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GENERAL INFORMATION

Introduction

The Orion 95-12 Ammonia Electrode 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 organic nitrogen after Kjeldahl digestion of the sample. Sample color and turbidity do not affect the measurement, and samples need not 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 manual. General analytical procedures, low-level procedures and a method for measuring ammonia in solutions that wet the membrane are given.

The Orion 95-12 comes with the following:

- forty loose membranes
- reusable membrane cap
- tweezers for handling membranes
- dispensing cap
- electrode filling solution
- electrode instruction manual.

Operator instructions for Orion Meters are outlined in the individual meter's instruction manual. Our Technical Service Chemists can be consulted for assistance and troubleshooting advice. Please refer to **Troubleshooting** Section for information on contacting Technical Services.

Required Equipment

Meter

The easiest type of meters to use is direct concentration readout specific ion meter, such as Orion EA940, 920A, 920Aplus, 720A, 720Aplus, 710A, 710Aplus, 290A, 290Aplus or 370. If unavailable, a pH/mV meter with readability to 0.1 mV could be used.

Magnetic Stirrer

Highly recommended for laboratory measurements.

Graph Paper

4-cycle semilogarithmic paper for preparing calibration curves (for use with digital pH/mV laboratory meters)

Required Solutions

Distilled or Deionized Water

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.

Standard Solutions	Orion
Ionic Strength Adjustor (ISA)	951211
Electrode Filling Solution	951202
0.1 M Ammonium Chloride Standard	951006
1000 ppm as Nitrogen Standard	951007

Solutions Prepared by Customer

For inner body check:

To check the operation of the electrode inner body.

Solution 1 — pH 4.01 Buffer with 0.1M NH_4Cl (or 0.1 M NaCl)

Take 200 mL of the pH 4.01 buffer solution, Orion 910104, add 1.07 g reagent-grade NH_4Cl (or 1.16g reagent-grade NaCl), stir to mix and label bottle as Solution 1. Store the buffer for repeated use. Discard buffer if turbidity develops.

Solution 2 — pH 7.00 Buffer with 0.1M NH_4Cl (0.1 M NaCl)

Take 200 mL of pH 7.00 buffer solution, Orion 910107, add 1.07 g reagent-grade NH_4Cl (or 1.16g reagent-grade NaCl), stir to mix and label bottle as Solution 2. Store the buffer for repeated use. Discard bottle if turbidity develops.

USING THE ELECTRODE

Set Up

Electrode Assembly

> ***NOTE:*** *Soak inner body in electrode filling solution for at least two hours before assembling new electrode. For best results, soak inner body overnight.*

Assemble electrode according to instructions below. The electrode is shipped dry with loose membranes and a loose membrane cap. Avoid excessive handling of the membrane during assembly; this may affect the membrane's hydrophobic properties, causing shortened membrane life. Use the tweezers provided. A membrane will last from one week to several months depending on usage.

> ***NOTE:*** *Membrane failure is characterized by a shift in electrode potential, drift, and poor response. See* ***Troubleshooting*** *section. Membrane failure may be apparent on visual inspection as dark spots or discoloration of the membrane.*

Electrode Preparation

NOTE: *Soak inner body in electrode filling solution for at least two hours before assembling electrode. For best results, soak inner body overnight.*

1. While holding the probe vertically, unscrew the top cap **(a)** and carefully remove the glass electrode inner body **(b)** from the electrode outer body **(c)** (See **Fig. 1**). Set cap with inner body aside carefully. Pour out remaining electrode filling solution from outer body if applicable, new probe will not have any filling solution in the body.

