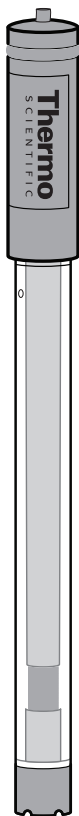


User Guide

High Performance
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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General Information

Introduction

The high performance ammonia ion selective electrode (ISE) allows fast, simple, economical, and accurate measurements of dissolved ammonia in aqueous solutions. This gas sensing electrode can also be used to measure the ammonium ion after conversion to ammonia or to measure organic nitrogen after Kjeldahl digestion of the sample. Sample color and turbidity do not affect the measurement and samples do not need to be distilled. Almost all anions, cations and dissolved species, other than volatile amines, do not interfere.

All apparatus and solutions required for measurement, electrode characteristics and electrode theory are discussed in this user guide. General analytical procedures, low-level procedures and a method for measuring ammonia in solutions that wet the membrane are given.

The High Performance Ammonia Electrode Includes:

- One preassembled outer body and membrane cap- includes outer body, membrane cap and membrane
- Twenty loose membranes
- Tweezers for handling loose membranes
- Electrode filling solution
- Dispensing cap for electrode filling solution
- User guide

There are two measurement techniques that are recommended for direct measurements of ammonia samples. The primary direct measurement technique is for ammonia samples with concentrations of 1 ppm ammonia as nitrogen and higher. The low-level measurement technique is for ammonia samples with concentrations of 10 ppm ammonia as nitrogen and lower. Refer to the **Analytical Techniques** section for details.

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.thermoscientific.com/water.

Required Equipment

1. Thermo Scientific Orion ISE meter, such as the Orion DUAL STAR meter, 4-Star pH/ISE meter or 5-Star pH/ISE/DO/conductivity meter.

Ammonia electrodes can be used on any ISE 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.thermoscientific.com/water for details.

2. Thermo Scientific Orion high performance ammonia ion selective electrode, Cat. No. 9512HPBNWP or 9512HP01.
3. Magnetic stirrer or Orion stirrer probe, Cat. No. 096019. The Orion stirrer probe can be used with the Orion DUAL STAR meter or 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 ammonia-free. Pass 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. 951209.
7. Ammonia calibration standards.

Cat. No.	Description
951006	0.1 M ammonia chloride standard
951007	1000 ppm ammonia as nitrogen standard
951207	100 ppm ammonia as nitrogen standard

8. Ionic Strength Adjuster (ISA), which provides a constant background ionic strength and adjusts the solution pH.

Cat. No.	Description
951211	Ammonia pH-adjusting ISA with pH-indicating blue dye, for samples that have a concentration of 1 ppm ammonia as nitrogen or higher
951210	Low Level Ammonia pH-adjusting ISA with pH-indicating blue dye, for samples that have a concentration of 10 ppm ammonia as nitrogen or lower
951011	Alkaline reagent (alternative low level ISA), for samples that have a concentration of 1 ppm ammonia as nitrogen or lower (does not contain pH-indicating blue dye)

Note: *If metallic ions are present in the samples, use Cat. No. 951211. See the Complexation Section for additional information.*

9. Ammonia electrode storage solution, Cat. No. 951213. Refer to the **Electrode Storage** section for detailed instructions on storage solution usage.

Electrode Setup

Electrode Assembly

Note: A new electrode is shipped without a membrane. You must install a preassembled outer body and membrane cap assembly or a new membrane before using the electrode.

Note: A new electrode is shipped dry. You must 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.

Assemble the electrode according to the instructions listed in the **Electrode Preparation with a Preassembled Outer Body and Membrane Cap Assembly** or **Electrode Preparation with Loose Membranes** section. Avoid excessive handling of the membrane during assembly; this may affect the hydrophobic properties of the membrane and cause a shortened membrane life. Use the tweezers provided. A membrane will last from one week to several months, depending on usage.

Electrode Preparation with a Preassembled Outer Body and Membrane Cap Assembly

1. Hold the electrode vertically and unscrew the electrode cap from the electrode body. See **Figure 1**.
2. Carefully remove the inner body from the outer body assembly. See **Figure 2**. Dispose of any electrode filling solution that is in the outer body.

Note: A new electrode is shipped dry. You must 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.

