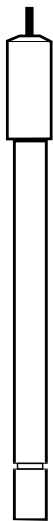


# User Guide

Standard  
Ammonia  
Ion Selective  
Electrode



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The specifications, descriptions, drawings, ordering information and part numbers within this document are subject to change without notice.

This publication supersedes all previous publications on this subject.

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# Introduction

This user guide contains information on the preparation, operation and maintenance for the ammonia ion selective electrode (ISE). General analytical procedures, electrode characteristics and electrode theory are also included in this user guide. Ammonia electrodes measure ammonia ions in aqueous solutions quickly, simply, accurately and economically. This gas sensing electrode can also be used to measure ammonium ions after conversion to ammonia or organic nitrogen after Kjeldahl digestion of the sample. Sample color and turbidity do not affect the measurements and samples do not need to be distilled. Almost all anions, cations and dissolved species, other than volatile amines, do not interfere with the measurements.

Technical Support Chemists can be consulted for assistance and troubleshooting advice. Within the United States call 1.800.225.1480 and outside the United States call 978.232.6000 or fax 978.232.6031. In Europe, the Middle East and Africa, contact your local authorized dealer. For the most current contact information, visit [www.thermo.com/contactwater](http://www.thermo.com/contactwater).

For the latest application and technical resources for Thermo Scientific Orion products, visit [www.thermo.com/waterapps](http://www.thermo.com/waterapps).

## **Ammonia Gas Sensing Combination ISE, Cat. No. 9512BNWP and 951201**

The ammonia combination electrode has the sensing and reference half-cells built into one electrode, which decreases the amount of required solutions and reduces waste. The ammonia combination electrode is available with a waterproof BNC connector, Cat. No. 9512BNWP, or a U.S. standard connector, Cat. No. 951201. Electrodes with a waterproof BNC connector can be used on any ISE or mV meter with a BNC connection.

The ammonia electrode includes the following:

- 40 loose membranes
- 1 reusable membrane cap
- Tweezers for handling the membranes
- Bottle of electrode filling solution with dispensing cap

# Required Equipment

1. Thermo Scientific Orion ISE meter, such as the 4-Star pH/ISE meter or 5-Star pH/ISE/DO/conductivity meter; equivalent ISE meter; or mV meter with a 0.1 mV resolution.

Ammonia electrodes can be used on any ISE or mV meter with a BNC or U.S. standard connection. The electrodes can also be used on meters with a variety of inputs when an adapter cable is used. Visit [www.thermo.com/water](http://www.thermo.com/water) for details.

2. Thermo Scientific Orion ammonia combination electrode, Cat. No. 9512BNWP or 951201.
3. Magnetic stirrer or Thermo Scientific Orion stirrer probe, Cat. No. 096019. The stirrer probe can be used with 3-Star, 4-Star and 5-Star benchtop meters.
4. Volumetric flasks, graduated cylinders and beakers.
5. Distilled or deionized water. All water must be free of ammonia. Pass the distilled or deionized water through an ion-exchange column containing a strong acidic cation exchange resin, such as Dowex 50W-X8.
6. Ammonia electrode filling solution, Cat. No. 951202
7. Ammonia calibration standards.

Cat. No.	Description
951006	0.1 M ammonia chloride (NH <sub>4</sub> Cl) standard
951007	1000 ppm ammonia as nitrogen (N) standard
951207	100 ppm ammonia as nitrogen (N) standard

8. Ammonia ionic strength adjuster (ISA), Cat. No. 951211. ISA provides a constant background ionic strength for samples and standards.

# Serial Dilutions

Serial dilution is the best method for the preparation of standards. Serial dilution means that an initial standard is diluted, using volumetric glassware, to prepare a second standard solution. The second standard is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.

1. **To prepare a  $10^{-2}$  M standard (170 ppm as  $\text{NH}_3$  and 140 ppm as N)** – Pipet 10 mL of the 0.1 M standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.
2. **To prepare a  $10^{-3}$  M standard (17.0 ppm as  $\text{NH}_3$  and 14.0 ppm as N)** – Pipet 10 mL of the  $10^{-2}$  M standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.
3. **To prepare a  $10^{-4}$  M standard (1.70 ppm as  $\text{NH}_3$  and 1.40 ppm as N)** – Pipet 10 mL of the  $10^{-3}$  M standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

To prepare standards with a different concentration use the following formula:

$$C_1 * V_1 = C_2 * V_2$$

$C_1$  = concentration of original standard

$V_1$  = volume of original standard

$C_2$  = concentration of standard after dilution

$V_2$  = volume of standard after dilution

For example, to prepare 100 mL of a 100 ppm ammonia as nitrogen (N) standard from a 1400 ppm ammonia as nitrogen (N) standard:

$$C_1 = 1400 \text{ ppm ammonia}$$

$$V_1 = \text{unknown}$$

$$C_2 = 100 \text{ ppm ammonia}$$

$$V_2 = 100 \text{ mL}$$

$$1400 \text{ ppm} * V_1 = 100 \text{ ppm} * 100 \text{ mL}$$

$$V_1 = (100 \text{ ppm} * 100 \text{ mL}) / 1400 \text{ ppm} = 7.14 \text{ mL}$$

# Electrode Setup

## Ammonia Electrode Preparation

**Note:** A new electrode is shipped with loose membranes and a reusable membrane cap. You must install a new membrane before using the electrode.

**Note:** A new electrode is shipped dry. Soak the inner body of the electrode in the electrode filling solution for at least two hours before using the electrode. For best results, soak the inner body overnight in electrode filling solution.

Avoid excessive handling of the membrane during assembly; this may affect the hydrophobic properties of the membrane and shorten the membrane life. Use the tweezers when handling the membrane. A membrane will last from one week to several months, depending on usage.

## Electrode Assembly

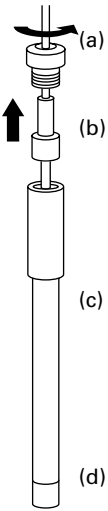
1. Hold the electrode vertically and unscrew the electrode cap (a) from the electrode body (c). See **Figure 1**.
2. Carefully remove the glass inner body (b) from the outer body (c). See **Figure 1**. Dispose of any electrode filling solution that is in the outer body.

**Note:** Soak the inner body of the electrode in the electrode filling solution for at least two hours before using the electrode. For best results, soak the inner body overnight in electrode filling solution.

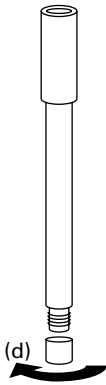
3. Unscrew the membrane cap (d) from the outer body. See **Figure 2**. Remove the membrane from the membrane cap if a membrane was previously installed.
4. Wear gloves and use tweezers to carefully grasp the corner of the white membrane from between wax paper separators. See **Figure 3**.

