

## Nitrogen, Total Kjeldahl

References: **Method 351.1**, Methods for Chemical Analysis of Water and Waste, EPA-600/4-79-020, U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268 (March 1979)

**Method SM 4500N<sub>org</sub>-C**, Standard Methods for the Examination of Water and Wastewater. APHA-AWWA-WEF. Standard Methods Online.

**Method SM 4500NH<sub>3</sub>-H**, Standard Methods for the Examination of Water and Wastewater. APHA-AWWA-WEF. Standard Methods Online.

**Method 10-107-06-2-D**, Methods for Automated Ion Analyzers, May 20, 1998.

### 1. Scope and Application

**Matrices:** Total Kjeldahl nitrogen can be determined in potable, surface, and saline waters as well as domestic and industrial wastewaters.

**Definitions:** See Alpha Laboratories Quality Manual Appendix A

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of the Tecator and/or Lachat Instrument and in the interpretation of Lachat data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability.

This method covers the determination of total kjeldahl nitrogen in drinking, surface and saline waters, and domestic and industrial wastes. The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia, but may not convert the nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semicarbazones and some refractory tertiary amines.

In waters and wastewaters the forms of nitrogen of greatest interest are, in order of decreasing oxidation state, nitrate, nitrite, ammonia, and organic nitrogen. All these forms of nitrogen, as well as nitrogen gas (N<sub>2</sub>), are biochemically interconvertible and are components of the nitrogen cycle. They are of interest for many reasons.

Organic nitrogen is defined functionally as organically bound nitrogen in the trinegative oxidation state. It does not include all organic nitrogen compounds. Analytically, organic nitrogen and ammonia can be determined together and have been referred to as "Kjeldahl nitrogen", a term that reflects the technique used in their determination. Organic nitrogen includes such natural materials as proteins and peptides, nucleic acids and urea, and numerous synthetic organic materials. Typical organic nitrogen concentrations vary from a few hundred micrograms per liter in some lakes to more than 20mg/L in raw sewage.

Ammonia is present naturally in surface and wastewaters. Its concentration generally is low in groundwaters because it adsorbs to soil particles and clays and is not leached readily from soils. It is produced largely by deamination of organic nitrogen containing compounds and by hydrolysis of

urea. At some water treatment plants ammonia is added to react with chlorine to form a combined chlorine residual.

In the chlorination of wastewater effluents containing ammonia, virtually no free residual chlorine is obtained until the ammonia has been oxidized. Rather, the chlorine reacts with ammonia to form mono- and dichloramines. Ammonia concentrations encountered in water vary from less than 10 µg ammonia nitrogen/L in some natural surface and groundwaters to more than 30 mg/L in some wastewaters.

In this discussion, organic nitrogen is referred to as organic N, nitrate nitrogen as  $\text{NO}_3\text{-N}$ , nitrite nitrogen as  $\text{NO}_2\text{-N}$ , and ammonia nitrogen as  $\text{NH}_3\text{-N}$ .

Total Kjeldahl nitrogen is defined as the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate  $(\text{NH}_4)_2\text{SO}_4$ , under the conditions of digestion described below.

Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free-ammonia value from the total Kjeldahl nitrogen value. This may be determined directly by removal of ammonia before digestion.

## 2. Summary of Method

The organic nitrogen is converted to ammonia via heating in the presence of concentrated sulfuric acid,  $\text{K}_2\text{SO}_4$ ,  $\text{HgSO}_4$ , and evaporated until  $\text{SO}_3$  fumes are obtained and the solution becomes colorless or pale yellow. The residue is cooled, diluted, and treated and made alkaline with a hydroxide-thiosulfate solution. The digestate is distilled at high pH into a solution of boric acid. The ammonia in the distillate is determined colorimetrically by the phenate method.

