

# Instructions



## accumet® Ammonia Combination Ion Selective Electrode

Catalog No.	Description	Connector	Refilling Solution
13-620-508	Ammonia Combination Electrode, Single Junction	US Std.	13-620-803A
13-620-509	Ammonia Combination Electrode, Single Junction	BNC	13-620-803A

### Performance Specifications

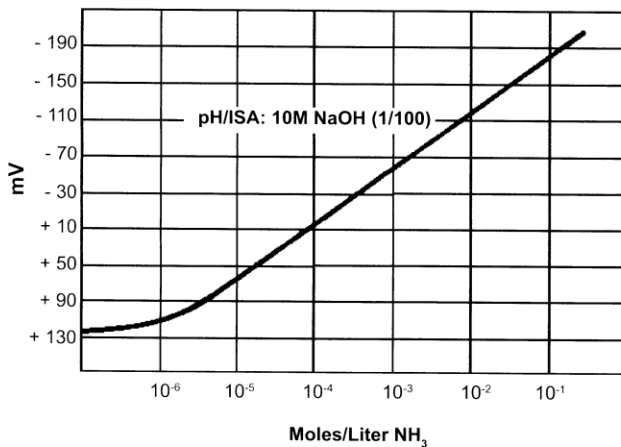
Concentration Range	5 x 10 <sup>-7</sup> M to 1M 0.01 ppm to 17,000 ppm NH <sub>3</sub>
Slope (out of box)	56 ± 3 mV/decade
Reproducibility	± 2%
Response Time	95% response in 30 seconds
Temperature Range	0° to 50°C (if calibrated at that temperature)
Pressure Range	0 to 10 PSI
pH Range	Above 11 pH
Interferences	Volatile amines
Temperature Compensation	No
On-Line Capability	Yes, pH control required
Body Material	Polypropylene

The accumet® Ammonia Electrode will quickly and accurately measure the concentration of ammonia or ammonium ion in aqueous solutions. This gas-sensing probe utilizes a pre-bonded semi-permeable membrane cap which separates the electrode's internal fill solution from the sample solution. The outer body is constructed of durable, break-resistant polypropylene.

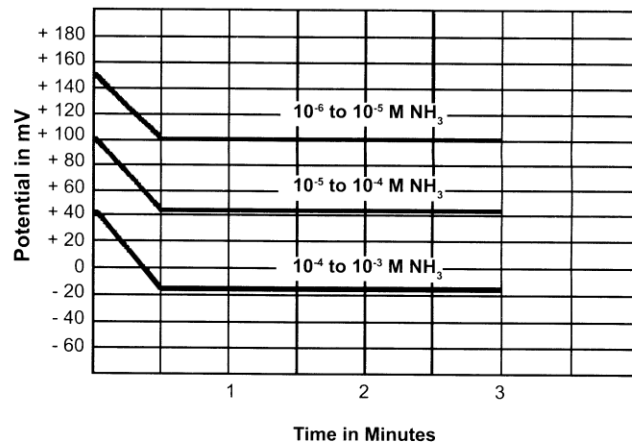
This quick, efficient method of ammonia analysis lends itself to diverse applications such as water, wastewater, biological samples, fertilizers, soil, and foodstuffs. Its ease of operation makes it particularly adaptable to quality control applications.

The probe responds to ammonia concentrations from 1 x 10<sup>-7</sup> to 1 x 10<sup>-1</sup> molar. The Nernstian response is shown in Figure 1. The excellent response time and stability are shown in Figure 2.

**Figure 1: Ammonia Calibration Curve**



**Figure 2: Ammonia Response Time**



## MATERIALS LIST

### Meter

Meters capable of reading to a minimum of 1.0 mV (0.1 millivolt preferred) may be used.

### pH Ionic Strength Adjuster (ISA)

Ammonia pH/ISA solution (Cat. No. 13-620-802) is recommended.

### Certified Standard Solutions

1000 ppm as Ammonia (Cat. No. 13-620-801)

### Internal Filling Solution

Accumet's Ammonia electrode internal filling solution (Cat. No. 13-620-803A) is recommended. Extra membrane caps are available in packs of three (Cat. No. 13-620-512).

## INSTALLATION

### Electrode Assembly

This electrode is shipped dry. Before using, unscrew the large cap and remove the inner glass electrode from the outer body. Fill the outer body with 2 to 3 ml of internal filling solution. Place the inner glass electrode into the outer body, and screw on the large cap until finger tight. Place the assembled electrode in an electrode holder and avoid trapping air bubbles at the bottom of the electrode.