**Note:** Do not touch the center of the membrane.

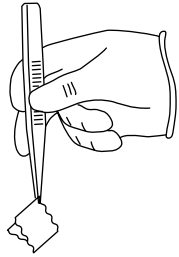




**Fig. 1**

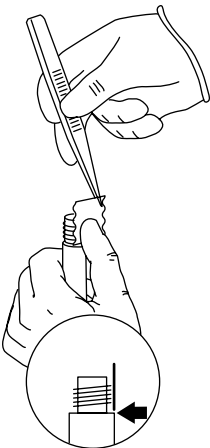


**Fig. 2**

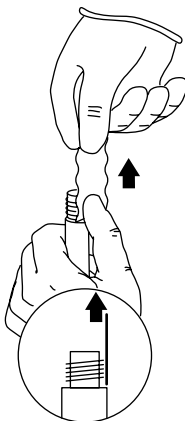


**Fig. 3**

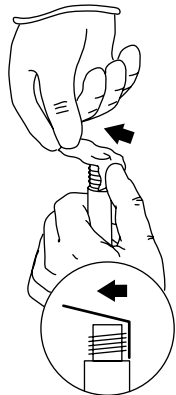
5. Hold the outer body oriented with the threads at the top. Align the straight edge of the membrane against the threaded shoulder and hold the membrane with your thumb. See **Figure 4**.
6. With the other hand, gently stretch the membrane upward and then across the opening. See **Figure 5** and **Figure 6**.



**Fig. 4**



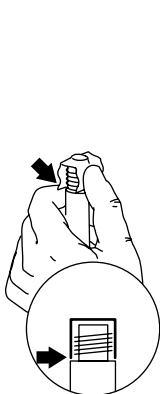
**Fig. 5**



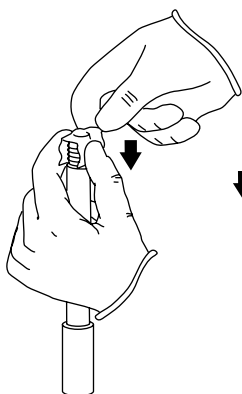
**Fig. 6**

7. Place the membrane down to align the other edge with the opposite shoulder. See **Figure 7**.
8. While holding each edge on both sides, gently stretch each serrated side of the membrane out and down over the threads and ensure that the membrane surface is smooth and without wrinkles. See **Figure 8**.
9. Smooth any loose material, taking care not to touch center of membrane. See **Figure 9**.

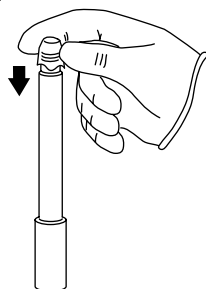
**Note:** Do not overstretch the membrane. The membrane is considered overstretched if the black body material can be seen through the membrane. Discard the membrane if it is overstretched and replace it with a new membrane. Continue from step 3.



**Fig. 7**



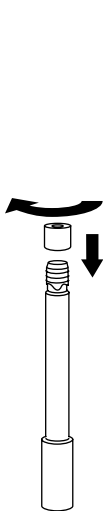
**Fig. 8**



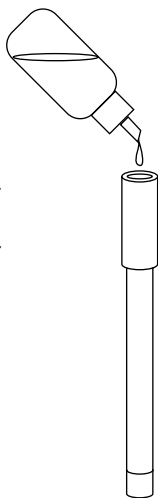
**Fig. 9**

10. Screw the membrane cap onto the outer body, being careful not to touch membrane. See **Figure 10**. Screw the membrane cap on half way and wrap any loose membrane material onto the threads and under the cap. Make sure that the cap is fully screwed on.
11. Fill the outer body with about 2.5 mL or 50 drops of electrode filling solution. See **Figure 11**.
12. Insert the inner body into the outer body. Ensure that the inner body is fully inserted in the top of the outer body and then screw on the electrode cap. See **Figure 12**.

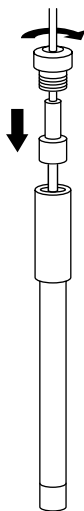
- Carefully shake the fully assembled electrode as if it were a clinical thermometer to remove air bubbles. Gently pull the spring loaded cable back and slowly release it to allow the filling solution to migrate between the membrane and inner body. See **Figure 13**.
- Rinse the electrode well and wipe it dry.
- Soak the electrode in a 10 ppm ammonia standard for at least 15 minutes before use.



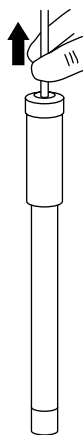
**Fig. 10**



**Fig. 11**



**Fig. 12**



**Fig. 13**

## Checking Electrode Operation (Slope)

These are general instructions that can be used with most meters to check the electrode operation. Refer to the meter user guide for more specific information.

This procedure measures electrode slope. Slope is defined as the change in millivolts observed with every tenfold change in concentration. Obtaining the slope value provides the best means for checking electrode operation.

1. If the electrode has been stored dry, prepare the electrode as described in the **Electrode Preparation** section.
2. Connect the electrode to a meter with a mV mode. Set the meter to the mV mode.
3. Add 100 mL of distilled water and 2 mL of ISA, Cat. No. 951211, to a 150 mL beaker. Stir the solution thoroughly.
4. Rinse the electrode with distilled water and place the electrode into the solution prepared in step 3.
5. Select either a 0.1 M ammonium chloride or 1000 ppm ammonia as nitrogen (N) standard. Pipet 1 mL of the standard into the beaker and stir the solution thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.
6. Pipet 10 mL of the same standard into the same beaker and stir the solution thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.
7. There should be a -54 to -60 mV difference between the two millivolt readings when the solution temperature is between 20 to 25 °C. If the millivolt potential is not within this range, refer to the **Troubleshooting** section.

## Measurement Units

Ammonia concentration can be measured in moles per liter (M), parts per million (ppm) or any convenient concentration unit.

**Table 1**  
**Concentration Unit Conversion Factors**

Moles/Liter (M)	ppm as NH <sub>3</sub>	ppm as N
1.0	17000	14000
10 <sup>-1</sup>	1700	1400
10 <sup>-2</sup>	170	140
10 <sup>-3</sup>	17	14
10 <sup>-4</sup>	1.7	1.4

## Sample Requirements

All samples must be aqueous and must not contain organic solvents. Contact Technical Support for information on using the electrode for specific applications.

The solution temperature must be less than 50 °C.

Samples and standards should be at the same temperature. A 1 °C difference in temperature for a 10<sup>-3</sup> M ammonia solution will give rise to about a 2% measurement error.

In all analytical procedures, ISA must be added to all samples and standards immediately before taking a measurement. After the addition of the ISA, all solutions should fall within a pH 11 to 14 range (the solution should have a blue color in this range) and have a total level of dissolved species below 1 M. If the total level of dissolved species is above 1 M, refer to the **Effect of Dissolved Species** section.

## Sample Storage

If possible, alkaline samples should be measured at once. The rate of ammonia loss at 25 °C from a stirred 100 mL basic solution in a 100 mL beaker is about 50% in six hours. If samples must be stored, make them slightly acidic (pH 6) by adding 0.5 mL of 1 M HCl to each 100 mL of sample, and place them in tightly capped vessels. Make stored samples basic by adding pH-adjusting ISA immediately before measurement.

## Measuring Hints

- Minimize the loss of ammonia from the sample by performing the following recommendations:
  - Store samples according to the procedure in the **Sample Storage** section.
  - Use beakers that minimize the ratio of surface area to volume.
  - Keep beakers that contain standards and samples covered between measurements.
- Add 2 mL of pH-adjusting ISA, Cat. No. 951211, to every 100 mL of sample or standard immediately before making measurements, and make sure the blue color is observed.
- Stir all standards and samples at a uniform, moderate rate. Place a piece of insulating material, such as Styrofoam or cardboard, between the magnetic stir plate and beaker to prevent measurement errors from the transfer of heat to the sample.
- Always use freshly prepared standards for calibration.
- Always rinse the electrode with distilled water between measurements and shake the electrode to remove the water and prevent sample carryover. Do not wipe or rub the electrode membrane.
- Allow all standards and samples to reach the same temperature for precise measurements.
- Verify the electrode calibration every two hours by placing the electrode in a fresh aliquot of the least concentrated standard used for calibration. If the value has changed by more than 2%, recalibrate the electrode.
- After immersing the electrode in a solution, check the electrode membrane for air bubbles and remove air bubbles by reimmersing the electrode in the solution and gently tapping it.
- For high ionic strength samples, prepare standards with a background composition similar to the sample.
- If the electrode response becomes sluggish, the membrane may contain a surface layer of contaminants. Restore the electrode performance by soaking the electrode in distilled water for about 5 minutes and then soaking the electrode in a 10 ppm ammonia standard solution for about 1 hour.

