pHOENIX ELECTRODE COMPANY
CALCIUM ELECTRODES
INSTRUCTION MANUAL

GENERAL INSTRUCTIONS

Introduction

The pHoenix Calcium Electrodes are used to quickly, simply, accurately, and economically measure calcium in aqueous solutions.

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 pHoenix Calcium Electrode, Cat. No. CAL1501, (reference electrode necessary), the pHoenix Calcium Ion Combination Glass Electrode, Cat. No. CAL1502, or the pHoenix Calcium Ion Combination Epoxy Electrode, Cat. No. CAL1503.

5. The pHoenix Single Junction Reference Electrode, Cat. No. 5731428 (for use with the CAL1501) with pHoenix Filling Solution, Cat. No. R001011, in the reference junction.

Required Solutions

1. Deionized or distilled water for solution and standard preparation.

2. pHoenix Calcium Standard, 0.1M $CaCl_2$, Cat. No. CALAS01. To prepare this solution from your own laboratory stock, half fill a one liter volumetric flask with distilled water and add 14.7 grams of reagent-grade calcium chloride ($CaCl_2.2H_2O$). Swirl the flask gently to dissolve the solid. Fill to the mark with distilled water, cap, and upend several times to mix the solution.

3. pHoenix Calcium Standard, 1000 ppm Ca^{+2}, Cat. No. CALAS02. To prepare this solution from you own laboratory stock, half fill a one liter volumetric flask with distilled water and add 3.67 grams of reagent-grade calcium chloride ($CaCl_2.2H_2O$). Swirl the flask gently to dissolve the solid. Fill to the mark with distilled

water, cap, and upend several times to mix the solution.

4. pHoenix Calcium Standard, 100 ppm Ca^{+2} as $CaCO_3$, Cat. No. CALAS03. To prepare this solution from your own laboratory stock, half fill a one liter volumetric flask with distilled water and add 0.15 grams of reagent-grade calcium chloride ($CaCl_2.2H_2O$). Swirl the flask gently to dissolve the solid. Fill to the mark with distilled water, cap, and upend several times to mix the solution.

5. pHoenix Ionic Strength Adjuster (ISA), 4 M KCl, Cat. No. CALIS01. To prepare this solution from your own laboratory stock, half fill a 1000 ml volumetric flask with distilled water and add 298 grams of reagent-grade potassium chloride (KCl). Swirl the flask gently to dissolve the solid. Fill to the mark with distilled water, cap, and upend several times to mix the solution.

6. EDTA titrant, 1M stock solution, for the titration of calcium. To prepare this titrant, add 37.2 grams of reagent grade $Na_2EDTA \cdot 2H_2O$, ethylenediaminetetraacetic acid dihydrate, disodium salt, to a 100 ml volumetric flask, add about 75 ml of distilled water, and swirl the flask gently to dissolve the solid. Fill to the mark with distilled water, cap, and upend several times to mix the solution.

GENERAL PREPARATION

Electrode Preparation

Remove the rubber caps covering the electrode tips and the rubber insert covering the filling hole of the reference electrode. Fill the combination electrode or the reference electrode with the filling solution shipped with the electrode to a level just below the fill hole. No preparation is required with a sealed reference electrode. Gently shake the electrode downward in the same manner as a clinical thermometer to remove any air bubbles which might be trapped behind the calcium membrane. Prior to first usage, or after long-term storage, immerse the calcium membrane in calcium standard for thirty minutes. The electrode is now ready for use.

Connect the electrodes to the proper terminals as recommended by the meter manufacturer.

Electrode Slope Check (with pH/mV meter) (check electrodes each day)

1. To a 150 ml beaker, add 100 ml of distilled water. Place the beaker on a magnetic stirrer and begin

stirring at a constant rate. After assuring that the meter is in the

millivolt mode, lower the electrode tips into the solution. If drifting or instability is observed, see the **TROUBLESHOOTING** section.

