# pHoenix Electrode Company Ammonium Ion Electrodes Instruction Manual

#### GENERAL INSTRUCTIONS

#### Introduction

The pHoenix Electrode Company Ammonium Ion Electrode is used to quickly, simply, accurately, and economically measure ammonium ions in aqueous solutions.

## 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. pHoenix Electrode Company Ammonium Ion Combination Electrodes, Cat. No. NH41502 (Glass), NH41508 (Epoxy).
- 5. pHoenix Electrode Company Reference Filling Solution, Cat. No. R001043, for use with both the Ammonium Ion Combination Glass Electrode NH41502 and the pHoenix Electrode Company Ammonium Ion Combination Epoxy Electrode NH41508.

#### Required Solutions

- 1. Deionized or distilled water for solution and standard preparation.
- 2. pHoenix Electrode Company Ionic Strength Adjuster, 5M NaCl, Cat. No. NH4IS01 to keep a constant background ionic strength present in the solution. To prepare the 5M NaCl ISA from your own laboratory stock, add 292 grams of reagent-grade sodium chloride (NaCl) to a 1000 ml volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid and fill to the mark with distilled water. Cap the flask and invert several times to mix the solution. Add 2 ml of ISA to every 100 ml of sample or standard solution for a back-ground ionic strength of 0.10M.

- 3. pHoenix Electrode Company Ammonium Standard, 0.1M  $\mathrm{NH_4Cl}$ , Cat. No. NH4AS01. To prepare this standard, add 5.34 grams of reagent-grade ammonium chloride to a 1 liter volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid and fill to the mark with distilled water. Cap the flask and invert several times to mix the solution.
- 4. pHoenix Electrode Company Ammonium Standard, 1000 ppm  $\mathrm{NH_4^{+1}}$ , Cat. No. NH4AS02. To prepare this standard, add 2.97 grams of reagent-grade ammonium chloride to a 1 liter volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid and fill to the mark with distilled water. Cap the flask and invert several times to mix the solution.

#### GENERAL PREPARATION

# Electrode Preparation

Remove any rubber cap covering the electrode tip and the rubber insert covering the filling hole of the reference electrode. Fill the combination electrode with the filling solution shipped with the electrode to a level just below the fill hole. Gently shake the electrode downward in the same manner as a clinical thermometer to remove any air bubbles which might be trapped behind the ammonium membrane. Prior to first usage, or after long term storage, immerse the ammonium electrode in ammonium standard for thirty minutes. The electrode is now ready for use.

Connect the electrode to the proper terminal(s) as recommended by the meter manufacturer.

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- 1. To a 150 ml beaker, add 100 ml of distilled water and 2 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 ammonium standard to the beaker. When the reading is stable, record the millivolt reading.

- 3. Using a pipet, add 10 ml of the standard 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  $56^{\pm}2\text{mV}$  indicates correct electrode operation, assuming the solution temperature is between  $20^{\circ}$  and  $25^{\circ}\text{C}$ . See the <u>Troubleshooting</u> section if the potential change is not within this range.

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

# Electrode Slope Check (with ion meter) (check electrodes each day)

- 1. Prepare standard ammonium solutions whose concentrations vary by tenfold. Use either the 0.1M  $\mathrm{NH_4^{+1}}$  or the 1000 ppm  $\mathrm{NH_4^{+1}}$  standard stock solutions. Use the serial dilution method for this preparation.
- 2. To a 150 ml beaker, add 100 ml of the lower 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. 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 with distilled water and blot dry.
- 5. To a 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 <u>Troubleshooting</u> section if the slope is not within this range.

#### **MEASUREMENT**

# Measuring Hints

The sensing membrane is normally subject to water uptake and might appear milky. This has no effect on performance.

All samples and standards should be at the same temperature for precise measurement, preferably ambient temperature.

Constant, but not violent, stirring is necessary for accurate measurement. Magnetic stirrers can generate sufficient heat to change the solution temperature. To counteract this effect, place a piece of insulating material, such as styrofoam sheet or asbestos sheet, between the stirrer and beaker.