The phenate method is based on the Berthelot reaction. Ammonia reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue. Sodium nitroprusside (nitroferricyanide) is added to enhance sensitivity. The absorbance of the reaction product is measured at 630nm, and is directly proportional to the ammonia concentration in the digestate.

### 2.1 Method Modifications from Reference

This method has been modified for soil digestion, Section 9.4.1.

## 3. Detection Limits

The RDL is determined to be 0.3 mg/L for liquid samples and 150 mg/Kg for soil or solid samples.

## 4. Interferences

### 4.1 Instrumental

Samples with a high concentration of TKN may carry-over into the next sample and therefore yield false high results in that next sample. If a sample with a low concentration follows a sample with a high concentration, re-analyze the low sample to ensure results are accurate.

### 4.2 Parameters

High nitrate concentrations (10X or more than the TKN level) result in low TKN values. The reaction between nitrate and ammonia can be prevented by the use of an anion exchange resin (chloride form) to remove the nitrate prior to the TKN analysis.

## 5. Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

**NOTE:** Both Phenol and Mercury used in this method are hazardous and general laboratory safety practices must be observed. Due to the Mercury used in this procedure, digestion must be done under a hood.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

## 6. Sample Collection, Preservation, and Handling

### 6.1 Sample Collection

The most reliable results are obtained on fresh samples. Use plastic or glass containers.

### 6.2 Sample Preservation

Samples may be preserved by addition of 2mL of concentrated  $H_2SO_4$  per liter if sample cannot be analyzed immediately. Refrigerate at 4°C.

### 6.3 Sample Handling

Even when properly preserved, conversion of organic nitrogen to ammonia may occur. Therefore samples should be analyzed as soon as possible.

## 7. Equipment and Supplies

**7.1 Digestion apparatus:** Kjeldahl Digestion System 20, Model 1015 Digester. Follow the instrument manufacturer's instructions.

**7.2 Distillation apparatus:** Tecator Instruments Automatic Distillation Unit: Follow the instrument manufacturer's instructions for proper operation.

**7.3 Automated Ion Analyzer:** Lachat Instruments

**7.4 Disposable polypropylene cups:** 250mL with covers.

**7.5 Glass Tuttlecaps:** For digestion.

**7.6 Glass Pipets:** Various volumes.

**7.7 Auto-pipettor with tips:** For 10mL capability.

**7.8 Analytical balances:** capable to weigh 0.1000g aliquots.

**7.9 Dilu Vials**

**7.10 Boiling chips**

## 8. Standards and Reagents

**8.1 Sodium Phenolate: CAUTION!** Wear gloves. Phenol causes severe burns and is rapidly absorbed into the body through the skin. In a 1L volumetric flask, dissolve 88mL of 88% liquified phenol or 83g crystalline phenol ( $C_6H_5OH$ ) in approximately 600mL DI water. While stirring, slowly add 32g sodium hydroxide (NaOH). Cool, dilute to the mark, and invert three times. Do **not** degas this reagent. Expires one month from date of preparation.

**8.2 Sodium Hypochlorite (approximate 2.6%):** In a 500mL volumetric flask, dilute 250mL Regular Chlorine bleach [5.25% sodium hypochlorite ( $NaOCl$ )] to the mark with DI water. Invert three times to mix. Expires one month from date of preparation.

**8.3 Sodium Nitroprusside (coloring agent):** In a 1L volumetric flask, dissolve 3.50g sodium nitroprusside (Sodium Nitroferricyanide [ $Na_2Fe(CN)_5NO_2 \cdot H_2O$ ]) dilute to the mark with DI water. Degas with helium to prevent bubble formation. Use He at 140kPa (20 lb/in<sup>2</sup>) through a helium degassing tube. Bubble He vigorously through the solution for one minute. Expires one month from date of preparation.

**8.4 Boric 1.5% Boric Acid Solution:** To a 1000mL volumetric flask add 15g Boric Acid. Dilute to the mark with DI water. Expires one month from date of preparation.

