Version 2.2
03-Mar-2011

TPS uniPROBE Fluoride (F^-) ISE

Introduction

The TPS Fluoride ISE belongs to a bold new line of ion sensors that offer superb versatility, performance, and savings. It is based on standard lanthanum fluoride crystal technology, where the crystal is bonded to a replaceable rubber tip that fits onto a combination electrode barrel.

- **Silicone rubber seal**

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

- **Replaceable tip**

The lanthanum fluoride 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.

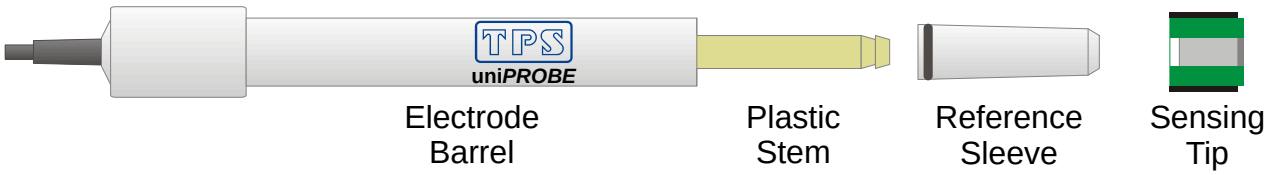
- **Replaceable Double Junction Reference Gel**

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, nitrate, ammonium, calcium, potassium, sodium, 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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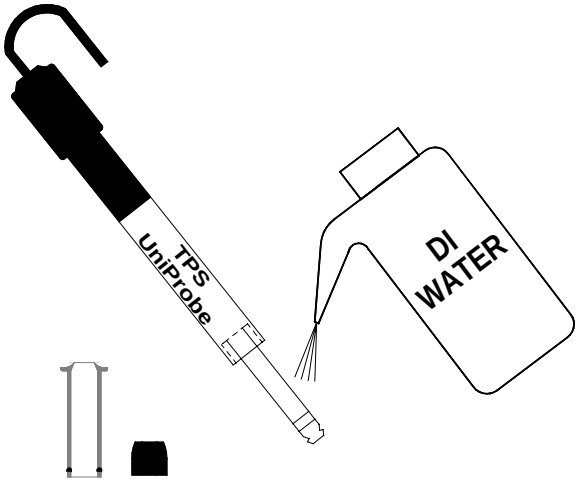
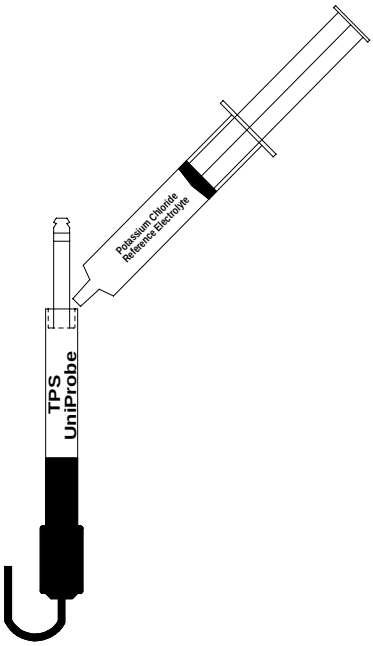
Preparing the Electrode

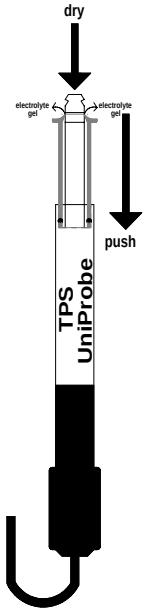
1. Remove the reference sleeve and rinse the plastic stem with deionised water.



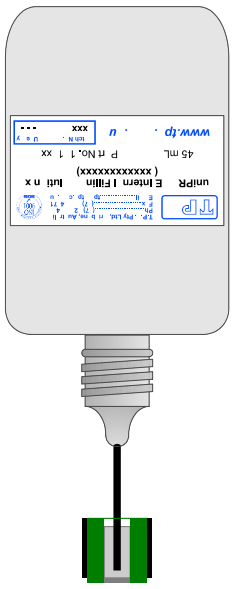
2. Fill the well around the stem with Potassium Chloride Reference Electrolyte Gel.



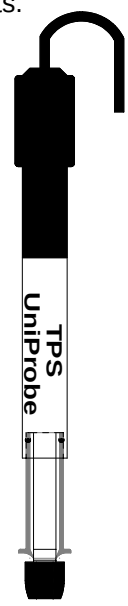
3. Slide the reference sleeve over the plastic stem until the black O ring is 4mm inside the body. Some force may be required. Reference Electrolyte Gel will be expelled from the end of the stem. Rinse with deionised water. Dry the end of the plastic stem with a tissue.



4. Fill a green fluoride 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 fluoride 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 fluoride concentrations in the linear portion of the response curve of the electrode ($1x10^{-4}$M to 1M F or 1.9ppm to 19000ppm F) standards are generally chosen one decade apart (e.g. 1.9ppm and 19ppm standards). Below 1.9ppm F, standards should be chosen closer together (e.g. 0.5ppm and 1.0ppm or 0.1ppm and 0.5ppm).
- Prepare the TPS Fluoride ISE as described above and connect it to the ion meter. If the LaF_3 rubber tip is new, allow the electrode to stabilise for about 15 minutes 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 may be required for maximum stability.
- Measure 25mL of each standard into 100mL beakers with magnetic stir bars. Always stir standards and samples for best results.
- Add 25mL of TISAB 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 LaF_3 crystal.
- 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 25mL 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 fluoride 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.

