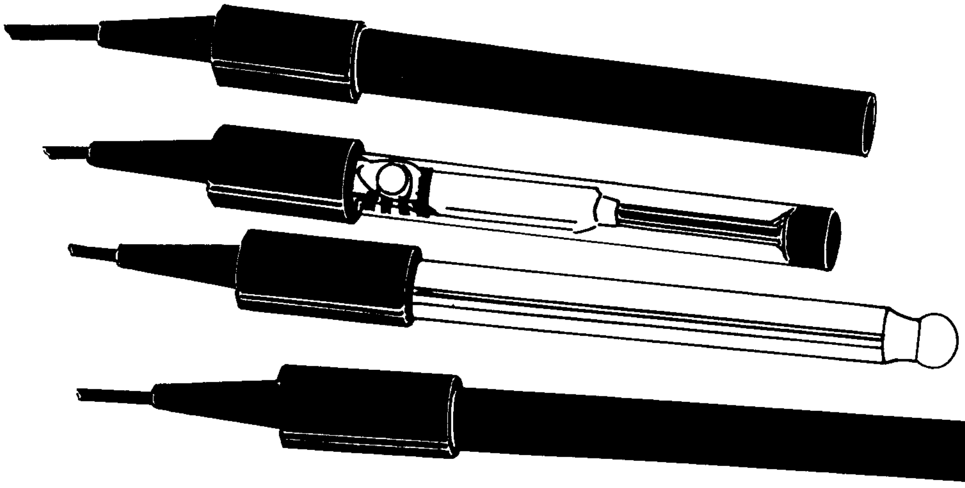
ISE-8710

Ammonia Gas-Sensing Electrodes



OMEGA®

An OMEGA Technologies Company

Operator's Manual

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SECTION 1 GENERAL DESCRIPTION

The OMEGA® Ammonia Gas-Sensing Electrode is used to quickly, simply, accurately, and economically measure dissolved ammonia in aqueous solutions. It can also be used to measure the ammonium ion after conversion to ammonia or organic nitrogen after Kjeldahl digestion of the sample. The measurement is not affected by sample color or turbidity and samples do not need to be distilled. Interferences from anions, cations, and dissolved species, other than volatile amines, do not occur. With a flow-thru cap, the electrode can be used in flow-thru applications.

SECTION 2 PREPARATION FOR MEASUREMENT

2.1 REQUIRED EQUIPMENT AND SOLUTIONS

1. A pH/mV meter or an ion meter, either line operated or portable.

2. Semi-logarithmic 4-cycle graph paper for preparing calibration curves when using the meter in the mV mode.

3. A magnetic stirrer.

4. Ammonia-free deionized or distilled water. Using a strongly acid exchange resin, such as Dowex 50W-X8, pass distilled or deionized water through the ion-exchange column.

5. The OMEGA Ammonia Electrode, ISE-8710.

6. Sodium Hydroxide Solution (10M), ISE-8710-R1.
   Add 1 mL of 10M NaOH to each 100 mL of standard or sample to adjust the solution pH to the operating range of the electrode. To prepare a 10M NaOH solution, fill a 100 mL volumetric flask half full of ammonia-free distilled water, add 40 grams of reagent-grade NaOH, swirl the flask to dissolve the pellets, and add distilled water to the mark.

7. Ammonia Chloride Standard, 0.1M NH_4Cl, ISE-8710-S1
   or Nitrogen Standard Solution, 1000 ppm, ISE-8710-S2
   To prepare a 0.1M NH_4Cl solution, fill a 100 mL volumetric flask half full of ammonia-free distilled water, add 0.535 grams of reagent-grade NH_4Cl, swirl the flask to dissolve the solid, and fill to the mark with distilled water. To prepare a 1000 ppm nitrogen standard, fill a 100 mL volumetric flask half full of ammonia-free distilled water, add 0.382 grams of reagent-grade NH_4Cl, swirl the flask to dissolve the solid, and fill to the mark with distilled water.

8. Ammonia Electrode Filling Solution, PHFS-8710

2.2 ELECTRODE ASSEMBLY

The electrode is shipped dry. Before using it, unscrew the big cap (at the top), remove the inner glass electrode from the outer body, and soak the inner glass electrode in internal fill solution for at least two hours. Fill the outer body half full with internal filling solution, place inner glass electrode into the outer body, and screw on the big cap till fingertight. After assembly, gently feel the membrane with fingertip to make sure that the inner glass electrode touches the membrane tightly.

2.2.1 Checking the Membrane

A small hole of any size on the membrane or the breakage of the membrane causes total failure of the measurements. It is recommended to check the membrane on every newly assembled electrode.

A simple and effective way is available: connect a newly assembled electrode to a pH/mV meter and place the electrode into DI water. Record the reading after stirring the DI water for about 15 minutes. Add proper buffer solution (see Required Solutions) to that DI water. A drastic change on the reading indicates the damage of the membrane.