**8.5 Mercuric Sulfate Solution:** Dissolve 8g red mercuric oxide ( $HgO$ ) in 50mL of 1:4 sulfuric acid (10.0mL concentrated  $H_2SO_4$  : 40mL distilled water) and dilute to 100mL with distilled water. Expires one month from date of preparation.

**8.6 Digestion Solution (Sulfuric Acid-Mercuric Sulfate-Potassium Sulfate):** Dissolve 267g  $K_2SO_4$  in 1300mL distilled water and 400mL concentrated  $H_2SO_4$ . Add 50mL mercuric sulfate (Section 8.5) solution and dilute to 2L with distilled water. Expires one month from date of preparation.

**8.7 Sodium Hydroxide-Sodium Thiosulfate Solution:** Dissolve 500g NaOH and 25g  $Na_2S_2O_3 \cdot 5H_2O$  in distilled water and dilute to 1L. Expires one month from date of preparation.

**8.8 0.2% Boric Acid Solution (Carrier Solution):** To a 2L volumetric flask, dissolve 4g Boric Acid ( $H_3BO_3$ ) in DI water. Degas by bubbling vigorously with Helium for one minute. Expires one month from date of preparation.

**8.9 Stock Standard, 1000ppm as  $NH_3$  (for calibration solutions):** Commercially prepared. Certificate of analysis is required.

**8.9.1 Intermediate Calibration Stock Standard, 100ppm as  $\text{NH}_3$ :** To a 100mL volumetric flask, add 10.0mL of Stock Standard (Section 8.9) and dilute to the mark with 0.2% Boric Acid solution (Section 8.8). Invert three times. Expires one month from date of preparation.

**8.9.1.1 Nine Working Calibration Standards:** Prepare the following standards in volumetric flasks:

**8.9.1.1.1 20.0ppm:** 40mL of 100ppm standard (Section 8.9.1) to 200mL with 0.2% Boric Acid solution (Section 8.8). Prepare fresh each day of use.

**8.9.1.1.2 10.0ppm:** 20mL of 100ppm standard (Section 8.9.1) to 200mL with 0.2% Boric Acid solution (Section 8.8). Prepare fresh each day of use.

**8.9.1.1.3 8.00ppm:** 8mL of 100ppm standard (Section 8.9.1) to 100mL with 0.2% Boric Acid solution (Section 8.8). Prepare fresh each day of use.

**8.9.1.1.4 4.00ppm:** 8mL of 100ppm standard (Section 8.9.1) to 200mL with 0.2% Boric Acid solution (Section 8.8). Prepare fresh each day of use.

**8.9.1.1.5 2.00ppm:** 2mL of 100ppm standard (Section 8.9.1) to 100mL with 0.2% Boric Acid solution (Section 8.8). Prepare fresh each day of use.

**8.9.1.1.6 1.00ppm:** 1mL of 100ppm standard (Section 8.9.1) to 100mL with 0.2% Boric Acid solution (Section 8.8). Prepare fresh each day of use.

**8.9.1.1.7 0.400ppm:** 4mL of 20ppm standard (Section 8.9.1.1.1) to 200mL with 0.2% Boric Acid solution (Section 8.8). Prepare fresh each day of use.

**8.9.1.1.8 0.200ppm:** 1mL of 20ppm standard (Section 8.9.1.1.1) to 100mL with 0.2% Boric Acid solution (Section 8.8). Alternately, this standard may be prepared utilizing autodilution of the 20ppm standard on the autosampler. Prepare fresh each day of use.

**8.9.1.1.9 0.100ppm:** 1mL of 20ppm standard (Section 8.9.1.1.1) to 200mL with 0.2% Boric Acid solution (Section 8.8). Alternately, this standard may be prepared utilizing autodilution of the 20ppm standard on the autosampler. Prepare fresh each day of use.

