

User Guide

Calcium
Ion Selective
Electrode



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This publication supersedes all previous publications on this subject.

TABLE OF CONTENTS

GENERAL INFORMATION	1
Introduction	1
Required Equipment	2
Required Solutions	2
BEFORE USING THE ELECTRODE	5
Electrode Assembly and Preparation	5
Checking Electrode Operation (Slope)	8
Recommendations for Optimum Results	9
Analytical Techniques	12
MEASUREMENT PROCEDURES	15
Direct Measurement	15
Small Volume Direct Measurement	19
Low-Level Measurements By Direct Measurement	22
Known Addition	25
Titration	32
ELECTRODE STORAGE	35
TROUBLESHOOTING	36
Troubleshooting Checklist	36
Troubleshooting Guide	38
Assistance	40
Warranty	40
ELECTRODE CHARACTERISTICS	41
Electrode Response	41
Limits of Detection	42
Reproducibility	42
Temperature Effects	43
Interferences	44
pH Effects	44
Electrode Life	44
Complexation and Precipitation	46
Theory of Operation	47
ORDERING INFORMATION	49
SPECIFICATIONS	50

GENERAL INFORMATION

Introduction

This user guide contains information on the preparation, operation and maintenance for the calcium ion selective electrode (ISE). General analytical procedures, electrode characteristics and electrode theory are also included in this user guide. Calcium electrodes measure free calcium ions in aqueous solutions quickly, simply, accurately and economically.

Technical Support Chemists can be consulted for assistance and troubleshooting advice. Within the United States call 1.800.225.1480 and outside the United States call 978.232.6000 or fax 978.232.6031. In Europe, the Middle East and Africa, contact your local authorized dealer.

Calcium ionplus® Sure-Flow® Plastic Membrane Combination ISE

The reference and sensing electrodes are built into one electrode, which decreases the amount of required solution and reduces waste. The built-in Sure-Flow reference junction prevents electrode clogging and provides fast and stable readings. The calcium ionplus combination ISE is available with a waterproof BNC connector, Cat. No. 9720BNWP.

Calcium Plastic Membrane Half-Cell ISE

The calcium half-cell electrode must be used with the single junction reference electrode, Cat. No. 900100. The calcium half-cell is available with a BNC connector, Cat. No. 9320BN.

Required Equipment

Meter– Thermo Scientific Orion ISE meter, such as the 4-Star pH/ISE meter or 5-Star pH/ISE/DO/conductivity meter. Calcium electrodes can be used on any ISE meter with a BNC or U.S. standard connection. The electrodes can also be used on meters with a variety of inputs when an adapter cable is used.

Reference Electrode– The 9320BN half-cell calcium electrode requires the Thermo Scientific Orion single junction reference electrode, Cat. No. 900100. Use the 4 M KCl saturated with Ag/AgCl filling solution, Cat. No. 900011.

Stirrer– Magnetic stirrer or stir probe, Cat. No. 096019. The stir probe can be used with 3-Star, 4-Star and 5-Star benchtop meters.

Labware– Volumetric flasks, graduated cylinders and beakers. Plastic labware is required for low-level cadmium measurements.

Required Solutions

Distilled or Deionized Water

Electrode Filling Solution

Use Optimum Results A filling solution with the 9720BNWP combination calcium electrode.

Use the 4 M KCl saturated with Ag/AgCl filling solution, Cat. No. 900011, with the single junction reference electrode that is used with the 9320BN half-cell calcium electrode.

Calcium Calibration Standards

0.1 M calcium standard, Cat. No. 922006

100 ppm calcium as calcium carbonate standard, Cat. No. 923206

1000 ppm calcium standard– Prepare a 1000 ppm calcium standard by transferring 25 mL of the 0.1 M calcium standard to a 100 mL volumetric flask and diluting to the mark with distilled water.

1000 ppm calcium as calcium carbonate standard– Prepare a 1000 ppm calcium as calcium carbonate standard by transferring 10 mL of the 0.1 M calcium standard to a 100 mL volumetric flask and diluting to the mark with distilled water.

Ionic Strength Adjustor (ISA), Cat. No. 932011– To adjust ionic strength of samples and standards

EDTA Titrant– For the titration of calcium. Prepare a 1 M stock solution by placing 37.2 g of reagent-grade Na_4EDTA [Sodium(tetra)ethylenediaminetetraacetic acid dihydrate] in a 100 mL volumetric flask and diluting to the mark with distilled water.

