Standard Operating Procedure for:

QuikChem® 8500 Flow Injection Analysis System Operation for Total Nitrogen (Lachat TN-R01.doc)

Missouri State University

and

Ozarks Environmental and Water Resources Institute (OEWRI)

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1 Identification of the method

Operation of the QuikChem® 8500 Flow Injection Analysis System.

2 Applicable matrix or matrices

This instrument can be used for natural water, sediment, and biomass samples.

3 Detection Limit

The applicable range is 0.2 to 10.0 mg/L. The method detection limit is 0.011 mg N/L. The method throughput is 45 injections per hour.

4 Scope of the method

This standard operating procedure provides Missouri State University (MSU) Ozarks Environmental and Water Resources Institute (OEWRI) laboratory personnel with guidance on the procedure for operation of the QuikChem® 8500 Flow Injection Analysis System.

This method is used to determine the total nitrogen concentration of drinking, ground, and surface waters.

5 Summary of method

5.1 The QuikChem Method 10-107-04-3-C is based on the oxidation of nitrogen compounds to nitrate using alkaline persulfate/UV in-line digestion.

5.2 Nitrate is quantitatively reduced to nitrite by passing the sample through a copperized cadmium column.

5.3 The nitrite (reduced nitrate plus original nitrite) undergoes diazotization with sulfanilamide under acidic conditions to form a diazonium ion.

5.4 The diazonium ion is coupled with N-(1-naphthyl) ethylenediamine dihydrochloride and makes a pink solution. That pink solution absorbs at 540 nm which is proportional to total nitrogen.

5.5 The digestion process occurs, the sample valve injects the sample, and the total nitrogen concentration is determined by flow injection analysis.

5.6 The desired performance criteria for this measurement are:

- 5.1 Detection limit: ≤0.1 mg TN/L
- 5.2 Precision: ± 20%
- 5.3 Accuracy: ± 20%
- 5.4 Minimum Quantification Interval: 0.1 mg TN/L

6 Definitions

6.1 Analytical batch: The set of samples processed at the same time.

6.2 Calibration standard: A solution prepared from the primary dilution standard solution or stock standard solutions. The calibration standards are used to calibrate the instrument response with respect to analyte concentration.

6.3 De-ionized water blank (DIB): This blank should not contain any concentration of analyte and is not processed or digested like the standards, checks, or samples. The de-ionized water blank should be less than the laboratory reagent blank (LRB).

6.4 Digestion Efficiency Check (DEC): This is a urea intermediate standard solution that is used to confirm effective digestion of nitrogen forms.

6.5 Field blank (FB) : An aliquot of deionized water treated as a sample in all aspects, including exposure to a sample bottle holding time, preservatives, and all pre-analysis treatments. The purpose is to determine if the field or sample transporting procedures and environments have contaminated the sample.

6.6 Field duplicate (FD): Two samples taken at the same time and place under identical circumstances which are treated identically throughout field and laboratory procedures. Analysis of field duplicates indicates the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

6.7 Laboratory control check sample (LCC): A solution prepared in the laboratory by dissolving a known amount of one or more pure compounds in a known amount of reagent water. Its purpose is to assure that the results produced by the laboratory remain within the acceptable limits for precision and accuracy. (This should not be confused with a calibrating standard).

6.8 Laboratory duplicate (LD): Two aliquots of the same environmental sample treated identically throughout a laboratory analytical procedure. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures.

6.9 Laboratory matrix spike (LS): An aliquot of a sample to which a known amount of analyte is added before sample preparation. The laboratory spike is used to evaluate analyte recovery in a sample matrix.

6.10 Laboratory reagent blank (LRB): An aliquot of deionized water treated as a sample in all aspects, except that it is not taken to the sampling site. The purpose is to determine if the if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

6.11 Method detection limit (MDL): The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero.

a. To calculate the MDL:
b. Prepare a solution with the concentration of TP near the estimated MDL
c. Analyze seven portions of this solution over a period of at least three days
d. Include all sample processing steps in the determination
e. Calculate the standard deviation (*s*).

f. From a table of the one-sided *t* distribution select the value of *t* for 7 – 1 = 6 degrees of freedom at the 99% level. This value is 3.14
g. The product 3.14 times *s* is the desired MDL.

6.12 Relative Percent Difference (RPD): calculated as the difference between a sample and duplicate results, divided by the average of the sample and duplicate results, multiplied by 100%.

6.13 Quality control check sample (QCC): A sample containing analytes of interest at known concentrations (true values). The quality control check sample is obtained from a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory performance using test materials that have been prepared independently from the normal preparation process.

