

## Title: AMMONIA POTENTIOMETRIC, ION SELECTIVE ELECTRODE SM 4500-NH<sub>3</sub> D

Approvals (Signature/Date):			
	8/29/13		08/29/2013
Tung Nguyen Technical Manager	Date	William Nash Health & Safety Coordinator	Date
	8-29-2013		08/29/2013
Maria Friedman Quality Assurance Manager	Date	Kirk Miltimore Laboratory Director	Date

**Copyright Information:**

This documentation has been prepared by TestAmerica Laboratories, Inc. and its affiliates ("TestAmerica"), solely for their own use and the use of their customers in evaluating their qualifications and capabilities in connection with a particular project. The user of this document agrees by its acceptance to return it to TestAmerica upon request and not to reproduce, copy, lend, or otherwise disclose its contents, directly or indirectly, and not to use it for any other purpose other than that for which it was specifically provided. The user also agrees that where consultants or other outside parties are involved in the evaluation process, access to these documents shall not be given to said parties unless those parties also specifically agree to these conditions.

**THIS DOCUMENT CONTAINS VALUABLE CONFIDENTIAL AND PROPRIETARY INFORMATION. DISCLOSURE, USE OR REPRODUCTION OF THESE MATERIALS WITHOUT THE WRITTEN AUTHORIZATION OF TESTAMERICA IS STRICTLY PROHIBITED. THIS UNPUBLISHED WORK BY TESTAMERICA IS PROTECTED BY STATE AND FEDERAL LAW OF THE UNITED STATES. IF PUBLICATION OF THIS WORK SHOULD OCCUR THE FOLLOWING NOTICE SHALL APPLY:**

©COPYRIGHT 2013 TESTAMERICA LABORATORIES, INC. ALL RIGHTS RESERVED

Facility Distribution No. \_\_\_\_\_

Distributed To: \_\_\_\_\_

## 1.0 SCOPE AND APPLICATION

This method is applicable to the measurement of ammonia-nitrogen in drinking, surface and saline water, domestic and industrial wastes. It has been modified to measure extractable ammonia in soil/solid samples by use of water leaching procedure followed by distillation.

Samples must be distilled prior to analysis.

See Attachment 1 for quantitation and QC acceptance limits.

Note that reporting limits (RLs) and method detection limits (MDLs) are subject to change based on annual MDL studies.

On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in "Validation of Methods" in the Quality Assurance Manual

## 2.0 SUMMARY OF METHOD

An aliquot of sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of boric acid. Ammonia is determined potentiometrically using an ion selective ammonia electrode and a pH meter having an expanded millivolt scale or a specific ion meter. The ammonia selective ion electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from the electrode internal solution of ammonium chloride. Dissolved ammonia ( $\text{NH}_3(\text{aq})$  and  $\text{NH}_4^+$ ) is converted to  $\text{NH}_3$  by raising the pH above 11 with a strong base. The  $\text{NH}_3$  diffuses through the membrane and changes the pH of the internal solution that is sensed by a pH electrode. Aqueous samples are measured directly whereas soils are leached using a 1:10 ratio of sample weight to volume of deionized water.

## 3.0 DEFINITIONS

There are no specific definitions associated with this SOP. See the QA Manual and Standard Method 4500-NH<sub>3</sub> for general definitions.

## 4.0 INTERFERENCES

- 4.1 Amines are a positive interference, which may be enhanced by acidification.
- 4.2 Mercury and silver interfere by complexing with ammonia. Thus the sample can not be preserved with mercuric chloride.

