

# Calcium Ion-Selective Electrode BNC

(Order Code CA-BNC)



The Vernier Calcium Ion-Selective Electrode BNC is used to measure the concentration of calcium ( $\text{Ca}^{2+}$ ) ions in aqueous samples. It is designed to be used with the Vernier Electrode Amplifier (order code EA-BTA) or Vernier Go Wireless<sup>®</sup> Electrode Amplifier (order code GW-EA).

## Inventory of Items Included with the Calcium ISE

- Ion-Selective Electrode with BNC terminated end, packed with a storage bottle
- 30 mL bottle of High Standard solution with SDS ( $1000 \text{ mg/L Ca}^{2+}$ )
- 30 mL bottle of Low Standard solution with SDS ( $10 \text{ mg/L Ca}^{2+}$ )
- Short-Term ISE Soaking Bottle

**NOTE:** Vernier products are designed for educational use. Our products are not designed nor are they recommended for any industrial, medical, or commercial process such as life support, patient diagnosis, control of a manufacturing process, or industrial testing of any kind.

Here is the general procedure to follow when using the Calcium ISE to measure mV:

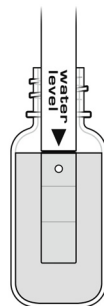
1. Connect the Calcium ISE to a Vernier electrode amplifier.
2. Connect the electrode amplifier to the interface (if required).
3. Start the data-collection software.
4. The software will automatically load a default data-collection setup. Change the units to mV, if necessary. You are now ready to collect data.

**Important:** Do not fully submerge the sensor.

## Preparing the Calcium ISE for Use

Soak the electrode in the High Standard solution (included with the ISE) for approximately 30 minutes. The ISE should not rest on the bottom of the container, and the small white reference contacts near the tip of the electrode should be immersed. Make sure no air bubbles are trapped below the ISE. **Important:** Do not leave the ISE soaking for more than 24 hours. **Important:** If you plan to use the electrode outside the range of the standards provided, you will need to prepare your own standards and use those for soaking.

**Note:** If the ISE needs to be transported to the field during the soaking process, use the Short-Term ISE Soaking Bottle. Remove



the cap from the bottle and fill it 3/4 full with High Standard. Slide the bottle's cap onto the ISE, insert it into the bottle, and tighten.

For long term storage, greater than 24 hours, make sure the sensor is stored in its storage bottle with the sponge slightly damp.

## Collecting Data

1. Make sure the sensor is connected to a Vernier electrode amplifier.
2. Connect the electrode amplifier to the interface (if required).
3. Start the data-collection software. The software will automatically load a default data-collection setup. Change the units to mV, if necessary.
4. Remove the storage bottle from the soaking solution (high standard). Thoroughly rinse the lower section of the probe, especially around the tip, using distilled or deionized water. Blot dry with a paper towel.
5. Insert the tip of the ISE into the aqueous sample to be tested. **Important:** Make sure the ISE is not resting on the bottom of the container, the white reference contacts near the tip of the electrode are immersed, and no air bubbles are trapped below the ISE. **Note:** Do not completely submerge the sensor.
6. Hold the ISE still until the reading stabilizes and record the displayed reading. **Note:** With some aqueous samples, especially those at high concentrations, it could take several minutes for the reading of the Calcium ISE to stabilize. If you know the approximate concentrations of your samples, it is best to analyze them from lowest concentration to highest.

## How the Ion-Selective Electrode Works

Combination Ion-Selective Electrodes consist of an ion-specific (sensing) half-cell and a reference half-cell. The ion-specific half-cell produces a potential which is measured against the reference half-cell depending on the activity of the target ion in the measured sample. The ion activity and the potential reading change as the target ion concentration of the sample changes. The relationship between the potential measured with the ISE and the ion activity, and thereby the ion concentration in the sample, is described by the Nernst equation:

$$E = E_o - 2.303 \frac{RT}{nF} \log(C + C_o)$$

$E$  = measured potential (mV) between the ion-selective and the reference electrode

$E_o$  = standard potential (mV) between the ion-selective and reference electrodes

$R$  = Universal gas constant ( $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )

$T$  = Temperature in K (Kelvin), with  $T(\text{K}) = 273.15 + t^\circ\text{C}$  where  $t$  is the temperature of the measured solution in  $^\circ\text{C}$ .