2. Using a pipet, add 1 ml of 0.1M, 1000 ppm, or 100 ppm (as calcium carbonate) standard and 2 ml of ISA to the beaker. When the reading is stable, record the mV reading.

3. Using a pipet, add 10 ml of the same calcium standard used above to the beaker. When the reading has stabilized, record the mV reading.

4. Determine the difference between the two readings. The electrode is operating correctly if the mV potential has changed by 27 " 2 mV, assuming the solution temperature is between 20^{o} and 25^{o}C. See 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.

Electrode Slope Check (with ion meter)
(check electrodes each day)

1. Prepare standard calcium solutions whose concentrations vary by tenfold. Use either the 0.1M Ca^{+2}, 1000 ppm Ca^{+2}, or the 100 ppm Ca^{+2} (as calcium carbonate) 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 tips into the solution. Assure that the meter is in the concentration mode.

3. Adjust the meter to the concentration of the standard and fix the value in the memory according to the meter manufacturer's instructions.

4. Rinse the electrodes with distilled water and blot dry.

5. To another 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 tips into the solution.

6. Adjust the meter to the concentration of the standard and fix the value in the memory.

7. Read the electrode slope according to the meter manufacturer's instructions. Correct electrode operation is indicated by a slope of 90-100%. See the **TROUBLESHOOTING** sections if the slope is not within this range.

MEASUREMENT

Measuring Hints

All samples and standards should be at the same temperature for precise measurement. A difference of 1^{o}C in temperature will result in a 4% measurement error.

The sensing membrane is normally subject to water uptake and might appear milky. This has no effect on performance.

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 a styrofoam sheet, between the stirrer and beaker.

Always rinse the electrode tips with distilled water and blot dry. Use a clean, dry tissue to prevent cross-contamination.

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

Always check to see that the membrane is free from air bubbles after immersion into standard or sample.

A slow responding electrode may be caused by interferences to the electrode. To restore proper performance, soak the electrode in distilled water for about 5 minutes to clean the membrane, rinse, and soak in diluted standard solution for about 5 minutes.

Dilute concentrated samples (over 0.1M) before measurement.

Recalibrate every few hours for routine measurement.

Sample Requirements

All samples and standards must be aqueous and not contain organics which can dissolve in the membrane or extract out the liquid ion exchanger.

The temperature of the standard solutions and of the sample solutions should be the same and below 40°C. About a 2% error will be introduced for a 1°C difference in temperature.

The pH range for the calcium ion electrode is 3-10. Neutralize samples outside this range with NaOH or HCl to bring them in range.

Interferences should be absent. If they are present, use the procedures found in the **Interferences** section to remove them.

Units of Measurement

Calcium concentrations are measured in units of ppm as calcium, ppm as $CaCO_3$, moles per liter, or any other convenient concentration unit. Table 1 indicates some of the concentration units.

TABLE 1: Concentration Unit Conversion Factors

ppm Ca^{+2}	ppm $CaCO_3$	moles/liter
4.01	10.0	1.0×10^{-4}
10.00	24.9	2.5×10^{-4}
40.10	100.1	1.0×10^{-3}
400.80	1000.9	1.0×10^{-2}

MEASUREMENT PROCEDURE

Direct Measurement

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 temperature of both sample solution and of standard solutions should be the same.

Direct Measurement of Calcium (using a pH/mV meter)

1. By serial dilution prepare three standard solutions from the 0.1M, 1000 ppm, or 100 ppm standard. The resultant concentrations should be 10^{-2}, 10^{-3}, and 10^{-4}M or 100, 10 and 1 ppm standards. Add 2 ml of ISA to each 100 ml of standard.