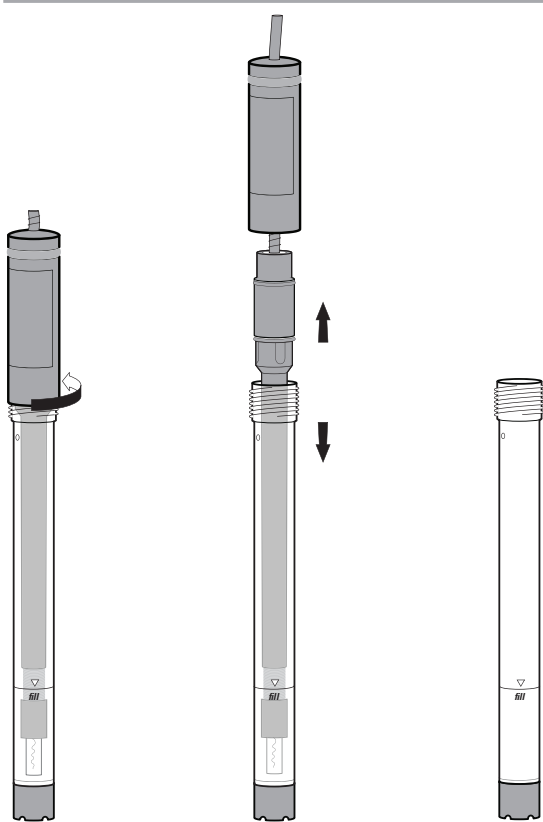


Figure 1

Figure 2

Figure 3

3. Select a new preassembled outer body and membrane cap assembly and verify that the membrane is not wrinkled or torn. See **Figure 3**.
4. Fill the preassembled outer body and membrane cap to the fill line with electrode filling solution. See **Figure 4**.
5. Insert the inner body into the preassembled outer body and membrane cap. Ensure that the inner body is fully inserted in the top of the outer body and then screw on the electrode cap. See **Figure 5**.
6. Gently tap the side of the electrode to remove air bubbles.
7. Soak the electrode in the ammonia electrode storage solution, Cat. No. 951213, for at least 15 minutes before use. Refer to the **Electrode Storage** section for detailed instructions on storage solution usage.

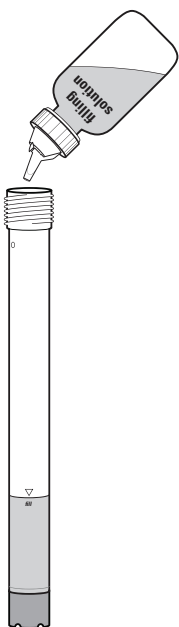


Figure 4

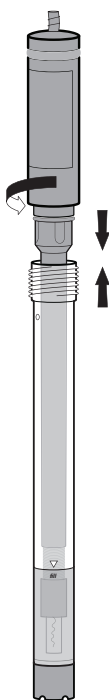


Figure 5

Electrode Preparation with Loose Membrane

1. Hold the electrode vertically and unscrew the electrode cap from the electrode body. See **Figure 6**.
2. Carefully remove the inner body from the outer body assembly. See **Figure 7**. Dispose of any electrode filling solution that is in the outer body.

Note: A new electrode is shipped dry. You must 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 from the outer body. See **Figure 8**. Remove the membrane from the membrane cap if a membrane was previously installed.

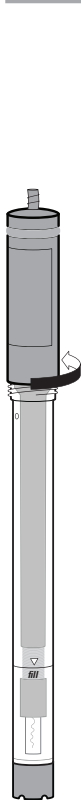


Figure 6

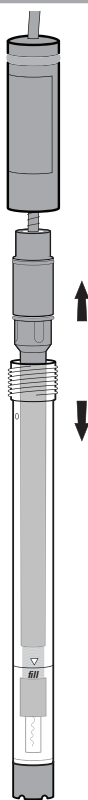


Figure 7



Figure 8

4. Wear gloves and use tweezers to carefully grasp the corner of the white membrane from between wax paper separators. See **Figure 9**.

Note: Do not touch the center of the membrane.

5. Hold the outer body oriented with the smaller diameter threads at the top. See **Figure 10**.
6. Align the serrated edge of the membrane against the threaded shoulder and hold the membrane with your thumb. See **Figure 11**.



Figure 9

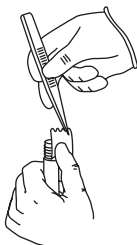


Figure 10

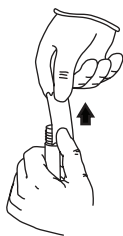


Figure 11

7. With the other hand, gently place the membrane across the opening. See **Figure 12**.
8. Then place the membrane down to align the other edge with the opposite shoulder. See **Figure 13**.
9. While holding each edge on both sides, gently place each smooth side of the membrane out and down over the threads and ensure that the membrane surface is smooth and without wrinkles. See **Figure 14**.
10. Smooth any loose material, taking care not to touch center of membrane. See **Figure 15**.



Figure 12



Figure 13

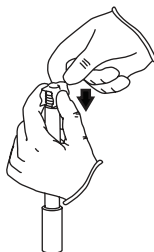


Figure 14

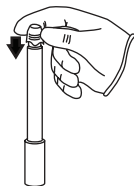


Figure 15

Note: Do not stretch the membrane.

