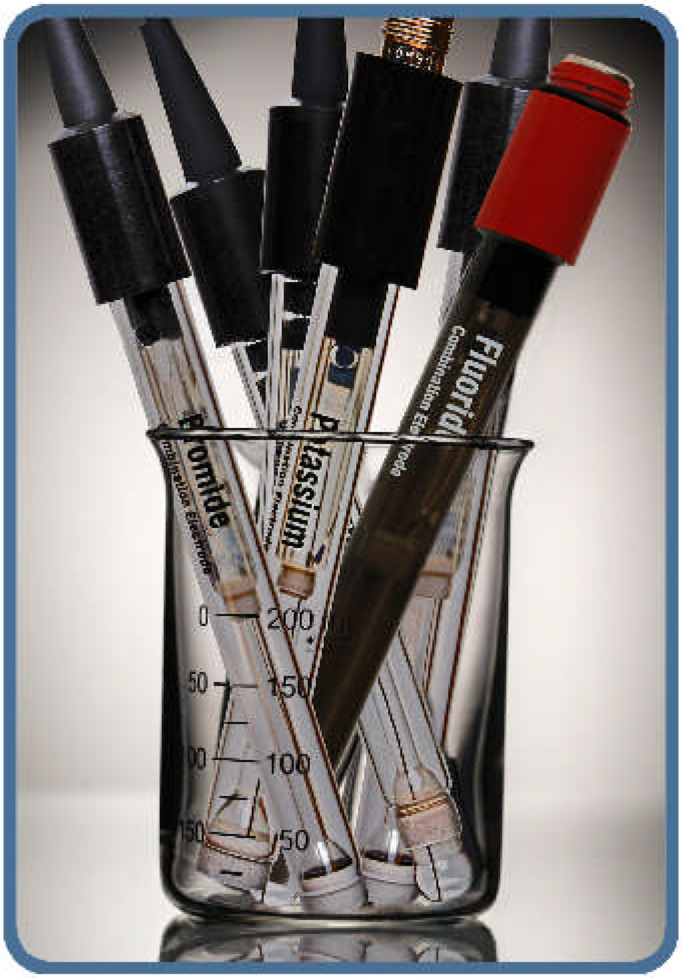
Van London Co.

"When Accuracy Matters"



Ammonia Gas Sensing Electrode

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GENERAL INSTRUCTIONS

Introduction

The Van London Co. Ammonia Gas-Sensing Electrode is used to measure dissolved ammonia in aqueous solutions. The measurement is not affected by sample color or turbidity. Interferences from anions, cations, and dissolved species, other than volatile amines, do not occur.

Required Equipment

1. An ion meter
2. Ammonia Gas Sensing Electrode
3. Ammonia Membranes
4. Tweezers, plastic syringe, pipets, volumetric flasks, 150 ml beakers

Required Solutions

1. Deionized or distilled water for solution preparation.
2. Van London Co. Ammonia Standard, 1000 ppm $NH_{3,}$ Cat.# NH3AS02.
3. Ammonia Electrode Ionic Strength Aduster (ISA) Solution, 10 M NaOH. To prepare this solution from your own laboratory stock, half fill a 1000 ml beaker with distilled water, add 400 grams of reagent-grade NaOH (sodium hydroxide). Swirl the flask gently under a hood to dissolve the solid. Allow to cool and fill to the mark with distilled water. Stir the solution and store in a plastic bottle.
4. Van London Co. Ammonia Electrode Filling Solution, Cat.# NH3IF01.

GENERAL PREPARATION

Electrode Preparation

Remove the small black shipping cap from the bottom of the electrode. Before using, grasp the black outer body with one hand and unscrew the cap at the top of the electrode with the other hand. Remove the inner pH glass electrode from the outer body. Rinse the glass electrode with deionized water to remove any KCl crystals. Store the black shipping cap for later use.

Fill the outer body with 2 to 3 ml of Electrode Filling Solution using the plastic syringe provided. **While holding the black outer body** insert the inner glass electrode back into the outer black body, and screw on the large cap until finger tight.

Note: Twisting of the black outer body after the glass inner body is inserted could result in the membrane being damaged. Be sure to screw the cap onto the body instead of screwing the body into the cap.

Connect the electrode to the meter with the BNC connector at the end of the cable as recommended by the meter manufacturer. To prevent air entrapment, place the electrode at a 20° angle from the vertical.