# Ammonia Electrode Storage

## Short Term Storage

Between measurements, rinse the electrode thoroughly with distilled water and store it in a  $10^{-3}$  M or 10 ppm ammonia standard with ISA added. When performing low level ammonia measurements, rinse the electrode thoroughly with distilled water and store it in a pH 4 buffer between measurements.

For overnight storage and storage up to one week, rinse the ammonia electrode thoroughly with distilled water and store it in a 0.1 M or 1000 ppm standard without any ISA.

**Note:** *If the electrode is accidentally left in the air and erratic results are obtained, the space between the inside of the membrane and the inner body may be dry. To make the electrode usable again, gently pull back the cable to allow solution to flow between the inner body and the membrane.*

## Long Term Storage

For storage over one week or if the electrode is stored indefinitely, disassemble the electrode completely and rinse the inner body, out body and membrane cap with distilled water. Dry and reassemble the electrode without filling solution or a membrane.

# Ammonia Electrode Maintenance

If the electrode response drifts or becomes sluggish, the membrane may contain a surface layer of contaminants. Restore the electrode performance by soaking the electrode in distilled water for about 5 minutes and then soaking the electrode in a 10 ppm ammonia standard solution for about 1 hour. If soaking the electrode does not restore normal electrode performance, replace the ammonia membrane.

A membrane will last from one week to several months depending on the usage. Membrane failure is characterized by a shift in the electrode potential, drift or poor response. Membrane failure may be apparent on visual inspection as dark spots or discoloration of the membrane.

Rinse the electrode with distilled water, obtain a new membrane and refer to the **Ammonia Electrode Preparation** section for instructions on installing a new membrane on the electrode.

# Analytical Techniques

A variety of analytical techniques are available to the analyst. The following is a description of these techniques.

**Direct Calibration** is a simple procedure for measuring a large number of samples. Only one meter reading is required for each sample. Calibration is performed using a series of standards. The concentration of the samples is determined by comparison to the standards. ISA is added to all solutions to ensure that samples and standards have similar ionic strength.

**Low Level Calibration** is similar to the direct calibration technique. This method is recommended when the expected sample concentration is less than  $4 \times 10^{-6}$  M ammonia (0.068 ppm as  $\text{NH}_3$  and 0.056 ppm as N). A minimum three point calibration is recommended to compensate for the electrode's non-linear response at these concentrations. A special calibration standard preparation procedure is the best means of preparing low level calibration standards.

**Incremental Techniques** provide a useful method for measuring samples, since a calibration is not required. The different incremental techniques are described below. They can be used to measure the total concentration of a specific ion in the presence of a large (50 to 100 times) excess of complexing agents. As in direct calibration, any convenient concentration unit can be used.

**Known Addition** is useful for measuring dilute samples, checking the results of direct calibration (when no complexing agents are present), or measuring the total concentration of an ion in the presence of an excess complexing agent. The electrode is immersed in the sample solution and an aliquot of a standard solution containing the measured species is added to the sample. From the change in potential before and after the addition, the original sample concentration is determined.

**Known Subtraction** is useful as a quick version of a titration, or for measuring species for which stable standards do not exist. It is necessary to know the stoichiometric ratio between standard and sample. For known subtraction, an electrode sensing the sample species is used. Stable standards of a species reacting completely with the sample in a reaction of known stoichiometry are necessary.



**Analate Addition** is often used to measure soluble solid samples, viscous samples, small or very concentrated samples, to diminish the effects of complex sample matrices, or to diminish the effects of varying sample temperatures. This method is not suitable for dilute or low concentration samples. Total concentration is measured even in the presence of complexing agents. The electrode is immersed in a standard solution containing the ion to be measured and an aliquot of the sample is added to the standard. The original sample concentration is determined from the change in potential before and after the addition.

**Analate Subtraction** is used in the measurement of ions for which no ion-selective electrode exists. The electrode is immersed in a reagent solution that contains a species that the electrode senses, and that reacts with the sample. It is useful when sample size is small, or samples for which a stable standard is difficult to prepare, and for viscous or very concentrated samples. The method is not suited for very dilute samples. It is also necessary to know the stoichiometric ratio between standard and sample.

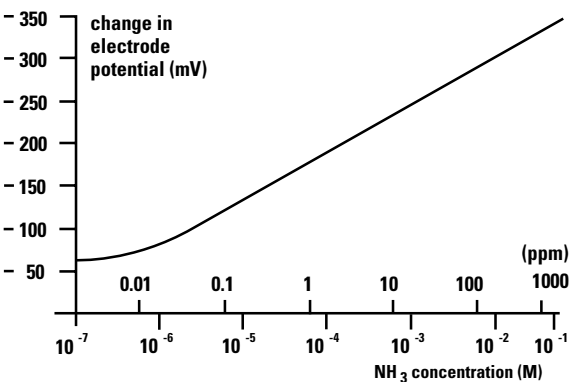
**Titrations** are quantitative analytical techniques for measuring the concentration of a species by incremental addition of a reagent (titrant) that reacts with the sample species. Sensing electrodes can be used for determination of the titration end point. Ion selective electrodes are useful as end point detectors, because they are unaffected by sample color or turbidity. Titrations are approximately 10 times more precise than direct calibration, but are more time-consuming.

# Direct Calibration Technique

## Typical Direct Calibration Curve

In the direct calibration procedure, a calibration curve is constructed either in the meter memory or on semi-logarithmic paper. Electrode potentials of standard solutions are measured and plotted on the linear axis against their concentrations on the log axis. In the linear regions of the curves, only two standards are needed to determine a calibration curve. In non-linear regions, more points must be taken. Procedures are given in the **Direct Calibration Technique** section for sample concentrations in the linear region of electrode response. The **Low Level Calibration Technique** section provides procedures for measurements in the non-linear region of electrode response.

**Figure 14**  
**Typical Direct Calibration Curve**



## Direct Calibration Overview

The following direct measurement procedures are recommended for moderate to high level measurements. Samples must be in the linear range of the electrode – greater than  $4 \times 10^{-6}$  M ammonia (0.068 ppm as  $\text{NH}_3$  and 0.056 ppm as N). A two point calibration is sufficient, although more points can be used. When using an ISE meter, sample concentrations can be read directly from the meter. When using a mV meter, a calibration curve can be prepared on semi-logarithmic graph paper, or a linear regression (against logarithmic concentration values) can be performed using a spreadsheet or graphing program.

### Calibration Hints

- Standard concentrations should bracket the expected sample concentrations.
- Always add 2 mL of ISA, Cat. No. 951211, per 100 mL of standard or sample.
- For high ionic strength samples that have an ionic strength of 0.1 M or greater, prepare standards with a background composition similar to that of the samples, or measure the samples using the known addition method.
- During calibration, measure the least concentrated standard first, and work up to the most concentrated standard.