11. Screw the membrane cap onto the outer body, being careful not to touch membrane. See **Figure 16**. Screw the membrane cap on half way and wrap any loose membrane material onto the threads and under the cap. Make sure the cap is fully screwed on.
12. Fill the outer body to the fill line with electrode filling solution. See **Figure 17**.
13. 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 18**.
14. Gently tap the side of the electrode to remove air bubbles.
15. Soak the electrode in the ammonia electrode storage solution, Cat. No. 951213, for at least 15 minutes before use. Refer to the **Electrode Storage** section for detailed instructions on storage solution usage.



Figure 16

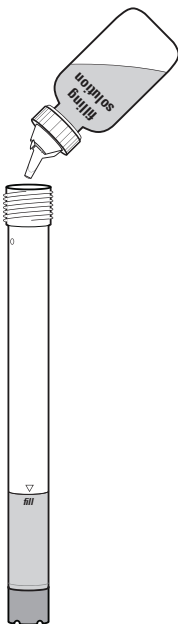


Figure 17

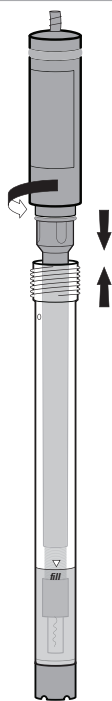


Figure 18

Checking Electrode Operation (Slope)

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

1. If the electrode has been stored dry, prepare the electrode as described in the **Electrode Preparation** section.
2. Connect the electrode to the meter.
3. Place 100 mL of distilled water into a 150 mL beaker. Add 2 mL of pH-adjusting ISA, Cat. No. 951211, or 2 mL of low level pH-adjusting ISA, Cat. No. 951210. Stir the solution thoroughly. Set the meter to the mV mode.
4. Rinse the electrode by immersing it in distilled water, blot it dry and place it into the solution prepared in step 3. To prevent air entrapment on the membrane surface, be sure to use an electrode holder that keeps the electrode at a 20° angle. If air bubbles appear on the sensing membrane, gently tap the electrode to remove the bubbles.
5. Select either a 0.1 M ammonium chloride or 1000 ppm ammonia as nitrogen standard. Pipette 1 mL of the standard into the beaker and stir the solution thoroughly. When a stable reading is displayed, after about 2 minutes, record the electrode potential in millivolts.
6. Pipette 10 mL of the same standard into the same beaker. Stir the solution thoroughly. When a stable reading is displayed, after about 2 minutes, 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 20-25 °C. If the millivolt potential is not within this range, refer to the **Troubleshooting** section.

Note: *If working with ammonia samples with concentrations of 1 ppm as nitrogen and lower, refer to the Low-Level Measurements by Direct Calibration section for a low-level checking electrode operation procedure.*

Units of Measurement

Ammonia can be measured in units of moles per liter (M), parts per million as ammonia, parts per million as nitrogen or any other convenient unit. See **Table 1**.

Table 1
Concentration Unit Conversion Factors

moles/liter (M)	ppm as nitrogen (N)	ppm as ammonia (NH ₃)
10 ⁻⁴	1.40	1.70
10 ⁻³	14.0	17.0
10 ⁻²	140	170
10 ⁻¹	1400	1700

Sample Requirements

Samples must be aqueous; they must not contain organic solvents. Contact Technical Support for recommendations on the use of the electrode in unusual applications. Samples and standards should be at the same temperature. A 1 °C difference in temperature will give rise to about 2% measurement error. In all analytical procedures, ISA must be added to all samples and standards immediately before measurement. After addition of the ISA, all solutions should fall within a pH 11 to 14 range (solutions should be blue in this range when using the pH-adjusting ISA, Cat. No. 951211, or low level pH-adjusting ISA, Cat. No. 951210.) and have a total level of dissolved species below 1 M. If the total level of dissolved species is above 1 M, see the **Effect of Dissolved Species** section.

Measuring Hints

- Store samples according to the **Sample Storage** section.
- Use beakers that minimize the ratio of surface area to volume.
- Keep beakers containing standards and samples covered between measurements.
- If working with samples that have a concentration of 1 ppm as nitrogen or higher, add 2 mL of pH-adjusting ISA (Cat. No. 951211) to every 100 mL of sample or standard. Once the ISA is added, a blue color should be observed.
- If working with samples that have a concentration of 10 ppm ammonia as nitrogen or lower, add 2 mL of low level pH-adjusting ISA (Cat. No. 951210) to every 100 mL of sample or standard. Once the low level ISA is added, a blue color should be observed.
- If alkaline reagent (Cat. No. 951011) is used instead of low level pH-adjusting ISA, add 1 mL of alkaline reagent to every 100 mL of standard or sample and use when working with ammonia samples that have concentrations of 1 ppm ammonia as nitrogen or lower.
- ISA should be added immediately before a calibration or measurement is made to prevent ammonia loss. Wait 2 minutes after the ISA is added before entering a calibration value or recording a measurement. This allows all of the ammonia in the sample to be fully converted to gas and will give more accurate calibrations and measurements.
- Between measurements, rinse the electrode by immersing it in distilled water.
- Be sure samples, standards and the electrode are at the same temperature.
- Samples and standards should be stirred using a magnetic stirrer or stirrer probe. Some magnetic stirrers generate enough heat to change solution temperature. Place a piece of insulating material such as cork or styrofoam between the beaker and the stirring plate to minimize this effect.
- Stir all standards and samples at a moderate, uniform rate.