Always rinse the electrode tip with distilled water and blot dry with a fresh tissue between readings to prevent solution carryover.

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

A slow or sluggish electrode response may indicate surface contamination of the ammonium electrode membrane. Soak the electrode tip in distilled water for about 5 minutes to clean the membrane. Rinse the membrane and soak in diluted standard solution for about 5 minutes to restore performance.

When measuring samples with high ionic strength, prepare standards with compositions similar to that of the sample.

Dilute concentrated samples (over 0.1M) before measurement.

Recalibrate every few hours for routine measurement.

#### Sample Requirements

Make sure that the samples and standards are at the same temperature. About a 2% error will be introduced for a  $1^{\circ}$ C difference in temperature. Temperature should normally be less than  $40^{\circ}$ C with intermittent measurements allowed to  $50^{\circ}$ C.

All samples and standards must be aqueous. They must not contain organic solvents.

Interferences found in Table 3 should be absent.

#### Units of Measurement

Ammonium concentrations are measured in units of parts per million as ammonium, parts per million as N, moles per liter, or any other convenient concentration unit. Table 1 indicates some of the concentration units.

Table 1: Concentration Unit Conversion Factors

$\underline{ppm}\ \underline{NH}_{\underline{4}}^{+}$	ppm N	$\underline{\text{moles/liter NH}_{\underline{4}}^+}$
1.80	1.40	1x10 <sup>-4</sup>
18.00	14.00	1x10 <sup>-3</sup>
180.00	140.00	1x10 <sup>-2</sup>

#### MEASUREMENT PROCEDURE

# Direct Measurement

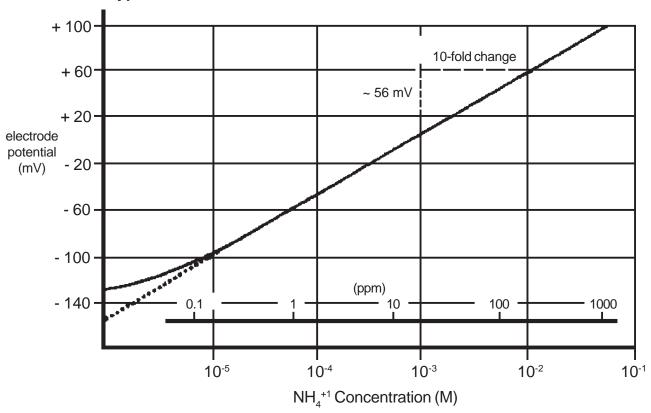
Direct Measurement is a simple procedure for measuring a large number of samples. A single meter reading is all that is required for each sample. The ionic strength of samples and standards should be made the same by adjustment with ISA for all ammonium solutions. The temperature of both sample solution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

## Direct Measurement of Ammonium (using a pH/mV meter)

- 1. Prepare  $10^{-2}$ ,  $10^{-3}$ , and  $10^{-4}M$  or 100, 10, and 1 ppm standards by serial dilution of the 0.1M or 1000 ppm standard. Add 2 ml of ISA per 100 ml of standard.
- 2. Place the most dilute solution  $(10^{-4}\text{M} \text{ or } 1 \text{ ppm})$  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 midrange solution  $(10^{-3}M \text{ or } 10 \text{ ppm})$  on the magnetic stirrer and begin stirring. After rinsing the electrode with distilled water and blotting dry, immerse the electrode tip in the solution. When the reading has stabilized, record the mV reading.
- 4. Place the most concentrated solution  $(10^{-2}M \text{ or } 100 \text{ ppm})$  on the magnetic stirrer and begin stirring. After rinsing the electrode(s) with distilled water and blotting dry, 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.

Figure 1
Typical Ammonium Electrode Calibration Curve



A calibration curve is constructed on semi-logarithmic paper when using a 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.

Extrapolate the curve down to about 1x10<sup>-5</sup>M or 0.2 ppm.

6. To a clean, dry 150 ml beaker, add 100 ml of sample and 2 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring. Place the electrode tip in the solution. When the reading has stabilized, record the millivolt reading. Determine the concentration directly from the calibration curve.