**8.9.1.1.10 0.050ppm:** 20mL of 0.100ppm standard (Section 8.9.1.1.9) to 40mL with 0.2% Boric Acid solution (Section 8.8). Alternately, this standard may be prepared utilizing autodilution of the 20ppm standard on the autosampler. Prepare fresh each day of use.

**8.9.1.2 Continuing Calibration Standards:**

**8.9.1.2.1 0.400ppm Low CCV:** 4mL of 20ppm standard (Section 8.9.1.1.1) to 200mL with 0.2% Boric Acid solution (Section 8.8).

**8.9.1.2.2 4.00ppm Hi CCV:** 8mL of 100ppm standard (Section 8.9.1) to 200mL with 0.2% Boric Acid solution (Section 8.8).

**8.10 Stock Standard, 1000ppm as TKN (for spike):** Commercially prepared. Certificate of analysis is required

**8.10.1 Intermediate spike Stock Standard, 200ppm as TKN:** To a 100mL volumetric flask, add 20.0mL of Stock Standard (Section 8.10) and dilute to the mark with 0.2% Boric Acid solution (Section 8.8). Invert three times. Expires one month from date of preparation.

**8.11 Stock Standard Solution, 1000ppm as  $\text{NH}_3$  (for ICV only):** Commercially prepared. Certificate of analysis is required. This must be from a different source than that used for Stock Standard (Section 8.9).

**8.11.1 Initial Calibration Verification Standards (ICV):**

**8.11.1.1 Hi ICV, 10ppm:** To a 100mL volumetric flask add 1mL of 1000ppm standard (Section 8.11). Dilute to the mark with 0.2% Boric Acid Solution (Section 8.8). Expires one month from date of preparation.

**8.11.1.2 Hi ICV, 8.0ppm:** To a 100mL volumetric flask add 0.8mL of 1000ppm standard (Section 8.11). Dilute to the mark with 0.2% Boric Acid Solution (Section 8.8). Expires one month from date of preparation.

**8.11.1.3 Low ICV, 1.0ppm:** To a 100mL volumetric flask add 10mL of 10ppm ICV (Section 8.11.1.1). Dilute to the mark with 0.2% Boric Acid Solution (Section 8.8). Expires one month from date of preparation.

**8.12 Stock Standard Solution, 1000ppm as TKN (for LCS):** Commercially prepared. Certificate of analysis is required. This must be from a different independent source than that used for Stock Standard (Section 8.10).

**8.12.1 LCS solution, 200ppm as TKN:** To a 100mL volumetric flask add 20mL of 1000ppm Stock Standard (Section 8.12) and dilute to the mark with DI water. Expires one month from date of preparation.

**8.13 6N Sodium Hydroxide Solution :** Dissolve 240g NaOH in distilled water and dilute to 1L. Expires six month from date of preparation.

## 9. Procedure

### 9.1 SET-UP

**9.1.1** Clean 250mL Tecator tubes by rinsing twice with approximately 0.5mL of 6N NaOH solution and 100mL RO water. Rinse twice again with DI water.

**9.1.2** Rinse glass tittlecaps under the hood in a 1000mL beaker with approximately 500mL DI and 1.0 mL of 6N NaOH. Allow to sit in this solution until use.

### 9.2 Initial Calibration

Calibrate the Lachat ion analyzer according to manufacturer's instructions.

#### 9.2.1 Calibration

Two boards are used to calibrate the Lachat instrument. Each curve has 7 calibration points. The correlation coefficient of each curve must be  $\geq 0.995$ , otherwise re-calibration is necessary. Prepare standard curves by plotting the peak areas of standards processed through the manifold against  $\text{NH}_3\text{-N}$  concentrations in standards.