- Verify calibration every two hours by placing the electrode in a fresh aliquot of the middle or high concentration standard used for calibration. If the value has changed, recalibrate the electrode.
- Always use fresh standards for calibration.
- After immersion in solution, check the electrode for any air bubbles on the membrane surface and remove bubbles by gently tapping the electrode.
- If electrode response is slow, replace the membrane and soak the electrode for at least 15 minutes in the ammonia electrode storage solution. Refer to the **Electrode Preparation** section.

Sample Storage

If possible, alkaline samples should be measured immediately. The rate of ammonia loss at room temperature 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 liter of sample, and place samples in tightly capped vessels. Make stored samples basic by adding ISA immediately before measurement.

For information on EPA regulations on ammonia sample storage, visit the Applications and Technical Resources section of our website at www.thermo.com/water.

Electrode Storage

Note: *The membrane must not be allowed to dry out. If the membrane is left out of solution, replace the membrane. Refer to the Electrode Preparation section.*

Storage between measurements– Store the electrode in the least concentrated calibration standard. Alternatively, the ammonia electrode storage solution, Cat. No. 951213, can be diluted and used for storage between measurements. Combine 2 mL of storage solution and 250 mL of deionized water and use this solution for storage between measurements.

Overnight storage and storage up to one week– Store the electrode in the ammonia electrode storage solution, Cat. No. 951213.

Storage over one week– Disassemble the electrode and rinse all the components with distilled water. Dry and reassemble the electrode without electrode filling solution and without a membrane. When preparing the electrode for use, follow the procedures in the **Electrode Preparation** section.

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.

Incremental Techniques provide a useful method for measuring samples, since calibration is not required. As in direct calibration, any convenient concentration unit can be used. 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 (50-100 times) excess of complexing agents.

- **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.
- **Titration**s 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.

Typical 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** section for concentrations in the linear region of electrode response. The **Low-Level Measurements By Direct Calibration** section provides procedures for measurements in the non-linear region of electrode response.

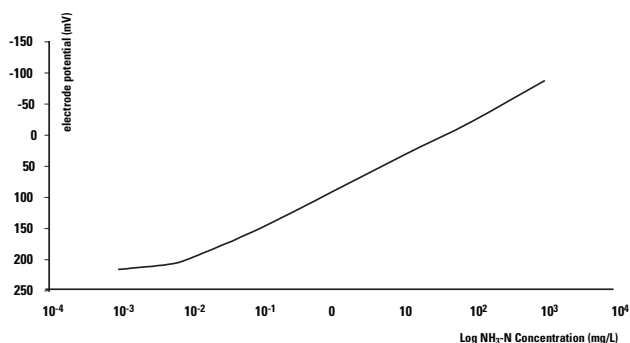


Figure 19: Typical Ammonia Electrode Calibration Curve

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. 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.

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 NH_4Cl standard (170 ppm as NH_3 and 140 ppm as N)**– Pipette 10 mL of the 0.1 M NH_4Cl standard into a 100 mL volumetric flask. Dilute to mark with deionized water and mix well.
2. **To prepare a 10^{-3} M NH_4Cl standard (17 ppm as NH_3 and 14 ppm as N)**– Pipette 10 mL of the 10^{-2} M NH_4Cl standard into a 100 mL volumetric flask. Dilute to mark with deionized water and mix well.
3. **To prepare a 10^{-4} M NH_4Cl standard (1.7 ppm as NH_3 and 1.4 ppm as N)**– Pipette 10 mL of the 10^{-3} M NH_4Cl standard into a 100 mL volumetric flask. Dilute to mark with deionized water and mix well.
4. **To prepare a 10^{-5} M NH_4Cl standard (0.17 ppm as NH_3 and 0.14 ppm as N)**– Pipette 10 mL of the 10^{-4} M NH_4Cl standard into a 100 mL volumetric flask. Dilute to mark with deionized water and mix well.

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

$$C_1 * V_1 = C_2 * V_2$$

where

C₁ = concentration of original standard

V₁ = volume of original standard

C₂ = concentration of standard after dilution

V₂ = volume of standard after dilution

For example, to prepare 100 mL of 25 ppm as NH₃ standard from a 500 ppm as NH₃ standard:

C₁ = 500 ppm as NH₃

V₁ = unknown

C₂ = 25 ppm as NH₃

V₂ = 100 mL

$$500 \text{ ppm} * V_1 = 25 \text{ ppm} * 100 \text{ mL}$$

$$V_1 = (25 \text{ ppm} * 100 \text{ mL}) / 500 \text{ ppm} = 5 \text{ mL}$$

To make the 25 ppm as NH₃ standard: Pipette 5 mL of the 500 ppm as NH₃ standard into a 100 mL volumetric flask. Dilute to mark with deionized water and mix well.