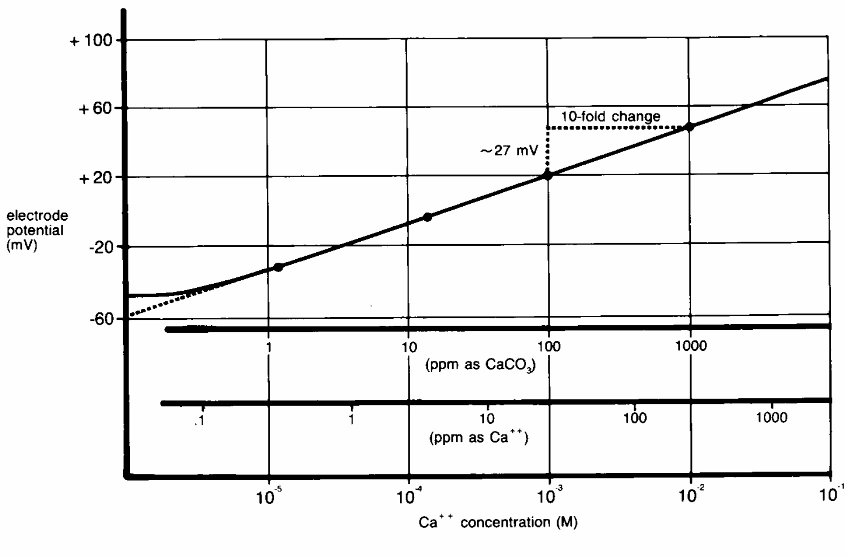
2. Place the most dilute solution ($1.0X10^{-4}$M or 1 ppm) in a 150 ml beaker on the magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tips into the solution. After the reading has stabilized, record the mV reading.

3. Place the mid-range solution ($1.0X10^{-3}$M or 10 ppm) in a 150 ml beaker on the magnetic stirrer and begin stirring. After rinsing the electrodes with distilled water, blot dry, and immerse the electrode tips in the solution. When the reading has stabilized, record the mV value.

4. Place the most concentrated solution ($1.0X10^{-2}$M or 100 ppm) in a 150 ml beaker on the magnetic stirrer and begin stirring. After rinsing the electrodes in distilled water, blot dry and immerse the electrode tips 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 1.

Figure 1
Typical calcium electrode calibration curve



A calibration curve is constructed on semi-logarithmic paper when using a pH/mV meter in the millivolt mode. 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 procedures.

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 at a constant rate. Rinse the electrode tips with distilled water, blot dry, and lower the electrode tips in the solution. When the reading has stabilized, record the mV reading. Using the calibration curve, determine the sample concentration.

7. The calibration should be checked every two hours. Assuming no change in ambient temperature, place the electrode tips in the mid-range standard. After the reading has stabilized, compare it to the original reading recorded in Step 3 above. A reading differing by more than 0.5 mV or a change in the ambient temperature will necessitate the repetition of Steps 2-5 above. A new calibration curve should be prepared daily.

Direct Measurement of Calcium (using an ion meter)

1. By serial dilution of the 0.1M, 1000 ppm, or 100 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 more dilute solution on the magnetic stirrer and begin stirring at a constant rate. Assure that the meter is in the concentration mode. Lower the electrode tips into the solution.

3. 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.

4. Rinse the electrode tips with distilled water and blot dry.

5. Place the more concentrated solution on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution.

6. 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.

7. For low level measurements, place the rinsed, dried electrodes 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.

8. Place 100 ml of the sample and 2 ml of ISA in a 150 ml beaker. Place the beaker on the magnetic stirrer and begin stirring.

9. Immerse the electrode tips in the solution and wait for the reading to stabilize. Read the concentration directly from the meter display.

10. The calibration should be checked every two hours. Assuming no change in ambient temperature, place the electrode tips in the first calcium standard. After the reading has stabilized, compare it to the original reading in Step 3 above. A reading differing by more than 0.5 mV or a change in ambient temperature will necessitate the repetition of Steps 2-6 above. The meter should be re-calibrated daily.