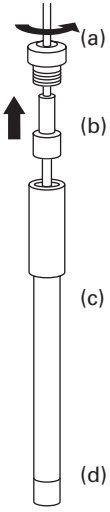

Fig. 1

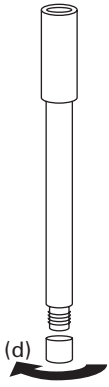

Fig. 2

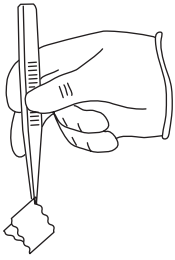

Fig. 3

2. Unscrew membrane cap **(d)** from outer body (See **Fig. 2**). Remove old membrane, if applicable.
3. Wearing gloves, use tweezers to carefully grasp corner of white membrane from between paper separators (See **Fig. 3**). Do not to touch center of membrane.

4. With free hand, grasp electrode outer body with threads oriented to the top. Align straight edge of membrane against threaded shoulder and hold with thumb (See **Fig. 4**). With other hand, gently stretch the membrane upwards (See **Fig. 5**), then across the opening (See **Fig. 6**), then down to align other edge with the opposite shoulder (See **Fig. 7**). While holding each edge on both sides, gently stretch each serrated side of the membrane out and down over threads making sure that membrane surface is smooth and without wrinkles (See **Fig. 8**). Smooth any loose material taking care not to touch center of membrane (See **Fig. 9**).

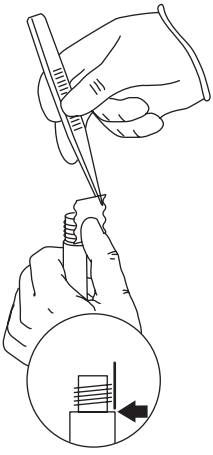

Fig. 4

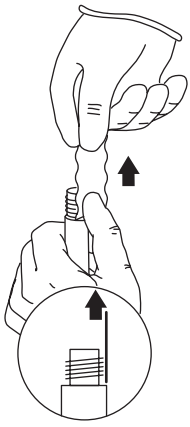

Fig. 5

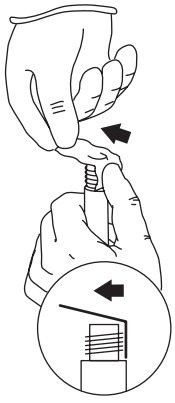

Fig. 6

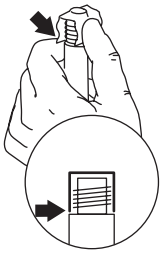

Fig. 7

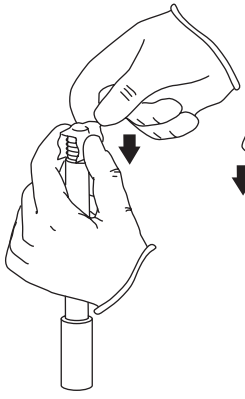

Fig. 8

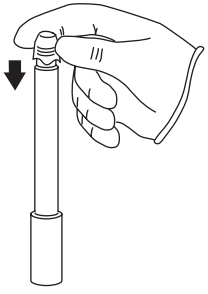

Fig. 9

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

5. Replace membrane cap being careful not to touch membrane center (See **Fig. 10**). Screw down half way and tuck any loose membrane material under cap while twisting. Make sure cap is fully screwed on.
6. Fill the outer body with 2.5 ml filling solution, or approximately 50 drops from the bottle (See **Fig. 11**).
7. Place inner body into outer body containing filling solution and screw on upper cap (See **Fig. 12**).
8. Carefully shake fully assembled electrode as if it were a clinical thermometer to remove bubbles. Gently pull spring loaded cable back and slowly release to allow filling solution to migrate between membrane and glass electrode inner body (See **Fig. 13**).