## Direct Calibration Setup

1. Prepare the electrode as described in the **Electrode Preparation** section.
2. Connect the electrode to the meter.
3. Prepare at least two standards that bracket the expected sample range and differ in concentration by a factor of ten. Standards can be prepared in any concentration unit to suit the particular analysis requirement. See the **Serial Dilution** section for instructions on how to prepare standards. All standards should be at the same temperature as the samples. For details on temperature effects on electrode performance, refer to the **Temperature Effects** section.

## Direct Calibration Procedure Using a Meter with an ISE Mode

**Note:** See the meter user guide for more specific information.

1. Add 100 mL of the less concentrated standard and 2 mL of ISA to a 150 mL beaker and stir the solution thoroughly.
2. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the less concentrated standard. Wait for a stable reading and adjust the meter to display the value of the standard, as described in the meter user guide.
3. Add 100 mL of the more concentrated standard and 2 mL of ISA to a second 150 mL beaker and stir the solution thoroughly.
4. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the more concentrated standard. Wait for a stable reading and adjust the meter to display the value of the second standard, as described in the meter user guide.
5. Record the resulting slope value. The slope should be between -54 and -60 mV when the standards are between 20 and 25 °C.
6. Add 100 mL of sample and 2 mL of ISA to a clean 150 mL beaker and stir the solution thoroughly.
7. Rinse the electrode with distilled water, blot it dry and place it into the sample. The concentration of the sample will be displayed on the meter.

**Note:** Other solution volumes may be used, as long as the ratio of solution to ISA remains 50:1.

## Direct Calibration Procedure Using a Meter with a mV Mode

**Note:** See the meter user guide for more specific information.

1. Set the meter to the mV mode.
2. Add 100 mL of the less concentrated standard and 2 mL of ISA to a 150 mL beaker and stir the solution thoroughly.
3. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the less concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
4. Add 100 mL of the more concentrated standard and 2 mL of ISA to a second 150 mL beaker and stir the solution thoroughly.
5. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the more concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
6. Using semi-logarithmic graph paper, prepare a calibration curve by plotting the millivolt values on the linear axis and the standard concentration values on the logarithmic axis.
7. Add 100 mL of sample and 2 mL of ISA to a clean 150 mL beaker and stir the solution thoroughly.
8. Rinse the electrode with distilled water, blot it dry and place it into the beaker. When a stable reading is displayed, record the mV value.
9. Using the calibration curve prepared in step 6, determine the unknown concentration of the sample.

**Note:** Other solution volumes may be used, as long as the ratio of solution to ISA remains 50:1.

# Low Level Calibration Technique

These procedures are for solutions that have a concentration of less than  $4 \times 10^{-6}$  M ammonia (0.068 ppm as  $\text{NH}_3$  and 0.056 ppm as N). For solutions low in ammonia but high in total ionic strength (greater than  $10^{-1}$  M), perform the same procedure by preparing a calibrating solution with a composition similar to the sample.

Accurate results require that the following conditions be met:

- Prepare at least three calibration standards that bracket the expected sample concentration.
- Adequate time must be allowed for electrode stabilization. Longer response time will be needed at low level measurements.
- Stir all standards and samples at a uniform rate.

## Low Level Setup

1. Prepare the electrode as described in the **Electrode Preparation** section.
2. Soak the electrode in a pH 4 buffer for several minutes.
3. Connect the electrode to the meter. Set the meter to the mV mode.
4. Select a standard solution. Use either a  $10^{-3}$  M ammonia standard or a 10 ppm ammonia as nitrogen standard.

## Low Level Calibration and Measurement

1. Add 100 mL of ammonia-free distilled water and 2 mL of ISA to an Erlenmeyer flask.
2. Rinse the electrode with distilled water, blot it dry and place it into the beaker. Stir the solution thoroughly.
3. Add increments of the  $10^{-3}$  M ammonia standard or 10 ppm ammonia as nitrogen standard to the beaker using the steps outlined in **Table 2**. Record the stable millivolt reading after each increment.
4. Soak the electrode in a pH 4 buffer for several minutes.
5. On semi-logarithmic paper, plot the concentration (log axis) against the millivolt potential (linear axis). Prepare a new calibration curve with fresh standards each day.
6. Measure 100 mL of sample and pour the solution into a clean 150 mL beaker. Rinse the electrode with distilled water, blot it dry and place the electrode into the sample.
7. Stir the solution thoroughly. When a stable reading is displayed, record the mV value.
8. Determine the sample concentration corresponding to the measured potential from the low level calibration curve.

**Table 2**  
**Calibration Curve For Low Level Calibrations**

Additions of standard to 100 mL distilled water and 2 mL ISA.

Step	Pipet Size	Volume Added	Concentration ppm	Concentration M
1	1 mL	0.1 mL	0.01	$9.8 \times 10^{-7}$
2	1 mL	0.1 mL	0.02	$2.0 \times 10^{-6}$
3	1 mL	0.2 mL	0.04	$3.9 \times 10^{-6}$
4	1 mL	0.2 mL	0.06	$5.8 \times 10^{-6}$
5	1 mL	0.4 mL	0.10	$9.7 \times 10^{-6}$
6	2 mL	2.0 mL	0.29	$2.9 \times 10^{-5}$
7	2 mL	2.0 mL	0.47	$4.7 \times 10^{-5}$

# Known Addition Technique

Known addition is a convenient technique for measuring samples in the linear range of the electrode (greater than  $4 \times 10^{-6}$  M ammonia, 0.068 ppm as  $\text{NH}_3$  or 0.056 ppm as N) because no calibration curve is required. It can be used to verify the results of a direct calibration or to measure the total concentration of an ion in the presence of a large excess of a complexing agent. The sample potential is measured before and after addition of a standard solution.

Accurate results require that the following conditions be met:

- Concentration should approximately double as a result of the addition.
- Sample concentration should be known to within a factor of three.
- Either no complexing agent or a large excess of the complexing agent may be present.
- The ratio of the uncomplexed ion to complexed ion must not be changed by addition of the standard.
- All samples and standards should be at the same temperature.
- With double or multiple known addition, the final addition should be 10 to 100 times the sample concentration.
- Add 2 mL of ISA to every 100 mL of sample before analysis.



## Known Addition Setup

1. Prepare the electrode as described in the **Electrode Preparation** section.
2. Connect the electrode to the meter.
3. Prepare a standard solution that will cause the ammonia concentration of the sample to double when added to the sample solution. Refer to **Table 3** for guidelines.
4. Determine the electrode slope by performing the procedure in the **Checking Electrode Operation (Slope)** section.
5. Rinse the electrode with distilled water.

**Table 3**  
**Guideline For Known Addition**

<b>Volume of Addition</b>	<b>Concentration of Standard</b>
1 mL	100 times sample concentration
5 mL	20 times sample concentration
10 mL*	10 times sample concentration

\* Most convenient volume to use

## Known Addition Using a Meter with a Known Addition Mode

**Note:** See the meter user guide for more specific information.

1. Set the meter to measure in the known addition mode.
2. Measure 100 mL of sample and 2 mL of ISA and pour the solutions into a 150 mL beaker. Rinse the electrode with distilled water and place it into the sample solution. Stir the solution thoroughly.
3. When a stable reading is displayed, set the meter as described in the meter user guide, if required.
4. Pipet the appropriate amount of the standard solution into the beaker. Stir the solution thoroughly.
5. When a stable reading is displayed, record the sample concentration.