Electrode Slope Check (for Ion meters which display mV)

1. To a clean, dry, 150 ml beaker, add 100 ml of distilled water and 2 ml of ISA. After assuring that the meter is in the millivolt mode, lower the electrode tip into the solution. Stir moderately. Remove air bubbles on the white Teflon membrane by redipping probe.
2. Using a pipet, add 1 ml of 1000 ppm standard into the solution. Stir moderately. After 1 minute, record the mV reading.
3. Using a pipet, add 10 ml of the 1000 ppm ammonia standard to the beaker. Stir moderately. After 1 minute, record the mV reading.
4. Determine the difference between the two readings. The electrode is operating correctly if a slope difference of 53-59 mV is found between 10ppm and 100 ppm, assuming the solution temperature is 25^{o}C. Slope is defined as the change in mV observed when the concentration changes by a factor of 10.
5. See the following **Checking Membrane** section if the slope is not within the 53-59 mV range. Otherwise, skip to the **Direct Measurement** section if the slope is correct.

Checking Membrane

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

1. Connect a newly assembled electrode to an Ion meter. Set meter to Concentration mode.
2. Lower the electrode tip in distilled water.
3. Record the reading after stirring the distilled water for about 15 minutes.
4. Add 2 ml ISA solution (10 m NaOH) to the distilled water. A drastic change in the ppm reading in a positive direction (>100 ppm) indicates damage of the membrane.
5. See the following **Changing Membrane** section if there is a drastic change in the ppm reading.
6. If no damage to the membrane is indicated, consult the **TROUBLESHOOTING** section in the back of this manual and repeat the Electrode Slope Check.

Changing Membrane (if damage of membrane has occurred)

1. Grasp the black outer body with one hand. Unscrew the cap at the top of the electrode with the other hand. Remove the inner pH glass body from the epoxy outer body. Carefully place the glass body aside.
2. Unscrew the bottom cap from the outer body. Remove the old white Teflon membrane from around the threads and electrode tip opening.
3. Using the tweezers provided, grab a new piece of white membrane material by the edge and remove from the separator paper. Then, with the hand not holding the tweezers, hold the electrode body up at the threads with thumb and forefinger. Place one edge of the membrane against the threads and hold in place with your thumb. Stretch the new membrane lengthwise across the electrode opening so that it smoothly covers the opening. Place the other edge of the membrane against the threads and hold in place with your forefinger.
4. Place the bottom cap gently over the membrane onto the threads and screw the bottom cap on until finger tight. Check that the membrane is free of wrinkles and holes or else repeat the above steps.
5. Using the syringe provided, fill the outer body with approximately 2-3 ml of Electrode Filling Solution.
6. While holding the black outer body, insert glass inner body into black outer body containing the electrode filling solution and screw on the upper cap until finger tight.
   Note: Twisting of the black outer body after the glass inner body is inserted could result in the membrane being damaged. Be sure to screw the cap onto the body instead of screwing the body into the cap.
7. Repeat the **Electrode Slope Check** above. Consult the **TROUBLESHOOTING** Section if the slope is not 53-59 mV after changing the membrane. Otherwise, proceed to the Measurement section which follows.

Measurement using an Ion Meter (in the Concentration Mode)

1. By serial dilution of the 1000 ppm ammonia standard, prepare two ammonia standards whose concentration is near the expected sample concentration. (e.g 10 ppm and 100 ppm) For example, to make a 100 ppm standard, pipet 10 ml of the 1000 ppm standard into a 100 ml volumetric flask and dilute to volume with deionized water. Next to make a 10 ppm standard, pipet 10 ml of the newly-made 100 ppm standard into a 100 ml volumetric flask and dilute to volume with deionized water. A 1 ppm standard is made by further dilution of the 10 ppm standard. Measure out 100 ml of each standard into individual 150 ml beakers.
2. Assure that the meter is in the concentration mode and set for a 2-point calibration.
3. Lower the electrode tip into the least concentrated solution. Begin stirring at a constant rate. Add 2 ml of ISA to the solution and continue stirring.
4. After 1 minute, adjust the meter to the concentration of the more dilute ammonia standard and fix the value in the memory according to the meter manufacturer's instructions.
5. Rinse the electrode tip with distilled water and blot dry.
6. Lower the electrode tip into the more concentrated solution. Begin stirring at a constant rate. Add 2 ml of ISA to the solution and continue stirring.

