



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



Version 2.2
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TPS uniPROBE Cyanide (CN⁻) ISE

Introduction

The TPS uniPROBE Cyanide ISE belongs to a bold new line of ion sensors that offer superb versatility, performance, and savings. The TPS Cyanide ISE is a solid state electrode made from a pressed pellet of AgI that develops a mV potential (voltage) proportional to the concentration of cyanide ions in solution. The Cyanide ISE can also serve as an iodide sensor.

- **Silicone rubber seal**

Fluid leakage around the AgI pellet is the most common mode of failure in a Cyanide ISE. This is due to the fact that there are no long lasting adhesive that will stick to the AgI, especially in an underwater environment. The silicone rubber tip forms a robust mechanical seal to the inert AgI 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 Cyanide 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 : *Cyanide ISE tips slowly dissolve when they are immersed into Cyanide samples. The higher the Cyanide concentration, the more rapidly the tip dissolves. This is the same for all brands of Cyanide ISE, and another reason why the replaceable tips of TPS uniPROBE series offers far better value for money.*

- **Replaceable Double Junction Reference Gel**

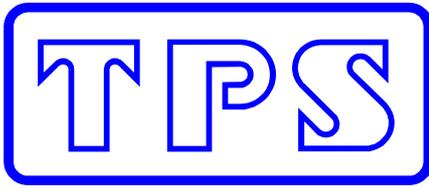
The double junction reference design allows the reference junction to be easily renewed by replacing the outer reference gel.

- **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



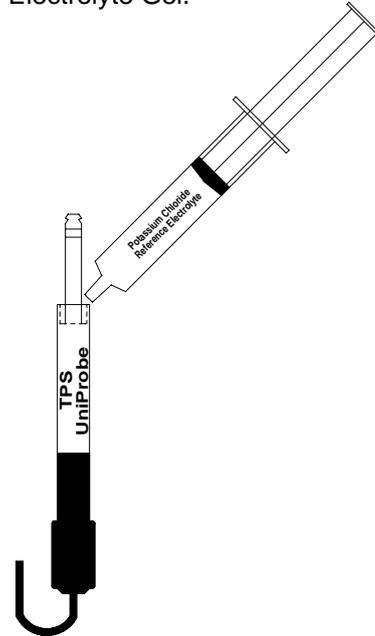
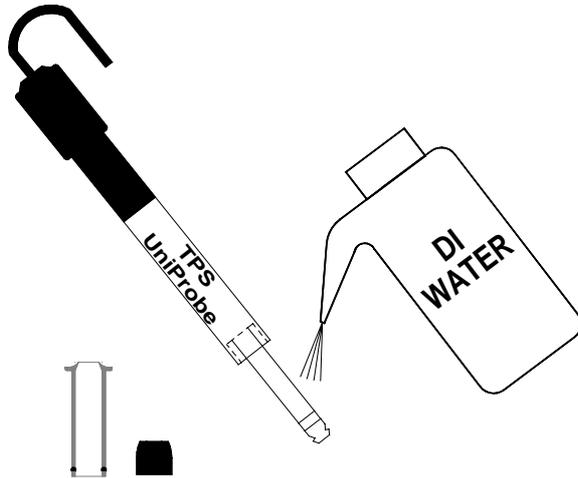


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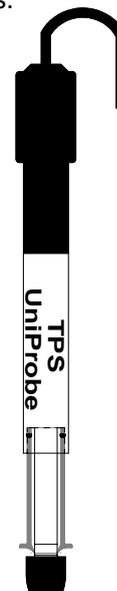
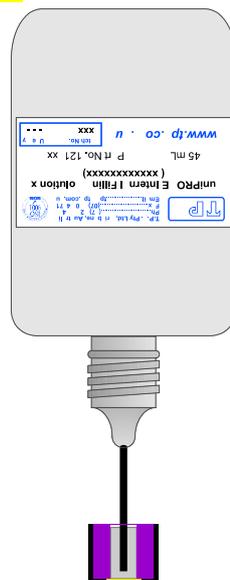
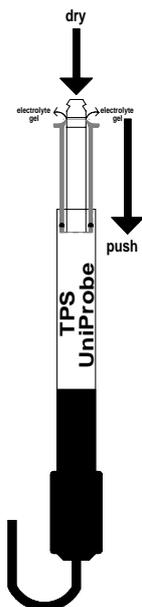