7. The electrode should be re-calibrated every 1-2 hours. Simply repeat Steps 2-5 above.

#### Direct Measurement of Ammonium (using an ion meter)

- 1. By serial dilution of the 0.1M or 1000 ppm ammonium standard, prepare two ammonium standards whose concentration is near the expected sample concentration. Measure out 100 ml of each standard into individual 150 ml beakers and add 2 ml of ISA to each.
- 2. Place the more dilute solution on the magnetic stirrer and begin stirring at a constant rate. Assure that the meter is in the concentration mode.
- 3. Lower the electrode tip into the solution.
- 4. Adjust the meter to the concentration of the ammonium standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
- 5. Rinse the electrode tip with distilled water and blot dry.
- 6. Place the more concentrated solution on the magnetic stirrer and begin stirring at a constant rate.
- 7. Lower the electrode tip into the solution.
- 8. Adjust the meter to the concentration of the ammonium standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
- 9. For low level measurements, place the rinsed, dried electrode into a solution containing 100 ml of distilled water and 2 ml of ISA. After stabilization, fix the blank value in the meter according to the meter manufacturer's instructions.
- 10. Place 100 ml of the sample and 2 ml of ISA in a 150 ml beaker, place it on the magnetic stirrer, and begin stirring.
- 11. Immerse the electrode tip in the solution and wait for the reading to stabilize. Read the concentration directly from the meter display.
- 12. The electrode should be re-calibrated every 1-2 hours. Simply repeat Steps 2-8 (2-9) above.

# Low Level Ammonium Determination (using a standard pH/mV meter)

This procedure is recommended for solutions with ionic strengths less than  $1.0 \times 10^{-2} M$ . If the solution is high in ionic strength, but low in ammonium, use the same procedure, but prepare a calibration solution with a composition similar to the sample.

- 1. Using 20 ml of stock ISA, dilute to 100 ml with distilled water.
- 2. Dilute 1 ml of the 0.1M standard to 100 ml to prepare a  $1.0 \times 10^{-3} M$  standard solution for measurements in moles per liter. Dilute 10 ml of the 1000 ppm standard to 100 ml to prepare a 100 ppm standard solution for measurements in ppm.
- 3. To a 150 ml beaker, add 100 ml of distilled water and 1 ml of low level ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.
- 4. Place the electrode tip in the solution. Assure that the meter is in the mV mode.
- 5. Add increments of the  $1.0 \times 10^{-3} M$  or 100 ppm standard as given in Table 2 below.
- 6. After the reading has stabilized, record the mV reading after each addition.

<u>Table 2</u>: Stepwise Calibration for Low Level Ammonium Measurements

		<u>Added</u>	<u>Concent</u>	<u>ration</u>
Step	<u> Pipet</u>	Volume (ml)	<u>M</u>	ppm
1	A	0.1	1.0X10 <sup>-6</sup>	0.1
2	A	0.1	2.0X10 <sup>-6</sup>	0.2
3	A	0.2	4.0X10 <sup>-6</sup>	0.4
4	A	0.2	6.0X10 <sup>-6</sup>	0.6
5	A	0.4	9.9X10 <sup>-6</sup>	1.0
6	В	2	2.9X10 <sup>-5</sup>	2.9
7	В	2	4.8X10 <sup>-5</sup>	4.8

Pipet A = 1 ml graduated pipet

Pipet B = 2 ml pipet

- 7. On semi-logarithmic graph paper, plot the mV reading (linear axis) against the concentration (log axis) as in Figure 1.
- 8. Rinse the electrode in distilled water and blot dry.
- 9. Measure out 100 ml of the sample into a 150 ml beaker, add 1 ml of low level ISA, and place the beaker on the magnetic stirrer. Begin stirring. Lower the electrode tip into the solution.
- 10. After the reading has stabilized, record the mV reading and determine the concentration from the low level calibration curve.
- 11. Prepare a new low level calibration curve daily. Check the calibration curve every 1-2 hours by repeating Steps 3-7 above.