Low Level Calcium Determination (using a pH/mV meter)

This procedure is recommended for solutions with ionic strengths less than $1.0X10^{-2}$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. Dilute 10 ml of the 0.1M standard to 1000 ml to prepare a $1.0x10^{-3}$M standard solution for measurements in moles per liter. Dilute 10 ml of the 1000 ppm or 1 ml of the 100 ppm standard to 1000 ml to prepare a 10 ppm standard solution for measurements in ppm.

2. Soak the calcium electrode for at least 1 hour in $1.0x10^{-3}$M or 100 ppm calcium standard solution.

3. To a 150 ml beaker, add 100 ml of distilled water. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.

4. Place the electrode tips in the solution. Assure that the meter is in the mV mode.

5. Add increments of the $1.0X10^{-3}M$ or 10 ppm standard as given in Table 2 below.

6. After the reading has stabilized, record the mV reading after each addition.

TABLE 2: Step-wise Calibration for Low Level Calcium Measurements

Step	Pipet	Added Volume (ml)	Concentration M	Concentration ppm
1	A	0.1	$1.0X10^{-6}$	$1.0X10^{-2}$
2	A	0.1	$2.0X10^{-6}$	$2.0X10^{-2}$
3	A	0.2	$4.0X10^{-6}$	$4.0X10^{-2}$
4	A	0.2	$6.0X10^{-6}$	$6.0X10^{-2}$
5	A	0.4	$9.9X10^{-6}$	$1.0X10^{-1}$
6	B	2	$2.9X10^{-5}$	$2.9X10^{-1}$
7	B	2	$4.8X10^{-5}$	$4.8X10^{-1}$

Pipet A = 1 ml graduated pipet
Pipet B = 2 ml pipet
Solutions: additions of $1.0x10^{-3}M$ or 10 ppm standard to 100 ml of distilled water.

7. On semi-logarithmic graph paper, plot the mV reading (linear axis) against the concentration (log axis) as in Figure 1.

8. Rinse the electrodes in distilled water and blot dry.

9. Measure out 100 ml of the sample into a 150 ml beaker and place the beaker on the magnetic stirrer and begin stirring. Lower the electrode tips into the solution. After the reading has stabilized, record the mV reading and determine the concentration from the low level calibration curve.

10. Prepare a new low level calibration curve daily. Check the calibration curve every 1-2 hours by repeating Steps 2-7 above.

Low Level Calcium Determination (using an ion meter)

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

Titration

The progressive 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 endpoint detectors since they are not influenced by solution color or turbidity. Though titration is more time consuming than direct measurement, it is about 10 times more accurate.

Titration of Calcium

The method outlined in this section makes use of the calcium ion electrode as a highly sensitive endpoint 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 the section **Required Solutions**. Dilute the EDTA to 10 to 20 times as concentrated as the suspected sample concentration. The sample should contain at least $1.0X10^{-3}$M calcium for a good detection of the endpoint.