7 Interferences

7.1 Chloride is a suspected interference. Seawater, when spiked at 5 mg N/L as ammonia, gave < 5% recovery.

7.2 Glassware or bottle contamination can be a problem in low level nitrogen determinations. Laboratory glassware is washed according to Preparation of Sample Bottles For Non-Metals Analyses (0150R01 Bottle Prep non-Metals.doc) which requires that glassware and sample bottles to be washed with Citranox, rinsed with deionized water, soaked in an 30% hydrochloric acid bath, and re-rinsed with deionized water.

7.3 Turbid samples can cause interference and may require filtration. Surface water samples may not require filtration but this should be verified with a sample containing high levels of solids. Results for wastewater influent may be up to 30% low when compared with a rigorous TKN digestion. If effluent samples are preserved and filtered, in-line digestion results will match the manual off-line digestion. If samples are not filtered, in-line results will be 1-15% low compared with off-line digestion. The laboratory manager and project supervisor should be consulted prior to analysis.

7.4 Deposition of reaction products on cell windows can interfere with analyses. Cell windows will be observed before analyses and scheduled maintenance should minimize any interference.

8 Health and safety

8.1 This analysis involves handling freshwater samples that may contain live microorganisms and therefore pose some threat of infection. Laboratory personnel who are routinely exposed to such water samples are encouraged to protect themselves from water borne illnesses by wearing clean disposable gloves and washing their hands frequently.

8.2 The calibration standards, samples, and most reagents used in this method pose no unusual hazard to an analyst employing standard safety measures including

protective clothing and safety goggles. Care must be taken when handling concentrated sulfuric acid, phosphoric acid, potassium persulfate, and cadmium. Analysts should review the MSDSs for all chemicals used in this analysis.

8.3 This procedure requires use of heated reagents under pressure. All safety directions for using the QuikChem® 8500 Flow Injection Analysis System should be followed carefully.

9 Personnel qualifications

Samples will be analyzed by Missouri State University (MSU) laboratory personnel who have received appropriate training from experienced personnel, prior coursework, and laboratory experience regarding the analyses, and who are familiar with all of MSU's sample handling and labeling procedures and appropriate SOPs. Prior to the first batch of sample analyses, the analyst will complete a demonstration of capability exercise.

10 Equipment and supplies

10.1 Balance -- analytical, capable of accurately weighing to the nearest 0.0001 g.

10.2 Chain of Custody Forms: used to describe the written record of the collection, possession and handling of samples. Chain of custody (COC) forms are located on a board in Temple Hall 125. Chain of custody forms should be completed as described in the Chain of Custody SOP # 1030R01.

10.3 Glassware -- Class A volumetric flasks and pipettes or plastic containers as required.

10.4 Flow injection analysis equipment designed to deliver and combine sample and reagents in the required order and ratios.

10.5 PVC PUMP TUBES MUST BE USED FOR THIS METHOD.

10.6 Protective Gloves: for protection against chemicals and from contaminants.

11 Reagents and standards

11.1 Deionized water (DI): Use deionized water that has been purified with a Barnstead/Thermolyne purification system that includes ion exchange and organic purification cartridges. Use this water for all procedures.

11.2 Reagent 1. Ammonium Chloride Buffer: Fumes are produced when making this reagent, prepare this reagent under a hood with proper ventilation. Dissolve 85.0 g ammonium chloride (NH4Cl) and 1.0 g disodium ethylenediamine tetraacetic acid dihydrate (Na2EDTA.2H2O) in approximately 800 mL of deionized water in a 1 L volumetric flask. Dilute to the mark and invert to mix. Adjust the pH to 8.5 with 15 N a sodium hydroxide solution. Reagent 1 can be stored in dark plastic for up to two months if refrigerated. ACS grade ammonium chloride has been found occasionally to contain significant nitrate contamination. An alternative recipe for the ammonium chloride buffer is: Add 500 mL DI water, 105 mL

concentrated hydrochloric acid (HCl), 95 mL ammonium hydroxide (NH4OH), and 1.0 g disodium EDTA. Dissolve to a 1 L volumetric and dilute to the mark. Invert to mix. Adjust the pH to 8.5 with HCl or 15 N NaOH solution.

11.3 Reagent 2. Sulfanilamide Color Reagent: Add 600 mL DI water to a 1 L volumetric flask. Then add 100 mL 85% phosphoric acid (H3PO4), 40.0 g sulfanilamide and 1.0 g N-(1-naphthyl)-ethylenediamine dihydrochloride (NED). Shake to wet, and stir to dissolve for 30 minutes. Dilute to the mark with DI water, and invert to mix. Store in a dark bottle and discard when the solution turns pink. (Some pink color is normal. Strong pink color indicates significant degradation of the NED.)

