

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



Version 2.1
18-Aug-2006

TPS uniPROBE Silver (Ag⁺) Ion ISE

Introduction

The TPS uniPROBE Silver Ion ISE belongs to a bold new line of ion sensors that offer superb versatility, performance, and savings. The Silver Ion ISE is a solid state electrode made from a pressed pellet of Ag₂S that develops a mV potential (voltage) proportional to the concentration of silver ion ions in solution. The Silver Ion ISE can also be used as a sulphide ion sensor.

- **Silicone rubber seal**

Fluid leakage around the Ag₂S pellet is the most common mode of failure in a Silver Ion ISE. This is due to the fact that there are no long lasting adhesive that will stick to the Ag₂S, especially in an underwater environment. The silicone rubber tip forms a robust mechanical seal to the inert Ag₂S pellet. Water will not affect the seal and temperature expansion and contraction is compensated for by the elasticity of the silicone rubber.

- **Replaceable tip**

The Silver Ion 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.

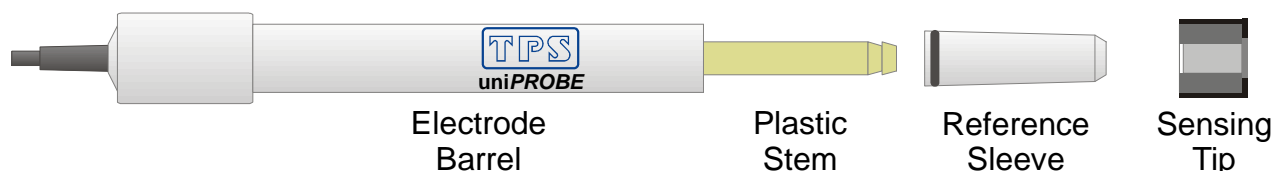
- **Replaceable Double Junction Reference Gel**

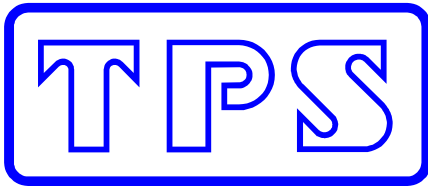
The double junction reference design allows the reference junction to be easily renewed by replacing the outer reference gel.

