Version 2.1
11-Aug-2006

TPS uniPROBE Calcium (Ca^{++}) ISE

Introduction

The TPS uniPROBE Calcium ISE belongs to a bold new line of ion sensors that offer superb versatility, performance, and savings. It is based on PVC membrane technology, where the membrane material is sealed to a replaceable silicone rubber tip that fits onto a combination electrode barrel.

- **Silicone rubber seal**

Silicone rubber forms a robust mechanical seal to the PVC membrane insert and the ISE barrel stem that will not deteriorate over extended periods under water.

- **Replaceable tip**

The calcium 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: To obtain maximum life from the sensing tips, store them in a refrigerator. When the sensor is not going to be used for an extended period, remove the tip, rinse with deionised water and also store in a refrigerator.***

- **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, fluoride, 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

Electrode Barrel | Plastic Stem | Reference Sleeve | Sensing Tip

TPS Pty Ltd
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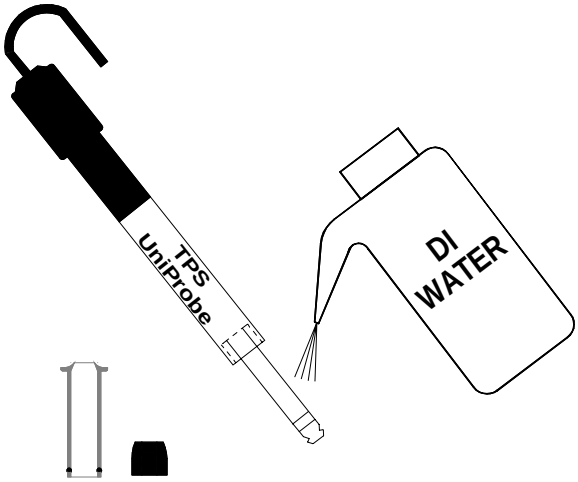
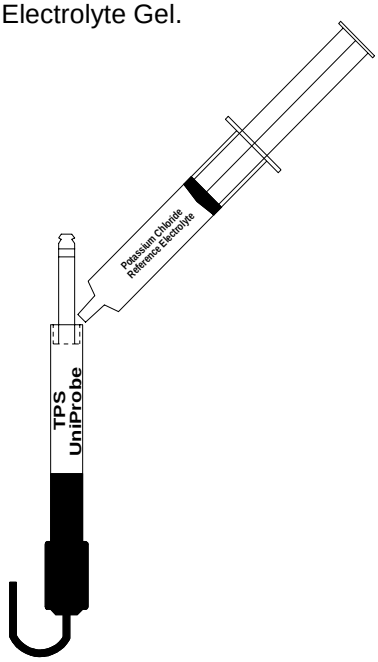
Preparing the Electrode

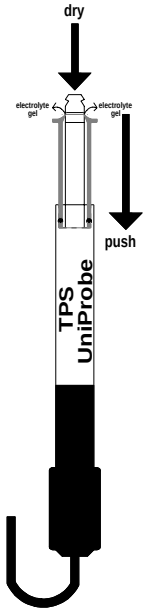
1. Remove the reference sleeve and rinse the plastic stem with deionised water.



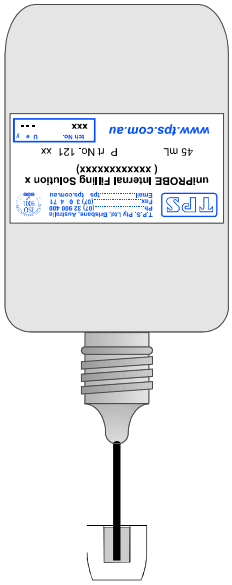
2. Fill the well around the stem with Potassium Chloride Reference Electrolyte Gel.



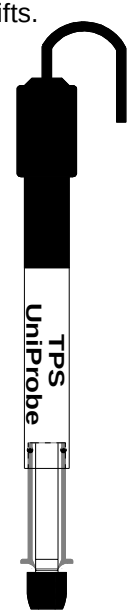
3. Slide the reference sleeve over the plastic stem until the black O ring is 4mm inside the body. Some force may be required. Reference Electrolyte Gel will be expelled from the end of the stem. Rinse with deionised water. Dry the end of the plastic stem with a tissue.



4. Fill a white calcium 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 (see example 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 Calcium ISE.

- The 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 calcium concentrations in the linear portion of the response curve of the electrode ($1x10^{-4}$M to 1M Ca^{+2} or 4.0ppm to 40100ppm Ca^{+2}) standards are generally chosen one decade apart (e.g. 4.0ppm and 40ppm standards). Below 4.0ppm Ca^{+2}, standards should be chosen closer together (e.g. 0.5ppm and 1.0ppm or 1.0ppm and 4.0ppm).
- Prepare the TPS Calcium ISE as described above and connect it to the ion meter. If the calcium 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 0.5mL of Calcium 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 membrane tip.
- When the potential reading is stable (<0.5mV/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 analyze 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 calcium 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.