## Known Addition Using a Meter with a Millivolt Mode

1. Set the meter to the relative millivolt mode. If a relative millivolt mode is not available, use the millivolt mode.
2. Measure 100 mL of sample and 2 mL of ISA and pour the solutions into a 150 mL beaker. Stir the solution thoroughly.
3. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker. When a stable reading is displayed, set the meter to read 0.0 mV. If the reading cannot be adjusted to 0.0 mV, record the actual mV value.
4. Pipet the appropriate amount of standard solution into the beaker. Stir the solution thoroughly.
5. When a stable reading is displayed, record the mV value. If the meter could not be set to 0.0 mV in step 3, subtract the first reading from the second reading to calculate  $\Delta E$ .
6. Use **Table 5** to find the Q value that corresponds to the change in potential,  $\Delta E$ . To determine the original sample concentration, multiply Q by the concentration of the added standard:

$$C_{\text{sample}} = Q * C_{\text{standard}}$$

$C_{\text{standard}}$  = standard concentration

$C_{\text{sample}}$  = sample concentration

Q = value from **Table 5**

The table of Q values is calculated for a 10% volume change. The equation for the calculation of Q for different slopes and volume changes is given below.

$$Q = (p * r) / \{(1 + p) * 10^{\Delta E/S} - 1\}$$

Q = value from **Table 5**

$\Delta E = E_2 - E_1$

S = slope of the electrode

p = volume of standard / volume of sample and ISA

r = volume of sample and ISA / volume of sample

## Calculating Known Addition for Samples using Lotus, Excel, or Quattro Spreadsheets

If it is more convenient, a simple spreadsheet can be set up to calculate the known addition results, using any ratio of sample to addition. A typical worksheet is shown in **Table 4**. The numbers shown are examples, but the formulas and their locations should be copied exactly.

**Table 4**  
**Known Addition Calculations using Lotus, Excel, or Quattro Spreadsheets**

A	B	C
1		Enter Value
2	Volume of sample and ISA (mL)	102
3	Volume of addition (mL)	10
4	Concentration of addition	10
5	Volume of sample	100
6	Initial mV reading	45.3
7	Final mV reading	63.7
8	Electrode slope	-59.2
9		
10		Derived Values
11	Delta E	+C7 - C6
12	Solution volume ratio	+C3/C2
13	Antilog term	+10 <sup>^</sup> (C11/C8)
14	Sample volume ratio	+C2/C5
15	Q term	+C12*C14/ (((1+C12)*C13)-1)
16	Calculated initial concentration in same units as addition	+C15*C4

**Note:** For Excel, use = instead of + at start of formulas.

**Table 5**  
**Q Values for a 10% volume change,**  
**slopes (in column heading) are in units of mV/decade**

$\Delta E$	Q Concentration Ratio			
	-57.2	-58.2	-59.2	-60.1
5.0	0.2894	0.2933	0.2972	0.3011
5.2	0.2806	0.2844	0.2883	0.2921
5.4	0.2722	0.2760	0.2798	0.2835
5.6	0.2642	0.2680	0.2717	0.2754
5.8	0.2567	0.2604	0.2640	0.2677
6.0	0.2495	0.2531	0.2567	0.2603
6.2	0.2436	0.2462	0.2498	0.2533
6.4	0.2361	0.2396	0.2431	0.2466
6.6	0.2298	0.2333	0.2368	0.2402
6.8	0.2239	0.2273	0.2307	0.2341
7.0	0.2181	0.2215	0.2249	0.2282
7.2	0.2127	0.2160	0.2193	0.2226
7.4	0.2074	0.2107	0.2140	0.2172
7.6	0.2024	0.2056	0.2088	0.2120
7.8	0.1975	0.2007	0.2039	0.2023
8.0	0.1929	0.1961	0.1992	0.2023
8.2	0.1884	0.1915	0.1946	0.1977
8.4	0.1841	0.1872	0.1902	0.1933
8.6	0.1800	0.1830	0.1860	0.1890
8.8	0.1760	0.1790	0.1820	0.1849
9.0	0.1722	0.1751	0.1780	0.1809
9.2	0.1685	0.1714	0.1742	0.1771
9.4	0.1649	0.1677	0.1706	0.1734
9.6	0.1614	0.1642	0.1671	0.1698
9.8	0.1581	0.1609	0.1636	0.1664
10.0	0.1548	0.1576	0.1603	0.1631
10.2	0.1517	0.1544	0.1571	0.1598
10.4	0.1487	0.1514	0.1540	0.1567
10.6	0.1458	0.1484	0.1510	0.1537
10.8	0.1429	0.1455	0.1481	0.1507
11.0	0.1402	0.1427	0.1453	0.1479
11.2	0.1375	0.1400	0.1426	0.1451
11.4	0.1349	0.1374	0.1399	0.1424
11.6	0.1324	0.1349	0.1373	0.1398
11.8	0.1299	0.1324	0.1348	0.1373

<b><math>\Delta E</math></b>	<b>Q Concentration Ratio</b>			
	<b>-57.2</b>	<b>-58.2</b>	<b>-59.2</b>	<b>-60.1</b>
12.0	0.1276	0.1300	0.1324	0.1348
12.2	0.1253	0.1277	0.1301	0.1324
12.4	0.1230	0.1254	0.1278	0.1301
12.6	0.1208	0.1232	0.1255	0.1278
12.8	0.1187	0.1210	0.1233	0.1256
13.0	0.1167	0.1189	0.1212	0.1235
13.2	0.1146	0.1169	0.1192	0.1214
13.4	0.1127	0.1149	0.1172	0.1194
13.6	0.1108	0.1130	0.1152	0.1174
13.8	0.1089	0.1111	0.1133	0.1155
14.0	0.1071	0.1093	0.1114	0.1136
14.2	0.1053	0.1075	0.1096	0.1118
14.4	0.1036	0.1057	0.1079	0.1100
14.6	0.1019	0.1040	0.1061	0.1082
14.8	0.1003	0.1024	0.1045	0.1065
15.0	0.0987	0.1008	0.1028	0.1048
15.5	0.0949	0.0969	0.0989	0.1009
16.0	0.0913	0.0932	0.0951	0.0971
16.5	0.0878	0.0897	0.0916	0.0935
17.0	0.0846	0.0865	0.0883	0.0901
17.5	0.0815	0.0833	0.0852	0.0870
18.0	0.0786	0.0804	0.0822	0.0839
18.5	0.0759	0.0776	0.0793	0.0810
19.0	0.0733	0.0749	0.0766	0.0783
19.5	0.0708	0.0724	0.0740	0.0757
20.0	0.0684	0.0700	0.0716	0.0732
20.5	0.0661	0.0677	0.0693	0.0708
21.0	0.0640	0.0655	0.0670	0.0686
21.5	0.0619	0.0634	0.0649	0.0664
22.0	0.0599	0.0614	0.0629	0.0643
22.5	0.0580	0.0595	0.0609	0.0624
23.0	0.0562	0.0576	0.0590	0.0605
23.5	0.0545	0.0559	0.0573	0.0586
24.0	0.0528	0.0542	0.0555	0.0569
24.5	0.0512	0.0526	0.0539	0.055
25.0	0.0497	0.0510	0.0523	0.0536
25.5	0.0482	0.0495	0.0508	0.0521
26.0	0.0468	0.0481	0.0493	0.0506