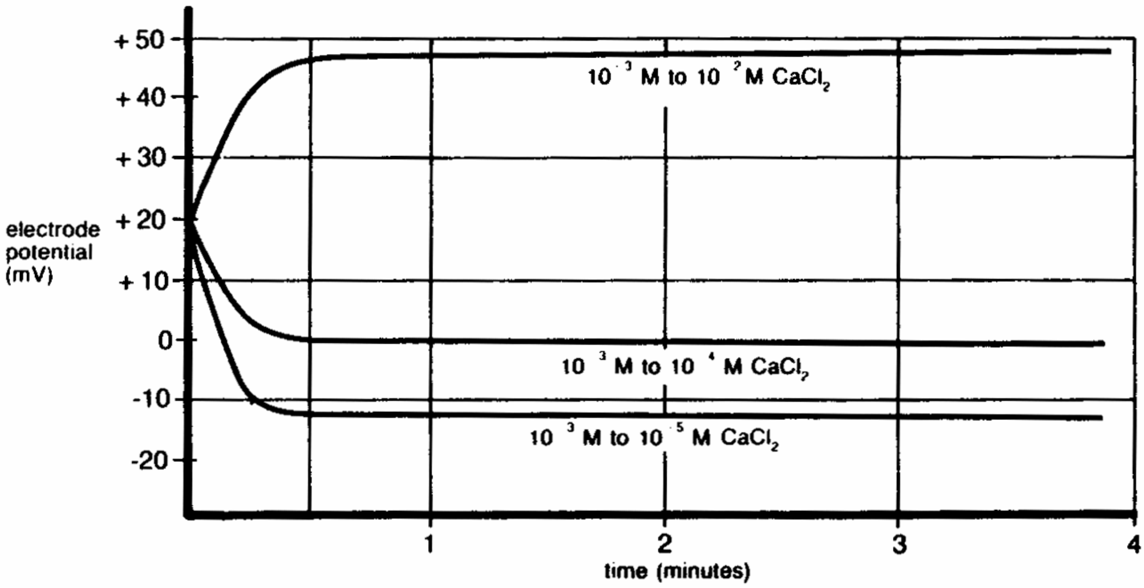
3. Fill a 50 ml buret with the EDTA solution. Pipet 100 ml of the sample into a 150 ml beaker, place the beaker on the magnetic stirrer and begin stirring at a constant rate. Adjust the sample to pH 10 by adding ammonia.

4. Position the buret tip in the beaker, slightly above the liquid level in the beaker and slightly off center. Position the electrode tips 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 endpoint.

6. Plot the milliliters of EDTA added against the mV potential on standard coordinate graph paper. (See Figure 2). The point of greatest potential change is the endpoint.

Figure 2
Typical electrode time response to step changes in $CaCl_2$



7. The calcium ion concentration from the unknown is calculated as follows.

$$V_tM_t$$

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

Where:

$M_{Ca}+2$ = concentration of calcium ion in the unknown (moles/liter)

V_t = volume of EDTA added at endpoint

M_t = EDTA concentration (moles/liter)

$V_{Ca}+2$ = volume of unknown sample

ELECTRODE CHARACTERISTICS

Reproducibility

Electrode measurements reproducible to "4% 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.

Interferences

Table 3 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 electrodes.

Electrode drift and slow response could indicate the presence of high interferences from the ions listed. Soak the electrode in distilled water for five minutes, then for five minutes in calcium standard solution to restore proper response.

TABLE 3: Concentration of Possible Interferences Causing a 10% Error at Various Levels of Calcium.

Interferences (moles/liter)	10^{-2}M	10^{-3}M	10^{-4}M
Mg^{+2}	$1.0X10^{+1}$	$1.0X10^{0}$	$1.0X10^{-1}$
Zn^{+2}	$1.0X10^{+1}$	$1.0X10^{0}$	$1.0X10^{-1}$
Ba^{+2}	$7.0X10^{0}$	$7.0X10^{-1}$	$7.0X10^{-2}$
K^{+1}	$4.0X10^{0}$	$4.0X10^{-1}$	$4.0X10^{-2}$

Na^{+1}	$2.0X10^{0}$	$2.0X10^{-1}$	$2.0X10^{-2}$
Ni^{+2}	$5.0X10^{-1}$	$5.0X10^{-2}$	$5.0X10^{-3}$
Cu^{+2}	$4.0X10^{-1}$	$4.0X10^{-2}$	$4.0X10^{-3}$
Fe^{+2}	$2.0X10^{-2}$	$2.0X10^{-3}$	$2.0X10^{-4}$
Sr^{+2}	$6.0X10^{-2}$	$6.0X10^{-3}$	$6.0X10^{-4}$
H^{+1}	$4.0X10^{-2}$	$4.0X10^{-3}$	$4.0X10^{-4}$
Hg^{+2}	$4.0X10^{-2}$	$4.0X10^{-3}$	$4.0X10^{-4}$
Pb^{+2}	$1.0X10^{-4}$	$1.0X10^{-5}$	$1.0X10^{-6}$

