

CALCIUM ION SELECTIVE ELECTRODES ISE-8740

Operator's Manual

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SECTION 1 GENERAL DESCRIPTION

The OMEGA® Calcium Ion Selective Electrodes are used to quickly, simply, accurately, and economically measure calcium ions in aqueous solutions.

SECTION 2 PREPARATION FOR MEASUREMENT

2.1 REQUIRED EQUIPMENT

1. A pH/mV meter or an ion meter, either line operated or portable.
2. Semi-logarithmic 4-cycle graph paper for preparing calibration curves when using the meter in the mV mode.
3. A magnetic stirrer.
4. The OMEGA Calcium Ion Electrode, ISE-8740 (reference electrode necessary).
5. OMEGA Double Junction Reference Electrode, PHE-3211.

2.2 REQUIRED SOLUTIONS

1. Deionized or distilled water for solution and standard preparation.
2. Ionic Strength Adjuster, ISE-8740-R1, 4M KCl, to adjust the pH and to keep a constant background ionic strength present in the solution. To prepare the 4M KCl ISA from your own laboratory stock, add 29.8 grams of reagent-grade potassium chloride (KCl) to a 100 mL volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid and fill to the mark with distilled water. Cap the flask and invert several times to mix the solution. Add 2 mL of ISA to every 100 mL of sample or standard solution for an ionic background strength of 0.10M.
3. OMEGA Calcium Standard, 0.1M CaCl₂, ISE-8740-S1. To prepare this standard, add 11.1 grams of reagent-grade calcium chloride to a 1 liter volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid and fill to the mark with distilled water. Cap the flask and invert several times to mix the solution.
4. Calcium Standard, 1000 ppm. To prepare this standard, add 250 mL of the 0.1M standard to a 1 liter volumetric flask and dilute to the mark with distilled water. Cap the flask and invert several times to mix the solution.

5. Calcium Standard, in ppm as CaCO_3 . To prepare a 1000 ppm stock solution, transfer 10 mL of the 0.1M standard to a 100 mL volumetric flask and dilute to the mark with distilled water. Cap the flask and invert several times to mix the solution.
6. Calcium Standard, 100 ppm as CaCO_3 . To prepare this solution, dilute 10 mL of the solution prepared in step 5 to 100 mL in a 100 mL volumetric flask, cap the flask, and invert several times to mix the solution.
7. EDTA titrant, 1M stock solution, for the titration of calcium. Add 37.2 grams of reagent grade $\text{Na}_4\text{EDTA}\cdot 2\text{H}_2\text{O}$, ethylenediamine-tetracetic acid dihydrate, tetra sodium salt, to a 100 mL volumetric flask, add about 75 mL of distilled water, and swirl the flask to dissolve the solid. Fill to the mark with distilled water, cap, and invert several times to mix the solution.

2.3 ELECTRODE PREPARATION

Remove the rubber cap covering the electrode tip and the rubber ban covering the filling hole of the reference electrode. Fill the reference electrode salt bridge with the appropriate filling solution.

Soak the tip of the calcium electrode in distilled water for 15 minutes, followed by standard calcium solution (10^{-3} M or 100 ppm) for 1 hour.

Connect the electrode to the proper terminal as recommended by the meter manufacturer.

NOTE

Do not be alarmed if white crystals form at end of electrode. This is normal with pH electrodes. These crystals are potassium chloride. Remove the shipping cap and rinse with distilled water to dissolve the crystals.

2.3.1 Electrode Slope Check (with standard pH/mV meter)

1. Check the electrodes on a daily basis. To a 150 mL beaker, add 100 mL of distilled water and 2 mL of ISA. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tip into the solution. If drifting or instability is observed, see the Troubleshooting section.
2. Using a pipet, add 1 mL of 0.1M or 1000 ppm calcium standard to the beaker. When the reading is stable, record the millivolt reading.

3. Again using a pipet, add 10 mL of the 0.1M or 1000 ppm calcium standard to the beaker. When the reading has stabilized, record the millivolt reading.
4. Determine the difference between the two readings. A difference of $29 \pm 2\text{mV}$ indicates correct electrode operation, assuming the solution temperature is between 20° and 25°C . Refer to the Troubleshooting section if the potential change is not within this range.

Slope is defined as the change in potential observed when the concentration changes by a factor of 10.