11.4 Reagent 3. Potassium Persulfate Oxidant: Add 900 mL DI water to a 1 L volumetric flask. Then add 49 g potassium persulfate (K2S2O4) and 10 mL disodium tetraborate decahydrate (Na2B2O7 ·10H20). Add a magnetic stirbar, stir solution until solids are dissolved, and dilute to the mark with DI water. Invert to mix.

11.5 Reagent 4. Buffer Solution for Digestion: Dissolve 25.0 g of disodium tetraborate decahydrate (Na2B4O7 ·10 H2O) and 3.0 g sodium hydroxide (NaOH) in approximately 900 mL DI water in a 1 L volumetric flask. Adjust to pH = 9.0 with sodium hydroxide or hydrochloric acid. Add a magnetic stirbar, stir solution until solids are dissolved, and dilute to the mark with DI water. Gentle heating may be required for complete dissolution. Invert to mix.

11.6 Nitrate solutions: Prepare two sets of the following, using different sources of potassium nitrate (e.g., different lot numbers from the same supplier or different suppliers). Use one to prepare calibration standards and the other to produce quality control standards. This standard is commercially available.

a. Stock nitrate solution (1.00 mg N/mL):
   1. Dry KNO_3 in an oven (105ºC) for 24 hours.
   2. Dissolve 7.218 g in water with 2 mL $CHCl_3$ (preservative) and dilute to 1 L.
   3. This solution is stable for at least 6 months.
   4. 1.00 mL = 1.00 mg NO_3-N.
   5. Commercially prepared nitrate solutions may be purchased instead.

b. Intermediate nitrate solution (0.10 mg N/mL):
   1. Dilute 25.0 mL nitrate stock solution to 250 mL.
   2. This solution is stable for six months.
   3. 1.00 mL = 0.100 mg NO_3-N.

11.7 Urea ($CO(NH_2)_2$) stock solution (1.00 mg N_{org}/mL):

a. Dissolve 536 mg urea and dilute to 250.0 mL.
b. Store in refrigerator.
b. 1.00 mL = 0.10 mg N_{org}.

11.8 Urea intermediate standard solution (0.100 mg N_{org}/mL):
- a. Dilute 10.0 mL urea stock solution to 100 mL with deionized water.
- b. Store in refrigerator
- c. Prepare monthly.
- d. 1.00 mL = 0.100 mg N_{org}.

11.9 Other compounds can be used for the digestion test solution, for example, glycine and glutamic acid.
- a. *Glycine digest-check stock solution (1 mL = 1.0 mg-N)*: Dissolve 3.98 g glycine (C2H5NO2•HCl, FW=111.5) in about 400 mL of DI water in a 500-mL volumetric flask. Dilute this solution to the mark with DI water and mix it thoroughly by manual inversion and shaking. Transfer the stock digest-check solution to a 500-mL Pyrex™ media bottle in which it is stable for 6 months at 4°C.

11.10 Preparation of nitrate calibration standards and checks: Prepare standards according to Table 1. Use within 24 hours.

Table 1. Preparation of nitrate calibration standards.

Standard solution	Prepare using	H_2SO_4 (mL)	Volume of standard solution (mL)	Final Volume (mL)	Concentration (mg NO_3-N/L)	Use
DIB	DI water	0.0	0.00	100.0	0.00	Calibration blank
LRB	DI water	0.4	0.00	100.0	0.00	Calibration blank
TN-1	Intermediate nitrate standard solution (0.10 mg N/L)	0.4	0.10	100.0	0.10	Calibration standard
TN-2		0.4	0.20	100.0	0.20	Calibration standard
TN-3		0.4	0.50	100.0	0.50	Calibration standard
TN-4		0.4	1.00	100.0	1.00	Calibration standard
TN-5		0.4	2.00	100.0	2.0	Calibration standard
TN-6		0.4	5.00	100.0	5.0	Calibration standard
LCC		0.4	1.00	100.0	1.0	Lab control check
QCC	Alternate intermediate nitrate standard*	0.4	1.00	100.0	1.0	Quality control check
DEC	Urea intermediate standard	0.0	2.0	100.0	2.0 mg N_{org}/L	Digestion efficiency check

LRB = Laboratory Reagent Blank; TN = Calibration standards; LCC = Laboratory Control Check; QCC = Quality Control Check; DEC = Digestion Efficiency Check
* Prepared using alternate nitrate standard solution, i.e., not the same standard used to prepare the calibration standards.