Preparing the Electrode

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 purple cyanide 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

Standard Addition Method

Due to the interaction of cyanide ions with the AgI pellet the potential has a tendency for long term drift. Standard addition methods help compensate for the drift to give more accurate results. Contact TPS for more information about standard addition methods.

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.

- Cyanide ions are in equilibrium with hydrogen ions in water to form hydrogen cyanide at a rate dependent on the pH of the solution. To minimize loss of hydrogen cyanide gas, the measurement of cyanide is best done at pH greater than 12.
- A general rule of thumb is to choose standards that bracket the expected concentration of the sample. For samples with cyanide concentrations in the linear portion of the response curve of the electrode ($1 \times 10^{-5} \text{M}$ to 1M CN^-) standards are generally chosen one decade apart. Below 0.3ppm CN^- , standards should be chosen closer together (e.g. 0.1ppm and 0.5ppm).
- Prepare the TPS Cyanide ISE as described above and connect it to the ion meter. If the Cyanide 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 5mL 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 ($<0.5 \text{mV/minute}$ 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 and in quick succession.



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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.

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 Cyanide.**
- 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.
- AgI pellet fouled. Polish the end of the AgI 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.
- Cyanide membrane has become debonded from the rubber tip. Replace the Cyanide tip with a new one.

Response

The TPS Cyanide 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 CN^{-} 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 Cyanide ISE is -57 ± 3 mV. The calibration curve becomes non-linear below 0.3ppm CN^{-} , 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 0.1ppm CN^{-} .



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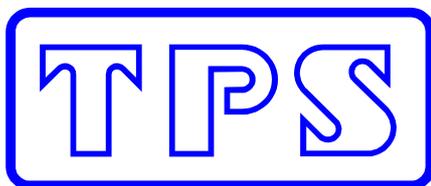


Interferences

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

Ions that interfere with CN ⁻ ISE	Excess that produces a 10% error
* Cl ⁻	* 106 times
* Br ⁻	* 5.10 ⁻³ times
* CN ⁻ /CN ⁻	* 5.10 ⁻⁶ times
* S ²⁻	* traces
* Cu ²⁺	* 5.10 ⁻²
*H ⁺	*affects determination of CN ⁻
* Hg ²⁺ , Ag ⁺ , Pb ²⁺ , TI ⁺	* affect solution to be analysed (precipitates)

Specifications:	
Concentration Range	0.1ppm CN ⁻ to 2600ppm CN ⁻ (5x10 ⁻⁶ M to 0.1M)
Linear Range.....	0.3ppm CN ⁻ to 2600ppm CN ⁻ (1x10 ⁻⁵ M to 0.1M)
Slope	-57mV/decade +/-3mV
Response Time	<30 seconds from 1.2ppm CN ⁻ to 12ppm CN ⁻



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Ordering Information

Part No

Complete TPS Cyanide ISE Analysis Kit	121590
Includes 1 x Combination ISE Body	121500
1 x Cyanide ISE Membrane / IFS / Electrolyte Kit.....	121592
1 x Cyanide ISE Instruction Manual	130050

Spare parts and accessories...

Combination Intermediate Junction ISE Barrel	121500
Cyanide ISE Membrane Kit.....	121592
Includes 1 x Purple Membrane tip	
1 x Internal Filling Solution (IFS), 45mL	121804
1 x External Reference Electrolyte Gel, 10mL	121811
Internal Filling Solution (IFS), 45mL.....	121804
External Reference Electrolyte Gel, 10mL	121811
Cyanide 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.