BEFORE USING THE ELECTRODE

Electrode Assembly and Preparation

Calcium Half-Cell Electrode, Cat. No. 9320BN

Remove the sensing module from the vial. Make sure that the rubber electrode washer on the sensing module is in place. See **Figure 1**. Screw the sensing module into the electrode body until the module is finger tight. To ensure electrical continuity, shake the electrode down like a clinical thermometer. Rinse the calcium electrode with distilled water and then soak it in a 100 ppm or 10^{-2} M calcium standard for 1 to 2 hours prior to initial use.

Do not immerse the electrode past the rubber electrode washer.

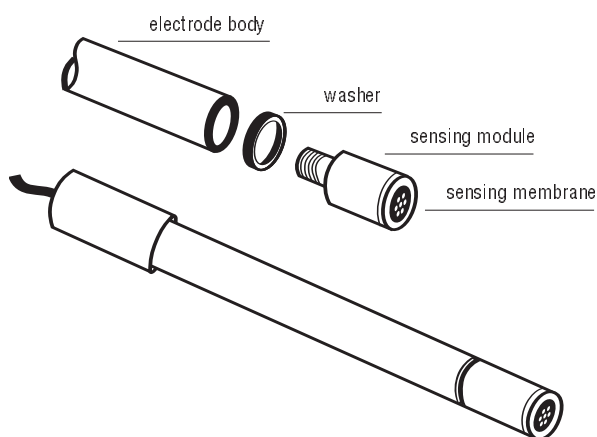


Figure 1
9320BN Electrode Assembly

Single Junction Reference Electrode, Cat. No. 900100

The single junction reference electrode is required for use with the calcium half-cell electrode. Fill the reference electrode according to instructions in the reference electrode user guide, using the 4 M KCl saturated with Ag/AgCl filling solution, Cat. No. 900011. **Do not use the filling solution that ships with the 900100 reference electrode because it contains interferences for calcium measurements.**

Calcium Combination Electrode, Cat. No. 9720BNWP

Note: Do not touch the sensing membrane or reference pellet during assembly.

1. Remove the sensing module from the vial. Make sure both O-rings are in place. Remove the handle from the box.
2. Take the outer body sleeve, with the fill hole end towards the cap, and gently push the inner stem through the outer body.
3. Slide the outer body sleeve, spring and cap down the electrode cable until the outer body sleeve is beyond the inner stem.
4. With one hand grasp the middle of the inner stem **without touching the reference pellet**. With your other hand, screw the sensing module onto the stem until it stops and the module is flush against the stem. Then tighten the module an additional one-quarter turn and stop. **Do not overtighten the module**. The module should be firmly attached to the stem.
5. Holding the electrode cable, slide the outer body, spring and cap over the inner stem.
6. Grasp the outer body sleeve, but do not touch the sensing membrane. With your other hand, pull on the cable and gently screw the cap onto the inner stem. Stop when an opposite force is felt. Do not overtighten or continue to turn the cap. The cap will not completely stop. If the inner body turns at all, the cap is too tight. Remove the cap and reassemble.
7. Hold the electrode with one hand. Press on the top of the cap with your thumb to make sure the electrode has a smooth flushing motion and reseats back onto the module.
8. Fill the outer body with Optimum Results A filling solution, Cat. No. 900061, up to the fill hole.
9. Press the cap to flush a few drops of filling solution out of the electrode. Release the cap and ensure that the outer body sleeve returns to its original position.

Note: The electrode filling solution should be added each day before use. The filling solution should be no lower than 1 inch from the fill hole and must be above the reference pellet. The filling solution level should always remain 1 inch above the sample level to ensure the proper flow rate.

10. Rinse the calcium electrode with distilled water and then soak it in a 100 ppm or 10^{-2} M calcium standard for 1 to 2 hours prior to initial use.