#### Low Level Ammonium Determination (using an ion meter)

Follow the procedure given for normal ammonium determinations using an ion meter and the blank correction procedure.

#### ELECTRODE CHARACTERISTICS

#### Reproducibility

Direct electrode measurements reproducible to  $\pm 2\%$  can be obtained if the electrode is calibrated every hour. Factors such as temperature fluctuations, drift, and noise limit reproducibility.

Reproducibility is independent of concentration within the electrode's operating range.

#### Interferences

Table 3 lists some common cations that, if present in high enough levels, will cause electrode interferences and measurement errors or electrode drift when using the ammonium ion electrodes.

Electrode drift and slow response could indicate the presence of high interference from the ions listed. Soak the electrode(s) in distilled water for an hour, then for two hours in ammonium standard solution to restore proper response.

Interferences			
(moles/liter)	$10^{-2} \underline{M} \underline{NH}_{\underline{4}}^{+1}$	$10^{-3} M NH_{4}^{+1}$	$10^{-4} M NH_{\underline{4}}^{+1}$
Cs <sup>+1</sup>	3.0X10 <sup>-3</sup>	3.0X10 <sup>-4</sup>	3.0X10 <sup>-5</sup>
$K^{+1}$	1.0X10 <sup>-2</sup>	1.0X10 <sup>-3</sup>	1.0X10 <sup>-4</sup>
Tl <sup>+1</sup>	6.0X10 <sup>-2</sup>	6.0X10 <sup>-3</sup>	6.0X10 <sup>-4</sup>
$\mathrm{H}^{+1}$	1.0X10 <sup>-1</sup>	1.0X10 <sup>-2</sup>	1.0X10 <sup>-3</sup>
$Ag^{+1}$	1.0X10 <sup>1</sup>	1.0	1.0X10 <sup>-1</sup>
+Tris <sup>+1</sup>	1.0X10 <sup>1</sup>	1.0	1.0X10 <sup>-1</sup>
Li <sup>+1</sup>	2.0X10 <sup>1</sup>	2.0	2.0X10 <sup>-1</sup>
Na <sup>+1</sup>	2.0X10 <sup>1</sup>	2.0	2.0X10 <sup>-1</sup>

 $+ {\rm Tris}^{+1}$  is the cation of tris(hydroxymethyl)aminomethane

Interferences			
(ppm)	100 ppm $NH_{\underline{4}}^+$	10 ppm $NH_{\underline{4}}^{+}$	$1 \text{ ppm } NH_{\underline{4}}^{+}$
Cs <sup>+1</sup>	1.0X10 <sup>2</sup>	1.0X10 <sup>1</sup>	1.0
$K_4^{+1}$	2.7X10 <sup>2</sup>	2.7X10 <sup>1</sup>	2.7
Tl <sup>+1</sup>	3.1X10 <sup>3</sup>	3.1X10 <sup>2</sup>	3.1X10 <sup>1</sup>
$\mathrm{H}^{+1}$	1.6pH	2.6рН	3.6pH
$Ag^{+1}$	2.7X10 <sup>5</sup>	2.7X10 <sup>4</sup>	2.7X10 <sup>3</sup>
+Tris <sup>+1</sup>	3.1X10 <sup>5</sup>	3.1X10 <sup>4</sup>	3.1X10 <sup>3</sup>
Li <sup>+1</sup>	3.5X10 <sup>4</sup>	3.5X10 <sup>3</sup>	3.5X10 <sup>2</sup>
Na <sup>+1</sup>	1.1X10 <sup>5</sup>	1.1X10 <sup>4</sup>	1.1X10 <sup>3</sup>

#### Temperature Influences

Samples and standards should be at the same temperature, since electrode potentials are influenced by changes in temperature. A  $1^{\circ}$ C difference in temperature results in a  $2^{\circ}$  error at the  $1.0 \times 10^{-3}$ M level.

