COLE-PARMER
Ammonia
Gas-Sensing Electrode
Instruction Manual

GENERAL INSTRUCTIONS

Introduction

The Cole-Parmer 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 from 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-through cap, the electrode can be used in flow-through applications.

Required Equipment

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. The Cole-Parmer Ammonia Electrode, Cat. No. 27502-00.

Required Solutions

1. Cole-Parmer Ammonia Standard, 0.1M NH_4Cl, Cat. No. 27503-00. To prepare a 0.1M NH_4Cl solution, dissolve 5.35 grams of reagent grade NH_4Cl in 500 ml of distilled water in a 1 liter volumetric flask and fill to the mark with distilled water. Cap the flask and invert several times to mix the solution.

2. Cole-Parmer Ammonia Standard, 1000 ppm NH_3 as N, Cat. No. 27503-01. To prepare a 1000 ppm solution, fill a l000 ml volumetric flask half full with distilled water, add 3.82 grams of reagent grade NH_4Cl , swirl to dissolve the solid, and fill to the mark with distilled water. Cap the flask and invert several times to mix the solution.

3. Ammonia Standard, 100 ppm NH_3 as N. To prepare a 100 ppm solution, fill a l000 ml volumetric flask half full with distilled water, add 0.382 grams of reagent grade NH_4Cl , swirl to dissolve the solid, and fill to the mark

with distilled water. Cap the flask and invert several times to mix the solution.

4. Cole-Parmer Ionic Strength Adjuster (ISA) Solution, 10 M NaOH, Cat. No. 27503-50.   To prepare a 10 M NaOH solution from your own stock, fill a 1000 ml beaker about half full with distilled water, add 400 grams of reagent-grade NaOH (sodium hydroxide), dissolve by swirling the flask under a hood, allow to cool and fill to the mark with distilled water. Stir the solution and store in a plastic bottle.

5. Ionic Strength Adjuster (ISA) Solution, 5M NaOH/.05M Disodium EDTA/10% Methanol with Color Indicator.   To prepare the ISA, fill a 1000 ml beaker half full with distilled water, add 200 grams of reagent-grade NaOH, stir the solution to dissolve the pellets, add 18.61 grams of disodium EDTA, and stir the solution again until all solids have dissolved. Allow solution to cool. In a separate 150 ml beaker, add a tiny amount (10-20 mg) of thymolphthalein to 100 ml of methanol and stir to dissolve. Pour the methanol solution into the 1000 ml beaker and stir to blend. The solution should turn a dark blue. Fill to the 1000 ml mark with distilled water and stir to blend.

6. Cole-Parmer Ammonia Electrode Filling Solution, Cat. No. 27503-71.

ELECTRODE PREPARATION

Electrode Assembly

The electrode is shipped dry. Before using it, unscrew the large cap (See Figure 5), and remove the inner glass electrode from the outer body. Fill the outer body with 2 to 3 ml of internal filling solution. Place inner glass electrode into the outer body, and screw on the large cap until finger tight. Place the assembled electrode in an electrode holder with a 20° angle from the vertical to avoid trapping air bubbles at the bottom of the electrode.

Checking Membrane

A small hole of any size on the membrane or the breakage of the membrane causes failure of the electrode. 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 tip in deionized water. Record the reading after stirring the deionized water for about 15 minutes. Add proper ISA solution (See **Required Solutions**) to the deionized

water.   A drastic change in the reading in a negative direction indicates damage of the membrane.

Changing Membrane

1.   Unscrew the top cap from the outer body and remove the inner glass body from the epoxy outer body. Carefully place the glass body aside.

2.   Unscrew the bottom cap from the outer body. Remove the old membrane from around the threads and electrode tip opening.

3.   Using the tweezers provided, grab a new piece of white membrane material by the edge and remove from the separator paper. Then, with the hand not holding the tweezers, hold the electrode body up at the threads with thumb and forefinger.   Place one edge of the membrane against the threads and hold in place with your thumb.   Stretch the new membrane lengthwise across the electrode opening so that it smoothly covers the opening.   Place the other edge of the membrane against the threads and hold in place with your forefinger.

4.   Place the bottom cap gently over the membrane onto the threads and screw the bottom cap on until fingertight. Check that the membrane is free of wrinkles and holes or else repeat the above steps.