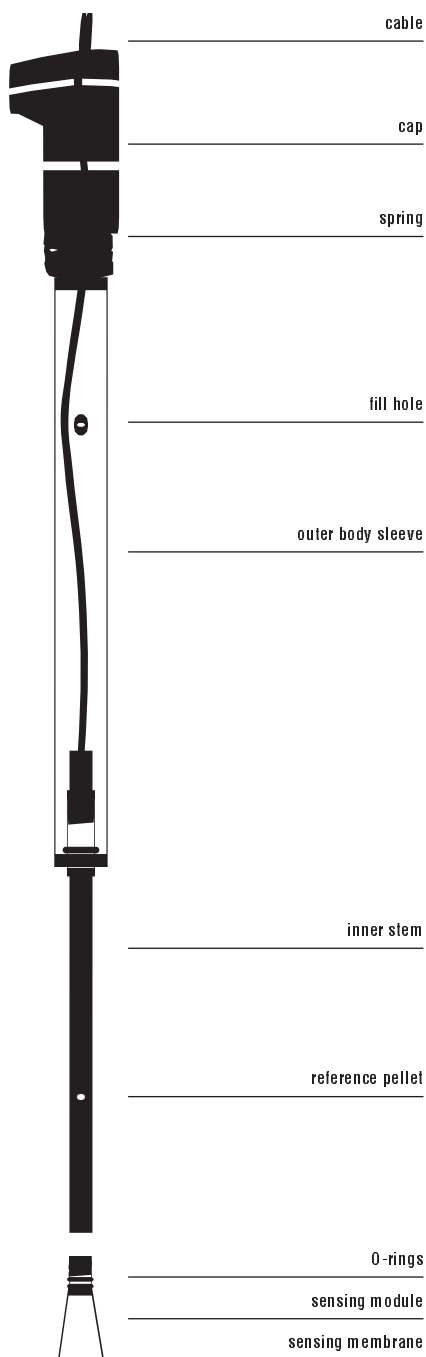


Figure 2:
9720BNWP
Electrode
Assembly

Checking Electrode Operation (Slope)

Use these general instructions to check electrode operation. Refer to the meter user guide for specific information.

This procedure measures electrode slope. Slope is defined as the change in millivolts observed with every tenfold (decade) change in concentration. Obtaining the slope value provides the best means for checking the electrode operation.

1. If the electrode(s) has been stored dry, prepare the electrode(s) as described in the **Electrode Assembly and Preparation** section.
2. Connect the electrode(s) to the meter as described in the meter user guide.
3. Select either 0.1 M or 1000 ppm calcium standard.
4. Place 100 mL of distilled water into a 150 mL beaker. Add 2 mL of ISA, Cat. No. 932011. Stir the solution thoroughly.
5. Set the meter to the mV mode.
6. Rinse the electrode(s) with distilled water, shake dry, and place in the solution prepared in step 4 above.
7. Pipette 1.0 mL of the standard into the beaker. Stir the solution thoroughly.
8. When a stable reading is displayed, record the electrode potential in millivolts.
9. Pipette 10.0 mL of the same standard into the same beaker. Stir the solution thoroughly.
10. When a stable reading is displayed, record the electrode potential in millivolts.
11. The difference between the first and second potential reading is defined as the slope of the electrode. The difference should be in the range of 25 to 30 mV/decade when the solution temperature is 25 ± 5 °C. If the slope is not within this range, re-soak the electrode as described in the **Electrode Assembly and Preparation** section. For other troubleshooting techniques refer to the **Troubleshooting** section.

Recommendations For Optimum Results

Units of Measurement

Measure calcium in units of moles per liter, parts per million as calcium, parts per million as calcium carbonate or any other convenient unit (see **Table 1**).

Table 1
Concentration Unit Conversion Factors

moles per liter	ppm as Ca^{2+}	ppm as CaCO_3	% Ca^{2+}
10^{-4}	4.0	10	0.0004
10^{-3}	40.1	100.0	0.004
10^{-2}	400.8	1000.9	0.04
10^{-1}	4008.0	10008.9	0.4

Sample Requirements

Samples must be aqueous and must not contain organic solvents. Consult our Technical Support Chemists for using the electrode in specific applications.

Sample temperature must be less than 40°C, with samples and standards at the same temperature. At the 10^{-3} M level, a 1 °C difference in temperature produces about a 4% error (9320BN) or 1.2% error (9720BNWP). For highly accurate results, use a water bath to control temperature variances.

Interferences should be absent. See the **Interferences** section for a list of possible interferences.

Important ISE Measurement Techniques

- Stir all standards and samples at a uniform rate during measurement. Magnetic stirrers may generate sufficient heat to change solution temperature. Place a piece of insulating material such as cork, cardboard or styrofoam between the stir plate and sample beaker.
- Always use fresh standards for calibration.
- Always rinse electrode(s) with distilled water thoroughly between measurements. Shake electrode after rinsing to prevent solution carryover.

Note: Do not wipe or rub the sensing membrane, as it will damage and contaminate the sensing membrane surface.

- Store the electrode(s) in a 10^{-2} M or 100 ppm calcium standard between measurements.
- Allow all standards and samples to come to the same temperature for precise measurements.
- After immersion in solution, check the calcium electrode for any air bubbles on the membrane surface. Remove air bubbles at the electrode surface by gently tapping the electrode.
- The calcium half-cell electrode should be immersed in solution approximately half the length of the calcium module.