Provided that temperature equilibria has occurred, the ammonium ion electrodes can be used at temperatures from  $0^{\circ}$  -  $40^{\circ}$ C. Room temperature measurements are recommended, since measurements at temperatures markedly different from room temperature may require equilibrium times up to one hour.

Table 4 indicates the variation of theoretical slope with temperature.

Table 4: Temperature vs Value for the Electrode Slope

$\underline{\text{Temp}}$ (°C)	"S" (slope)
0	54.20
10	56.18
20	58.16
25	59.16
30	60.15
40	62.13
50	64.11

#### Electrode Response

Plotting the electrode mV potential against the ammonium concentration on semi-logarithmic paper results in a straight line with a slope of about 56mV per decade. Refer to Figure 1.

The time needed to reach 99% of the stable electrode potential reading, the electrode response time, varies from one minute or less for ammonium concentration above  $1.0 \times 10^{-5} M$  to several minutes near the detection limit. Refer to Figure 2.

+ 75  $10^{-3}$  M to  $10^{-2}$  M NH $_{4}$ CI + 50 + 25 electrode 0 potential (mV) - 25 10<sup>-3</sup> M to 10<sup>-4</sup> M NH<sub>4</sub>Cl - 50  $10^{-3}$  M to  $10^{-5}$  M NH<sub>4</sub>CI - 75 - 100 · 2 1 3 Time (minutes)

Figure 2
Typical Electrode Time Response to Step Changes in NH,CI

#### Detection Limit

The upper limit of detection is 1M in pure ammonium chloride solutions. The upper limit of detection is above  $1.0 \times 10^{-1} \mathrm{M}$  when other ions are present, but the possibility of a liquid junction potential developing at the reference electrode and the "salt extraction effect" are two limiting factors. Some salts may be extracted into the electrode membrane at high salt concentrations causing deviation from theoretical response. Calibrate the electrode at four or five intermediate points, or dilute the sample, to measure samples between  $1.0 \times 10^{-1} \mathrm{M}$  and 1M.

The slight water solubility of the ion exchanger in the sensing module, which causes deviation from theoretical response, determines the lower limit of detection. The theoretical response at low levels of ammonium chloride compared to actual response is shown in Figure 1. A low level measurement is recommended if ammonium measurements are made below  $1.0 \times 10^{-5} M$  (0.18 ppm as ammonium).

#### pH Effects

Hydrogen ion interferes with measurements of low levels of ammonium ion although the electrode can be used over a wide pH range. Table 3 should be used to determine the minimum pH at which low level ammonium measurements can be made without more than a 10% error due to hydrogen ion interference.

#### Electrode Life

The ammonium electrode will last six months in normal laboratory use. On-line measurement 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 electrode replacement is required.

#### Electrode Storage

The ammonium electrode may be stored in  $1.0 \times 10^{-2} M$  ammonium standard for short periods of time. For storage over 3 weeks, rinse and dry the ammonium membrane electrode and cover the tip with any protective cap shipped with the electrode. The reference portion of the combination electrode should be drained of filling solution, and the rubber insert placed over the filling hole.

#### ELECTRODE THEORY

#### Electrode Operation

The pHoenix Electrode Company ammonium ion electrodes are composed of an epoxy or glass body and a sensing membrane. This sensing membrane contains a liquid internal filling solution in contact with a gelled organophilic membrane containing an ammonium selective ion exchanger.

An electrode potential develops across the membrane when the membrane is in contact with an ammonium solution. Measurement of this potential against a constant reference potential with a digital pH/mV meter or with a specific ion meter depends on the level of free ammonium ion in solution. The level of ammonium ions, corresponding to the measured potential, is described by the Nernst equation:

$$E = E_0 + S \log X$$

where:

E = measured electrode potential

E = reference potential (a constant)

S = electrode slope ( 56 mV/decade)

X = level of ammonium ions in solution

The activity, X, represents the effective concentration of the ions in solution. Total ammonium concentration,  $C_{\rm t}$ , includes free ammonium ions,  $C_{\rm p}$ , plus bound or complexed ammonium ions,  $C_{\rm p}$ . Since the ammonium electrodes only respond to free ion, the free ion concentration is:

$$C_f = C_t - C_b$$

The activity is related to the free ion concentration,  $\textbf{C}_{_{\! f}}\text{,}$  by the activity coefficient,  $\gamma$  , by:

$$X = \gamma C_f$$

Activity coefficients vary, depending on total ionic strength, I, defined as:

$$I = \frac{1}{2} \sum_{x} C_{x} Z_{x}^{2}$$

where:

 $C_x = concentration of ion X$ 

 $Z_{v}$  = charge of ion X

 $\Sigma$  = sum of all of the types of ions in the solution.