**9.2.1.1** Channel 1 is used to generate a calibration curve on the low range from 0.00 – 2ppm.

**9.2.1.2** Channel 2 is used to generate a calibration curve on the high range from 0 – 20ppm.

Alternative method: One board can be used to calibrate the Lachat instrument. Ten point calibration curve will be used with calibration standards 10.0, 8.0, 4.0, 2.0, 1.0, 0.4, 0.2, 0.1, 0.05 mg/l each and blank. The correlation coefficient must be  $\geq 0.995$ , otherwise re-calibration is necessary. Prepare standard curves by plotting the peak areas of standards processed through the manifold against  $\text{NH}_3\text{-N}$  concentrations in standards

Calibration coefficient will be calculated using Lachat software. All calibration points are back calculated by Lachat software and should be within 10% from true concentration, except 2 lowest points of calibration curve. % recoveries for the low range will be wider, but shouldn't exceed 100% and correlation coefficient will not be worse than 0.995. The standards for the calibration curve are recalculated manually to prove the software calculations are within +/- 10% of the true concentrations.

**9.2.2 Initial Calibration Verification (ICV)**

Prior to sample analysis, an ICV is analyzed at 1.0ppm (Section 8.10.1.2) to verify the low calibration curve on Channel 1. Another ICV is analyzed at 10ppm (Section 8.10.1.1) to verify the high calibration curve on Channel 2. Both ICVs must yield results  $\pm 10\%$  of their true value, otherwise re-calibration is necessary.

**Note:** if instrument is calibrated using one board calibration, then both ICV's (Low and High), will be evaluated and high ICV will be 8.0 mg/l ICV standard (Section 8.11.1.2)

**9.2.3 Initial Calibration Blank (ICB)**

Following the ICV is the analysis of an ICB. The ICB consists of an aliquot of 0.2% Boric Acid (Section 8.8). Results must be less than  $< 0.05\text{mg/L}$ .

**9.3 Standardization (Continuing Calibration Verification)**

Analyze the following after every 10 samples and at the completion of analysis:

**0.400ppm Low CCV,** (Section 8.9.1.2.1)

**4.0ppm Hi CCV,** (Section 8.9.1.2.2)

**Blank, 0.2% Boric Acid Solution.** (Section 8.8)

**9.4 Equipment Operation and Sample Analysis**

**9.4.1 Aqueous Sample Digestion:** Add 50mL of homogenized sample or a portion diluted to 50mL with DI water, to pre-washed Tecator tubes that are numbered to correspond with the samples.

**Soil/Solid Sample Digestion:** Weigh 0.1g of homogenized soil/solid sample into dilu vial and record the weight in the laboratory notebook. Transfer to a pre-washed, pre-numbered Tecator tube and add 50mL of DI water.

In a similar manner, for each matrix, prepare the QC samples to be digested with the batch (refer to Sections 10.2.1, 10.3.1, 10.7 and 10.8)

Then add approximately 1g of black boiling chips to each tube. Move to hood before adding 10mL of Digestion Solution (Section 8.6) to each tube with a calibrated pipettor.

Rinse glass tittlecaps with DI and place one onto the top of each Tecator tube. Place Tecator tube rack onto Tecator digestion block and turn temperature control knob to "4" which represents approximately 250°C. (Temperature should never exceed 300°C.) Cook for approximately 2 hours to SO<sub>3</sub> fumes. The remaining mixture will be clear or pale yellow in color. Remove tube from digestion block and allow to cool to ~80 °C before adding DI to the 90mL mark on the tube.

**9.4.2 Distillation:** To minimize contamination, leave distillation apparatus assembled after steaming out and until just before starting sample distillation. Make the digestate alkaline by careful addition of 20mL of sodium hydroxide-thiosulfate solution (Section 8.7) without mixing. Do not mix until the digestion tube has been connected to the distillation apparatus. Connect the Tecator tube to the Tecator distillation unit's stopper as defined in the manual. Distill for 3 minutes 40 seconds as defined in the manual and collect distillate in 20mL boric acid solution (Section 8.4). Distill at maximum rate with the tip of the delivery tube below the surface of boric acid receiving solution. Collect at least 90mL distillate. Dilute to 150mL with DI water. Refrigerate at 0-4°C if Lachat analysis is delayed.