2.2.2 Changing the Membrane

Unscrew the small cap (at the bottom) from the outer body, and remove the membrane base out from the small cap with a screw-driver. Cut the O-ring which wraps the membrane onto the base; and discard the old membrane. Lay a piece of new membrane (20mm x 20mm) onto the base, the shiny side of the membrane faces the base opening. Then, put a small O-ring (supplied) on the top of the cone-shaped membrane mounting tool, and slide the O-ring down to the bottom of the cone. Place the cone with the O-ring on it onto the membrane, gently slide the O-ring into the groove on the base to wrap the membrane. Do not push the cone too hard while sliding down the O-ring into the groove, or the membrane may be damaged. Trim the excessive membrane, screw the base into place, and re-assemble the electrode.

2.3 Connecting the Electrode

Connect the electrode to the meter in the same manner as any other combination electrode. No external reference electrode is required. To prevent air entrapment, mount the electrode at a 20° angle from the vertical.

NOTE

Do not be alarmed if white crystals form at end of electrode. This is normal with pH electrodes. These crystals are potassium chloride. Remove the shipping cap and rinse with distilled water to dissolve the crystals.

2.3.1 Checking the Electrode Slope

The electrode slope is the change in potential (mV) observed when the concentration changes by a factor of ten. The electrode slope should be checked on a daily basis.

To check the slope:

1. Measure out 100 mL of ammonia-free distilled water and 1 mL of 10M NaOH and transfer to a 150 mL beaker. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip into the solution and make sure the meter is in the mV mode.

2. Pipet 1 mL of the 0.1M or 1000 ppm standard into the solution. Adjust the calibration control (offset adjustment) to zero.

3. Pipet 10 mL of the 0.1M or 1000 ppm standard into the solution. If the electrode is operating properly, a reading of 56+/-2mV should appear on the meter, assuming the solution temperature is between 20° and 25°C. If the change in potential is not within this range, see Troubleshooting section.

SECTION 3 MEASUREMENT PROCEDURE

3.1 MEASURING HINTS

To minimize ammonia loss from samples:

1. Samples should be measured immediately after preparation or collection.

2. If immediate measurement is impossible, store the samples according to the instructions in the Sample Storage section.

3. The ratio of surface area to volume in the beaker should be minimized.

4. Beakers containing the samples or the standard should be kept covered between measurements.

5. Immediately before measurement, add 1mL 10M NaOH to 100 mL of sample or standard.

6. Samples, standards, and electrode must be at the same temperature.

7. Rinse the electrode with ammonia-free distilled water between measurements.

8. Stir samples and standards using a magnetic stirrer.

9. Use an insulating material, such as gauze or styrofoam between the beaker and the magnetic stirrer to minimize heat transfer from the magnetic stirrer to the solution in the beaker.

3.2 SAMPLE REQUIREMENTS

Standards and samples must be at the same temperature, since a 1°C difference in temperature will result in a measurement error of approximately 2%.

10M NaOH must be added to standards and samples before measurement. When the 10M NaOH is added, all standards and samples should be in the range of pH 11 to 14 and have a total level of dissolved species below 1M. If the total level is greater than 1M, see the Effect of Dissolved Species section.

3.3 UNITS OF MEASUREMENT

Measurement of ammonia can be expressed in units of moles/liter, ppm as nitrogen, ppm as ammonia or other convenient concentration unit. Table 3-1 lists conversion units.

TABLE 3-1
Concentration Unit Conversion

moles/liter	ppm N	ppm NH_3
10^{-2}	140	170
10^{-3}	14.0	17.0
10^{-4}	1440	1770

3.4 MEASUREMENT PROCEDURES

3.4.1 Direct Measurement

Direct measurement is the simplest, fastest method for measuring over a wide range of concentration. The temperature of the standards and the samples should be the same. Only one meter reading need be taken for each sample.

The graph in Figure 3-1 illustrates the convenience of direct measurements in the $4x10^{-6}$ to 1M ammonia range. For low-level measurements (below 4×10^{-6}M NH_3, 0.07 ppm NH_3, 0.06 ppm N), the rate of ammonia diffusion through the membrane is slow, and the rate of equilibrium between the ammonium in the internal filling solution and ammonia is slow. Such samples are best measured by using special low-level techniques. Above a concentration of 1M ammonia, dilution before measurement is required to minimize ammonia diffusion out of the sample.

1. Using serial dilution of the 0.1M or of the 1 00 ppm standards, prepare 10^{-2} M (100 ppm), 10^{-3} M (10 ppm), and 10^{-4} M (1 ppm) standards.

2. Put 100 mL of the 10^{-3}M (10 ppm) standard into a 150 mL beaker. Place the beaker on the magnetic stirrer and begin stirring. Place the tip of the electrode in the solution and add 1 mL of 10M NaOH to the standard. Set the meter in the mV mode. Adjust the calibration control (offset adjustment) to zero.

3. Put 100 mL of the 10^{-4}M (1 ppm) standard into a 150 mL beaker. Place the beaker on the magnetic stirrer and begin stirring. After rinsing the electrode with ammonia-free distilled water, immerse the tip of the electrode in the solution and add 1 mL of 10M NaOH to the standard. Record the value when the reading has stabilized.