2.3.2 Electrode Slope Check (with ion meter)

1. Check the electrodes on a daily basis. Prepare standard calcium solutions whose concentrations vary by tenfold. Use either the 0.1M Ca^{+2} or the 1000 ppm Ca^{+2} standard stock solutions. Use the serial dilution method for this preparation.
2. To a 150 mL beaker, add 100 mL of the lower value standard and 2 mL of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip into the solution.
3. Assure that the meter is in the concentration mode.
4. Adjust the meter to the concentration of the standard and fix the value in the memory according to the meter manufacturer's instructions.
5. Rinse the electrode with distilled water and blot dry.
6. To a 150 mL beaker, add 100 mL of the higher value standard and 2 mL of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip into the solution.
7. Adjust the meter to the concentration of the standard and fix the value in the memory.
8. Read the electrode slope according to the meter manufacturer's instructions. Correct electrode operation is indicated by a slope of 90-100%. Refer to the Troubleshooting section if the slope is not within this range.

SECTION 3 MEASUREMENT PROCEDURE

3.1 MEASURING HINTS

All samples and standards should be at the same temperature for precise measurement, preferably ambient temperature.

Constant, but not violent, stirring is necessary for accurate measurement. Magnetic stirrers can generate sufficient heat to change the solution temperature. To counteract this effect, place a piece of insulating material, such as styrofoam sheet or asbestos sheet, between the stirrer and beaker.

Always rinse the electrode tip with distilled water and blot dry with a fresh tissue between readings to prevent solution carryover. Do not wipe or rub the sensing membrane.

Check the electrode for air bubbles adhering to the membrane surface after immersion in solution. Agitate the electrode gently to remove the air bubbles.

A slow or sluggish electrode response may indicate surface contamination of the membrane. Soak the electrode tip in distilled water for about 5 minutes to clean the membrane. Rinse the membrane and soak in diluted standard solution for about 1 hour to restore performance.

When measuring samples with high ionic strength, prepare standards with compositions similar to that of the sample.

Dilute concentrated samples (over 0.1M) before measurement.

3.2 SAMPLE REQUIREMENTS

Make sure that the samples and standards are at the same temperature. About a 2% error will be introduced for a 1°C difference in temperature. Temperature should be less than 40°C.

All samples and standards must be aqueous. They must not contain organic solvents. Interferences found in Table 4-1 should be absent.

3.3 UNITS OF MEASUREMENT

Calcium ion concentrations are measured in units of parts per million as calcium parts per million as CaCO₃, moles per liter, or any other convenient concentration unit. Table 3-1 indicates some of the concentration units.

TABLE 3-1
CONCENTRATION UNIT CONVERSION FACTORS

<u>ppm Ca⁺²</u>	<u>ppm CaCO₃</u>	<u>moles/liter Ca⁺²</u>	<u>%Ca⁺²</u>
4.0	10	1 x 10 ⁻⁴	0.0004
40.1	100.1	1 x 10 ⁻³	0.004
400.8	1000.9	1 x 10 ⁻²	0.04
4008.0	10008.9	1 x 10 ⁻¹	0.4

3.4 MEASUREMENT PROCEDURES

Direct measurement is a simple procedure for measuring a large number of samples. A single meter reading is all that is required for each sample. The ionic strength of samples and standards should be made the same by adjustment with ISA for all calcium samples. The temperature of both sample solution and of standard solutions should be the same.

Titration is the progression and quantitative addition of a reagent to a measured sample until neither active species (reagent or sample) is in excess. Ion selective electrodes are excellent end point detectors since they are not influenced by solution color or turbidity. Though titrations are more time-consuming than direct measurement, they are about 10 times more accurate.

3.4.1 Direct Measurement (using a standard pH/mV meter)

1. By serial dilution, prepare 10^{-2} , 10^{-3} , and 10^{-4} M or 100, 10, and 1 ppm standards by serial dilution of the 0.1M or 1000 ppm standard. Add 2 mL of ISA per 100 mL of standard.
2. Place the most dilute solution (10^{-4} M or 1 ppm) on the magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tip into the solution. When the reading has stabilized, record the mV reading.
3. Place the midrange solution (10^{-3} M or 10 ppm) on the magnetic stirrer and begin stirring. After rinsing the electrode with distilled water and blotting dry, immerse the electrode tip in the solution. When the reading has stabilized, record the mV reading.
4. Place the most concentrated solution (10^{-2} M or 100 ppm) on the magnetic stirrer and begin stirring. After rinsing the electrode with distilled water and blotting dry, immerse the electrode tip in the solution. When the reading has stabilized, record the mV reading.
5. Using the semi-logarithmic graph paper, plot the mV reading (linear axis) against the concentration (log axis). A typical calibration curve can be found in Figure 3-1.