Interferences

(ppm)	1000 ppm $CaCO_3$	100 ppm $CaCO_3$	10 ppm $CaCO_3$
Mg^{+2}	$2.43X10^{5}$	$2.43X10^{4}$	$2.43X10^{3}$
Zn^{+2}	$6.53X10^{5}$	$6.53X10^{4}$	$6.53X10^{3}$
Ba^{+2}	$9.60X10^{5}$	$9.60X10^{4}$	$9.60X10^{3}$
K^{+1}	$1.56X10^{5}$	$1.56X10^{4}$	$1.56X10^{3}$
Ni^{+2}	$2.94X10^{4}$	$2.94X10^{3}$	$2.94X10^{2}$
Cu^{+2}	$2.54X10^{4}$	$2.54X10^{3}$	$2.54X10^{2}$
Fe^{+2}	$1.11X10^{4}$	$1.11X10^{3}$	$1.11X10^{2}$
Sr^{+2}	$5.20X10^{3}$	$5.20X10^{2}$	$5.20X10^{1}$
H^{+1}	1.4 pH	2.4 pH	3.4 pH
Hg^{+2}	$8.0X10^{3}$	$8.0X10^{2}$	$8.0X10^{1}$
Pb^{+2}	$2.0X10^{1}$	2.0	$2.0X10^{-1}$

Complexation

Sulfate, bicarbonate, and carbonate are the most common species that complex calcium ions. The level of calcium ions, 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 $5X10^{-4}$M (50 ppm). To avoid formation of $CaCO_3$ or formation of the $CaHCO_3^+$ complex, the pH of the solution should be less than 7, and the total carbonate/bicarbonate concentration should be less than $3X10^{-3}$M (280 ppm carbonate).

Temperature Influences

Samples and standards should be at the same temperature, since electrode potentials are influenced by changes in temperature. A 1^oC difference in temperature results in a 4% error at the $1.0X10^{-3}$M level.

Provided that temperature equilibria has occurred, the calcium electrodes can be used at temperatures from 0^o-40^oC. Room temperature measurements are recommended, since measurements at temperatures quite different from room temperature may require equilibrium times up to one hour. Table 4 indicates the variation of theoretical slope with temperature.

TABLE 4: Temperature vs. Value for the Electrode Slope

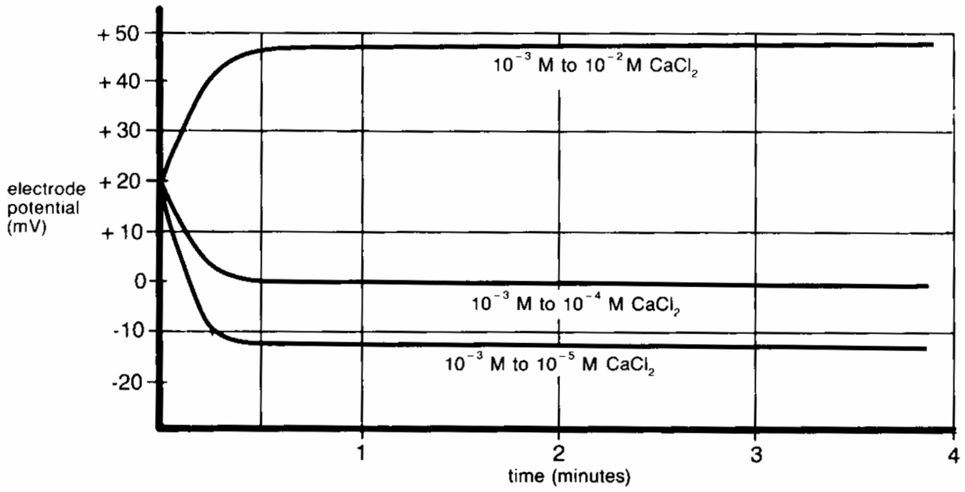
Temp (^oC)	"S"
0	27.10
10	28.10
20	29.08
25	29.58
30	30.07
40	31.07

Electrode Response

Plotting the mV potential against the calcium concentration on semi-logarithmic paper results in a straight line with a slope of about 27 mV per decade. (Refer to Figure 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 $1.0x10^{-4}$M to several minutes near the detection limit. (Refer to Figure 3.)

