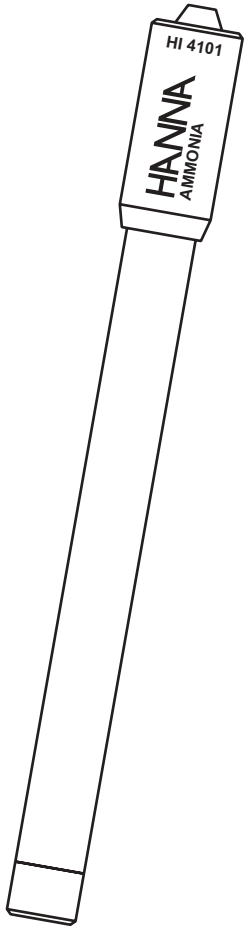


Instruction Manual

HI 4101

Ammonia
Ion
Selective Electrode

HANNA® instruments
With Great Products, Come Great Results™

HI 4101 Ammonia Electrode

I. Introduction:

The Hanna HI 4101 Ammonia gas selective electrode is a combination electrode designed for the measurement of ammonia in aqueous solutions such as waste water samples, wine, beer. Ammonium ions are also measured by conversion to ammonia gas upon ISA addition.

II. Specifications

Type:	NH_3 gas sensing electrode with glass pH internal, Ag/ AgCl reference and gas permeable PTFE membrane.
Species Measured:	NH_4^+, NH_3
Measurement Range:	1.0 M to 1x 10^{-6} M 17000 to 0.02 ppm
Interfering ions:	Surfactants, wetting agents, volatile amines.
Operating Temperature:	0 to 40°C
Operating pH:	>11 pH
Dimensions:	12 mm (OD) X 120 mm (insertion) 0.47"x 4.72"
Wetted materials:	Delrin®, body and cap PTFE gas membrane
Connection:	BNC

III. Theory of Operation:

The ammonia electrode is a complete potentiometric cell that contains both a silver/silver chloride (Ag/AgCl) reference and a pH measurement element. These elements are housed within a thermoplastic body in a chloride ion-containing electrolyte, and are isolated from the sample by a gas permeable membrane made of polytetrafluoroethylene (PTFE).

Dissolved gas in the sample solution diffuses into the membrane and changes the pH in the thin film of electrolyte on the surface of the pH glass. Diffusion continues until the partial pressures of the gas in the sample and thin film are equal. The change in pH is proportional to the concentration of dissolved gas in the sample solution.

The Nernst expression for an ammonia sensor is expressed in the equation below. Note that the potential is a function of the ammonia gas, which in turn is related to the hydroxyl ion concentration. The glass internal, Ag/AgCl reference, and Henry's law constant are rolled into the E' and E^o constants. The Nernst equation for the sensor becomes the equation noted below:

$$E = E' - 2.3RT/nF \log [A] = E^o - 0.059 \log [OH^-]$$

E = observed potential

E' = Reference and fixed internal voltages

R = gas constant (8.314 J/K Mol)

n = Charge on ion (equivalents/mol)

A_{ion} = ion activity in sample

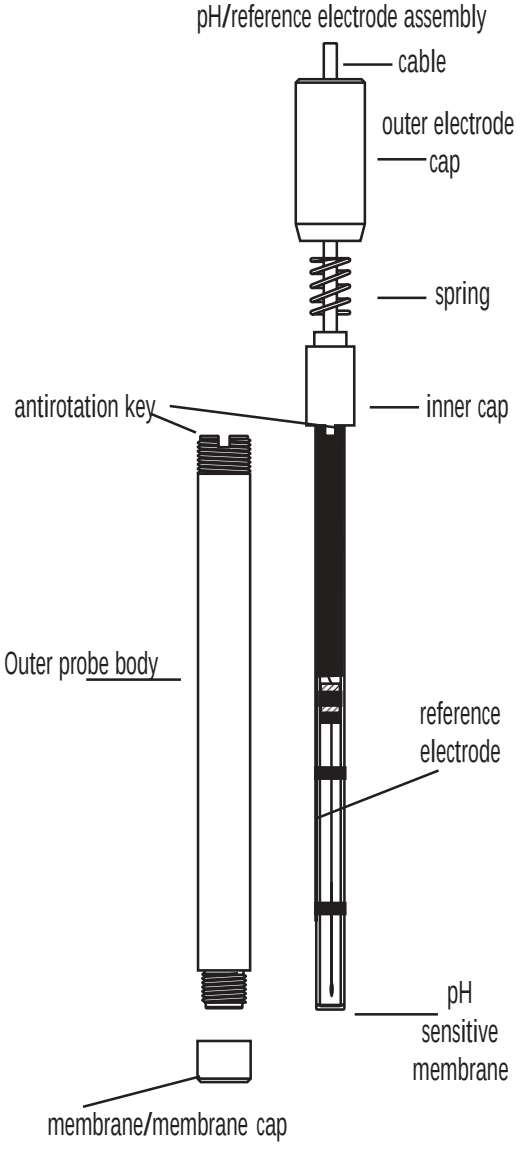
T = absolute temperature in K

F = Faraday constant (9.648×10^4 C/equivalent)

The mV should decrease in a Nernstian manner as the ammonia partial pressure increases in the sample.

IV. Design Elements

The Hanna HI 4101 ammonia gas sensor has 3 main parts. These are the membrane/membrane cap, outer probe body with antirotation key and the pH/reference assembly which includes the outer electrode cap, spring, inner cap and pH/reference electrode assembly.



V. Equipment Required:

- Hanna HI 4222 pH/ISE/mV meter or other suitable ion or pH/mV meter. (Note: log/linear graph paper is useful if an ISE meter is not available).
- Hanna HI 180 magnetic stirrer or equivalent with stirring bars. (Note: Isolate beakers from stirrer motor heat by placing insulating material such as foam or cork between them).
- 2 or 3 necked flask with stoppers or
- Hanna HI 76404 electrode holder or equivalent with Beakers or other suitable measurement vessel with plastic sealing film or wrap.

