

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



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03-Mar-2011

TPS uniPROBE Bromide (Br^-) ISE

Introduction

The TPS uniPROBE Bromide ISE belongs to a bold new line of ion sensors that offer superb versatility, performance, and savings. The TPS Bromide ISE is a solid state electrode made from a pressed pellet of AgBr that develops a mV potential (voltage) proportional to the concentration of bromide ions.

- **Silicone rubber seal**

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

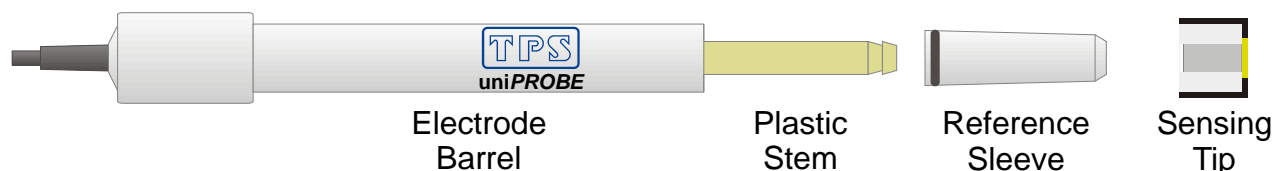
- **Replaceable Double Junction Reference Gel**

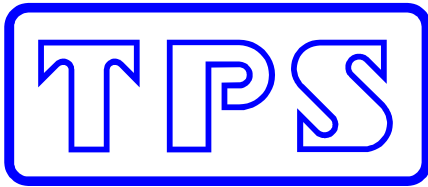
The double junction reference design allows the reference junction to be easily renewed by replacing the outer reference gel.

- **Interchangeable sensor tips**

In many instances the same electrode barrel can be used with other sensing tips, such as chloride, iodide, 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