4. Put 100 mL of the 10^{-2}M (100 ppm) standard into a 150 mL beaker. Place the beaker on the magnetic stirrer and begin stirring. After rinsing the electrode with ammonia-free distilled water, immerse the tip of the electrode in the solution and add 1 mL of 10M NaOH to the standard. Record the value when the reading has stabilized.

5. Using standard semi-logarithmic paper, plot the mV value (linear axis) vs. concentration (log axis). A typical calibration curve appears in Figure 3-1.

6. Measure 100 mL of sample, put it into a 150 mL beaker, place the beaker on the stirrer, and begin stirring. After rinsing the electrode with ammonia-free distilled water, immerse the tip of the electrode in the solution, and add 1 mL of 10M NaOH to the sample. Wait for the reading to stabilize and record the value. Using the calibration curve, determine the sample concentration.

3.4.2 Known Addition

The known addition technique is useful for measuring total ammonia ion concentration in the absence of, or in the presence of a large excess (50 to 100 times) of complexing agent. It is a convenient method of measuring occasional samples, since no calibration is necessary.

The known addition method requires that the concentration approximately doubles as a result of the addition. As a result, sample concentration must be known within a factor of three. In the absence of complexing agents, total concentration of ammonia can be measured down to 4×10^{-6} M (0.07 ppm NH_3 or 0.06 ppm N) or in the presence of a large excess (50 to 100 times) of complexing agent.

1. Using the 0.1M or 1000 ppm standard, prepare a dilution about 10 times as concentrated as the sample concentration.

2. Measure out 100 mL of sample solution and add it to a 150 mL beaker. Add 1 mL of 10M NaOH. Place the beaker on the magnetic stirrer and begin stirring. Rinse the electrode and place the electrode tip in the solution.

3. Make sure the meter in the mV mode. Adjust the calibration control (offset adjustment) to zero.

4. Add 10 mL of standard, by pipet, into the beaker. After the reading has stabilized, record the potential and determine the change in potential.

5. Find the concentration ratio, Q, that corresponds to the change in potential, from Table 3-3. The original total concentration is determined by multiplying Q by the concentration of the added standard:

$$Co = QCs$$

where:

CO = total sample concentration
Q = reading from Table 3-3
Cs = concentration of added standard

Table 3-3 (Q values) is calculated for a 10% volume change for electrode with slopes of 59mV. To calculate Q for different slopes and volume changes:

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

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

3.4.3 Low Level Determination

As the concentration of ammonia decreases, response time increases. If the internal filling solution is diluted with ammonia-free distilled water (1:10), response at low levels can improve. Measurements of a sample containing less than 4 x 10^{-6} M ammonia (0.07 ppm NH_3 or 0.06 ppm as N) can be speeded up by first placing the electrode tip in an ammonia-free pH 4 buffer, then into the sample. Always keep standards and samples covered. Work with large solution volumes to minimize surface-area-to-volume ratio, thereby avoiding ammonia absorption from air. Allow 5-10 minutes for a stable reading in a low-level solution.

1. Measure out 100 mL of a pH 4 buffer solution, add it to a 150 mL beaker, place beaker on magnetic stirrer, and begin stirring. Place the electrode tip in the solution for about 3 minutes.

2. Prepare a serial dilution the 0.1M or 1000 ppm standard to 10^{-2}M or 100 ppm.

3. To a 250 mL erlenmeyer flask, add 100 mL of ammonia-free distilled water and 1 mL of 10M NaOH. Place on magnetic stirrer and begin stirring. After rinsing the electrode, place the tip in this calibration solution. Make sure that the meter is in the mV mode.

4. Using a 1 mL graduated pipet (A) and a 2 mL pipet (B), add increments of the 10^{-2}M or 100 ppm dilution to the calibration solution using the steps outlined in Table 2. Allow the reading to reach equilibrium and record the electrode potential (linear axis) on semi-logarithmic paper to obtain the calibration curve.

5. After rinsing the electrode, immerse the electrode tip in pH 4 buffer for 3 minutes. Be sure to use the magnetic stirrer.

6. Place 100 mL of the sample into a 150 mL beaker, add 1 mL of 10M NaOH, place the beaker on the magnetic stirrer,and begin stirring. After rinsing the electrode, immerse the tip in the solution. When the reading has stabilized, record the mV potential.

7. Determine the concentration from the calibration curve. (Prepare a new low-level calibration curve on a daily basis using freshly prepared solutions).

TABLE 3-2

Additions of 10^{-2}M or 100 ppm Standard to 1 liter Ammonia-Free Distilled Water and 10 mL 10M NaOH

Step	Pipet	Added Volume	Resulting M	Concentration ppm
1	A	0.10 mL	9.9×10^{-7}	0.01
2	A	0.10	2.0×10^{-6}	0.02
3	A	0.20	4.0×10^{-6}	0.04
4	A	0.02	5.9×10^{-6}	0.06
5	A	0.40	9.9×10^{-6}	0.10
6	B	2.00	3.0×10^{-5}	0.30
7	B	2.00	4.9×10^{-5}	0.49

3.5 MEMBRANE WETTING SOLUTIONS

Since the membrane of the ammonia membrane is gas-permeable and hydrophobic, liquid water does not penetrate the membrane holes and does not wet it. A non-aqueous solution, or a solution containing a surfactant which wets the membrane, will wet the membrane. Non-aqueous samples, such as latex paints or nylon, and those containing surfactants, such as sewage, cause measurement difficulties. The electrode must be suspended above the sample to measure ammonia in such samples.