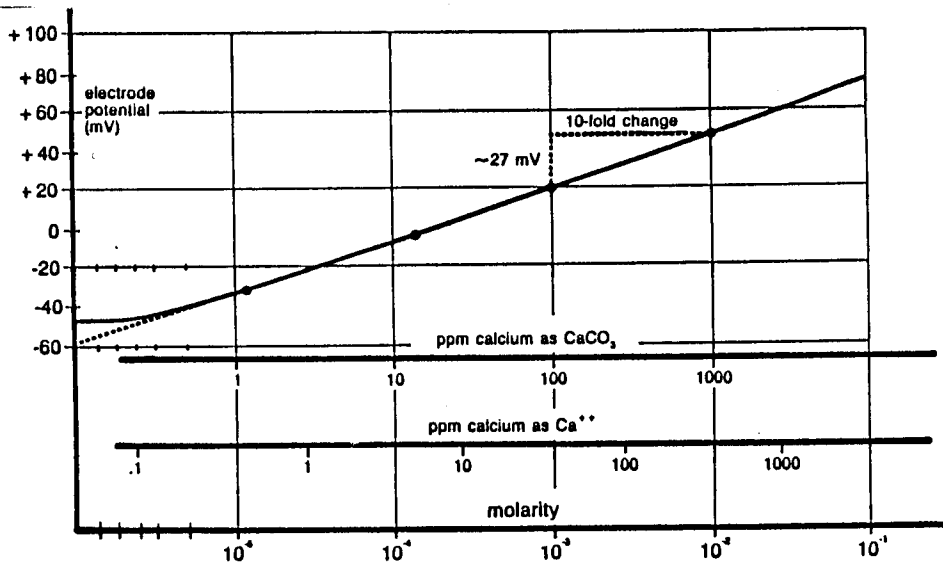


Figure 3-1. Typical Calcium Electrode Calibration Curve

A calibration curve is constructed on semi-logarithmic paper when using a pH/mV meter in the direct measurement procedure. The measured electrode potential in mV (linear axis) is plotted against the standard concentration (log axis). In the linear region of the curve, only three standards are necessary to determine a calibration curve. In the non-linear region, additional points must be measured. The direct measurement procedures given are for the linear portion of the curve. The non-linear portion of the curve requires the use of low level procedure.

Extrapolate the curve down to about $1 \times 10^{-5}M$ or 0.4 ppm.

6. To a clean, dry 150 mL beaker, add 100 mL of sample and 2 mL of ISA. Place the beaker on the magnetic stirrer and begin stirring. Place the electrode tip in the solution. When the reading has stabilized, record the millivolt reading. Determine the concentration directly from the calibration curve.
7. The electrode should be re-calibrated every 1-2 hours. Repeat steps 2-5.

3.4.2 Direct Measurement of Calcium (using an ion meter)

1. By serial dilution of the 0.1M or 1000 ppm calcium standard, prepare two calcium standards whose concentration is near the expected sample concentration. Measure out 100 mL of each standard into individual 150 mL beakers and add 2 mL of ISA to each.

2. Place the most dilute solution on the magnetic stirrer and begin stirring at a constant rate. Assure that the meter is in the concentration mode.
3. Lower the electrode tip into the solution.
4. Adjust the meter to the concentration of the calcium standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
5. Rinse the electrode tip with distilled water and blot dry.
6. Place the most concentrated solution on the magnetic stirrer and begin stirring at a constant rate.
7. Lower the electrode tip into the solution.
8. Adjust the meter to the concentration of the calcium standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
9. For low level measurements, place the rinsed, dried electrode into a solution containing 100 mL of distilled water and 2 mL of ISA. After stabilization, fix the blank value in the meter according to the meter manufacturer's instructions.
10. Place 100 mL of the sample and 2 mL of ISA in a 150 mL beaker, place it on the magnetic stirrer, and begin stirring.
11. Immerse the electrode tip in the solution and wait for the reading to stabilize. Read the concentration directly from the meter display.
12. The electrode should be re-calibrated every 1-2 hours. Simply repeat steps 2-8 (9).