12 Sample collection, preservation, shipment and storage

12.9 Samples are collected in 500-mL plastic bottles and preserved with concentrated sulfuric acid (H_2SO_4) to pH <2 – CAUTION: highly corrosive; will cause chemical burns to exposed skin, wear protective gloves.

12.10 Sample bottles are stored on ice for transport to the laboratory.

12.11 Preserved and refrigerated samples can be stored for up to 28 days.

13 Quality Control

13.1 Quality control program: The minimum requirements of the quality control program for this analysis consist of an initial demonstration of laboratory capability and the periodic analysis of laboratory reagent blanks and other laboratory solutions as a continuing check on performance. The laboratory must maintain performance records that define the quality of the data that are generated.

a. Analyses of matrix spike and matrix spike duplicate samples are required to demonstrate method accuracy and precision and to monitor matrix interferences (interferences caused by the sample matrix). The procedure and QC criteria for spiking are described in Sections 15.2 and 13.4.
b. Analyses of laboratory blanks are required to demonstrate freedom from contamination.
c. The laboratory shall, on an ongoing basis, demonstrate through calibration verification and analysis of the ongoing precision and recovery sample that the analysis system is in control.
d. The laboratory should maintain records to define the quality of data that is generated.

13.2 Initial demonstration of performance. The following must be satisfied before the analytical procedure may be used for samples and before a new analyst may analyze samples.

a. Method Detection Limit (MDL) – To establish the ability to detect the analyte, the analyst shall determine the MDL by carrying through 7 or more separately prepared reagent blank solutions through the analytical procedures in Section 15. The average value, X, and the standard deviation of the values, s, shall be calculated. The MDL is equal to 3s (3 x standard deviation). The MDL and average value, X, should both be less than or equal to 0.1 mg N/L.

b. Initial Precision and Recovery – To establish the ability to generate acceptably precise and accurate results, the operator shall perform 10 replicates of a mid-range standard (0.50 mg NO_3-N/L), according to the procedure in Section 11. Using the results of the replicates compute the average value, S, and the standard deviation, s, for the analyte. The

value of X should be within 10% of the true value. The standard deviation should be less than or equal to 10% of the average value.

13.3 The DIB, LRB, LCC, QCC and DEC should be measured along with the standards at the start of the analytical cycle. The criteria are listed in Table 2.

Table 2. Quality control solution and acceptable ranges.

Solution	Acceptable range	Comments
DIB	< 0.005 mg TN/L	Less than LRB
LRB	≤ 0.005 mg TN/L	Ideally less than or equal to the required detection limit
LCC	0.180 - 0.220 mg TN/L	Within ± 10% of the true value
QCC	0.180 - 0.220 mg TN/L	Within ± 10% of the true value
AMP	0.180 - 0.220 mg TN/L	Within ± 10% of the true value

13.4 With each sample batch of ten samples, the following should also be run (acceptance criteria noted in Table 3):

Table 3. Quality control samples and acceptance criteria.

Solution	Acceptance Criteria
DIB	< 0.001 mg TN/L
LRB	Ideally < 0.001 mg TN/L
LCC	0.180 - 0.220 mg TN/L or 100 ± 10%recovery
LD	greater of ± 20% or ± 0.005 mg TN/L
FD	greater of ± 20% or ± 0.005 mg TN/L
LS-1 and LS-2	both 100 ± 20% recovery

14 Calibration and standardization

Calibration: Obtain a standard curve by plotting absorbance of standards (including the reagent blank) versus concentration. The data will be fit to a linear equation using a spreadsheet program such as Excel.