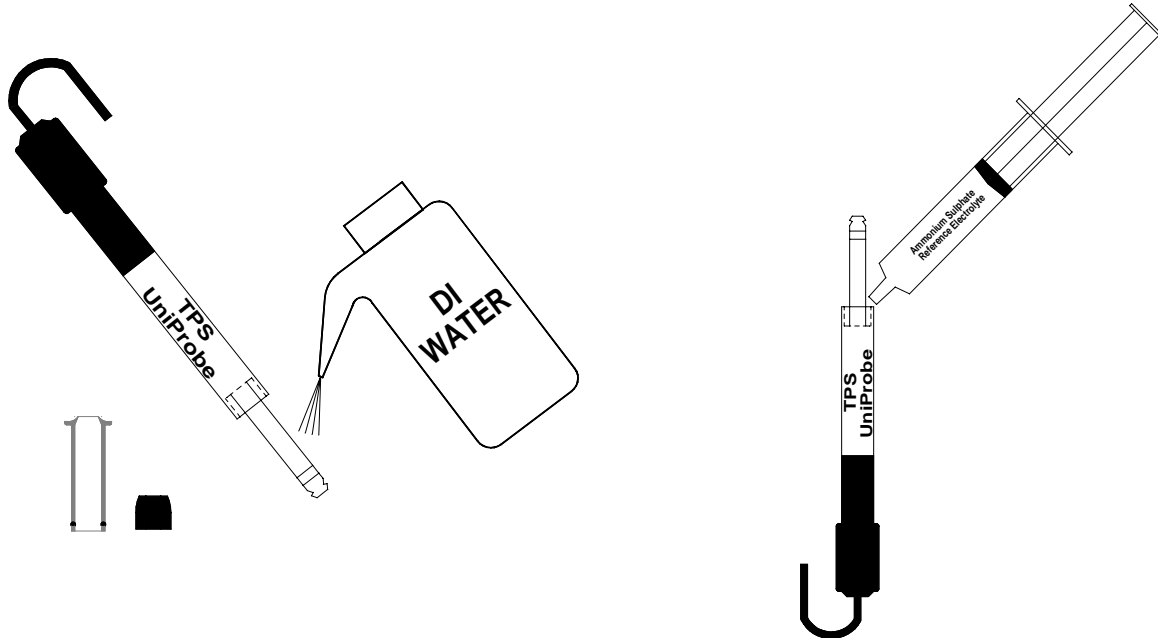


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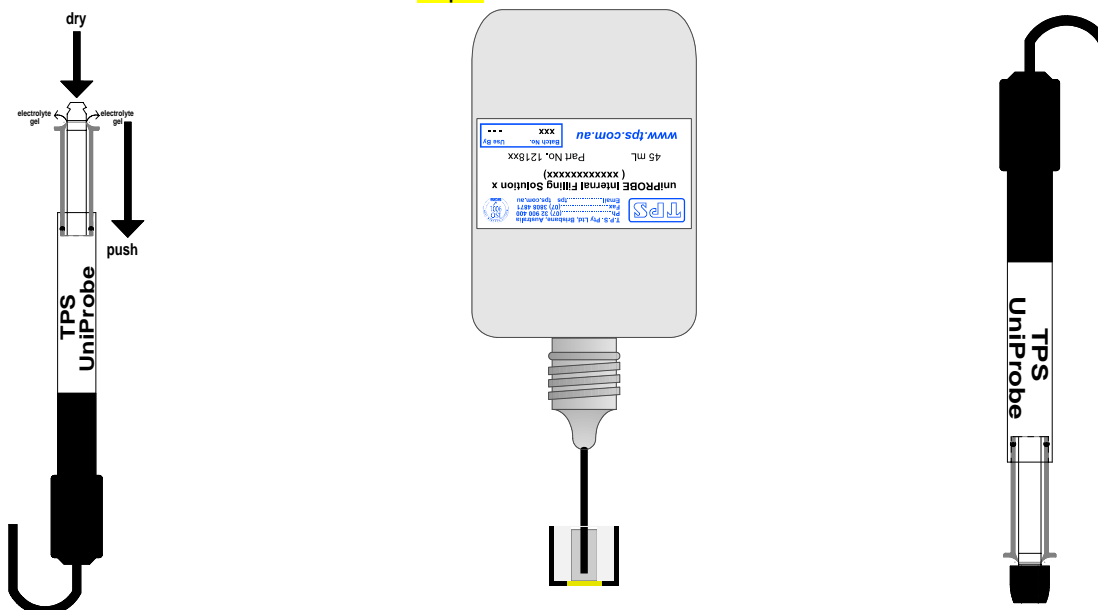


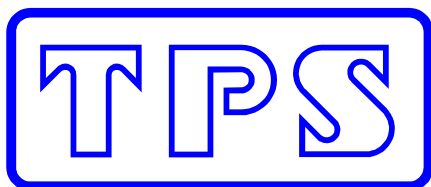
Preparing the Electrode

1. Remove the reference sleeve and rinse the plastic stem with deionised water.
2. Fill the well around the stem with Ammonium Sulphate 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 translucent bromide 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 the ISE overnight or until the reading no longer drifts.





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Analysis

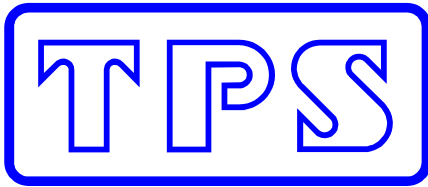
Direct Method

The direct method involves measuring the mV potential of known standards to produce a calibration graph of mV vs. concentration (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 Bromide 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 bromide concentrations in the linear portion of the response curve of the electrode ($1 \times 10^{-5} \text{M}$ to 1M Br or 0.8ppm to 80000ppm Br) standards are generally chosen one decade apart (e.g. 0.8ppm and 8.0ppm standards). Below 0.8ppm Br, standards should be chosen closer together (e.g. 0.1ppm and 0.5ppm or 0.08ppm and 0.1ppm).
- Prepare the TPS Bromide ISE as described above and connect it to the ion meter. If the bromide rubber tip is new, allow the electrode to stabilise overnight if possible or until the reading is stable 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 ($<0.2\text{mV}/\text{minute}$ 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 bromide 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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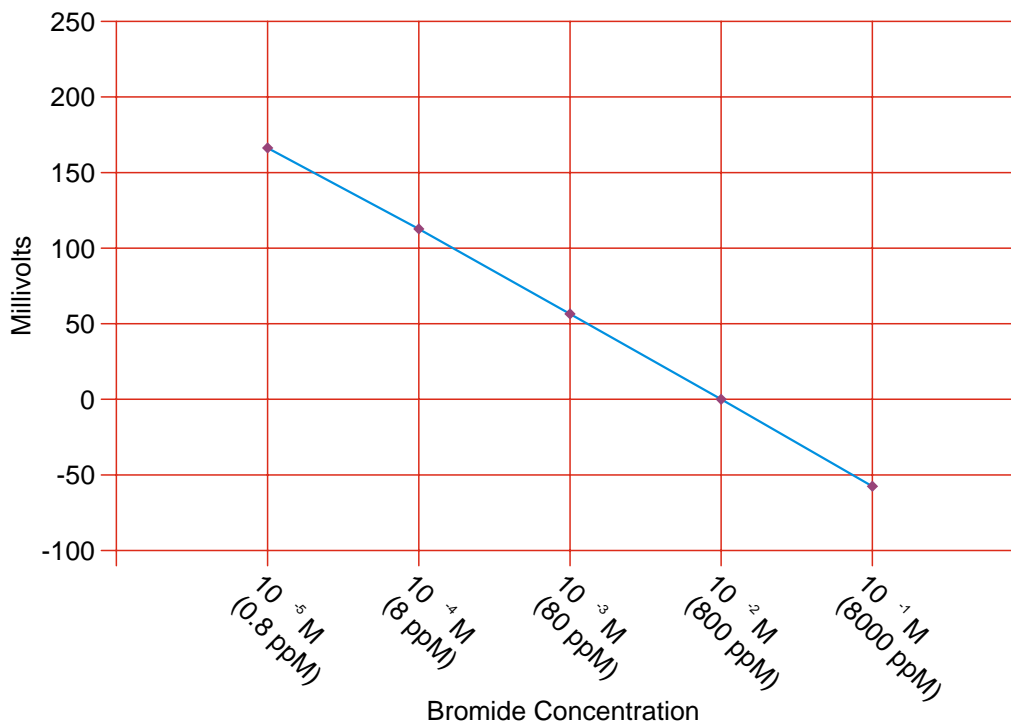
Troubleshooting