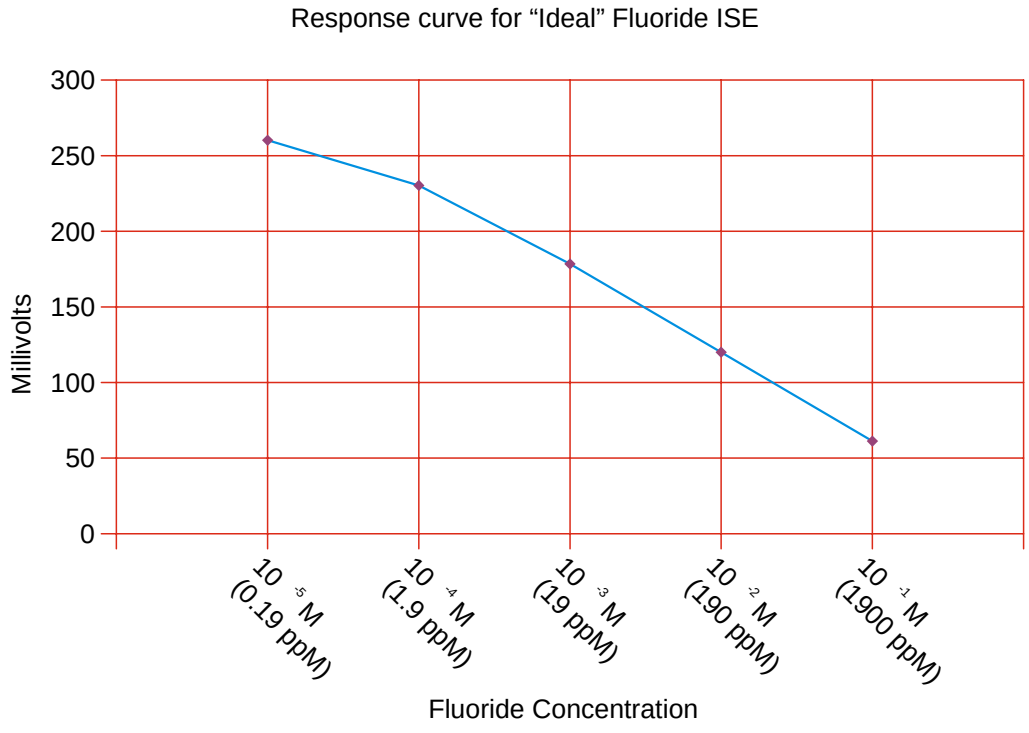
Troubleshooting

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 Fluoride.**

- 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.
- Lanthanum fluoride tip has become fouled. Wipe the end of the crystal dry with a soft tissue. Clean the end of the crystal with the rubber from the end of a pencil. Try not to scratch the crystal.
- Standards contaminated or gone bad. Re-make standards. Check response.
- Lanthanum fluoride crystal has become debonded from the rubber tip. Replace the lanthanum fluoride tip with a new one. Return the rubber tip to TPS for possible rejuvenation.

Fluoride ISE Response



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The TPS Fluoride 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 F^{-} and NO_3^{-} have a theoretical slope of -59 (n=-1), while ions like Ca^{+2} have a theoretical slope of +29 (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 fluoride ISE is –57 +/-3 mV. The calibration curve becomes non-linear below 1.9ppm F, 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 0.02ppm F.

Interferences

The fluoride ISE is highly selective for fluoride and suffers from only a few interferences. Hydroxide ions will affect the reading, which is why TISAB is added to buffer the standards and samples to a constant pH. Metal ions such as Al^{+3}, $Fe^{+2/3}$, and complex fluoride and prevent it from being sensed by the electrode. TISAB contains a strong complexing agent that displaces the F ion from the metal ion and allows it to be sensed by the electrode.

Reference:

TISAB Solution = 0.06M CDTA / 1M sodium citrate / 1M NaCl / adjusted to pH 6.0 – 6.5 with 40% NaOH

Specifications:
Concentration Range ..... 0.02ppm F to 19000ppm F ($1x10^{-6}$M to 1M)
Linear Range..... 1.9ppm F to 19000ppm F ($1x10^{-4}$M to 1M)
Slope.....-57mV/decade +/-3mV
Response Time.....<1 minute for 90% of final value

Ordering Information

	Part No
Complete TPS Fluoride ISE Analysis Kit	121560
Includes 1 x Combination ISE Body	121500
1 x Fluoride ISE Membrane / IFS / Electrolyte Kit	121562
1 x 1000ppm F^- Standard (200mL)	121564
1 x TISAB Solution (200mL)	121820
1 x Fluoride ISE Instruction Manual	130050

Spare parts and accessories…

Combination Intermediate Junction ISE Barrel	121500
Fluoride ISE Membrane Kit	121562
Includes 1 x Green Membrane tip	
1 x Internal Filling Solution (IFS), 45mL	121806
1 x External Reference Electrolyte Gel, 10mL	121811
Internal Filling Solution (IFS), 45mL	121806
External Reference Electrolyte Gel, 10mL	121811
1000ppm F^- Standard (200mL)	121564
1000ppm F^- Standard (1 Litre)	121566
TISAB Solution (200mL)	121820
TISAB Solution (1 Litre)	121822
Fluoride 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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