



Manufacturers of Instruments for  
pH, Redox, Specific Ions,  
Conductivity, Salinity,  
Dissolved Oxygen,  
Humidity, Temperature,  
for Research and Industry



Version 2.2  
11-Aug-2006

## TPS uniPROBE Ammonium ( $\text{NH}_4^+$ ) Membrane ISE

### Introduction

The TPS uniPROBE Ammonium ISE belongs to a bold new line of ion sensors that offer superb versatility, performance, and savings. It is based on PVC membrane technology, where the membrane material is sealed to a replaceable silicone rubber tip that fits onto a combination electrode barrel.

- **Silicone rubber seal**

Silicone rubber forms a robust mechanical seal to the PVC membrane insert and the ISE barrel stem that will not deteriorate over extended periods under water.

- **Replaceable tip**

The ammonium sensor tip is easily removed from the electrode body. This allows the internal filling solution to be replenished in the event that it dries out, or the entire tip can be replaced at considerable savings if it becomes inoperable. **NOTE: To obtain maximum life from the sensing tips, store them in a refrigerator. When the sensor is not going to be used for an extended period, remove the tip, rinse with deionised water and also store in a refrigerator.**

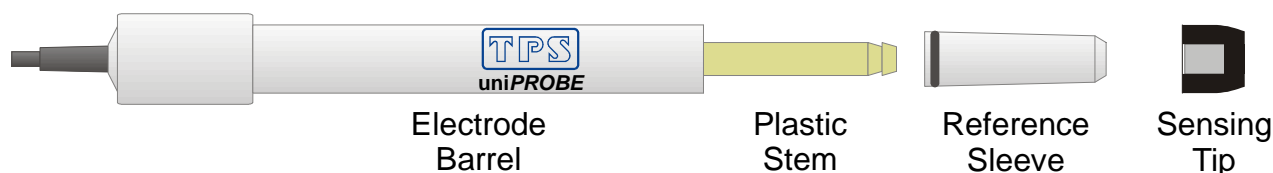
- **Replaceable Double Junction Reference Gel**

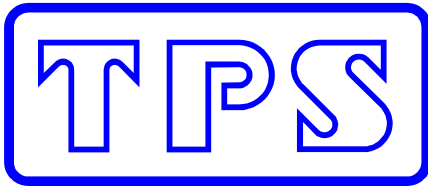
The double junction reference design allows the reference junction to be easily renewed by replacing the outer reference gel.

- **Interchangeable sensor tips**

In many instances the same electrode barrel can be used with other sensing tips, such as chloride, nitrate, calcium, fluoride, potassium, sodium, and others. These tips can be ordered separately. In some instances a different reference cartridge will be required. Consult your TPS representative.

