AMMONIUM ION ELECTRODES
INSTRUCTION MANUAL

GENERAL INSTRUCTIONS

The   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) ISE-8711 and ISE-8712 Ammonium Ion Electrodes

5. The PHE-4202 (for use with ISE-8711) with PHFS-A250 fill solution in the inner junction and with PHFS-1043 fill solution in the outer junction.

Required Solutions

1) Deionized or distilled water for solution and standard preparation.

2)   Ionic Strength Adjuster, 5M NaCl, 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)   Ammonium Standard, 0.1M NH_4Cl,
        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)   Ammonium Standard, 1000 ppm NH_4^{+1},
        To prepare this standard, add 2.97 gramsof 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(s) covering the electrode tip(s) and the rubber inserts covering the filling holes of the reference electrode. Fill the combination electrode or the reference electrode with the filling solution shipped with the electrode to a level just below the fill hole. No preparation is required for a sealed reference electrode. 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(s) to the proper terminal(s) as recommended by the meter manufacturer.

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

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(s) into the solution.

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.

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

2

Determine the difference between the two readings. A difference of $56 \pm 2mV$ 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 electrodes each day)

Prepare standard ammonium solutions whose concentrations vary by tenfold. Use either the 0.1M NH_4^{+1} or the 1000 ppm NH_4^{+1} standard stock solutions. Use the serial dilution method for this preparation.

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(s) into the solution.

Assure that the meter is in the concentration mode.

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

Rinse the electrode(s) with distilled water and blot dry.

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(s) into the solution.

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

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

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(s) 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°C difference in temperature. Temperature should normally be less than 40°C with intermittent measurements allowed to 50°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.

4

TABLE 1: Concentration Unit Conversion Factors

ppm NH_4^+	ppm N	moles/liter NH_4^+
1.80	1.40	1×10^{-4}
18.00	14.00	1×10^{-3}
180.00	140.00	1×10^{-2}

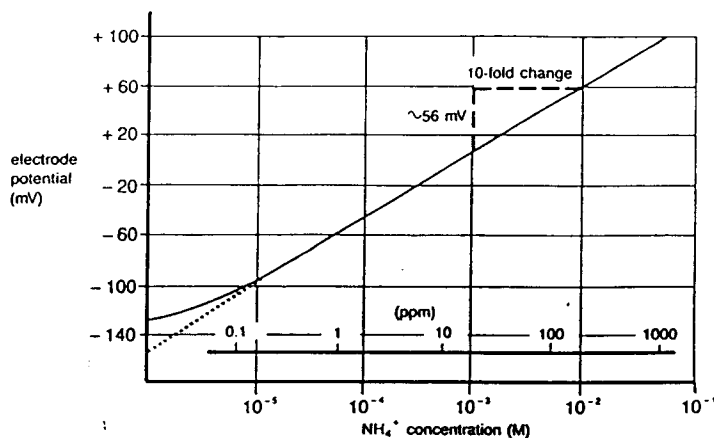## Measurement Procedure

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 ammonium samples. The temperature of both sample solution and of standard solutions should be the same.

Direct Measurement of Ammonium (using a standard 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}M or 1 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(s) into the solution. When the reading has stabilized, record the mV reading.

3) Place the mid-range solution (10^{-3}M or 10 ppm) on the magnetic stirrer and begin stirring. After rinsing the electrode(s) with distilled water and blotting dry, immerse the electrode tip(s) in the solution. When the reading has stabilized, record the mV reading.

4) Place the most concentrated solution (10^{-2}M or 100 ppm) on the magnetic stirrer and begin stirring. After rinsing the electrode(s) with distilled water and blotting dry, immerse the electrode tip(s) 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 direct measurement procedure. 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 1×10^{-5}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(s) in the solution. When the reading has stabilized, record the millivolt reading. Determine the concentration directly from the calibration curve.

7. The electrode(s) 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(s) 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(s) 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(s) 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(s) 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(s) in the solution and wait for the reading to stabilize. Read the concentration directly from the meter display.

12. The electrodes 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 1.0×10^{-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 1.0×10^{-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(s) in the solution. Assure that the meter is in the mV mode.

5. Add increments of the 1.0×10^{-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.

TABLE 2: Step-wise Calibration for Low Level Ammonium Measurements

Step	Pipet	Added Volume (ml)	Concentration M	ppm
1	A	0.1	1.0×10^{-6}	0.1
2	A	0.1	2.0×10^{-6}	0.2
3	A	0.2	4.0×10^{-6}	0.4
4	A	0.2	6.0×10^{-6}	0.6
5	A	0.4	9.9×10^{-6}	1.0
6	B	2	2.9×10^{-5}	2.9
7	B	2	4.8×10^{-5}	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(s) 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(s) 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 ±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.

TABLE 3: Concentration of Possible Interferences Causing a 10% Error at Various Levels of NH_4Cl; Background Ionic Strength is 0.12M NaCl.