$F$  = Faraday constant ( $96485 \text{ C mol}^{-1}$ )

$n$  = valence of the ion

$C$  = concentration of ion to be measured

$C_o$  = detection limit

Since  $R$  and  $F$  are constant, they will not change. The electrical charge of the ion (valence) to be measured is also known. Therefore, this equation can be simplified as:

$$E = E_o - S \cdot \log(C + C_o)$$

where  $S = -2.303 \frac{RT}{nF}$  is the ideal slope of the ISE.

The following table describes **ideal behavior**:

Ion Examples	n (valence of ion)	S (at 25 °C), mV/decade
Calcium (Ca <sup>2+</sup> )	+2	+29.58
Potassium (K <sup>+</sup> ), Ammonium (NH <sub>4</sub> <sup>+</sup> )	+1	+59.16
Nitrate (NO <sub>3</sub> <sup>-</sup> ), Chloride (Cl <sup>-</sup> )	-1	-59.16

Assuming  $C_0$  is near zero, the equation can be rewritten as:

$$C = 10^{[(E - E_o) / S]}$$

allowing for the calculation of the ion concentration.

It is very important to note that this table reflects ideal behavior. Ion-selective electrodes have slopes that are typically lower than ideal. It is generally accepted that an ISE slope from 88–101% of ideal is allowable. The slope ( $S$ ) is an indicator of ISE performance. If the slope changes significantly over time it may indicate that it is necessary to replace the ISE sensor tip.

### Convert Potential to Concentration (Optional)

To measure the mV readings from an aqueous sample, calibration is not required. To convert mV readings to concentration (mg/L or ppm), you will use a modified version of the Nernst Equation:

$$C = 10^{[(E - E_o) / S_m]}$$

$C$  = concentration of ion to be measured (mg/L or ppm)

$E$  = measured potential of sample (mV)

$E_o$  = measured potential (mV) at a  $C = 1$  mg/L Ca<sup>2+</sup> concentration

$S_m$  = measured electrode slope in mV/decade

The value of  $S_m$ , the measured electrode slope, is determined by measuring the potential of two standard solutions, and solving the equation below:

$$S_m = -[(\text{Low Standard} - \text{High Standard}) / \# \text{ of decades}^*]$$

\*A decade is defined as the factor of the difference between the two standard solutions. For example, the difference between a 1mg/L standard and a 100 mg/L standard is 2 decades (a factor of 100 difference, or  $1 \times 10^2$ ).

### Example Calculation, converting mV to mg/L

For this example, the measured quantities are shown in the chart below:

Solution	Measured Potential
1 mg/L Ca <sup>2+</sup> standard	1 mV
10 mg/L Ca <sup>2+</sup> standard	30 mV
1000 mg/L Ca <sup>2+</sup> standard	82 mV
unknown sample	50 mV

$$S_m = - \frac{(30 \text{ mV} - 82 \text{ mV})}{2 \text{ decades}} = +26 \text{ mV/decade}$$

$$C = 10^{[(50 \text{ mV} - 1 \text{ mV}) / +26 \text{ mV/decade}]} = 77 \text{ ppm Ca}^{2+}$$

### Using the Calcium ISE with Other Vernier Sensors

Some combinations of sensors interfere with each other when placed in the same solution. The degree of interference depends on many factors. For more information, see [www.vernier.com/til/638/](http://www.vernier.com/til/638/)

### Storing the Ion-Selective Electrode

Proper care and storage are important for optimal longevity of your Calcium ISE.

- Long-term storage of the ISE (longer than 24 hours): Moisten the sponge in the bottom of the long-term storage bottle with distilled water. When you finish using the ISE, rinse it off with distilled water and blot it dry with a paper towel. Loosen the lid of the long-term storage bottle and insert the ISE. **Note:** The tip of the ISE should NOT touch the sponge. Also, make sure the white reference mark is inside the bottle. Tighten the lid. This will keep the electrode in a humid environment, which prevents the reference junctions from completely drying out.
- Short-term wet storage (less than 24 hours): Fill the Short-Term ISE Soaking bottle 3/4 full with High Standard. Loosen the cap, insert the electrode into the bottle, and tighten.