### TPS uniPROBE ISE Probe Parts



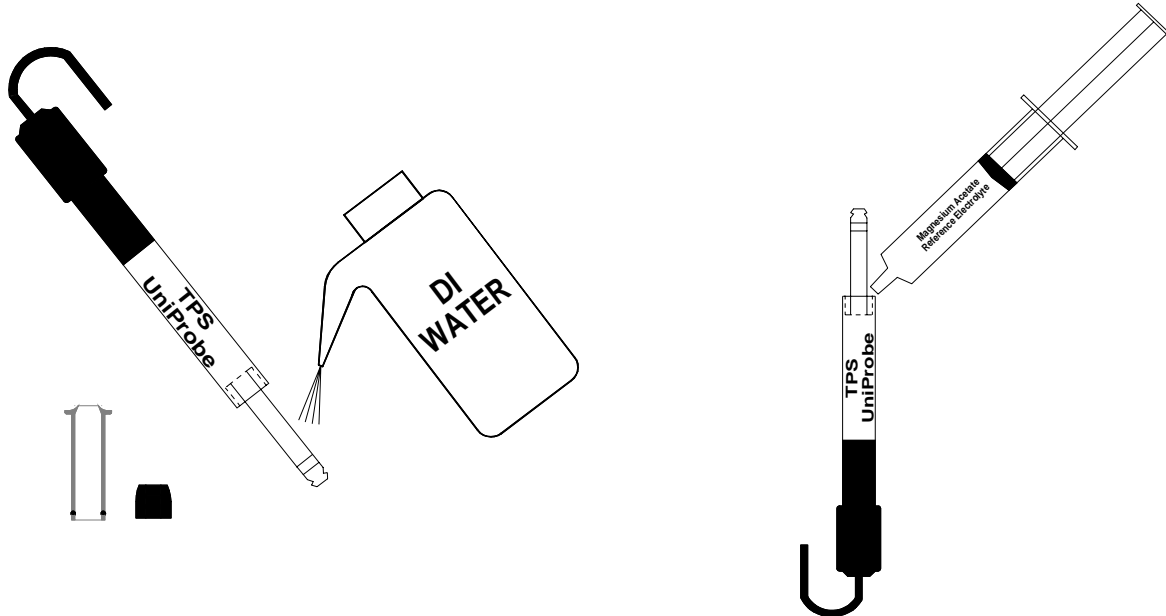


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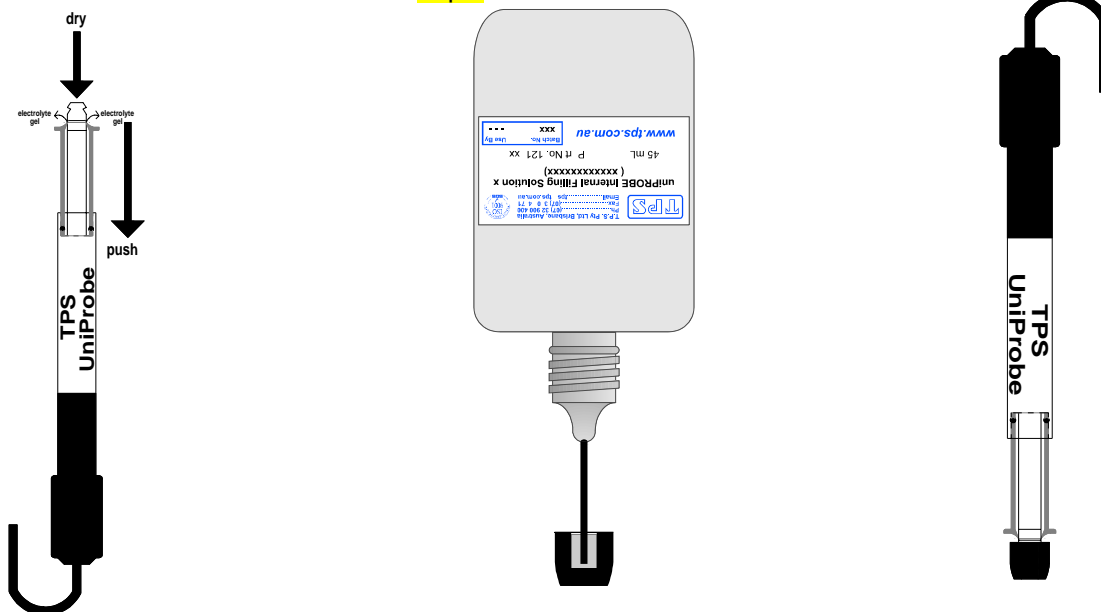


## Preparing the Electrode

1. Remove the reference sleeve and rinse the plastic stem with deionised water.
2. Fill the well around the stem with Magnesium Acetate Reference Electrolyte Gel.



3. Slide the reference sleeve over the plastic stem until the black O ring is 4mm inside the body. Some force may be required. Reference Electrolyte Gel will be expelled from the end of the stem. Rinse with deionised water. Dry the end of the plastic stem with a tissue.
4. Fill a black ammonium silicone rubber tip with Internal Filling Solution. Before filling, fit the black tube supplied into the nozzle of the bottle. Carefully insert the tube into the sensing tip and fill it from the bottom up. This procedure prevents air traps.
5. Gently push the tip onto the plastic stem until it stops. DO NOT FORCE IT BEYOND THE STOP POSITION. DO NOT TOUCH THE SENSING SURFACE. Rinse with deionised water. Condition overnight if possible or until there is no drift.