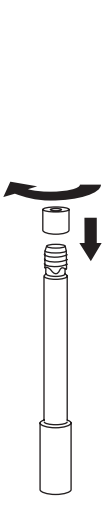

Fig. 10

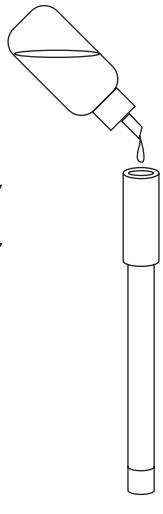

Fig. 11

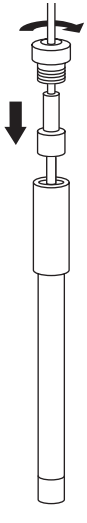

Fig. 12

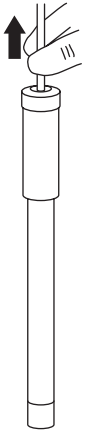

Fig. 13

9. Rinse the electrode well and wipe dry.

Checking Electrode Operation (Slope)

These are general instructions, which can be used with most meters to check electrode operation. See individual meter instruction manuals 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 electrodes have been stored dry, prepare the electrodes as described under the section entitled **Electrode Preparation**.
2. Connect electrodes to the meter. For an electrode with a BNC connector, turn the connector clockwise to attach to the meter. For an electrode with a U.S. Standard connector, insert reference pin-tip connector and the sensing electrode connector into appropriate jacks on the meter. Non-Orion meters may require special adaptors. Consult your meter instruction manual.
3. Place 100 mL distilled water into a 150 mL beaker. Add 2 mL pH-adjusting ISA, Orion 951211. Stir thoroughly. Set the meter to the mV mode.
4. Rinse electrode with distilled water and place in the solution prepared in step 3 above. To prevent air entrapment on the membrane surface, be sure to use an electrode holder that keeps the electrode at a 20˚ angle. If bubbles appear on the sensing membrane, tap electrode gently to remove.
5. Select either 0.1 M or 1000 ppm ammonium chloride standard. Pipet 1 mL of the standard into the beaker, stir 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. Stir thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.
7. Take the first potential reading and subtract it from the second one. The difference should be in the range of -54 to -60 mV/decade when the solution temperature is between 20-25 ˚C. If the potential is not within this range, refer to **Troubleshooting**.

Before Analysis

Units of Measurement

Ammonia can be measured in units of moles per liter, 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	ppm as N	ppm as 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. Consult Our Technical Service Chemists for 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, pH-adjusting 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 (solution should be blue 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, see section entitled **Effect of Dissolved Species**.

Measuring Hints

Minimize NH_3 loss from sample by following the recommendations below:

- Store samples according to procedure in Sample Storage.
- Use beakers that minimize the ratio of surface area to volume.
- Keep beakers containing standards and samples covered between measurements.

- Add 2 mL of pH-adjusting ISA to 100 mL of sample or standard immediately before making measurements, and make sure the blue color is observed.
- Between measurements, rinse the electrode with distilled water.
- Be sure samples, standards, and electrodes are at the same temperature.
- Samples and standards should be stirred using a magnetic stirrer. Some magnetic stirrers generate enough heat to change solution temperature. Placing a piece of insulating material such as cork or styrofoam between the beaker and the stirring plate can minimize this effect.
- Verify calibration every two hours by placing electrodes in a fresh aliquot of the first standard solution used for calibration. If value has changed, recalibrate the electrode.
- Always use fresh standards for calibration.
- After immersion in solution, check electrode for any air bubbles on membrane surface and remove by shaking the electrode as you would with a thermometer or lightly tapping of the electrode.
- If electrode response is slow, the membrane may contain a surface layer of contaminant. Restore performance by soaking electrode in distilled water for about 5 minutes, then rinse and soak in a standard solution for about 1 hour before use.

Sample Storage

If possible, alkaline samples should be measured at once. 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 them in tightly capped vessels. Make stored samples basic with pH-adjusting ISA immediately before measurement.

Analytical Procedures

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 in 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 an alternate method 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 electrodes are 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 electrodes are 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 electrodes are immersed in a reagent solution which 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. Specific instructions for known subtraction, analate addition and analate subtraction, can be found in the Orion meter instruction manuals. 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

Set Up

1. Prepare the electrode as described in **Electrode Assembly** and **Electrode Preparation**.
2. Connect electrode to meter.
3. Prepare two standards which 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 **Temperature Effects**.)