Direct Calibration Using a Meter with an ISE (Concentration) Mode

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

1. Measure 100 mL of the less concentrated standard into a 150 mL beaker. Add 2 mL of pH-adjusting ISA. Stir the solution thoroughly.
2. Rinse the electrode by immersing it in distilled water, blot it dry and place it into the beaker with the less concentrated standard. Wait about 2 minutes for a stable reading and then adjust the meter to display the value of the standard, as described in the meter user guide.
3. Measure 100 mL of the more concentrated standard into a second 150 mL beaker. Add 2 mL of pH-adjusting ISA. Stir the solution thoroughly.
4. Rinse the electrode by immersing it in distilled water, blot it dry and place it into the beaker with the more concentrated standard. Wait about 2 minutes for a stable reading and then 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 to -60 mV when the standards are between 20-25 °C.
6. Measure 100 mL of the sample into a 150 mL beaker. Add 2 mL of pH-adjusting ISA. Stir the solution thoroughly.
7. Rinse the electrode by immersing it in distilled water, blot it dry and place it into sample. Wait about 2 minutes and the concentration will be displayed on the meter.

Note: Smaller volumes of solutions may be used as long as the ratio of standard or sample to pH-adjusting ISA does not change. For example, 50 mL of standard or sample requires the addition of 1 mL of pH-adjusting ISA.

Direct Calibration Using a Meter with a Millivolt Mode

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

Low-Level Measurements By Direct Calibration

These procedures are for solutions with a concentration of 10 ppm ammonia as nitrogen (7×10^{-4} M, 12 ppm as ammonia) or less. For solutions low 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
- ISA should be added immediately before a calibration or measurement is made to prevent ammonia loss. Wait at least 2 minutes after the ISA is added before entering a calibration value or recording a measurement.

Electrode response is relatively slow at low levels of ammonia and is faster going in the direction of increasing concentration. When measuring low levels of ammonia, keep samples and standards covered and work with large solution volumes to minimize surface-area-to-volume ratio. This avoids ammonia absorption from air. Time response is slow at ammonia concentrations of 0.1 ppm ammonia as nitrogen and lower. Allow up to 5 minutes for a stable reading in a low-level standard or sample.

Setup

1. Prepare the electrode as described in the **Electrode Preparation** section.
2. Soak the electrode in ammonia electrode storage solution for at least 15 minutes. After, soak the electrode in deionized water for about 2 to 5 minutes.
3. Rinse the electrode by immersing it in distilled water and then blot it dry.
4. Connect the electrode to the meter.

Low-Level Checking Electrode Operation (Slope)

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

1. Place 100 mL of distilled water into a 150 mL beaker. Add 2 mL of low level pH-adjusting ISA, Cat. No. 951210. Stir the solution thoroughly. Set the meter to the mV mode.
2. Rinse the electrode by immersing it in distilled water, blot it dry and place it into the solution prepared in step 1. To prevent air entrapment on the membrane surface, be sure to use an electrode holder that keeps the electrode at a 20° angle. If air bubbles appear on the sensing membrane, gently tap the electrode to remove the bubbles.
3. Select either a 100 ppm ammonia as nitrogen standard or 10 ppm ammonia as nitrogen standard. Pipette 1 mL of the standard into the beaker and stir the solution thoroughly. When a stable reading is displayed, after at least 2 minutes, record the electrode potential in millivolts.
4. Pipette 10 mL of the same standard into the same beaker. Stir the solution thoroughly. When a stable reading is displayed, after at least 2 minutes, record the electrode potential in millivolts.
5. There should be a 54 to 60 mV difference between the two millivolt readings when the solution temperature is between 20-25 °C. If the millivolt potential is not within this range, refer to the **Troubleshooting** section.

Low-Level Calibration

1. Prepare a 1 ppm ammonia as nitrogen standard by pipetting 10 mL of the 100 ppm ammonia as nitrogen standard into a 1 L volumetric flask and diluting to the mark with deionized water.
2. Prepare a 0.1 ppm ammonia as nitrogen standard by pipetting 50 mL of the 1 ppm ammonia as nitrogen standard into a 500 mL volumetric flask and diluting to the mark with deionized water.
3. Prepare a 0.01 ppm ammonia as nitrogen standard by pipetting 50 mL of the 0.1 ppm ammonia as nitrogen standard into a 500 mL volumetric flask and diluting to the mark with deionized water.
4. Measure 50 mL of each standard and pour the standards into separate, clean beakers. Just prior to calibration, add 1 mL of low-level pH-adjusting ISA, Cat. No. 951210, to each beaker. Wait at least 2 minutes after the ISA is added before entering any calibration values.
5. Set the meter measurement mode to ISE. If using a Thermo Scientific Orion Star Series meter or equivalent meter, it is recommended to set the stirrer speed to 3 and the read type to continuous. It is also recommended in the ISE setup mode to set the resolution to 3, the units to mg/L, the range to low and to turn on the blank correction feature.
6. Perform a three point calibration using the 0.01 ppm ammonia as nitrogen, 0.1 ppm ammonia as nitrogen and 1 ppm ammonia as nitrogen standards. Between standards, rinse the electrode by immersing it in distilled water and then blot it dry. Stir all solutions throughout the procedure. Calibrate daily using fresh solutions.