Since water vapor reacts with ammonia in the gas phase, placing the ammonia electrode in a closed system containing water vapor will allow measurements of solutions above 10^{-3} M (14 ppm) ammonia to be taken.

Ammonia in samples containing non-aqueous solutions or surfactants can be measured by adjusting the sample pH to 11-13 with 10M NaOH. After measuring the sample, transfer it to an erlenmeyer flask large enough to contain approximately 2/3 volume of air after sample addition. Place a magnetic stir bar in the flask, fit the flask with an one-hole rubber stopper (opening large enough to insert the electrode snugly), and insert the electrode until it is just above the level of liquid in the flask. The closed flask now forms an air-tight closed system with the gas phase saturated with water vapor. The partial pressure of ammonia is in equilibrium with the solution.

For gas phase measurements, calibrate the electrode in a closed flask using standards or use the known addition method in the closed flask. The response time for the ammonia electrode will be longer in the gas phase than if it were actually immersed in a surfactant-free, aqueous solution.

TABLE 3-3
VALUES OF Q VS. ΔE for 10% VOLUME CHANGE

ΔE	Q	ΔE	Q	ΔE	Q	ΔE	Q
5.0	0.297	10.0	0.160	20.0	0.0716	30.0	0.0394
5.1	0.293	10.2	0.157	20.2	0.0707	30.2	0.0390
5.2	0.288	10.4	0.154	20.4	0.0698	30.4	0.0386
5.3	0.284	10.6	0.151	20.6	0.0689	30.6	0.0382
5.4	0.280	10.8	0.148	20.8	0.0680	30.8	0.0378
5.5	0.276	11.0	0.145	21.0	0.0671	31.0	0.0374
5.6	0.272	11.2	0.143	21.2	0.0662	31.2	0.0370
5.7	0.268	11.4	0.140	21.4	0.0654	31.4	0.0366
5.8	0.264	11.6	0.137	21.6	0.0645	31.6	0.0362
5.9	0.260	11.8	0.135	21.8	0.0637	31.8	0.0358
6.0	0.257	12.0	0.133	22.0	0.0629	32.0	0.0354
6.1	0.253	12.2	0.130	22.2	0.0621	32.2	0.0351
6.2	0.250	12.4	0.128	22.4	0.0613	32.4	0.0347
6.3	0.247	12.6	0.126	22.6	0.0606	32.6	0.0343
6.4	0.243	12.8	0.123	22.8	0.0598	32.8	0.0340
6.5	0.240	13.0	0.121	23.0	0.0591	33.0	0.0336
6.6	0.237	13.2	0.119	23.2	0.0584	33.2	0.0333
6.7	0.234	13.4	0.117	23.4	0.0576	33.2	0.0329
6.8	0.231	13.6	0.115	23.6	0.0569	33.6	0.0326
6.9	0.228	13.8	0.113	23.8	0.0563	33.8	0.0323
7.0	0.225	14.0	0.112	24.0	0.0556	34.0	0.0319
7.1	0.222	14.2	0.110	24.2	0.0549	34.2	0.0316
7.2	0.219	14.4	0.108	24.4	0.0543	34.4	0.0313
7.3	0.217	14.6	0.106	24.6	0.0536	34.6	0.0310
7.4	0.214	14.8	0.105	24.8	0.0530	34.8	0.0307
7.5	0.212	15.0	0.103	25.0	0.0523	35.0	0.0304
7.6	0.209	15.2	0.1013	25.2	0.0517	36.0	0.0289
7.7	0.207	15.4	0.0997	25.4	0.0511	37.0	0.0275
7.8	0.204	15.6	0.0982	25.6	0.0505	38.0	0.0261
7.9	0.202	15.8	0.0967	25.8	0.0499	39.0	0.0249
8.0	0.199	16.0	0.0952	26.0	0.0494	40.0	0.0237
8.1	0.197	16.2	0.0938	26.2	0.0488	41.0	0.0226
8.2	0.195	16.4	0.0924	26.4	0.0482	42.0	0.0216
8.3	0.193	16.6	0.0910	26.6	0.0477	43.0	0.0206
8.4	0.190	16.8	0.0897	26.8	0.0471	44.0	0.0196
8.5	0.188	17.0	0.0884	27.0	0.0466	45.0	0.0187
8.6	0.186	17.2	0.0871	27.2	0.0461	46.0	0.0179
8.7	0.184	17.4	0.0858	27.4	0.0456	47.0	0.0171
8.8	0.182	17.6	0.0846	27.6	0.0450	48.0	0.0163
8.9	0.180	17.8	0.0834	27.8	0.0445	49.0	0.0156
9.0	0.178	18.0	0.0822	28.0	0.0440	50.0	0.0149
9.1	0.176	18.2	0.0811	28.2	0.0435	51.0	0.0143
9.2	0.174	18.4	0.0799	28.4	0.0431	52.0	0.0137
9.3	0.173	18.6	0.0788	28.6	0.0426	53.0	0.0131
9.4	0.171	18.8	0.0777	28.8	0.0421	54.0	0.0125
9.5	0.169	19.0	0.0767	29.0	0.0417	55.0	0.0120
9.6	0.167	19.2	0.0756	29.2	0.0412	56.0	0.0115
9.7	0.165	19.4	0.0746	29.4	0.0408	57.0	0.0110
9.8	0.164	19.6	0.0736	29.6	0.0403	58.0	0.0105
9.9	0.162	19.8	0.0726	29.8	0.0399	59.0	0.0101