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## Analysis

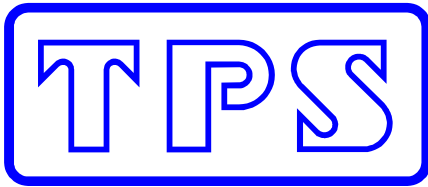
### *Direct Method*

The direct method involves measuring the mV potential of known standards to produce a calibration graph of mV vs. concentration (see sample 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 Ammonium 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 ammonium concentrations in the linear portion of the response curve of the electrode ( $1 \times 10^{-5} \text{M}$  to  $1 \text{M}$   $\text{NH}_4^+$  or 0.14ppm to 14000ppm  $\text{NH}_4^+\text{-N}$ ) standards are generally chosen one decade apart (e.g. 1.4ppm and 14ppm standards). Below 0.14ppm  $\text{NH}_4^+\text{-N}$ , standards should be chosen closer together (e.g. 0.1ppm and 0.5ppm or 0.02ppm and 0.05ppm).
- Prepare the TPS Ammonium ISE as described above and connect it to the ion meter. If the ammonium rubber tip is new, allow the electrode to stabilise (overnight if possible or until there is no drift) 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 5mL of Ammonium ISAB 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 ( $<0.2 \text{mV/minute}$  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 ammonium standard. For long term storage, remove the rubber tip and rinse the inside of it with deionised water. Store it dry. Remove the reference sleeve and rinse the electrode stem with deionised water. Place the reference sleeve over the electrode stem. Store it dry.



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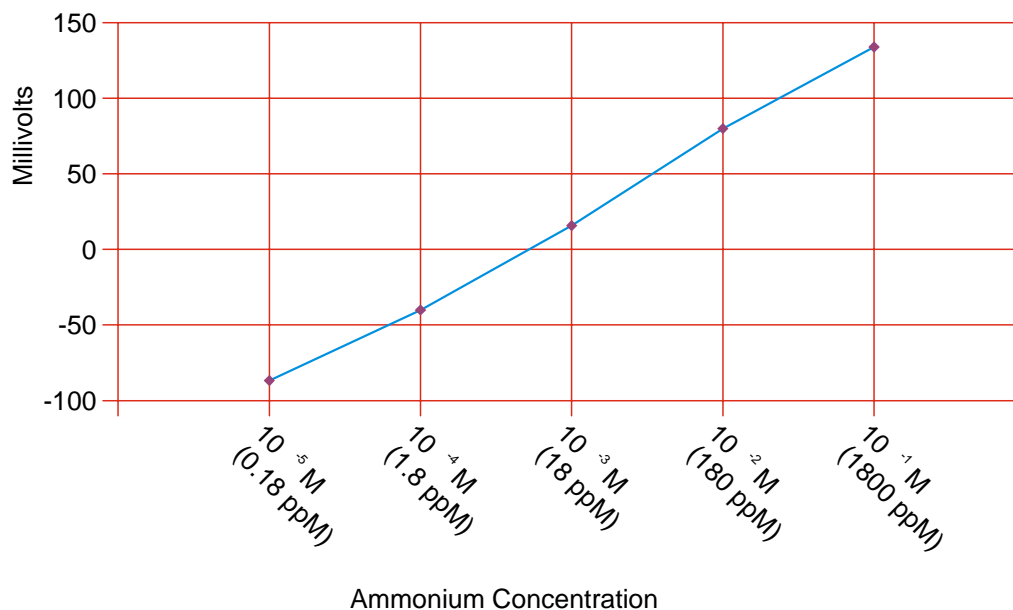
## Troubleshooting

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 cation ( + ) when measuring Ammonium.**
- Rubber tip has developed a short or dried out. Remove the rubber tip and rinse the inside with deionised water. This would be a good time to replenish the reference electrolyte as well. Prepare the electrode for use as described above. Check the response.
- Standards contaminated or gone bad. Re-make standards. Check response.
- Ammonium membrane has become debonded from the rubber tip. Replace the ammonium tip with a new one.