15 Procedure

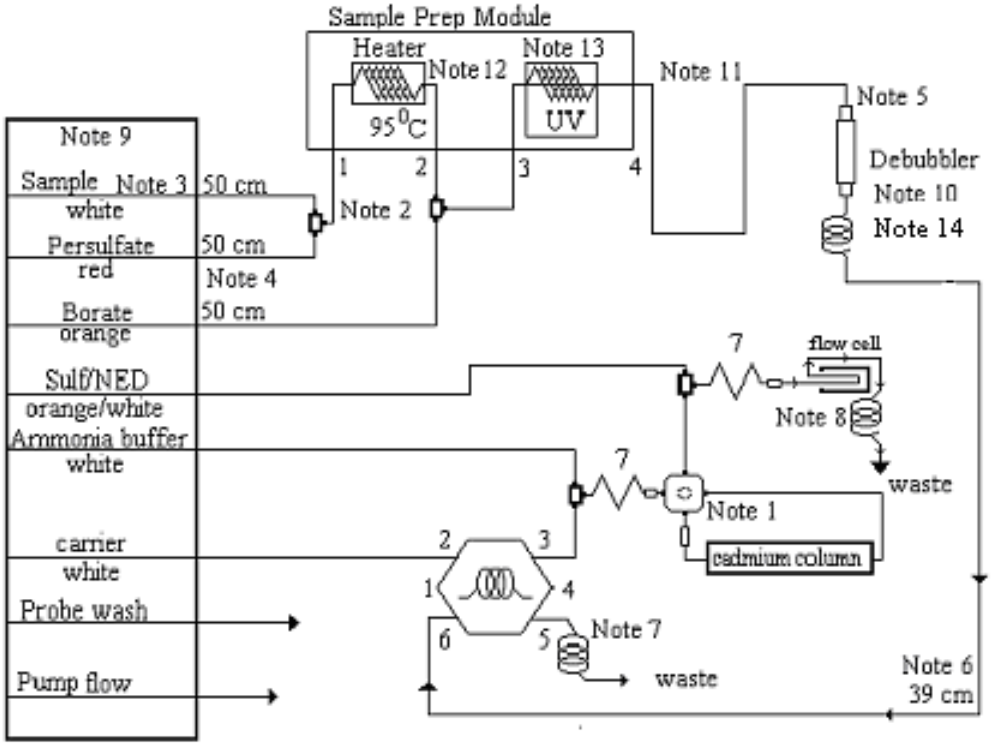
15.1 Prepare reagents, standards, and digestion check solutions as described in section 11.

15.2 Preparation of laboratory matrix spike (LS): Prepare two LS samples using 10-mL aliquots of a water sample (or a smaller aliquot diluted to10 mL) from the same sample. Spike each with 0.10 mL intermediate urea standard solution.

(This should increase observed concentration by 1.0 mg/L.) Carry each through the analysis procedure.

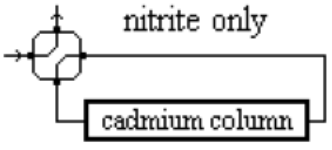
15.3 Check manifold setup by referring to the manifold diagram and notes below. Put lines in from bottom up. Start with carrier then reagents. Length of coil is in cm from end to end of the coil support. If length of coil is given in inches in the diagram, measure from hole to hole of the coil support. Set temperature of heater to temperature under heater block symbol.

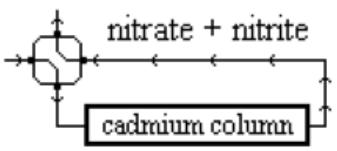
TOTAL NITROGEN MANIFOLD DIAGRAM



Carrier: DI water
AE Sample Loop: 8.5 cm
QC8000 Sample Loop: 14 cm
Interference Filter: 540 nm

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





Note 2: Tee's '1'and '2' are mounted on left side of manifold board.

Note 3: From sampler to tee fitting ‘1’: The white pump tube is cut 2 cm outside of the tabs on both sides. The outlet of the sample pump tube is connected to tee fitting ‘1’ with 50 cm of 0.8 mm id manifold tubing.

Note 4: Persulfate (red) and borate (orange) pump tubes are connected to tees ‘1’ and ‘2’ with 50 cm lengths of 0.8 mm id manifold tubing.

Note 5: The Tubular Membrane Debubbler is mounted vertically (up and down) on the sample prep module. Two small brown (Ultem) collars are used to connect the tubular membrane to the pump tube adapters. The flow inlet is at the top and the outlet at the bottom. The flow inlet is connected to the outlet of the UV. The metal pins should be removed from the tube adapter fittings. To get the best results from the debubbler, the tubular membrane should be replaced every two days.

Note 6: The outlet of the tubular membrane debubbler is connected to port 6 of the valve using a 39 cm length of 0.5 mm (0.022 in.) i.d. Teflon tubing.

Note 7: The 100 cm back pressure loop is 0.5 mm (0.022in.) i.d. tubing.

Note 8: The 200 cm back pressure loop is 0.5 mm (0.022 in) i.d. tubing.

Note 9: PVC pump tubes must be used for this method.

Note 10: Remove the stainless steel pins from the PTA’s for the debubbler.

Note 11: 45 cm 0.032” i.d. tubuing between the In-Line heater and the debubbler.

Note 12: Heater (inside of the sample prep module): 1200 cm of tubing is wrapped on a high temperature heater with 90 cm remaining for connection at the inlet and outlet. The outlet of tee ‘1’ is connected to the heater inlet, and the heater outlet is connected to inlet of tee ‘2’. Tee’s ‘1’ and ‘2’ are mounted on the chemistry manifold board.