3.4.3 Low Level Determination (using a standard pH/mV meter)

This procedure is recommended for solutions with ionic strengths less than $1 \times 10^{-2}M$. If the solution is high in ionic strength, but low in calcium, use the same procedure, but prepare a calibration solution with a composition similar to the sample.

1. Using 25 mL of stock ISA, dilute to 100 mL with distilled water.
2. Dilute 1 mL of the 0.1M standard to 1000 mL to prepare a $1.0 \times 10^{-4}M$ standard solution for measurement in moles per liter. Dilute 1 mL of the 1000 ppm standard to prepare a 10 ppm standard solution for measurements in ppm.
3. Soak the calcium ion electrode for at least 1 hour in the $10^{-3}M$ or 100 ppm calcium standard solution.

4. To a 150 mL beaker, add 100 mL of distilled water and 1 mL of low level ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.
5. Place the electrode tip in the solution. Assure that the meter is in the mV mode.
6. Add increments of the 1.0×10^{-4} M or 10 ppm standard as given in Table 3-2.
7. After the reading has stabilized, record the mV reading after each addition.

TABLE 3-2
STEPWISE CALIBRATION FOR LOW LEVEL CALCIUM MEASUREMENTS

<u>Step</u>	<u>Pipet</u>	<u>Added Volume (mL)</u>	<u>Concentration</u>	
			<u>ppm</u>	<u>M</u>
1	A	0.1	1.0×10^{-2}	1.0×10^{-7}
2	A	0.1	2.0×10^{-2}	2.0×10^{-7}
3	A	0.2	4.0×10^{-2}	4.0×10^{-7}
4	A	0.2	6.0×10^{-2}	6.0×10^{-7}
5	A	0.4	1.0×10^{-1}	9.9×10^{-7}
6	B	2.0	2.9×10^{-2}	2.9×10^{-6}
7	B	2.0	4.8×10^{-1}	4.8×10^{-6}

Pipet A = 1 mL graduated pipet

Pipet B = 2 mL pipet

Solutions: additions of 1.0×10^{-4} M or 10 ppm standard to 100 mL of distilled water and 1 mL of low level ISA.

8. On semi-logarithmic graph paper, plot the mV reading (linear axis) against the concentration (log axis) as in Figure 3-1.
9. Rinse the electrode in distilled water and blot dry.
10. Measure out 100 mL of the sample into a 150 mL beaker, add 1 mL of low level ISA, and place the beaker on the magnetic stirrer. Begin stirring. Lower the electrode tip into the solution.
11. After the reading has stabilized, record the mV reading and determine the concentration from the low level calibration curve.
12. Prepare a new low level calibration curve daily. Check the calibration curve every 1-2 hours by repeating steps 3-7.

3.4.4 Low Level Determination (using an ion meter)

Follow the procedure given for normal calcium determinations using an ion meter and the blank correction procedure.

3.5 TITRATION OF CALCIUM

The method outlined in this section makes use of the calcium ion electrode as a highly sensitive end point detector for calcium-containing samples. The titrant used is EDTA.

EDTA complexes calcium as well as other cations. The sample pH can be adjusted to pH 10 by adding ammonia to eliminate unwanted ion complexes. Masking agents can be added in some cases.

1. Soak the calcium ion electrode tip in $10^{-3}M$ or 100 ppm calcium standard solution for a minimum of one hour prior to use.
2. Prepare the stock EDTA titrant as given in Section 2.2, Required Solutions. Dilute the EDTA to 10 to 20 times as concentrated as the suspected sample concentration. The sample should contain at least $1.0 \times 10^{-3} M$ calcium for a good detection of the end point.
3. Fill a 50 mL buret with the EDTA solution. Pipet 100 mL of the sample into a 150 mL beaker, place the beaker on the magnetic stirrer and begin stirring at a constant rate. Adjust the sample to pH 10 by adding ammonia.
4. Position the buret tip in the beaker, slightly above the liquid level in the beaker and slightly off center. Position the electrode tip in the solution about half-way between the center of the beaker and the beaker wall.
5. Begin adding the EDTA in 0.5 mL to 1.0 mL increments and about 0.1 mL to 0.2 mL increments as the potential begins to change more rapidly. Record the mV potential after each addition. Continue the additions several milliliters past the end point.
6. Plot the milliliters of EDTA added against the mV potential on standard coordinate graph paper. Refer to Figure 3-2. The point of greatest potential change is the end point.
7. The calcium ion concentration from the unknown is calculated as follows:

$$M_{Ca^{+2}} = \frac{V_t M_t}{V_{Ca^{+2}}}$$

where:

