. Then start the run by clicking the green arrow. Save the run by adding an R to the end (*i.e.*, save WG145889 as WG145889R).

11.10 **Run Completion & Data Export**

11.10.1 After the analysis has ended save the data file by selecting "Run" (upper left hand corner of display) "Save File As," type the workgroup number for the file name. Print a copy of the data by clicking on the "Tools," "Custom Report," and printer icon. Close the run file by selecting "Run" and "Close."

11.10.2 Reopen the file and click on the "Run" tab in the "Run Properties" display box. Click on "Export Data to File" box.

11.10.3 Under "Tools" choose "Custom Report." Click on the arrows to ensure all required information is included. Make sure all samples appear on the chromatogram. To alter the format go under "Report" and choose "Format." The # of peaks per chart can be changed under "Charts." To zoom in or out on the chromatogram, alter the view under the channel view on the main page (this changes the view in Custom Report).

11.10.4 If the workgroup is ready for review, send it directly to U:\Waitload\FIA1 or … \FIA2. Then copy and paste the file into U:\Autoload\FIA1 or … \FIA2 directory.

11.10.5 If a workgroup needs additional editing ("R" group, dilution factors must be entered, soils data must be entered) then send the workgroup to U:\Waitload\FIA1 or …\FIA2.

11.10.6 If the file does not export check the software export to the Waitload directory. Click on "Configuration," "Options," "Data Export," and "Data Items." Verify data is being exported to either U:\Autoload\FIA1 or U:\Waitload\FIA2. If not then change the directory. Click the "Ominion 2.0 format," "Accept" "Ominion 2.0 format" and "Close." Then try exporting the file again.

11.10.7 If the workgroup was sent to Waitload, go to the data drive on the network and locate U:\Waitload\FIA1 or U:\Waitload\FIA2.

11.10.8 Find the appropriate workgroup and the "R" group, if applicable.

11.10.9 Double click on the correct file to open and confirm the correct dilution factors will upload (change if necessary).

11.10.10 If "R" group was analyzed, copy data from the "R" group; open the original workgroup and paste "R" group data to end of the original workgroup data.

11.10.11 Save the file and send the workgroup to U:\Autoload\FIA1 or …\FIA2.

11.10.12 Review the workgroup in SAGE (AREV), completing a data review checklist (FRMWC006). Attach all raw data and supporting documentation and turn in for secondary review (SREV).

Table 12.1: QC Standards, Frequency, Limits, and Corrective Action

QC Standard	Frequency	Limits	Required Corrective action if QC fails
Calibration	First workgroup of the day	$r \leq 0.995$	Recalibrate
Column efficiency check	Once after ICV/ICB for each new calibration	NO_3 value $\geq$ 90% of NO_2 value	Repack column and reanalyze efficiency check standards. If new calibration curve is created, efficiency check must be performed again.
ICV	After calibration.	90 – 110%	1 retest OK then recalibrate. Redo all samples associated with a failed ICV.
CCV	Every 10 samples and end.	90 – 110%	Re-analyze affected samples.
PQV	One per batch for DW samples	70 – 130%	1 retest OK then redo all DW samples.
ICB	After ICV	3X (-MDL) $\leq$ sx < MDL	1 retest OK then recalibrate.
CCB	After every CCV	3X (-MDL) $\leq$ sx < MDL	Re-analyze associated samples. Client samples <MDL can be accepted and reported with the appropriate qualifier if bracketing CCB fails high.
LFB (water)	1 per 20 samples	90 – 110%	1 retest OK then redo all samples.
LFB (soil/sludge)	1 per 20 samples	90 – 110%	1 retest OK then redo all samples.
AS	1 per 10 water samples and 1 per 20 soils samples	90 – 110%	If LFB and instrument QC passes, qualify associated data with the appropriate qualifier(s).
DUP	1 per 10 water samples and 1 per 20 soils samples	RPD <20	1 retest OK then redo associated H_2O samples if [sx] > 10x MDL. Flag data for soils.
PBS	One per soils extract batch	3X (-MDL) $\leq$ sx < MDL	REDO all samples < 10 x PBS. Client samples <MDL can be accepted and reported with the appropriate qualifier if the PBS fails high.