<b>ΔE</b>	<b>Q Concentration Ratio</b>			
	<b>-57.2</b>	<b>-58.2</b>	<b>-59.2</b>	<b>-60.1</b>
26.5	0.0455	0.0467	0.0479	0.0491
27.0	0.0442	0.0454	0.0466	0.0478
27.5	0.0429	0.0441	0.0453	0.0464
28.0	0.0417	0.0428	0.0440	0.0452
28.5	0.0405	0.0417	0.0428	0.0439
29.0	0.0394	0.0405	0.0416	0.0427
29.5	0.0383	0.0394	0.0405	0.0416
30.0	0.0373	0.0383	0.0394	0.0405
31.0	0.0353	0.0363	0.0373	0.0384
32.0	0.0334	0.0344	0.0354	0.0364
33.0	0.0317	0.0326	0.0336	0.0346
34.0	0.0300	0.0310	0.0319	0.0328
35.0	0.0285	0.0294	0.0303	0.0312
36.0	0.0271	0.0280	0.0288	0.0297
37.0	0.0257	0.0266	0.0274	0.0283
38.0	0.0245	0.0253	0.0261	0.0269
39.0	0.0233	0.0241	0.0249	0.0257
40.0	0.0222	0.0229	0.0237	0.0245
41.0	0.0211	0.0218	0.0226	0.0233
42.0	0.0201	0.0208	0.0215	0.0223
43.0	0.0192	0.0199	0.0205	0.0212
44.0	0.0183	0.0189	0.0196	0.0203
45.0	0.0174	0.0181	0.0187	0.0194
46.0	0.0166	0.0172	0.0179	0.0185
47.0	0.0159	0.0165	0.0171	0.0177
48.0	0.0151	0.0157	0.0163	0.0169
49.0	0.0145	0.0150	0.0156	0.0162
50.0	0.0138	0.0144	0.0149	0.0155]
51.0	0.0132	0.0137	0.0143	0.0148
52.0	0.0126	0.0131	0.0136	0.0142
53.0	0.0120	0.0125	0.0131	0.0136
54.0	0.0115	0.0120	0.0125	0.0130
55.0	0.0110	0.0115	0.0120	0.0124
56.0	0.0105	0.0110	0.0115	0.0119
57.0	0.0101	0.0105	0.0110	0.0114
58.0	0.0096	0.0101	0.0105	0.0109
59.0	0.0092	0.0096	0.0101	0.0105
60.0	0.0088	0.0092	0.0096	0.0101

# Electrode Characteristics

## Electrode Response

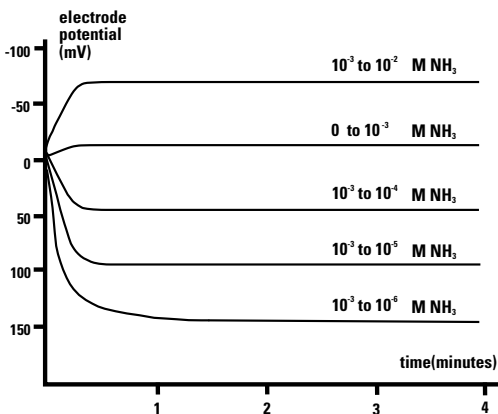
The electrode potential plotted against concentration on semi-logarithmic paper results in a straight line with a slope of about -54 to -60 mV per decade change in concentration.

The electrode exhibits good time response (95% of response in one minute or less) for ammonia concentrations above  $4 \times 10^{-6}$  M ammonia (0.068 ppm as  $\text{NH}_3$  and 0.056 ppm as N). Below this value, response times are longer and ammonia absorption from the air may become a source of error. Above 1.0 M, ammonia is rapidly lost to the air. Samples above 1.0 M ammonia concentration can be diluted before measurement.

For solutions with low concentration in ammonia but high in total ionic strength, perform the same procedure with one change – prepare a calibration solution with a background composition similar to the sample. Accurate measurement requires that the following conditions be met:

- Adequate time must be allowed for electrode stabilization. Longer response time will be needed for low level measurements.
- Remember to stir all standards and samples at a moderate, uniform rate. When plotted on semi-logarithmic paper, electrode potential response as a function of ammonia concentration is a straight line with a slope of about -58 mV per decade.

**Figure 15**  
**Typical Electrode Response to Ammonia Concentrations**





## 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 hourly calibrations, direct electrode measurements reproducible to  $\pm 2\%$  can be obtained.

## Temperature Effects

A change in temperature will cause electrode response to shift and change slope. **Table 6** lists the variation of theoretical response with temperature. At  $10^{-3}$  M, a  $1\text{ }^{\circ}\text{C}$  temperature change gives rise to a 2% error. Samples and standards should be at the same temperature. Note that the higher the temperature, the faster the ammonia loss from solution.

**Table 6**  
**Theoretical Slope vs. Temperature Values**

Temperature ( $^{\circ}\text{C}$ )	Slope (mV)
0	-54.20
10	-56.18
20	-58.16
25	-59.16
30	-60.15
40	-62.13

## Interferences

Volatile amines interfere with electrode measurements. Most gases do not interfere as they are converted to the ionic form in basic solution. 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 in the solution and about the same level of dissolved species. Also, some metallic ions complex ammonia, causing falsely low results in direct measurements. The pH adjusting ISA, Cat. No. 951211, removes interferences from metallic ions.

## pH Effects

The pH of all standards and samples must be adjusted above 11 before they can be measured.

## Complexation

Ammonia forms metal complexes with a number of metal ions: mercury, silver, copper, gold, nickel, cobalt, cadmium, and zinc. Most of these metals are removed in the form of hydroxide complexes or precipitates in basic solution. 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 pH adjusting ISA inhibits the formation of some these common metal complexes in the sample, because it contains a high concentration of hydroxide ion and a reagent that removes mercury and silver ions.

## Effect of Dissolved Species

Water vapor is a potential electrode interference. Water can move across the membrane as water vapor, changing the concentration of the electrode filling solution under the membrane. Such changes will be seen as electrode drift. Water vapor transport across the membrane is not a problem if the total level of dissolved species in solution (osmotic strength) is below 1 M or the electrode and sample temperatures are the same. Addition of 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 measurement. Dilution should not reduce the ammonia level below  $10^{-5}$  M. 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 electrode filling solution is adjusted. To adjust the electrode filling solution, add 4.25 grams of solid  $\text{NaNO}_3$  to each 100 mL electrode filling solution.

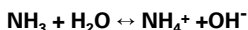
## Membrane Life

A membrane will last from one week to several months, depending on usage. Membrane failure is characterized by a shift in electrode potential, drift or poor response. Refer to the **Ammonia Electrode Maintenance** section for instructions on changing the membrane. Before replacement, refer to the **Troubleshooting** section to make sure that the difficulties are caused by the membrane.

# Theory of Operation

The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from the electrode filling 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 filling solution and, to a small extent, reacts reversibly with water in the filling solution.



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

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \text{constant}$$

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

$$[\text{OH}^-] = [\text{NH}_3] \cdot \text{constant}$$

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

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

where:

- E** = measured electrode potential
- E<sub>0</sub>** = reference potential
- OH<sup>-</sup>** = hydroxide concentration in solution
- S** = electrode slope (-59.2 mV/decade)

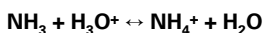
Since the hydroxide concentration is proportional to ammonia concentration, electrode response to ammonia is also Nernstian.

$$E = E_0 - S \log [\text{NH}_3]$$

The reference potential, E<sub>0</sub>, is partly determined by the internal reference element that responds to the fixed level of chloride in the filling solution.