- $M_{Ca^{+2}}$ = concentration of calcium ion in the unknown (moles/liter)
- V_t = volume of EDTA added at end point
- M_t = EDTA concentration (moles/liter)
- $V_{Ca^{+2}}$ = volume of unknown sample

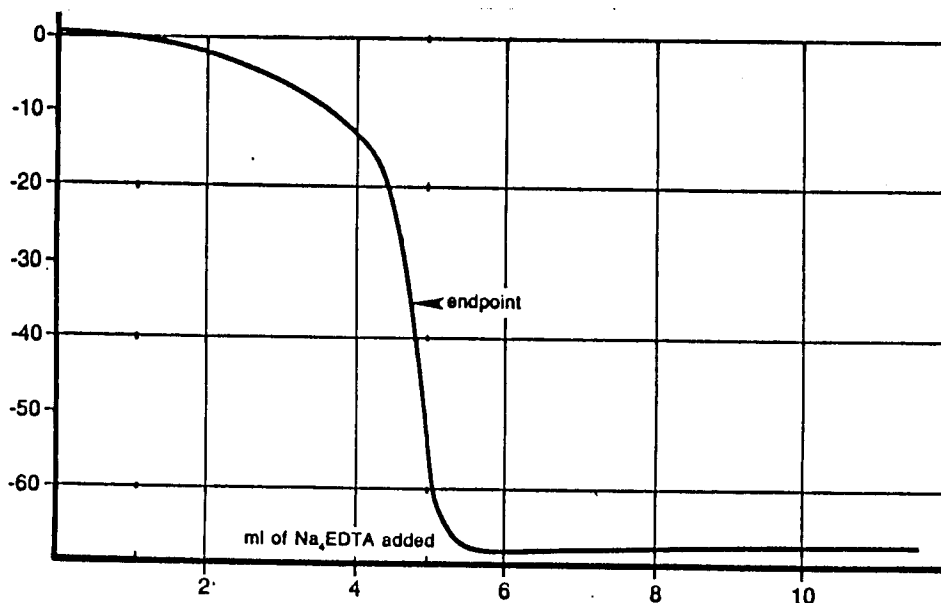


Figure 3-2. Typical Titration of 100mL of $5 \times 10^{-3} \text{M CaCl}_2$ (pH adjusted to 10 with ammonia) with 0.1 Na_4EDTA

SECTION 4 ELECTRODE CHARACTERISTICS

4.1 REPRODUCIBILITY

Direct electrode measurements reproducible to $\pm 2\%$ can be obtained if the electrode is calibrated every hour. Factors such as temperature fluctuations, drift, and noise, limit reproducibility. Reproducibility is independent of concentration within the electrode's operating range.

4.2 INTERFERENCES

Table 4-1 lists some common cations that, if present in high enough levels, will cause electrode interferences and measurement errors, or electrode drift when using the calcium ion electrodes.

Electrode drift and slow response could indicate the presence of high interference from the ions listed. Soak the electrode in distilled water for an hour, then for two hours in calcium standard solution to restore proper response.

TABLE 4-1
CONCENTRATION OF POSSIBLE INTERFERENCES CAUSING A 10% ERROR AT
VARIOUS LEVELS OF CALCIUM CHLORIDE
 (Background ionic strength is 0.08M KCl)

<u>Interferences</u> (moles/liter)	<u>10⁻²M Ca⁺²</u>	<u>10⁻³M Ca⁺²</u>	<u>10⁻⁴M Ca⁺²</u>
Mg ⁺²	1.0 x 10 ¹	1.0	1.0 x 10 ⁻¹
Zn ⁺²	1.0 x 10 ¹	1.0	1.0 x 10 ⁻¹
Ba ⁺²	7.0	7.0 x 10 ⁻¹	7.0 x 10 ⁻²
K ⁺¹	4.0	4.0 x 10 ⁻¹	4.0 x 10 ⁻²
Li ⁺¹	3.0	3.0 x 10 ⁻¹	3.0 x 10 ⁻²
Tris ⁺¹	3.0	3.0 x 10 ⁻¹	3.0 x 10 ⁻²
Na ⁺¹	2.0	2.0 x 10 ⁻¹	2.0 x 10 ⁻²
NH ₄ ⁺¹	2.0	2.0 x 10 ⁻¹	2.0 x 10 ⁻²
Ni ⁺²	5.0 x 10 ⁻¹	5.0 x 10 ⁻²	5.0 x 10 ⁻³
Cu ⁺²	4.0 x 10 ⁻¹	4.0 x 10 ⁻²	4.0 x 10 ⁻³
Fe ⁺²	2.0 x 10 ⁻²	2.0 x 10 ⁻³	2.0 x 10 ⁻³
Sr ⁺²	6.0 x 10 ⁻²	6.0 x 10 ⁻³	6.0 x 10 ⁻⁴
H ⁺¹	4.0 x 10 ⁻²	4.0 x 10 ⁻³	4.0 x 10 ⁻⁴
Hg ⁺²	4.0 x 10 ⁻²	4.0 x 10 ⁻³	4.0 x 10 ⁻⁴
Pb ⁺²	1.0 x 10 ⁻⁴	1.0 x 10 ⁻⁵	1.0 x 10 ⁻⁶

