51927-88

HACH®

sension™

Ammonia Gas Sensing Combination Electrode

Model 51927-00

te/dk 08/01 1ed

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SPECIFICATIONS

Specifications subject to change without notice.

Concentration Range*
0.06 to 17,000 mg/L NH_3
0.05 to 14,000 mg/L NH_3-N

Temperature Range
Operating: 0 to 50 °C

Storage: -40 to 60 °C

pH Range
> pH 11; Ionic Strength Adjustor raises pH above 11

Slope
–57 ±3 mV/decade in linear concentration range

Response Time
95% response in three minute(s) or less in linear range

Ammonia Membrane Modules
Replaceable membrane modules; module life depends on sample composition

Internal Filling Solution
Refillable

Electrode Storage
Dry in air (membrane in sealed vial), or in Ammonia Storage Solution. See *Storing the Electrode* on page *51*.

Electrode Resistance
<500 Megohm

Electrode Connector
BNC (twist type)

Dimensions
Electrode length: 14 cm (5.5 in.)
Electrode diameter: 1.3 cm (0.5 in.)
Cable length: 91 cm (36 in.)

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* In this manual, concentrations are expressed in mg/L (ppm) NH_3-N and moles/L (M).

SAFETY PRECAUTIONS

Please read this entire manual before unpacking, setting up, or operating this instrument. Pay particular attention to all danger and caution statements. Failure to do so could result in serious injury to the operator or damage to the equipment.

To ensure the protection provided by this equipment is not impaired, do not use or install this equipment in any manner other than that which is specified in this manual.

Use of Hazard Information

If multiple hazards exist, this manual will use the signal word (Danger, Caution, Note) corresponding to the greatest hazard.

DANGER
Indicates a potentially or imminently hazardous situation which, if not avoided, could result in death or serious injury.

CAUTION
Indicates a potentially hazardous situation that may result in minor or moderate injury.

NOTE
Information that requires special emphasis.

Precautionary Labels

Read all labels and tags attached to the instrument. Personal injury or damage to the instrument could occur if not observed.

⚠ This symbol, if noted on the instrument, references the instruction manual for operational and/or safety information.

SECTION 1 INTRODUCTION

1.1 Electrode Description

The Hach Ammonia Electrode measures ammonia gas or ammonium ions in aqueous solutions that have been converted to gas by the addition of a strong base. The electrode (*Figure 1*) is a complete electrochemical cell consisting of a glass pH electrode and a reference electrode.

Figure 1 Ammonia Gas Sensing Electrode

The gas-permeable membrane separates the sample from a thin layer of electrolyte that is pressed between the pH bulb and the membrane. At high pH, ammonium is converted to ammonia gas. The gas diffuses through the membrane and causes a pH change in the thin layer of electrolyte. The potential across the pH glass changes as a result of the pH change and the electrode measures the change in potential. The measured pH change is proportional to the ammonia concentration in the solution (see *SECTION 5* on page *53*).

The ammonia electrode will measure ammonia gas or ammonium ion (converted to gas by strong base) in a variety of aqueous samples. Applications include water, wastewater, boiler feedwaters, fertilizers, biological samples, fish tanks, and more. An air gap accessory is available for samples that may foul or destroy the membrane (see *Section 1.4* on page *14* for more information).

1.2 Preparing the Electrode For Use

Before using a new Ammonia Electrode or an electrode that has been stored dry, remove the protective cap from the end. Prepare the electrode as follows:

1. Unscrew the top cap. Carefully remove the internal glass electrode from the outer body.

   Note: *A white membrane is mounted at the tip of the outer body.*

2. Soak the inner body in Ammonia Electrode Filling Solution for at least two hours before assembling the electrode. For best results, soak overnight in a small diameter test tube or within the ammonia electrode outer body. Make sure that the ring-shaped ceramic reference junction is immersed.

3. Fill the outer body with 3.5 mL of Internal Fill Solution.

4. Rinse the internal glass electrode with deionoized water. Blot dry. Return the electrode to the filled outer body.

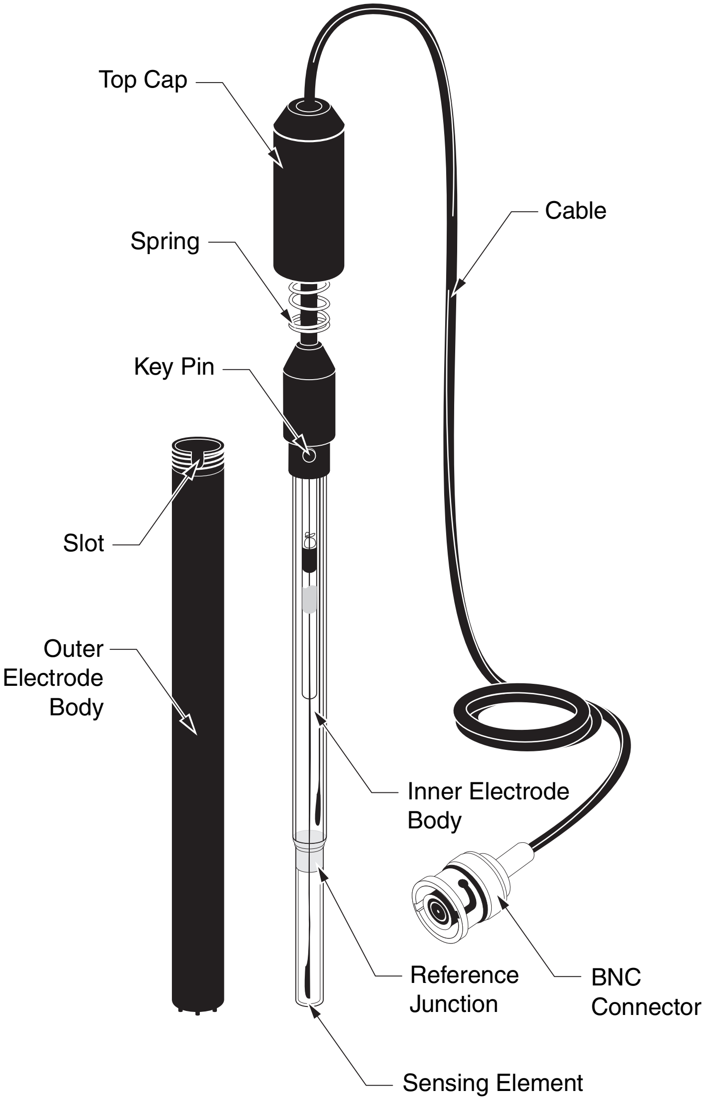
   Note: *Make sure that the key pin at the top of the internal glass electrode is seated in the slot at the top of the outer body.*

5. Reinstall the threaded top cap onto the top of the ammonia electrode body. Finger-tighten the cap until snug. Do not over-tighten.

6. Place the electrode in the electrode holder. To clean the electrode, immerse the electrode tip in deionized water and stir for 5 minutes.

7. Shake the fully assembled electrode as if it were a mercury thermometer to remove bubbles.

Figure 2 Assembling the Electrode



1.2.1 Ammonia Modules and Membranes

The ammonia electrode is shipped with three ammonia modules. Each module is a bonded white ammonia membrane within a screw cap assembly.

Avoid excessive handling of the modules during assembly. Excessive handling may affect the membrane's hydrophobic properties, causing shorter electrode life. A module will last from one week to several months, depending on usage and sample matrix.

Membrane failure will cause a shift in electrode potential, drift and poor response. Replace the membrane module if:

1. The electrode response becomes very slow.
2. The results are not reproducible.
3. The slope becomes too low or shifts.
4. Visual inspection detects dark spots or discoloration of the membrane.

1.2.2 Replacing the Internal Filling Solution

Replenish the filling solution if the electrode is left out in the air for more than one hour. If electrode drift occurs with a relatively new membrane module, the filling solution may need replacing.

1. Unscrew the membrane module. Pour out the filling solution.
2. Rinse the pH bulb and reference wire with deionized water and gently blot dry.
3. Fill the module with about 3.5 mL of new solution.
4. Screw the membrane module onto the electrode body. Excess filling solution will be expelled.

1.2.3 Conditioning the Electrode

1.2.3.1 New or Stored Longer Than One Week

Place the assembled electrode into the Ammonia Electrode Storage Solution for at least 60 minutes. Check the electrode's response following the directions in *Section 1.3*.

1.2.3.2 Between Samples

Place the electrode in Ammonia Electrode Storage Solution for at least one minute. This reinitializes the electrode for the next measurement.

1.2.3.3 Overnight and Up to One Week

Keep the electrode in 1000-ppm ammonia standard **without Ionic Strength Adjustor** (ISA) or in the Ammonia Electrode Storage Solution. Never let the membrane dry out. Hach recommends covering the storage beaker and electrode body with Parafilm® to prevent solution evaporation.

1.2.3.4 Longer Than One Week

Unscrew the membrane and clean all parts of the cap and body in deionized water. Re-assemble and store dry until reconditioning for use.

1.3 Checking The Ammonia Electrode Slope

1. If using a Hach meter, select the mV mode according to the meter's instruction manual.
2. If using a Hach *sension*™*2* meter, go to *step 3*.

   If using a *sension4* meter:

   a. Press **SETUP.** Use the Up Arrow to scroll to **Stabilizing....**

   b. Press **ENTER**. Enter a stability criteria of 0.1 mV/min., then press **ENTER**.

   c. Press **EXIT** to return to Reading mode.

3. Select two standards above 0.5 mg/L NH_3-N that are a decade (factor of 10) apart and fall within a concentration range that is close to the sample concentration range.

***Note:** Properly condition the electrode before checking the slope.*

4. Using a 25-mL graduated cylinder, measure 25 mL of each standard into separate 50-mL plastic beakers. Add a stir bar to each beaker.

5. Add the contents of one Ammonia Ionic Strength Adjustor (ISA) Powder Pillow, or add 0.5 mL of Ammonia ISA solution to the 50-mL beaker with the lowest ammonia concentration. Rinse the electrode well with deionized water and blot dry.

6. Place the beaker on a magnetic stirrer and stir at a moderate rate. The solution should turn blue.

7. Place the electrode into the beaker being stirred. When a steady mV reading is obtained, record the potential.

8. Remove the electrode and rinse with deionized water. Blot dry with a paper towel.

9. Prepare the higher standard as in *steps 4* and *5*. Immerse the electrode in this standard.

10. Record the mV potential when it is stable.

11. Subtract the first mV reading from the second reading. The potential should have changed –57 ±3 mV.

1.4 Measuring Hints

These hints will improve the accuracy of the calibration curve and sample measurements.

- Two alternatives exist for handling solutions that contain oils, sludge, waste, or surfactants. One is to digest the sample before measurement using a total kjeldahl nitrogen (TKN) procedure. The procedure will measure all the free NH_4^+ or NH_3 in the sample, as well as the nitrogen from amines converted to NH_4^+ during digestion. The second choice is to use an air gap accessory. This will only measure the free NH_4^+ or NH_3 in the sample and is not appropriate for measuring aminated nitrogen.

- To improve response time and the reproducibility of the electrode, immerse it in Ammonia Storage Solution for at least 15 minutes after it is first assembled. Between samples or standards, immerse it in the Storage Solution for 1 minute. This re-establishes a neutral pH between the sensing glass and the membrane before the next measurement. Rinse the electrode with deionized water before placing it in a sample or standard.

- Check the electrode for accuracy after every hour of use in fresh calibration standard. Recalibrate if necessary.
- Make sure all samples and standards are at the same temperature (within 1 °C). If a previous calibration is used, it should have been prepared at the same temperature as the samples being measured.
- Use a magnetic stirrer and stir bar; stir at a constant rate. This speeds response time and permits a lower detection limit.
- For best accuracy, especially at low levels where long sample stirring is necessary, use a Hach electromagnetic stirrer that won't heat the sample (see Accessories). Or, place an insulating pad (cardboard or foam) between the sample container and stirrer.
- Excessive mixing or stirring causes rapid diffusion of ammonia out of the sample, making measurements inaccurate. Do not vortex the sample.
- Add the correct amount of Ionic Strength Adjustor (ISA) to each standard and sample so the ionic strength is constant (see *Section 5.5* on page *55*).
- Measure samples and standards within 15 minutes after adding ISA because ammonia gas can escape out of the solution. Covering low-concentration samples and standards with parafilm (leave a hole for the electrode) reduces ammonia loss. The air gap accessory also minimizes ammonia loss and prolongs membrane life.
- Keep stored samples in tightly capped bottles to prevent NH_3 contamination from the atmosphere. Pour samples just before measuring. Do not leave them out too long or they will become contaminated with atmospheric NH_3. Recap the standards immediately.