VI. Solutions Required for Calibration:

Ionic Strength Adjuster (ISA):	HI 4001-00
Hanna 0.1 M standard:	HI 4001-01
Hanna 100 ppm N standard:	HI 4001-02*
Hanna 1000 ppm N standard:	HI 4001-03*

*Please Note: These calibration standards are ppm as NH_3-N.

See Section XVII for additional solutions used for maintenance.

Using volumetric pipettes and glassware make dilutions of the standard to bracket the concentration of the samples. Standards with concentrations less than 10^{-3}M should be prepared fresh daily. Store solution in a tightly sealed bottle without ISA added. 2 mL of HI 4001-00 ISA should be added to each 100 mL sample of standard and samples just prior to measurement. ISA adjusts the pH of the sample or standard to about pH 11 thus converting ammonium ion to ammonia. It also provides samples and standards a constant ionic strength background that stabilizes the solutions activity coefficient and permits concentration to be measured directly. The ISA provides color indication to verify it has been added to the solution and a complexing agent to remove metal ions (i.e copper, zinc) from solution. These

ions are capable of reducing the ammonia concentration. If other volumes of sample/standard are used, add ISA at 2 parts per 100 parts standard/sample.

VII. General Guidelines

- Calibration standards and sample solutions should have the same ionic strength. ISA should be added to both samples and standards immediately before taking measurements.
- Calibration standards and sample solutions should be at the same temperature. Thermally insulate solution vessel from magnetic stirrer with cork or other insulating medium.
- Calibration standards and sample solutions should be stirred at the same rate using identical sized stir bars.
- Surface coating or "wetting" the PTFE membrane will effect the response. Inspect sensor before using. Replace PTFE membrane if damage is evident.
- Rinse electrode with distilled or deionized water between samples and dab dry with lab wipe or other soft disposable absorbent toweling.
- Check calibration every 1-2 hours.
- Position sensors at an angle of approximately 20° to lessen bubble adherence from solution out-gassing due to temperature change.
- Close container with plastic wrap or use 2 or 3 necked flask to prevent gas from leaving.
- Gently pulling cable will permit an exchange of fill solution at membrane surface. Re-Calibration is required.

VIII. Inner Electrode Check

Before assembling the electrode for the **first time** or if reactivating it after storage, the inner electrode assembly should be conditioned and then tested as a pH electrode.

Prepare pH test solutions HI 4000-47-4 and HI 4000-47-7 by mixing and dissolving each buffer packet in separate containers with 50 mL deionized water. These pH solutions contain chloride ions and pH buffers that are used to verify the inner electrode (pH internal) is operational. See Section XVII for replacement accessories and maintenance items.

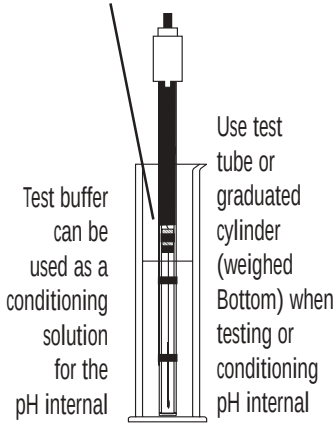
For a new sensor:

Remove the protective shipping cap from the glass inner electrode.

For existing sensor:

Unscrew the upper cap on the top of the electrode and carefully withdraw the internal pH/reference assembly.

For stable readings, glass should be covered to the bottom of the long black band.



- If sensor has been stored or shipped dry, it should be "conditioned" by soaking the pH/reference assembly 1 hour or more in one of the pH test solutions.
- Avoid touching the pH glass with your fingers.
- Attention: The pH/reference assembly is fragile! Support the upper portion of the internal cell while immersing the glass and reference assembly. A tall narrow container with weighted bottom is best. The pH test solution should cover the bottom of the large black ban.

Test: Connect the BNC connector on the electrode cable to a pH/mV (mV or ORP mode) meter. Carefully immerse the sensor assembly into one of the buffers. When the measurment stabilizes record the mV generated. Rinse sensor tip in deionized water and dab dry between buffers to prevent solution carry-over. Do not rub the glass. Take a measurement in the second buffer and record mV. Pay attention to minus sign if present.

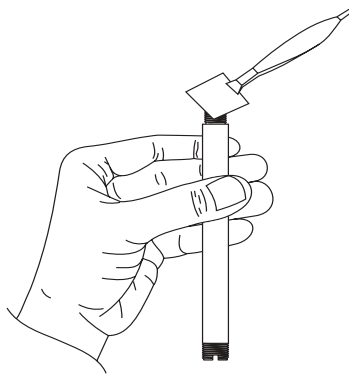
Calculate the difference in mV between the two solutions. Example of typical values:

HI 4000-47- 7	-90.2 mV
HI 4000-47-4	80.66 mV
Difference 170.8 mV =	80.6-(-90.2)

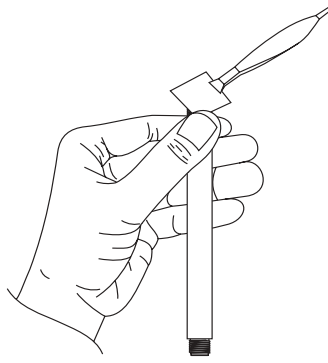
A calculated value equal or greater than 160 mV is acceptable for ambient temperatures between 20° and 25°C.

IX. Electrode Preparation

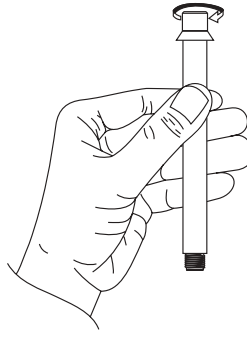
1) Remove glass internal from sensor body and perform inner electrode check. (See section VIII).
2) Install membrane on the outer probe body. Use tweezers provided and avoid touching working area of membrane with your fingers as skin oil will change the hydrophobic properties. Discard the paper backing (blue) found between white PTFE membranes. Hold membrane at corner with tweezers and drape over lower opening of outer probe body.



