

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



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## TPS uniPROBE Sulphide ( $S^{2-}$ ) ISE

### Introduction

The TPS uniPROBE Sulphide ISE belongs to a bold new line of ion sensors that offer superb versatility, performance, and savings. The Sulphide ISE is a solid state electrode made from a pressed pellet of  $Ag_2S$  that develops a mV potential (voltage) proportional to the concentration of sulphide ions in solution. The Sulphide ISE can also be used as a silver ion sensor.

- **Silicone rubber seal**

Fluid leakage around the  $Ag_2S$  pellet is the most common mode of failure in a Sulphide ISE. This is due to the fact that there are no long lasting adhesive that will stick to the  $Ag_2S$ , especially in an underwater environment. The silicone rubber tip forms a robust mechanical seal to the inert  $Ag_2S$  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 Sulphide 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.

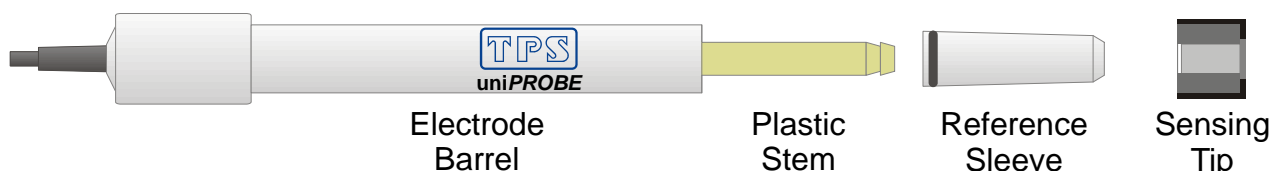
- **Replaceable Double Junction Reference Gel**

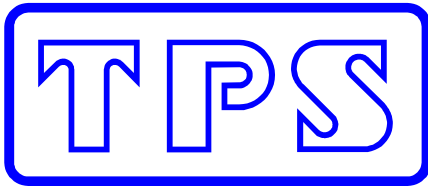
The double junction reference design allows the reference junction to be easily renewed by replacing the outer reference gel.

- **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



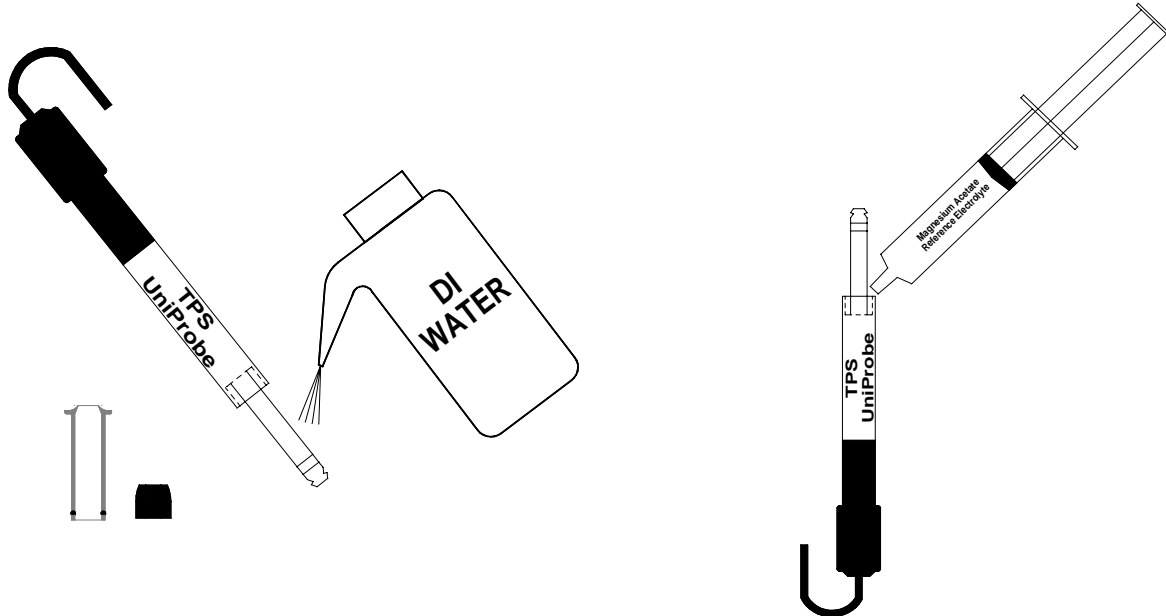


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## Preparing the Electrode

1. Remove the reference sleeve and rinse the plastic stem with deionised water.
2. Fill the well around the stem with Potassium Chloride 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 sulphide silicone rubber tip with 0.1 M 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