In the case of high and constant ionic strength relative to the sensed ion concentration, the activity coefficient,  $\gamma$ , is constant and the activity, X, is directly proportional to the concentration.

To adjust the background ionic strength to a high and constant value, ionic strength adjuster (ISA) is added to samples and standards. The recommended ISA for ammonium is sodium chloride, NaCl. Solutions other than this may be used as long as ions that they contain do not interfere with the electrode's response to ammonium ions.

The reference electrode must also be considered. When two solutions of different composition are brought into contact with one another, liquid junction potentials arise. Millivolt potentials occur from the interdiffusion of ions into the two solutions. Electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions, since ions diffuse at different rates. When making measurements, it is important to remember that this potential be the same when the reference is in the standardizing solution as well as in the sample solution or the change in liquid junction potential will appear as an error in the measured electrode potential.

The composition of the liquid junction filling solution in the reference electrode is most important. The speed with which the positive and negative ions in the filling solution diffuse into the sample should be as nearly equal as possible, that is, the filling solution should be equitransferant. No junction potential can result if the rate at which positive and negative charge carried into the sample is equal.

Strongly acidic (pH = 0-2) and strongly basic (pH = 12-14) solutions are particularly troublesome to measure. The high mobility of hydrogen and hydroxide ions in samples make it impossible to mask their effect on the junction potential with any concentration of an equitransferant salt. One must either calibrate the electrode(s) in the same pH range as the samples or use a known increment method for ion measurement.

#### TROUBLESHOOTING GUIDE

The goal of troubleshooting is the isolation of a problem through checking each of the system components in turn: the meter, the glassware, the electrode, the standards & reagents, the sample, and the technique.

#### Meter

The meter may be checked by following the checkout procedure in the instrument instruction manual.

#### Glassware

Clean glassware is essential for good measurement. Be sure to wash the glassware well with a mild detergent and rinse very well with distilled or deionized water. Clean glassware will drain without leaving water droplets behind.

#### Electrode

The electrode may be checked by using the procedure found in the sections entitled **Electrode Slope Check**.

- 1. Be sure to use distilled or deionized water when following the procedures given in **Electrode Slope Check**.
- 2. If the electrode fails to respond as expected, see the sections Measuring Hints and Electrode Response. Repeat the slope check.

- 3. If the electrode still fail to respond as expected, substitute another ammonium ion electrode that is known to be in good working order for the questionable electrode. If the problem persists and you are using an electrode pair, try the same routine with a working reference electrode.
- 4. If the problem persists, the reagent may be of poor quality, interferences in the sample may be present or the technique may be faulty. See **Standards & Reagents**, **Sample**, and **Technique** sections below.
- 5. If another electrode is not available for test purposes, or if the electrode in use is suspect, review the instruction manual and be sure to:
  - Clean and rinse the electrode(s) thoroughly.
  - Prepare the electrode(s) properly.
  - Use the proper filling solution.
  - Adjust the pH and the ionic strength of the solution by the use of the proper ISA.
  - Measure correctly and accurately.
  - Review Troubleshooting Hints.

#### Standards & Reagents

Whenever problems arise with the measuring procedure that has been used successfully in the past, be sure to check the standard and reagent solutions. If in doubt about the credibility of any of the solutions, prepare them again. Errors may result from contamination of the ISA, incorrect dilution of standards, poor quality distilled/deionized water, or a simple mathematical miscalculation.