If Using Meter with Direct Concentration Readout Capability:

NOTE: *See individual meter instruction manuals for more specific information.*

1. Measure 100 mL of the more dilute standard into a 150 mL beaker. Add 2 mL of ISA. Stir thoroughly.
2. Rinse electrodes with distilled water, blot dry and place into the beaker. Wait for a stable reading then adjust the meter to display the value of the standard as described in the meter instruction manual.
3. Measure 100 mL of the more concentrated standard into a second 150 mL beaker. Add 2 mL of ISA. Stir thoroughly.
4. Rinse electrodes with distilled water, blot dry and place into the beaker with more concentrated standard. Wait for a stable reading then adjust the meter to display the value of the second standard, as described in the meter instruction manual.
5. Measure 100 mL of the sample into a 150 mL beaker. Add 2 mL of ISA. Stir thoroughly.
6. Rinse electrodes with distilled water, blot dry and place into sample. The concentration will be displayed on the meter. In the direct calibration procedure, a calibration curve is constructed on semilogarithmic 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. The direct measurement procedures in the manual are given for concentrations in the region of linear electrode response. Low level measurement procedures are given for measurements in the non-linear region.

If Using Meter with Millivolt Readout Only:

1. Adjust the meter to measure mV.
2. Measure 100 mL of the more dilute standard into a 150 mL beaker. Add 2 mL of ISA. Stir thoroughly.
3. Rinse electrodes with distilled water, blot dry and place into the beaker. When a stable reading is displayed, 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 ISA. Stir thoroughly.
5. Rinse electrodes with distilled water, blot dry and place into the second beaker. When a stable reading is displayed, record the mV value and corresponding standard concentration.
6. Using semilogarithmic 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. Measure 100 mL of the sample into a 150 mL beaker. Add 2 mL of ISA. Stir thoroughly.
8. Rinse electrodes with distilled water, blot dry and place 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.

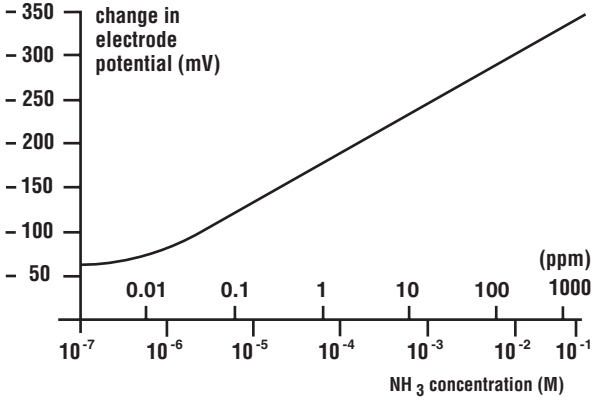

Figure 14: Typical Ammonia Electrode Calibration Curve

Low-Level Measurements By Direct Calibration

These procedures are for solutions with an ammonia concentration of less than 4×10^{-6} M (0.07 ppm NH_3). For solutions low in ammonia but high in total ionic strength, perform the same procedure with one change: prepare a calibration solution with a 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 at low-level measurements
- Remember to stir all standards and samples at a uniform rate

Electrode response is relatively slow at low levels of ammonia and is faster going in the direction of increasing concentration. Diluting the electrode filling solution with distilled water 1:10 can improve response at low levels. To speed up the measurement of a sample containing less than 4×10^{-6} M ammonia (0.07 ppm NH_3 or 0.06 ppm as N), the electrode is first placed in an ammonia-free pH 4 buffer, then into the sample. 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 low levels. Allow 5-10 minutes for a stable reading in the pH 4 buffer or a low-level solution.

Set Up

1. Prepare electrode as described under Electrode Assembly and Electrode Preparation.
2. Place electrode in a pH 4 buffer solution for several minutes. Stir all solutions throughout the procedure.
3. Prepare a 10^{-3} M or 10 ppm standard by serial dilution of the 0.1 M or 1000 ppm standard.
4. Connect electrode to the meter.