1.5 The Air Gap Accessory

The Ammonia Electrode uses a fine, porous membrane to separate the sample solution from a thin layer of electrolyte that coats the pH sensing bulb inside the electrode. In a closed system saturated with water vapor, the ammonia electrode reacts to ammonia in the gas phase. Measurements of solutions above 10^{-3} M (14 mg/L) ammonia are possible under these conditions. Ammonia gas diffuses through the air space between the membrane and solution, then through the membrane. The air space has slightly different diffusion characteristics than the membrane, which **increases the response time**.

The membrane of the ammonia electrode is gas-permeable and hydrophobic. Liquid water does not wet it or penetrate the pores. If a sample solution is nonaqueous, or if it contains a surfactant which wets the membrane, the liquid penetrates the membrane. This causes difficulties in samples such as sewage, which contains surfactants, and samples which are nonaqueous, such as latex paint or nylon. To measure ammonia in such samples, use the Air Gap Accessory, which suspends the electrode above the sample and provides a closed system.

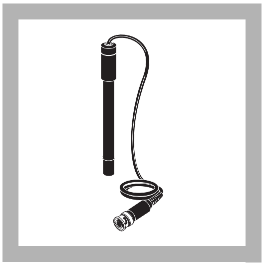
The Air Gap Accessory optimizes performance and extends the usable lifetime of the membrane module. Samples containing substances known to cause membrane failure (e.g., surfactants, oils, fats) can be measured repeatedly with this accessory. Slopes, absolute mV readings, and response times may change significantly when the Air Gap Accessory is used. Therefore, both **calibrations and measurements should be made with the Air Gap Accessory**.

Method 10000

NITROGEN, AMMONIA IN WATER

(0.1 to 1000 mg/L NH_3-N)

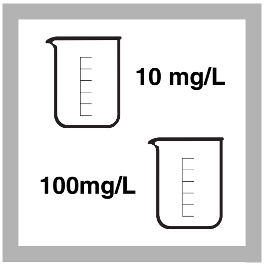
Using a Hach *sension*™ Meter



1. Prepare the electrode as described in *Section 1.2* on page *10*.

2. Rinse the electrode and place it in the Ammonia ISE Storage Solution with the sensor module on to condition for at least 15 minutes.

Note: *Before removing the electrode from the storage solution, the reading on the meter should be below 0.1 mg/L. This ensures the electrode is properly conditioned. After every hour of continuous use, place the electrode in the storage solution for 10 minutes to thoroughly recondition. Check with a 10 mg/L NH_3-N standard for accuracy and recalibrate if necessary.*

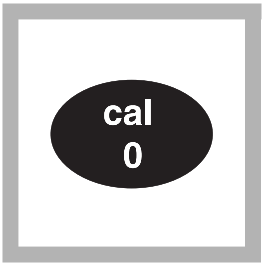


3. For calibration, use two ammonia standards of 10 and 100 mg/L NH_3-N. For more accurate analysis, bracket the expected sample concentration with two standards that are one decade apart in concentration.

4. After conditioning, connect the Ammonia ISE to the pH/ISE meter. Verify that BNC is selected in Setup 1 of the Setup menu.

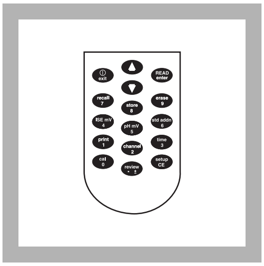
Note: *One BNC and one five-pin connector are on the back of the meter. Choose the BNC connector for the ammonia electrode.*

5. Press **ISE/mV** until the display shows **mg/L** or other selected concentration units.

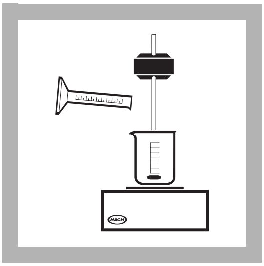


6. Press **CAL**. The display will show **CAL**, **?**, **mg/L**, and the active keys. The units will be flashing. Use the arrow keys to select the desired units, then press **ENTER**.

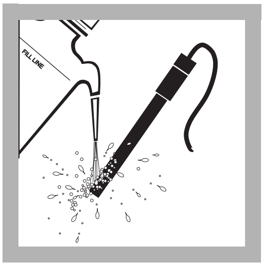
7. The display will show **Standard 1 ?** and _ _ _ _ or the value of standard 1 from the previous calibration.



8. If necessary, use the number keys to change the value to match the concentration of the standard. **Do not** press **ENTER** yet.

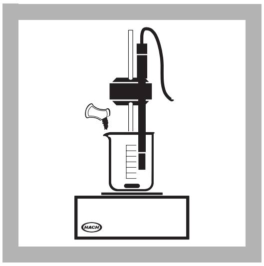


9. Transfer 25 mL of the 10-mg/L NH$_3$-N standard to a 50-mL beaker. Add a stir bar to the beaker. Place the beaker on a magnetic stirrer and stir at a moderate rate.



10. Remove the electrode from the storage solution. Rinse it with deionized water and blot dry. Place it into the 10-mg/L NH$_3$-N standard.

Note: *Be sure no air bubbles are trapped under the tip of the electrode.*

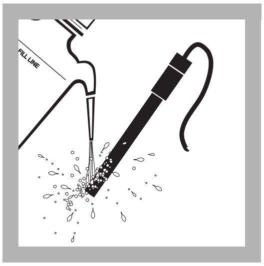


11. Add the contents of one Ammonia Ionic Strength Adjustor Powder Pillow to the standard and immediately press **ENTER**.

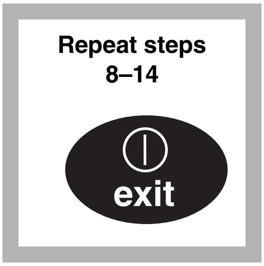
Note: *At high pH, ammonia solutions lose ammonia to the atmosphere, lowering the concentration. It is important to take measurements as soon as possible after the solution is basic.*

12. **Stabilizing...** will be displayed until the reading is stable.

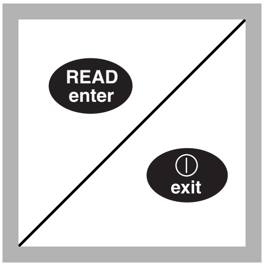
13. The display will show **Standard 2 ?** and _ _ _ _ or the value of standard 2 from the previous calibration.



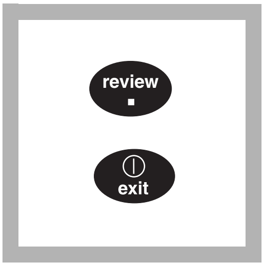
14. Remove the electrode from the standard. Rinse with deionized water and blot dry. Place in storage solution for one minute.



15. Repeat *steps 8-14* for each standard. After the last standard is measured, press **EXIT.**

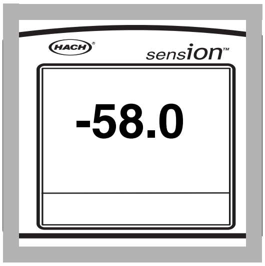


16. The display will show **Store?**. Press **ENTER** to store the calibration or **EXIT** to leave the calibration mode without storing the calibration values.

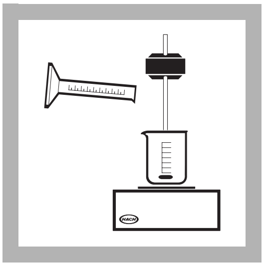


17. Press **REVIEW**. Use the Up arrow key to scroll to the last slope value. It should be -57 ±3 mV/decade. Press **EXIT** to return to the measurement mode.

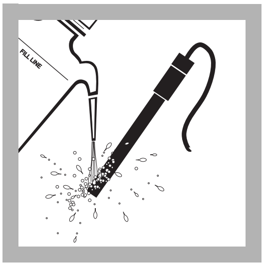
***Note:** If the slope does not approximate -57 ±3 mV/decade, recalibration may be necessary. If the slope is still incorrect after recalibration, replace the ammonia module.*



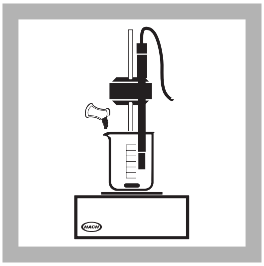
18. Be sure the slope displayed is within the range recommended in *Electrode Response* on page *54*.



19. Transfer 25 mL of the sample to a 50-mL beaker. Add a stir bar to the beaker. Place the beaker on a magnetic stirrer and stir at a moderate rate.

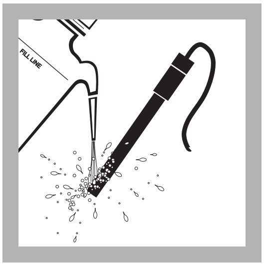


20. Remove the electrode from the storage solution. Rinse it with deionized water and blot dry. Place it into the sample.



21. Add the contents of one Ammonia Ionic Strength Adjustor Powder Pillow to the sample.

22. The display will show **Stabilizing...** until the reading is stable. Record or store the measurement value.



23. Remove the electrode from the sample. Rinse it with deionized water and blot it dry. Place it in the storage solution for at least one minute.

Repeat *steps 19-23* for each sample.

Sampling and Storage

Collect samples in glass or plastic containers of convenient size. Clean new bottles by washing with deionized or distilled water. Fill the sample bottle completely and stopper immediately. Analyze the sample as soon as possible.

Ammonia may be lost more quickly when sample temperatures are above 50 °C, so it is important to collect samples at less than 40 °C, or use a cooling coil between the bottle and sampling point.

If chlorine is present, treat the sample immediately with sodium thiosulfate. Add one drop of 0.1 N Sodium Thiosulfate Standard Solution for each 0.3 mg of chlorine present in a one liter sample.

If prompt analysis is not possible, preserve the sample with 0.8 mL of concentrated sulfuric acid per liter. Use a *sens***ion** pH meter to be sure the pH of the preserved sample is between 1.5 and 2. Some wastewater samples may require more sulfuric acid to achieve this pH. Store the sample at 4 °C. Samples preserved in this manner may be stored up to 28 days.

Before analysis, neutralize the sample to pH 7 with 5 N sodium hydroxide. Do not let the pH go above 10. Correct the test results for the volume addition.

Do not use mercuric chloride as a preservative because ammonia complexes with mercuric ions.

Accuracy Check

To verify measurement accuracy, run a standard addition spike on the sample. This provides more complete information about possible inaccuracies, because the measurement includes any interferences that may be present in the actual sample.

The spike should roughly double the measured concentration without significantly diluting the sample. To run a standard addition sample, use *Table 1* to determine the concentration and volume of standard to spike your sample. It is important to accurately transfer the volume of original sample. Simply add the amount and concentration specified in *Table 1* to the sample and record the reading when it is stable. Do not allow the sample to stand too long before spiking, as ammonia will be lost to the atmosphere. Then proceed with the calculations. Generally, results from 90-110% recovery are considered acceptable.

Table 1 Spiking volumes

Measured Sample Concentration (mg/L)	Measured Sample Volume (mL)	Standard Concentration (mg/L)	Standard Volume (mL)
0.1–0.6	25	100	0.1
0.6–1.0	25	100	0.2
1.0–1.5	25	100	0.3
1.5–3.0	25	100	0.5
3–6	25	100	1.0
6–10	25	100	2.0
10–15	25	100	3.0
15–25	25	1000	0.5
25–35	25	1000	0.7
35–50	25	1000	1.0
50–100	25	1000	2.0

Calculate percent recovery as follows:

$$\%\ \text{Recovery} = \frac{100(X_s - X_u)}{K}$$

Where:

X_s = measured value for spiked sample in mg/L
X_u = measured value for unspiked sample adjusted for dilution by the spike, in mg/L
K = known value of the spike in the sample in mg/L

Calculations:

1. $$X_u = \frac{X_i \times V_u}{V_u + V}$$

Where:

X_i = measured value of unspiked sample in mg/L
V_u = volume of separate unspiked portion in mL
V = volume of spike in mL

2. $K = \frac{C \times V}{V_u + V}$

Where:

C = concentration of standard used in spike in mg/L

V = volume of spike in mL

V_u = volume of separate portion before spike in mL

3. Final calculation using X_u and K:

$$\% \text{ Recovery} = \frac{100(X_s - X_u)}{K}$$

Example: A sample was analyzed and read 5.0 mg/L NH_3-N. As directed in *Table 1*, a 1.0-mL spike of 100-mg/L NH_3-N standard was added to the 25-mL sample, giving a result of 8.75 mg/L.