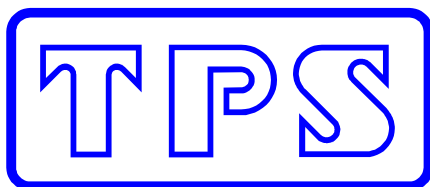
Poor response / poor slope / no slope

- 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 anion ($-$) when measuring Bromide.**
- 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.
- AgBr pellet fouled. Polish the end of the AgBr pellet with fine polishing cloth (1200grit). Wet the polishing cloth. Grasp the electrode by the rubber tip and rotate it against the polishing cloth on a hard flat surface.
- Standards contaminated or gone bad. Re-make standards. Check response.
- Bromide membrane has become debonded from the rubber tip. Replace the bromide tip with a new one.

Bromide ISE Response

Response curve for "Ideal" Bromide ISE





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The TPS Bromide 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:

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

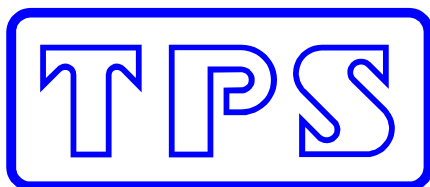
where E is the measured voltage, E° is a constant, S is the slope factor, and [Ion] is the concentration of the ion to which it responds. The relationship between the measured potential and the concentration is logarithmic, which explains why potentiometric sensors are described as having exceptional 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 Br^{-} and NO_3^{-} have a theoretical slope of -59 (n=-1), while ions like Ca^{+2} have a theoretical slope of +28.5 (n=+2). 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 Bromide ISE is -57 +/-3mV. The calibration curve becomes non-linear below 0.8ppm Br^{-} , 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 0.08ppm Br^{-} .

Interferences

The Bromide ISE is subject to interference from iodide, sulphide, cyanide, silver, and mercury ions. See table below. Hydroxide ions will affect the reading, which is why ISAB is added to buffer the standards and samples to a constant pH.

Ions that interfere with Br ISE	Excess that produces a 10% error
* OH-	3×10^4 times
* Cl ⁻	5×10^2 times
* I ⁻ /CN ⁻	2×10^{-2} times
* S ²⁻	Trace levels
* Cu ²⁺	5×10^{-2}
* Hg ²⁺ , Ag ⁺ , Pb ²⁺ , Tl ⁺	affect solution to be analysed (precipitates)

Specifications:	
Concentration Range	0.08ppm Br to 80000ppm Br ($1 \times 10^{-6}M$ to 1M)
Linear Range.....	0.8ppm Br to 80000ppm Br ($1 \times 10^{-5}M$ to 1M)
Slope	-57mV/decade +/-3mV
Response Time	<30 seconds from 0.8ppm Br to 8.0ppm Br



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Ordering Information

Part No

Complete TPS Bromide ISE Analysis Kit	121600
Includes 1 x Combination ISE Body	121500
1 x Bromide ISE Membrane / IFS / Electrolyte Kit	121602
1 x 1000ppm Br ⁻ Standard (200mL)	121604
1 x 5M NaNO ₃ ISAB Solution (200mL).....	121826
1 x Bromide ISE Instruction Manual.....	130050

Spare parts and accessories...

Combination Intermediate Junction ISE Barrel	121500
Bromide ISE Membrane Kit	121602
Includes 1 x Natural (Translucent) Membrane tip	
1 x Internal Filling Solution (IFS), 45mL	121804
1 x External Reference Electrolyte Gel, 10mL	121812
Internal Filling Solution (IFS), 45mL.....	121804
External Reference Electrolyte Gel, 10mL	121812
1000ppm Br ⁻ Standard (200mL)	121604
1000ppm Br ⁻ Standard (1 Litre)	121606
5M NaNO ₃ ISAB Solution (200mL)	121836
5M NaNO ₃ ISAB Solution (1 Litre)	121838
Bromide 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
• 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.