Figure 3
Typical electrode time response to step changes in $CaCl_2$



Limits of Detection

The upper limit of detection in pure calcium chloride solutions is 1M. In the presence of other ions, the upper limit of detection is above 1.0×10^{-1}M, 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 infuse 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 lower limit of detection is influenced by the slight water solubility of the ion exchanger used in the sensing portion of the electrode. Refer to Figure 1 for a comparison of the theoretical response to actual response at low levels of calcium chloride.

pH Effects

The operating range of the calcium electrode is from pH 3 to pH 10. Use at other pH values can adversely affect the membrane. Hydrogen ion interferes with measurements of very low levels of calcium. Hydroxide ion will complex calcium ions.

Electrode Life

The calcium electrode will last six months in normal laboratory use. On-line measurement might shorten operational lifetime to several months. In time, the response time will increase and the calibration slope will decrease to the point calibration is difficult and electrode replacement is required.

Electrode Storage

The calcium electrodes may be stored for short periods of time in $1.0X10^{-2}$M calcium standard. For longer storage (longer than two weeks), rinse and dry the calcium membrane and cover the tip with any protective cap shipped with the electrodes. The reference portion of the combination electrode (or the outer chamber of the reference electrode) should be drained of filling solution, if refillable, and the rubber insert placed over the filling hole.

ELECTRODE THEORY

Electrode Operation

The pHoenix 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:

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

where:
- E = measured electrode potential
- E_o = reference potential (a constant)
- S = electrode slope (-27 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, a, by:

$$X = a\ C_f$$

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

$$I = 23C_xZ_x^2$$

where: C_x = concentration of ion X
Z_x = charge on ion X
3 = sum of all of the types of ions in the solution

In the case of high and constant ionic strength relative to the sensed ion concentration, the activity coefficient, a, 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 adjuster (ISA) is added to samples and standards. The recommended ISA for calcium is potassium chloride, KCl. Solutions other than this may be used as ISA's 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 inter-diffusion 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 equitransferent. No junction potential can result if the rate at which positive and negative charge carried into the sample is equal.

TROUBLESHOOTING GUIDE

The goal of troubleshooting is the isolation of a problem through checking each of the system components in turn: the meter, the

glass-ware, the electrodes, the standards & reagents, the sample, and the technique.

Meter

The meter may be checked by following the check-out procedure in the instrument instruction manual.

Glass-ware

Clean glass-ware will drain clean. That is, when rinsed with distilled or deionized water, the water does not bead on the inside walls of the glass-ware.

Electrodes

The electrodes may be checked by using the procedure found in the sections entitled **Electrode Slope Check**.

1. Be sure to use distilled or deionized water when following the procedures given in **Electrode Slope Check.**

2. If the electrode fails to respond as expected, see the section **Measuring Hints**. Repeat the slope check.

3. If the electrodes still fail to respond as expected, substitute another calcium electrode that is known to be in good working order for the questionable electrode. If the problem persists and you are using an electrode pair, try the same routine with a working reference electrode.

4. If the problem persists, the standards and/or reagents may be of poor quality, interferences in the sample may be present or the technique may be faulty. (See **Standards & Reagents**, **Sample**, and **Technique** sections below.)

5. If another electrode is not available for test purposes, or if the electrode in use is suspect, review the instruction manual and be sure to:

   - Clean and rinse the electrodes thoroughly.
   - Prepare the electrodes properly.

- Use the proper filling solution.
- Adjust the pH of the solution according to the method being used for the analysis.
- Measure correctly and accurately.
- Review **TROUBLESHOOTING HINTS**.