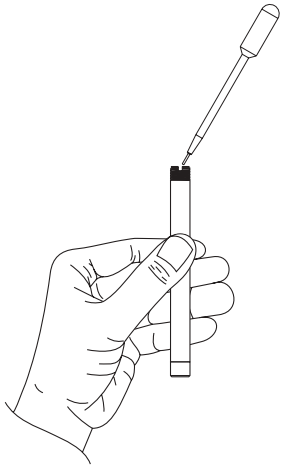
3) Hold one corner against the threads with thumb while gently stretching membrane over opening and capturing opposite membrane corner against threads . Smooth excess membrane material around the threads.



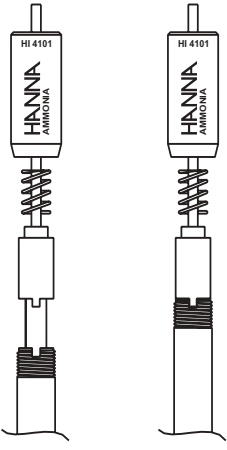
4) Screw outer membrane cap onto body
thus capturing the membrane between the cap and outer body threads.



5.) Using dropper provided, add about 2 mL of ammonia internal electrolyte HI 4001-40 into outer probe body.



6) Insert and position the inner glass/reference assembly into the outer body so that the anti-rotation key sits in the cut out on the outer probe body.



7) Holding the electrode upright, slide spring and electrode cap down cable and screw cap on outer body until fully engaged. Do not invert electrode. Do not overtighten.

8) Install assembled electrode in gas sensor test vessel or in electrode holder and connect cable connector to pH/mV meter.

X. Quick Check of Electrode Slope

- Connect BNC (connector) to pH/mV/ISE meter.
- Place meter in mV mode.
- Place 100 mL of deionized water into a vessel with stir bar. Add 2 mL of ISA Hanna HI 4001-00.
- Place sensor into prepared sample.
- Add 1 mL of 1000 ppm or 0.1 M Ammonia standard to beaker. Record the mV value when stable.
- Add an additional 10 mL of standard to the solution. Record the mV when reading has stabilized. This value should be less than the previous noted (more negative).
- Determine the difference between the two mV values. An acceptable value for this slope is 54±4 mV at ambient temperatures between 20 and 25°C.

XI. Corrective action

- Verify that the upper cap has been screwed in all the way.
- Verify electrode is connected properly to meter and the meter is is powered.
- Verify ISA has been added in the correct ratio to the standard.
- Examine the white membrane and check for electrolyte that might have leaked through the PTFE film. Replace membrane if damaged.
- If sensor does not change mV verify the the glass assembly is operational (See section VIII).

XII. Sample Handling

- Keep samples stored in tightly covered bottles to prevent ammonia loss or ammonia contamination from other sources.
- Alkaline samples must be measured at once or acidified for storage. (HCl may be added to bring pH to 6).
- Acidic samples such as wine or juice may require addition ISA. Samples should be approximately pH 11 for measurement.
- Measure sample and standards quickly after adding ISA because ammonia gas will escape from the solution.
- For solutions containing organically bound nitrogen such as oil, sludge, waste, or samples which may contain surfactants; digest sample first using a total Kjeldahl nitrogen (TKN) procedure. This involves oxidation with hot sulfuric acid which converts bound nitrogen to ammonium ions. Consult Method 4500-N_{org} from Standard Methods for the Examination of Water and Wastewater.
- For samples found to penetrate or "wet" the membrane, measurements may be made above the sample in a small headspace of a sealed system such as HI 4000-71 test vessel, provided the concentration of NH_3 is greater than 10^{-3} M. The headspace should be saturated with water vapor and the membrane end of the electrode suspended in the gas sample above the sample with ISA added. Expect a longer response time from the sensor when gas phase measurements are made.

XIII. Direct Calibration and Measurement

The direct method can be used in the linear working regions of the sensor. (See figure for typical sensor response). A direct reading ISE meter (HI 4222 or equivalent) determines concentration of the unknown by a direct reading after calibrating the meter with the standards. The meter is calibrated with two or more freshly made standards that are in the measurement range of the unknowns. HI 4001-00 ISA is added just before measurement of the standard or sample. Covering the vessel to prevent gas loss is advised.

A pH/mV meter in mV mode and semi-log graph paper may also be used. Two or freshly prepared standards that are in the measurement range of the unknowns (with ISA added), are measured in mV mode on the meter. These standards are plotted on semilog graph paper and their points are connected to form a straight-line curve. When samples are measured, their mV values are converted to concentration by following the mV to the concentration axis on the semi-log plot.

Method 4500-NH_3 D. from Standard Methods for the Examination of Water and Wastewater is a direct measurement method for water samples.
For both direct reading and mV convertion, ISA is added prior to measurement and the vessel should be covered to prevent gas loss.

In the lower concentration ranges the electrode calibration becomes less linear, many more calibration points are needed, and calibration will need to be repeated more frequently. Known addition method may also be used in these regions provided the actual slope of the sensor has been determined.

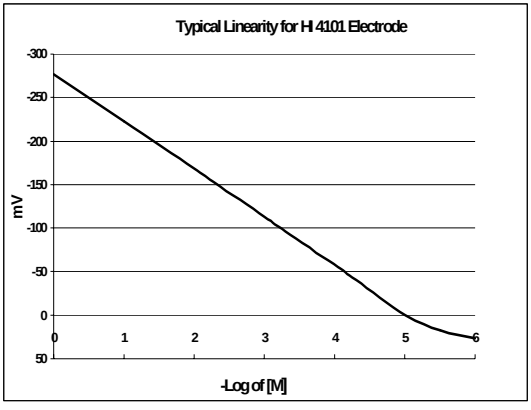
Direct Measurement Procedure

1) Follow section IX to prepare sensor.
2) Follow section VI to prepare standards and solutions.