<u>Interferences</u> (ppm)	<u>1000 ppm CaCO₃</u>	<u>100 ppm CaCO₃</u>	<u>10 ppm CaCO₃</u>
Mg ⁺²	2.43 x 10 ⁵	2.43 x 10 ⁴	2.43 x 10 ³
Zn ⁺²	6.53 x 10 ⁵	6.53 x 10 ⁴	6.53 x 10 ³
Ba ⁺²	9.60 x 10 ⁵	9.60 x 10 ⁴	9.60 x 10 ³
K ⁺¹	1.56 x 10 ⁵	1.56 x 10 ⁴	1.56 x 10 ³
Li ⁺¹	2.08 x 10 ⁴	2.08 x 10 ³	2.08 x 10 ²
Tris ⁺¹	3.63 x 10 ⁵	3.63 x 10 ⁴	3.63 x 10 ³
Na ⁺¹	4.60 x 10 ⁴	4.60 x 10 ³	4.60 x 10 ²
NH ₄ ⁺¹	3.40 x 10 ⁴	3.40 x 10 ³	3.40 x 10 ²
Ni ⁺²	2.94 x 10 ⁴	2.94 x 10 ³	2.94 x 10 ²
Cu ⁺²	2.54 x 10 ⁴	2.54 x 10 ³	2.54 x 10 ²
Fe ⁺²	1.11 x 10 ⁴	1.11 x 10 ³	1.11 x 10 ²
Sr ⁺²	5.20 x 10 ³	5.20 x 10 ²	5.20 x 10 ¹
H ⁺¹	1.4 pH	2.4 pH	3.4 pH
Hg ⁺²	8.0 x 10 ³	8.0 x 10 ²	8.0 x 10 ¹
Pb ⁺²	2.0 x 10 ¹	2.0	2.0 x 10 ⁻¹

4.3 TEMPERATURE INFLUENCES

Samples and standards should be at the same temperature, since electrode potentials are influenced by changes in temperature. A 1°C difference in temperature results in a 4% error at the 1.0 x 10⁻³ M level.

Provided that temperature equilibria has occurred, the calcium ion selective electrodes can be used at temperatures from 0 to 40°C. Room temperature measurements are recommended, since measurements at temperatures markedly different from room temperature may require equilibrium times up to one hour.

Table 4-2 indicates the variation of theoretical slope with temperature.

TABLE 4-2
TEMPERATURE VS. VALUE FOR THE ELECTRODE SLOPE

Temp. (°C)	S
0	27.10
10	28.10
20	29.08
25	29.58
30	30.07
40	31.07
50	32.06

4.4 ELECTRODE RESPONSE

Plotting the electrode mV potential against the calcium concentration on semi-logarithmic paper results in a straight line with a slope of about 25-30 mV per decade. Refer to Figure 3-1.

The time needed to reach 99% of the stable electrode potential reading, the electrode response time, varies from one minute or less for calcium concentration above $1.0 \times 10^{-5}M$ to several minutes near the detection limit. Refer to Figure 4-1.