11.10.13 Record all pertinent workgroup analysis information in the instrument logbook.

11.11 **Lachat Cleaning and Maintenance Procedure**

11.11.1 Remove all NO_2 pump tubes from the reagents and place them in water.

11.11.2 Take the NO_3NO_2 tubes for buffer and carrier and place them in the buffer.

11.11.3 Pump buffer through reduction column for ~ 5 minutes or until column is filled with buffer.

11.11.4 Turn reduction column off-line, place pump tubes in water and continue pumping water until the manifolds are adequately rinsed. Then take the tubes out of the H_2O and pump air until the lines are cleared.

11.11.5 Routine maintenance must be performed monthly, semiannually and annually as prescribed by the LACHAT FIA User Manual. Refer to the manual for maintenance procedures. Record routine maintenance in instrument maintenance logs.

12.0 QUALITY CONTROL

Quality control samples must be analyzed with each workgroup as required by the method and other regulatory agencies. See Table 12.1 for QC types, acceptance limits and required corrective actions.

13.0 CALCULATIONS, DATA REPORTING & ARCHIVING

13.1 Linear Least Square Regression Calibration Model With No Curve Weighting

y = mx + b

Where: y = concentration (C_x) in mg/L
m = slope
x = peak area (Vs), A_x
b = y-intercept

Slope (m)

$$m = \frac{\left(\sum_i^n w_i x_i y_i \times \sum_i^n w_i\right) - \left(\sum_i^n w_i x_i \times \sum_i^n w_i y_i\right)}{\left(\sum_i^n w_i \times \sum_i^n w_i x_i^{\,2}\right) - \left(\sum_i^n w_i x_i\right)^2}$$

y-intercept (b)

$$b = \frac{\left(\sum_i^n w_i x_i^{\,2} \times \sum_i^n w_i y_i\right) - \left(\sum_i^n w_i x_i \times \sum_i^n w_i x_i y_i\right)}{\left(\sum_i^n w_i \times \sum_i^n w_i x_i^{\,2}\right) - \left(\sum_i^n w_i x_i\right)^2}$$

Calibration Coefficient (R)

$$R = \frac{\left(\sum_i^n w_i \times \sum_i^n w_i x_i y_i\right) - \left(\sum_i^n w_i x_i \times \sum_i^n w_i y_i\right)}{\sqrt{\left(\left(\sum_i^n w_i \times \sum_i^n w_i {x_i}^2\right) - \left(\sum_i^n w_i x_i\right)^2\right) \times \left(\left(\sum_i^n w_i \times \sum_i^n w_i {y_i}^2\right) - \left(\sum_i^n w_i y_i\right)^2\right)}}$$

Where: (variables for slope, intercept, and calibration correlation)
w_i = weighting factor (for non-weighted calibration curves $w_i = 1$ for all standards)
x_i = peak area for the i^{th} calibration standard
y_i = expected concentration for the i^{th} calibration standard
$i \rightarrow n$ = calibration points in order of decreasing concentration

NOTE: FRMQA049 may be used to calculate slope, intercept, calibration coefficient, and concentrations. Use the worksheet titled "ESTD LIN EW IO". Lachat software calculates the linear equation from plotting the sample concentration, Cx, versus peak area, Ax. Enter the calibration levels, C1 through C7 in fields A20 through A26. Enter peak areas measured for each standard in fields C20 through C26. Enter standard concentrations in fields B20 through B26. Make sure all weighting factors are set to 1 (fields D20 through D26). The calculated linear calibration curve values are displayed in fields D32 (slope), D33 (y-intercept), D34 (correlation coefficient). Sample concentrations can be calculated in the lower table by entering sample IDs starting with column A47 and peak area in column C47. The calculated sample concentrations are listed starting with column D47 and computed using equation, y = mx + b.

13.2 Aqueous matrices are reported in mg/L. Soil extracts are reported in mg/Kg, and sludge samples are reported as % mass. Raw data values are multiplied by any dilution factor(s).