7. After 1 minute, adjust the meter to the concentration of the more concentrated ammonia standard and fix the value in the memory according to the meter manufacturer's instructions.
8. Add 100 ml of the sample and 2 ml of ISA in a 150 ml beaker. Lower the electrode tip into the solution. Begin stirring at a constant rate. Ensure that the meter is in sample mode.
9. After 1 minute, read the concentration directly from the meter display.
10. The electrode should be re-calibrated every 2-3 hours. Simply repeat Steps 2-7 above.

Low Level Ammonia (<0.5 ppm) Determination (for Ion meters which display mV)

As the concentration of ammonia decreases, the rate of ammonia diffusion through the membrane is slow, the rate of equilibrium between the ammonium in the internal filling solution and ammonia is slow, and thus the response time increases. If the internal filling solution is diluted with ammonia-free distilled water (1:10), response at low levels can improve. Measurements can be speeded up by first placing the electrode tip in an ammonia-free pH 4 buffer, then into the sample. Always keep standards and samples covered. Work with large solution volumes to minimize surface-area-to-volume ratio, thereby avoiding ammonia absorption from air. Allow 5 - 10 minutes for a stable reading in the pH 4 buffer or a low-level solution.

Use the following low level ammonia measurement procedure in the non-linear portion of the calibration curve. This procedure is used for ammonia samples containing less than 0.5 ppm ammonia.

1. Measure out 100 ml of a pH 4 buffer solution, add it to a 150 ml beaker, place the beaker on the magnetic stirrer, and begin stirring. Place the electrode tip in the solution for about 3 minutes.
2. By serial dilution, prepare a 100 ppm ammonia standard by diluting the 1000 ppm standard solution.
3. To a 2500 ml Erlenmeyer flask, add 1000 ml of distilled water and 10 ml of 10M NaOH. Place on magnetic stirrer and begin stirring. After rinsing the electrode, place the tip in this calibration solution. Assure that the meter is in the mV mode.
4. Using a 1 ml graduated pipet (A) and a 2 ml pipet (B), add increments of the 100 ppm dilution to the calibration solution using the steps outlined in Table 2. Allow the reading to reach equilibrium and record the electrode potential after each step. Plot the concentration (log axis) vs. the electrode potential (linear axis) to obtain the calibration curve.
5. After rinsing the electrode, immerse the electrode tip in pH 4 buffer for 3 minutes. Be sure to use the magnetic stirrer.
6. Place 1000 ml of the sample into a 1000 ml beaker, add 10 ml of 10M NaOH, place the beaker on the magnetic stirrer, and begin stirring. After rinsing the electrodes, immerse the tip in the solution. When the reading has stabilized, record the mV potential.
7. Determine the concentration from the calibration curve. (Prepare a new low-level calibration curve on a daily basis using freshly prepared solutions).

TABLE 2: Additions of 100 ppm Standard to 1000 ml Distilled Water and 10 ml 10M NaOH

Step	Pipet	Added Volume(ml)	Concentration ppm
1	A	0.10	0.01
2	A	0.10	0.02
3	A	0.20	0.04
4	A	0.20	0.06
5	A	0.40	0.10
6	B	2.00	0.30
7	B	2.00	0.49

Measuring Hints

As ammonia electrodes are used or stored for long periods, they will experience some deterioration in performance and slope errors will increase. By using the meter's calibration controls this error can be corrected. If an electrode is able to be calibrated and is stable and responsive, it is still a functional electrode and may be used in service even though it no longer meets "new" electrode specifications.

Samples should be measured immediately after collection. Samples should be stored in sealed containers if immediate measurement is not possible.

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

The ISA, 10M NaOH, should be added just before measurement.

All samples and standards should be at the same temperature for precise measurement. A difference of 1°C in temperature will result in approximately a 2% error.

Always rinse the electrode with distilled water and blot dry between measurements. Use a clean, dry tissue to prevent cross-contamination.

Constant, but not violent, stirring is necessary for accurate measurement.

Always check to see that the membrane is free from air bubbles after immersion into standard or sample.

Dilute concentrated samples (over 5000 ppm) before measurement.

Use fresh standards for calibration. Re-calibrate every few hours for routine measurement.