- Standards should bracket the measurement range of interest and differ from each other by a factor of 10 in the linear regions.
- Standards and solutions should be at the same temperature. 2 mL of ISA is added to each 100 mL of sample and standard. A color change should occur to indicate the ISA has been added.
- Protect these solutions from loss of dissolved gas by covering and using promptly.

3) Follow section VII; General Guidelines to optimize test set-up.
4) During calibration it is best to start with lower concentration samples first. Wait for a stable reading before reading/recording values.
5) To prevent carry over and contamination of samples, rinse sensors with deionized water and blot dry between samples.
6) Between measurements suspend sensor tip in a small sample of NH_3 Conditioning solution; HI 4001-45. Rinse body with deionized water and blot dry before placing in next sample.

Typical calibration curve for HI 4101 Ammonia ISE



XIV. Other Measurement Techniques

Known addition

An unknown concentration of ammonia can be determined by adding a known amount (volume and concentration) of ammonia standard to a known volume of the sample. This technique is extremely useful for ammonia as the sensor may drift from calibrated values over time, however the slopes remain constant. With known addition, the standard and sample are measured within minutes of one another. The technique can use an ideal sensor slope, but actual slopes at the temperature of measurement should be determined and used if possible. This will improve accuracy. Known addition is Method 4500-NH_3 E. from Standard Methods for the Examination of Water and Wastewater.

1) The volume of the unknown sample (V_{Sample}) is measured accurately and placed into the closed sample vessel. The sensor is secured in the vessel and then the vessel is placed on a stirrer.
2) ISA is added at 1 part per 50 parts sample.
3) When the measurement is stable the mV value is noted.
4) A known amount, volume ($V_{Standard}$) and concentration ($C_{Standard}$), of NH_3 standard is then added to the sample. mV values are again noted when the measurement is stable.
5) The mV change is then calculated (ΔE).
6) Using the measured and calculated values, the sample concentration (C_{Sample}) can be determined.

$$C_{sample} = \frac{C_{standard} V_{standard}}{(V_T)10^{\Delta E/S} - (V_{S'})} \left(\frac{V_{S'}}{V_{sample}} \right)$$

$$(V_{sample} + V_{standard} + V_{ISA}) = V_T$$

$$(V_{sample} + V_{ISA}) = V_{S'}$$

7) The procedure can be repeated with a second standard addition to verify slope and operation of the method.

Note:

This method is preprogrammed in the Hanna HI 4222pH/ISE/mV meter, which simplifies the method greatly and permits repeated determinations easily.

Example:

Ammonia determination with known addition:

1. A 50 mL sample of unknown (V_{SAMPLE}) is placed in an clean vessel with an electrode. 1 mL of ISA is added to the sample and the color change is noted. The sample is covered and permitted to mix. The mV is then recorded when the sensor has stabilized.
2. 5 mL ($V_{STANDARD}$) of 0.1 M ($C_{STANDARD}$) standard is then added to the vessel and is permitted to mix. The mV value decreases as the concentration increases. (Note: for other concentration samples, add a known volume and concentration of standard to produce a 30 mV change or greater.
3. The unknown ammonia concentration in the original sample (C_{SAMPLE}) can then be determined by using the equation provided.

XV. Storage and Care of the HI 4101 sensor

The HI 4101 sensor can be stored assembled and ready to use in HI 4001-45 Conditioning solution overnight or between measurements. After overnight storage, gently pull on the cable to compress the spring mechanism thus permitting electrolyte to exchange from the bulk to the thin film between the membrane and glass. Calibration is required after doing this.

For longer term storage (over a week), disassemble the sensor completely and rinse off the internal pH/reference assembly, the outer body and the membrane cap. Discard the white PTFE membrane. (Note: keep black membrane cap). Cover the glass tip with the protective shipping cap and store parts securely in the original shipping box. When reassembling the sensor follow section IX.

XVI. Conversion Tables

For NH_3	Multiply by
Moles/L (M) NH_3 to ppm NH_3 (mg/L)	1.70×10^4
ppm NH_3 (mg/L) to M (Moles/L)	5.882×10^{-5}

For N-NH3 (ppm as nitrogen)	Multiply by
Moles/L (M) NH_3 to ppm N-NH_3 (mg/L)	1.40×10^4

XVII. HI 4101 Accessories and Replacement Parts

For Calibration :

Code	
HI 4001-00	Ionic Strength Adjuster (500 mL)
HI 4001-01	Hanna 0.1 M standard (500 mL)
HI 4001-02*	Hanna 100 ppm N standard (500 mL)
HI 4001-03*	Hanna 1000 ppm N standard (500mL)
HI 4001-30	Nitrate test kit (Bulk pkg)

*Please Note: These calibration standards are ppm as NH_3-N.

For Maintenance:

HI 4001-40	Hanna Ammonia Fill solution (4 X 30 mL)
HI 4001-45	Hanna Ammonia conditioning solution (500 mL)
HI 4000-47	Bulk package of 10 each HI 4000-47-4 and HI 4000-47-7 buffer packets
HI 4000-52	Replacement membrane cap
HI 4001-51	Replacement membranes kit (20 pieces)
HI 4000-51	Replacement pH/reference electrode assembly
HI 740155P	Capillary Pipettes (20 piece)
HI 740159	Plastic tweezers (1 piece)

MAN4101 10/08 R5

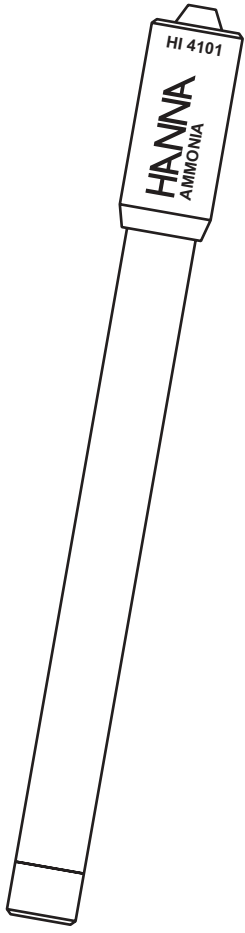
WARRANTY

Hanna Instruments Ion Selective Electrodes are warranted to be free of defects in material and workmanship for 6 months from date of purchase when used for their intended purpose and maintained according to instructions. If they fail to work when first used contact your dealer immediately. Damage due to accidents, misuse, misapplication, tampering or lack of prescribed maintenance is not covered.

