Version 2.2
03-Mar-2011

TPS uniPROBE Chloride (Cl^-) ISE

Introduction

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

- **Silicone rubber seal**

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

Electrode Barrel | Plastic Stem | Reference Sleeve | Sensing Tip

TPS Pty Ltd
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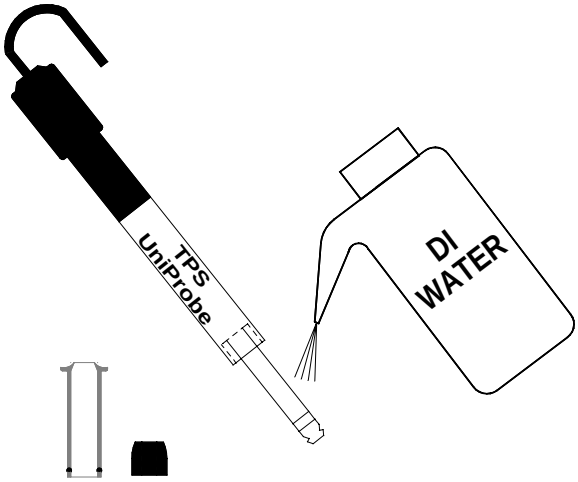
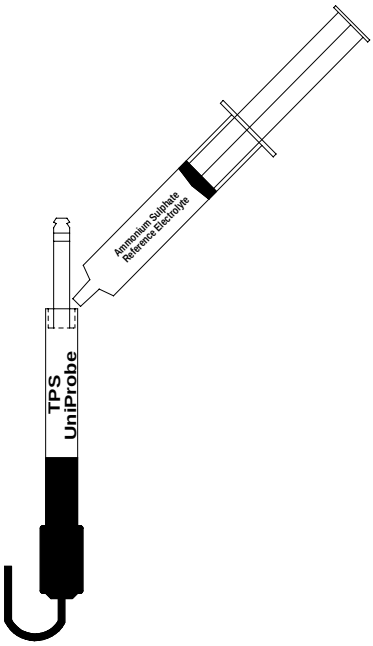
Preparing the Electrode

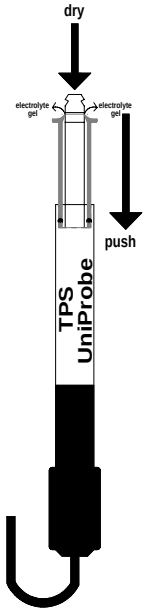
1. Remove the reference sleeve and rinse the plastic stem with deionised water.



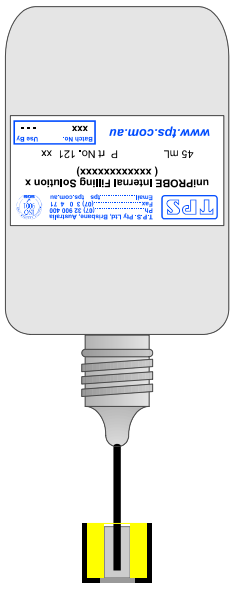
2. Fill the well around the stem with Ammonium Sulphate Reference Electrolyte Gel.



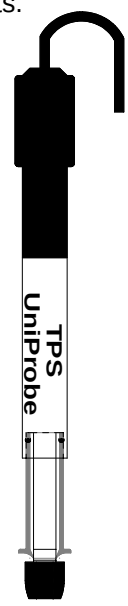
3. Slide the reference sleeve over the plastic stem until the black O ring is 4mm inside the body. Some force may be required Reference Electrolyte Gel will be expelled from the end of the stem. Rinse with deionised water. Dry the end of the plastic stem with a tissue.



4. Fill a yellow chloride 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, 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. Below are specific tips for using the Chloride 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 chloride concentrations in the linear portion of the response curve of the electrode ($1x10^{-4}$M to 1M Cl or 3.5ppm to 35000ppm Cl) standards are generally chosen one decade apart (e.g. 3.5ppm and 35ppm standards). Below 3.5ppm Cl, standards should be chosen closer together (e.g. 0.5ppm and 1.0ppm or 0.3ppm and 0.5ppm).
- Prepare the TPS Chloride ISE as described above and connect it to the ion meter. If the chloride 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 (<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 chloride 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.