SECTION 4 ELECTRODE CHARACTERISTICS

4.1 REPRODUCIBILITY

Electrode measurements to +/-2% can be obtained if the electrode is calibrated on a hourly basis and if limiting factors are kept at a minimum. Factors, such as temperature fluctuation, drift, and noise, limit reproducibility. Reproducibility is independent of concentration within operating range of the electrode.

4.2 INTERFERENCES

Volatile amines interfere with the operation of the ammonia electrode. Most gases, since they are converted to the ionic form in basic solutions, do not interfere with ammonia electrode measurement. The level of ions in solution can change the solubility of ammonia, though ionic species cannot cross the gas-permeable membrane and are not considered direct electrode interferences. The level of ions in sample solution and standards do not interfere, given that they are equal. The same holds true for dissolved species. Low results can occur in direct measurements, due to the presence of some metallic ions and their complexation effect on ammonia.

4.3 TEMPERATURE INFLUENCES

Table 4-1 gives the variation of theoretical response with temperature. The electrode response will shift and change slope with change in temperature. Standards and samples should be at the same temperature. A 2% error results with a 1°C temperature change for a 10^{-3}M solution. Gases are expelled from a solution at a faster rate as the temperature increases.

4.4 ELECTRODE RESPONSE

Electrode potential response as a function of ammonia concentration is a straight line with a slope of about 58 mV/decade, when plotted on semi-logarithmic paper. See Figure 3-1.

For ammonia concentrations above 4×10^{-6} M (0.07 ppm NH_3 or 0.06 ppm N), the electrode exhibits good response time - 95% of total mV reading in one minute or less. Response times are longer below this value and ammonia absorption from the air may become a source of error. Ammonia is rapidly lost to the air above a concentration of 1M. Dilution may be used if ammonia concentrations are above 1M. Response times of the ammonia electrode to step changes in ammonia concentration are shown in Figure 4-1. If electrode slope is found to be slow during operation, the following solutions will be necessary to check the inner body: pH 4 and pH 7.

Disassemble the ammonia electrode. If the electrode is dry, soak the glass tip of the inner body in Ammonia Electrode Internal Filling Solution (PHFS-8710) for at least two hours.

Rinse the electrode thoroughly with ammonia-free distilled water. Put 100 mL of pH 7 buffer in a 150 mL beaker, place the beaker on the magnetic stirrer, and begin stirring. Immerse the tip of the inner body in the solution so that the reference element is covered. Make sure the meter is in the mV mode. Record the meter reading.

Rinse the inner body thoroughly in ammonia-free distilled water. Put 100 mL of pH 4 buffer in a 150 mL beaker, place the beaker on the magnetic stirrer, and begin stirring. Immerse the tip of the inner body in the solution so that the reference element is covered. Observe the change in the meter reading carefully. In less than 30 seconds after immersion, the reading should change 100 mV. The meter reading should stabilize in 3-4 minutes, with a difference greater than 150 mV, if the inner body sensing elements are operating properly.

4.5 ELECTRODE STORAGE

If erratic results are obtained from accidently leaving the electrode in air, the space between the sensing element and the inside of the membrane may be dry. To remedy this situation and allow new filling solution to flow into the space, withdraw the glass electrode from the membrane by pulling the cable slightly.

For low-level measurements, immerse the tip of the electrode in pH 4 buffer between measurements.

For normal-range measurements, keep the electrode tip immersed in a 0.001M or 10 ppm standard with added NaOH.

If storing the ammonia electrode overnight or over the weekend, immerse the tip in the 0.1M standard without added NaOH. Do not store overnight in the pH 4 buffer.

For longer periods of time, completely disassemble the electrode, rinse the inner body, the outer body, and the cap with distilled water. After drying, reassemble the electrode without filling solution.

4.6 EFFECTS OF DISSOLVED SPECIES

One common substance that is a potential electrode interference is water vapor. The concentration of the internal filling solution under the membrane is changed when water, in the form of water vapor, moves across the electrode membrane. These changes will be seen as electrode drift. If 1) the total level of dissolved species in solution -the osmotic strength- is below 1M and 2) the sample and electrode temperature are the same, water vapor transport is not a problem.