## 5.0 SAFETY

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

### 5.1 Specific Safety Concerns or Requirements.

Personal Protective Equipment Required: Safety Glasses/Face Shield, Lab coat, Nitrile/Cut-resistant Gloves

## 5.2 Primary Materials Used

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

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sodium tetraborate decahydrate	Irritant	Not listed by OSHA	Causes eye, skin, and respiratory tract irritation. Chronic exposure may cause reproductive disorders and teratogenic effects.
Ammonia	Corrosive Poison	50 ppm-TWA	Vapors and mists cause irritation to the respiratory tract. Causes irritation and burns to the skin and eyes
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

## 6.0 EQUIPMENT AND SUPPLIES

### 6.1 Equipment

- 6.1.1 pH meter with expanded mV scale or ion specific meter
- 6.1.2 Ammonia selective electrode (Orion or equivalent)
- 6.1.3 Gerhardt Vapodest distillation unit, Buchi-B-324 distillation unit, or equivalent

### 6.2 Supplies

- 6.2.1 Distillation tubes
- 6.2.2 100 mL glass beakers
- 6.2.3 50 mL graduated cylinders, class A
- 6.2.4 50 uL and 1000 uL pipettes
- 6.2.5 Kimwipes™
- 6.2.6 pH paper (1-14)
- 6.2.7 Potassium Iodide – starch indicator.
- 6.2.8 50 mL volumetric flasks, class A

## 7.0 REAGENTS AND STANDARDS

**7.1 Reagents**

All purchased and prepared reagents must be made from a traceable (NIST) source material, if available, and documentation of this traceability must be maintained by the laboratory.

- 7.1.1 Ammonia pH adjustment buffer (ISA) (Orion 951211 or equivalent)
- 7.1.2 Sodium Hydroxide, pellets, certified ACS
- 7.1.3 Sodium tetraborate decahydrate ( $\text{Na}_2\text{B}_4\text{O}_7$ ), powder or granular, ACS grade or equivalent
- 7.1.4 Boric Acid ( $\text{H}_3\text{BO}_3$ ), powder, certified ACS
- 7.1.5 Alkaline Reagent (Orion 951011 or equivalent).
- 7.1.6 Electrode filling solution (Orion 951209 or equivalent)
- 7.1.7 Thymolphthalein indicator solution, 0.05%, in 90% ethyl alcohol
- 7.1.8 Laboratory Reagent Grade Water (DI water)
- 7.1.9 Ottawa Sand, or equivalent

**7.2 Standards**

All purchased standards must be accompanied by a Certificate of Analysis (C of A) which is kept available at the laboratory in order to demonstrate traceability of the standard to certified (NIST-traceable, if available) source material.

- 7.2.1 Thermo Scientific -Ion Ammonia standard (1000  $\mu\text{g/ml}$ ) or Ammonia as Nitrogen standard (1000  $\mu\text{g/ml}$ ), or equivalent.
- 7.2.2 Ricca Ammonia standard (1000  $\mu\text{g/ml}$ ) or Ammonia as Nitrogen standard (1000  $\mu\text{g/ml}$ ) or equivalent (for second source).

**8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE**

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

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters	Polyethylene bottle	250 mL	$\text{H}_2\text{SO}_4$ , pH < 2; Cool >0 to 6°C	28 Days	40 CFR Part 136.3
Soils	Brass drilling sleeve or glass jar	4 Oz jar	Cool >0 to 6°C	28 Days	N/A

Water samples are most commonly sampled in polyethylene bottles with the pH adjusted to  $\leq 2$  with  $\text{H}_2\text{SO}_4$  (approx. 2 mL) at the time of collection.

**9.0 QUALITY CONTROL**

**9.1 Sample QC**



The following quality control samples are prepared with each batch of samples. Each of these QC samples may be re-analyzed once if it doesn't pass, prior to sample analysis, in order to verify the failure wasn't due to a physical or mechanical problem.

#### **9.1.1 Method Blank (MB)**

Prepare and analyze a method blank (MB) for each matrix and with every batch of 20 samples, or less. Check that there is no analyte detected at or above the reporting limit. If the method blank shows contamination, re-prepare all samples in the batch unless:

- The samples are ND (flag the result accordingly and write an NCM).
- The sample result is > 10x the blank level (flag the result accordingly and write an NCM).