Measuring Ammonia in Solutions that Wet the Membrane

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

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

To measure ammonia in samples containing surfactants, or nonaqueous solutions, adjust the sample pH to 11-13 with pH-adjusting ISA. Transfer the solution to a 125 mL Erlenmeyer flask containing a magnetic stirring bar. Fit the neck of the flask with a rubber stopper that has 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. Minimum air space between solution and electrode is necessary for best time response.

Measuring Organic Nitrogen

For information concerning the measurement of organic nitrogen, 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.thermoscientific.com/water.

Nitrate Analysis Test Kit , Cat. No. 700005

The nitrate analysis test kit includes one 475 mL bottle each of alkaline reagent (Cat. No. 951011), reducing reagent (Cat. No. 700006), 100 ppm nitrate as nitrogen standard (Cat. No. 930707), 100 ppm ammonia as nitrogen standard (Cat. No. 951207); two 50 mL bottles of electrode filling solution (Cat. No. 951203); and application procedure number 115: "Nitrate Measurement in Environmental Samples".

Application Notes

For application notes, such as measuring ammonia in wastewater, please visit www.thermoscientific.com/water and select the applications link.

Known Addition

Known Addition is a convenient technique for measuring samples because no calibration curve is needed. 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 measurement requires 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.
- In general, either no complexing agent or a large excess of the complexing agent must be present.
- 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.

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, upon addition to the sample, will cause concentration of the ammonia to double. Refer to **Table 2** as a guideline.
4. Determine the slope of the electrode by performing the procedure in the **Checking Electrode Operation (Slope)** section.
5. Rinse the electrode between solutions by immersing it in distilled water and then blot it dry.

Using a Meter with a Known Addition Mode:

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

1. Set the meter to the known addition mode.
2. Measure 100 mL of the sample into a beaker.
3. Rinse the electrode by immersing it in distilled water, blot it dry and then place it in the sample solution. Add 2 mL of pH-adjusting ISA. Stir the solution thoroughly.
4. When a stable reading is displayed, after about 2 minutes, set the meter as described in the meter user guide, if required.
5. Pipette the appropriate amount of the standard solution into the beaker. Stir the solution thoroughly.
6. When a stable reading is displayed, record the sample concentration.

Using a Meter with a Millivolt Mode:

1. Set the meter to relative millivolt mode.
2. Measure 100 mL of the sample into a 150 mL beaker. Add 2 mL of pH-adjusting ISA. Stir the solution thoroughly.
3. Rinse the electrode by immersing it in distilled water, blot it dry and then place it in the sample solution. When a stable reading is displayed, after about 2 minutes, set the millivolt reading to zero. If the reading cannot be set to zero, record the mV value.
4. Pipette 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 zeroed in step 3, subtract the first reading from the second to find ΔE .

6. From **Table 3**, find the Q value that corresponds to the change in potential, ΔE . To determine the original sample concentration, multiply Q by the concentration of the added standard:

$$C_{\text{sam}} = QC_{\text{std}}$$

where:

C_{std} = standard concentration

C_{sam} = sample concentration

Q = reading from known addition table

The table of Q values is calculated for a 10% volume change for electrodes with slope in the range of -57.2 to -60.2 mV. The equation for the calculation of Q for different slopes and volume changes is given below:

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

where:

Q = reading from known addition table

ΔE = $E_2 - E_1$

S = slope of the electrode

$p = \frac{\text{volume of standard}}{\text{volume of sample}}$

Table 2

Volume of Addition	Concentration of Standard
1 mL	100 x sample concentration
5 mL	20 x sample concentration
10 mL*	10 x sample concentration

* Most convenient volume to use

Table 3
Known Addition Table for an added volume one-tenth the sample
volume. Slopes (in the column headings) are in units of mV/decade.

ΔE	Q Concentration Ratio			
	(-57.2)	(-58.2)	(-59.2)	(-60.1)
Monovalent				
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	0.2073
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
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

ΔE	Q Concentration Ratio			
	Monovalent	(-57.2)	(-58.2)	(-59.2)
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
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 exhibits good time response (one minute or less) for ammonia concentrations above 1 ppm ammonia as nitrogen. 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.