**9.4.3 Ammonia analysis of distillate:** Follow the manufacturer's instructions for the proper operation of the ion analyzer. The following are specific notes for this analysis.

Sample throughput:	90 samples/hr; 40 sec/sample
Pump speed:	35
Cycle period:	40 s
Inject to start of peak period:	25 s
Inject to end of peak period:	63 s

**9.4.4 System Notes:**

**9.4.4.1** Allow 15 minutes for heating unit to warm up to 60°C.

**9.4.4.2** System IV GAIN: 175 x 1.

**9.4.4.3** If standards are not distilled, samples should be multiplied by procedure dilution (final volume 150mL) divided by initial volume.

**9.4.4.4** If baseline drifts, peaks are too wide, or other problems with precision arise, clean the manifold by the following procedure:

**9.4.4.4.1** Place all reagent lines in deionized water and pump to clear reagents (2-5 minutes).

**9.4.4.4.2** Place reagent lines and carrier in 1M hydrochloric acid (1 volume concentrated HCl added to 11 volumes of deionized water) and pump for several minutes.

**9.4.4.4.3** Place all lines in deionized water and pump until the HCl is thoroughly washed out.

**9.4.4.4.4** Resume pumping reagents.

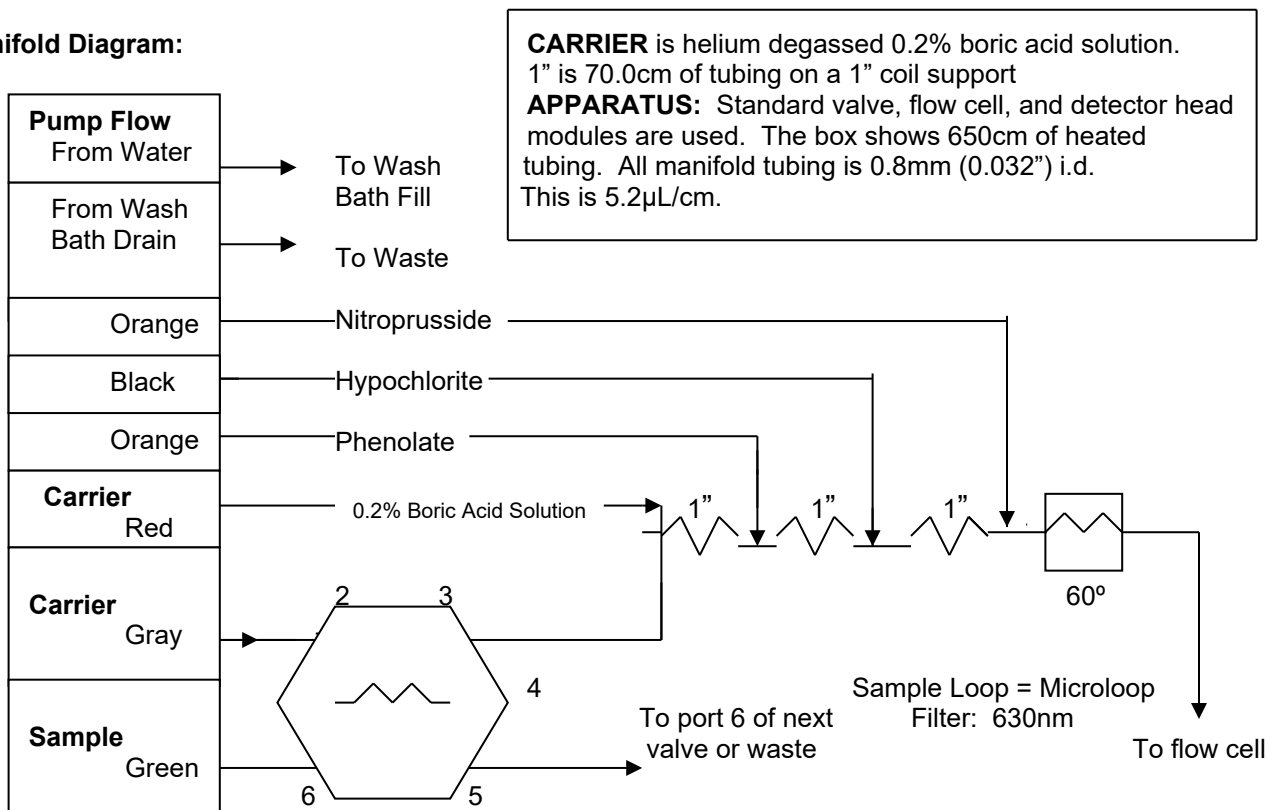


**9.4.4.5** If samples are colored or are suspected to show a background absorbance, this interference should be subtracted. This can be done by diluting or by the following procedure:

- 9.4.4.5.1** Calibrate the system in the normal manner.
- 9.4.4.5.2** Disable the check standard or DQM features and analyze the samples.
- 9.4.4.5.3** Place reagent and carrier lines in DI water and allow the baseline to stabilize.
- 9.4.4.5.4** Inject samples again without recalibrating.
- 9.4.4.5.5** Subtract the "background" concentration from the original concentration to give the corrected concentration.

$$\text{Original Concentration} - \text{Background Concentration} = \text{Corrected Concentration.}$$

#### Manifold Diagram:



## 9.5 Preventative Maintenance

- 9.5.1** All lines are flushed at the end of each run.
- 9.5.2** All equipment is kept clean.

## 9.6 Calculations

Prepare standard curves by plotting peak areas of standards processed through the manifold against  $\text{NH}_3$  -N concentrations in standards. Compute sample  $\text{NH}_3$  -N concentration by comparing sample peak areas with standard curve, as determined by the Lachat instrument software.