#### **9.1.2 Laboratory Control Sample (LCS)**

Prepare and analyze a primary source laboratory control sample (LCS) for every batch of 20 samples or less. The LCS recovery must be within laboratory acceptance limits (see Attachment 1). If the LCS is outside of these limits, re-prepare the entire batch and/or re-calibrate the system unless:

- The LCS recovery is above the upper limit and samples are ND. Flag sample results accordingly and initiate an NCM

LCS Duplicate (LCD) is performed only when insufficient sample is available for the MS/MSD or when requested by the client/project/contract.

#### **9.1.3 Matrix Spike and Matrix Spike Duplicate**

The source sample for MS/MSD is randomly selected, unless specifically requested by a client. Prepare and analyze a matrix spike (MS) and a matrix spike (MSD) duplicate for each matrix and with every batch of 20 samples, or less. The recovery and relative percent difference must be within laboratory acceptance limits (see Attachment 1), unless there is obvious matrix interference. In the case of matrix interference, flag the results accordingly and initiate an NCM.

### **9.2 Instrument QC**

The following instrument QC samples are run with each analytical sequence. Each of these QC samples may be re-analyzed once if it does not pass, in order to verify the failure wasn't due to a physical or mechanical problem. Re-analysis must be performed before the analysis of any associated batch QC or client samples. Note that instrument QC standards do not undergo the distillation procedure.

#### **9.2.1 Initial Calibration (ICAL)**

Prepare a calibration curve by plotting standard millivolt potential against its corresponding concentration values expressed as a logarithm using a linear regression program. An acceptable calibration curve must meet the following conditions:

- The absolute value of the correlation coefficient of the linear regression calculation must be  $\geq 0.995$ .
- The calibration blank result must be less than the reporting limit.
- The ICV recovery must be within  $\pm 15\%$  of the true value

If these criteria are not met:

- Re-prepare the calibration standards and repeat the calibration.

Refer to the "Calibration Curves" SOP.

### **9.2.2 Initial Calibration Verification (ICV) 2.5 mg/L**

Immediately after the initial calibration, analyze the Secondary source (ICV) standard.

Verify that that its response is within 15% of the true value.

- If not, re-prepare and re-analyze the ICV standard.
- If the ICV is still out of control, re-calibrate the system

### **9.2.3 Continuing Calibration Verification (CCV) 4 mg/L**

Analyze a CCV standard after every 10 sample aliquots or less and at the end of the sequence. The recovery must be within  $\pm 15\%$  of the true value. If the CCV is outside recovery limits, re-analyze once. If it is still out, the instrument must be recalibrated and samples not bracketed by acceptable CCVs must be re-analyzed, unless:

- If the CCV is out high, any ND samples may be reported with an NCM.

### **9.2.4 Initial and Continuing Calibration Blank (ICB/CCB)**

Follow every ICV with an ICB and every CCV with a CCB, the ICB/CCB must read less than the method RL. If the ICB/CCB is above the RL, re-analyze once. If it is still out, the instrument must be recalibrated and samples not bracketed by acceptable ICBs/CCBs must be re-analyzed unless all affected samples are ND, in which case, they may be reported.

- The samples are ND (flag the result accordingly and write an NCM).
- The sample result is  $> 10x$  the blank level (flag the result accordingly and write an NCM).

## **10.0 PROCEDURE**

### **10.1 Reagent Preparation**

NOTE: Reagents and standards may be prepared at final volumes other than those listed, provided the component ratios are maintained and the specific weights and volumes used are documented.

#### **10.1.1 Sodium Hydroxide (1 N)**

Prepare this solution by dissolving 40 g of NaOH in reagent grade water and dilute to 1 L. Store at room temperature. Shelf life is six months.

#### **10.1.2 Sodium tetraborate decahydrate solution (0.024 M)**

Prepare this solution by dissolving 9.5 g of  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  in 1 L of reagent grade water. Store the solution at room temperature. Shelf life is six months.

#### **10.1.3 Borate Buffer**

Prepare this solution by adding 88 mL of 0.1 N NaOH to 500 mL of 0.025 M Sodium tetraborate decahydrate solution and dilute to 1 L. Store at room temperature. Shelf life is six months.