Calculate the percent recovery as follows:

1. $X_u = \frac{5.0 \text{ mg/L} \times 25 \text{ mL}}{25 \text{ mL} + 1 \text{ mL}} = 4.81 \text{ mg/L}$

2. $K = \frac{100 \text{ mg/L} \times 1 \text{ mL}}{25 \text{ mL} + 1 \text{ mL}} = 3.85 \text{ mg/L}$

3. $\%R = \frac{100 \times (X_s - X_u)}{K} = \frac{100 \times (8.75 - 4.81)}{3.85} = 102.3 \text{ \% Recovery}$

Method Performance

Precision

In a single lab using a standard solution of 5.0 mg/L and two electrodes with a single *sens**ion2*** meter, a single operator obtained a standard deviation of 0.095 mg/L ammonia nitrogen. Each electrode was exposed to seven test solutions and the meter default stability criteria was 0.5 mV/min. Between test solutions, electrodes were rinsed and placed in the storage solution until a reading of <0.1 mg/L was obtained.

Interferences

Volatile low molecular weight amines cause a positive interference.

Mercury and silver interfere by complexing with ammonia.

High concentrations of dissolved ions affect the measurement. For calibration use standard solutions that have about the same total concentration of dissolved species as the sample.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Ammonia Electrode Filling Solution, 60 mL	3 mL	each	44472-26
Ammonia Electrode Storage Solution	1 mL	500 mL	25412-49
Ammonia Ionic Strength Adjustor Powder Pillows	1	100/pkg	44471-69
Ammonia ISA Solution	1 mL	500 mL	28243-49
Ammonia (Nitrogen) Standard Solutions:			
10 mg/L NH_3-N	25 mL	500 mL	153-49
100 mg/L NH_3-N	25 mL	500 mL	24065-49
Water, deionized	100 mL	4 L	272-56

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Ammonia Electrode, BNC Connector	1	each	51927-00
Beaker, 50 mL, polypropylene	1	each	1080-41
Bottle, wash	1	500 mL	620-11
sension™*2* Portable pH/ISE Meter	1	each	51725-00
sension™*4* Laboratory pH/ISE Meter	1	each	51775-00
Stir Bar, 22.2 x 4.76 mm	1	each	45315-00
Select one based on available voltage:			
Stirrer, electromagnetic, 115 V, with stand and stir bar	1	each	45300-01
Stirrer, electromagnetic, 230 V, with stand and stir bar	1	each	45300-02

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Sulfuric Acid, concentrated	500 mL	979-49

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Air Gap Assembly	each	50253-00
Ammonia Electrode Membrane Modules	5/pkg	51927-11
Cylinder, graduated, glass	100 mL	508-42
Electrode Washer	each	27047-00

NITROGEN, AMMONIA IN WASTEWATER (0.1–10 mg/L NH_3-N)

USPEA accepted for reporting*

Calibration

Prepare ammonia standard working solutions of 10.0, 1.0 and 0.1 mg/L ammonia nitrogen from a 100-mg/L stock solution. Prepare the standards daily before use. Higher or lower concentration ranges (0.05–1400 mg/L NH_3-N) can be obtained by calibrating the meter with different standard solutions.

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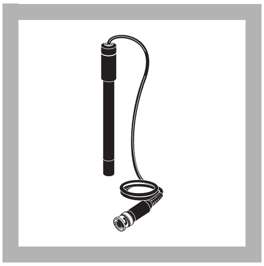
* Manual distillation is not required if comparability data on representative samples in company files show the distillation is not necessary. Manual distillation will be required to resolve any controversies.

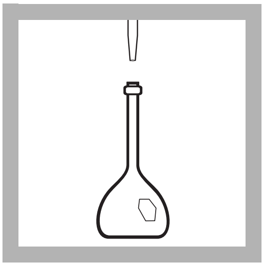
PROCEDURE



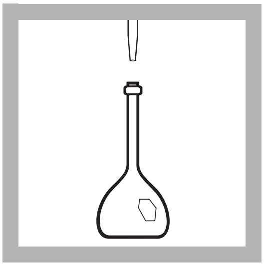
1. Assemble the electrode as described in *Section 1.2* on page *10*.

2. Rinse the electrode with deionized water. Place it in the Ammonia ISE storage solution with the sensor module on to condition for at least 15 minutes.

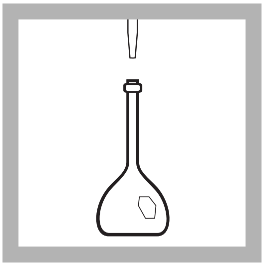
Note: *Before removing the electrode from the storage solution, the reading on the meter should be below 0.1 mg/L. This ensures the electrode is properly conditioned. After every hour of continuous use, place the electrode in the storage solution for 10 minutes to thoroughly recondition. Check with a 10 mg/L* NH_3*-N standard for accuracy and recalibrate if necessary.*



3. During the conditioning period prepare three standards. Make a 10-mg/L NH_3-N standard by pipeting 25 mL of 100-mg/L NH_3-N Standard into a 250-mL volumetric flask. Dilute to the mark with ammonia -free deionized water.



4. Prepare a 1.0-mg/L NH_3-N standard by pipeting 25 mL of the 10-mg/L standard into a 250-mL volumetric flask. Dilute to the mark with ammonia-free deionized water.

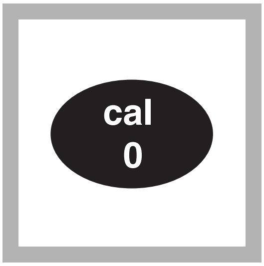


5. Prepare a 0.1-mg/L NH_3-N standard by pipeting 25 mL of the 1.0-mg/L NH_3-N standard into a 250-mL volumetric flask. Dilute to the mark with ammonia -free deionized water.

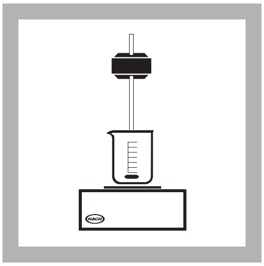
6. Connect the Ammonia ISE to the pH/ISE meter. Verify that BNC is selected in Setup 1 of the Setup menu.

***Note:** One BNC and one five-pin connector are on the back of the meter. Choose the BNC for the ammonia electrode.*

7. Turn the meter on. Press **ISE/mV** until the display shows **mg/L** or other chosen concentration units.

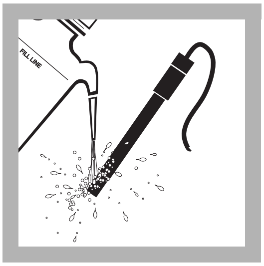


8. Press **CAL**. The display will show **CAL**, **?**, **mg/L,** and the active keys. The units will be flashing. Use the arrow keys to select the desired units, then press **ENTER**.



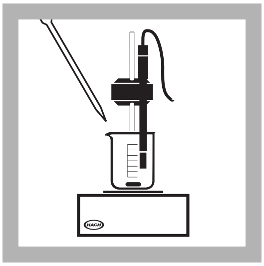
9. Transfer 100 mL of the 0.1-mg/L NH_3-N standard to a 150-mL beaker. Add a stir bar to the beaker. Place the beaker on a magnetic stirrer and stir at a moderate rate.

***Note:** Placing the electrode back into the storage solution prepares it for the next standard. Leave it in the storage solution for at least one minute before proceeding to the next standard.*



10. Remove the electrode from the storage solution. Rinse it with deionized water and blot dry. Place the electrode into the 0.1-mg/L NH_3-N standard.

***Note:** Be sure no air bubbles are trapped under the tip of the electrode.*



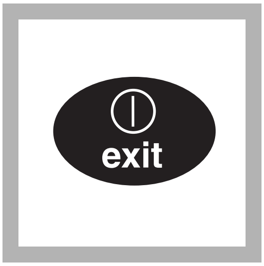
11. Pipet 2.0 mL of Ammonia ISA Solution into the standard. Immediately proceed to the next step.

12. The display will show **Standard 1?** and the value from the previous calibration. Press **ENTER** to accept the numerical value or use the number keys to change the value to match the concentration of the standard, then press **ENTER**.

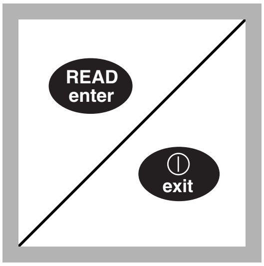
13. **Stabilizing...** will be displayed until the reading is stable. The display will show **Standard 2** and _ _ _ _ or the value of standard 2 from the previous calibration.

Repeat steps 9–14

14. Rinse the electrode with deionized water. Place it in the storage solution for one minute. Repeat *steps 9-14* for the 1.0- and 10-mg/L standards.



15. After the last standard is measured, press **EXIT**.

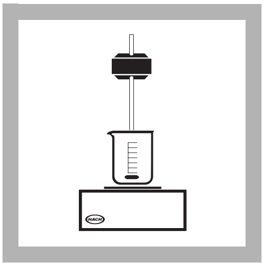


16. The display will show **Store?**. Press **ENTER** to store the calibration or **EXIT** to leave the calibration mode without storing the calibration values.

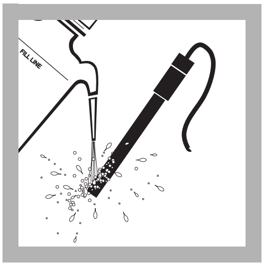
17. Press **REVIEW**. Use the Up arrow key to scroll to the second slope value. It should be -57 ±3 mV/decade. Press **EXIT** to return to measurement mode.

Note: *If the slope is not –57 ±3 mV/decade, recalibration may be necessary. If the slope is still incorrect after recalibration, replace the ammonia module.*

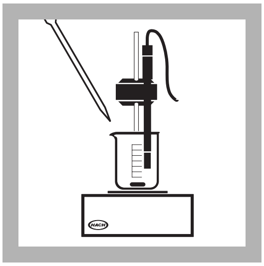
18. Remove the electrode from the last standard. Rinse it with deionized water, and place it in the storage solution.



19. Transfer 100 mL of sample to a 150-mL beaker. Add a stir bar to the beaker. Place the beaker on a magnetic stirrer and stir at a moderate rate.



20. Remove the electrode from the storage solution. Rinse it with deionized water and blot dry. Place it into the sample.



21. Pipet 2.0 mL of Ammonia ISA solution into the sample and proceed immediately to the next step.

Note: *At high pH, ammonia solutions lose ammonia to the atmosphere, lowering the concentration. It is important to take measurements as soon as possible after the solution is basic.*

Note: *For most wastewater samples, 1 mL of 10 N NaOH (or equivalent ISA) is sufficient to increase the pH above 11. If in doubt, check the pH with pH paper (Cat. No. 385-33) and add additional NaOH in 0.1 mL increments until the pH exceeds 11.*

Repeat steps 18–22

22. **Stabilizing...** will be displayed until the reading is stable. Record or store the measurement value.

Repeat *steps 18–22* for other samples.

Note: *Stabilization will take about 1 to 2 minutes for concentrations above 1.0 mg/L NH_3-N and longer for lower concentrations. Slow downward drift in concentration indicates probable loss of ammonia to the atmosphere. Record the highest value that is stable.*

Note: *For the distillation procedure in this manual, the capture volume after distillation and the sample volume before distillation is 250 mL, so the concentration from this step is the actual concentration.*

Note: *After every hour of continuous use the electrode should be placed in the storage solution for a 10 minute period for thorough reconditioning. Check with a 10 mg/L NH_3-N standard for accuracy and recalibrate if necessary.*

Sampling and Storage

Collect samples in glass or plastic containers of convenient size. Clean new bottles by washing with deionized or distilled water. Fill the sample bottle completely and stopper immediately. Analyze the sample as soon as possible.

Ammonia may be lost from samples at temperatures above 50 °C, so it is important to collect samples at less than 40 °C, or use a cooling coil between the bottle and sampling point if necessary.

If chlorine is present, treat the sample immediately with sodium thiosulfate. Add one drop of 0.1 N Sodium Thiosulfate Standard Solution for each 0.3 mg of chlorine present in a one liter sample.

If prompt analysis is not possible, preserve the sample with 0.8 mL of concentrated sulfuric acid per liter. Use a *sens**ion***™ pH meter to be sure the pH of the preserved sample is between 1.5 and 2. Some wastewater samples may require more sulfuric acid to achieve this pH. Store the sample at 4 °C. Samples preserved in this manner may be stored up to 28 days.

Before analysis, neutralize the sample to pH 7 with 5 N sodium hydroxide. Do not let the pH go above 10. Correct the test results for the volume addition.

Do not use mercuric chloride as a preservative because ammonia complexes with mercuric ions.

Accuracy

To verify measurement accuracy, run a standard addition spike on the sample. This provides more complete information about possible inaccuracies, because the measurement includes any interferences that may be present in the actual sample. The spike should roughly double the measured concentration without significantly diluting the sample.

To run a standard addition sample, use *Table 2* to prepare a spiked sample for analysis based on the measured sample concentration. To prepare the spiked sample, add 100 mL of the sample and the appropriate volume and concentration of standard to the distillation flask. Then proceed through the analysis, including the distillation. Generally, results from 90–110% recovery are considered acceptable.