Hanna Instruments reserves the right to modify the design, construction or appearance of its products without advance notice.

HANNA® instruments
With Great Products, Come Great Results™

www.hannainst.com



Instruction Manual

HI 4101

Ammonia
Ion
Selective Electrode

HANNA® instruments
With Great Products, Come Great Results™

HI 4101 Ammonia Electrode

I. Introduction:

The Hanna HI 4101 Ammonia gas selective electrode is a combination electrode designed for the measurement of ammonia in aqueous solutions such as waste water samples, wine, beer. Ammonium ions are also measured by conversion to ammonia gas upon ISA addition.

II. Specifications

Type:	NH_3 gas sensing electrode with glass pH internal, Ag/ AgCl reference and gas permeable PTFE membrane.
Species Measured:	NH_4^+, NH_3
Measurement Range:	1.0 M to 1x 10^{-6} M 17000 to 0.02 ppm
Interfering ions:	Surfactants, wetting agents, volatile amines.
Operating Temperature:	0 to 40°C
Operating pH:	>11 pH
Dimensions:	12 mm (OD) X 120 mm (insertion) 0.47"x 4.72"
Wetted materials:	Delrin®, body and cap PTFE gas membrane
Connection:	BNC

III. Theory of Operation:

The ammonia electrode is a complete potentiometric cell that contains both a silver/silver chloride (Ag/AgCl) reference and a pH measurement element. These elements are housed within a thermoplastic body in a chloride ion-containing electrolyte, and are isolated from the sample by a gas permeable membrane made of polytetrafluoroethylene (PTFE).

Dissolved gas in the sample solution diffuses into the membrane and changes the pH in the thin film of electrolyte on the surface of the pH glass. Diffusion continues until the partial pressures of the gas in the sample and thin film are equal. The change in pH is proportional to the concentration of dissolved gas in the sample solution.

The Nernst expression for an ammonia sensor is expressed in the equation below. Note that the potential is a function of the ammonia gas, which in turn is related to the hydroxyl ion concentration. The glass internal, Ag/AgCl reference, and Henry's law constant are rolled into the E' and E^o constants. The Nernst equation for the sensor becomes the equation noted below:

$$E = E' - 2.3RT/nF \log [A] = E^o - 0.059 \log [OH^-]$$

E = observed potential

E' = Reference and fixed internal voltages

R = gas constant (8.314 J/K Mol)

n = Charge on ion (equivalents/mol)

A_{ion} = ion activity in sample

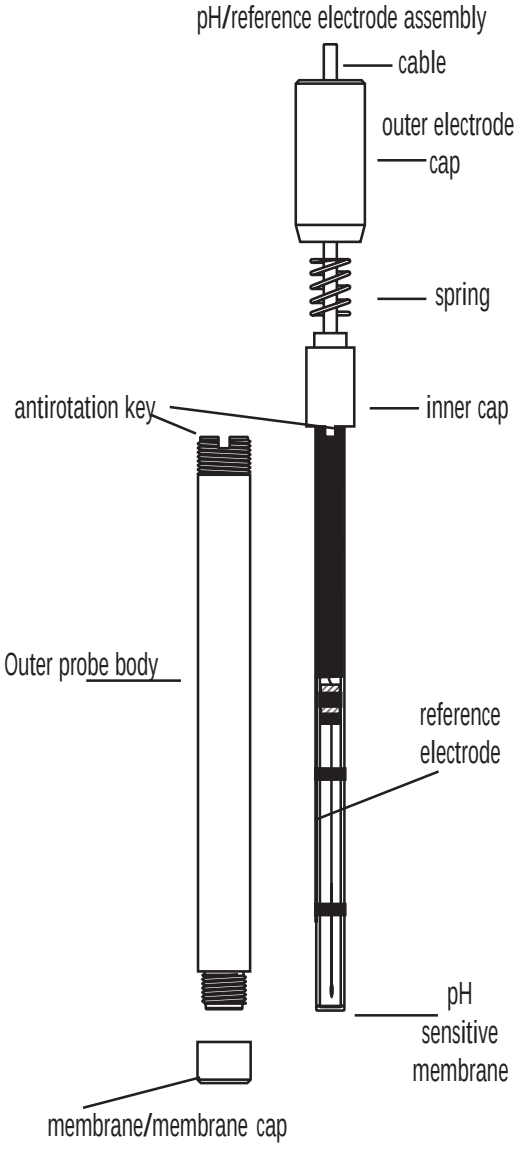
T = absolute temperature in K

F = Faraday constant (9.648×10^4 C/equivalent)

The mV should decrease in a Nernstian manner as the ammonia partial pressure increases in the sample.

IV. Design Elements

The Hanna HI 4101 ammonia gas sensor has 3 main parts. These are the membrane/membrane cap, outer probe body with antirotation key and the pH/reference assembly which includes the outer electrode cap, spring, inner cap and pH/reference electrode assembly.



V. Equipment Required:

- Hanna HI 4222 pH/ISE/mV meter or other suitable ion or pH/mV meter. (Note: log/linear graph paper is useful if an ISE meter is not available).
- Hanna HI 180 magnetic stirrer or equivalent with stirring bars. (Note: Isolate beakers from stirrer motor heat by placing insulating material such as foam or cork between them).
- 2 or 3 necked flask with stoppers or
- Hanna HI 76404 electrode holder or equivalent with Beakers or other suitable measurement vessel with plastic sealing film or wrap.