5.   Using the syringe provided, fill the outer body with approximately 2 ml of inner filling solution.

6.   Place glass inner body into epoxy outer body containing the internal filling solution and screw on the upper cap until fingertight.

Connecting the Electrode to the Meter

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.

Electrode Slope Check (with standard pH/mV meter)
                    (check electrode each day)

1. To a 150 ml beaker, add 100 ml of distilled water and 1 ml of ISA. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tip into the solution.

2. Using a pipet, add 1 ml of 0.1M or 1000 ppm ammonia

standard to the beaker. When the reading has stabilized,
record the millivolt reading.

   3. Using a pipet, add 10 ml of the same ammonia used above
      to the beaker. When the reading has stabilized, record
      the millivolt reading.

   4. Determine the difference between the two readings. A
      difference of 56 ± 3 mV indicates correct electrode
      operation, assuming the solution temperature is between
      20° and 25°C. See the **TROUBLESHOOTING** section if the
      potential change is not within this range.

Slope is defined as the change in potential observed when the
concentration changes by a factor of 10.

Electrode Slope Check (with ion meter)
                    (check electrode each day)

   1. Prepare standard ammonia solutions whose concentrations
      vary by tenfold. Use either the 0.1M or 1000 ppm ammonia
      standard.   Use the serial dilution method for this
      preparation.

   2. To a 150 ml beaker, add 100 ml of the lower value
      standard and 1 ml of ISA. Place the beaker on the
      magnetic stirrer and begin stirring at a constant rate.
      Lower the electrode tip into the solution. Assure that
      the meter is in the concentration mode.

   3. Adjust the meter to the concentration of the standard
      and fix the value in the memory according to the meter
      manufacturer's instructions.

   4. Rinse the electrode and blot dry.

   5. To another 150 ml beaker, add 100 ml of the higher value
      standard and 2 ml of ISA. Place the beaker on the
      magnetic stirrer and begin stirring at a constant rate.
      Lower the electrode tip into the solution.

   6. Adjust the meter to the concentration of the standard
      and fix the value in the memory.

   7. Read the electrode slope according to the meter
      manufacturer's instructions. Correct electrode operation
      is indicated by a slope of 90-100%.   See the
      TROUBLESHOOTING section if the slope is not within this
      range.

MEASUREMENT

Sample Storage

Samples should be measured immediately after preparation or collection, if possible. Wait only long enough for temperature equilibration between the sample and the electrode. If stirring a 100 ml basic solution in a 150 ml beaker, the rate of ammonia loss at room temperature is about 50% in six hours. The loss of CO_2 increases with increasing temperature.

If the samples cannot be measured immediately, make them slightly acidic (pH 6) by adding 0.5 ml of 1M HCl to each liter of sample and store in tightly capped vessels. Prior to measurement, add 10M NaOH to make the samples slightly basic.

Sample Requirements

Standards and samples must be at the same temperature, since a $1^{\circ}C$ difference in temperature will result in a measurement error of approximately 2%. All samples must be aqueous.

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. In this range, all ammonium species are converted to ammonia. Adding the 10 M NaOH adjusts the total level of dissolved species below 1M. If the total level is greater than 1M, the sample should be diluted before measurement. See the **Effect of Dissolved Species** section for a further explanation.

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 1 lists conversion units.

TABLE 1: Concentration Unit Conversion

moles/liter	ppm N	ppm NH_3
10^{-2}	140.0	170.0
10^{-3}	14.0	17.0
10^{-4}	1.4	1.7

Measuring Hints

- Samples should be measured immediately after collection. Samples should be stored according to the directions given

in **Sample Storage** if immediate measurement is not possible.

- The ratio of surface area to volume in the beaker should be minimized. Beakers containing the samples or the standard should be kept covered between measurements.

- The ammonia ISA, 10 M NaOH, should be added <u>just</u> <u>before</u> <u>measurement</u>.

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

- The electrode should be rinsed with distilled water between measurements. Blot dry with a fresh tissue between reading to prevent solution carryover.

- Samples and standards should be stirred using a magnetic stirrer. An insulating material, such as gauze or styrofoam, should be used between the beaker and the magnetic stirrer to minimize heat transfer from the magnetic stirrer to the solution in the beaker.

