Version 2.2
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TPS Ammonia (NH_3^-) ISE

Introduction

Ammonia ion (NH_3) concentration is a concern in industrial processes, agriculture, and environmental pollution. It forms an equilibrium in water with ammonia (NH_3), normally a gaseous species, which is dependant upon the pH of the solution.

$$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^-$$

The TPS Ammonia ISE measures ammonia concentration in water by responding to the ammonia (NH_3) gas in equilibrium with the solution. The ammonia gas diffuses through a microporous hydrophobic membrane on the electrode and reacts with the water on the other side of the membrane to cause the pH to rise. This pH change is registered by a pH sensitive glass membrane inside the electrode and results in an potential (voltage) change proportional to the ammonia concentration in solution. Around neutral pH the equilibrium lies far to the right and the majority of the species is ammonia. While in strong ammonia solutions the TPS Ammonia ISE is capable of detecting the ammonia of a neutral solution, it is much more advantageous to adjust the pH of a sample solution to greater than pH10 and drive the equilibrium to the left in order to obtain a measurable signal, and hence achieve a lower detection limit.

Note : Due to the specific way in which the Ammonia ISE operates, Specific Ion meters must be set to Monovalent Anion (-) when measuring Ammonia.

TPS ISE Probe Parts

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Preparing the Electrode

1. Unscrew the Ammonia Membrane Module from the electrode body.
2. Fill the Ammonia Membrane Module with 1000ppm NH_3-N Standard to about the middle of the internal threads (about 1mL).

Note: If you plan to measure samples with ammonia concentrations in the low range of the electrode (<1.4ppm N), it is best to use a 10:1 dilution of the 0.1M Ammonium Chloride Filling Solution to fill the Ammonia Membrane Module. This imparts greater sensitivity to the electrode in this concentration range.

3. Screw the Ammonia Membrane Module back onto the electrode body. Make sure the module is snug against the shoulder of the electrode body.
4. Thoroughly rinse the electrode with deionised water and blot dry. Avoid damaging the membrane on the module
5. Allow the electrode to condition in a low ammonia standard for about 15 minutes before analysis.

Analysis

Direct Method

The *direct method* involves measuring the mV potential of known standards to produce a calibration graph of mV vs. concentration (see example graph below). The mV potential of the sample is then measured and correlated to a concentration on the calibration graph. TPS Specific Ion meters are able to take the readings from the electrodes in the different standards and electronically generate the calibration graph to be used to determine the unknown sample concentration. Each meter has included in its manual a step-by-step procedure for calibrating the meter and measuring the sample. Below are specific tips for using the Ammonia ISE.

- A general rule of thumb for choosing standards to calibrate the electrode is to use standards that bracket the expected concentration of the sample. For samples with ammonia concentrations in the linear portion of the response curve of the electrode ($1x10^{-4}$M to $1x10^{-1}$M NH_3 or 1.4ppm to 1400ppm NH_3-N) standards are generally chosen one decade apart (e.g. 1.4ppm and 14ppm standards). Below 1.4ppm NH_3-N, standards should be chosen closer together (e.g. 0.5ppm and 1.0ppm or 0.1ppm and 0.5ppm).
- Prepare the TPS Ammonia ISE as described above and connect it to the ion meter. If the ammonia membrane module is new, allow the electrode to stabilise for about 15 minutes before beginning to take measurements.
- Measure 50mL of each standard into 100mL beakers with magnetic stir bars. Always stir standards and samples for best results.
- Add 0.5mL of 10M NaOH to each standard. Place the lowest concentration standard on the stir plate, and begin stirring.
- Place the electrode into the solution and dislodge any air bubbles that may have stuck to the surface of the membrane tip.

- When the potential reading is stable (<0.2mV/minute drift) enter the reading into the meter as described by the meter manual.
- Repeat the steps above for the other standard. Rinse the electrode with deionised water and blot dry with a tissue before placing it in the next standard. The calibration is complete.
- Take 50mL of each sample you are to analyse and repeat the procedures above. Rinse the electrode with deionised water between samples. For best results, measure standards and samples at the same temperature.

Storage

For overnight or short-term storage, place the electrode in a beaker of 1000ppm standard. For long term storage, remove the module, rinse it with deionised water and place it back on electrode dry.