VI. Solutions Required for Calibration:

Ionic Strength Adjuster (ISA):	HI 4001-00
Hanna 0.1 M standard:	HI 4001-01
Hanna 100 ppm N standard:	HI 4001-02*
Hanna 1000 ppm N standard:	HI 4001-03*

*Please Note: These calibration standards are ppm as NH_3-N.

See Section XVII for additional solutions used for maintenance.

Using volumetric pipettes and glassware make dilutions of the standard to bracket the concentration of the samples. Standards with concentrations less than 10^{-3}M should be prepared fresh daily. Store solution in a tightly sealed bottle without ISA added. 2 mL of HI 4001-00 ISA should be added to each 100 mL sample of standard and samples just prior to measurement. ISA adjusts the pH of the sample or standard to about pH 11 thus converting ammonium ion to ammonia. It also provides samples and standards a constant ionic strength background that stabilizes the solutions activity coefficient and permits concentration to be measured directly. The ISA provides color indication to verify it has been added to the solution and a complexing agent to remove metal ions (i.e copper, zinc) from solution. These

ions are capable of reducing the ammonia concentration. If other volumes of sample/standard are used, add ISA at 2 parts per 100 parts standard/sample.

VII. General Guidelines

- Calibration standards and sample solutions should have the same ionic strength. ISA should be added to both samples and standards immediately before taking measurements.
- Calibration standards and sample solutions should be at the same temperature. Thermally insulate solution vessel from magnetic stirrer with cork or other insulating medium.
- Calibration standards and sample solutions should be stirred at the same rate using identical sized stir bars.
- Surface coating or "wetting" the PTFE membrane will effect the response. Inspect sensor before using. Replace PTFE membrane if damage is evident.
- Rinse electrode with distilled or deionized water between samples and dab dry with lab wipe or other soft disposable absorbent toweling.
- Check calibration every 1-2 hours.
- Position sensors at an angle of approximately 20° to lessen bubble adherence from solution out-gassing due to temperature change.
- Close container with plastic wrap or use 2 or 3 necked flask to prevent gas from leaving.
- Gently pulling cable will permit an exchange of fill solution at membrane surface. Re-Calibration is required.

VIII. Inner Electrode Check

Before assembling the electrode for the **first time** or if reactivating it after storage, the inner electrode assembly should be conditioned and then tested as a pH electrode.

Prepare pH test solutions HI 4000-47-4 and HI 4000-47-7 by mixing and dissolving each buffer packet in separate containers with 50 mL deionized water. These pH solutions contain chloride ions and pH buffers that are used to verify the inner electrode (pH internal) is operational. See Section XVII for replacement accessories and maintenance items.

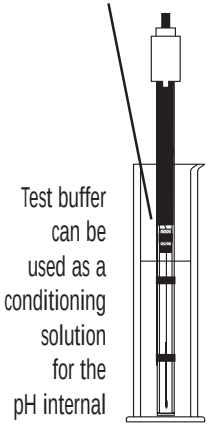
For a new sensor:

Remove the protective shipping cap from the glass inner electrode.

For existing sensor:

Unscrew the upper cap on the top of the electrode and carefully withdraw the internal pH/reference assembly.

For stable readings, glass should be covered to the bottom of the long black band.



- If sensor has been stored or shipped dry, it should be "conditioned" by soaking the pH/reference assembly 1 hour or more in one of the pH test solutions.
- Avoid touching the pH glass with your fingers.
- Attention: The pH/reference assembly is fragile! Support the upper portion of the internal cell while immersing the glass and reference assembly. A tall narrow container with weighted bottom is best. The pH test solution should cover the bottom of the large black ban.

Test: Connect the BNC connector on the electrode cable to a pH/mV (mV or ORP mode) meter. Carefully immerse the sensor assembly into one of the buffers. When the measurment stabilizes record the mV generated. Rinse sensor tip in deionized water and dab dry between buffers to prevent solution carry-over. Do not rub the glass. Take a measurement in the second buffer and record mV. Pay attention to minus sign if present.

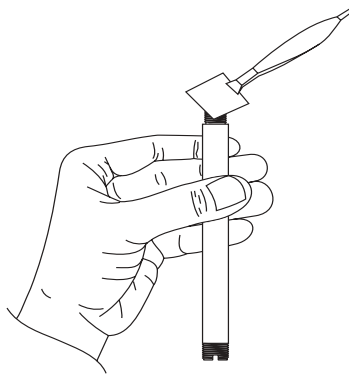
Calculate the difference in mV between the two solutions. Example of typical values:

HI 4000-47- 7	-90.2 mV
HI 4000-47-4	80.66 mV
Difference 170.8 mV =	80.6-(-90.2)

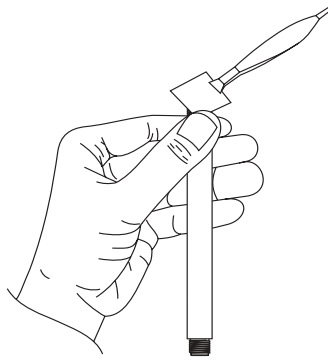
A calculated value equal or greater than 160 mV is acceptable for ambient temperatures between 20° and 25°C.

IX. Electrode Preparation

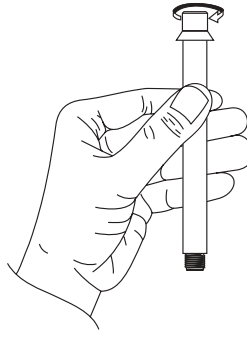
1) Remove glass internal from sensor body and perform inner electrode check. (See section VIII).
2) Install membrane on the outer probe body. Use tweezers provided and avoid touching working area of membrane with your fingers as skin oil will change the hydrophobic properties. Discard the paper backing (blue) found between white PTFE membranes. Hold membrane at corner with tweezers and drape over lower opening of outer probe body.