Note: Do not immerse the calcium half-cell electrode past the rubber electrode washer.

Immerse the reference electrode to the same depth as the calcium half-cell electrode.

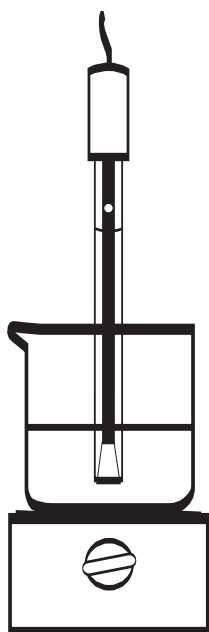


Figure 3

1. Uncover fill hole during measurement.
2. Use fresh standard.
3. Stir all samples and standards.
4. Filling solution level must be higher than sample level, and at least one inch above the reference pellet.
5. Immerse reference junction.
6. Place insulation between stirrer and beaker.

Note: Do not immerse the calcium half-cell electrode past the rubber electrode washer.

Analytical Techniques

Guide to Measuring Techniques

	Direct	Small Volume Measurement	Low-Level Direct	Known Addition	Titration Addition
Recommended concentration range	0.02 to 40,100 ppm Ca ²⁺	0.02 to 40,100 ppm Ca ²⁺	0.4 ppm Ca ²⁺ and lower	0.4 to 40,100 ppm Ca ²⁺	0.4 to 40,100 ppm Ca ²⁺
Large number of samples	X	X (9720BNWP only)	X	X	X
Small sample volumes		X (9720BNWP only)		X	X
Reduced chemical usage		X (9720BNWP only)			X
Field measurements	X	X (9720BNWP only)		X	
Ionic strength greater than 0.1 M				X	X
Occasional sampling				X	X

A variety of analytical techniques are available to the analyst. The best technique is dependent upon the sample matrix. The following section describes the recommended techniques for calcium determination.

Direct Measurement is a simple procedure for measuring a large number of samples. This method requires only one meter reading for each sample. Calibration is performed in a series of standards. The concentration of the samples is determined by comparison to the standards. Addition of ISA to all solutions ensures that samples and standards have similar ionic strength, proper pH, and reduces the effects of interfering ions. When measuring small sample volumes or to reduce chemical usage, follow the **Small Volume Direct Measurement** method, using the 9720BNWP combination calcium electrode.

Low-Level Measurement is similar to direct measurements. Use this method when the expected sample concentration is less than 10^{-5} M or 0.4 ppm. Using a minimum of three calibration standards compensates for the electrode's non-linear response at low concentrations. This procedure describes the best means of preparing low-level calibration standards.

Known Addition is an alternate method useful when measuring only a few samples, when samples have a high (>0.1 M) ionic strength, or have a complicated background matrix. Refer to the **Theory of Operation** section for an explanation of these effects. The electrodes are immersed in the sample solution and an aliquot of a standard solution containing the measured species is added to the sample. From the change in potential before and after the addition, the original sample concentration is determined. As in direct calibration, any convenient concentration unit can be used.

Titrations are quantitative analytical techniques for measuring the concentration of a species by incremental addition of a reagent (titrant) that reacts with the sample species. Sensing electrodes can be used to determine the titration end point. Ion selective electrodes are unaffected by sample color or turbidity, making them excellent endpoint detectors. Titration are approximately 10 times more precise than direct calibration, but are more time-consuming.

MEASUREMENT PROCEDURES

Direct Measurement

The following direct measurement procedures are recommended for high-level measurements, when all samples fall within the linear range of the electrode, greater than 0.4 ppm or 10^{-5} M calcium. A two point calibration is sufficient, though more points can be used if desired. Using ISE meters, read sample concentrations directly from the meter. Refer to the meter's user guide for calibration details. When using a mV meter, prepare a calibration curve on semi-logarithmic graph paper, or a linear regression can be performed at the user's discretion using a spreadsheet or graphing program.

For Improved Accuracy

- The standard concentrations should bracket the expected sample concentration.
- Always dilute samples and standards in a 50:1 ratio with ISA. For example, 100 mL of sample and 2 mL of ISA.
- Verify this procedure by measuring a standard of known concentration as an unknown or by spiking a sample with calcium standard.
- For high ionic strength samples, having an ionic strength of 0.1 M or greater, prepare standards with a composition similar to that of the samples, measure the samples using the known addition method or dilute the samples.
- During calibration, measure the least concentrated standard first and work up to the most concentrated.
- The best method for preparation of standards is serial dilution. This procedure involves preparing an initial standard that is diluted to prepare a second standard solution, using volumetric glassware. The second is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.
- Review the **Important ISE Measurement Techniques** section.

