COLE-PARMER REPLACEABLE MEMBRANE
CALCIUM ION ELECTRODES
INSTRUCTION MANUAL

GENERAL INSTRUCTIONS

Introduction

The Cole-Parmer Calcium Ion Electrodes are used to quickly, simply, accurately, and economically measure calcium in aqueous solutions. The primary advantage of combination ion-selective probes with replaceable sensing membranes is that when the sensing membrane fails or loses performance for whatever cause, it can be immediately replaced without discarding any other portion of the combination electrode. This results in time and cost savings.

Another distinct advantage of this replaceable membrane design is that when the sensing membrane fails or loses performance for whatever cause, membrane replacement has no unfortunate side effects on the performance of the reference electrode. There is no danger of reference electrolyte leakage upon replacing the membrane. The membrane replacement assembly is separated from the reference electrolyte/reference junction so that the membrane may be replaced without disturbing the reference electrolyte solution.

Yet another advantage of these ISE probes is the option of interchangeable sensing membranes, where one can select a membrane for a particular analytical ion. A single combination ISE body can be used to measure a variety of analytical ions by simple replacement of the membrane cartridge. This offers benefits in multiple ion analysis whereby an electrode kit containing various replaceable membranes can be made available for the analysis of different ions done on an occasional basis.

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 Cole-Parmer Replaceable Membrane Calcium Combination Ion Electrode, Cat. No. 27505-06

Required Solutions

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

2. Cole-Parmer Ionic Strength Adjuster (ISA), 4 M KCl, Cat. No. 27503-52. 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.

3. Cole-Parmer Calcium Standard, 1000 ppm Ca^{+2}, Cat. No. 27503-05. To prepare this solution from your 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. 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 black protective cap covering the electrode tip and lower the rubber sleeve covering the filling hole of the reference chamber to expose the fill hole. Fill the combination electrode with the reference filling solution shipped with the electrode to a level just below the fill hole. 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.

Connecting the Electrode to the Meter

Connect the electrode to the meter according to the meter manufacturer's instructions. No external reference electrode is required. To prevent air entrapment, mount the electrode at a 20^{o} angle from the vertical.

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

A small hole of any size around the membrane seal or breakage of the membrane causes failure of the electrode. It is recommended to check the membrane on every newly assembled electrode.

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.

2. Using a pipette, add 1 ml of 1000 ppm standard and 2 ml of ISA to the beaker. When the reading is stable, record the mV reading.

3. Using a pipette, 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° and 25°C. See the **TROUBLESHOOTING** section if the potential change is not within this range.

5. 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)

A small hole of any size around the membrane seal or breakage of the membrane causes failure of the electrode. It is recommended to check the membrane on every newly assembled electrode.

1. Prepare standard calcium solutions whose concentrations vary by tenfold. Use the 1000 ppm Ca^{+2} standard stock solution. 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.

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 electrodes with distilled water and blot dry.

6. 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.

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%. See the **TROUBLESHOOTING** sections if the slope is not within this range.

Changing the Membrane Cartridge (when necessary)

1. Unscrew the bottom cap from the outer body. Remove the old membrane cartridge from the bottom cap by pushing out the cartridge with the tool provided with the electrode.

2. Insert the new membrane cartridge into the bottom cap by pushing in the cartridge using the opposite end of the tool until it seats.

3. Invert the outer body and check that there is inner filling solution inside the center chamber. Using the syringe provided, fill the outer body with inner filling solution if necessary.

4. Place the bottom cap onto the outer body threads and screw the bottom cap onto the outer body until fingertight. Check that the assembled cap is not leaking at the bottom of the electrode or else repeat the above steps.

5. 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. Immerse the calcium electrode in calcium standard for thirty minutes. The electrode is now ready for use.

6. Connect the electrode to the meter and repeat the electrode slope check

MEASUREMENT

Measuring Hints

1. 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.

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

3. 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.

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

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

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

7. 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

* Make sure that the samples and standards are at the same temperature. About a 2% error will be introduced for a 1^{o}C difference in temperature. Temperature should normally be less than 40^{o}C with intermittent measurements allowed to 50^{o}C. .

* All samples and standards must be aqueous. They must not contain organic solvents.

* Interferences found in Table 3 should be absent.

Units of Measurement

Calcium concentrations are measured in units of parts per million as calcium, parts per million 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	$1.0X10^{-4}$
10.00	24.9	$2.5X10^{-4}$
40.10	100.1	$1.0X10^{-3}$
400.80	1000.9	$1.0X10^{-2}$

MEASUREMENT PROCEDURE

Direct Measurement

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 ammonium samples. 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 1000 ppm standard. The resultant concentrations should be 100, 10 and 1 ppm standards. Add 2 ml of ISA to each 100 ml of standard.