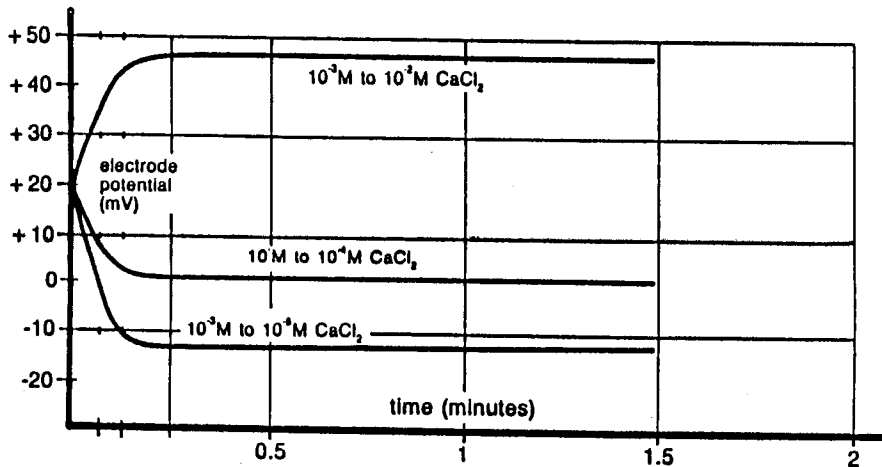


Figure 4-1. Typical Electrode Response to Step Changes in CaCl₂

4.5 ELECTRODE STORAGE

The electrodes may be stored in 1.0×10^2 M calcium standard for short periods of time. For storage over three weeks, rinse and dry the indicating electrode and cover the tip with the rubber cap. The salt-bridge of the reference electrode should be drained of filling solution, the rubber band placed over the filling hole and the rubber cap replaced on the electrode tip.

4.6 DETECTION LIMIT

The upper limit of detection is 1M in pure calcium chloride solutions. The upper limit of detection is above 1.0×10^{-1} M when other ions are present, but the possibility of a liquid junction potential developing at the reference electrode and the "salt extraction effect" are two limiting factors. Some salts may be extracted into the electrode membrane at high salt concentrations, causing deviation from theoretical response. Calibrate the electrode at four or five intermediate points, or dilute the sample, to measure samples between 1.0×10^{-1} M and 1M.

The slight water solubility of the ion exchanger in the sensing module, which causes deviation from theoretical response, determines the lower limit of detection. The theoretical response at low levels of calcium chloride compared to actual response is shown in Figure 4-1. A low level measurement is recommended if calcium measurements are made below 1.0×10^{-5} M (0.04 ppm as Ca^{+2} or 1 ppm as CaCO_3).

4.7 pH EFFECTS

Hydrogen ion interferes with measurements of low levels of calcium ion, although the electrode can be used over a wide pH range. Table 4-1 should be used to determine the minimum pH of which low level calcium measurements can be made without more than a 10% error due to hydrogen ion interference.

Sufficient hydroxide ion will be present to form a precipitate with calcium ion at a high pH. Since the electrode only measures the free calcium ion in the solution, it will not measure the calcium precipitated as calcium hydroxide. Use 1M HCl, when necessary, to adjust the pH to below 11 for samples and standards to avoid precipitation.

4.8 COMPLEXATION AND PRECIPITATION

Hydroxide, sulfate, bicarbonate, carbonate, and EDTA are the most common species that complex calcium ions. The level of calcium ion, the level of the complexing ion, the pH of the solution, and the total ionic strength of the solution determine the extent of the complexation. Complexation reduces the free calcium ion concentration and, since the electrode responds only to free calcium ions, a false reading results.

To avoid formation of CaSO_4 , the sulfate concentrations must be less than 5×10^{-4} M (50 ppm). To avoid CaCO_3 or formation of the CaHCO_3^+ M complex, the pH of the solution should be less than 7, and the total carbonate/bicarbonate concentration should be less than 3×10^{-3} M (280 ppm carbonate).

4.9 THEORY OF OPERATION

The calcium electrode consists of an electrode body containing an ion exchanger in a sensing module. This sensing module contains a liquid internal filling solution in contact with a gelled organophilic membrane containing a calcium selective ion exchanger.

An electrode potential develops across the membrane when the membrane is in contact with a calcium solution. Measurement of this potential against a constant reference potential with a digital pH/mV meter or with a specific ion meter depends on the level of free calcium ion in solution. The level of calcium ions, corresponding to the measured potential, is described by the Nernst equation:

$$E = E_0 + S \log X$$

where:

- E = measured electrode potential
- E_0 = reference potential (a constant)
- S = electrode slope (29 mV/decade)
- X = level of calcium ions in solution

The activity, X, represents the effective concentration of the ions in solution. Total calcium concentration, C_t , includes free calcium ions, C_f , plus bound or complexed calcium ions, C_b . Since the calcium electrodes only respond to free ion, the free ion concentration is:

$$C_f = C_t - C_b$$

The activity is related to the free ion concentration, C_f , by the activity coefficient, ζ , by:

$$X = \zeta C_f$$

Activity coefficients vary, depending on total ionic strength, I, defined as:

$$I = 1/2 \sum C_x Z_x^2$$

where:

- C_x = concentration of ion X
- Z_x = charge of ion X
- \sum = sum of all types of ions in the solution.