### Checking the Membrane

A small hole of any size on the membrane or breakage of the membrane causes a failure of the electrode. Check the membrane on every newly assembled electrode.

1. Connect a newly assembled electrode to a pH/mV meter.
2. Lower the electrode tip into distilled water.
3. Record the reading after stirring the distilled water for about 15 minutes.
4. Add proper ISA solution (see Materials List) to the distilled water. A drastic change in the reading in a negative direction indicates damage of the membrane.

### Changing the Membrane Cap

1. Unscrew the top cap from the outer body and remove the inner glass body from the epoxy outer body. Carefully place the glass body aside.
2. Unscrew the old bottom cap from the outer body.
3. Place the new bottom cap gently onto the threads and screw the bottom cap on until fingertight.
4. Fill the outer body with approximately 2 ml of inner filling solution with the syringe provided.
5. Place the glass inner body into the epoxy outer body containing the internal filling solution and screw on the upper cap until fingertight.

### Connecting the Electrode to the Meter

Connect the electrode to the meter in the same manner as any other combination electrode. No external reference electrode is required.

## CALIBRATION AND SAMPLE MEASUREMENT

### Manual Plotting

The millivolt potentials of ammonia standard solutions,  $10^{-4}\text{M}$ ,  $10^{-3}\text{M}$ , and  $10^{-2}\text{M}$  for example, are measured with the ammonia electrode. A calibration curve can then be constructed on semilog graph paper or in a spreadsheet program. Plot concentration on the log scale and mV on the linear scale. A slope of  $-59 \pm 4$  mV (assuming solutions were measured between  $20^\circ$  and  $30^\circ\text{C}$ ) indicates correct electrode operation.

For accurate measurements, the standards and the samples should be at the same temperature. Ammonia pH/Ionic Strength Adjuster (ISA) is added to both standards and samples to "swamp out" standard and sample differences in ionic strength.

The following steps are typical for calibration and sample measurement by this direct, manual plotting method:

1. Connect the electrode plugs to the appropriate electrode terminals on the meter.
2. Prepare ammonia standards,  $10^{-4}\text{M}$ ,  $10^{-3}\text{M}$ ,  $10^{-2}\text{M}$ , etc..., by serial dilution of a  $10^{-1}\text{M}$  Ammonium Chloride standard solution.
3. Measure 100 ml of the lowest concentration standard and 2 ml of the pH/ISA into a beaker. Stir moderately.
4. Immerse the electrode into the standard solution.
5. Set the meter to the mV display mode.

6. Record the mV reading once it has stabilized.
7. Remove, rinse, and blot dry the electrode.
8. Repeat steps 3-7 for several solutions over the concentration range of interest.
9. Plot millivolt readings versus concentration (log axis).
10. Measure the potential of sample solution under identical conditions as the standards. Read the sample ammonia concentration from the calibration curve.

### Instrumental Calibration

Consult the meter's instruction manual for the proper specific calibration procedure. The following steps are typical:

1. Place the electrode into the first standard solution. Add pH/ISA solution.
2. Place the meter into the concentration calibration mode.
3. Enter the concentration of the first standard.
4. Enter the mV reading of the standard once it has stabilized.
5. Place the electrode into a second standard solution. Add pH/ISA. (Rinse the electrode between measurements to prevent sample carry over).
6. Enter the concentration value and the associated millivolt reading as before for each additional standard.

The instrument is now calibrated and ready for samples (100 mL sample and 2 mL of pH/ISA). Correct electrode operation is indicated by an efficiency of  $-1.00 + 0.08$  or a slope of  $-59 + 4$  mV (assuming solutions were measured between  $20^\circ$  and  $30^\circ\text{C}$ ).

7. Measure the potential of sample solution under identical conditions as the standards. Read the sample ammonia concentration from the meter.

### Known Addition

The Known Addition technique is useful when the ionic strength of the sample solution is high, or high levels of complexing agents are present. No calibration is necessary; therefore, the method is also useful where occasional samples are encountered.

The method requires that the concentration of the standard solution, the electrode slope and the volumes of both the standard and sample solutions be known. The potential (mV) of the sample is measured, the potential of the sample plus standard is measured, and the sample concentration is derived from the following equation:

$$\text{Equation 1} \quad C_s = \frac{C_{\text{std}} V_{\text{std}}}{(V_s + V_{\text{std}}) 10^{\Delta E/S} - V_s}$$

$C_s$	=	Concentration of the sample	$C_{\text{std}}$	=	Concentration of the standard
$V_s$	=	Volume of the sample	$V_{\text{std}}$	=	Volume of the standard
$\Delta E$	=	Change in potential on addition of standard			
$S$	=	Electrode Slope			