13.3 SAGE qualifies data with a concentration less than the MDL ("U") or less than the PQL ("B").

13.4 SAGE calculates sample NO_3 values by subtracting the NO_2 values from the NO_3-NO_2 values.

13.5 Samples exceeding the highest standard must be diluted and reanalyzed. Samples on a dilution that upload with a "U" or "B" qualifier must be reanalyzed on a smaller dilution. Data may be appropriately qualified if the sample required dilution due to matrix, reactivity, insufficient volume and data is reported with a "U" or "B" qualifier.

13.6 Method Detection Limit (MDL) / Practical Quantitation Limit (PQL):

▭ $N\text{-}NO_3$	MDL = 0.02 mg/L	PQL = 0.10mg/L
▭ $N\text{-}NO_2$	MDL = 0.01mg/L	PQL = 0.05mg/L
▭ $N\text{-}NO_3/NO_2$	MDL= 0.02mg/L	PQL = 0.10mg/L
▭ $N\text{-}NO_2$-KCL	MDL = 0.1 mg/Kg	PQL = 0.5 mg/Kg
▭ $N\text{-}NO_3/NO_2$-KCL	MDL = 0.2 mg/Kg	PQL = 0.5 mg/Kg

13.7 Refer to SOPAD044 for details of instrument data backup and archiving.

13.8 Retrieval of archived data files:

1. Go to Labweb.

2. Change the internet address to 'http://saloon'.

3. Log onto the internet by typing user name and password.

4. Click on 'Archive', 'Instrument', 'FIA1' or 'FIA2', 'Program Files', 'Lachat', 'Omnion', 'Data', 'ACZ Methods', 'NO3&NO2'.

5. Search directory for desired workgroup to retrieve.

6. Right click on workgroup file name (WGnumber), select 'Save Target As…' and save file to local desk top computer in C;//Program File/Lachat/Omnion/Data/ACZ Methods/NO3NO2 directory.

7. Click 'Close' after saving file.

8. Open Omnion software and open the saved archive file in the NO3NO2 directory.

13.9 The Sludge dilution factor (DF) is determined with the following equation:

$$\mathrm{DF} = \frac{V_f}{(W \times \%\mathrm{Solids}) \times 10000}$$

Where: V_f = Final Volume in Ml
W = sample weight in grams
10000 = Conversion factor from mg/L to %mass.

NOTE: The "solid fraction" of the equation is derived from the Soils Department "Percent Solid" or "Sludge" workgroup data. An Excel spreadsheet available on each PC in the Lachat Lab will perform this calculation. Dilution factors must be altered in the raw data in Waitload before going to Autoload if necessary and changes noted on the workgroup bench sheet.

13.10 Relative Percent Difference (RPD) is determined using the following equation:

$$\mathrm{RPD} = \frac{(S - D)}{[(S + D) / 2]} \times 100\%$$

Where: S = Sample Value
D = Duplicate Value

13.11 Percent Recovery (%R) for the LFB is determined using the following equation:

$$\%\,R = [\text{Measured Value} / \text{True Value}] * 100\%$$

13.12 Percent recovery for spiked samples is determined using the following equation:

$$\%R = [(X_s - X_u) / C_t] * 100\%$$

Where: X_s = measured concentration of the spiked sample
X_u = measured concentration of the unspiked sample (if > MDL)

C_t = true concentration of the spike added

14.0 METHOD PERFORMANCE / DETECTION LIMITS

14.1 **Method Detection Limit Study (MDL):** An MDL study is required for water only and must be performed for initial method development; **every six months**[2]**;** and whenever, in the judgment of the analyst, a change in analytical performance caused by a change in instrument hardware, operating conditions or location would dictate the MDL be re-determined. The MDL study must be performed on 3 different days.

14.1.1 Spike at least seven aliquots of reagent blank at 1 – 5x MDL and process as described in this SOP. The analysis must include at least a passing calibration and ICV/ICB. Enter the results into MDL form in Lab Web (FRMAD031). Print the form and sign it. Attach all raw data and supporting documentation and submit the data package to the department supervisor for review. Refer to §SOPAD001 for additional information.

14.2 **Demonstration of Capability (DOC):** A successful Initial DOC must be completed and approved by the QA/QC department for each analyst prior to independent generation of client data. A continuing DOC (CDOC) must be performed on an annual basis. All DOCs must include a passing calibration, ICV/ICB and CCV/CCB. The average recovery must be within the laboratory control standard (LFB, LCSW, or LCSS) limits defined in §12 of this SOP. One IDOC/CDOC is required for aqueous matrices.