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

ELECTRODE CHARACTERISTICS

Reproducibility

Electrode measurements reproducible to ±2% can be obtained if the electrode is calibrated every hour. Factors such as temperature fluctuation, drift, and noise limit reproducibility.

Interferences

Volatile amines interfere with the operation of the ammonia electrode. Most gases, since they are converted to the ionic form in basic solutions, do not interfere with ammonia electrode measurement. The level of ions in solution can change the solubility of ammonia, though ionic species cannot cross the gas-permeable membrane and are not considered direct electrode interferences. The level of ions in sample solution and standards do not interfere, given that they are equal. The same holds true for dissolved species. Low results can occur in direct measurements, due to the presence of some metallic ions and their complexation effect on ammonia. Electrode drift and slow response could indicate the presence of high interferences. Soak the electrode in distilled water for five minutes, then soak for five minutes in 100 ppm standard solution with ISA added, to restore proper response.

Complexation

Metal complexes are formed with ammonia and a number of metal ions. Complexes of mercury, copper, gold, silver, nickel, zinc, cobalt, and cadmium are removed in the form of hydroxide complexes or precipitates in basic solution. Use of the recommended ISA (10M NaOH solution) inhibits the formation of metal complexes in the sample, since it contains a high concentration of hydroxide ions.

Temperature Influences

The electrode response will shift and change slope with change in temperature. Standards and samples should be at the same temperature. A 2% error results with a 1^{o}C temperature change for a 10 ppm solution. Gases like NH_3 are expelled from a solution at a faster rate as the temperature increases.

The electrodes can be used at temperatures from 0° - 50°C. Room temperature measurements are recommended, since measurements at temperatures quite different from room temperature may require equilibrium times up to one hour.

Electrode Response

Plotting the electrode mV potential against the ammonia concentration results in a straight line with a slope of 56±3 mV per decade (10ppm – 100ppm) at 25°C.

For ammonia concentrations above 10 ppm NH_3, the electrode exhibits good time response (95% of total mV reading in 30 seconds or less). Response times are longer below this value and ammonia loss to air may become a source of error.

Limits of Detection

The upper limit of detection in pure ammonia solutions is 17,000 ppm. Ammonia is rapidly lost to the air above a concentration of 17,000 ppm. Dilution may be used if ammonia concentrations are above 1M. Also dilute samples between or calibrate the electrode at 4 or 5 intermediate points.

The lower limit of detection is around 20 ppb. Ammonia measurements below 0.5 ppm (500 ppb) should employ low level procedures.

pH Effects

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

Electrode Life

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

Since ammonia electrodes have a limited shelf life, it is important to have a backup electrode which is in working condition when required.

Electrode Storage

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

For low level measurements (below 0.5 ppm), immerse the tip of the electrode in pH 4 buffer between measurements.

For normal range measurements, keep the electrode tip immersed in a 10 ppm standard with added NaOH between measurements. If storing the ammonia electrode overnight or over the weekend, immerse the tip in the 1000 ppm standard without added NaOH. Do not store overnight in pH 4 buffer.

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

TROUBLESHOOTING HINTS

*Remember to remove the black protective shipping cap on the bottom of the electrode and fill the outer body with Ammonia Electrode Filling Solution prior to first use.

Symptom	**Possible Causes**	**Next Step**
Out of Range Reading	defective meter	check meter with shorting strap (see meter instruction manual)
	defective inner pH glass body	refer to **Checking the Electrode Inner Body** following this section
	electrode not plugged in properly	unplug electrode from meter and reset
	electrode outer body not filled	fill black outer body as instructed in **Electrode Preparation**
	air bubble on membrane	remove air bubble by re-dipping electrode
	electrode not in solution	put electrode insolution
Noisy or Unstable Reading (readings continuously or randomly changing.)	insufficient internal filling solution	fill outer body of electrode with proper amount of internal filling solution
	defective meter	check meter with shorting strap (see meter instruction manual)
	bottom cap loose	ensure that bottom cap is screwed on tight enough to close gap between bottom cap and body
	defective inner pH glass body	refer to **Checking the Electrode Inner Body** following this section
	air bubble on membrane	remove air bubble by re-dipping electrode
	meter or stirrer improperly grounded	check meter and stirrer for grounding
Drift (reading slowly changing in one direction)	internal filling solution leakage	ensure that membrane is installed properly
	incorrect internal filling solution	refill outer body of electrode using filling solution shipped with electrode
	total sample level of dissolved species above 1M	dilute sample
	electrode in sample too long; NH_3 loss	reduce surface area to volume ratio, slow down rate of stirring, avoid hightemperatures
	membrane failure (wet, perforation, discoloration)	replace membrane
	samples and standards at different temperatures	allow samples and standards to come to same temperature before measurement
	heat generated by magnetic	place insulating material between stirrer and