#### 10.1.4 Alkaline Reagent Conditioning Solution

Add 1 mL of the Alkaline Reagent to 100 mL of a 1 ppm ammonia standard.

### 10.2 Standard Preparation

#### 10.2.1 Working Calibration Standards

Prepare the calibration standards by diluting the appropriate volume of the calibration stock standard (1000 ppm NH<sub>3</sub> as N) with reagent grade water. Add approximately 40 mL of reagent grade water into a clean 50 volumetric flask. Pipette the appropriate volume of stock standard to each flask. Dilute to 50 mL with reagent grade water. Calibration standards, including ICV and CCV are NOT distilled.

Name	Concentration (mg/L)	μL primary standard added (1000 ppm NH <sub>3</sub> as N)	μL secondary standard added (1000 ppm NH <sub>3</sub> as N)	Final Vol (mL)
Calib Blank ICB/CCB	0	none	--	50
Cal 1	0.1	5	--	50
Cal 2	0.5	25	--	50
Cal 3	2.0	100	--	50
Cal 4	5.0	250	--	50
ICV	2.5	--	125	50
CCV	4.0	200	--	50

#### 10.3 Batch QC Preparation

Prepare the batch QC by adding the appropriate volume of the stock standard (1000 ppm NH<sub>3</sub> as N) to a **50 mL graduated cylinder** containing the specified matrix. Bring to a final volume of 50 mL. Batch QC samples are distilled in the same manner as client samples.

Name	Matrix	Preparation	Concentration	μL primary standard added (1000 ppm NH <sub>3</sub> as N)
MB	Water	Reagent water	0 mg/L	--
MB	Solid	5g sand + reagent water	0 mg/L	--
LCS/LCSD	Water	Reagent water	2.5 mg/L	125
LCS/LCSD	Solid	5g sand + reagent water	25 mg/Kg	125
MS/MSD	Water	Source sample	2.5 mg/L	125
MS/MSD	Solid	5g source sample + reagent water	25 mg/Kg	125

#### 10.4 Distillation Unit Initialization

Run the cleaning program on the distillation unit before every batch of samples is distilled.

Program Parameter	Setting
H2O (sec)	13 sec
NaOH (sec)	0
Delay (sec)	0
Distill (sec)	420
Steam (%)	100
Aspir/suction time	20 sec

## 10.5 Sample Preparation

### 10.5.1 General Sample Provisions

- Samples must be at room temperature before analysis.
- Test the pH of all water samples using pH paper. Do not allow the pH paper to come in contact with sample directly. Take a sample aliquot using a disposable pipette and drop the aliquot on pH paper to determine the sample pH. Record the pH measurement in the LIMS Worksheet. If not properly preserved to pH < 2, add a few drops of H<sub>2</sub>SO<sub>4</sub> and re-test the pH to verify the sample is properly preserved. Initiate an NCM if the sample was improperly preserved. Record the H<sub>2</sub>SO<sub>4</sub> lot number in the LIMS Worksheet.
- Label 100 mL glass beakers with the descriptions of the QA/QC samples, and the lab number for the environmental samples.

### 10.5.2 Water samples

- Using a 50 mL graduated cylinder, pour 50 mL of the sample into a distillation tube.
- Add 2.5 mL of Borate buffer.
- Adjust the pH to 9.5 with 1 N NaOH using thymolphthalein indicator. Add 2-3 drops of thymolphthalein into the sample tube. Add NaOH dropwise until it turns blue. Add a few boiling chips.

### 10.5.3 Soil samples

- Weigh out 5 g or less of soil into a 50 mL centrifuge tube and quantitatively transfer the sample into a digestion tube. Record the exact amount used.
- Add 50 mL of reagent grade water, 2.5 mL of Borate buffer and adjust the pH to 9.5 with 1 N NaOH using thymolphthalein indicator. Add 2-3 drop of thymolphthalein into the sample tube. Add NaOH dropwise until it turns blue. Add a few boiling chips.
- NOTE: a method blank and LCS for soils must be prepared and distilled in the same manner using glass beads and reagent grade water.