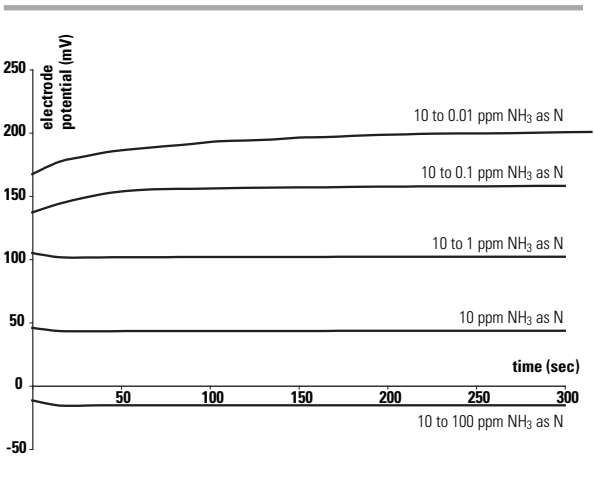


Figure 20: Typical Electrode Response To Step Changes in Ammonia Concentration

Temperature Effects

A change in temperature will cause electrode response to shift and change slope. **Table 4** lists the variation of theoretical response with temperature. At 10^{-3} M, a 1 °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 4

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

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. Note that the low-level pH-adjusting ISA, Cat. No. 951210, and alkaline reagent, Cat. No. 951011, do not remove 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, Cat. No. 951211, 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. Note that the low-level pH-adjusting ISA, Cat. No. 951210, and alkaline reagent, Cat. No. 951011, do not inhibit the formation of common metal complexes in the sample.

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 g solid NaNO_3 to each 100 mL electrode filling solution.

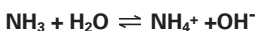
Membrane Life

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 **Troubleshooting** section.

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
- E₀** = reference potential
- OH⁻** = hydroxide concentration in solution
- S** = electrode slope (-59.2 mV/decade)

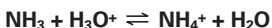
Since the hydroxide concentration is proportional to ammonia concentration, electrode response to ammonia is also Nernstian.

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

The reference potential, E₀, 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 21**). 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.

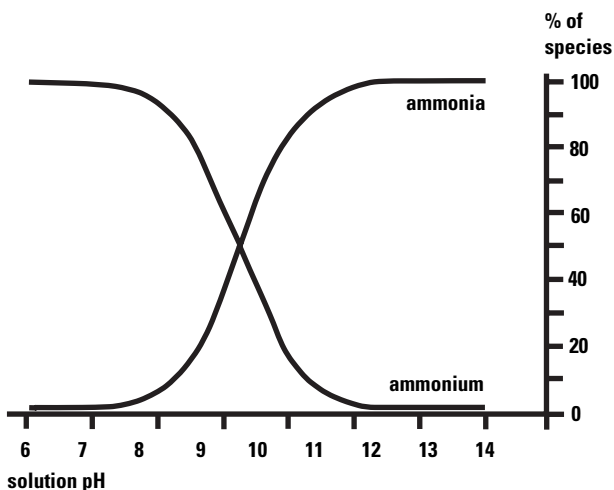


Figure 21: Percent of Ammonia and Ammonium as a Function of pH

Troubleshooting

Troubleshooting Checklist

Symptom: Off-scale or over-range reading

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

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.

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

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

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

Electrode not in solution– Insert the electrode in solution.

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

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 **Electrode Preparation** section for instructions.

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

Standards contaminated or made incorrectly– Prepare fresh standards.

ISA not used or incorrect ISA used– Use pH-adjusting ISA, Cat. No. 951211, when working with ammonia samples that have concentrations of 1 ppm ammonia as nitrogen or higher. Add 2 mL of pH-adjusting ISA to every 100 mL of standard and sample.

Use low level pH-adjusting ISA, Cat. No. 951210, when working with ammonia samples that have concentrations of 10 ppm ammonia as nitrogen or lower. Add 2 mL of low level pH-adjusting ISA to every 100 mL of standard and sample. If alkaline reagent (Cat. No. 951011) is used instead of low level pH-adjusting ISA, add 1 mL of alkaline reagent to every 100 mL of standard or sample and use when working with ammonia samples that have concentrations of 1 ppm ammonia as nitrogen or lower.

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

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.

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

ISA not used– Use the recommended ISA.

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.

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

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

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

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

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

Both ISA solutions used for one analysis– Use only one type of ISA for each calibration and measurement set. Use pH-adjusting ISA, Cat. No. 951211, with ammonia samples that are 1 ppm and higher. Use low-level pH-adjusting ISA, Cat. No. 951210, with ammonia samples that are 10 ppm and lower. It is especially important to only use one type of ISA if the alkaline reagent (Cat. No. 951011) is used instead of low level pH-adjusting ISA, to ensure that the dilution ratio is the same for the calibration and measurement set.