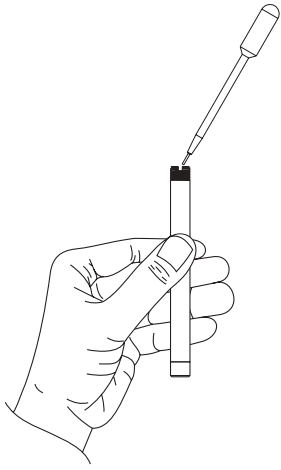
3) Hold one corner against the threads with thumb while gently stretching membrane over opening and capturing opposite membrane corner against threads . Smooth excess membrane material around the threads.



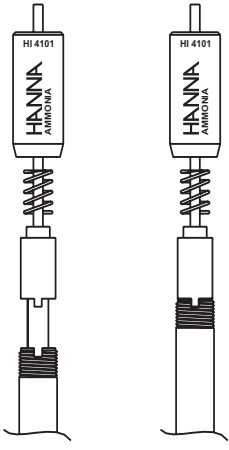
4) Screw outer membrane cap onto body thus capturing the membrane between the cap and outer body threads.



5.) Using dropper provided, add about 2 mL of ammonia internal electrolyte HI 4001-40 into outer probe body.



6) Insert and position the inner glass/reference assembly into the outer body so that the anti-rotation key sits in the cut out on the outer probe body.



7) Holding the electrode upright, slide spring and electrode cap down cable and screw cap on outer body until fully engaged. Do not invert electrode. Do not overtighten.

8) Install assembled electrode in gas sensor test vessel or in electrode holder and connect cable connector to pH/mV meter.

X. Quick Check of Electrode Slope

- Connect BNC (connector) to pH/mV/ISE meter.
- Place meter in mV mode.
- Place 100 mL of deionized water into a vessel with stir bar. Add 2 mL of ISA Hanna HI 4001-00.
- Place sensor into prepared sample.
- Add 1 mL of 1000 ppm or 0.1 M Ammonia standard to beaker. Record the mV value when stable.
- Add an additional 10 mL of standard to the solution. Record the mV when reading has stabilized. This value should be less than the previous noted (more negative).
- Determine the difference between the two mV values. An acceptable value for this slope is 54±4 mV at ambient temperatures between 20 and 25°C.

XI. Corrective action

- Verify that the upper cap has been screwed in all the way.
- Verify electrode is connected properly to meter and the meter is is powered.
- Verify ISA has been added in the correct ratio to the standard.
- Examine the white membrane and check for electrolyte that might have leaked through the PTFE film. Replace membrane if damaged.
- If sensor does not change mV verify the the glass assembly is operational (See section VIII).

XII. Sample Handling

- Keep samples stored in tightly covered bottles to prevent ammonia loss or ammonia contamination from other sources.
- Alkaline samples must be measured at once or acidified for storage. (HCl may be added to bring pH to 6).
- Acidic samples such as wine or juice may require addition ISA. Samples should be approximately pH 11 for measurement.
- Measure sample and standards quickly after adding ISA because ammonia gas will escape from the solution.
- For solutions containing organically bound nitrogen such as oil, sludge, waste, or samples which may contain surfactants; digest sample first using a total Kjeldahl nitrogen (TKN) procedure. This involves oxidation with hot sulfuric acid which converts bound nitrogen to ammonium ions. Consult Method 4500-N_{org} from Standard Methods for the Examination of Water and Wastewater.
- For samples found to penetrate or "wet" the membrane, measurements may be made above the sample in a small headspace of a sealed system such as HI 4000-71 test vessel, provided the concentration of NH_3 is greater than 10^{-3} M. The headspace should be saturated with water vapor and the membrane end of the electrode suspended in the gas sample above the sample with ISA added. Expect a longer response time from the sensor when gas phase measurements are made.

XIII. Direct Calibration and Measurement

The direct method can be used in the linear working regions of the sensor. (See figure for typical sensor response). A direct reading ISE meter (HI 4222 or equivalent) determines concentration of the unknown by a direct reading after calibrating the meter with the standards. The meter is calibrated with two or more freshly made standards that are in the measurement range of the unknowns. HI 4001-00 ISA is added just before measurement of the standard or sample. Covering the vessel to prevent gas loss is advised.

A pH/mV meter in mV mode and semi-log graph paper may also be used. Two or freshly prepared standards that are in the measurement range of the unknowns (with ISA added), are measured in mV mode on the meter. These standards are plotted on semilog graph paper and their points are connected to form a straight-line curve. When samples are measured, their mV values are converted to concentration by following the mV to the concentration axis on the semi-log plot.

Method 4500-NH_3 D. from Standard Methods for the Examination of Water and Wastewater is a direct measurement method for water samples.
For both direct reading and mV convertion, ISA is added prior to measurement and the vessel should be covered to prevent gas loss.

In the lower concentration ranges the electrode calibration becomes less linear, many more calibration points are needed, and calibration will need to be repeated more frequently. Known addition method may also be used in these regions provided the actual slope of the sensor has been determined.

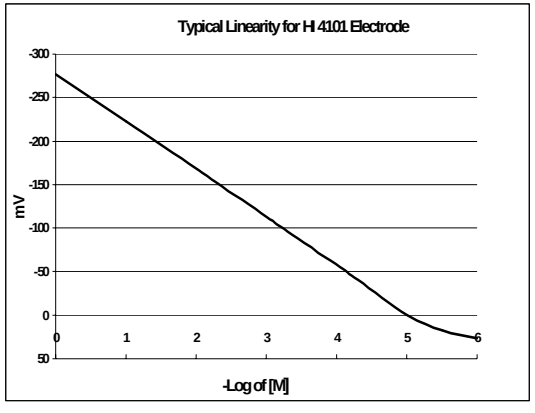
Direct Measurement Procedure

1) Follow section IX to prepare sensor.
2) Follow section VI to prepare standards and solutions.