### Specifications

Range (mV)	-450 mV to +1100 mV (EA-BTA) -1100 mV to +1100 mV (GW-EA)
Range (concentration)	1 to 40,000 mg/L (or ppm)
Reproducibility (precision)	±30 mV
Interfering ions	Pb <sup>2+</sup> , Hg <sup>2+</sup> , Si <sup>2+</sup> , Fe <sup>2+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup> , NH <sub>3</sub> , Na <sup>+</sup> , Li <sup>+</sup> , K <sup>+</sup> , Ba <sup>2+</sup> , Zn <sup>2+</sup> , Mg <sup>2+</sup>
pH range	2–8 (no pH compensation)
Temperature range	0–40°C (no temperature compensation)
Electrode slope	+26 ±2 mV/decade at 25°C
Electrode resistance	100 MΩ
Minimum sample size	must be submerged 2.8 cm (1.1 in)

## Maintaining and Replacing the ISE Standard Calibration Solutions

Having accurate standard solutions is essential for performing good calibrations. The two standard solutions that were included with your ISE can last a long time if you take care not to contaminate them. At some point, you will need to replenish your supply of standard solutions. Vernier sells replacement standards in 500 mL volumes. Order codes are:

CA-LST: Calcium Low Standard, 10 mg/L  $\text{Ca}^{2+}$

CA-HST: Calcium High Standard, 1000 mg/L  $\text{Ca}^{2+}$

To prepare your own standard solutions, use the information in the table below.

**Note:** Use glassware designed for accurate volume measurements, such as volumetric flasks or graduated cylinders. All glassware must be very clean.

Standard Solution	Concentration (mg/L or ppm $\text{Ca}^{2+}$ )	Preparation Method using High Quality Distilled Water
Calcium ( $\text{Ca}^{2+}$ ) ISE High Standard	1000 mg/L as $\text{Ca}^{2+}$	2.771 g $\text{CaCl}_2$ / 1 L solution or 3.669 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ / 1 L solution
Calcium ( $\text{Ca}^{2+}$ ) ISE Low Standard	10 mg/L as $\text{Ca}^{2+}$	Dilute the High Standard by a factor of 100 (from 1000 mg/L to 10 mg/L).*
Calcium ( $\text{Ca}^{2+}$ ) ISE 1 mg/L Standard	1 mg/L as $\text{Ca}^{2+}$	Dilute the Low Standard by a factor of 10 (from 10 mg/L to 1 mg/L).**

\*Perform two serial dilutions as described below.

- Combine 100 mL of the High Standard with 900 mL of distilled water. Mix well.
- Combine 100 mL of the solution made in Step a with 900 mL of distilled water. Mix well.

\*\*Perform a serial dilution as described below.

- Combine 100 mL of the Low Standard with 900 mL of distilled water. Mix well.

## Calcium ISE Replacement Membrane Modules

The Calcium Ion-Selective Electrode has a PVC membrane with a limited life expectancy. It is warranted to be free from defects for a period of twelve (12) months from the date of purchase; it is possible, however, that you may get somewhat longer use than the warranty period. If you start to notice a reduced response (e.g., distinctly different voltages or voltage ranges during calibration), it is probably time to replace the membrane module. **Important:** Do not order membrane modules far in advance of the time you will be using them; the process of degradation takes place even when they are stored on the shelf.

## Using Ionic Strength Adjuster Solutions to Improve Accuracy

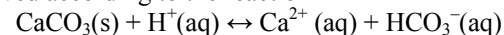
For optimal results at low concentrations of calcium ions, a standard method for taking measurements with the Calcium Ion-Selective Electrode (ISE) is to add ionic strength adjuster (ISA) solutions to each of your standard solutions and samples.

Adding an ISA ensures that the total ion activity in each solution being measured is nearly equal, regardless of the specific ion concentration. This is especially important when measuring very low concentrations of calcium ions. The ISA contains no ions common to the Calcium ISE itself. **Note:** The additions of ISA solutions to samples or standards described below do not need to have a high level of accuracy—combining the ISA solution and sample solution counting drops using a disposable Beral pipet works fine.