Note: *If distillation was not required, and you want to run a standard addition, the following calculations are not correct. Use the calculations following Table 1 on page 24.*

Table 2 Spiking volumes

Measured Sample Concentration (mg/L)	Measured Sample Volume (mL)	Standard Concentration (mg/L)	Standard Volume (mL)
0.1–0.3	100	100	0.2
0.3–0.5	100	100	0.4
0.5–0.7	100	100	0.6
0.7–0.9	100	100	0.8
0.9–1.1	100	100	1.0
1.0–3.0	100	100	2.0
3.0–6.0	100	100	4.0

Calculate percent recovery as follows:

$$\%\ \text{Recovery} = \frac{100(X_s - X_u)}{K}$$

Where:

X_s = measured value for spiked sample in mg/L (*step 22*)
X_u = measured value for unspiked sample adjusted for dilution by the spike, in mg/L (*step 22*)
K = known value of the spike in the sample in mg/L

Calculations:

1. $$X_u = \frac{X_i \times V_u}{V_u + V}$$

Where:

X_i = measured value for spiked sample in mg/L
X_u = volume of separate unspiked portion in mL
V = volume of spike in mL

2. $K = \frac{C \times V}{V_u + V}$

Where:

C = concentration of standard used in spike in mg/L
V = volume of spike in mL
V_u = volume of separate distillate (100 mL)

3. Final calculation plugging in X_u and K:

$$\% \text{ Recovery} = \frac{100(X_s - X_u)}{K}$$

Example:
A 100-mL wastewater sample was analyzed and read 5.0 mg/L NH_3-N. As directed in *Table 2*, a 4.0-mL spike of 100-mg/L NH_3-N standard was added to the 100-mL sample, giving a final reading of 8.75 mg/L.

Calculate the percent recovery as follows:

1. $X_u = \frac{5.0 \text{ mg/L} \times 100}{100 + 4} = 4.8 \text{ mg/L}$

2. $K = \frac{100 \text{ mg/L} \times 4 \text{ mL}}{104 \text{ mL}} = 3.85 \text{ mg/L}$

3. $\%R = \frac{100 \times (X_s - X_u)}{K} = \frac{100 \times (8.75 - 4.80)}{3.85} = 103\% \text{ Recovery}$

Method Performance

Precision
In a single lab using a standard solution of 0.8 mg/L and two electrodes with a single *sension*™*2* meter, a single operator obtained a standard deviation of 0.01 mg/L ammonia nitrogen. Each electrode was exposed to seven test solutions and a default stability criteria was 0.5 mV/min. Between test solutions, the electrodes were rinsed and placed in the storage solution until a reading of <0.1 ppm was obtained.

Interferences

Volatile low molecular weight amines give a positive interference. Mercury and silver interfere by complexing with ammonia. Distillation prior to ammonia analysis removes all inorganic interferences that complex ammonia.

Comparison Table of USEPA and Hach Method

Feature	EPA Method 350.3	Hach Method 10001
Range	0.03–1400 mg/L NH_3-N	0.05–1400 mg/L NH_3-N
Preservation	2 mL H_2SO_4/L, 4 °C, 28 days	2 mL H_2SO_4/L, 4 °C, 28 days
Stock Solution(s)	1000 mg/L NH_3-N	1000 mg/L NH_3-N, 100 mg/L NH_3-N
Standard Solution(s)	10 mg/L NH_3-N	10 mg/L NH_3-N, 1 mg/L NH_3-N, 0.1 mg/L NH_3-N
Sample Size	100 mL	100 mL
NaOH Used	1 mL 10 N	1 mL 10 N
pH Note	pH of solution after NaOH addition must be >11	pH of solution after NaOH addition must be >11
NaOH Caution	Do not add NaOH before immersing the electrode	Do not add NaOH before immersing the electrode
Electrode	Hydrophobic gas permeable membrane	Hydrophobic gas permeable membrane
Electrode Internal Solution	Ammonium Chloride	Ammonium Chloride
Electrometer	pH meter with expanded mV scale of specific ion meter	pH meter with expanded mV scale of specific ion meter

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Ammonia Electrode Filling Solution, 60 mL	drops	each	44472-26
Ammonia Electrode Storage Solution	20 mL	500 mL	25412-49
Ammonia Nitrogen Standard Solution, 100 mg/L NH_3-N	100 mL	500 mL	24065-49
Water, deionized	100 mL	4 L	272-56
Ammonia ISA Solution	2 mL/100 mL sample	500 mL	28243-49

REQUIRED APPARATUS

Ammonia Electrode, combination, BNC	1	each	51927-00
Beaker, 150 mL, polypropylene	1	each	1080-44
Bottle, wash	1	500 mL	620-11
Flask, volumetric, Class A, 250 mL	1	each	14574-46
Pipet, volumetric, Class A, 25.00 mL	2	each	14515-40
Pipet, TenSette®, 1.0-10.0 mL	1	each	19700-10
sension™***4*** Laboratory pH/ISE Meter	1	each	51775-00
Stir Bar, 22.2 x 4.76 mm (7/16 x 3/16 in.)	1	each	45315-00
Select one based on available voltage:			
Stirrer, electromagnetic, 115 V, with stand and stir bar	1	each	45300-01
Stirrer, electromagnetic, 230 V, with stand and stir bar	1	each	45300-02

OPTIONAL REAGENTS

Ammonia Nitrogen Standard Solution, 1000 mg/L NH_3-N	1L	23541-53
pH Paper, 9.0–12.0 pH units	5 rolls/pkg	385-33
Sulfuric Acid, concentrated	500 mL	979-49

OPTIONAL APPARATUS

Air Gap Assembly	each	50253-00
Ammonia Electrode Membrane Modules	4/pkg	51927-11
Cylinder, graduated, glass	100 mL	508-42
Electrode Washer	each	27047-00
Pipet tips for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet tips for 19700-10 TenSette Pipet	50/pkg	21997-96
Pipet, Volumetric, Class A, 1.00 mL	each	14515-35
sension™***2*** Portable pH/ISE Meter	each	51725-00
TenSette® Pipet, 0.1-1.0 mL	each	19700-01

Method 10002

NITROGEN, AMMONIA KNOWN ADDITION METHOD (≥0.8 mg/L NH_3-N) For Wastewater

Standard Method 4500-NH3G USEPA Accepted for reporting wastewater analyses (with distillation)*

Because an accurate measurement requires that the concentration approximately double as a result of the addition, the approximate sample concentration must be known within a factor of three.

Use *Table 3* to determine how to dilute a 1000 mg/L NH_3-N stock solution to use as a spiking solution. Pipet the appropriate amount of 1000-mg/L NH_3-N standard into a 100-mL volumetric flask and dilute to the mark with ammonia-free water.

Make the spiking solution before beginning the procedure. Known addition is also a convenient check on the results of direct measurement.

Table 3 Making Spiking Solutions

Expected Sample Concentration (mg/L)	mL of 1000-mg/L NH_3-N	Standard Concentration
0.8–4.0	2	20 mg/L
2.5–7.5	5	50 mg/L
5–15	10	100 mg/L
12–50	25	250 mg/L
25–75	50	500 mg/L
50–150	100	1000 mg/L

Slope Determination

Determine the slope before performing standard additions of the sample. Use the 100 mg/L and 1000-mg/L NH_3-N stock solutions to determine the slope. Check the electrode occasionally to determine if it is functioning properly and to determine its exact slope value. The frequency of this operation depends on the harshness of your sample.

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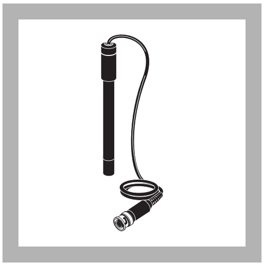
* Manual distillation is not required if comparability data on representative samples in company files show the distillation is not necessary. Manual distillation will be required to resolve any controversies.



1. Prepare the electrode as described in *Section 1.2* on page *10*.

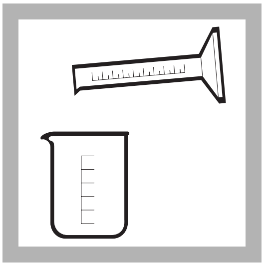
Note: *Only the Hach sens**ion**™**4** can perform Standard Additions.*

2. Rinse the electrode and place it in the Ammonia ISE Storage Solution to condition for at least 15 minutes.

Note: *Before removing the electrode from the storage solution, the reading on the meter should be below 0.1 mg/L. This ensures the electrode is properly conditioned. After every hour of continuous use, place the electrode in the storage solution for 10 minutes to thoroughly recondition. Check with a 10 mg/L NH_3-N standard for accuracy and recalibrate if necessary.*

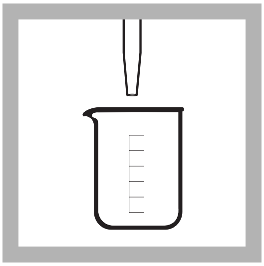
3. Connect the Ammonia ISE to the pH/ISE meter. Verify that BNC is selected in Setup 1 of the Setup menu.

Note: *Two BNC and two five-pin connectors are on the back of the meter. Choose a BNC for the ammonia electrode.*



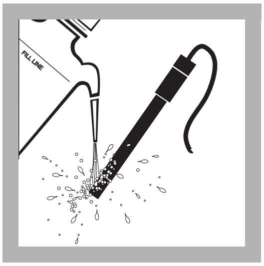
4. Accurately transfer 100 mL of NH_3-N free deionized water to a 150-mL beaker using a volumetric pipet or graduated cylinder. Add a stir bar to the beaker. Place the beaker on a magnetic stirrer and stir at a moderate rate.

Note: *Stirring at a constant, moderately fast rate speeds response and improves accuracy.*



5. Pipet 1.0 mL of 10 N NaOH solution into the sample.

Note: *The 10-mL Hach TenSette Pipet works conveniently for this addition, as well as the remainder of the additions in this procedure.*

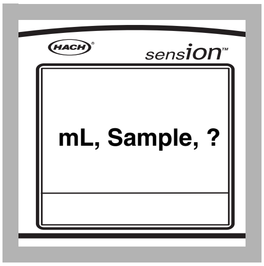


6. Remove the electrode from the storage solution. Rinse it with deionized water and blot dry. Place the electrode in the sample.

Note: *Be sure no air bubbles are trapped under the tip of the electrode. Remove bubbles by lightly tapping the electrode or by tilting the electrode to 20°.*

7. Turn the meter on. Press **STD ADDN**. Press the arrow keys until the display shows the desired units. Press **ENTER**.

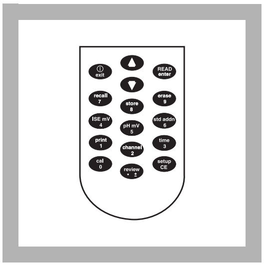
8. The display will show **Slope** and the slope value for the last calibration (default is –59.2 mV). Press **ENTER** to accept the numerical value or use the number keys to change the slope value. Press **ENTER** to accept the new value.



9. The meter will prompt for the sample volume (in mL). The display will show **mL**, **Sample**, **?**, and _ _ _ _. Use the number keys to enter the sample volume, then press **ENTER**.

10. The display will show **Stabilizing...** until the baseline reading is stable. The meter will then prompt for the standard volume. The display will show **mL**, **Standard**, **?**, and _ _ _ _.

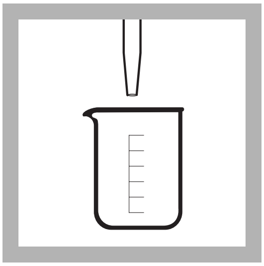
Note: *Place the electrode in the storage solution for at least one minute to prepare it for the next standard.*



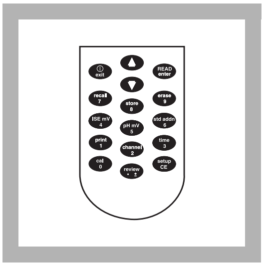
11. Use the number keys to enter the volume of standard to be used (for example, 1.0 mL). Press **ENTER**.

Note: *Obtain the standard concentration and volume from Table 4 on page 41 after estimating the sample concentration.*

12. The display will show **Standard**, **?**, and **mg/L** (or chosen units).



13. Add the volume of a known standard (listed in *Table 4*) to the beaker and proceed as quickly as possible through the rest of the procedure.



14. Use the number keys to enter the concentration of the standard used (for example, 1000 mg/L). Press **ENTER.**

15. **Sample+Standard** and **Stabilizing...** will be displayed until the reading is stable.

16. The meter will calculate and display the adjusted value for the original sample. Record or store this value as usual.