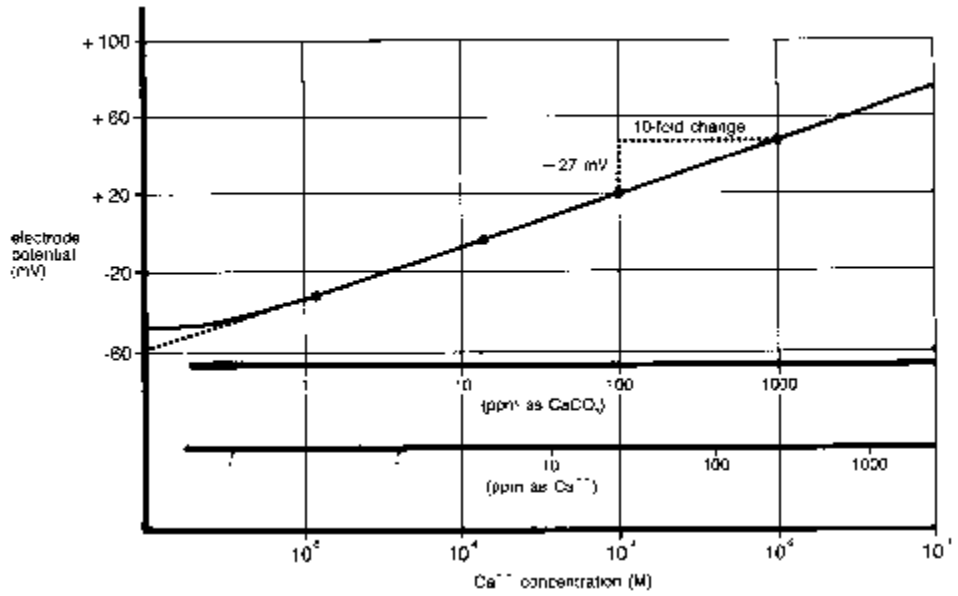
2. Place the most dilute solution (1 ppm) in a 150 ml beaker on the magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tips into the solution. When the reading has stabilized, record the mV reading.

3. Place the mid-range solution (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 (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 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 procedures. Extrapolate the curve down to about 0.2 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 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 1-2 hours. Simply repeat Steps 2-5 above.

Direct Measurement of Calcium (using an ion meter)

1. By serial dilution of the 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 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 1000 ppm 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 10 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 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	Pipette	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	$4.8X10^{-5}$	$4.8X10^{-1}$

Pipette A = 1 ml graduated pipette
Pipette B = 2 ml pipette
Solutions: additions of 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 1000 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 50 ppm calcium for a good detection of the endpoint.

3. Fill a 50 ml buret with the EDTA solution. Pipette 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.

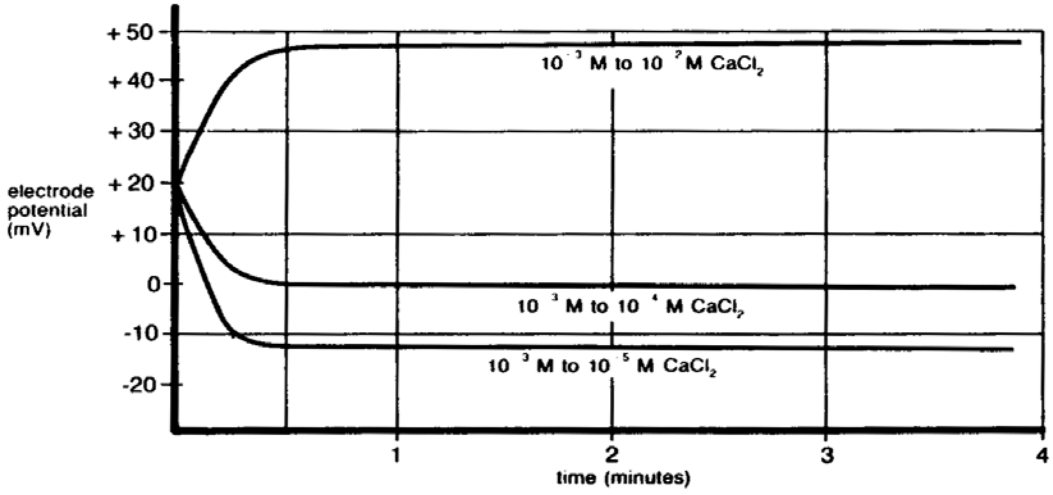
4. Position the buret tip in the beaker, slightly above the liquid level in the beaker and slightly off center. Position the electrode tips in the solution about half way

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.

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

where

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

V_t = volume of EDTA added at 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}	$1.56X10^{5}$	$1.56X10^{4}$	$1.56X10^{3}$
Na^{+1}	$4.60X10^{4}$	$4.60X10^{3}$	$4.60X10^{2}$
Ni^{+2}	$2.94X10^{4}$	$2.94X10^{3}$	$2.94X10^{2}$
Cu^{+2}	$2.54X10^{4}$	$2.54X10^{3}$	$2.54X10^{2}$

(ppm)	1000 ppm $CaCO_3$	100 ppm $CaCO_3$	10 ppm $CaCO_3$
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 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 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 40 ppm 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 (^{o}C)	"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 ppm)$1.0x10^{-4}$M to several minutes near the detection limit. (Refer to Figure 3.)

