Van London Co.

"When Accuracy Matters"

Calcium Ion Selective Electrode

www.VanLondon.com
info@VanLondon.com

Toll Free (800) 522-7920
Local (832) 456-6641

GENERAL INSTRUCTIONS

Introduction

The Van London Co. Calcium Ion Selective Electrode is used to quickly, simply, accurately, and economically measure calcium in aqueous solutions.

Required Equipment

1. An ion meter
2. Calcium Ion Sensing Electrode
3. Plastic syringe, pipets, volumetric flasks, 150 ml beakers

Required Solutions

1. Deionized or distilled water for solution preparation.
2. Van London Co. Calcium Standard, 1000 ppm Ca^{+2}, Cat. No. CALAS02.
3. Ionic Strength Adjuster (ISA), 4 M KCl, Cat. No. CALIS01.
4. Calcium Electrode Reference Fill Solution, Cat# R001013.

GENERAL PREPARATION

Electrode Preparation

Remove the rubber cap covering the electrode tip and the rubber insert covering the filling hole of the reference electrode. Fill the combination 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 may be trapped behind the calcium membrane. Connect the electrode to the proper terminals of the meter as recommended by the meter manufacturer. Store the black shipping cap for later use.

Electrode Slope Check (for Ion meters which display mV)

1. To a clean, dry, 150 ml beaker, add 100 ml of distilled water and 2 ml of ISA. After assuring that the meter is in the millivolt mode, lower the electrode tip into the solution. Stir moderately. Remove air bubbles on the clear plastic membrane by redipping probe.
2. Using a pipet, add 1 ml of 1000 ppm calcium standard into the solution. Stir moderately. After 1 minute, record the mV reading.
3. Using a pipet, add 10 ml of the 1000 ppm calcium standard to the beaker. Stir moderately. After 1 minute, record the mV reading.
4. Determine the difference between the two readings. The electrode is operating correctly if a slope difference of 26±2 mV is found, assuming the solution temperature is 25°C. Slope is defined as the change in mV observed when the concentration changes by a factor of 10.

Measurement using an Ion Meter (in the Concentration Mode)

1. By serial dilution of the 1000 ppm calcium standard, prepare two calcium standards whose concentration is near the expected sample concentration. (e.g. 10 ppm and 100 ppm) For example, to make a 100 ppm standard, pipet 10 ml of the 1000 ppm standard into a 100 ml volumetric flask and dilute to volume with deionized water. Next to make a 10 ppm standard, pipet 10 ml of the newly-made 100 ppm standard into a 100 ml volumetric flask and dilute to volume with deionized water. A 1 ppm standard is made by further dilution of the 10 ppm standard. Measure out 100 ml of each standard into individual 150 ml beakers.
2. Assure that the meter is in the concentration mode and set for a 2-point calibration.
3. Lower the electrode tip into the least concentrated solution. Begin stirring at a constant rate. Add 2 ml of ISA to the solution and continue stirring.

4. After 1 minute, adjust the meter to the concentration of the more dilute calcium standard and fix the value in the memory according to the meter manufacturer's instructions.
5. Rinse the electrode tip with distilled water and blot dry.
6. Lower the electrode tip into the more concentrated solution. Begin stirring at a constant rate. Add 2 ml of ISA to the solution and continue stirring.
7. After 1 minute, adjust the meter to the concentration of the more concentrated calcium standard and fix the value in the memory according to the meter manufacturer's instructions.
8. Add 100 ml of the sample and 2 ml of ISA in a 150 ml beaker. Lower the electrode tip into the solution. Begin stirring at a constant rate. Ensure that the meter is in sample mode.
9. After 1 minute, read the concentration directly from the meter display.
10. The electrode should be re-calibrated every 2-3 hours. Simply repeat Steps 2-7 above.

Measuring Hints

As calcium electrodes are used or stored for long periods, they will experience some deterioration in performance and slope errors will increase. By using the meter's calibration controls this error can be corrected. If an electrode is able to be calibrated and is stable and responsive, it is still a functional electrode and may be used in service even though it no longer meets "new" electrode specifications.

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

Constant, but not violent, stirring is necessary for accurate measurement.

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

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

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 standard solution for about 5 minutes.

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

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

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

ELECTRODE CHARACTERISTICS

Reproducibility

Electrode measurements reproducible to ±2% can be obtained if the electrode is calibrated every hour. Factors such as temperature fluctuation, drift, and noise limit reproducibility.

Interferences

Certain cations are electrode interferences and will cause electrode malfunction, drift or measurement errors if present in high enough levels. The level of interfering common cations that will cause a 10% error at three levels of calcium is given in Table 1.