Note 13: The UV-254 lamp (inside of the sample prep module) has 550 cm of tubing wrapped around the UV lamp with about 50 cm of tubing remaining at each end for connections. The outlet of tee ‘2’ is connected to the UV inlet, and the UV outlet is connected to the tubular membrane debubbler.

Note 14: 10 cm of tan PEEK, part number 28031 are added after the debubbler.

15.4 Turn the main switch of the power strip on.

15.5 Line/Pump Startup:

a. Pull lines to ends of cartridge to ensure proper tension on the line.
b. Clamp the cartridges to the pump. Clamp pump cartridges down only when pump on and rolling. Snap cartridge in one end and then the other.
c. Set tension on lines, by clicking the tabs on top of the cartridge back one click.

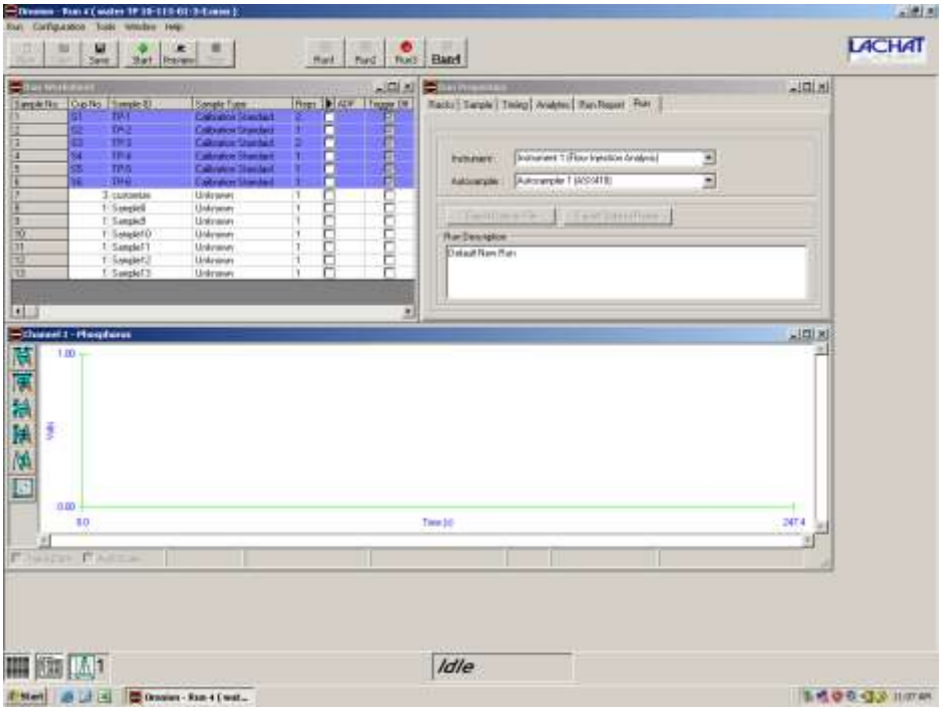
d. Keep pump speed on 35 (10 rev/50 sec ±1 sec) unless method calls for changes. Never slow speed for any heated method. “OL” means that the pump is overheating and that no liquid is going through the tubes.
e. Tubes can pop off of the cartridges, if that occurs slow the pump down and place tubes in fluid to be drawn through.
f. Use the correct type of pump tube for the reagent flowing through it. Tubes are made of PVC (clear) or Durprene (tan color) and have different diameters for different flow rates. Use PVC tube for high pressure flows with appropriate adapter collars. Never mix the tubes in line.
g. Flip Cd column on manifold to off line.
h. Place the tube ends in DI water and run deionized water through all the lines for at least 5 minutes to check for leaks and flush potential contaminants.

15.6 If the method requires the use of the heating unit, turn on the heater and set the temperature as defined by the manifold diagram. Allow more than 20 minutes for the heating unit in the sample prep module to warm to 95°C. There is tubing wrapped around the heating unit and it will bake and crimp if liquid is not running through it when the heating unit is on. Always have liquid (deionized water or reagents) flowing through the tubes when the heater is on especially if the temperature is above 80°C.

15.7 Check that the wash bath line for the auto sampler valve is in deionized water.

15.8 Load rack with calibration standards first, then blanks, samples, duplicates, etc. See diagram for auto sampler sequence. Align preloaded sample rack in auto sampler tray with the calibration standards on the left closest to the computer. Don’t manually move probe if green light is on. Flip switch in back to be able to move probe manually. Align feet of rack in tray.