Measurement

1. Measure 100 mL of ammonia-free distilled water in an Erlenmeyer flask and add 2 mL of pH-adjusting ISA.
2. Rinse the electrode with distilled water, and place into flask. Stir thoroughly.
3. Add increments of the 10^{-3} M or 10 ppm standard to the calibration solution using the steps outlined in **Table 2**. Measure the electrode potential after each increment and plot on semilogarithmic paper the concentration (log axis) against the potential (linear axis).
4. Rinse the electrode and place in pH 4 buffer for several minutes.
5. Measure 100 mL of sample into a beaker.
6. Rinse the electrode and place in sample solution. Add 2 mL of pH-adjusting ISA to each 100 mL sample. Stir thoroughly. Wait for a stable reading and record data. Determine the concentration from the low-level calibration curve.
7. Prepare a new low-level calibration curve daily by using fresh solutions.

Table 2
Preparation of Calibration Curve For Low Level Measurements

Additions of 10^{-3} M or 10 ppm standard to 100 mL distilled water, plus 2 mL pH-adjusting ISA. "A" is a 1 mL graduated pipet. "B" is a 2 mL pipet.

Step	Pipet Size	Added Volume	Concentration ppm	Molarity
1	A	0.10 mL	0.01	9.8×10^{-7}
2	A	0.10 mL	0.02	2.0×10^{-6}
3	A	0.20 mL	0.04	3.9×10^{-6}
4	A	0.20 mL	0.06	5.8×10^{-6}
5	A	0.40 mL	0.10	9.7×10^{-6}
6	B	2.00 mL	0.29	2.9×10^{-5}
7	B	2.00 mL	0.47	4.7×10^{-5}

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 may 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.

Set Up

1. Prepare the electrode as described under **Electrode Assembly** and **Electrode Preparation**.
2. Connect electrodes to the meter.
3. Upon addition to the sample, prepare a standard solution which will cause concentration of the ammonia to double. Refer to **Table 3** as a guideline.
4. Determine the slope of the electrode by performing the procedure under **Checking Electrode Operation (Slope)**.
5. Rinse electrode between solutions with distilled water.

If Using Meter with Direct Known Addition Readout Capability:

NOTE: *See individual meter instruction manuals for more specific information.*

1. Set up meter to measure in the known addition mode.
2. Measure 100 mL of the sample into a beaker.
3. Rinse electrodes with distilled water, then place in sample solution. Add 2 mL of ISA. Stir thoroughly.
4. When a stable reading is displayed, calibrate the meter as described in the meter instruction manual.
5. Pipet the appropriate amount of the standard solution into the beaker. Stir thoroughly.
6. When a stable reading is displayed, record the sample concentration.

If Using Meter with Millivolt Readout Only:

Use this procedure when no instructions for known addition are available in the meter instruction manual.

1. Set the meter to relative millivolt mode.
2. Measure 100 mL of the sample into a 150 mL beaker. Add 2 mL of ISA. Stir thoroughly.
3. Rinse electrodes with distilled water, blot dry and place into beaker. When a stable reading is displayed, set the reading to 000.0 by turning the calibration control. If the reading cannot be set to 000.0, record the mV value.
4. Pipet the appropriate amount of standard solution into the beaker. Stir 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 4**, find the value, Q, that corresponds to the change in potential, ΔE. To determine the original sample concentration, multiply Q by the concentration of the added standard:

$C_{sam} = QC_{std}$

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

$\Delta E = E_2 - E_1$

S = slope of the electrode

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

Table 3

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

Electrode Storage

Between measurements, keep the electrode tip immersed in a 10^{-3} M or 10 ppm standard with added ISA. For low-level measurements, keep the electrode in a pH 4 buffer between measurements. Do not store overnight in a pH 4 buffer.

For overnight or week-long storage, the electrode tip should be immersed in 0.1 M or 1000 ppm standard without added ISA.