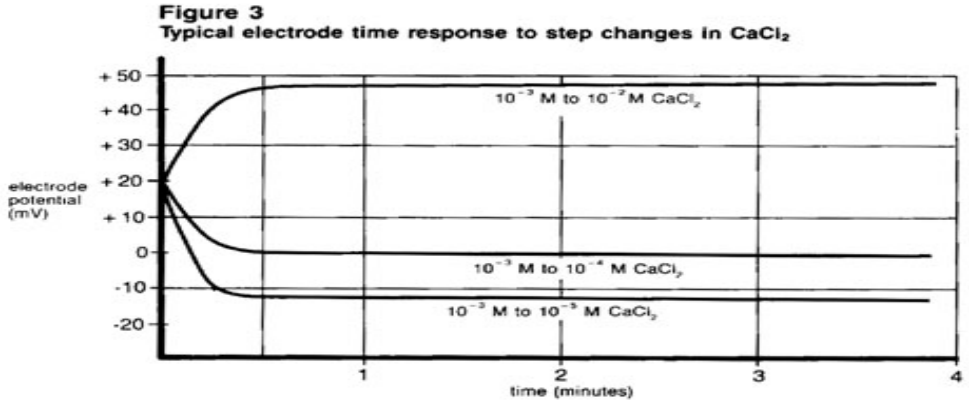


Figure 3
Typical electrode time response to step changes in $CaCl_2$

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 $1.0x10^{-1}$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 $1.0x10^{-1}$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 membrane cartridge replacement is required.

Electrode Storage

The Cole-Parmer Replaceable Membrane Calcium Ion Electrodes may be stored for short periods of time in 100 ppm 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 should be drained of filling solution and the rubber sleeve placed over the filling hole.

ELECTRODE THEORY

Electrode Operation

The Cole-Parmer Calcium Electrode consists of an electrode body containing an ion exchanger in a membrane cartridge. 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, γ, by:

$$X = \gamma C_f$$

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

$$I = \tfrac{1}{2}\Sigma C_x Z_x^2$$

where: C_x = concentration of ion X
Z_x = charge on ion X
Σ = 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, γ, 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.

Strongly acidic (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 electrode(s) in the same pH range as the samples or use a known increment method for ion

measurement.

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 is the easiest component to eliminate as a possible cause of error. Most meter are provided with an instrument check-out procedure in the instruction manual and a short strap for convenience in troubleshooting. Consult the manual for complete instructions and verify that the instruments operates as indicated.

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, replace membrane cartridge as outlined in the section **Changing the Membrane Cartridge.**

4. If the measurement problems still exist, the standards may be of poor quality, the sample may contain interferences or complexing agents, or the technique may be in error. See Standard, Sample, and Technique sections below.

5. 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 Cole-Parmer and ask for the Technical Services Department.

TROUBLESHOOTING HINTS

SYMPTON	POSSIBLE CAUSES	NEXT STEP
Out of Range Reading	defective meter	check meter with shorting strap (see meter instruction manual)
	electrode(s) not plugged in properly	unplug electrode(s) and reseat
Filled	reference electrode not filled	be sure reference is filled
	air bubbles on membrane	remove bubble by re-dipping electrode
	electrodes not in solution	put electrode(s) in solution
Incorrect Answer" (but calibrate is good)	incorrect scaling of semilog paper	plot millivolts on the linear axis. On the log curve 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 conversion	apply correct factor: 10^{-3}M= 18ppm NH_4^+=14ppm as N
	sample carryover	rinse electrodes thoroughly between samples
Drift (reading changing in one direction)	samples and standard at difference temperatures	allow solutions slowly to come to room temperature before measurement
	electrode exposed to interferences	soak electrode ammonium standard
	incorrect reference filling solution	use recommended filling solution

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
	defective electrode	replace membrane cartridge
	electrode exposed to interferences	soak electrode in ammonium standard
	air bubble on membrane	remove bubble by re-dipping probe
Noisy or unstable readings (readings continuously or randomly changing)	defective meter	check meter with shoring strap
	air bubble on membrane	remove bubble by re-dipping electrode
	defective electrode	replace membrane cartridge
Interferences	electrode exposed to interferences	soak electrode in ammonium standard
	meter or stirrer not grounded	ground meter or stirrer
	outer filling solution level too low	fill electrode to level just below fill hole

SPECIFICATIONS

Concentration Range:	1M to $5x10^{-6}$M (18,000 ppm to 0.01 ppm)
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
27505-06	Calcium Ion Electrode, combination, epoxy body, Replaceable membrane.
27503-05	Calcium Standard, 1000 ppm Ca^{+2}
27503-52	Calcium ISA (Ionic Strength Adjustor), 4 M KCl
27505-56	Replacement Membrane Kit containing 3 membrane cartridges, o-rings, inner filling solution and reference filling solution

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