- 9.6.1** If the sample has a concentration of less than 2ppm, calculate results by using the low curve generated on Channel 1.
- 9.6.2** If the sample concentration is greater than 2ppm, calculate results by using the high curve generated on Channel 2.

Alternative method: use only one Channel and calculate all results from one channel.

To compute final results for aqueous samples, multiply the direct reading by the dilution factor based on the initial preparation volume.

$$\text{TKN mg/L} = \text{mg/L direct reading} \times \text{dilution factor}$$

To compute results for soil/solid samples, multiply the direct reading by the extraction final volume (150mL) and then divide by the weight of the sample used for extraction (Section 9.4.1), and multiply by a dilution factor as necessary.

$$\text{TKN mg/Kg} = \left[ \frac{(\text{mg/L direct reading}) \times \text{extraction final volume (150mL)}}{\text{Sample weight (g)}} \right] \times \text{dilution factor}$$

## 10. Quality Control and Data Assessment

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation.

### 10.1 Demonstration of Capability

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. Each time a method modification is made, the analyst is required to repeat the procedure.

When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must locate and correct the source of the problem and repeat the test for failed parameters of the method.

Repeated failure confirms a general problem with the measurement system or analytical technique of the analyst. If the failure repeats, locate and correct the source of the problem and repeat the test for all parameters listed in the method.

### 10.2 Blank

- 10.2.1** The Distillation Blank is 50mL of DI. Distill one per batch of 20 samples or less. Subtract any blank greater than 0.3mg/L from all samples and QC.

- 10.2.2** The Analytical Blank (ICB) for the Lachat analysis is not distilled and is 0.2% Boric Acid Solution (Section 8.8).

The ICB is run after the initial calibration verification standards (ICV) and another is run after the continuing calibration standards (CCV).

### 10.3 Laboratory Control Samples (LCS)

- 10.3.1 Distillation:** Distill a Low and a Hi LCS with each batch of 20 samples or less. The results from the Hi LCS are reported for the batch. The Low LCS is used to verify the low curve, but is not reported.