	stirrer	beaker
	defective inner pH glass body	refer to **Checking the Electrode Inner Body** following this section
	electrode exposed to air for extended period	hold electrode by outer body and pull gently on electrode cable. Internal filling solution will flow under membrane and restore electrode response
Low Slope or No Slope	standards contaminated or incorrectly made	prepare fresh standards
	ISA not used	use recommended ISA
	standard used as ISA	use ISA
	electrode exposed to air for extended period	hold electrode by outer body and gently pull on electrode cable. Internal filling solution will flow under membrane and restore electrode response
	membrane failure (wet, perforation, discoloration)	replace membrane
	defective inner pH glass body	refer to **Checking the Electrode Inner Body** following this section
"Incorrect Answer" but calibration curve is good)	incorrect standards	prepare fresh standards
	wrong units used	apply correct conversion factor: 10^{-3}M = 17 ppm as NH_3 = 14 ppm as N
	ISA added to standards and Not samples	add same proportions of ISA to standards and samples
	sample carryover	rinse electrodes thoroughly between samples

<u>Checking the Electrode Inner Body (Glass pH electrode)</u>

If the electrode slope is found to be low during operation, disassemble the ammonia electrode. Grasp the black outer body with one hand and unscrew the cap at the top of the electrode with the other hand. Remove the inner pH glass electrode from the outer body. Rinse the glass electrode with deionized water to remove any KCl crystals. If the glass pH electrode is dry, soak the glass tip of the inner body in Ammonia Electrode Filling Solution for at least two hours.

Rinse the glass pH electrode thoroughly with distilled water. Put 100 ml of pH 7 buffer in a 150 ml beaker. Place the beaker on the magnetic stirrer, and begin stirring. Immerse the tip of the glass pH electrode in the solution so that the reference element is covered. Make sure that the meter is in the mV mode. Record the meter reading when stable.

Rinse the glass pH electrode thoroughly in distilled water. Put 100 ml of pH 4 buffer (0.1M NaCl added) in a 150 ml beaker, place the beaker on the magnetic stirrer, and begin stirring. Immerse the tip of the glass pH electrode in the solution so that the reference element is covered. Observe the change in the meter reading carefully. In less than 30 seconds after immersion, the reading should change 100 mV. The meter reading should stabilize in 3 - 4 minutes, with a difference greater than 150 mV if the glass pH electrode sensing element is operating properly.

SPECIFICATIONS

Concentration Range:	0.01 to 17000 ppm NH_3
	5×10^{-7}M to 1 M
pH Range:	above 11
Slope:	53 – 59 mV between 10ppm – 100ppm at 25°C
Temperature Range:	0° to 50°C
Interferences:	Volatile amines
Reproducibility:	± 2%
Size:	110 mm length
	12 mm diameter
	1 m cable length
Storage:	store electrodes in 0.1M NH_4Cl

ELECTRODE THEORY

Electrode Operation

A gas-permeable membrane is used to separate the electrode's internal solution from the sample solution in the Van London Co. Ammonia Gas-Sensing Electrode. The sample diffuses dissolved ammonia through the membrane until the partial pressure of ammonia is the same on both sides of the membrane. The partial pressure of ammonia is proportional to the ammonia concentration.

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

$$NH_3 + H_2O \text{ ---> } NH_4^+ + OH^-$$

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

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

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

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

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

$$E = E_o - S \log [OH^-]$$

where S is the slope of the electrode.

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

$$E = E_o^1 - S \log [NH_3]$$

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

Ammonia Chemistry

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

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

The relative amounts of the ammonium ion and of ammonia is determined by the solution's pH. Virtually, all the ammonia is converted to ammonium ion where hydrogen ion is readily available, as in acid solution. Half the ammonia will be in the form of ammonium ion at a pH of about 9.3. (See Figure 3).

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

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

at 25°C, X = 0.1
where pK ~ 9

The ratio of ammonium to ammonia is given by:

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

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