For storage over one week or if the electrode is stored indefinitely, disassemble completely and rinse the inner body, out body, and bottom cap with distilled water. Dry and reassemble electrode without filling solution or membrane. When rebuilding, follow procedure in **Electrode Assembly** and **Electrode Preparation**.

If the electrode is accidentally left in the air and erratic results are obtained, the space between the inside of the membrane and the sensing element may be dry. To make the electrode usable again, pull back the cable slightly to allow solution flow between the sensor and the membrane.

Table 4

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			
Monovalent	**(-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	02.056	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
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)**	**(-60.1)**
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

TROUBLESHOOTING

Troubleshooting Checklist

Symptom	Possible Causes
Off-scale or Over-range reading	Defective meter
	Defective inner body
	Electrodes not plugged in properly
	Electrode filling solution not added
	Air bubble on membrane
	Electrodes not in solution
Noisy or unstable readings (erratic-rapidly changing)	Insufficient electrode filling solution
	Defective meter
	Bottom cap loose
	Defective inner body
	ISA not used
Drift (Reading slowly changing in one direction)	Meter or stirrer improperly grounded
	Electrode filling solution leakage
	Incorrect electrode filling solution
	Total level of dissolved species above 1 M
	Electrode in sample too long;
	Membrane failure (wet, perforation, discoloration)

Next Step

Perform meter checkout procedure (see meter instruction manual)

Refer to Troubleshooting Guide (check inner body operation)

Unplug electrodes and reseat

Fill outer body of electrode with proper amount of Electrode filling solution

Remove bubble by redipping electrode in solution

Put electrodes in solution

Fill outer body of electrode with proper amount of Electrode filling solution

Perform meter checkout procedure (see meter instruction manual)

Ensure that bottom cap is screwed on tight enough to close gap between bottom cap and body

Check inner body operation

Use recommended ISA, Orion No. 951211

Check meter and stirrer for grounding

Ensure that membrane is installed properly

Refill outer body of electrode using filling solution shipped with electrode

Dilute solution

Reduce surface-area-to-volume loss ratio, slow rate of stirring, avoid high temperatures

Replace membrane

Troubleshooting Checklist (cont.)

Symptom	Possible Causes
	Solutions not at constant temperature
	Heat generated by magnetic stirrer
	Defective inner body
	Electrode exposed to air for extended period
	Samples and standards at different temperatures
Low slope or No slope	Standards contaminated or incorrectly made
	ISA not used
	Standard used as ISA
	Electrode exposed to air for extended period
	Membrane failure (wet, perforation, discoloration)
	Defective inner body
"Wrong Answer" (But calibration curve is OK)	Incorrect scaling of semilog paper
	Incorrect sign
	Incorrect standards
	Wrong units used
	Complexing agents in sample
	ISA added to standards and not samples

Next Steps

Allow solutions to come to room temperature before use

Place insulating material between stirrer and beaker

Check inner body operation

Hold electrode by outer body and pull up on electrode cable. Electrode filling solution will flow under membrane and restore electrode response

Allow solutions to come to room temperature before measurement

---

Prepare fresh standards

Use recommended ISA, Orion No. 951211

Use ISA!

Hold electrode by outer body and pull up on electrode cable. Electrode filling solution will flow under membrane and restore electrode response

Replace membrane

Check inner body operation

Plot millivolts on the linear axis. On the log axis, be sure concentration numbers within each decade are increasing with increasing concentration

Be sure to note sign of millivolt value correctly

Prepare fresh standards

Apply correct conversion factor:
10^{-3} M = 17 ppm as NH_3 = 14 ppm as N

Use known addition or titration techniques, or a decomplexing procedure

Add some proportion of ISA to standards and samples

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: 1) Meter, 2) Electrodes, 3) Standard, 4) Sample, and 5) Technique.

Meter

The meter is the easiest component to eliminate as a possible cause of error. Orion meters are provided with an instrument checkout procedure in the instruction manual and a shorting strap for convenience in troubleshooting. Consult the manual for complete instructions and verify that the instrument operates as indicated and is stable in all steps.