## 10.6 Sample Distillation Procedure

- On the distillation unit enter the following parameters to distill the samples.

Program Parameter	Setting
H <sub>2</sub> O (sec)	0
NaOH (sec)	0



Program Parameter	Setting
Delay (sec)	0
Distill (sec)	117
Steam (%)	85%
Aspir/Suction time	OFF

- Place the digestion tube on the distillation apparatus.
- Recover the distillate in a 50 mL graduated cylinder containing 10 mL of 2% boric acid solution. Bring up to final volume of 50 mL with reagent grade water.

### 10.7 Millivolt Meter Set-up

- Attach the ammonia probe to the pH meter.
- Make sure the Ammonia electrode is filled with the electrode filling solution. Plug the electrode into the pH meter. Rinse the probe with reagent grade water, discarding the water into a glass beaker. Dry the probe with a Kimwipe.
- Soak the assembled electrode for 15 minutes in a 1 ppm ammonia standard with Alkaline Reagent before using.
- Immerse the electrode in a beaker of Reagent Grade water add 1mL ISA solution. After adding ISA, press mV button immediately. Verify the millivolt reading is approximately in the range of 190 to 200. If it is not, soak the electrode longer and/or rinse and refill the electrode.
- For overnight storage, soak probe in electrode filing solution.

### 10.8 Calibration

**10.8.1** Add a small magnetic stirrer bar to each of the standards and place on the stir plate. Allow the standard to mix thoroughly.

**10.8.2** Lower the probe into the standard and add 1 mL ISA solution. After adding ISA, press the mV button immediately. Press the mV button again to ensure the reading is stable.

**10.8.3** For a new calibration, load the calibration standards in ascending concentration order followed by the ICV. Verify all calibration criteria are met before proceeding.

**10.8.4** To continue using a previous calibration, recall the calibration file, analyze a calibration blank and midpoint standard. Verify acceptance criteria are met before proceeding.

### 10.9 Sample Analysis

**10.9.1** Soak the assembled electrode for 15 minutes in a 1ppm ammonia standard with Alkaline Reagent before using the electrode.

**10.9.2** Add a small magnetic stirrer bar to each of the 50 mL samples, including the blank, LCS, MS and MSD samples. Gently stir the sample on the magnetic stirring plate. Be sure to mix the sample well before immersing the electrode into the sample. If the sample is not mixed well, it may affect the result. Maintain the same stirring rate throughout calibration and testing procedure to minimize possible loss of ammonia from the solution.

**10.9.3** Immerse the electrode into the sample.

**10.9.4** Add 1 mL of ammonia pH ISA adjustment buffer to every sample while the sample is being stirred. (This buffer will increase the pH of the samples to  $\geq 11$ )

**10.9.5 Note:** If the addition of ISA does not turn the sample blue, add more ISA (approximately 0.5-1 mL) until the sample appears blue. This is necessary because the pH must be  $\geq 11$  prior to sample analysis.

**10.9.6** Once the mV reading stabilizes, record it on the Ammonia Worksheet (Attachment 2).

**10.9.7** Rather than rinsing the electrode with a reagent grade water wash bottle between measurements, **dip** the electrode in reagent grade water between measurements. For the best accuracy and precision, rinse the electrode a second time by dipping it in a second beaker of reagent grade. Wipe off the excess water with a Kimwipe.

**10.9.8** Between samples, store the assembled electrodes in the 1 ppm ammonia standard with Alkaline Reagent.

**10.9.9** A typical daily run sequence is listed below:

1	Blank
2	ICAL (0.1 – 5.0 ppm)
3	ICV (2 <sup>nd</sup> source)
4	ICB
5	LCS (1 <sup>st</sup> source)
6	MB
7	8 samples (including MS/MSD; 1 <sup>st</sup> source)
8	CCV (1 <sup>st</sup> source)/CCB
9	10 samples
10	CCV (1 <sup>st</sup> source)/CCB

## 10.10 Preventative Maintenance

**10.10.1** As needed replace, the ammonia internal filling solution and the white ammonia membrane on the electrode. Allow the electrode to sit in the electrode filling solution for one hour before analyzing samples. The electrode should be stored in the electrode filling solution between analyses.