## Ammonium Ion

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



The relative amount of ammonia and ammonium ion is determined by the solution pH. See **Figure 16**. In acid solution, where hydrogen ion is readily available, virtually all the ammonia is converted to ammonium ion. At a pH of about 9.3, half the ammonia will be in the form of ammonium ion.

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

$$\frac{[\text{NH}_4^+]}{[\text{H}_3\text{O}^+][\text{NH}_3]} = \frac{[\text{NH}_4^+]}{10^{-\text{pH}} [\text{NH}_3]} = K 10^{9.3}$$

at 25 °C  $\mu = 0.1$  and  $\text{pK} = 9.3$ .

The ratio of ammonium to ammonia is given by:

$$\frac{[\text{NH}_4^+]}{[\text{NH}_3]} = K 10^{-\text{pH}} = 10^{9.3-\text{pH}}$$

Martell, A.; Smith, R., *Critical Stability Constants*, Plenum Press. New York, NY, 1974.

The exact value of K will vary with both temperature and ionic strength. For example, while the pK, at 25 °C and  $\mu = 0.1$ , is given as 9.3 (as in the discussion above) an increase in ionic strength to  $\mu = 1.0$  yields a pK of 9.4.

## Partial Pressure of Ammonia

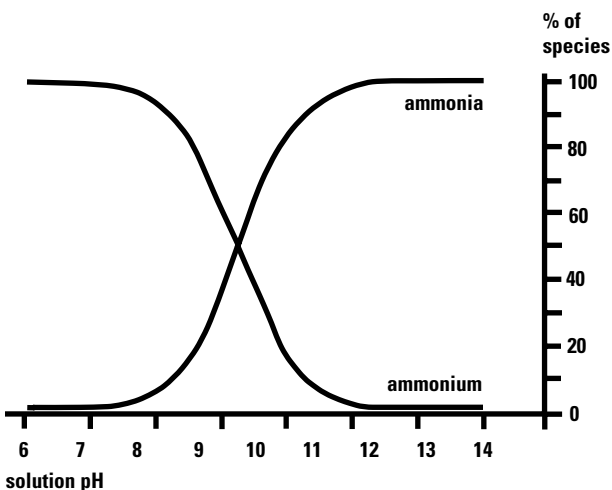
As discussed in the **Theory of Operation** section, the ammonia electrode responds to the partial pressure of dissolved ammonia gas. The partial pressure of dissolved ammonia gas is related to the ammonia concentration by Henry's Law:

$$K_h = \frac{[\text{NH}_3] \text{ aqueous}}{P_{\text{NH}_3}} = 56 \text{ moles/liter} \cdot \text{atm. (25 }^\circ\text{C)}$$

The Henry's Law constant,  $K_h$ , 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.

**Figure 16**  
**Percent of Ammonia and Ammonium as a Function of pH**



## Measuring Ammonia in Solutions that Wet the Membrane

The membrane of the ammonia electrode is gas-permeable and hydrophobic, meaning that liquid water does not wet it and does not penetrate the holes. If a sample solution is nonaqueous, or if it contains a surfactant that wets the membrane, liquid will penetrate the membrane. This causes difficulties in samples such as sewage that contain surfactants, and samples that are nonaqueous, such as latex paint or nylon. To measure ammonia in these samples, the electrode should be suspended above the sample in a stoppered flask.

If the ammonia electrode is placed in a closed system saturated with water vapor, it reacts to ammonia in the gas phase. Measurements of solutions above  $10^{-3}$  M (17 ppm as  $\text{NH}_3$  and 14 ppm as N) ammonia are possible under these conditions.

To measure ammonia in samples containing surfactants or nonaqueous solutions, adjust the sample pH to between 11 and 13 with ISA. Transfer the solution to a 125 mL Erlenmeyer flask containing a magnetic stir bar. Fit the neck of the flask with a rubber stopper with a hole large enough to hold the electrode snugly. The closed flask forms an airtight system whose gas phase is saturated with water vapor and has a partial pressure of ammonia in equilibrium with the solution.

Normal analytical techniques may be used with the electrode in the gas phase. Calibrate the electrode in a closed flask of standards, or make a standard addition to the closed flask of sample. The electrode in the gas phase has a longer response time than if it were actually in a surfactant-free aqueous solution. A minimum air space between solution and electrode is necessary for best time response.

### Organic Nitrogen

For information concerning the measurement of organic nitrogen, contact our Technical Support Chemists and request the Orion Guide to Water and Wastewater Analysis.

# Troubleshooting

Follow a systematic procedure to isolate the problem. The measuring system can be divided into four components for ease in troubleshooting: meter, electrode, sample/application and technique.

## Meter

The meter is the easiest component to eliminate as a possible cause of error. Thermo Scientific Orion meters include an instrument checkout procedure and shorting cap for convenience in troubleshooting. Consult the meter user guide for directions.

## Electrode

1. Rinse the electrode thoroughly with distilled water.
2. Verify the electrode performance by performing the procedure in the **Checking Electrode Operation (Slope)** section.
3. If the electrode fails this procedure, review the **Measuring Hints** section. Clean the electrode thoroughly as directed in the **Electrode Maintenance** section. Drain and refill the electrode with fresh filling solution.
4. Repeat the procedure in the **Checking Electrode Operation (Slope)** section.
5. If the electrode still does not perform correctly, perform the procedure in the **Checking the Inner Body** section to determine if the inner body is working properly.
6. If the electrode passes the procedure in the **Checking the Inner Body** section, but measurement problems persist, the sample may contain interferences or complexing agents, or the technique may be in error.
7. Before replacing a faulty electrode, review this user guide and be sure to thoroughly clean the electrode; correctly prepare the electrode; use the proper filling solution, ISA and standards; correctly measure the samples and review the **Troubleshooting Checklist** section.

## Sample/Application

The quality of results depends greatly upon the quality of the standards. Always prepare fresh standards when problems arise, it could save hours of frustrating troubleshooting! Errors may result from contamination of prepared standards, accuracy of dilution, quality of distilled water, or a mathematical error in calculating the concentrations.

The best method for preparation of standards is serial dilution. Refer to the **Serial Dilution** section. The electrode and meter may operate with standards, but not with the sample. In this case, check the sample composition for interferences, incompatibilities or temperature effects. Refer to the **Sample Requirements, Temperature Effects** and **Interferences** sections.

## Technique

If trouble persists, review operating procedures. Review calibration and measurement sections to be sure proper technique has been followed. Verify that the expected concentration of the ion of interest is within the limit of detection of the electrode.

Check the method of analysis for compatibility with your sample. Direct measurement may not always be the method of choice. If a large amount of complexing agents are present, known addition may be the best method. If working with low level samples, follow the procedure in the **Low Level Calibration** section.

## Assistance

After troubleshooting all components of your measurement system, contact Technical Support. Within the United States call 1.800.225.1480 and outside the United States call 978.232.6000 or fax 978.232.6031. In Europe, the Middle East and Africa, contact your local authorized dealer. For the most current contact information, visit [www.thermo.com/contactwater](http://www.thermo.com/contactwater).