- Standards should bracket the measurement range of interest and differ from each other by a factor of 10 in the linear regions.
- Standards and solutions should be at the same temperature. 2 mL of ISA is added to each 100 mL of sample and standard. A color change should occur to indicate the ISA has been added.
- Protect these solutions from loss of dissolved gas by covering and using promptly.

3) Follow section VII; General Guidelines to optimize test set-up.
4) During calibration it is best to start with lower concentration samples first. Wait for a stable reading before reading/recording values.
5) To prevent carry over and contamination of samples, rinse sensors with deionized water and blot dry between samples.
6) Between measurements suspend sensor tip in a small sample of NH_3 Conditioning solution; HI 4001-45. Rinse body with deionized water and blot dry before placing in next sample.

Typical calibration curve for HI 4101 Ammonia ISE



XIV. Other Measurement Techniques

Known addition

An unknown concentration of ammonia can be determined by adding a known amount (volume and concentration) of ammonia standard to a known volume of the sample. This technique is extremely useful for ammonia as the sensor may drift from calibrated values over time, however the slopes remain constant. With known addition, the standard and sample are measured within minutes of one another. The technique can use an ideal sensor slope, but actual slopes at the temperature of measurement should be determined and used if possible. This will improve accuracy. Known addition is Method 4500-NH_3 E. from Standard Methods for the Examination of Water and Wastewater.

1) The volume of the unknown sample (V_{Sample}) is measured accurately and placed into the closed sample vessel. The sensor is secured in the vessel and then the vessel is placed on a stirrer.
2) ISA is added at 1 part per 50 parts sample.
3) When the measurement is stable the mV value is noted.
4) A known amount, volume ($V_{Standard}$) and concentration ($C_{Standard}$), of NH_3 standard is then added to the sample. mV values are again noted when the measurement is stable.
5) The mV change is then calculated (ΔE).
6) Using the measured and calculated values, the sample concentration (C_{Sample}) can be determined.

$$C_{sample} = \frac{C_{standard} V_{standard}}{(V_T)10^{\Delta E/S} - (V_{S'})} \left(\frac{V_{S'}}{V_{sample}} \right)$$

$$(V_{sample} + V_{standard} + V_{ISA}) = V_T$$

$$(V_{sample} + V_{ISA}) = V_{S'}$$

7) The procedure can be repeated with a second standard addition to verify slope and operation of the method.

Note:

This method is preprogrammed in the Hanna HI 4222pH/ISE/mV meter, which simplifies the method greatly and permits repeated determinations easily.

Example:

Ammonia determination with known addition:

1. A 50 mL sample of unknown (V_{SAMPLE}) is placed in an clean vessel with an electrode. 1 mL of ISA is added to the sample and the color change is noted. The sample is covered and permitted to mix. The mV is then recorded when the sensor has stabilized.
2. 5 mL ($V_{STANDARD}$) of 0.1 M ($C_{STANDARD}$) standard is then added to the vessel and is permitted to mix. The mV value decreases as the concentration increases. (Note: for other concentration samples, add a known volume and concentration of standard to produce a 30 mV change or greater.
3. The unknown ammonia concentration in the original sample (C_{SAMPLE}) can then be determined by using the equation provided.

XV. Storage and Care of the HI 4101 sensor

The HI 4101 sensor can be stored assembled and ready to use in HI 4001-45 Conditioning solution overnight or between measurements. After overnight storage, gently pull on the cable to compress the spring mechanism thus permitting electrolyte to exchange from the bulk to the thin film between the membrane and glass. Calibration is required after doing this.

For longer term storage (over a week), disassemble the sensor completely and rinse off the internal pH/reference assembly, the outer body and the membrane cap. Discard the white PTFE membrane. (Note: keep black membrane cap). Cover the glass tip with the protective shipping cap and store parts securely in the original shipping box. When reassembling the sensor follow section IX.

XVI. Conversion Tables

For NH_3	Multiply by
Moles/L (M) NH_3 to ppm NH_3 (mg/L)	1.70×10^4
ppm NH_3 (mg/L) to M (Moles/L)	5.882×10^{-5}

For N-NH3 (ppm as nitrogen)	Multiply by
Moles/L (M) NH_3 to ppm N-NH_3 (mg/L)	1.40×10^4

XVII. HI 4101 Accessories and Replacement Parts

For Calibration :

Code	
HI 4001-00	Ionic Strength Adjuster (500 mL)
HI 4001-01	Hanna 0.1 M standard (500 mL)
HI 4001-02*	Hanna 100 ppm N standard (500 mL)
HI 4001-03*	Hanna 1000 ppm N standard (500mL)
HI 4001-30	Nitrate test kit (Bulk pkg)

*Please Note: These calibration standards are ppm as NH_3-N.

For Maintenance:

HI 4001-40	Hanna Ammonia Fill solution (4 X 30 mL)
HI 4001-45	Hanna Ammonia conditioning solution (500 mL)
HI 4000-47	Bulk package of 10 each HI 4000-47-4 and HI 4000-47-7 buffer packets
HI 4000-52	Replacement membrane cap
HI 4001-51	Replacement membranes kit (20 pieces)
HI 4000-51	Replacement pH/reference electrode assembly
HI 740155P	Capillary Pipettes (20 piece)
HI 740159	Plastic tweezers (1 piece)

MAN4101 10/08 R5

WARRANTY

Hanna Instruments Ion Selective Electrodes are warranted to be free of defects in material and workmanship for 6 months from date of purchase when used for their intended purpose and maintained according to instructions. If they fail to work when first used contact your dealer immediately. Damage due to accidents, misuse, misapplication, tampering or lack of prescribed maintenance is not covered.

Hanna Instruments reserves the right to modify the design, construction or appearance of its products without advance notice.

HANNA® instruments
With Great Products, Come Great Results™

www.hannainst.com