Samples of low osmotic strength are automatically adjusted to the correct level through addition of 10M NaOH. If samples have osmotic strengths greater than 1M, they should be diluted before measurement. However, this dilution should not reduce the ammonia level below 10^{-5}M. If dilution is not possible for the reason mentioned above, the sample can be measured by adjusting the osmotic strength of the internal filling solution. The total level of dissolved species in the internal filling solution may be adjusted by adding 0.425 grams of reagent- grade sodium nitrate ($NaNO_3$) to 10 mL of the internal filling solution.

4.7 THEORY OF OPERATION

The Ammonia Gas-Sensing Electrode uses a hydrophobic gas-permeable membrane to separate the electrode's internal solution from the sample solution. The sample diffuses dissolved ammonia through the membrane until the partial pressure of ammonia is the same on both sides of the membrane. The partial pressure of ammonia is proportional to the ammonia concentration.

The ammonia that diffuses through the membrane dissolves in the internal filling solution, reacting reversibly with water in the filling solution, to a small extent:

$$NH_3 + H_2O \qquad NH_4^+ + OH^- \qquad (1)$$

The equilibrium equation gives rise to the equilibrium constant in the following equation:

$$\text{constant} = \frac{[NH_4^+]\ [OH^-]}{[NH_3]} \qquad (2)$$

The ammonium ion concentration can be considered fixed, since the internal filling solution contains ammonium chloride at a sufficiently high level. As a result:

$$[OH^-] = [NH_3] \times \text{constant} \qquad (3)$$

The electrode sensing element's potential, with respect to the internal reference element, varies in an Nernstian manner with changes in the hydroxide level:

$$E = E_o - S \log [OH^-] \qquad (4)$$

where S is the slope of the electrode.

Because the hydroxide concentration is proportional to the ammonia concentration (3), electrode response to ammonia is also Nernstian:

$$E = E_o^1 - S \log [NH_3] \qquad (5)$$

E_o^1 represents the reference potential and is partly determined by the internal reference element which responds to the fixed level of chloride in the internal filling solution.

Partial Pressure of Ammonia

As discussed above, the ammonia electrode responds to the partial pressure of dissolved ammonia gas. Henry's Law relates the ammonia concentration to the partial pressure of dissolved ammonia by:

$$K_h = \frac{[NH_3]aq}{P_{NH3}} = \frac{56 \text{ moles}}{\text{liter.atm.}} \quad \text{at } 25°C$$

K_b, Henry's Law Constant, varies with the level of dissolved species and with temperature. As an example, the constant is about 20% lower in 1M NaCl than in distilled water.

Standards and samples should contain the same level of dissolved species and be at the same temperature to keep Henry's Law Constant close to the same value.

4.8 AMMONIUM ION EFFECT

As mentioned earlier, ammonia dissolved in water to form the ammonium ion. Ammonia also reacts with hydrogen ions to form ammonium ions;

$$NH_3 + H_3O \quad NH_4^+ + H_2O \qquad (1)$$

The relative amounts of the ammonium ion and of ammonia is determined by the solution's pH. Virtually, all the ammonia is converted to ammonium ion where hydrogen ion is readily available, as in acid solution. Half the ammonia will be in form of ammonium ion at a pH of about 9.3. See Figure 4-2.

It is possible to calculate the ration of ammonia to ammonium ion, theoretically, if the pH is known. A.Martell and R.Smith in Critical Stability Constants, Plenum Press, New York, 1974, state:

$$\frac{[NH_4^+]}{[H_3O^+]\ [NH_3]} = \frac{(NH_4^+]}{10^{-pH}[NH_3]} = K = 10^{-9.3} \qquad (2)$$

at 25°C, = 0.1
where pk = 9.3

The ratio of ammonium to ammonia is given by:

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

Both temperature and ionic strength will cause the exact value of K to vary. If, for example, while the pH at 25°C and = 0.1 is 9.3, an increase in ionic strength to = 1.0 yields a pH of 9.4, at 25°C.