**10.10.2** Record all performed maintenance in the instrument maintenance logbook.

**10.10.3** If an instrument is unusable or has limitation to its use, it must be tagged accordingly until such a time the problem has been corrected. Record the problem, solution, and verification of proper operation into the instrument maintenance logbook.

## 11.0 CALCULATIONS / DATA REDUCTION

### 11.1 Accuracy

$$\text{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

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

**11.2 Precision (RPD)**

$$\text{Matrix Duplicate (MD)} = \frac{|\text{orig. sample value} - \text{dup. sample value}|}{[(\text{orig. sample value} + \text{dup. sample value})/2]} \times 100$$

**11.3 Concentration**

Calculate the concentration of ammonia in the sample by plotting the raw sample millivolt reading against the calibration curve to get the log of the concentration:

$$L = \frac{m - i}{s}$$

Where L = log of raw sample concentration (mg/L)  
 s = calibration curve slope (mV / log (conc))  
 m = millivolt reading of sample  
 i = calibration curve intercept (mV)

Calculate the inverse log to get the concentration in mg/L. Apply prep and dilution factors as necessary:

$$C = 10^L \times \frac{V}{A} \times D$$

Where C = sample concentration in mg/L or mg/kg (soils)  
 V = volume of sample analyzed (mL)  
 A = aliquot of sample prepared (mL or g)  
 D = dilution factor

Report all results as mg/L (or mg/kg) NH<sub>3</sub> as N unless otherwise directed.

**Conversion from mg/L (or mg/kg) NH<sub>3</sub> as N to mg/L NH<sub>3</sub>.**

$$(\text{mg/L NH}_3 \text{ as N}) \times 1.21 = \text{mg/L NH}_3$$

**Conversion from mg/L (or mg/kg) NH<sub>3</sub> to mg/L NH<sub>3</sub> as N.**

$$(\text{mg/L NH}_3) \times 0.82 = \text{mg/L NH}_3 \text{ as N}$$

**11.4 Data Review**

**11.4.1** Whenever a sample is analyzed for BOTH ammonia-nitrogen (NH<sub>3</sub>-N) and total Kjeldahl nitrogen (TKN), all data review personnel must be aware that, in theory, NH<sub>3</sub>-N results cannot be greater than TKN results. Both must be expressed as nitrogen and in the same units. (TKN is the sum of all digested organic nitrogen plus any ammonia in the sample.) Similarly, organic nitrogen results, TKN – NH<sub>3</sub>-N cannot be negative.

**11.4.2** Due to variability in the method and the sample matrix, some allowances will be made for results that do not meet this relationship:

- If NH<sub>3</sub>-N is greater than TKN, the data for both methods must be checked.

- If no data errors are found and the  $\text{NH}_3\text{-N}$  is no more than 10 % greater than the TKN result, the data may be reported.
- If the  $\text{NH}_3\text{-N}$  is more than 10 % greater than the TKN result, the sample **MUST** be re-analyzed for one or both tests.
- If organic nitrogen is being calculated and the  $\text{NH}_3\text{-N}$  concentration is greater than TKN by 10 % or less, organic nitrogen will be reported as "ND" and an NCM must be written stating "Ammonia concentration exceeded TKN concentration. Results are within acceptable variability limits for the methods."

## 12.0 METHOD PERFORMANCE

### 12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure as described in laboratory's SOP, IR-QA-MDL. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. Ammonia by ISE MDLs are performed annually.