***Note:** When recalling data for standard additions,* **STANDARD ADDITONS** *will appear in the display with the data.*

Sampling and Storage

Collect samples in glass or plastic containers of convenient size. Clean new bottles by washing with deionized or distilled water. Fill the sample bottle completely and stopper immediately. Analyze the sample as soon as possible.

Ammonia may be lost more quickly from samples at temperatures above 50 °C, so it is important to collect samples at less than 40 °C, or use a cooling coil between the bottle and sampling point if necessary.

If chlorine is present, treat the sample immediately with sodium thiosulfate. Add one drop of 0.1 N Sodium Thiosulfate Standard Solution for each 0.3 mg of chlorine present in a one liter sample.

If prompt analysis is not possible, preserve the sample with 0.8 mL of concentrated sulfuric acid per liter. Use a *sension* pH meter to be sure the pH of the preserved sample is between 1.5 and 2. Some wastewater samples may require more sulfuric acid to achieve this pH. Store the sample at 4 °C. Samples preserved in this manner may be stored up to 28 days.

Before analysis, neutralize the sample to pH 7 with 5 N sodium hydroxide. Do not let the pH go above 10. Correct the test results for the volume addition.

Do not use mercuric chloride as a preservative as ammonia complexes with mercuric ions.

Accuracy

To verify measurement accuracy, run a standard addition spike on the sample. This provides more complete information about possible inaccuracies, because the measurement includes any interferences that may be present in the actual sample.

The spike should roughly double the measured concentration without significantly diluting the sample. To run a standard addition sample, use *Table 4* to determine the concentration and volume of standard to spike your sample. It is important that the volume of sample transferred is accurate. Simply add the amount and concentration specified in *Table 4* to the sample while performing the standard addition method on the sample. Do not allow the sample to stand too long before spiking, as ammonia will be lost to the atmosphere. Then proceed with the calculations. Generally, results from 90-110% recovery are considered acceptable.

Note: *If distillation was not required, and you want to run a standard addition, the following calculations are not correct. Use the calculations following Table 1 on page 24.*

Table 4 Spiking Volumes For Known Additions

Measured Sample Concentration (mg/L)	Measured Sample Volume (mL)	Standard Concentration (mg/L)	Standard Volume (mL)
0.8–1.0	100	100	1.0
1–3	100	100	2.0
3–6	100	100	4.0
6–9	100	100	8.0
9–12	100	100	10.0
12–20	100	1000	2.0
20–40	100	1000	4.0
40–60	100	1000	6.0
60–75	100	1000	8.0

Calculate percent recovery as follows:

$$\%\ \text{Recovery} = \frac{100(X_s - X_u)}{K}$$

Where:

X_s = measured value for spiked sample in mg/L
X_u = measured value for unspiked sample adjusted for dilution by the spike, in mg/L
K = known value of the spike in the sample in mg/L

Calculations

1. $$X_u = \frac{X_i \times V_u}{V_u + V}$$

Where:

X_i = measured value of unspiked sample in mg/L
V_u = volume of separate unspiked portion in mL
V = volume of spike in mL

2. $$K = \frac{C \times V}{V_u + V}$$

Where:

C = concentration of standard used in spike in mg/L
V = volume of spike in mL
V_u = volume of separate portion before spike in mL

3. Final calculation plugging in X_u and K:

$$\%\ \text{Recovery} = \frac{100(X_s - X_u)}{K}$$

Example:
A sample was analyzed and read 5.0 mg/L NH_3-N. As directed in *Table 4*, a 4.0-mL spike of 100-mg/L NH_3-N standard was added to another 100-mL sample, giving a final standard addition result of 8.75 mg/L.

Calculate the percent recovery as follows:

1. $$X_u = \frac{5.0\ \text{mg/L} \times 100\ \text{mL}}{100\ \text{mL} + 4\ \text{mL}} = 4.81\ \text{mg/L}$$

2. $$K = \frac{100\ \text{mg/L} \times 4\ \text{mL}}{100\ \text{mL} + 4\ \text{mL}} = 3.85\ \text{mg/L}$$

3. $$\%R = \frac{100 \times (X_s - X_u)}{K} = \frac{100 \times (8.75 - 4.81)}{3.85} = 102.3\ \%\ \text{Recovery}$$

Method Performance

Precision

In a single lab using a standard solution of 5.0 mg/L and two electrodes with a single *sension4* meter, a single operator obtained a standard deviation of 0.08 mg/L ammonia nitrogen. Each electrode was exposed to seven test solutions and a default stability of 0.5 mV/min. Between test solutions, the electrodes were rinsed and placed in storage solution until a reading of 0.1 mV was obtained.

Interferences

Volatile low molecular weight amines give a positive interference. Mercury and silver interfere by complexing with ammonia. Distillation prior to ammonia analysis removes all inorganic interferences, such as metals which complex ammonia.

Comparison of Standard Method and Hach Method

Feature	EPA Method 350.3	Hach Method 10001
Range	≥0.8 mg/L NH_3-N	≥0.8 mg/L NH_3-N
Preservation	2 mL H_2SO_4/L, 4 °C, 28 days	2 mL H_2SO_4/L, 4 °C, 28 days
Stock Solution(s)	1000 mg/L NH_3-N	1000 mg/L NH_3-N
Sample Size	100 mL	100 mL
NaOH Used	1 mL 10 N	1 mL 10 N
Electrode	Hydrophobic gas permeable membrane	Hydrophobic gas permeable membrane
Electrode Internal Solution	Ammonium Chloride	Ammonium Chloride
Electrometer	pH meter with expanded mV scale of specific ion meter	pH meter with expanded mV scale of specific ion meter
Concentration Ratio Table	Table 4500-NH_3 IV	Table 4500-NH_3 IV encoded in software

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Ammonia Electrode Filling Solution	3 mL	50 mL	44472-26
Ammonia Electrode Storage Solution	5 mL	500 mL	25412-49
Ammonia Nitrogen Standard, 1000 mg/L NH_3-N	varies	1 L	23541-53
Sodium Hydroxide Solution, 10 N	10 mL	500 mL	25450-49
Water, deionized	100 mL	4 L	272-56

REQUIRED APPARATUS

Ammonia Electrode	1	each	51927-00
Beaker, 50 mL, polypropylene	1	each	1080-41
Bottle, wash		500 mL	620-11
Cylinder, graduated, 100-mL	1	each	508-42
sension™*4* Laboratory pH/ISE Meter	1	each	51775-00
Stir Bar, 22.2 x 4.76 mm	1	each	45315-00
TenSette® Pipet, 1.0-10.0 mL	1	each	19700-10
Pipet tips for 19700-10 TenSette Pipet		50/pkg	21997-96
Select one based on available voltage:			
Stirrer, electromagnetic, 115 V, with stand and stir bar	1	each	45300-01
Stirrer, electromagnetic, 230 V, with stand and stir bar	1	each	45300-02

OPTIONAL REAGENTS

pH Paper, pH 9.0-12.0	5 rolls/pkg	385-33
Sulfuric Acid, concentrated	500 mL	979-49

OPTIONAL APPARATUS

Ammonia Electrode Membrane Modules	4/pkg	51927-11
Electrode Washer	each	27047-00
Pipet, Volumetric, Class A	1.00 mL	14515-35
Pipet, Volumetric, Class A	10.00 mL	14515-38
Pipet, Volumetric, Class A	100.0 mL	14515-42
TenSette® Pipet, 0.1-1.0 mL	each	19700-01
Pipet tips for 19700-01 TenSette Pipet	50/pkg	21856-96
sension™*2* Portable pH/ISE Meter	each	51725-00

Method 10007

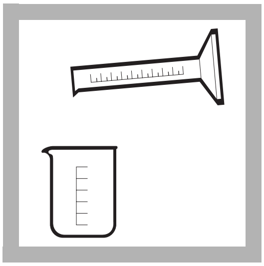
MEASURING LOW LEVELS OF AMMONIA

For samples below 0.5 mg/L NH_3-N

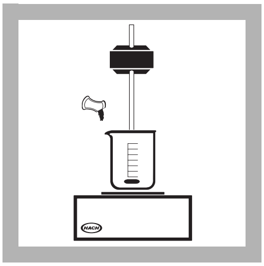
The electrode response is nonlinear below 0.5 mg/L NH_3-N (3.6 X 10^{-5} M). Low ammonia concentrations in the nonlinear range can be determined by plotting a calibration curve, or by using the *sension*™*2* or *sension*™*4* pH/ISE Meter. Use several standards per decade to increase accuracy. Repeat or check the calibration more often in this less stable, less reproducible region. Use one of the calibration standards as a frequent check on the stability of the calibration.

The method below measures all the standards in one beaker, with spikes of ammonia standard added to incrementally raise the ammonia level. Response time will be slightly longer in the low-level range. If using a Hach *sension4* meter, set the stability criteria to 0.1 mV/min. Stirring at a constant rate is important and using a chart recorder helps visualize the change in the potential.

Procedure

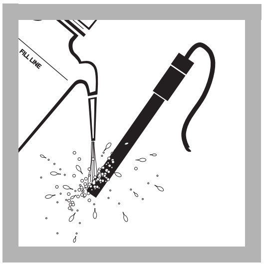


1. Fill a carefully cleaned 600-mL beaker with 400 mL of deionized ammonia-free water. Add a stir bar.

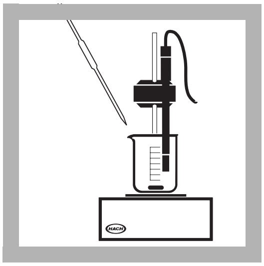


2. Add the contents of 8 powder pillows (0.8 g) of Ammonia ISA. Place the beaker on a magnetic stirrer and stir at a moderate rate.

***Note:** If the 400 mL of <u>sample</u> requires more than 8 powder pillows of ISA to raise the pH above 11 (solution turns blue) run the calibration with the amount of ISA necessary to accomplish that. Before calibrating, verify one ISA powder pillow added to 50 mL of sample results in a blue color.*

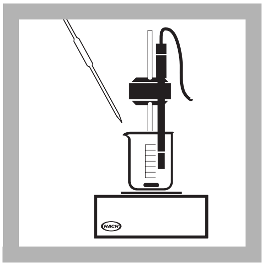


3. Rinse the electrode thoroughly with deionized water and place it into the beaker.

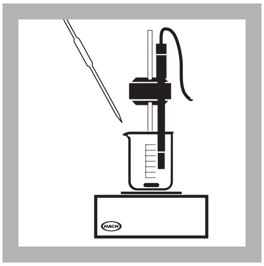


4. Add 0.20 mL of 100-mg/L NH_3-N Standard Solution (makes a 0.05 mg/L solution). Wait for the potential to stabilize; this may take up to five minutes. Record the potential, or enter the concentration into an ISE meter calibration program.

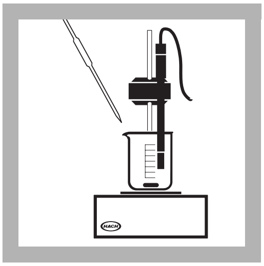
***Note:** The TenSette Pipet is useful for the repetitive additions used in this method.*



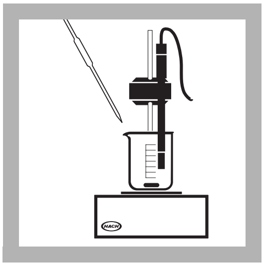
5. Add 0.10 mL of 100-mg/L NH_3-N Standard Solution (makes a 0.075 mg/L solution). Record the potential when it stabilizes, or enter the concentration into an ISE meter calibration program.



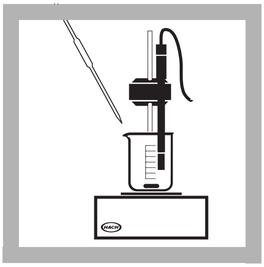
6. Add 0.10 mL of 100-mg/L NH_3-N Standard Solution (makes a 0.10 mg/L solution). Record the potential when it stabilizes, or enter the concentration into an ISE meter calibration program.



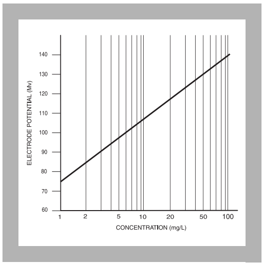
7. Add 0.20 mL of 100-mg/L NH_3-N Standard Solution (makes a 0.15 mg/L solution). Record the potential when it stabilizes, or enter the concentration into an ISE meter calibration program.



8. Add 0.60 mL of 100-mg/L NH_3-N Standard Solution (makes a 0.30 mg/L solution). Record the potential when it stabilizes, or enter the concentration into an ISE meter calibration program.