14.2.1 Prepare a **DOC** solution at **1– 4x the PQL** and analyze 4 individual aliquots according to the SOP. Include a passing calibration, ICV/ICB and CCV/CCB. Enter the results on the DOC form in Labweb (FRMAD023), attach all raw data and supporting documentation, and turn in to the department supervisor for review. Refer to §SOPAD001for additional information and CDOC options.

NOTE: The **IDOC** solution must be prepared from a different source than the calibration standards. The **IDOC** must be a single-blind sample (*i.e.,* the person performing the IDOC cannot know the true value of the DOC solution). The IDOC solution may be obtained from a reputable vendor, prepared by the department supervisor, or prepared by another analyst approved by the QA/QC department to perform the procedure. The IDOC solution must have an SCN or PCN and the IDOC documentation must state who prepared the solution. As part of an analyst's **IDOC** a successful MDL study must be performed by the analyst (§14.1). The MDL study must be analyzed on 3 different days for an IDOC.

14.3 **Linear Calibration Range Study (LCR):** A successful LCR during initial method development and whenever the calibration range is extended.

14.3.1 Calibrate the instrument. R must be > 0.995 or recalibrate before proceeding. Analyze each calibration standard as a sample, bracketing them with a passing ICV/ICB and CCV/CCB. Compare the observed concentration of each to the actual concentration. The values must agree within +/- 10%. If this is not the case, determine the cause of the discrepancy and perform another study. Enter results on FRMQA029; attach all raw data and supporting documentation; and turn in to the

[2] Colorado Department of Public Health and Environment [2004 audit report].

department supervisor for review. Refer to §SOPAD013 for instructions on extending the calibration range.

NOTE: EPA353.2 requires the LCR to be verified every 6 months; however, Jim O'Dell of the EPA confirmed that the intent of the LCR is to establish the upper limit of the calibration range. ACZ's procedure requires daily instrument calibration and dilution of samples with a concentration greater than the high calibration standard; therefore, verification of the LCR every 6 months does not provide a quality control measurement pertinent to laboratory activities and is not required for this procedure.

15.0 DOCUMENTATION

15.1 Record daily OTCR efficiencies and other OTCR information in the OTCR logbook.

15.2 Record the pertinent information for all prepared standards and reagents in SAGE or the Wet Chem Standards/Reagent Logbook. Include analyst's initials, prep date, expiration date, and the PCN or SCN of any stock standard or reagent used.

NOTE: For working standards, documentation of preparation of C2 (CCV) shall indicate that all calibration standards were prepared in tandem.

15.3 Record all work completed, maintenance performed and any problems in the instrument logbook. Initial and date each logbook entry.

15.4 Label each standard or reagent prepared in §8.0 with the following information:

- standard name
- SCN (or other unique ID)
- preparer's initials
- expiration date
- prep date

15.5 Include the following information with the workgroup:

- Instrument ID
- Dilution factors noted on bench sheet, review checklist form (FRMWC006.10.15.21), or Sample Dilution Worksheet, (FRMWC026.02.08.01).
- Analysis date, start time and completion time.
- Analyst's initials.
- Any remarks about analysis or samples.

15.6 The SOP Revision Form (FRMQA030) must be filled out and approved by the QA/QC department before changes are made to this procedure.

16.0 WASTE MANAGEMENT/POLLUTION PREVENTION

16.1 All waste is collected in waste receptacle next to the instrument, which is regularly emptied into the neutralization system. Refer to ACZ's Waste Management Plan for additional disposal details.

17.0 DEFINITIONS

17.1 **Initial Calibration Verification (ICV) –** A solution of method analyte(s) of known concentration and obtained from a source external to the laboratory and different from the source used to prepare the calibration standards. Analysis of the ICV confirms the validity of the instrument calibration. The ICV is equivalent to the QCS referenced in the method. The prepared concentration should be ~ 50% of the high calibration standard.

17.2 **Initial Calibration Blank (ICB) –** Reagent blank analyzed immediately after the ICV and used to confirm that no background contamination is present in the calibration blank.