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

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

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

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

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

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 **Electrode Preparation** section.

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

Incorrect electrode filling solution used– Fill the electrode using the correct electrode filling solution, Cat. No. 951209.

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

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

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

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

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

Troubleshooting Guide

The most important principle in troubleshooting is to isolate the components of the system and check each in turn. The components of the system are the meter, electrode, standard, sample 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 in the meter user guide and a shorting strap for convenience in troubleshooting. Consult the user guide for complete instructions and verify that the instrument operates as indicated and is stable in all steps.

Electrode

1. Rinse the electrode thoroughly with distilled water.
2. Perform **Checking Electrode Operation (Slope)** procedure.
3. If the electrode fails this procedure, replace the membrane and soak the electrode as directed in the **Electrode Preparation** section.
4. Repeat the **Checking Electrode Operation (Slope)** procedure.
5. If the electrode still does not perform correctly, perform the **Checking Inner Body** procedure to determine if the inner body is working properly.

Checking Inner Body:

Solution 1– pH 4.01 buffer with 0.1 M NH_4Cl or 0.1 M NaCl

Take 100 mL of pH 4.01 buffer, Cat. No. 910104, and add 0.54 g of reagent-grade NH_4Cl or 0.58 g 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.

Solution 2– pH 7.00 Buffer with 0.1 M NH_4Cl or 0.1 M NaCl

Take 100 mL of pH 7.00 buffer, Cat. No. 910107, and add 0.54 g of reagent-grade NH_4Cl or 0.58 g 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 $\pm 1\text{ }^{\circ}\text{C}$.

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. Rinse the inner body with distilled water and immerse it in pH 7 buffer with 0.1 M NH_4Cl added. Make sure that the coiled reference wire is completely covered. Stir the solution throughout the procedure. Record the millivolt reading after two minutes.

Rinse the inner body in distilled water and place in the pH 4 buffer with 0.1 M NH_4Cl added. Watch the change in 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.

6. If the stability and slope check out properly, but measurement problems still persist, the sample may contain interferences or complexing agents, or the technique may be in error. Refer to the **Standard, Sample,** and **Technique** sections.
7. Before replacing a “faulty” electrode, review the instruction manual and be sure to:
 - Clean the electrode thoroughly
 - Prepare the electrode properly
 - Use proper electrode filling solution, ISA and standards
 - Review the **Troubleshooting Checklist** section

Standard

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 by serial dilution. Refer to the **Direct Calibration** section.

Sample

If the electrode works properly in standards but not in the sample, look for possible interferences, complexing agents or substances that could alter the electrode response or physically damage the electrode. If possible, determine the composition of the samples and check for problems. Refer to the **Sample Requirements**, **Interferences**, and **pH Requirements** sections.

Technique

Check the method of analysis for compatibility with your sample. Direct measurement may not always be the method of choice. If large amounts of complexing agents are present, known addition may be best method. If the sample is viscous, analate addition may solve the problem. If working at low levels, be sure to follow the low-level measurement technique. Also, be sure that the expected concentration of the ion of interest is within the electrode's limit of detection. If problems persist, review operational procedures and instruction manuals to be sure that proper technique has been followed. Refer to the **Measuring Hints** and **Analytical Techniques** sections.

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.thermoscientific.com/water.

Warranty

For the most current warranty information, visit www.thermoscientific.com/water.

Ordering Information

Cat. No.	Description
9512HPBNWP	High performance ammonia electrode with waterproof BNC connector
9512HP01	High performance ammonia electrode with U.S. standard connector
951214	Loose membranes, box of 20
951215	Preassembled outer body and membrane cap assembly, 3 pack
951211	Ammonia pH-adjusting ISA with pH-indicating blue dye, 475 mL bottle
951210	Ammonia low level pH-adjusting ISA with pH-indicating blue dye, 475 mL bottle
951213	Ammonia electrode storage solution, 475 mL bottle
951209	Electrode filling solution, 60 mL bottle
951006	0.1 M NH ₄ 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

Note: Use 951214 and 951215 only with the 9512HPBNWP and 9512HP01 high performance ammonia electrodes

Specifications

Concentration Range

5 x 10⁻⁷ to 1 M

0.01 to 17,000 ppm as ammonia (NH₃)

0.01 to 14,000 ppm as nitrogen (N)

pH Range

Samples and standards must be adjusted above pH 11

Temperature Range

0 to 50 °C

Electrode Resistance

Less than 1,500 megohms

Slope

-54 to -60 mV (in the linear range of the electrode, with all solutions at 25 °C ± 4 °C and with all solutions at same temperature within ± 1° C)

Response Time

1 minute or less (at higher concentrations and with ideal electrode conditions)

Size

Electrode Length: 115 mm

Body Diameter: 12 mm

Cap Diameter: 16 mm

Cable Length: 1 meter

Note: Specifications subject to change without notice



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