- Check the electrode for air bubbles adhering to the membrane surface after immersion in solution. Agitate the electrode gently to remove the air bubbles.

MEASUREMENT PROCEDURE

Direct Measurement

A simple procedure for measuring a large number of samples. A single meter reading is all that is required for each sample. The ionic strength of samples and standards should be made the same by adjustment with ISA for all ammonia solutions. The temperature of both sample solution and standard solutions should be the same.
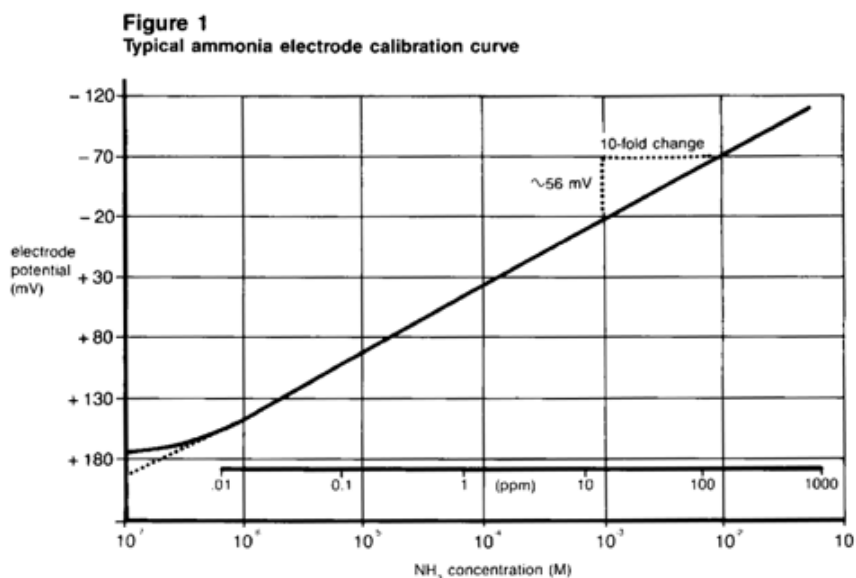
Direct Measurement of Ammonia (using a standard pH/mV meter)

1. By serial dilution of the 0.1M or 1000 ppm standards, prepare 10^{-2}, 10^{-3}, and 10^{-4}M or 100 and 10 ppm ammonia standards. Add 1 ml of ISA per 100 ml of standard. Prepare standards with a composition similar to the samples if the samples have an ionic strength above 0.1M.

2. Place the most dilute solution (10^{-4}M or 10 ppm) on the magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tip into the solution. When the reading has stabilized, record the mV reading.

3. Place the mid-range solution (10^{-3}M or 100 ppm) on the magnetic stirrer and begin stirring. After rinsing the

electrode in distilled water, blot dry and immerse the
electrode tip in the solution. When the reading has
stabilized, record the mV reading.

4. Place the most concentrated solution (10^{-2}M or 1000 ppm)
on the magnetic stirrer and begin stirring. After rinsing
the electrode in distilled water, blot dry, and immerse the
electrode tip in the solution. When the reading has
stabilized, record the mV reading.

5. Using the semi-logarithmic graph paper, plot the mV
reading (linear axis) against the concentration (log axis).
A typical calibration curve can be found in Figure 1.
Extrapolate the calibration curve down to about 1.0×10^{-5}M.

Figure 1
Typical ammonia electrode calibration curve

A calibration curve is constructed on semi-logarithmic
paper when using the pH/mV meter in the millivolt
mode. The measured electrode potential in mV (linear
axis) is plotted against the standard concentration
(log axis). In the linear region of the curve, only
three standards are necessary to determine a
calibration curve. In the non-linear region,
additional points must be measured. The direct
measurement procedures given are for the linear
portion of the curve. The non-linear portion of the
curve requires the use of low level procedures.

6. To a clean, dry 150 ml beaker, add 100 ml of the sample
and 1 ml of ISA. Place the beaker on the magnetic stirrer
and begin stirring at a constant rate. After rinsing the
electrode tip with distilled water and blotting dry, lower
the electrode tip into the solution. When the reading has
stabilized, record the mV reading. Determine the
concentration directly from the calibration curve.