- **Interchangeable sensor tips**

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

TPS uniPROBE ISE Probe Parts



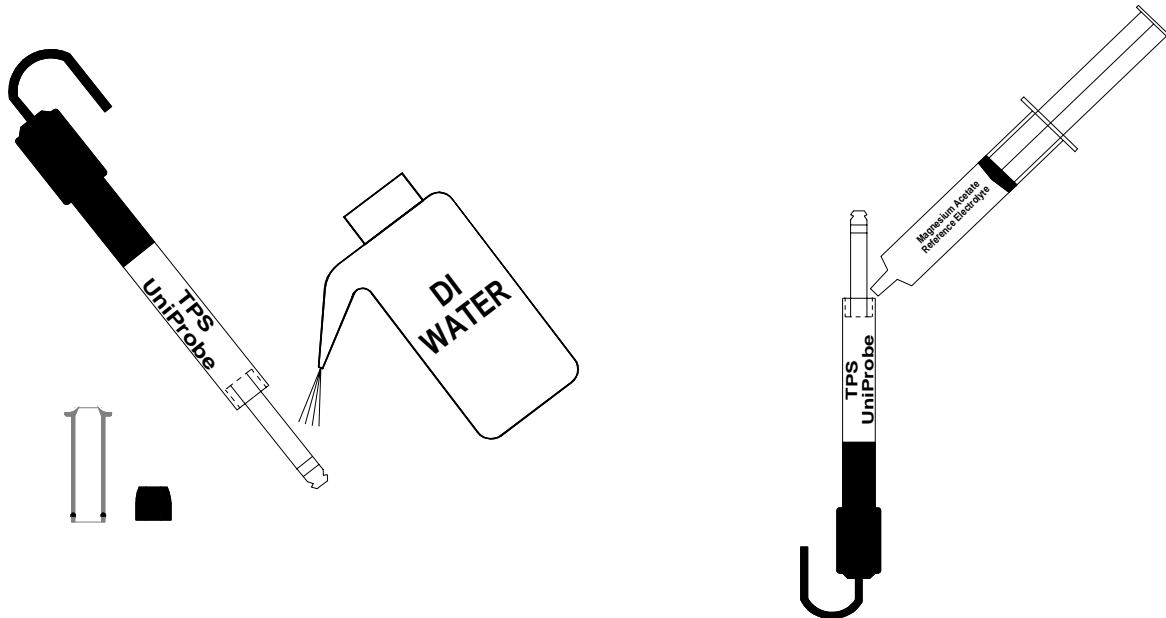


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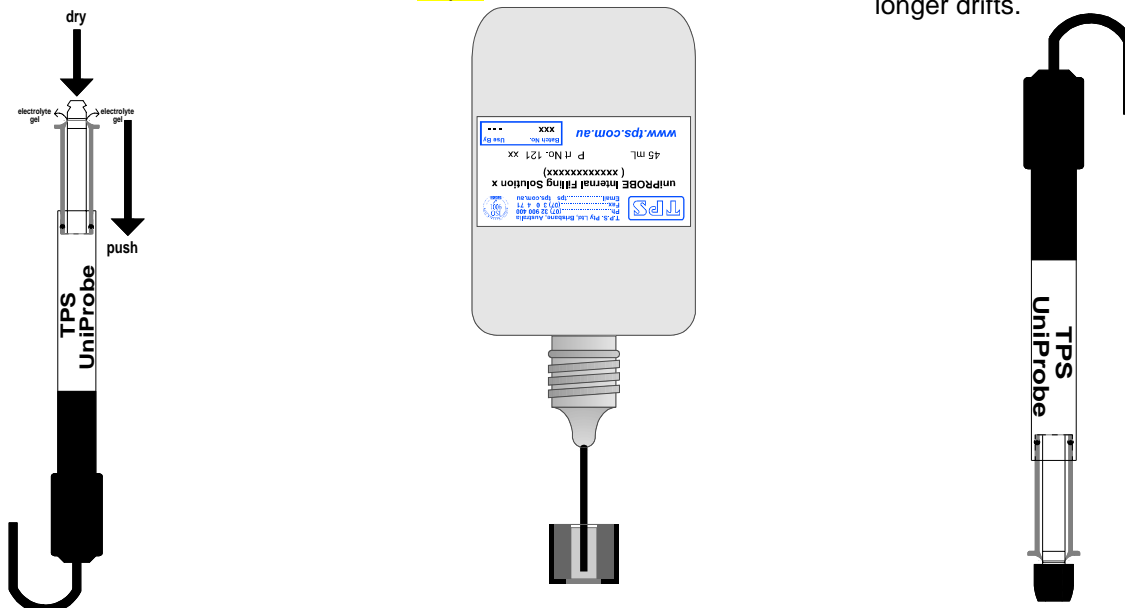


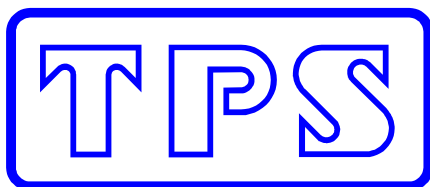
Preparing the Electrode

1. Remove the reference sleeve and rinse the plastic stem with deionised water.
2. Fill the well around the stem with 10% Potassium Nitrate 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 silver ion silicone rubber tip with 0.1M KCl 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 the ISE overnight, if possible, or until the reading no longer drifts.





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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. 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.

Silver Ion Analysis

- A general rule of thumb is to choose standards that bracket the expected concentration of the sample. For samples with silver ion concentrations in the linear portion of the response curve of the electrode ($1 \times 10^{-4} \text{M}$ to 1M Ag^+) standards are generally chosen one decade apart (e.g. $1 \times 10^{-4} \text{M}$ and 1×10^{-3} standards). Below $1 \times 10^{-4} \text{M Ag}^+$, standards should be chosen closer together.
- Prepare the TPS Silver Ion ISE as described above and connect it to the ion meter. If the Silver Ion rubber tip is new, allow the electrode to stabilise overnight if possible, or until the reading no longer drifts, before beginning to take measurements. **Note:** If the ISE barrel had just previously been used with a tip designed for a different ion, then overnight conditioning will be required for maximum stability.
- Measure 50mL of each standard into 100mL beakers with magnetic stir bars. Always stir standards and samples for best results.
- Add 1mL of 5M NaNO_3 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 pellet.
- When the potential reading is stable (<1 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 deionised water. 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