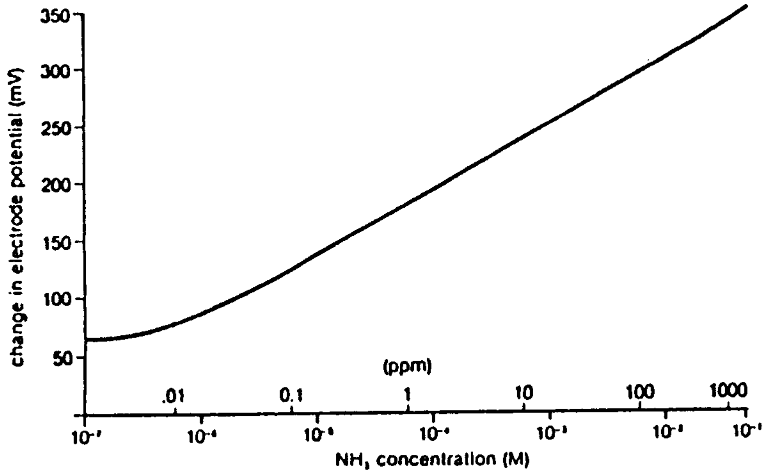

Figure 4-1. Typical Response of Ammonia Electrode

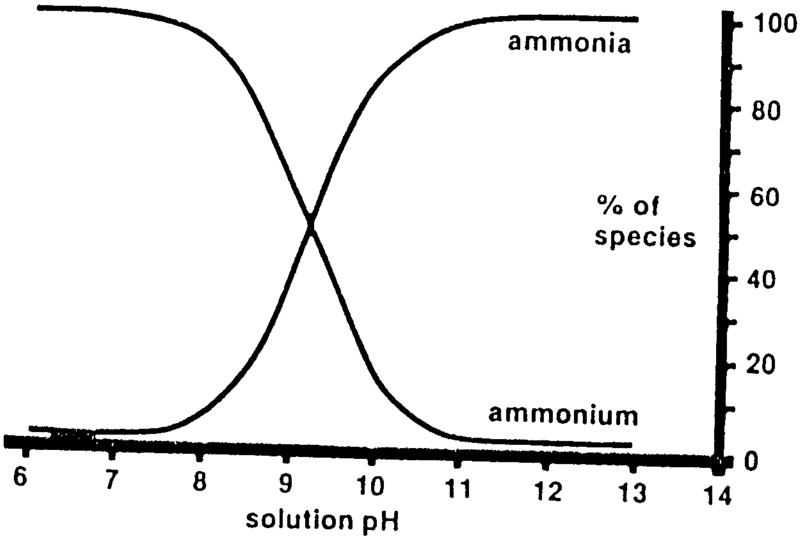

Figure 4-2. Percent of Ammonia and Ammonium as a Function of pH

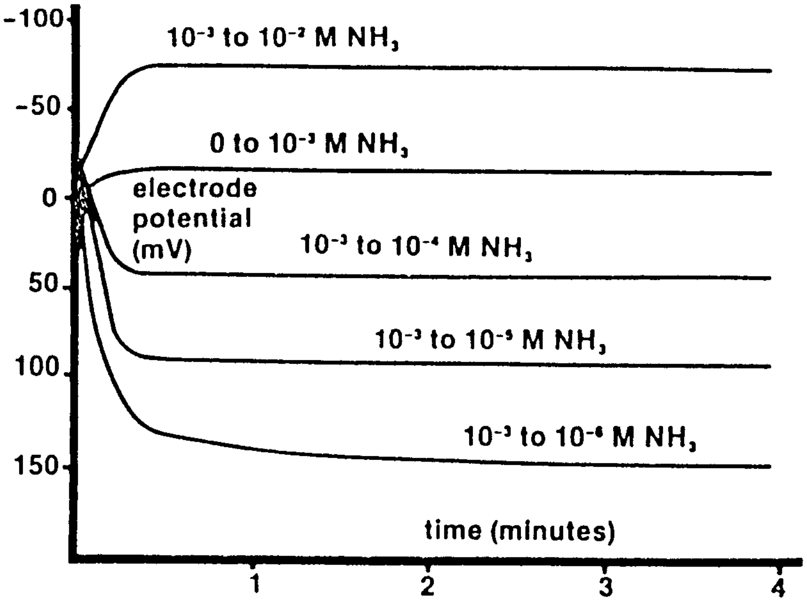

Figure 4-3. Typical Electrode Response to Step Changes in Ammonia Concentration

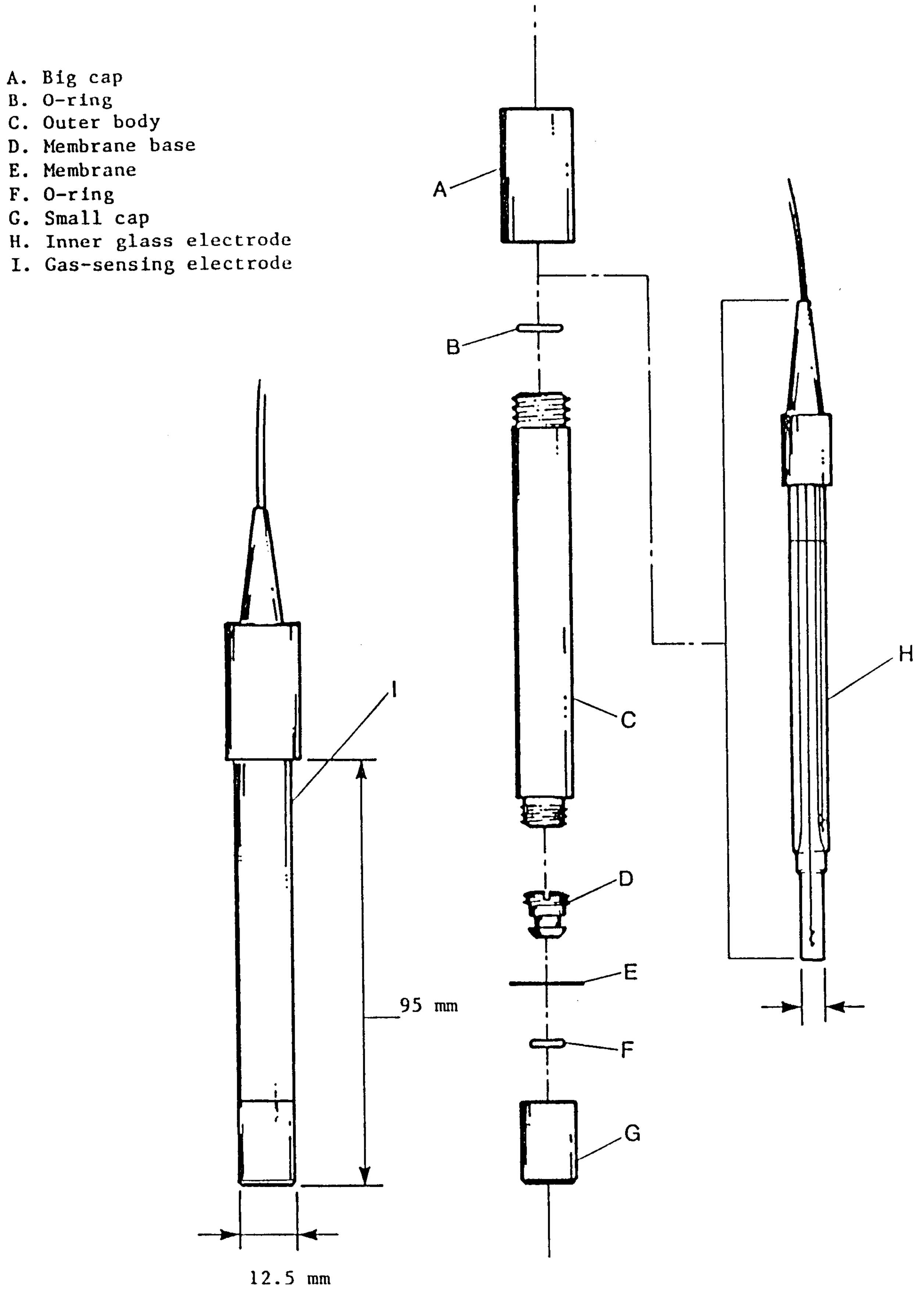

Figure 4-4. Ammonia Electrode

TABLE 4-1
VALUES OF THEORETICAL SLOPE VS. TEMPERATURE

temp	slope (mV)
0°C	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

SECTION 5 TROUBLESHOOTING

SYMPTOM	POSSIBLE CAUSES	NEXT STEP
Out of range reading	Defective meter	Check meter with shorting strap
	Electrode not plugged in properly	Reseat electrode
	Reference electrode junction is dry	Hold cap and lift outer sleeve to expel a few drops of filling solution
	Reference electrode not filled	Be sure reference electrode is filled
	Calibration control not turned far enough	Continue turning the calibration control
Noisy or unstable readings	Defective meter	Check meter with shorting strap
	Wrong reference electrode	Do not use calomel or Ag/AgCl (frit or fiber type) reference electrode
	TISAB not used	Use recommended TISAB
	Meter or stirrer not grounded	Ground meter or stirrer
Drift (reading changing in one direction)	Samples and standards at different temperatures	Allow solutions to come to room temperature before measurement