17.3 **Continuing Calibration Verification (CCV) –** A solution of analyte(s) of known concentration(s) used to confirm the continued calibration of the instrument. It is analyzed after every 10 samples, including the final sample in the run. The CCV is equivalent to the IPC.

17.4 **Continuing Calibration Blank (CCB) –** This is the same solution as the calibration blank. It is intended to detect baseline drift in the calibration of the instrument and must be analyzed immediately after each CCV including the final CCV.

17.5 **Preparation Blank Soil (PBS) –** A reagent blank carried through the entire sample preparation scheme with the samples. It is intended to confirm the absence of contamination in the prep stages. The prep blank is not required for non-digested analysis.

17.6 **Laboratory Fortified Blank (LFB) –** This solution is the same as the calibration blank, but has been spiked with a known concentration of the pertinent method analytes. The LFB is treated exactly like a sample and confirms that the spiking procedure is accurate.

17.7 **Analytical Spike (AS) –** A volume of sample to which a known amount of analyte is added. It is prepared in the same manner as the LFB, only spiking into sample. The AS is intended to demonstrate the absence or presence of interfering elements in an unknown matrix and is equivalent to the LFM referenced in the method.

17.8 **Duplicate (DUP)** – Two aliquots of a sample are analyzed in the same workgroup, under identical circumstances. Analysis of a duplicate indicates the precision associated with the procedure.

17.9 **Relative Percent Difference (RPD) –** The difference between two replicates (a sample and its duplicate) divided by the average of those two replicates and then multiplied by 100.

17.10 **Method Detection Limit (MDL)** – The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

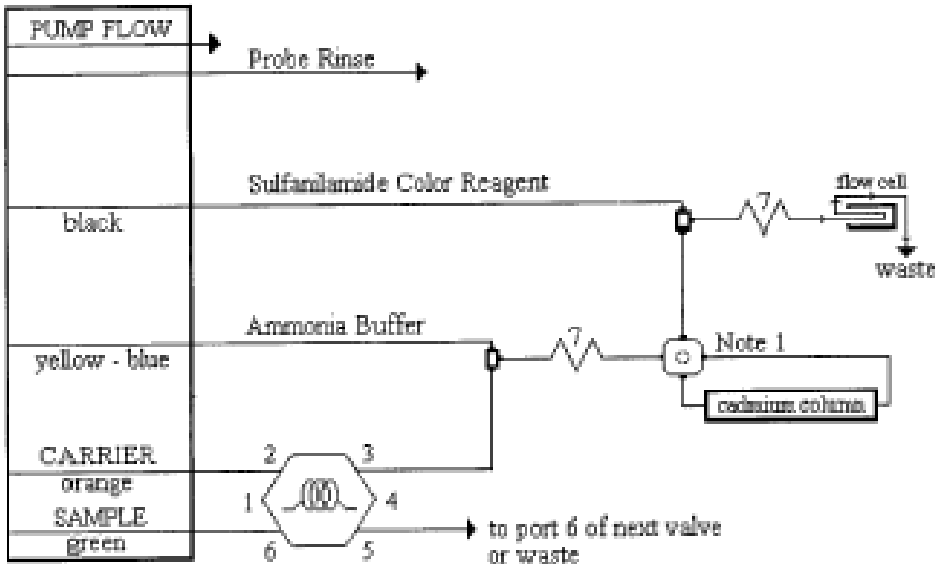
17.11 **Practical Quantitation Limit (PQL)** – The lowest level that can be reliably achieved within methods specified limits during routine operations.

17.12 **Practical Quantitation Verification (PQV)** – A standard is analyzed to verify the analysis accuracy at the reporting limit.