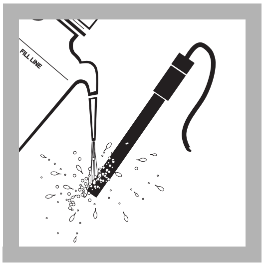


9. Add 1.20 mL of 100-mg/L NH_3-N Standard Solution (makes a 0.60 mg/L solution). Record the potential when it stabilizes, or enter the concentration into an ISE meter calibration program. Store the electrode in Ammonia Electrode Storage Solution until sample measurement.

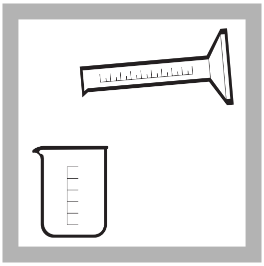


10. Enter the calibration into the meter. If you do not have a meter, plot the concentration vs. potential on semi-logarithmic graph paper. The concentration goes on the log axis, the potential goes on the linear axis.

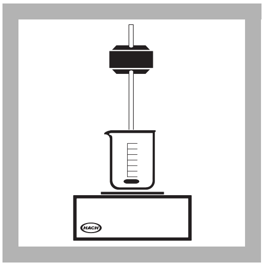
Sample Analysis



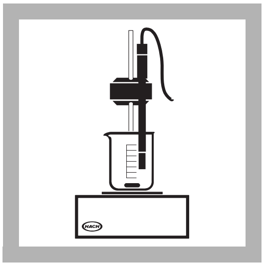
1. To determine the sample concentration, rinse the electrode and blot it dry.



2. Add at least 50 mL of sample to a 100-mL beaker. Add the appropriate amount of ISA for the sample volume (one ISA Powder Pillow for every 50 mL or the amount used in *step 2* to adjust for the sample pH).



3. Place stir bar in the sample beaker and stir at a moderate rate on an electromagnetic stirrer.



4. Place the electrode in the sample. Record the potential when it is stable. Read the concentration from the ISE meter or the calibration curve.

REQUIRED REAGENTS AND APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Ammonia Electrode Filling Solution	varies	59 mL	44472-26
Ammonia Electrode Storage Solution	20 mL	500 mL	25412-49
Ammonia Ionic Strength Adjustor Powder Pillows	varies	100/pkg	44471-69
Ammonia (Nitrogen) Standard Solution, 100 mg/L NH_3-N	2.4 mL	500 mL	24065-49
Water, deionized	varies	4 L	272-56
Ammonia Electrode, BNC	1	each	51927-00
Beaker, 50 mL, polypropylene	1	each	1080-41
Bottle, wash, 500 mL	1	each	620-11
Pipet Tips, for 19700 TenSette® Pipet	varies	50 pkg	21856-96
*sens***ion**™*2* Portable pH/ISE Meter	1	each	51725-00
*sens***ion**™*4* Laboratory pH/ISE Meter	1	each	51775-00
Stir Bar, 22.2 x 4.76 mm	1	each	45315-00
TenSette® Pipet, 0.1-1.0 mL	1	each	19700-01
Select one based on available voltage:			
Stirrer, electromagnetic, 115 V, with stand and stir bar	1	each	45300-01
Stirrer, electromagnetic, 230 V, with stand and stir bar	1	each	45300-02

SECTION 4 ELECTRODE MAINTENANCE

4.1 Storing the Electrode

4.1.1 Short-term Storage

Between measurements or for low-level measurements, keep the electrode tip immersed in Ammonia Electrode Storage Solution. If the storage solution is not available, use pH 4 buffer. For low-level measurements, keep the electrode in a pH 4 buffer between measurements.

Do not store the electrode overnight in pH 4 buffer or storage solution.

4.1.2 Long-term Storage

Overnight to One-Week Storage
Immerse the electrode tip in a 0.1 M or 1000 mg/L standard. **Do not add ISA.**

Longer than One Week
Disassemble the electrode completely and rinse the inner body, outer body, and bottom cap with deionized water. Dry and reassemble the electrode without filling solution or a membrane. When reassembling, follow the instructions in *Section 1.2* on page *10*.

If the electrode is accidently left in the air and erratic results are observed, the space between the inside of the membrane and the sensing element may be dry. If this occurs, withdraw the glass electrode from the membrane by gently pulling back on the cables. New filling solution will flow into the space.

After storage, condition the electrode for at least one hour.

SECTION 5 ELECTRODE CHARACTERISTICS

5.1 Theory of Operation

The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from the electrode internal solution. Dissolved ammonia in the sample solution diffuses through the membrane until the partial pressure of ammonia is the same on both sides of the membrane. In any given sample, the partial pressure of ammonia will be proportional to its concentration. Ammonia diffusing through the membrane dissolves in the internal filling solution and, to a small extent, reacts reversibly with water in the filling solution:

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$$

The relationship between ammonia, ammonium ion, and hydroxide is given by the following equation:

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = \text{constant}$$

The internal filling solution contains ammonium chloride at a sufficiently high level so that the ammonium ion concentration can be considered fixed. Thus:

$$[OH^-] = [NH_3] \times \text{constant}$$

The potential of the electrode sensing element with respect to the internal reference element is described by the Nernst equation:

$$E = E_0 - S \log [OH^-]$$

Where:

E = measured electrode potential
E_o = reference potential
OH^- = hydroxide concentration in solution
S = electrode slope (–59.2 mV/decade)

Since the hydroxide concentration is proportional to the ammonia concentration, electrode response to ammonia is also Nernstian.

$$E = E_0 - S \log [NH_3]$$

The reference potential, E_o, is partly determined by the internal reference element which responds to the fixed level of chloride in the internal filling solution.

5.2 Electrode Response

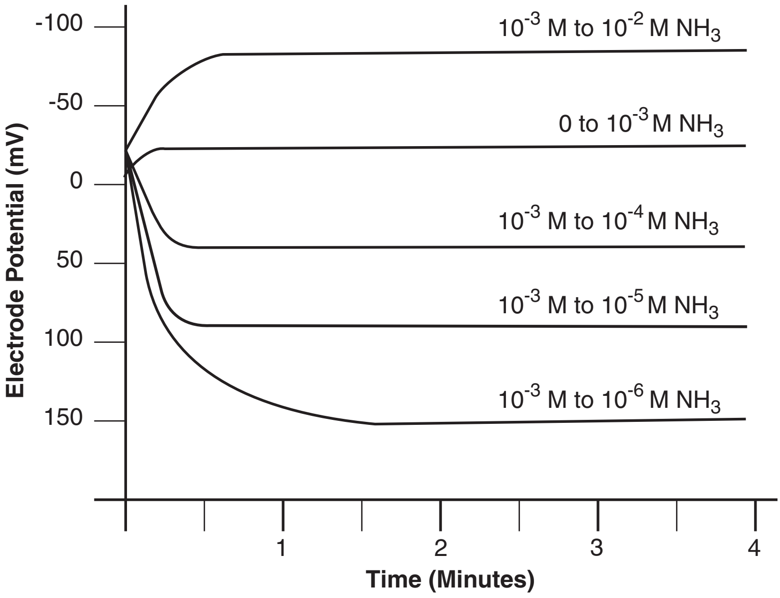
The electrode exhibits good time response (95% response in one minute or less) for ammonia concentrations above 4 x 10^{-5} M (0.68 mg/L NH_3 or 0.56 mg/L N). Below this value response times are longer, and ammonia absorption from the air may become a source of error. Above 1 M, ammonia is rapidly lost to the air. Samples above 1 M ammonia concentration can be diluted before measurement. *Figure 3* shows response time of the ammonia electrode to step changes in ammonia concentration.

For solutions low in ammonia but high in total ionic strength, prepare a calibration solution with a composition similar to the sample. Accurate measurement requires these conditions:

- Allow adequate time for electrode stabilization. Longer response time will be needed at low levels.
- Stir standards and samples at a uniform rate.

When plotted on semilogarithmic paper, electrode potential response as a function of ammonia concentration is a straight line with a slope of about -58 mV per decade.

Figure 3 **Response to Step Changes**



5.3 Reproducibility

Reproducibility is limited by factors such as temperature fluctuations, drift, and noise. Within the operating range of the electrode, reproducibility is independent of concentration. With calibration every hour, measurements to ±2% can be obtained.

5.4 Temperature Effects

A change in temperature will cause electrode response to shift and change slope. *Table 5* lists the variation of theoretical response with temperature. At 10^{-3} M, a 1 °C temperature change causes a 2% error. Samples and standards should be at the same temperature (for convenience, room temperature). As the temperature increases, so does the ammonia loss.

Table 5 Theoretical Slope vs. Temperature

Temperature (°C)	Slope (mV)
0	-54.20
5	-55.20
10	-56.18
15	-57.17
20	-58.16
25	-59.16
30	-60.15
35	-61.14
40	-62.13

5.5 Effect of Ionic Strength

Water vapor is a potential electrode interference. Water can move across the membrane as water vapor, changing the concentration of the internal filling solution under the membrane. Such changes will be seen as electrode drift. Water vapor transport across the membrane is not a problem if:

1. The total level of dissolved species in solution (osmotic strength) is below 1 M.

2. Electrode and sample temperatures are the same.

Adding ammonia ISA to samples of low osmotic strength automatically adjusts them to the correct level. Samples with osmotic strengths above 1 M should be diluted before measuring ammonia levels below 10^{-5}. Samples with high osmotic strengths (above 1 M) and low ammonium levels (below 10^{-5} M) can be measured without dilution if the osmotic strength of the internal filling solution is adjusted. To adjust the internal filling solution, add 4.25 g solid $NaNO_3$ to each 100 mL internal filling solution.

5.6 Interferences

Volatile amines interfere with electrode measurement. Most gases do not interfere as they are converted to ionic form in basic solutions. Ionic species cannot cross the gas-permeable membrane and are not direct electrode interferences. However, the level of ions in solution can change the solubility of ammonia. Standards and samples should have about the same level of ions and dissolved species.

Ammonia forms metal complexes with a number of metal ions: mercury, silver, copper, gold, nickel, cobalt, cadmium, and zinc. At pH 11, most of these metals form hydroxide complexes or precipitate. When hydroxide is present at the 0.1 M level and the ammonia concentration is below 10^{-3} M, only mercury will appreciably complex ammonia. The total ammonia level of the sample will be measured if the mercury in the sample is preferentially bound to some other species. Iodide is recommended for this purpose, since it forms a soluble mercury complex at all pH levels. Use of Ammonia ISA inhibits the formation of some common metal complexes in the sample because it contains a high concentration of hydroxide ion.

5.7 Ammonium Ion

When ammonia is dissolved in water it reacts with hydrogen ion to form ammonium ion:

$$NH_3 + H_30^+ \Leftrightarrow NH_4^+ + H_20$$

The relative amount of ammonia and ammonium ion is determined by the solution pH. In acid solutions, where hydrogen ion is readily available, virtually all the ammonia is converted to ammonium ion. At a pH of about 9.3, half of the ammonia will be in the form of ammonium.

Theoretically, it is possible to calculate the ratio of ammonia to ammonium ion, if the pH is known. The equilibrium constant of the reaction is:

$$NH_4^+ + H_2O \Leftrightarrow NH_3 + H_3O^+$$

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

$$pKa = \log_{10}(Ka) = -\log_{10}\left(\frac{[NH_3][H_3O^+]}{[NH_4^+]}\right)$$

$$\text{Since: } -\log_{10}([H_3O^+]) = pH\text{ , } pK_a = -\log_{10}\left(\left[\frac{NH_3}{NH_4^+}\right]\right) + pH$$

$$\log_{10}\left(\left[\frac{NH_3}{NH_4^+}\right]\right) = pH - pK_a$$

$$\frac{[NH_3]}{[NH_4^+]} = 10^{(pH - pK_a)}$$

at 25°, $\mu = 0.1$ and pK = 9.3. The ratio of ammonium to ammonia is given by:

$$\frac{[NH_4{}^+]}{[NH_3]} = (K10 - pH) = 10^{9.3 - pH}$$

5.8 Partial Pressure of Ammonia

As discussed in *Theory of Operation*, the ammonia electrode responds to the partial pressure of dissolved ammonia gas. The partial pressure of dissolved ammonia gas is related to the ammonia concentration by Henry's Law:

$$Kh = \frac{NH_3\text{ aqueous}}{pNH_3} = 56\text{ moles/liter} - \text{atm } (25\ ^\circ C)$$

The Henry's Law constant, Kh, varies both with temperature and the level of dissolved species. For example, the constant is about 20% lower in 1 M NaCl than in distilled water.

To keep the Henry's Law constant close to the same value, standards and samples should contain the same level of dissolved species and be about the same temperature.

5.9 Electrode Life

A membrane will last from one week to several months depending on usage (membrane failure is characterized by a shift in electrode potential, drift, and poor response).

Membrane failure may be apparent on visual inspection as dark spots or discoloration of the membrane.