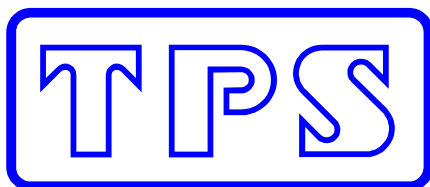
The direct method involves measuring the mV potential of known standards to produce a calibration graph of mV vs. concentration. The mV potential of the sample is then measured and correlated to a concentration on the calibration graph. TPS Specific Ion meters are able to take the readings from the electrodes 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.

### Sulphide Analysis

- A general rule of thumb is to choose standards that bracket the expected concentration of the sample. For samples with sulphide concentrations in the linear portion of the response curve of the electrode ( $1 \times 10^{-4} \text{M}$  to  $1 \text{M S}^{-2}$ ) standards are generally chosen one decade apart (e.g.  $1 \times 10^{-4} \text{M}$  and  $1 \times 10^{-3}$  standards). Below  $1 \times 10^{-4} \text{M S}^{-2}$ , standards should be chosen closer together.
- Prepare the TPS Sulphide ISE as described above and connect it to the ion meter. If the Sulphide 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 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 pellet.
- When the potential reading is stable ( $<1.0 \text{mV/minute}$  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 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 divalent anion (  $^{2-}$  ) when measuring Sulphide.**
- 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.
- Ag<sub>2</sub>S pellet fouled. Polish the end of the Ag<sub>2</sub>S 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.
- Sulphide membrane has become de-bonded from the rubber tip. Replace the Sulphide tip with a new one.

## Response

The TPS Sulphide 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<sup>o</sup> 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 S<sup>-2</sup> have a theoretical slope of -28.5 (n=-2), while ions like K<sup>+</sup> have a theoretical slope of +59 (n=+1). By plotting the measured potential (E) of several standards versus the log<sub>10</sub> 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 Sulphide ISE is -30 +/-5mV. The calibration curve becomes non-linear below about 1x10<sup>-4</sup>M S<sup>-2</sup>.

## Interferences

The Sulphide ISE is subject to interference from silver, and mercury ions. See table below. Hydrogen ions will affect sulphide readings, which is why 10M NaOH is added to buffer the standards and samples to a basic pH.

Ions that interfere with I <sup>-</sup> ISE	Excess that produces a 10% error
H <sup>+</sup>	affects determination of S <sup>-2</sup>
Hg <sup>2+</sup> , Ag <sup>+</sup> , Pb <sup>2+</sup> , Tl <sup>+</sup>	affect solution to be analysed (precipitates)



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<b>Specifications:</b>	
Concentration Range .....	0.03ppm S <sup>-2</sup> to 32000ppm S <sup>-2</sup> (1x10 <sup>-5</sup> M to 1M)
Linear Range.....	0.3ppm S <sup>-2</sup> to 32000ppm S <sup>-2</sup> (1x10 <sup>-5</sup> M to 1M)
Slope .....	-30mV/decade +/-5mV
Response Time .....	<30 seconds from 3ppm to 30ppm

### Ordering Information

Part No

<b>Complete TPS Sulphide ISE Analysis Kit .....</b>	<b>121610</b>
Includes	
1 x Combination ISE Body .....	121500
1 x Sulphide ISE Membrane / IFS / Electrolyte Kit.....	121613
1 x ISE Instruction Manual .....	130050

### Spare parts and accessories...

Combination Intermediate Junction ISE Barrel .....	121500
Sulphide ISE Membrane Kit.....	121613
Includes	
1 x Black Membrane tip	
1 x Internal Filling Solution (IFS), 45mL.....	121808
1 x External Reference Electrolyte Gel, 10mL .....	121811
Internal Filling Solution (IFS), 45mL.....	121808
External Reference Electrolyte Gel, 10mL.....	121811
Sulphide 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>
• Fluoride	Green
• Chloride	Yellow
• Iodide	Purple
• Cyanide	Purple
• Bromide	Natural
• Sulphide	Black

**Ammonia is also available, but is not interchangeable with the other uniPROBE sensor tips and does not include the external electrolyte gel.**