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7. The calibration should be checked every two hours. Assuming no change in ambient temperature, place the electrode tip in the mid-range standard. After the reading has stabilized, compare it to the original reading recorded in Step 3 above. A reading differing by more than 0.5 mV or a change in the ambient temperature will necessitate the repetition of Steps 2-5 above. A new calibration curve should be prepared daily.

Direct Measurement of Ammonia (using an ion meter)

1. By serial dilution of the 0.1M or 1000 ppm ammonia standard, prepare two ammonia standards whose concentration is near the expected sample concentration. Measure out 100 ml of each standard into individual 150 ml beakers and add 1 ml of ISA to each.

2. Place the most dilute solution on the magnetic stirrer and begin stirring at a constant rate. Assure that the meter is in the concentration mode. Lower the electrode tip into the solution.

3. Adjust the meter to the concentration of the ammonia standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.

4. Rinse the electrode with distilled water and blot dry.

5. Place the most concentrated solution on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip into the solution.

6. Adjust the meter to the concentration of the ammonia standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.

7. For low level measurements, place the rinsed, dried electrode into a solution containing 100 ml of distilled water and 1 ml of ISA. After stabilization, fix the blank value in the meter according to the meter manufacturer's instructions.

8. Place 100 ml of the sample and 1 ml of ISA in a 150 ml beaker. Place the beaker on the magnetic stirrer and begin stirring.

9. Immerse the electrode tip in the solution and wait for the reading to stabilize. Read the concentration directly from the meter display.

10. The calibration should be checked every two hours. Assuming no change in ambient temperature, place the

electrode tip in the first ammonia standard. After the reading has stabilized, compare it to the original reading in Step 3 above. A reading differing by more than 0.5 mV or a change in ambient temperature will necessitate the repetition of Steps 2-6 above. The meter should be re-calibrated daily.

Low Level Ammonia Determination (using a pH/mV meter)

As the concentration of ammonia decreases, the rate of ammonia diffusion through the membrane is slow, the rate of equilibrium between the ammonium in the internal filling solution and ammonia is slow, and thus the response time increases. If the internal filling solution is diluted with ammonia-free distilled water (1:10), response at low levels can improve. Measurements 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 the pH 4 buffer or a low-level solution.

Use the following low level ammonia measurement procedure in the non-linear portion of the calibration curve. See Figure 1. This procedure is used for ammonia samples containing less than 1.0×10^{-5}M ammonia.

1. Measure out 100 ml of a pH 4 buffer solution, add it to a 150 ml beaker, place the beaker on the 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 2500 ml erlenmeyer flask, add 1000 ml of distilled water and 10 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 after each step. Plot the concentration (log axis) vs. the electrode potential (linear axis) on semilogarithmic 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 1000 ml of the sample into a 1000 ml beaker, add 10 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 2: Additions of 10^{-2}M or 100 ppm Standard to 1000 ml Distilled Water and 10 ml 10M NaOH

Step	Pipet	Added Volume (ml)	Concentration M	ppm
1	A	0.10	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	0.20	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

Ammonia Measurements in Membrane Wetting Solutions

Since the membrane of the ammonia electrode 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 penetrate 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 a 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. 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.

ELECTRODE CHARACTERISTICS

Reproducibility

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

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.

Effect 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 temperatures 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.

Complexation

Metal complexes are formed with ammonia and a number of metal ions. Complexes of mercury, copper, gold, silver, nickel, zinc, cobalt, and cadmium are removed in the form of hydroxide complexes or precipitates in basic solution. When ammonia concentration is below 10^{-3}M and hydroxide is present at the 10^{-1}M level, the only appreciable complex formed will be between mercury and ammonia. Since the total ammonia level of a sample will be measured if the mercury is preferentially bound to another species, addition of iodide is recommended for this purpose. Use of the recommended ISA (10M NaOH solution) inhibits the formation of metal complexes in the sample, since it contains a high concentration of hydroxide ions.