SECTION 6 TROUBLESHOOTING

This section contains a series of decision trees based on the symptoms that result from a problem or a combination of problems. The symptoms are listed below along with the page number of the decision tree that will help solve the problem(s) that may cause the symptom.

Before using a decision tree, check the pH bulb per *Section 6.1*

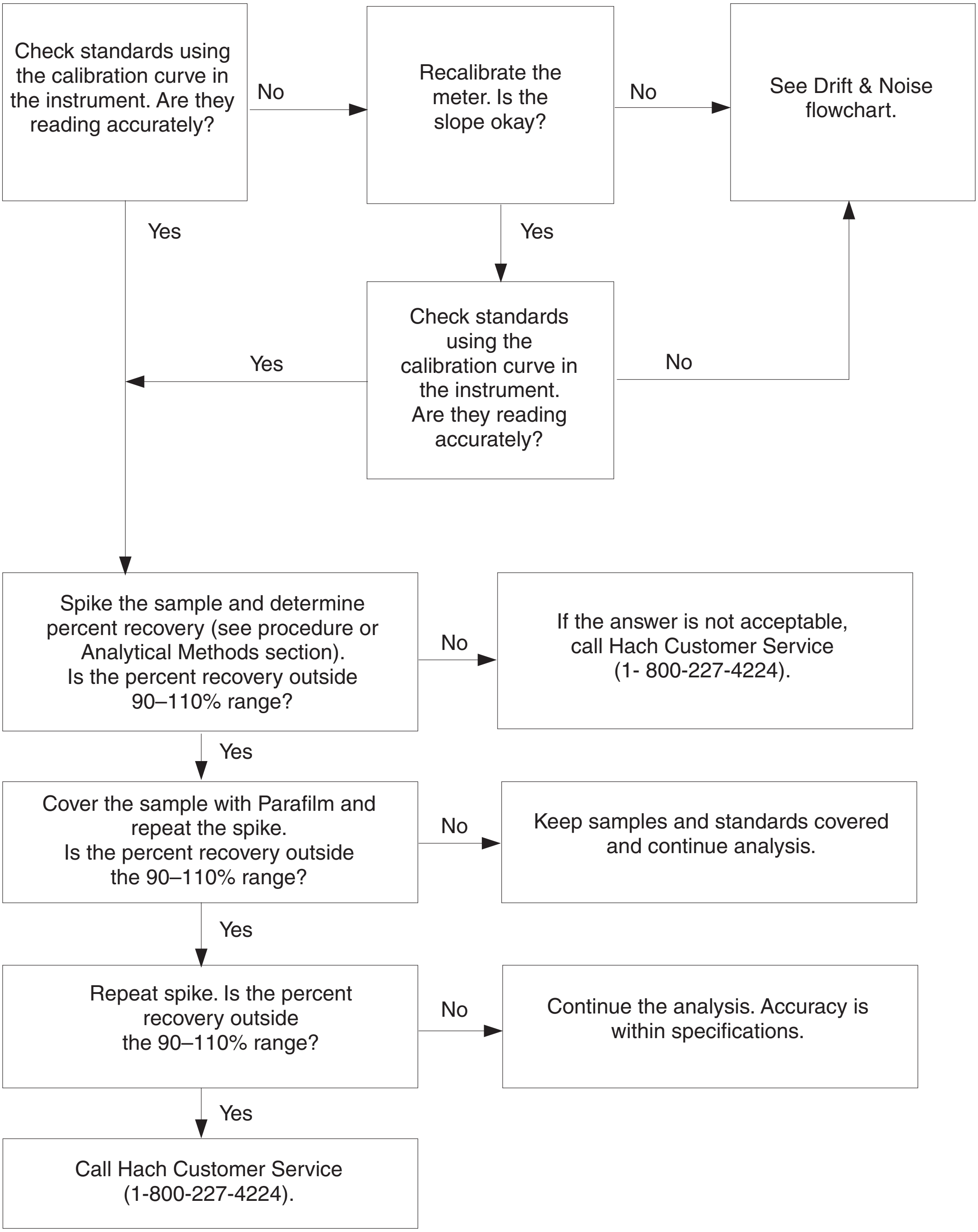
Symptom	Page
Inaccurate readings	60
Imprecise readings	60
Low slope or no slope	61
Drift in the meter reading	63
Slow response time	63
Error messages or no key response	See meter manual

6.1 Checking pH Bulb Function

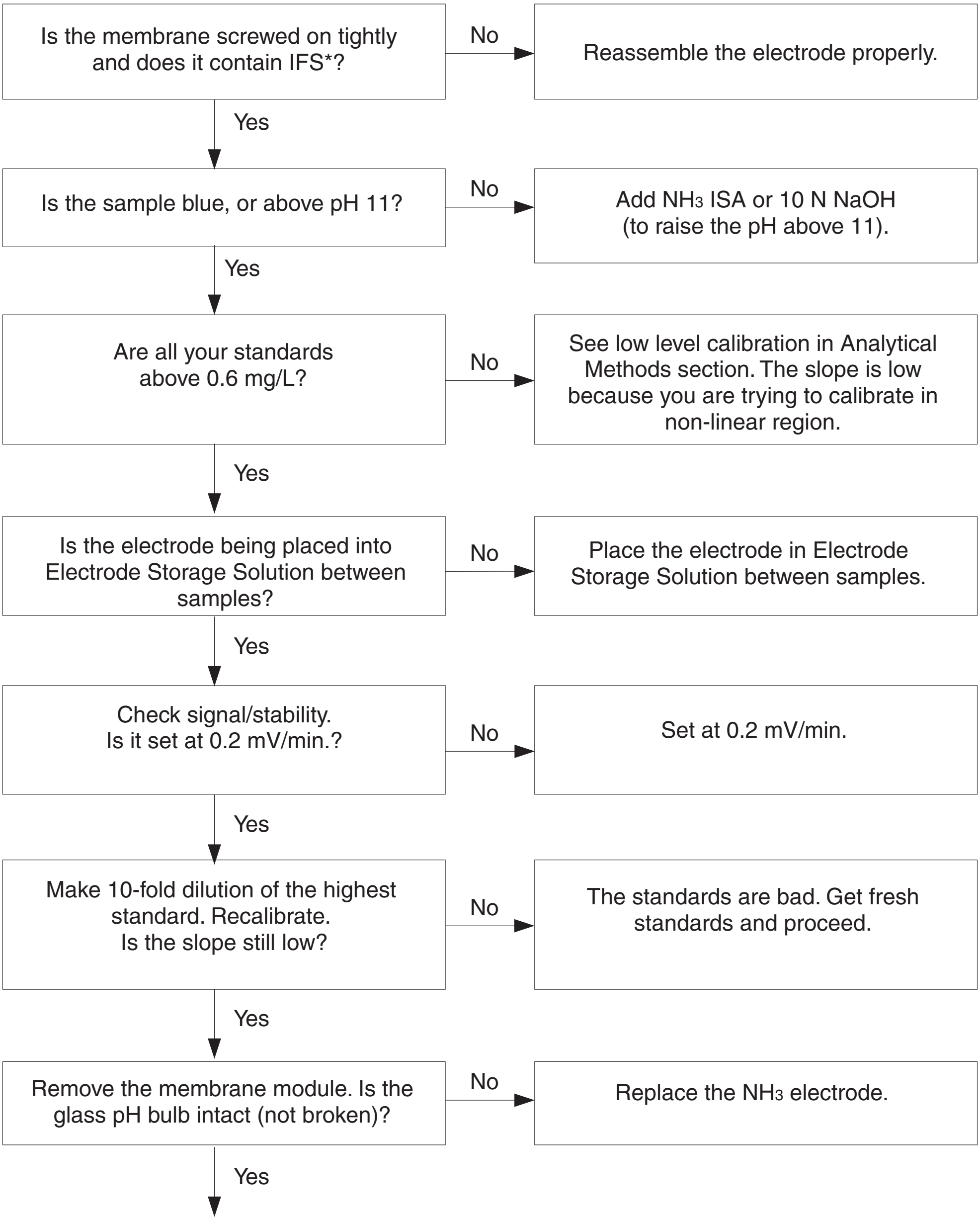
1. Unscrew the Ammonia Membrane Module and remove it.
2. Rinse the electrode with deionized water.
3. Use pH 4 and 7 buffers (add 0.5 gram sodium chloride per 50 mL of buffer). Carefully immerse the pH bulb in the pH 4 buffer. Record the mV reading.
4. Immerse the pH bulb in the pH 7 buffer. Record the mV reading.
5. Subtract the pH 7 mV reading from the pH 4 mV reading. Divide the difference by 3. The answer should be -57 ±3 mV.

6.2 Decision Trees

Symptom: Accuracy or precision is in question.



Symptom: Low Slope



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*Internal Filling Solution

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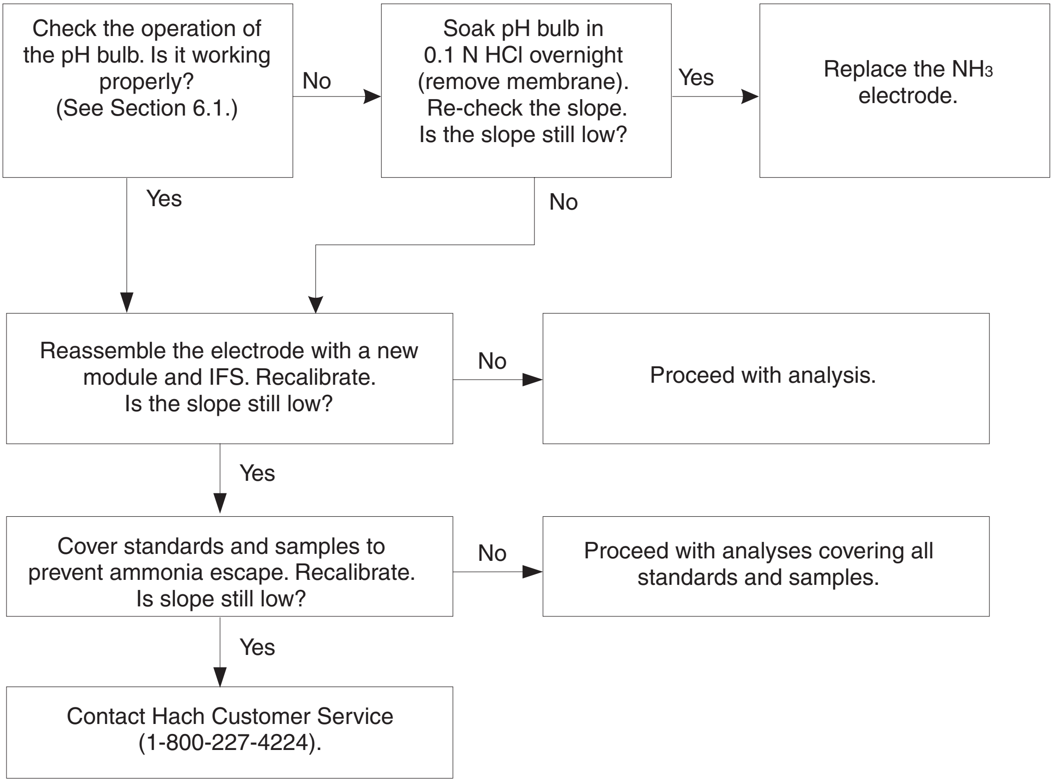
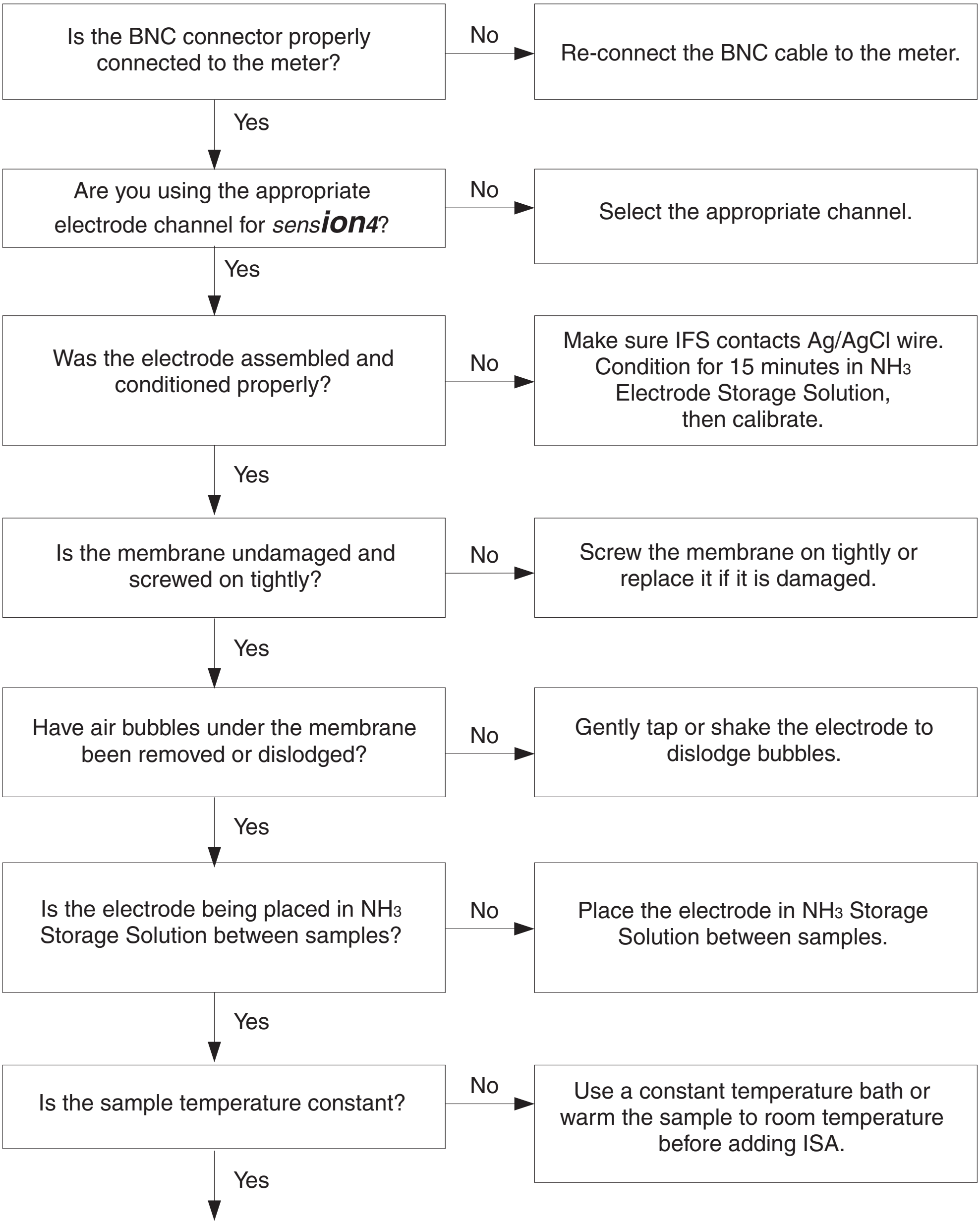