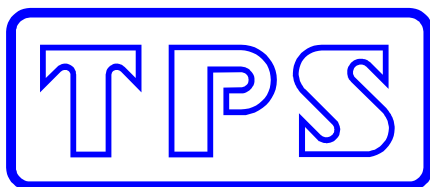
- First, make sure all electrical connections are tight and the meter is set up correctly on the right channel. **The meter must be set to monovalent cation (+) when measuring Silver.**
- Rubber tip has developed a short or dried out. Remove the rubber tip and rinse the inside with deionised water. This would be a good time to replenish the reference electrolyte as well. Prepare the electrode for use as described above. Check the response.
- Ag₂S pellet fouled. Polish the end of the Ag₂S pellet with fine polishing cloth (1200 grit). Wet the polishing cloth. Grasp the electrode by the rubber tip and rotate it against the polishing cloth on a flat hard surface.
- Standards contaminated or gone bad. Re-make standards. Check response.
- Silver Ion membrane has become de-bonded from the rubber tip. Replace the Silver Ion tip with a new one.

Response

The TPS Silver Ion 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:

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

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 I⁻ and NO₃⁻ have a theoretical slope of -59 (n=-1), while ions like Ag⁺ have a theoretical slope of +59 (n=+1). By plotting the measured potential (E) of several standards versus the log₁₀ 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 Silver Ion ISE is +57 +/-5mV. The calibration curve becomes non-linear below 1x10⁻⁴M Ag⁺.



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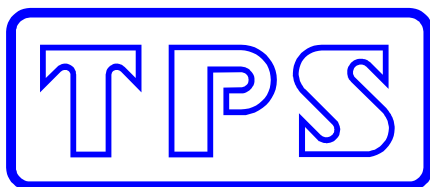


Interferences

The Silver Ion ISE is subject to interference from any salts that precipitate Ag⁺ ions. This includes Cl⁻, Br⁻, I⁻, carbonate, cyanide, sulphide and sulphate. Mercury ions also interfere.

Ions that interfere with I ⁻ ISE	Excess that produces a 10% error
Cl ⁻ , Br ⁻ , I ⁻ , carbonate, cyanide, sulphide and sulphate	traces
* Hg ²⁺ , Ag ⁺ , Pb ²⁺ , Tl ⁺	* affect solution to be analysed (precipitates)

Specifications:	
Concentration Range	1x10 ⁻⁶ to 1M
Linear Range.....	1x10 ⁻⁴ M to 1M
Slope	57mV/decade +/-5mV
Response Time	<30 seconds from 1x10 ⁻⁴ to 1x10 ⁻³ M



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Ordering Information

Part No

Complete TPS Silver ISE Analysis Kit	121620
Includes 1 x Combination ISE Body	121500
1 x Silver ISE Membrane / IFS / Electrolyte Kit.....	121612
1 x 1000ppm Ag ⁺ Standard (200mL).....	121626
1 x 5M NaNO ₃ ISAB Solution (200mL).....	121836
1 x Silver ISE Instruction Manual	130050

Spare parts and accessories...

Combination Intermediate Junction ISE Barrel	121500
Silver ISE Membrane Kit.....	121612
Includes 1 x Black Membrane tip	
1 x Internal Filling Solution (IFS), 45mL	121808
1 x External Reference Electrolyte Gel, 10mL	121814
Internal Filling Solution (IFS), 45mL.....	121808
External Reference Electrolyte Gel, 10mL	121814
1000ppm Ag ⁺ Standard (200mL)	121624
1000ppm Ag ⁺ Standard (1 Litre)	121626
5M NaNO ₃ ISAB Solution (200mL)	121836
5M NaNO ₃ ISAB Solution (1 Litre)	121838
Silver 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.

Species	Tip Colour Code
• 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.