18.0 TABLES & DIAGRAMS

Table 6.1: N-NO3NO2 Hold Times
Table 6.2: N-NO2 Hold Times
Table 8.1: QC Standards
Table 8.2: Working Calibration Standards
Table 12.1: QC Standards, Frequency, Limits, and Corrective Action
Figure 20.1: Recopperization Manifold

Figure 18.1: Nitrate/Nitrite Manifold



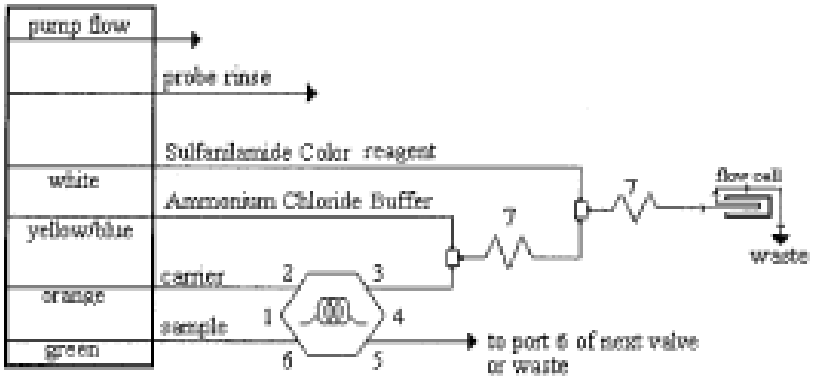
Carrier: Helium Degassed DI water
Manifold Tubing: 0.8 mm (0.032 in) i.d. This is 5.2 µL/cm.
AE Sample Loop: 17 cm x 0.8 mm i.d.
QC8000 Sample Loop: 22.5 cm x 0.8 mm i.d.
Interference Filter: 520 nm

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

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

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

Figure 18.2: Nitrite Manifold



Carrier: **DI water**
Manifold Tubing: **0.8 mm (0.032 in) i.d.** This is **5.2 µL/cm.**
AE Sample Loop: 10 cm
QC8000 Sample Loop: 15.5 cm
Interference Filter: 520 nm

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

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

19.0 CORRECTIVE ACTION

19.1 For QC samples that do not meet the method acceptance criteria, refer to Table 12.1. For retests that will occur past the method hold time, check first with the department supervisor to determine if the reanalysis should be conducted.

19.2 For any SOP/method deviation fill out section 1 of a corrective action report (FRMQA001). If necessary, the department supervisor and/or project manager may provide additional information in the appropriate sections; however, QA/QC does not need to close a minor corrective action. Attach a copy of the minor corrective action report to all workgroups affected. A minor corrective action is for documentation purposes –any SOP or method deviation may be noted on the data review checklist or on the workgroup bench sheet in lieu of using FRMQA001.

19.3 For any system failure a major corrective must be opened and the problem investigated. A department supervisor or the QA/QC Officer can open a major corrective action. The corrective action will be assigned a unique tracking number by the QA/QC Officer and will be closed by the QA/QC Officer once the failure has been resolved. Use FRMQA001 (in Labweb).

20.0 APPENDIX A: Procedure To Recopperize and Repack Cadmium Column

20.1 Remove used cadmium from column. By unscrewing the column connection on one end of the column and removing the foam plug. Pour out the cadmium into a 600 mL beaker.

20.2 Add approximately 80 mL of acetone to the granules and gently swirl. Then decant the acetone to an organic waste container. Repeat this step until the acetone does not turn cloudy.

20.3 Add 100 – 150 mL Type I H_2O to the beaker. Gently swirl the cadmium granules in the beaker and decant the cloudy water solution. Repeat several times until the water solution does not turn cloudy.

20.4 Add approximately 50 – 100 mL of 1M HCl solution to the granules and gently swirl. Decant acid and repeat this step, if necessary, to produce more uniform color in cadmium granules.

20.5 Copperize the cadmium granules by adding the approximately 50 – 100 mL of 2% $CuSO_4$ solution and swirling the granules until the granules begin to darken. Decant the 2 % $CuSO_4$ solution. Repeat this step one to three more times until fine brown reddish precipitate forms.

20.6 Decant the $CuSO_4$ solution and add approximate 100 mL of ammonia buffer solution. The cadmium can be covered and stored in this solution for future use or is ready to pack into the column.

20.7 Remove the old foam from both ends of the column. Place new foam plug on inlet side of the column. The cadmium column can be repacked as shown in Figure 20.11 or in-line, while connected to the manifold after the NO_3NO_2 valve.

20.8 Start pumping buffer solution to fill the empty column with buffer.

20.9 Then carefully add cadmium granules into the column. Once the column is uniformly packed with the granules then place a new foam plug on the outlet side of the column and reconnect the column to the manifold.