An example follows:

The electrodes were placed into 100 mL of sample and 1 mL of 10N NaOH. The mV reading of this solution was -20.0 mV. After the addition of 10 mL of a 100 ppm ammonia standard the mV reading was 52.1 mV. The slope of the electrode was previously determined to be -58.0 mV. With this information the ammonia concentration can be determined by substitution into equation 1.

$$C_{\text{std}} = 100 \text{ ppm}; V_{\text{std}} = 10 \text{ ml}; V_s = 101 \text{ ml}; S = -58.0 \text{ mV}; \Delta E = -52.1 - (-20.0) = 32.1 \text{ mV}$$

$$\text{Therefore: } C_s = \frac{(100 \text{ ppm}) (10 \text{ ml})}{(102 \text{ ml} + 10 \text{ ml})10^{-32.1/58} - 101 \text{ ml}} = \frac{1000}{(112)(3.58) - 101} \text{ ppm} = \frac{1000}{296} \text{ ppm} = \underline{3.38 \text{ ppm NH}_3}$$

NOTE: For best results, the concentration should approximately double as a result of the addition

### STORAGE OF ELECTRODE

Between measurements, the electrode can be stored wet or dry. For short term storage, up to one week, it is best to store the electrode in  $10^{-2}\text{M}$  ammonium chloride solution (without added NaOH).

For long term storage, drain the internal solution, rinse the body and cap with distilled water, and store disassembled unit dry.

Use of the electrode in nonaqueous media can wet the membrane, promote penetration of the sample liquid into the elec-

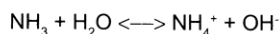
trode, and result in electrode failure. Aqueous solutions containing surfactants can do likewise. For such samples, it is best to measure ammonia with the electrode suspended above the sample in a closed system.

For best performance, change the internal filling solution (Cat. No. 13-620-803A) every 2-3 weeks.

## THEORETICAL CONCEPTS

The Ammonia Electrode is capable of measuring the concentration of ammonia in aqueous solution without interference from sample turbidity and color. The electrode detects ammonia gas as it diffuses through a hydrophobic gas-permeable membrane and reaches partial pressure equilibrium on both sides of the membrane. The amount of ammonia that has passed through the membrane is proportional to the concentration of ammonia in solution.

Having diffused through the membrane, the ammonia dissolves in the internal fill solution, and reacts as follows with water:



The above relationship reduces to:

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \text{constant}$$

As the internal solution has an essentially constant ammonium ion concentration, the above equation can be expressed as:

$$[\text{OH}^-] = [\text{NH}_3] \text{ Constant}$$

which relates the ammonia concentration to hydroxide concentration, and therefore pH.

The potential of the internal glass electrode varies with hydroxide ion concentration, and, therefore, ammonia concentration, in Nernstian fashion:

$$E = E^0 - 2.3 \frac{RT}{nF} \log[\text{NH}_3]$$

At 25°C, the potential decreases 59 mV for each decade increase in ammonia concentration.

It is necessary that all dissolved ammonia exist in the free, gaseous state which is detected by the electrode. To achieve this, pH/ionic strength adjustment buffer is added to standards and samples. The ISAB raises the solution pH to over 12, where more than 99.9% of the ammonia exists in the free, gaseous state.

## INTERFERENCES

Volatile amines interfere with electrode measurements resulting in high results. Easily hydrolyzable nitrogen containing organic material may also interfere.

Certain metallic ions (Hg, Ag, Cu, Au, Ni, Co, Zn) complex ammonia and can cause low results. The addition of the pH/ISA (10M NaOH) normally eliminates the ammonia-metal ion complexation. Residual chlorine can interfere by forming chloramines.

Gases such as CO<sub>2</sub>, SO<sub>2</sub>, and H<sub>2</sub>S do not interfere as they are converted to ionic species in the highly alkaline medium. Ionic species cannot cross the membrane, and therefore, cannot interfere with electrode measurements.

## ISE PROBLEM AREAS

Symptom A - Slope Variation

### Problem

Inconsistent temperature

Symptom B - Sub-Nernstian Slope

### Problem

Solvent penetration of membrane

Membrane surface contamination

Inadequate stirring

Ionic strength of solution too low

Incorrect standards

Presence of interferences

Symptom C - Noise

### Problem

Check internal fill solution

Static electricity

## ISE "DO'S AND DONT'S"

1. DO start standardization with solutions at the lowest concentration first.
2. DO stir solutions during measurement.
3. DO all measurements at a constant temperature.
4. DO adjust the ionic strength of all standards and samples.
5. DON'T allow the electrode membrane to contact organic solvents, particularly cyclic organics.