Add the 1.0 M KCl ISA solution (7.46 g KCl / 100 mL solution) to the  $\text{Ca}^{2+}$  standard or to the solution being measured, in a ratio of 1 part of ISA (by volume) to 50 parts of total solution (e.g., 1 mL of ISA to 50 mL of total solution, or 2 drops of ISA to 5 mL of total solution).

## Calcium in the Environment

Your Calcium Ion-Selective Electrode (ISE) can be used to determine the concentration of aqueous  $\text{Ca}^{2+}$  ions, in the range of 1.8 to 40,100 mg/L. It can be especially useful in determining “hardness of water.” Calcium ions are often found in freshwater samples as a result of water flowing over soil and mineral deposits containing limestone, chalk, magnesite, or dolomite. In one common reaction, limestone is dissolved according to the reaction



This reaction and others similar to it produce water with a relatively high concentration of  $\text{Ca}^{2+}$  ions, and lesser concentrations of  $\text{Mg}^{2+}$  and  $\text{Fe}^{3+}$  ions—known as hard water.

## Water Hardness as $\text{Ca}^{2+}$

Many methods of determining water hardness use “total hardness,” or the sum of hardness due to  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . The  $\text{Ca}^{2+}$  concentration of freshwater usually exceeds that of  $\text{Mg}^{2+}$ , thus determining the  $\text{Ca}^{2+}$  concentration alone is a good indicator of water hardness—we will refer to this measurement as “calcium hardness.” For best results, calibrate the Calcium ISE using the 10 mg/L and 1000 mg/L standards.

Using the standard solutions described here, measurements will be in units of mg/L  $\text{Ca}^{2+}$ . Units of calcium hardness are usually expressed as “calcium hardness as  $\text{CaCO}_3$ .” To convert from units of mg/L of  $\text{Ca}^{2+}$  (150 mg/L is used in this example) to units of calcium hardness as mg/L  $\text{CaCO}_3$ :

$$\frac{150 \text{ mg } \text{Ca}^{2+}}{1 \text{ L}} \times \frac{100 \text{ g } \text{CaCO}_3}{40 \text{ g } \text{Ca}^{2+}} = 375 \text{ mg/L } \text{CaCO}_3$$

It is important to remember that total hardness, the sum of calcium and magnesium levels, will be about 1.5 times higher than a calcium hardness value. Water hardness varies considerably in different parts of the United States, from levels of less than 60 mg/L (total hardness as  $\text{CaCO}_3$ ) in Washington, Oregon, Louisiana, Mississippi, Tennessee, and New England, to levels exceeding 250 mg/L in Midwestern states

(Ohio, Indiana, Illinois, Iowa, Nebraska, South Dakota, and Oklahoma). Water with a hardness as  $\text{CaCO}_3$  level greater than 120 mg/L is considered to be “hard,” while levels exceeding 180 mg/L are referred to as “very hard.” Total water hardness, the sum of calcium and magnesium hardness in mg/L  $\text{CaCO}_3$ , can be determined by titration with EDTA. A protocol can be found in our lab book *Water Quality with Vernier*. A plot of  $\ln [\text{Ca}^{2+}]$  (natural log of calcium ion concentration) vs. volume is used to determine the equivalence point. The second derivative can be used to calculate the point of maximum inflection at the equivalence point of the titration.

## Warranty

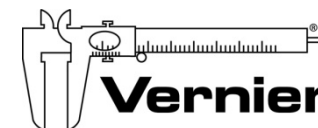
Vernier warrants this product to be free from defects in materials and workmanship for a period of five years from the date of shipment to the customer. This warranty does not cover damage to the product caused by abuse or improper use. ISE modules are covered by a one-year warranty.

## Related Products

- Ammonium Ion-Selective Electrode: NH4-BNC
- Chloride Ion-Selective Electrode: CL-BNC
- Nitrate Ion-Selective Electrode: NO3-BNC
- Potassium Ion-Selective Electrode: K-BNC
- Electrode Amplifier: EA-BTA
- Go Wireless Electrode Amplifier: GW-EA

## Replacement Products

- Standard High Calcium ISE Solution: CA-HST
- Standard Low Calcium ISE Solution: CA-LST
- Calcium Replacement Module: CA-MOD



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