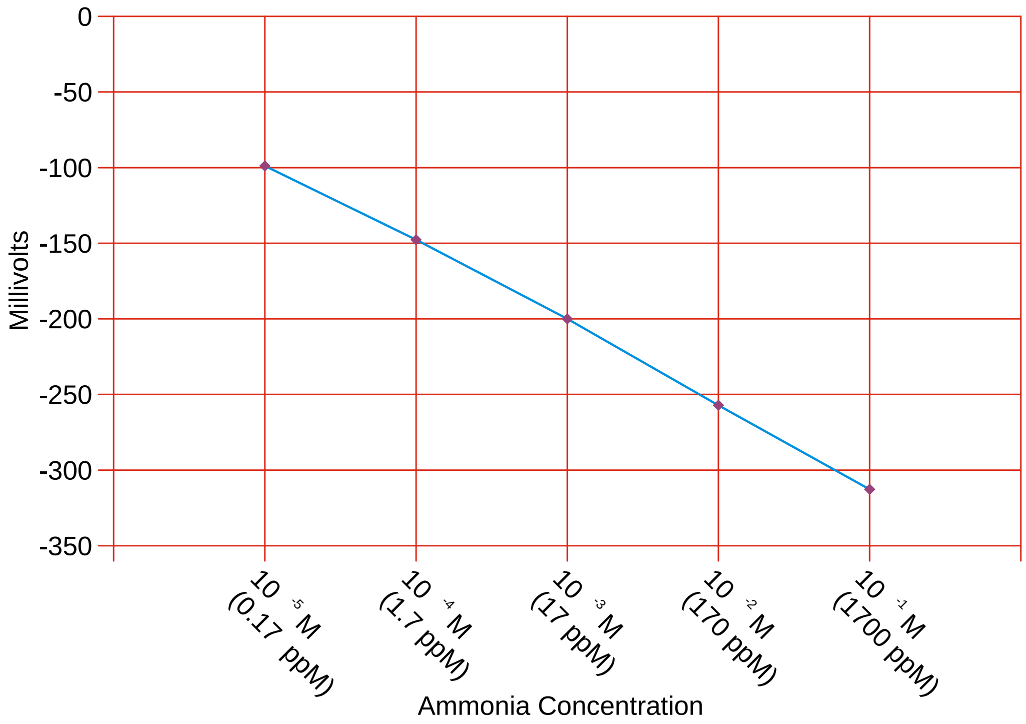
Troubleshooting

Poor response / poor slope / no slope

- First, make sure all electrical connections are tight and the meter is set up correctly on the right channel. **The meter must be set to monovalent anion ($^{-}$) when measuring Ammonia.**
- Membrane Module out of filling solution. Remove membrane module and rinse the inside of membrane module with deionised water. Refill the module with new filling solution and place back on the electrode. Check the response.
- Standards contaminated or gone bad. Re-make standards. Cover beakers with a piece of parafilm and cut a small hole in the parafilm to fit the electrode. This helps prevent the loss of ammonia, especially for low concentration standards.
- Ruptured or leaking membrane module. This is usually manifested by an extremely negative reading in all standards and samples. Replace the module with a new one.
- Broken pH glass bulb. All standards and samples read about the same. Replace the electrode.

Ammonia ISE Response

Response curve for “Ideal” Ammonia ISE



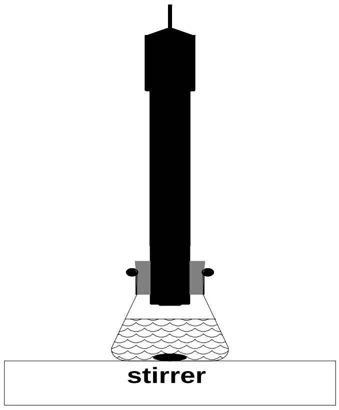
The TPS Ammonia ISE is a potentiometric sensor, meaning that is develops a potential (or voltage) proportional to the concentration of the ion to which it responds. The mathematical equation that describes this relationship is called the Nernst Equation:

$$E = E^{o} + S \log_{10} [\text{Ion}]$$

where E is the measured voltage, E^{o} is a constant, S is the slope factor, and [Ion] is the concentration of the ion to which it responds. The relationship between the measured potential and the concentration is logarithmic, which explains why potentiometric sensors are described as having exceptional working ranges, but limited accuracy. The slope factor, S, is dependent on the temperature of the solution, which is why it is best to measure both standards and samples at the same temperature. It has a theoretical value of about 59/n mV at 25°C, where n is the charge of the ion being measured. Ions such as F^- and NO_3^- have a theoretical slope of -59 (n=-1), while ions like NH_4^+ have a theoretical slope of +59 (n=+1). The ammonia ISE is a complicated issue, since it is a gas sensing electrode, and actually correlates the mV potential to the OH^- concentration. It has a theoretical slope factor of -59. By plotting the measured potential (E) of several standards versus the $\log_{10}$ of their concentration, it is possible to generate a linear calibration curve. The slope of the calibration curve for the TPS Ammonia ISE has an acceptable range of -57 +/-3 mV. The calibration curve becomes non-linear below 1.4ppm N, where the electrode starts to reach the limits of its capabilities. At this point the slope begins to fall until it reaches the detection limit of 0.02ppm N.

Interferences

The ammonia ISE has no ionic interferences, since ions cannot pass through the gas permeable membrane. Volatile amines can pass through the membrane and will impart a positive interference on the ammonia reading. Surfactants in a sample will wet the membrane, causing it to lose its hydrophobic quality and allow ions to pass through, thus destroying its response. If surfactants are a problem, it is possible to set up an apparatus for measuring ammonia through an air gap, which prevents direct contact of the membrane with the sample. Standards should also be measured through the air gap, when setting up the calibration curve. The response time will be longer.



Air Gap Assembly

Specifications:
Concentration Range ....0.02ppm N to 1400ppm N (1.4×10^{-6}M to 0.1M)
Linear Range..1.4ppm N to 1400ppm N (1×10^{-4}M to 0.1M)
Slope ....-57 mV/decade +/-3mV
Response Time .... <1 minute for 90% of final result from 10ppm N to 100ppm N

Ordering Information

	Part No
Complete TPS Ammonia ISE Analysis Kit	121700
Includes 1 x Combination ISE Body	ESNH3B
1 x Ammonia ISE Membrane / IFS Kit	121702
1 x 1000ppm NH_4^+ / NH_3 Standard (200mL)	121524
1 x Ammonia ISE Instruction Manual	130050

Spare parts and accessories…

Ammonia ISE Body	ESNH3B
Ammonia ISE Membrane Kit	121702
Includes 3 x Ammonia Membrane tips	
1 x Internal Filling Solution (IFS), 45mL	121807
Internal Filling Solution (IFS), 45mL	121807
1000ppm NH_4^+ / NH_3 Standard (200mL)	121524
1000ppm NH_4^+ / NH_3 Standard (1 Litre)	121526
Ammonia ISE Instruction Manual	130050

The uniPROBE Ammonia ISE body is not interchangeable with the other uniPROBE sensor tips.

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