	Incorrect reference	Use recommended fill solution
	Membrane dirty	Remove organic deposits
	Glassware used	Use plastic labware

SYMPTOM	**POSSIBLE CAUSE**	**NEXT STEP**
Low slope or no slope	Standards contaminated	Prepare fresh standards
	Standard used as TISAB	Use TISAB
"Incorrect Answer" (but calibration curve is good)	Incorrect scaling of semilog paper	Plot millivolts on the linear axis. On the log be sure concentration numbers within each decade are increasing with increasing concentration
	Incorrect sign	Be sure to note sign of millivolt reading correctly
	Incorrect standards	Prepare fresh standards

Where Do I Find Everything I Need for Process Measurement and Control? OMEGA...Of Course!

TEMPERATURE

- ☑ Thermocouple, RTD & Thermistor Probes, Connectors, Panels & Assemblies
- ☑ Wire: Thermocouple, RTD & Thermistor
- ☑ Calibrators & Ice Point References
- ☑ Recorders, Controllers & Process Monitors
- ☑ Infrared Pyrometers

PRESSURE/STRAIN FORCE

- ☑ Transducers & Strain Gages
- ☑ Load Cells & Pressure Gauges
- ☑ Displacement Transducers
- ☑ Instrumentation & Accessories

FLOW/LEVEL

- ☑ Rotameters, Gas Mass Flowmeters & Flow Computers
- ☑ Air Velocity Indicators
- ☑ Turbine/Paddlewheel Systems
- ☑ Totalizers & Batch Controllers

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- ☑ Industrial Water & Wastewater Treatment
- ☑ pH, Conductivity & Dissolved Oxygen Instruments