## Ammonium ISE Response

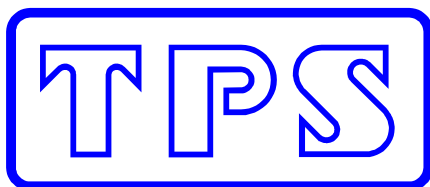
Response curve for "Ideal" Ammonium ISE



The TPS Ammonium ISE is a potentiometric sensor, meaning that it 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:

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

where E is the measured voltage,  $E^{\circ}$  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.



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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 ( $n=+1$ ). 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. In reality, the slope of the calibration curve has an acceptable range, which for the Ammonium ISE is +57 +/-3mV. The calibration curve becomes non-linear below 0.14ppm  $NH_4^+$ -N without ISAB or 1.0ppm with ISAB, 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  $NH_4^+$ -N.

### Interferences

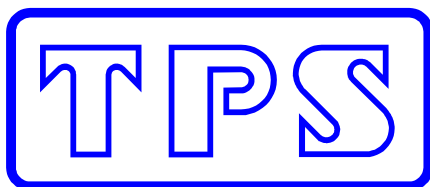
The ammonium membrane ISE is for fresh water use only due to the high levels of interfering ions in salt and brackish water. Potassium is a severely interfering ion, but is seldom encountered in high concentrations in natural waters.

<b>Specifications:</b>	
Concentration Range .....	0.02ppm $NH_4^+$ -N to 14000ppm $NH_4^+$ -N ( $1 \times 10^{-6}M$ to 1M)
Linear Range.....	0.2ppm $NH_4^+$ -N to 14000ppm $NH_4^+$ -N ( $1 \times 10^{-5}M$ to 1M)
Slope .....	+57 mV/decade +/-3mV
Response Time .....	<30 seconds from 1.4ppm $NH_4^+$ -N to 14ppm $NH_4^+$ -N

### References

Ma, S.C., Chaniotakis, N.A. and Meyerhoff, M.E., Anal. Chem. 60, 2293 (1988)

Ammonium ISAB = 1.5M Magnesium Acetate



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## Ordering Information

Part No

<b>Complete TPS Ammonium ISE Analysis Kit</b> .....	121520
Includes 1 x Combination ISE Body .....	121500
1 x Ammonium ISE Membrane / IFS / Electrolyte Kit.....	121522
1 x 1000ppm NH <sub>4</sub> <sup>+</sup> Standard (200mL).....	121524
1 x Ammonium ISAB Solution (200mL).....	121824
1 x Ammonium ISE Instruction Manual .....	130050

## Spare parts and accessories...

Combination Intermediate Junction ISE Barrel .....	121500
Ammonium ISE Membrane Kit.....	121522
Includes 2 x Black / White Membrane tips	
1 x Internal Filling Solution (IFS), 45mL .....	121801
1 x External Reference Electrolyte Gel, 10mL .....	121813
Internal Filling Solution (IFS), 45mL.....	121801
External Reference Electrolyte Gel, 10mL .....	121813
1000ppm NH <sub>4</sub> <sup>+</sup> Standard (200mL) .....	121524
1000ppm NH <sub>4</sub> <sup>+</sup> Standard (1 Litre) .....	121526
Ammonium ISAB Solution (200mL) .....	121824
Ammonium ISAB Solution (1 Litre) .....	121826
Ammonium ISE Instruction Manual.....	130050

**uniPROBE Membrane Kits are available for the following Ions. All Membrane Kits are supplied with 1 or more colour-coded sensing tips, 45mL internal filling solution and 10mL external electrolyte gel.**

<b>Species</b>	<b>Tip Colour Code</b>
• Nitrate	Red / White
• Ammonium	Black / White
• Calcium	White / White
• Sodium	Blue / White
• Potassium	Natural / White
• Fluoride	Green
• Chloride	Yellow
• Iodide	Purple
• Cyanide	Purple
• Bromide	Natural
• Sulphide	Black
• Silver	Black

**Ammonia is also available, but is not interchangeable with the other uniPROBE sensor tips.**