### 12.2 Demonstration of Capabilities

Every analyst must perform an Initial Demonstration of Capability (IDOC) before performing analyses on any client samples. An IDOC consists of 4 consecutive LCS samples at 1 to 4 times the RL with an average recovery and RSD within laboratory acceptance limits. An on-going DOC must be performed annually. An ODOC can be 4 consecutive LCSs at mid-level or a passing PT.

### 12.3 Training Requirements

The analyst must have documented training, including reading of the SOP and source methods, conducted by the department manager, senior chemist, or other analyst with training documentation and a passing DOC.

## 13.0 POLLUTION CONTROL

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

## 14.0 WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the laboratory's Waste Disposal SOP (IR-EHS-WASTE). The following waste streams are produced when this method is carried out:

**Sodium hydroxide waste:** This waste is generated in the cyanide and ammonia tests. The waste is collected in a 2.5 gal carboy satellite container. Waste bulked as NaOH/pyridine.

**Soil waste** – Generated by analyst/technicians after samples have been prepared and analyzed in the Wetchem area. This waste is stored in 55-gallon closed head metal drum in the Wetchem area. Sample archive technicians label the drum with a preprinted label of Non-RCRA Hazardous waste solid. The drum is removed from the Wetchem area to the main waste storage area by sample archive technicians. Analyst/technicians let the sample archive technicians know when they need to removed this drum.

**Non-Hazardous Waste:** Non-Hazardous waste is disposed of by pouring the samples water that have been extracted into the sink, measuring the pH and neutralizing the water using soda ash, and then draining the neutralized contents into the sewer system. The soil generated in these tests is collected in the 55-gallon closed head metal drum in the wetchem area. Sample archive technicians label the drum with a preprinted label of Non-RCRA Hazardous waste solid.

Wetchem analysts/technicians are responsible for neutralizing this waste in the glassware washing room.

**Unused standards or reagents.** If the standard or reagent is hazardous and can not be collected with one of the waste streams generated in the method, then the analysts and technicians will take this standard or reagent and place it on the shelves labeled “hazardous waste” in the main waste storage area. The waste material must be labeled with the words “Hazardous Waste”, contents and the date taken to the waste storage area. The waste material will be lab packed (example: mercury standard). If the waste material can be collected in the satellite waste container for one of the waste streams of the method, then pour the standard in the right satellite container, rinse the original container, and collect the rinsate in the satellite container. The original container can be placed in the regular trash. (Example, buffer solutions pH 4).

**15.0 REFERENCES / CROSS-REFERENCES**

- 15.1 Method 4500-NH3 D, “Ammonia-Selective Electrode Method”, Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998.
- 15.2 Method 4500-NH3 B, “Preliminary Distillation Step”, Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998.
- 15.3 40 CFR Parts 122, 136, 141, 143, 430, 455, 465 Final Rule, 12 March 2007 (“Method Update Rule”, effective 04/11/07)
- 15.4 CA-Q-S-005, Calibration Curves (General)
- 15.5 IR-QA-MDL, Determination of Method Detection Limits

**16.0 METHOD MODIFICATIONS**

Item	Method 4500-NH3 B & D	Modification



1	Sec. 4b 4500-NH3 D	The volume used for both the calibration standards and samples is 50 mL. The lower volume is cost and time effective, and it does not affect the detection limit or accuracy of the analysis.
2	Sec. 4b 4500-NH3 D	The ammonia pH ISA adjustment buffer is used in place of 10N NaOH. The buffer raises the pH of samples to 11.
3	Sec. 1b 4500-NH3 D	There is a modification for the analysis of solid matrix samples. (Soluble Ammonia)
4	Sec. 4b 4500-NH3 B	In lieu of pH meter, thymolphthalein indicator is used for adjusting pH. Its transition range is at approximately pH 9.3-10.5

## 17.0 ATTACHMENTS

- 17.1 **Attachment 1:** Analysis Information
- 17.2 **Attachment 2:** Worksheet
- 17.3 **Attachment 3:** Data Review Checklist

## 18.0 REVISION HISTORY

This section has been added beginning with Revision 0. Only details of the last two revisions are incorporated into this SOP. Prior revisions are documented in the QA files.