#### Sample

Look for possible interferences, complexing agents, or substances which could affect the response or physically damage the sensing electrode (or the reference electrode) if the electrode(s) work perfectly in the standard, but not in the sample.

Try to determine the composition of the samples prior to testing to eliminate a problem before it starts. See Measuring Hints, Sample Requirements, and Interferences.

# Technique

Be sure that the electrode's limit of detection has not been exceeded.

Be sure that the analysis method is clearly understood and that Good Laboratory Practice has been followed.

Refer to the instruction manual again. Reread  $\underline{\text{General Preparation}}$  and  $\underline{\text{Electrode}}$  Characteristics.

If trouble still persists, call your pHoenix Electrode Company distributor and ask for the Technical Services Department.

# TROUBLESHOOTINGHINTS

Symptom	Possible Causes	Next Step
Out of Range Reading	defective meter	check meter with shorting strap see meter instruction manual
	defective electrode	check electrode operation
	electrode not plugged in properly	unplug electrode and reseat
	reference electrode not filled	be sure reference electrode is filled
	air bubble on membrane	remove air bubble by re-dipping electrode
	electrode not in solution	put electrode in solution
Noisy or Unstable Readings	defective meter	check meter with shorting strap
(readings continuously or rapidly changing)	air bubble on membrane	remove air bubble by re-dipping electrode
	ISA not used	use recommended ISA
	meter or stirrer not grounded	ground meter or stirrer
	defective electrode	replace electrode
	electrode exposed to interferences	soak electrode in ammonium standard
Drift (reading slowly changing in one direction)	samples and standards at different temperatures	allow solutions to come to room temperature before measurement
	electrode exposed to complexing agents	check section entitled Complexation
	incorrect reference filling solution	use recommended filling solution
Low Slope or No Slope	standards contaminated or incorrectly made	prepare fresh standards
	ISA not used	use recommeded ISA
	standard used as ISA	use ISA

**Symptom Possible Causes Next Step** check section entitled electrode exposed to complexing **Complexation** agents air bubble on membrane remove bubble by re-dipping electrode "Incorrect Answer" incorrect scaling of semi-log plot millivolts on the linear axis. (but calibration is good) On the log axis, be sure concenpaper tration numbers within each decade are increasing with increasing concentration incorrect sign be sure to note sign of millivolt number correctly incorrect standards prepare fresh standards wrong units used apply correct conversion factor:  $10^{-3}M = 18 \text{ ppm NH}_{4}^{+} =$ 14 ppm as N complexing agents in sample check section entitled **Complexation SPECIFICATIONS** Concentration Range: 1M to  $5X10^{-6}M$  (18,000 ppm to 0.01 ppm) pH Range: 4 to 10 Temperature Range:  $0^{\circ}$  to  $40^{\circ}$ C Resistance: 100 megaohms Reproducibility: ±2% Samples: aqueous solutions only; no organic solvents Size: 110 mm length 12 mm diameter 1 m cable length

store in dilute ammonium standard

Storage:

# ORDERING INFORMATION

Part Number	Description
NH41502	Ammonium Ion Electrode, combination, glass body
NH41508	Ammonium Ion Electrode, combination, epoxy body
NH4AS01	Ammonium Standard, 0.1 M NH <sub>4</sub> Cl
NH4AS02	Ammonium Standard, 1000 ppm $\mathrm{NH_4^{+1}}$
NH4IS01	Ammonium ISA (Ionic Strength Adjustor) 5 M NaCl
R001043	Reference Electrode Filling Solution, 0.1 M NaCl, for both the NH41502 and NH41508 electrodes
TABLE OF CONTENTS	
<pre>introduction required equipment</pre>	
electrode preparat electrode slope ch	
measuring hints sample requirement	
direct measurement direct measurement (using a pH/ direct measurement (using an ic	(mV meter)of ammoniumon meter)a determination(mV meter)

Electrode Characteristics
interferences9
temperature influences11
electrode response11
limits of detection12
pH effects13
electrode life13
electrode storage13
Electrode Theory
Troubleshooting Guide
Troubleshooting Hints18
Specifications
Ordering Information
Table of Contents