TABLE 1: Concentration of Possible Interferences Causing a 10% Error at Various Levels of Calcium .

(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	$2.0X10^{-1}$

If the electrode is exposed to high levels of interfering ions which cannot be removed, the electrode reading may drift and the response may become sluggish. Restore performance by soaking in distilled water for 30 minutes followed by soaking in calcium standard for 30 minutes.

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

The electrode response will shift and change slope with change in temperature. Standards and samples should be at the same temperature. A 2% error results with a 1^oC temperature change for a 10 ppm solution.

The electrode can be used at temperatures from 0° - 40°C. Room temperature measurements are recommended, since measurements at temperatures quite different from room temperature may require equilibrium times up to one hour.

Electrode Response

Plotting the mV potential against the calcium concentration results in a straight line with a slope of 26±2 mV per decade. For calcium concentrations above 10 ppm Ca^{+2}, the electrode exhibits good time response (95% of total mV reading in 30 seconds or less). Response times are longer below this value.

Limits of Detection

Calcium concentration down to 0.5 ppm calcium can be measured in neutral solutions. Since sample contamination can be a factor in low level calcium measurements, care must be taken in making determinations below 1.0 ppm. The upper limit of detection in pure calcium chloride solutions is Saturated.

pH Effects

The operating range of the calcium electrode is from pH 3 to pH 10.

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.

Since calcium electrodes have a limited shelf life, it is important to have a backup electrode which is in working condition when required.

Electrode Storage

The calcium electrode may be stored for short periods of time in 10 ppm calcium solution. For longer storage (longer than two weeks), rinse and dry the sensing tip and cover the membrane tip with any protective cap shipped with the electrode. 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.

TROUBLESHOOTING HINTS

Symptom	Possible Causes	Next Step
Out of Range Reading	defective meter	check meter with shorting strap (see meter instruction)
	defective electrode	check electrode operation
	electrodes not plugged in properly	unplug electrodes and reset
	reference electrode not filled	be sure reference electrode is filled
	air bubble on membrane	remove bubble by re-dipping electrode
	electrodes not in solution	put electrodes in solution
Noisy or Unstable Readings (readings continuously or rapidly changing)	defective meter	check meter with shorting strap
	air bubble on membrane	remove bubble by re-dipping electrode
	defective electrode	replace electrode
	ISA not used	use recommended ISA
	meter or stirrer not grounded	ground meter or stirrer
	electrode exposed to interferences	soak electrode in calcium standard
	outer filling solution level too low	fill electrode to level just below the fill hole
Drift (reading slowly changing one direction)	samples and standards at different temperatures	allow solutions to come to room come to room temperature before measurement
	electrode exposed to interferences	soak electrode in calcium 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
	electrode exposed to interferences	soak electrode in calcium standard
	defective electrode	check electrode operation
	air bubble on membrane	remove bubble by re-dipping probe
Incorrect Answer	incorrect standards	prepare fresh standard
	wrong units used	apply correct conversion factor: 10^{-3}M = 40 ppm Ca^{+2}= 100 ppm as $CaCO_3$
	sample carryover	rinse electrodes thoroughly between samples

SPECIFICATIONS

Concentration Range:	saturated solutions to 0.5 ppm
pH Range:	3 to 10
Slope:	26±2 mV between 10 ppm and 100 ppm at 25°C
Temperature Range:	0° to 40°C
Interferences:	Pb^{+2}, Hg^{+2}, Cu^{+2}, Ni^{+2}
Reproducibility:	± 2%
Size:	110 mm length 12 mm diameter 1 m cable length
Storage:	store in dilute calcium standard
Samples:	aqueous solutions only no organic solvents

ELECTRODE THEORY

Electrode Operation

The calcium electrode consists of an electrode body containing a liquid internal filling solution in contact with a gelled organophilic membrane containing a calcium ion exchanger. When the membrane is in contact with a solution containing free calcium ions, an electrode potential develops across the membrane. This electrode potential is measured against a constant reference potential, using a standard pH/mV meter or an ion meter. The level of calcium ions, corresponding to the measured potential, is described by the Nernst equation:

$$E = E' - S \log X$$

where: E = measured electrode potential
E’ = reference potential (a constant)
S = electrode slope (-26 mV/decade)
X = level of calcium ions in solution

The activity, X, represents the effective concentration of the ions in solution. The total calcium ion concentration, C_t, is the sum of free calcium ion, C_f, and complexed or bound calcium ion, C_b. The electrode is able to respond to only the free ions, whose concentration is :

$$C_f = C_t - C_b$$

Since calcium ions form very few stable complexes, the free ion concentration may be equated to the total ion concentration.

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 ions 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 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.