### 18.1 **Revision 2, dated 31 October 2012**

- This revision supersedes IR-WET-NH3ISE, revision 1 (09/17/10)
- Revised Standard Preparation section
- Revised Sample Preparation section
- Revised Demonstration of Capabilities
- Revised Sample QC and Instrument QC sections.
- Revised Standards and Reagents sections.
- Change all Element references to TALS
- Added Soil Wastes in Waste Management
- Revised by YZ, DD and LH.

### 18.2 **Revision 3, dated 30 August 2013**

- This revision supersedes IR-WET-NH3ISE, revision 1 (10/12/12)
- Created table for preparation of all batch QC
- Specified that batch QC be prepared in graduated cylinders, in the same manner as samples.
- Removed undistilled sample section – all samples must be distilled
- Revised typical daily run sequence section to include ICV/ICB
- Added acceptance criteria for ICB
- Noted that instrument QC standards do not undergo the distillation procedure
- Revised distillation unit parameters
- Revised distillation to require collection in a final volume of 50 mL, not 100 mL
- Added 0.1 mg/L calibration point and removed 1.0 mg/L calibration point
- Clarified how probe performance is checked and how often the filling solution and membrane must be changed.
- Revised Attachment 2 (Worksheet)
- Revised by YZ, DC, DD and LH

**Attachment 1  
 Analysis Information**

**TestAmerica Irvine**

**Analytical Method Information**

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
<b>Ammonia-N, ISE in Water (SM4500NH3-D)</b>								
Preservation: 4 C, H2SO4								
Container: 250 mL Poly			Amount Required: 100 ml			Hold Time: 28 days		
Ammonia-N	0.1	0.50 mg/l			75 - 125	15	85 - 115	15
<b>Ammonia-N, ISE in Soil (SM4500NH3-D MOD.)</b>								
Preservation: 4 C, Cool								
Container: 4 oz Jar			Amount Required: 50 grams			Hold Time: 28 days		
Ammonia-N	1.0	5.0 mg/kg			75 - 125	15	85 - 115	15

Uncontrolled Document



**Attachment 3  
 Data Review Checklist**

**AMMONIA DATA REVIEW CHECKLIST  
 SM 4500-NH3-D**

Method: \_\_\_\_\_ Analysis Date: \_\_\_\_\_ 2<sup>nd</sup> Level Reviewer: \_\_\_\_\_  
 Prep Batch: \_\_\_\_\_ Analyst Initials: \_\_\_\_\_ Review Date: \_\_\_\_\_

Item to Review	Analyst	2 <sup>nd</sup> Level	Notes/Specific Criteria
<b>Calibration</b>			
4 Calibration points + Blank used for curve			
Calibration curve meets acceptance criteria, $r \geq 0.995$			
Second source verification (ICV) analyzed and passes (85-115%)			
No reported results above the high calibration standard			
CCVs every 10 samples/end of run and within limits (85-115%)			
CCBs after every CCV and read less than RL			
<b>Sample Preparation Batch:</b>			
Water samples preserved with sulfuric acid to pH<2			
All samples prepared and analyzed within holding time of 28 days			
Batch contains no greater than 20 samples			
Method Blank reads < RL			
LCS recovery within limits 85-115%			
MS/MSD within limits 75-125%, RPD 15%			
<b>Data Documentation:</b>			
All standards used are uniquely identified and are not expired			
All errors are crossed out with a single line, initialed and dated			
Unused data is clearly identified			
The analyst's signature/initials are on the logsheet page			
All qualifiers correctly applied and CARs written, as required			
All dilution factors applied correctly and entered into LIMS			
Analysis and prep times accurately entered into LIMS			
All initial and final results from print-out match LIMS entries			
All calculation correct (final results, recovery, RPD)			

Q:\DATA\_REVCHKLIST\WETCHEM\Ammonia\_NH3D\_Check\_r0.doc  
 Rev: 08/27/2010