Direct Calibration Using a Meter with an ISE Mode

Note: See the meter user guide for more specific information.

1. Measure 100 mL of the less concentrated standard and 2 mL of ISA and pour into a 150 mL beaker. Stir the solution thoroughly.
2. Rinse the electrode(s) with distilled water, blot them dry and place the electrode(s) into the beaker with the less concentrated standard. Wait for a stable reading and then adjust the meter to display the value of the standard, as described in the meter user guide.
3. Measure 100 mL of the more concentrated standard and 2 mL of ISA and pour into a second 150 mL beaker. Stir the solution thoroughly.
4. Rinse the electrode(s) with distilled water, blot them dry and place the electrode(s) into the beaker with the more concentrated standard. Wait for a stable reading and then adjust the meter to display the value of the second standard, as described in the meter user guide.
5. Record the resulting slope value. The slope should be between 25 to 30 mV when the standards are between 20-25 °C.
6. Measure 100 mL of the sample and 2 mL of ISA and pour into a clean 150 mL beaker. Stir the solution thoroughly.
7. Rinse the electrodes with distilled water, blot them dry and place the electrodes into the sample. The concentration of the sample will be displayed on the meter.

Direct Calibration Using a Meter with a Millivolt Mode

1. Set the meter to the mV measuring mode.
2. Measure 100 mL of the less concentrated standard and 2 mL of ISA and pour into a 150 mL beaker. Stir the solution thoroughly.
3. Rinse the electrode(s) with distilled water, blot them dry and place the electrode(s) into the beaker with the less concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
4. Measure 100 mL of the more concentrated standard and 2 mL of ISA and pour into a second 150 mL beaker. Stir the solution thoroughly.
5. Rinse the electrode(s) with distilled water, blot them dry and place the electrode(s) into the beaker with the more concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
6. Using semi-logarithmic graph paper, prepare a calibration curve by plotting the millivolt values on the linear axis and the standard concentration values on the logarithmic axis.
7. Measure 100 mL of the sample and 2 mL of ISA and pour into a clean 150 mL beaker. Stir the solution thoroughly.
8. Rinse the electrode(s) with distilled water, blot them dry and place the electrode(s) into the beaker. When a stable reading is displayed, record the mV value.
9. Using the calibration curve prepared in step 6, determine the unknown concentration of the sample.

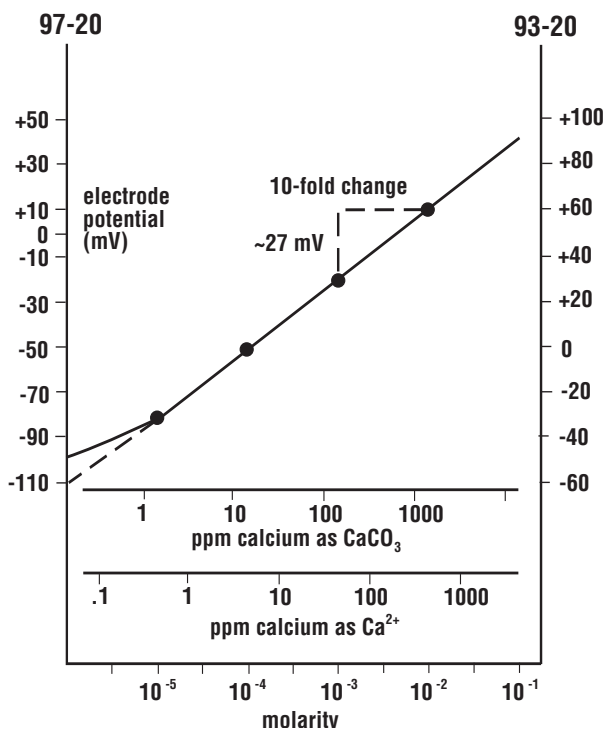


Figure 4
Typical Calcium Electrode Calibration Curve

During the direct measurement procedure, a calibration curve is constructed automatically by the ISE meter. Alternately, a calibration curve may be plotted by hand using semi-logarithmic paper. Measured electrode potentials of standard solutions are plotted on the linear axis against their concentrations on the log axis. In the linear regions of the curves, only two standards are needed to determine a calibration curve. In non-linear regions more points must be taken for accuracy. The direct measurement procedures in the manual are given for concentrations in the region of linear electrode response. When measuring in the non-linear region follow the low-level measurement procedure. This curve serves as an example only. Actual mV values may differ.