**10.3.1.1 Low 4.0ppm LCS:** Add 1mL of 200ppm LCS solution (Section 8.10.2) to 50 mL DI. This is used for the Low 0 - 6 ppm curve.

**10.3.1.2 Hi 40ppm LCS:** Add 10mL of 200ppm LCS solution (Section 8.10.2) to 50 mL DI. This is used for the Hi 0 - 60 ppm curve.

### 10.4 Initial Calibration Verification Standards

- 10.4.1 Lachat Analysis:** The ICVs are not distilled. Analyze the following after calibration of the Lachat instrument. Recoveries must be within 10% of the true value, otherwise recalibration of the instrument is necessary.

**10.4.1.1 Low ICV, 1.0ppm** (Section 8.10.1.2)

**10.4.1.2 Hi ICV, 10ppm** (Section 8.10.1.1); **HI ICV** will be 8.0 ppm (Section 8.10.1.2) in case of one board calibration.

### 10.5 Continuing Calibration Verification Standards

- 10.5.1 Lachat Analysis:** The CCVs are not distilled. Analyze the following after every ten samples and at the completion of analysis. Recoveries must be within 10% of the true value.

If recoveries fall outside of this range, the cause for the failure is determined and corrected, and the instrument is recalibrated. All samples that were analyzed since the last CCV that was within range are reanalyzed.

**10.5.1.1 0.4ppm Low CCV** (Section 8.9.1.2.1)

**10.5.1.2 4.0ppm Hi CCV** (Section 8.9.1.2.2)

### 10.6 Interference Check Standards

None.

### 10.7 Matrix Spike

One per batch of 20 samples or less. Prior to distillation, add 2mL of 200ppm Spiking Solution (Section 8.9.2) per 50mL of sample.

### 10.8 Duplicates

Distill one duplicate sample per batch of 20 samples or less.

## 10.9 Control Limits

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained.

Control limits for the method parameters are generated by the QC staff. The control limits are calculated based on in-house performance data. The limits are compared to the control limits found in the reference method.

## 10.10 Analytical Sequences

### 10.10.1 Distillation Sequence:

3 Rinse tubes  
Blank 1  
Low LCS  
Hi LCS  
Rinse  
Samples (each sample must be followed by rinse, except between sample and its spike or sample and its duplicate)  
Duplicate  
Spike  
Rinse  
Shut-down

### 10.10.2 Lachat Analytical Sequence:

Instrument Calibration  
DQM = Hi 4.0ppm CCV  
Low 0.4ppm CCV  
CC Blank  
Low 1.0ppm ICV  
Hi 10ppm ICV or 8.0 ppm ICV  
IC Blank  
Samples  
DQM : Run after every 10 samples and at completion of analysis  
Rinse reagent lines with 1M HCl for 5 to 10 minutes  
DI water rinse for 5 to 10 minutes  
Air rinse 5 to 10 minutes.  
Shut-Down.

## 11. Method Performance

### 11.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/1732. These studies performed by the laboratory are maintained on file for review.

## 11.2 Demonstration of Capability Studies

Refer to Alpha SOP/1734, 1739 for further information regarding IDC/DOC Generation.

### 11.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

### 11.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

## 12. Corrective Actions

Holding time exceedence, improper preservation and observed sample headspace are noted on the nonconformance report form.

Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

Review of standards, blanks and standard response for acceptable performance occurs for each batch of samples. Record any trends or unusual performance on a nonconformance action form.

If the CV or LCS recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked samples is suspect and is only reported for regulatory compliance purposes with the appropriate nonconformance action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time.

## 13. Pollution Prevention

See Chemical Hygiene Plan for pollution prevention operations.

## 14. Waste Management

See Chemical Hygiene Plan SOP/1728 for waste handling and disposal.

**NOTE: TKN Lachat waste contains Mercury and must be deposited into TKN/Lachat waste stream in the Waste Room.**