Symptom: The meter reading is slow, drifting, jumpy or dramatically offset.



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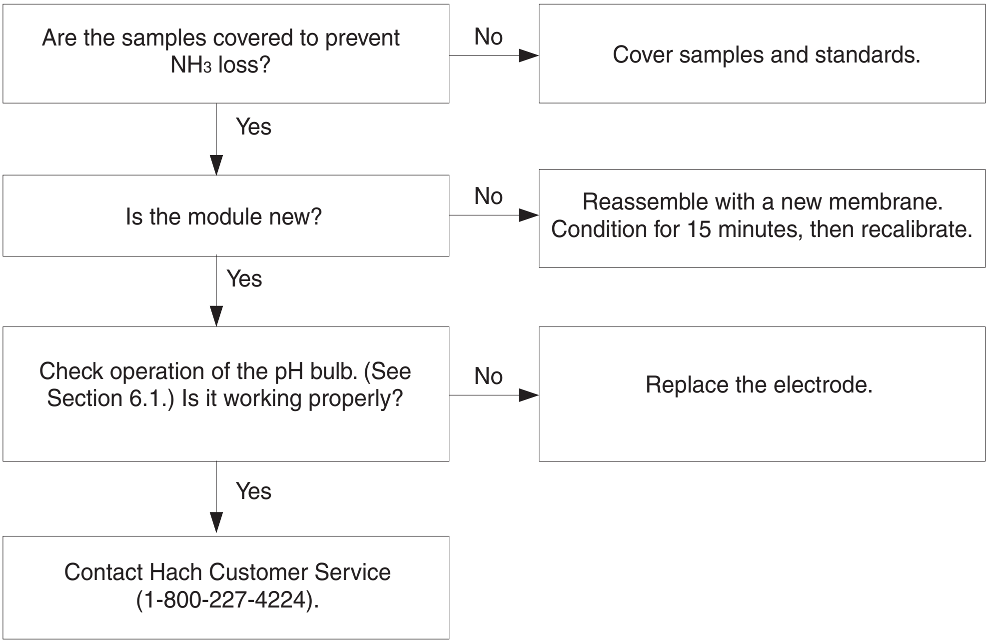

*Electrodes left in samples for more than 15 minutes will show some drift due to ammonia gas loss. To decrease drift, use an air gap assembly. (This will increase response time.)

ELECTRODE SERVICE REQUEST QUESTIONNAIRE

If the electrode still malfunctions after following the troubleshooting guide, our service representatives want to help solve any problems as quickly as possible. To help them with this process, please have the following information when calling:

1. The electrode catalog number.
2. Model of the meter the electrode is being used with.
3. Complete lot code of the electrode.
4. Date the electrode was purchased.
5. How long the electrode has been in use.
6. How often the electrode is being used.
7. Types of samples being tested.
8. Has ISA been used in all samples and standards?
9. How the electrode is stored between samples.
10. Slope of the electrode after a typical calibration.
11. If the electrode is new, how was it conditioned?
12. Any maintenance that has been done on the electrode.
13. Any long-term storage periods and how it was stored.
14. Does a visual inspection show any cracks, discoloration, broken wires, crystals, etc.
15. Description of the problem.

GLOSSARY

Acid —A chemical compound that contributes hydrogen ions (H^+) to an aqueous solution or causes the pH to be less than 7.0.

Acidic—A solution or system with a pH less than 7.0.

Activity—The measure of work performed by an ion as it moves through a system. The activity is dependent upon the concentration of all ions in the system and the charge associated with the ion.

Alkali—A solution or system with a pH greater than 7.0.

Alkalinity—Capacity of water to accept hydrogen (H^+) ions. Characteristic of the presence of carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), and hydroxyl (OH^-) ions.

Anion—A negatively charged ion (i.e., NO_3^-, Cl^-).

Base—A compound that contributes hydroxide ions (OH^-) to an aqueous solution or causes the pH to be greater than 7.0.

Buffer— 1. A compound, mixture of compounds, or solution which when added to a system changes the pH to a specified, known value.

2. The ability of a solution or system to resist change in pH when either an acid or a base is added.

Buffering Capacity—A measurement of the amount of acid or base which can be added to a solution before the pH changes.

Cation—A positively charged ion (i.e., NH_4^+, Ca_2^+).

Chelating Agents—Organic compounds that can withdraw ions from solution, forming complexes in which the species removed is not available for measurement. The complex formed may or may not be insoluble.

Decade—Any two standards with a concentration ratio of 10; i.e.,

$$\frac{\text{Concentration of higher standard}}{\text{Concentration of lower standard}} = 10$$

Dilution Factor—A numerical value by which results must be multiplied in order to obtain the actual value of the sample. For example, if one mL of sample is diluted to 10 mL then the result obtained must be multiplied by 10 to obtain the value for the sample before dilution.

Electrolyte—A solution comprised of dissolved ions used to facilitate electrical conductance and ionic transport. In electrochemistry, the composition is usually potassium chloride (KCl), sodium chloride (NaCl), ammonium chloride (NH_4Cl), or ammonium sulfate ($(NH_4)_2SO_4$).

Inert—Does not react with other substances.

Ion—An atom, group of atoms or molecule that is electrically charged as the result of gaining or losing electrons. An ion resulting from the gain of electrons becomes negative (anion); an ion resulting from the loss of electrons becomes positive (cation).

Ionic Strength Adjustor—A powder or solution that changes the ionic strength of a sample and adjusts the pH. Typically used to mask or moderate common interferences while adjusting the pH to the optimum operating range.

ISA—See Ionic Strength Adjustor.

Linear Response Region—The operating range of the electrode where the calibration curve is a straight line.

Nonlinear Response Region—The operating range of the electrode where the calibration is not a straight line. It is usually at the lowest concentration range of the electrode

pH—A relative numerical measurement of the acidic, neutral, or alkali nature of a solution or system. Mathematically defined as the negative log of the hydrogen ion concentration.

Potential—The capacity of a system to perform work. When two ions of opposite charge are separated, a potential develops from the tendency of the ions to come together. Each ion would need to exert work to come together. The amount of work that each ion would need to exert to come together is the potential.

Salt—An ionic compound.

TISAB—Total Ionic Strength Adjustor Buffer; See Ionic Strength Adjustor.

GENERAL INFORMATION

At Hach Company, customer service is an important part of every product we make.

With that in mind, we have compiled the following information for your convenience.

CONVERSION TABLES

Table 6 Ammonia Concentration Conversions

Moles/L (M)	mg/L NH_3 (ppm)	mg/L NH_3-N (ppm)	mg/L NH_4^+ (ppm)
1×10^{-1}	1700	1400	1800
1×10^{-2}	170	140	180
1×10^{-3}	17	14	18
1×10^{-4}	1.7	1.4	1.8
1×10^{-5}	0.17	0.14	0.18
1×10^{-6}	0.017	0.014	0.018

Table 7 Ammonia Unit Conversions

To convert from...	To...	Multiply by...
moles/L (M)	mg/L NH_3	17,000
mg/L NH_3	mg/L NH_3^--N	0.822
mg/L NH_3^--N	mg/L NH_4^+	1.29
mg/L NH_3	moles/L (M)	5.87×10^{-5}
mg/L NH_3^--N	mg/L NH_3	1.22
mg/L NH_4^+	mg/L NH_3^--N	0.776

HOW TO ORDER

By Telephone:	**By Mail:**
6:30 a.m. to 5:00 p.m. MST Monday through Friday (800) 227-HACH (800-227-4224) **By FAX:** (970) 669-2932	Hach Company P.O. Box 389 Loveland, CO 80539-0389 U.S.A.

Ordering information by E-mail: orders@hach.com

Information Required

- Hach account number (if available)
- Your name and phone number
- Purchase order number
- Brief description or model number
- Billing address
- Shipping address
- Catalog number
- Quantity

Technical and Customer Service (U.S.A. only)

Hach Technical and Customer Service Department personnel are eager to answer questions about our products and their use. Specialists in analytical methods, they are happy to put their talents to work for you.
Call **1-800-227-4224** or E-mail **techhelp@hach.com**.

International Customers

Hach maintains a worldwide network of dealers and distributors. To locate the representative nearest you, send E-mail to **intl@hach. com** or contact:

In Canada, Latin America, Africa, Asia, Pacific Rim:
Telephone: (970) 669-3050; FAX: (970) 669-2932

In Europe, the Middle East, or Mediterranean Africa:
HACH Company, c/o
Dr. Bruno Lange GmbH
Willstätterstr. 11
D-40549 Düsseldorf
Germany
Telephone: +49/[0]211.52.88.0
Fax: +49/[0]211.52.88.231

REPAIR SERVICE

Authorization must be obtained from Hach Company before sending any items for repair. Please contact the HACH Service Center serving your location.

In the United States:
Hach Company
100 Dayton Avenue
Ames, Iowa 50010
(800) 227-4224 (U.S.A. only)
Telephone: (515) 232-2533
FAX: (515) 232-1276

In Canada:
Hach Sales & Service Canada Ltd.
1313 Border Street, Unit 34
Winnipeg, Manitoba
R3H 0X4
(800) 665-7635 (Canada only)
Telephone: (204) 632-5598
FAX: (204) 694-5134
E-mail: canada@hach.com

In Latin America, the Caribbean, the Far East, the Indian Subcontinent, Africa, Europe, or the Middle East:
Hach Company World Headquarters
P.O. Box 389
Loveland, Colorado, 80539-0389
U.S.A.
Telephone: (970) 669-3050
FAX: (970) 669-2932
E-mail: intl@hach.com

WARRANTY

Hach warrants most products against defective materials or workmanship for at least one year from the date of shipment; longer warranties may apply to some items.

HACH WARRANTS TO THE ORIGINAL BUYER THAT HACH PRODUCTS WILL CONFORM TO ANY EXPRESS WRITTEN WARRANTY GIVEN BY HACH TO THE BUYER. EXCEPT AS EXPRESSLY SET FORTH IN THE PRECEDING SENTENCE, HACH MAKES NO WARRANTY OF ANY KIND WHATSOEVER WITH RESPECT TO ANY PRODUCTS. HACH EXPRESSLY DISCLAIMS ANY WARRANTIES IMPLIED BY LAW, INCLUDING BUT NOT BINDING TO ANY WARRANTY OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE.

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Catalog descriptions, pictures and specification, although accurate to the best of our knowledge, are not a guarantee or warranty.

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