In the case of high and constant ionic strength relative to the sensed ion concentration, the activity coefficient, ζ , is constant and the activity, X, is directly proportional to the concentration.

To adjust the background ionic strength to a high and constant value, ionic strength adjustor (ISA) is added to samples and standards. The recommended ISA for calcium is potassium chloride, KCl. Solutions other than this may be used as long as ions that they contain do not interfere with the electrode's response to calcium ions.

The reference electrode must also be considered. When two solutions of different composition are brought into contact with one another, liquid junction potentials arise. Millivolt potentials occur from the interdiffusion of ions into the two solutions. Electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions, since ions diffuse at different rates. When making measurements, it is important to remember that this potential be the same when the reference is in the standardizing solution as well as in the sample solution, or the change in liquid junction potential will appear as an error in the measured electrode potential.

The composition of the liquid junction filling solution in the reference electrode is most important. The speed with which the positive and negative ions in the filling solution diffuse into the sample should be as nearly equal as possible, that is, the filling solution should be equitransferant. No junction potential can result if the rate at which positive and negative charge carried into the sample are equal.

Strongly acidic (pH = 0-2) and strongly basic (pH = 12-14) solutions are particularly troublesome to measure. The high mobility of hydrogen and hydroxide ions in samples make it impossible to mask their effect on the junction potential with any concentration of an equitransferant salt. One must either calibrate the electrodes in the same pH range as the samples or use a known increment method for ion measurement.

SECTION 5 TROUBLESHOOTING

SYMPTOM	POSSIBLE CAUSES	NEXT STEP
Out of range reading	Defective meter	Check meter with shorting strap
	Electrodes not plugged in properly	Reseat electrodes
	Reference electrode not filled	Be sure reference electrode is filled
	Air bubbles on membrane	Remove bubble by redipping electrode
	Calibration control not turned far enough	Continue turning the calibration control
"Incorrect Answer" (but calibration curve is good)	Incorrect scaling of semilog paper	Plot millivolts on the linear axis. On the log axis, be sure concentration numbers within each decade are increasing with increasing concentration
	Incorrect sign	Be sure to note sign of millivolt number correctly
	Incorrect standards	Prepare fresh standards
	Wrong units used	Apply correct conversion factor: $10^{-3}\text{M} = 40 \text{ ppm}$ $\text{Ca}^{+2} = 100 \text{ ppm as CaCO}_3$.
	Complexing agents in sample	Use titration or decomplexing procedure
	Drift (reading slowly changing in one direction)	Samples and standards at different temperatures
Electrode exposed to interferences		Soak electrode in calcium standard
Incorrect reference filling solution		Use recommended filling solution

TROUBLESHOOTING (Cont'd)

SYMPTOM	POSSIBLE CAUSES	NEXT STEP
Low slope or no slope	Standards contaminated or incorrectly made	Prepare fresh standards
	ISA not used	Use recommended ISA
	Standard used as ISA	Use ISA
Noisy or unstable readings (continuously or rapidly changing)	Electrode exposed to interferences	Soak electrode in calcium standard
	Defective meter	Check meter with shorting strap
	Wrong reference electrode	Do not use calomel or Ag/AgCl (frit or fiber-type) reference electrode
	Air bubble on membrane	Remove bubble by redipping electrode
	ISA not used	Use recommended ISA
	Meter or stirrer not grounded	Ground meter or stirrer

SECTION 6 SPECIFICATIONS

CONCENTRATION RANGE: 1M to 5×10^{-7} M
(4.01×10^4 ppm to 2.0×10^{-2} ppm)

pH RANGE: 2.5 to 11

TEMPERATURE RANGE: 0 to 40°C

RESISTANCE: 1 to 4 Mohm

REPRODUCIBILITY: $\pm 2\%$

SAMPLES: Aqueous solutions only; no organic solvents

SIZE: 110 mm in length
12 mm in diameter
1 m cable length