15.9 Software Setup:
b. The input data system parameters are saved as the water TN 10-107-04-3-C template and mirror parameters from QuikChem Method 10-107-04-3-C.
c. Access software by clicking Omnion 3.0 on the desktop. Open the Total Nitrogen folder and double click on the water TN 10-107-04-3-C.omn file for the TN template. The templates contain the correct time to valve, standards, carrier, and reagents.
d. The Omnion screen contains the Run Worksheet, Run Properties, and Channel 1 – Nitrogen graph. See figure below.



e. Set up the Run Worksheet to match the sample sequence. Add sample rows to match the number of calibration standards, checks, samples, duplicates, spikes, and blanks for the run. To add a row right click in the grey area of the Run Worksheet box and insert or append one or many rows. ID each sample appropriately.

f. Check that the manifold matches the manifold diagram.

15.10 Place the tubes in the reagents in the order illustrated in the manifold diagram. Use a chem wipe to clean the lines and glass weights before putting each in the reagent bottles. Where applicable, always start pumping the buffer solution first. Allow reagents to run through lines for at least 5 minutes.

15.11 Flip column on manifold to on line if a Cd column is used in the manifold diagram.

15.12 Checks prior to analysis:

a. Check that the reagent lines are in the correct reagents and that the reagents match the preparation instructions.

b. Check that your standard solutions are in the correct standard vials and are set in the correct sequence in the Run Worksheet.

c. Check that the waste lines are connected and direct waste to a container that is not close to being full. Check waste container often throughout procedure.

d. Check system notes in the method and manifold diagram.

e. Check that the heater, if used, is at the correct temperature. If not wait.

15.13 When the run worksheet is set up and all components of the Lachat system are ready, click Start to run the template and analyze the entire rack of samples.

15.14 Shutdown:

a. Flip column on manifold to off line.

b. Remove reagent lines from each reagent and rinse with DI water before placing them in the DI H_2O container. Pump DI H_2O through lines for at least 10 minutes. The method may recommend a rinse solution, place all reagent lines into the recommend rinse solution and pump for the recommended time at standard speed.

c. Keep running liquid through the manifold until the temperature of the heater has reached 60°C if heater used.

d. Remove the lines from the DI H_2O and allow all liquid to be pumped out of the manifold.

e. Release the cartridges from the pump and turn the pump off. If instrument is not going to be used for the next week, release the tubes from one cartridge end.

f. Turn the power strip off.

g. Remove samples from the auto sampler tray and store appropriately. Leave auto sampler tray with instrument, do not store samples in tray.

h. Remove all reagents used and store appropriately.

15.15 Store data on computer in your folder or on removable media. Access data at c: Program Lachat Ominion data folder. Log off.

15.16 Clean all countertops that were used and replace any materials that the next user would need i.e. chem wipes or DI H_2O for the wash bath line for the auto sampler.

15.17 Properly dispose of waste accumulated in the waste container under the Lachat unit as instructed by the laboratory manager.

16 Data acquisition, calculations, and reporting

16.1 Calculation of concentrations: The concentration of each solution will be calculated based on the linear equation for the regression data. The concentrations will represent the concentration of analyte in the aliquot. Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard will be diluted and reanalyzed.

16.2 Calculation of water sample concentrations, corrected for dilution: For samples for which dilution was required, the concentration in the original water sample is calculated using equation 1.

a. Equation 1: $C_{sample} = C_{analysis} \times \frac{(10.0\ mL/V_{aliquot})}{V_{aliquot}}$

b. Where: C_{sample} is the concentration in the original water sample,

$C_{analysis}$ is the concentration of the solution as determined in (16.1),
and $V_{aliquot}$ is the volume of the aliquot diluted to 10 mL in (15.2.b).

16.3 Reporting results: Results should be reported to 0.001 mg TP/L precision.

16.4 The evaluation of MDL and precision require calculation of standard deviation. Standard deviations should be calculated as indicated below, where n = number of samples, x = concentration in each sample. Note: This is the sample standard deviation calculated by the STDEV function in Microsoft Excel.

$$s = \left(\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{n-1} \right)^{1/2}$$

16.5 Calculation of recoveries: Recovery of matrix spike solutions shall be calculated as indicated below, where S = concentration observed for spiked sample, U = concentration observed for unspiked sample, and 0.200 is the concentration increase expected upon spiking. Both S and U are concentrations based on (16.1), i.e., not adjusted for dilution of an aliquot. The factor 1.02 corrects for the small volume change upon spiking.

$$\%\ recovery = \frac{1.02 \times S - U}{0.200}$$

The LS 13 320 includes a software package with a multi-component Standard Operating Procedure (SOP). The SOP is divided into two distinct components; an SOM (Standard Operating Method) and a Preference (.prf) file. The SOM includes all aspects of the analysis relating to the instrument settings. The Preference file (.prf) includes choices relating to data presentation and output formats. Data is stored as ".$ls" files that the LS 13 320 software uses for data presentation. Standard templates have been prepared and include all system parameters. The TN standard template is used for this analysis.