Electrodes

1. Rinse electrode thoroughly with distilled water.
2. Check electrode operation (slope).
3. If electrode fails this procedure, soak ammonia electrode again as directed in **Electrode Preparation** and **Electrode Assembly**.
4. Repeat step 2, Checking Electrode Operation.
5. If the electrode still does not perform as described, determine whether the ammonia inner body is working properly.

Checking inner body:

> ***NOTE:*** *This is a troubleshooting procedure. If electrode slope is found to be low during operation, disassemble electrode and check inner body.*

Disassemble ammonia electrode. If the electrode is dry, first 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 in pH 7 buffer solution with 0.1 M NH_4Cl added. Make sure that the reference wire is covered (see **Required Solutions** for preparation). Stir throughout the procedure. Record the millivolt reading after two minutes.

> ***NOTE:*** *Use caution so that the buffer solution comes into contact with the reference wire, but not the protective rubber sleeve. If contact is made with the sleeve, be sure to thoroughly rinse electrode with deionized water.*

Rinse the inner body in distilled water and place in the pH 4 buffer solution with 0.1 M NH_4Cl added (See **Required Solutions** for preparation). Watch the change in meter reading carefully. The reading should change 100 mV in less than 30 seconds after immersion in the pH 4 buffer solution. The mV difference between pH 7 and pH 4 should be greater than 150 mV if the inner body sensing elements are operating correctly after three minutes.

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. See **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 filling solutions, ISA and standards
    - Measure correctly
    - Review **Troubleshooting Checklist**

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! Error 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. This means that an initial standard is diluted, using volumetric glassware, to prepare a second standard solution. The second is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.

Sample

If the electrode works properly in standards but not in the sample, look for possible interferences, complexing agents, or substances which could affect response or physically damage the sensing electrode or the reference electrode. If possible, determine the composition of the samples and check for problems. See **Sample Requirements**, **Interferences**, and **pH Requirements**.

Technique

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 best. 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. Reread **Measuring Hints** and **Analytical Procedures**.

Assistance

For the most current warranty information, visit www.thermo.com.

After troubleshooting all components of your measurement system, contact The Technical Edge℠ for Orion products. Within the United States call 1.800.225.1480, 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.

ELECTRODE CHARACTERISTICS

Electrode Response

The electrode exhibits good time response (95% response in one minute or less) for ammonia concentrations above 4×10^{-6} M (0.07 ppm NH_3 or 0.06 ppm 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 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 at low level measurements.
- Remember to stir all standards and samples at a uniform rate. When plotted on semilogarithmic paper, electrode potential response as a function of ammonia concentration is a straight line with a slope of about -58 mV per decade.

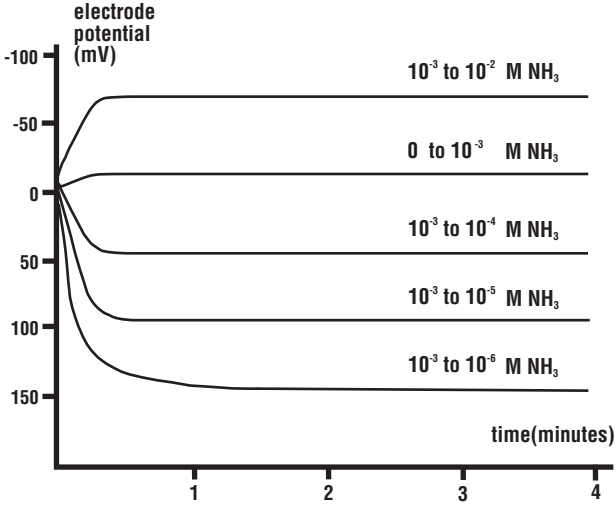

Figure 15: To Step Changes in Ammonia Concentration Typical Electrode Response

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. Reproducibility can be obtained to ± 2% when calibration is performed every hour.