Interferences (moles/liter)	$10^{-2}M\ NH_4^{+1}$	$10^{-3}M\ NH_4^{+1}$	$10^{-4}M\ NH_4^{+1}$
Cs^{+1}	3.0×10^{-3}	3.0×10^{-4}	3.0×10^{-5}
K^{+1}	1.0×10^{-2}	1.0×10^{-3}	1.0×10^{-4}
Tl^{+1}	6.0×10^{-2}	6.0×10^{-3}	6.0×10^{-4}
H^{+1}	1.0×10^{-1}	1.0×10^{-2}	1.0×10^{-3}
Ag^{+1}	1.0×10^{1}	1.0	1.0×10^{-1}
$+Tris^{+1}$	1.0×10^{1}	1.0	1.0×10^{-1}
Li^{+1}	2.0×10^{1}	2.0	2.0×10^{-1}
Na^{+1}	2.0×10^{1}	2.0	2.0×10^{-1}

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

Interferences (ppm)	100 ppm NH_4^+	10 ppm NH_4^+	1 ppm NH_4^+
Cs^{+1}	1.0×10^{2}	1.0×10^{1}	1.0
K_4^{+1}	2.7×10^{2}	2.7×10^{1}	2.7
Tl^{+1}	3.1×10^{3}	3.1×10^{2}	3.1×10^{1}
H^{+1}	1.6pH	2.6pH	3.6pH
Ag^{+1}	2.7×10^{5}	2.7×10^{4}	2.7×10^{3}
$+Tris^{+1}$	3.1×10^{5}	3.1×10^{4}	3.1×10^{3}
Li^{+1}	3.5×10^{4}	3.5×10^{3}	3.5×10^{2}
Na^{+1}	1.1×10^{5}	1.1×10^{4}	1.1×10^{3}

Temperature Influences

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

Provided that temperature equilibria has occurred, the ammonium ion

electrodes car. be used at temperatures from 0° - 50°C continuously and 40° - 50°C intermittently. 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

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 $1.0X10^{-5}M$ to several minutes near the detection limit. Refer to Figure 2.

Figure 2
Typical electrode time response to step changes in NH₄Cl
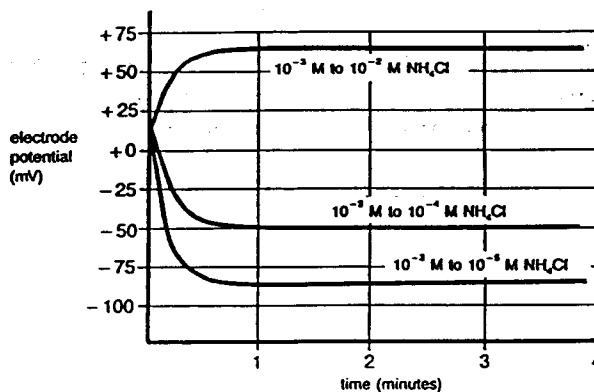
Electrode Storage

Ion Electrodes may be stored in $1.0X10^{-2}M$ 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(s). The reference portion of the combination electrode (or the outer

chamber of the reference electrode) should be drained of filling solution, if refillable, and the rubber insert placed over the filling hole.

Detection Limit

The upper limit of detection is 1M in pure ammonium chloride solutions. The upper limit of detection is above $1.0X10^{-1}M$ 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 $1.0X10^{-1}M$ 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 $1.0X10^{-5}M$ (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 THEORY

Electrode Operation

The ammonium electrode consists of an electrode body containing an ion exchanger in a sensing module. This sensing module 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:

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

where:

E = measured electrode potential
E_o = 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_t, includes free ammonium ions, C_f, plus bound or complexed ammonium ions, C_b. 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, C_f, by the activity coefficient, γ, by:

$$X = \gamma \ C_f$$

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

$$I = 1/2 \ C_x Z_x^2$$

where:

C_x = concentration of ion X
Z_x = charge of ion X
= 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, γ, 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 inter-diffusion of ions into the two

13

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

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) Electrodes, 3) Standard, 4) Sample, and 5) Technique.

Meter

The meter is the easiest component to eliminate as a possible cause of error. Most meter 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.

Electrodes

1. Rinse electrode(s) thoroughly with distilled water.

2. Perform **Electrode Slope Check**.

3. If electrode(s) fail this procedure, see the section on **Measuring Hints**.

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

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

Standard

The quality or results depends greatly upon the quality of the standards. ALWAYS prepare fresh standard 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 standard concentrations.

Sample

If the electrode works properly in standard 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. See **Sample Requirements** and **Interferences.** Try to determine the composition of the samples prior to testing to eliminate a problem before it starts.

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 the instruction manual to be sure that proper technique has been followed.

Troubleshooting Hints

Symptom	Possible Causes	Next Step
Out of Range Reading	defective meter	check meter with shorting strap (see meter instruction manual)
	electrode(s) not plugged in properly	unplug electrode(s) and reseat
	reference electrode not filled	be sure reference electrode is filled
	air bubbles on membrane	remove bubble by redipping electrode
	electrodes not in solution	put electrode(s) in solution
"Incorrect Answer" (but calibration curve is good)	incorrect scaling of semilog 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 number correctly
	incorrect standards	prepare fresh standards
	wrong units used	apply correct conversion factor: $10^{-3}M = 18$ ppm $NH_4^+ = 14$ ppm as N
	sample carryover	rinse electrodes thoroughly between samples

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 interferences	soak electrode in ammonium standard
	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 recommended ISA
	standard used as ISA	use ISA
	defective electrode	check electrode operation
	electrode exposed to interferences	soak electrode in ammonium standard
	air bubble on membrane	remove bubble by redipping probe
Noisy or Unstable Readings (readings continuously or randomly changing)	defective meter	check meter with shorting strap
	air bubble on membrane	remove bubble by redipping electrode
	defective electrode	replace electrode
	electrode exposed to interferences	soak electrode in ammonium standard
	meter or stirrer not grounded	ground meter or stirrer
	outer filling solution level too low	fill electrode to level just below fill hole

SPECIFICATIONS

Concentration Range:	1M to 5×10^{-6}M (18,000 ppm to 0.01 ppm)
pH Range:	4 to 10
Temperature Range:	$0°$ to $40°$C (continuous) $40°$ to $50°$C (intermittent)
Resistance:	100 megaohms
Reproducibility:	$\pm 2\%$
Samples:	aqueous solutions only; no organic solvents
Size:	110 mm length 12 mm diameter 1 m cable length
Storage:	electrode should be stored in dilute ammonium standard

TABLE OF CONTENTS

M-3965