16.6 The support data for QuikChem Method 10-107-04-3-C is presented in Section 12 of the original method. Individual linear equations from the regression data will be used for each batch analyzed and method detection limits, precision, and accuracy will be determined for each individual batch to ensure quality control.

17 Computer hardware and software

17.1 Word: This document was prepared using Microsoft
Word: The Word document file name for this SOP is: Lachat TN-R01.doc

17.2 Excel: Quality control checks are created using Excel.

18 Method performance

18.1 The desired performance criteria for this measurement are:

a. Detection limit: ≤0.1 mg TN/L
b. Precision: ± 20%
c. Accuracy: ± 20%
d. Minimum Quantification Interval: 0.1 mg TN/L

18.2 The applicable range is 0.2 to 10 mg N/L. The statistically determined method detection limit is 0.011 mg N/L. The method throughput is 45 injections per hour.

19 Pollution prevention

All wastes from these procedures shall be collected and disposed of according to existing waste policies within the MSU Chemistry Department. Volumes of reagents made should mirror the number of samples being analyzed. These adjustments should be made to reduce waste

20 Data assessment and acceptable criteria for quality control measures

20.1 The analyst should review all data for correctness (e.g., calculations).

20.2 Precision values are calculated for pairs of duplicate analyses. The desired precision is ± 20%.

20.3 The desired detection limit is 0.1 mg N/L. The deionized water blank (DIB) should be less than the laboratory reagent blank (LRB).

20.4 Percent recovery is calculated for LCC, QCC and spiked samples. Record these values on the bench sheet. The desired recoveries are; 100 ± 10% for LCC and QCC and 100 ± 20% for spiked samples.

20.5 The data will be reviewed by the OEWRI QA/QC manager.

21 Corrective actions for out-of-control or unacceptable data

21.1 Quality control charts will be created for charting precision (REP), accuracy (LCC and QCC) and laboratory reagent blank (LRB) and laboratory matrix spikes (LS) values.

21.2 The results for precision, accuracy and LRB data are compared to the acceptable values for this analysis; ± 20%, 100 ± 10% (LCC and QCC), 100 ± 20% (LS) and 0.1 mg N/L, respectively.

21.3 If a precision value exceeds 20% then the analyst should note that the data are associated with an out-of-control duplicate analysis in the data report given to the QA/QC manager. The upper control limit (UCL) = 20%.

21.4 If an accuracy value exceeds the UCL for LCC or LS, then the analyst should note that the data are associated with an out-of-control LCC (or LS) analysis in the data report given to the QA/QC manager. The limit is 100 ± 10% (or ± 20%).

21.5 If a LRB value exceeds 0.1 mg N/L then the analyst should note that the data are associated with a LRB value that exceeds the detection limit of 0.1 mg N/L in the data report given to the QA/QC manager.

21.6 If there is sufficient volume of sample remaining for all samples, the analytical batch may be re-analyzed. Quality control data from the first run must be recorded on the control charts.

21.7 If data are unacceptable for any reason, the analyst should review their analytical technique prior to conducting this analysis again.

22 Waste management

22.1 The wastes generated in this method are hazardous because of a low final pH. The samples may be neutralized by the addition of water in accumulation container (e.g., a large beaker or flask). Add sufficient amounts of water to adjust the pH to between 2 and 12.5. When the pH is > 5 (for acidic wastes) the solution can be discarded in the laboratory drain followed by an equal volume of water.

22.2 Outdated chemicals are discarded following the procedures of the MSU Environmental Management Department.

23 References

23.1 U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020, Revised March 1983, Method 365.4

23.2 Determination of Nitrogen in Water: Comparison of a Continuous-flow method with online UV Digestion with the original Kjeldahl method, Hennie Kroon, Analytica Chemica Acta, 276, (1993) 287-293.

23.3 Lachat Instruments Inc., QuikChem Method 10-107-04-1-C revised by Diane Pritzlaff on 11 January 1996.

24 Tables, diagrams and flowcharts

Tables and flowcharts can be found within this document.