Temperature Effects

A change in temperature will cause electrode response to shift and change slope. **Table 5** lists the variation of theoretical response with temperature. At 10^{-3} M, a 1 ˚C temperature change 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 5

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.

pH Effects

See **Theory of Operation**.

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 Orion Ammonia pH-adjusting ISA inhibits the formation of some these common metal complexes in the sample, because it contains a high concentration of hydroxide ion.

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 pH-adjusting 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.

Electrode Life

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

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

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

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

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

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

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

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

where:

E	=	measured electrode potential
E_0	=	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.

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

The reference potential, E_0 is partly determined by the internal reference element which 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:

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

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:

$$\frac{[NH_4^+]}{[H_3O+][NH_3]} = \frac{[NH_4^+]}{10\text{-}pH[NH_3]} = K10^{-9.3}$$

at 25 °C μ= 0.1
and pK = 9.3. The ratio of ammonium to ammonia is given by:

$$\frac{[NH_4^+]}{[NH_3]} = K\,10^{-pH} = 10^{9.3\text{-}pH}$$

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 μ = 0.1, is given as 9.3 (as in the discussion above) an increase in ionic strength to μ = 1.0 yields a pK of 9.4.

Partial Pressure of Ammonia

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

$$K_h = \frac{[NH_3]\ \text{aqueous}}{P_{NH_3}} = 56\ \text{moles/liter} — \text{atm. (25 °C)}$$

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

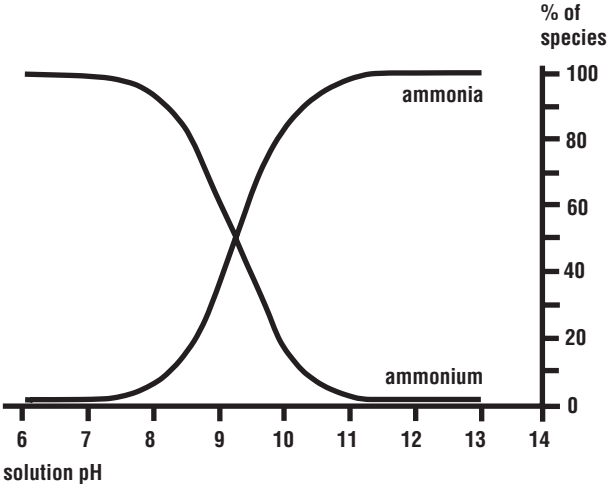

Figure 16: Percent of Ammonia and Ammonium as a Function of pH

Measuring Ammonia

In Solutions That Wet The Membrane

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

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 (14 ppm) ammonia are possible under these conditions.

To measure ammonia in samples containing surfactants, or nonaqueous solutions, adjust the sample pH to 11-13 with ISA. Transfer the solution to a 125 mL Erlenmeyer flask containing a magnetic stirring bar. The neck of the flask is fitting with a rubber stopper with a hole large enough to hold the electrode snugly. The closed flask forms an air-tight 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 Service Chemists and request Orion's Guide to Water and Wastewater Analysis.

ORDERING INFORMATION

Orion	Description
9512BN	Ammonia Electrode, BNC Connector
951211	Ionic Strength Adjustor (ISA), 475 mL
951202	Electrode Filling Solution, 60 mL bottle
951204	Membranes, box of 20
951006	Standard Solution, 0.1M NH_4Cl
951007	Standardizing Solution, NH_4Cl, 1000 ppm as N
951205	Bonded Membrane Caps, 3 per pack

SPECIFICATIONS

Concentration Range
1 M to 5 x 10^{-7} M
(0.01 to 17,000 ppm NH_3 or 0.01 to 14,000 ppm 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%

Minimum Sample Size
2.5 mL in a 30 mL beaker

Size
Electrode Length: 14.9 cm
Body Diameter: 12 mm
Cap Diameter: 16 mm
Cable Length: 110 cm

Specifications subject to change without notice.