Standards & Reagents

Whenever problems arise with the measuring procedure that has been used successfully in the past, be sure to check the standard and reagent solutions. If in doubt about the credibility of any of the solutions, prepare them again. Errors may result from contamination of the ISA, incorrect dilution of standards, poor quality distilled/deionized water, or a simple mathematical miscalculation.

Sample

Look for possible interferences, complexing agents, or substances which could affect the response or physically damage the sensing electrode (or the reference electrode) if the electrodes work perfectly in the standard, but not in the sample.

Try to determine the composition of the samples prior to testing to eliminate a problem before it starts. (See **Measuring Hints**, **Sample Requirements**, and **Interferences.**)

Technique

Be sure that the electrodes' limit of detection has not been exceeded. Be sure that the analysis method is clearly understood and is compatible with the sample. Refer to the instruction manual again. Reread **GENERAL PREPARATION** and **ELECTRODE CHARACTERISTICS**.

If trouble still persists, call pHoenix Electrode Company at 1-800-522-7920 and ask for the Technical Services Department.

TROUBLESHOOTING HINTS

Symptom	Possible Causes	Next Step
Out of Range Reading	defective meter	check meter with shorting strap (see meter instruction manual)
	defective electrode	check electrode operation
	electrodes not plugged in properly	unplug electrodes and reseat
	reference electrode not filled	be sure reference electrode is filled
	air bubbles on membrane	remove bubbles by re-dipping electrode
	electrodes not in solution	put electrodes in solution
Noisy or Unstable Readings (readings continuously or randomly changing	defective meter	check meter with shorting strap
	air bubble on membrane	remove bubble by re-dipping electrode
	meter or stirrer not grounded	ground meter or stirrer
	outer filling solution too low	fill electrode to level just below fill hole
	defective electrode	replace electrode
	electrode exposed to interferences	soak electrode in calcium standard
"Incorrect Answer" (but calibration curve is good)	incorrect scaling of semi-log 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: $1.0x10^{-3}M$ = 40 ppm Ca^{+2} = 100 ppm as $CaCO_3$
	sample carryover	rinse electrodes thoroughly between samples
Drift (reading slowly changing in one direction)	samples and standards at different temperatures	allow solutions to come to room temperature before measure.
	electrode exposed to interferences	soak electrode in calcium standard
	incorrect reference filling solution	use recommended filling solution
	incorrect pH	adjust to pH 3-10 with NaOH or HCl
Low Slope or No Slope	standards contaminated or incorrectly made	prepare fresh standards
	defective electrode	check electrode operation
	air bubble on membrane	remove bubble by re-dipping probe
	electrode exposed to interferences	soak electrode in calcium standard

standard used as ISA	use ISA
ISA not used	use ISA

SPECIFICATIONS

Concentration Range:	1M to $5x10^{-6}$M
pH Range:	3 to 10
Temperature Range:	0^{o} to 40^{o}C
Resistance:	100 Mohms
Reproducibility:	"4%
Samples:	aqueous solutions only; no organic solvents
Size:	110 mm length 12 mm diameter 1 m cable length
Storage:	store in dilute calcium standard

ORDERING INFORMATION

P/N	DESCRIPTION
CAL1501	Calcium Electrode, mono (reference electrode necessary), PVC body
CAL1502	Calcium Electrode, combination, glass body
CAL1503	Calcium Electrode, combination, epoxy body
5731428	Reference Electrode, single junction, epoxy body, for use with the CAL1501
CALAS01	Calcium Standard, 0.1M $CaCl_2$
CALAS02	Calcium Standard, 1000 ppm Ca^{+2}
CALAS03	Calcium Standard, 100 ppm Ca^{+2} as $CaCO_3$
CALIS01	Calcium ISA (Ionic Strength Adjustor), 4 M KCl
R001011	5731428 Reference Electrode Filling Solution & CAL1503 Combination Electrode Filling Solution, 4M KCl (saturated with AgCl)
R001013	CAL1502 Combination Electrode Filling Solution, 4 M KCl

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