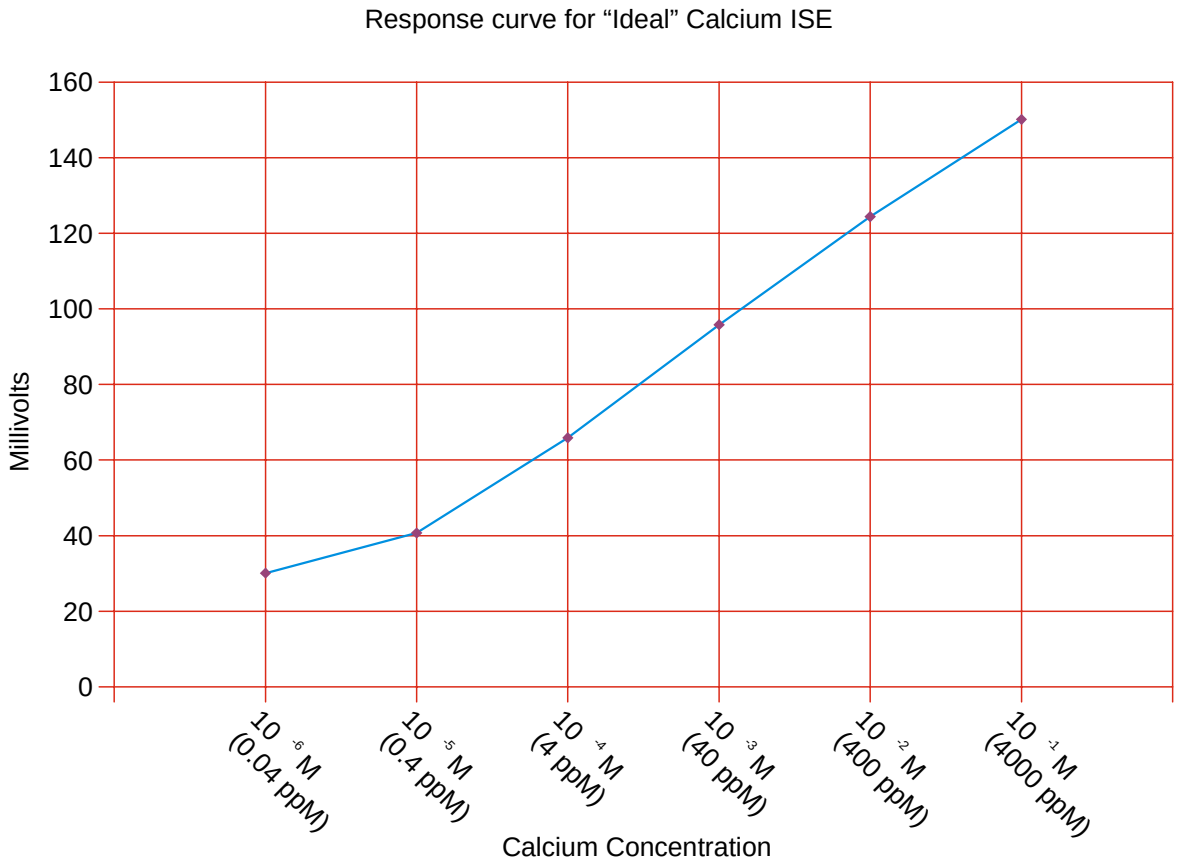
Troubleshooting

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 divalent cation ($^{++}$) when measuring Calcium.**

- 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.
- Standards contaminated or gone bad. Re-make standards. Check response.
- Calcium membrane has become debonded from the rubber tip. Replace the calcium tip with a new one.

Calcium ISE Response



The TPS Calcium 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 calcium ISE is +28 +/-3mV. The calibration curve becomes non-linear below 0.4ppm Ca^{+2} without ISAB or 1.0ppm with ISAB, 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 0.04ppm Ca^{+2}.

Reference:

- Gehrig, P., Rusterholz, B., and Simon, W. Chimia *43*, 377 (1989).

- Calcium ISAB Solution = Saturated KCl

Specifications:
Concentration Range ..... 0.04ppm Ca^{+2} to 40100ppm Ca^{+2} ($1x10^{-6}$M to 1M)
Linear Range..... 0.4ppm Ca^{+2} to 40100ppm Ca^{+2} ($1x10^{-5}$M to 1M)
Slope.....+28 mV/decade +/-3mV
Response Time.....<30 seconds from 4.0ppm Ca^{+2} to 40ppm Ca^{+2}

Interferences

The Calcium ISE is subject to interference from pH and Magnesium ions. See the table below. Hydrogen ions will affect the reading, which is why standards and samples should be run at around pH6 to 8.

Ions that interfere with Br ISE	**Excess that produces a 10% error**
H^+	H^+ level 500 times higher than Ca^{+2} level.
Mg^{+2}	Mg^{+2} level 10,000 times higher than Ca^{+2} level.

Ordering Information

	Part No
Complete TPS Calcium ISE Analysis Kit	121530
Includes 1 x Combination ISE Body	121500
1 x Calcium ISE Membrane / IFS / Electrolyte Kit	121532
1 x 1000ppm Ca^{+2} Standard (200mL)	121534
1 x Calcium ISAB, Saturated KCl Solution (200mL)	121832
1 x Calcium ISE Instruction Manual	130050

Spare parts and accessories…

Combination Intermediate Junction ISE Barrel	121500
Calcium ISE Membrane Kit	121542
Includes 2 x White / White Membrane tips	
1 x Internal Filling Solution (IFS), 45mL	121802
1 x External Reference Electrolyte Gel, 10mL	121811
Internal Filling Solution (IFS), 45mL	121802
External Reference Electrolyte Gel, 10mL	121811
1000ppm Ca^{+2} Standard (200mL)	121534
1000ppm Ca^{+2} Standard (1 Litre)	121536
Calcium ISAB Solution, Saturated KCl (200mL)	121832
Calcium ISAB Solution, Saturated (1 Litre)	121834
Calcium 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
• Nitrate	Red / White
• Ammonium	Black / White
• Calcium	White / White
• Sodium	Blue / White
• Potassium	Natural / White
• Fluoride	Green
• Chloride	Yellow
• Iodide	Purple
• Cyanide	Purple
• Bromide	Natural
• Sulphide	Black
• Silver	Black

Ammonia is also available, but is not interchangeable with the other uniPROBE sensor tips.

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