Temperature Influences

Table 4 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.
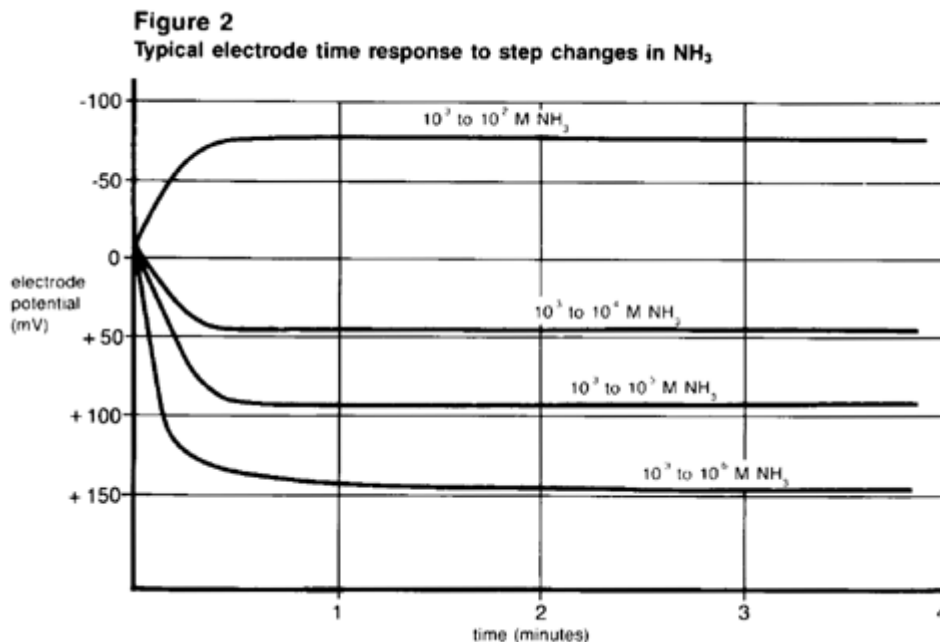
TABLE 4: Values of Theoretical Slope vs. Temperature

Temp.($^{\circ}$C)	"S"
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

Electrode Response

Electrode potential response to ammonia concentration is a straight line with a slope of about 56 mV/decade, when plotted on semilogarithmic paper. See Figure 1.

For ammonia concentrations above 4×10^{-6}M (0.07 ppm NH_3 or 0.06 ppm N), the electrode exhibits good time response (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. Response times of the

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ammonia electrode to step changes in ammonia are shown in Figure 2.

Figure 2
Typical electrode time response to step changes in NH$_3$

Limits of Detection

The upper limit of detection in pure ammonia solutions is 1M. Ammonia is rapidly lost to the air above a concentration of 1M. Dilution may be used if ammonia concentrations are above 1M. Also dilute samples between 1M and 10^{-1}M or calibrate the electrode at 4 or 5 intermediate points.

The lower limit of detection is around 1 x 10^{-6} M. Refer to Figure 1 for a comparison of the theoretical response to the actual response at low levels of ammonia. Ammonia measurements below 10^{-5}M NH$_3$ should employ low level procedures.

pH Effects

The ammonia electrode can be used over the pH range 11 to 14. It is necessary to adjust the sample pH to above 11 using the recommended ISA to convert all ammonium species in solution to ammonia.

Electrode Life

The ammonia electrode will last six months in normal laboratory use. On-line measurements might shorten operational lifetime to several months. In time, the response time will increase and the calibration slope will decrease to the point calibration is difficult and membrane replacement is required.

Electrode Storage

If erratic results are obtained from accidentally 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 between measurements.
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 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.

ELECTRODE THEORY

Electrode Operation

The Cole-Parmer 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:

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

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

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

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

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

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

$$E = E_o - S \log [OH^-]$$
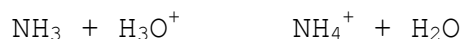
where S is the slope of the electrode.
Because the hydroxide concentration is proportional to the ammonia concentration, electrode response to ammonia is also Nernstian:
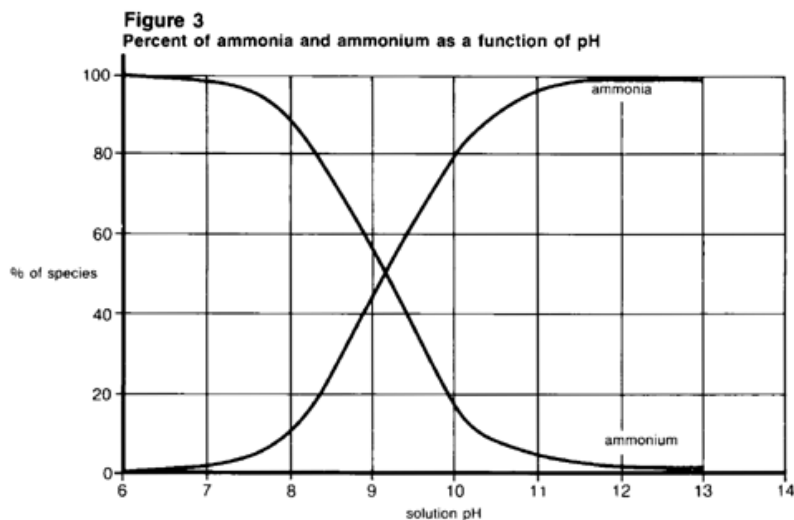
$$E = E_o^1 - S \log [NH_3]$$

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.

Ammonia Chemistry

As mentioned earlier, ammonia dissolves in water to form the ammonium ion. Ammonia also reacts with hydrogen (hydronium) ions to form ammonium ions:

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

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 the form of ammonium ion at a pH of about 9.3. See Figure 3.

Figure 3
Percent of ammonia and ammonium as a function of pH

It is possible to calculate the ratio of ammonia to ammonium ion, theoretically, if the pH is known. A. Martell and R. Smith in <u>Critical</u> <u>Stability</u> <u>Constants</u>, Plenum Press, New York,

1974, state:

$$\frac{[NH_4^+]}{[H_3O^+]\,[NH_3]} = \frac{[NH_4^+]}{10^{-pH}[NH_3]} = K \sim 10^{-9.3}$$

at 25°C,   X = 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 pK at 25°C and X = 0.1 is 9.3, an increase in ionic strength to X = 1.0 yields a pK of 9.4, at 25°C.

TROUBLESHOOTING

Troubleshooting Guide

The most important principal in troubleshooting is to isolate the components of the system and check each in turn. The components of the system are: 1) Meter, 2) Electrode, 3) Standard, 4) Sample, and 5) Technique.

Meter

The meter is the easiest component to eliminate as a possible cause of error. Most meters are provided with an instrument check-out 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.

Electrode

1. Rinse electrode thoroughly with distilled water.

2. Perform **Electrode Slope Check**.

3. If electrode fails this procedure, re-soak ammonia electrode as directed in **Electrode Assembly** and **Checking Membrane**.

4. Repeat **Electrode Slope Check**.

5. If the electrode still does not perform as described, determine whether the ammonia electrode inner body is working properly as directed in **Checking the Electrode Inner Body.**

6. If the stability and the slope check out properly, but measurement problems persist, the standards may be of poor quality, the sample may contain interference or complexing agents, or the technique may be in error. See **Standard, Sample** and **Technique** sections below.

7. Before replacing a "faulty" electrode, review the instruction manual and be sure to:
   - clean and rinse the electrode thoroughly
   - prepare the electrode properly
   - use proper filling solution, buffer, and standards
   - measure correctly
   - review **Troubleshooting Hints**

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 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 and Interferences.**

Technique

Check the method of analysis for compatibility with your

sample. Direct measurement may not always be the method of choice.
Also, be sure that the expected concentration of the ion of interest is within the electrode's limits of detection.

If problems persist, review operational procedures and instruction manual to be sure that proper technique has been followed. Call Cole-Parmer at 1-800-323-4340 and ask for the Technical Services Department to answer any questions.