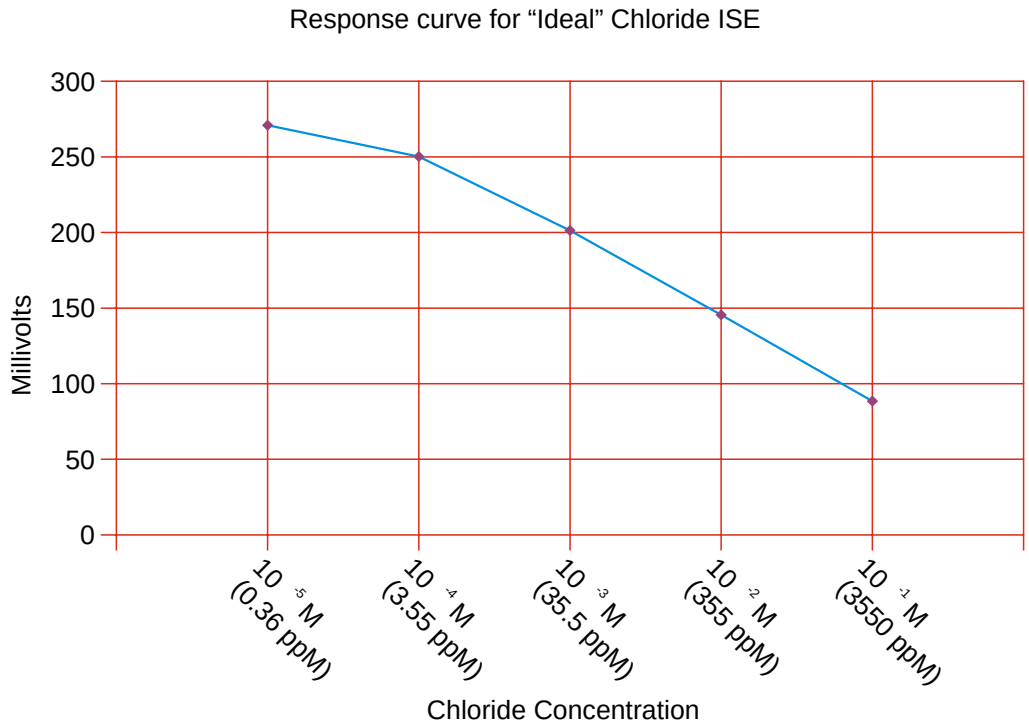
Troubleshooting

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 Chloride.**

- 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.
- AgCl pellet fouled. Polish the end of the AgCl 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.
- Chloride membrane has become de-bonded from the rubber tip. Replace the chloride tip with a new one.

Chloride ISE Response



The TPS Chloride 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:

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

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 Cl^- and NO_3^- have a theoretical slope of -59 (n=-1), while ions like K^+ 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 Chloride ISE is -57 +/-3mV. The calibration curve becomes non-linear below 3.5ppm Cl^-, 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 0.35ppm Cl^-.

Interferences

The chloride ISE is subject to interference from bromide, 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 Cl ISE	**Excess that produces a 10% error**
* OH^-	* 80 times
* Br^-	* 3.10^{-3} times
* I^-/CN^-	* 5.10^{-6} times
* S^{2-}	* traces
* Cu^{2+}	* 15 times
* Hg^{2+}, Ag^+, Pb^{2+}, Tl^+	* affect solution to be analysed (precipitates)

Specifications:
Concentration Range ..... 0.35ppm Cl to 35000ppm Cl ($1x10^{-5}$M to 1M)
Linear Range..... 3.5ppm Cl to 35000ppm Cl ($1x10^{-4}$M to 1M)
Slope ..... -57mV/decade +/-3mV
Response Time ..... <30 seconds from 3.5ppm Cl to 35ppm Cl

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Ordering Information

		Part No
Complete TPS Chloride ISE Analysis Kit		121570
Includes	1 x Combination ISE Body	121500
	1 x Chloride ISE Membrane / IFS / Electrolyte Kit	121572
	1 x 1000ppm Cl^- Standard (200mL)	121574
	1 x 5M $NaNO_3$ ISAB Solution (200mL)	121836
	1 x Chloride ISE Instruction Manual	130050

Spare parts and accessories…

Combination Intermediate Junction ISE Barrel		121500
Chloride ISE Membrane Kit		121572
Includes	1 x Yellow 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 Cl^- Standard (200mL)		121572
1000ppm Cl^- Standard (1 Litre)		121576
5M $NaNO_3$ ISAB Solution (200mL)		121836
5M $NaNO_3$ ISAB Solution (1 Litre)		121838
Chloride 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.

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