For the latest application and technical resources for Thermo Scientific Orion products, visit [www.thermo.com/waterapps](http://www.thermo.com/waterapps).

## Warranty

For the most current warranty information, visit [www.thermo.com/water](http://www.thermo.com/water).



## Checking the Inner Body

1. Prepare a pH 4.01 buffer with 0.1 M  $\text{NH}_4\text{Cl}$  or 0.1 M NaCl – Combine 100 mL of pH 4.01 buffer, Cat. No. 910104, and 0.54 grams of reagent-grade  $\text{NH}_4\text{Cl}$  or 0.58 grams of reagent-grade NaCl. Thoroughly stir the solution and label the bottle as Solution 1. Store the buffer for repeated use. Discard the buffer if turbidity develops.
2. Prepare a pH 7.00 buffer with 0.1 M  $\text{NH}_4\text{Cl}$  or 0.1 M NaCl – Combine 100 mL of pH 7.00 buffer, Cat. No. 910107, and 0.54 grams of reagent-grade  $\text{NH}_4\text{Cl}$  or 0.58 grams of reagent-grade NaCl. Thoroughly stir the solution and label the bottle as Solution 2. Store the buffer for repeated use. Discard the buffer if turbidity develops.

**Note:** *The temperature of the buffers and distilled water must be  $25\text{ }^\circ\text{C} \pm 4\text{ }^\circ\text{C}$  and all solutions should be at same temperature within  $\pm 1\text{ }^\circ\text{C}$ .*

3. Disassemble the ammonia electrode. If the electrode is dry, soak the glass tip of the inner body in filling solution for at least two hours.
4. Connect the electrode to a meter with a mV mode. Set the meter to the mV mode.
5. Rinse the inner body with distilled water and place it in the pH 7 buffer with 0.1 M  $\text{NH}_4\text{Cl}$  or 0.1 M NaCl added. Make sure that the coiled reference wire is completely covered. Stir the solution throughout the procedure. Record the millivolt reading after two minutes.
6. Rinse the inner body in distilled water and place it in the pH 4 buffer with 0.1 M  $\text{NH}_4\text{Cl}$  or 0.1 M NaCl added. Watch the change in the meter reading carefully. The reading should change by 100 mV in less than 30 seconds after immersion in the pH 4 buffer. After three minutes, the mV difference between pH 7 and pH 4 should be greater than 150 mV if the inner body is operating correctly.

# Troubleshooting Checklist

## Symptom: Off-scale or over-range reading

Membrane failure – Replace the membrane. Refer to the **Ammonia Electrode Preparation** section for instructions.

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Inner body not properly conditioned – Soak the inner body in electrode filling solution for at least two hours. For best results, soak the inner body overnight.

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Inner body defective – Refer to the **Troubleshooting** section and perform the checking the inner body procedure.

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Electrode filling solution not added – Fill the electrode up to the fill line with electrode filling solution.

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Air bubble on the membrane – Remove bubbles by gently tapping the side of the electrode.

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Electrode not in solution – Insert the electrode in solution.

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Electrode not plugged into the meter properly – Unplug and reconnect the electrode.

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Defective meter – Perform the meter checkout procedure (refer to the meter user guide).

## Symptom: Low slope or no slope

Membrane failure – Replace the membrane. Refer to the **Ammonia Electrode Preparation** section for instructions.

---

Inner body defective – Refer to the **Troubleshooting** section and perform the checking the inner body procedure.

---

Standards contaminated or made incorrectly – Prepare fresh standards, refer to the **Serial Dilution** section.

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ISA not used or incorrect ISA used – Add pH adjusting ISA, Cat. No. 951211, to all standards and samples immediately before measurements are taken.

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Electrode exposed to air for extended period – Replace the membrane. Refer to the **Ammonia Electrode Preparation** section for instructions.

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**Symptom: Noisy or unstable readings (erratic, rapidly changing)**

Insufficient electrode filling solution – Fill the electrode up to the fill line with electrode filling solution.

---

Membrane cap loose – Ensure that the membrane cap is screwed on tight enough to close the gap between the cap and body.

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Inner body defective – Refer to the **Troubleshooting** section and perform the checking the inner body procedure.

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ISA not used – Use the recommended ISA, Cat. No. 951211.

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Defective meter – Perform the meter checkout procedure (refer to the meter user guide).

**Symptom: Wrong answer but calibration curve is correct**

Standards contaminated or made incorrectly – Prepare fresh standards, refer to the **Serial Dilution** section.

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Incorrect scaling of semi-logarithmic paper – Refer to the **Direct Calibration Technique** section.

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Incorrect millivolt sign used – Make sure to correctly record the sign of mV values.

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Incorrect units used – Apply the correct conversion factor:  
 $10^{-3} \text{ M} = 17 \text{ ppm as } \text{NH}_3 = 14 \text{ ppm as N}$

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Complexing agents in sample – Use known addition, titration techniques or a decomplexing procedure.

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ISA added to standards, but not samples – Add the same proportion of ISA to all standards and samples.

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**Symptom: Drift (reading slowly changing in one direction)**

Membrane failure – Replace the membrane. Refer to the **Ammonia Electrode Preparation** section for instructions.

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Inner body defective – Refer to the **Troubleshooting** section and perform the checking the inner body procedure.

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Ammonia loss from sample sitting too long – Reduce the surface area to volume ratio, slow the rate of stirring and avoid high temperatures.

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Filling solution leaking – Ensure that the membrane is installed properly. Refer to the **Ammonia Electrode Preparation** section.

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Electrode not assembled properly – Ensure that the inner body is fully inserted in the top of the outer body when assembling the electrode. Refer to the **Ammonia Electrode Preparation** section.

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Samples and standards at different temperatures – Allow solutions to come to room temperature before measurement.

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Incorrect electrode filling solution used – Fill the electrode using the correct electrode filling solution, Cat. No. 951202.

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Total level of dissolved species above 1 M – Dilute solutions.

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Meter or stirrer improperly grounded – Check meter and stirrer for grounding issues.

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Solutions not at constant temperature – Allow solutions to come to room temperature before use.

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Magnetic stirrer generating heat – Place insulating material between the magnetic stirrer and beaker.

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Electrode exposed to air for extended period – Replace the membrane. Refer to the **Ammonia Electrode Preparation** section for instructions.

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# Ordering Information

<b>Cat. No.</b>	<b>Description</b>
9512BNWP	Ammonia electrode with waterproof BNC connector
951201	Ammonia electrode with U.S. standard connector
951204	Loose membranes, box of 20
951211	pH adjusting ISA, 475 mL bottle
951202	Electrode filling solution, 60 mL bottle
951006	0.1 M NH <sub>4</sub> Cl standard, 475 mL bottle
951007	1000 ppm ammonia as nitrogen standard, 475 mL bottle
951207	100 ppm ammonia as nitrogen standard, 475 mL bottle

# Specifications

## Concentration Range

5 x 10<sup>-7</sup> M to 1 M

0.01 ppm to 17,000 ppm as NH<sub>3</sub>

0.01 to 14,000 ppm as N)

## pH Range

Samples and standards must be adjusted to above pH 11

## Temperature Range

0 to 50 °C

## Electrode Resistance

Less than 5,000 megohms

## Reproducibility

± 2%

## Size

Body Diameter: 12 mm

Body Length: 150 mm

Cap Diameter: 16 mm

Cable Length: 1 meter

*\* Specifications are subject to change without notice*



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