Troubleshooting Hints

<u>Symptom</u>	<u>Possible Causes</u>	<u>Next Step</u>
Out of Range Reading	defective meter	perform meter check out procedure (see meter instruction manual)
	defective inner body	refer to **Checking the Electrode Inner Body**
	electrode not plugged in properly	unplug electrode and reseat
	internal filling solution not added	fill outer body of electrode with proper amount of internal filling solution
	air bubble on membrane	remove bubble by re-dipping electrode
	electrode not in solution	put electrode in solution
Noisy or Unstable Reading (readings continuously or randomly changing)	insufficient internal filling solution	fill outer body of electrode with proper amount of internal filling solution
	defective meter	perform meter check-out procedure (see meter instruction manual)
		ensure that bottom

	bottom cap loose	cap is screwed on tight enough to close gap between bottom cap and body
	defective inner body	refer to **Checking the Electrode Inner Body**
	air bubbles on membrane	remove bubbles by redipping electrode
	meter or stirrer improperly grounded	check meter and stirrer for grounding
Drift (reading slowly changing in one direction)	internal filling solution leakage	ensure that membrane is installed properly
	incorrect internal filling solution	refill outer body of electrode using filling solution shipped with electrode
	total level of dissolved species above 1M	dilute solution
	electrode in sample too long; NH_3 loss	reduce surface area-to-volume ratio, slow down rate of stirring, & avoid high temperatures
	membrane failure (wet, perforation, discoloration)	replace membrane
	samples & standards not at constant temperature	allow samples & standards to come to room temperature before use
	heat generated by magnetic stirrer	place insulating material between stirrer and beaker
	defective inner body	

		refer to **Checking the Electrode Inner Body**
	electrode exposed to air for extended period	hold electrode by outer body and pull on electrode cable internal filling solution will flow under membrane and restore electrode response
Low Slope or No Slope	standards contaminated or incorrectly made	prepare fresh standards
	buffer not used	use recommended buffer
	standard used as buffer	use buffer
	electrode exposed to air for extended period	hold electrode by outer body and pull up on electrode cable internal filling solution will flow under membrane and restore electrode response
	membrane failure (wet, perforation, discoloration)	replace membrane
	defective inner body	refer to **Checking the Electrode Inner Body**
"Incorrect Answer" (but calibration curve is good)	incorrect scaling of semi-log paper	plot millivolts on the linear axis. On the log axis, be sure concentration numbers within each decade are increasing with increasing concentration

incorrect sign	be sure to note sign of millivolt value correctly
incorrect standards	prepare fresh standards
wrong units used	apply correct conversion factor: $10^{-3}M$ = 17 ppm as NH_3 = 14 ppm as N
buffer added to standards and not samples	add same proportions of buffer to standards and samples
sample carryover	rinse electrodes thoroughly between samples

Checking the Electrode Inner Body

If the electrode slope is found to be low during operation, the following solutions will be necessary to check the inner body:

- pH 4 Buffer (0.1M NaCl added)
Add 2.9 grams of reagent-grade NaCl to 500 ml of pH 4 buffer. Dissolve the solid. The solution may be stored for repeated use.

- pH 7 Buffer (0.1M NaCl added)
Add 2.9 grams of reagent-grade NaCl to 500 ml of pH 7 buffer. Dissolve the solid. The solution may be stored for repeated use.

Disassemble the ammonia electrode. If the electrode is dry, soak the glass tip of the inner body in Cole-Parmer Ammonia Electrode Filling Solution (Cat. No. 27503-71) for at least two hours.

Rinse the electrode thoroughly with distilled water. Put 100 ml of pH 7 buffer (0.1M NaCl added) 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 that the meter is in the mV mode. Record the meter reading.

Rinse the inner body thoroughly in distilled water. Put 100 ml of pH 4 buffer (0.1M NaCl added) 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.

SPECIFICATIONS

Concentration Range: 5×10^{-7}M to 1 M NH_3
(0.01 to 17000 ppm NH_3)
(0.01 to 14000 ppm as N)

pH Range: above 11

Temperature Range: 0° to 50°C

Inner Body Resistance: ~1000 Mohm

Reproducibility: $\pm$ 2%

Size: 110 mm length
12 mm diameter
1 m cable length

Storage: store electrodes in 0.1M NH_4Cl

ORDERING INFORMATION

P/N	Description
27502-00	Ammonia Gas Sensing Electrode
275xx-xx	Ammonia Membrane Kit, bag of 20 membranes and spare o-ring
27503-71	Ammonia Electrode Filling Solution
27503-00	Ammonia Standard, 0.1M NH_4Cl
27503-01	Nitrogen Standard, 1000 ppm NH_3 as N
27503-50	Ammonia Ionic Strength Adjuster (ISA) Solution, 10 M NaOH

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