Small Volume Direct Measurement

Using the Sure-Flow reference design, the 9720BNWP combination calcium electrode allows measurement of sample volumes as small as 5 mL with a modified direct measurement procedure. This technique is applicable to any sample where reduced chemical usage of standards and ISA is important. This small volume measurement is well-suited for field testing as the combination reference electrode conveniently reduces equipment, setup and sampling time. All samples should be greater than 0.4 ppm or 10^{-5} M calcium. As with the previous **Direct Measurement** section, a two point calibration is sufficient, though more points can be used if desired. Use a direct concentration meter (ISE meter) or a pH/mV meter with 0.1 mV resolution. The following procedure recommends using 25 mL of sample. Smaller sample volumes can be used, as long as the final volume of solution is sufficient to cover the reference junction of the electrode. Do not allow the sensing membrane to touch the sample container.

For Improved Accuracy:

- Use the 9720BNWP combination calcium electrode.
- The standard concentrations should bracket the expected sample concentration.
- Always dilute samples and standards in a 50:1 ratio with ISA.
- Verify this procedure by measuring a standard of known concentration as an unknown or by spiking a sample with calcium standard.
- For high ionic strength samples, having an ionic strength of 0.1 M or greater, prepare standards with a composition similar to that of the samples, measure the samples using the known addition method or dilute the samples.
- During calibration, measure the least concentrated standard first and then proceed in order of increasing concentration.
- The best method for preparation of standards is serial dilution. This procedure involves preparing an initial standard that is diluted to prepare a second standard solution, using volumetric glassware. The second is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.
- Review the **Important ISE Measurement Techniques** section.

Small Volume Direct Calibration Using a Meter with an ISE Mode and the 9720BNWP Combination Calcium Electrode

Note: See the meter user guide for more specific information.

1. Measure 25 mL of the less concentrated standard and 0.5 mL of ISA and pour into a 150 mL beaker. Stir the solution thoroughly.
2. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker with the less concentrated standard. Wait for a stable reading and then adjust the meter to display the value of the standard, as described in the meter user guide.
3. Measure 25 mL of the more concentrated standard and 0.5 mL of ISA and pour into a second 150 mL beaker. Stir the solution thoroughly.
4. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker with the more concentrated standard. Wait for a stable reading and then adjust the meter to display the value of the second standard, as described in the meter user guide.
5. Record the resulting slope value. The slope should be between 25 to 30 mV when the standards are between 20-25 °C.
6. Measure 25 mL of the sample and 0.5 mL of ISA and pour into a clean 150 mL beaker. Stir the solution thoroughly.
7. Rinse the electrode with distilled water, blot it dry and place the electrodes into the sample. The concentration of the sample will be displayed on the meter.

Note: Other solution volumes may be used, as long as the ratio of solution to ISA remains 50:1.

Direct Calibration Using a Meter with a Millivolt Mode and the 9720BNWP Combination Calcium Electrode

1. Set the meter to the mV measuring mode.
2. Measure 25 mL of the less concentrated standard and 0.5 mL of ISA and pour into a 150 mL beaker. Stir the solution thoroughly.
3. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker with the less concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
4. Measure 25 mL of the more concentrated standard and 0.5 mL of ISA and pour into a second 150 mL beaker. Stir the solution thoroughly.
5. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker with the more concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
6. Using semi-logarithmic graph paper, prepare a calibration curve by plotting the millivolt values on the linear axis and the standard concentration values on the logarithmic axis.
7. Measure 25 mL of the sample and 0.5 mL of ISA and pour into a clean 150 mL beaker. Stir the solution thoroughly.
8. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker. When a stable reading is displayed, record the mV value.
9. Using the calibration curve prepared in step 6, determine the unknown concentration of the sample.

Low Level Measurements By Direct Measurement

Use this method when measuring solutions with a calcium concentration of less than 0.4 ppm or 10^{-5} M, those within the non-linear range of the electrode. Low-level measurements require at least three standards to compensate for the electrode's non-linearity.

For Improved Accuracy:

- If some samples have low-level concentrations and some have higher concentrations, dilute the higher concentrations down to the low-level range. The electrode's time response at low-levels is faster when it is not exposed to high concentrations.
- Ideally, calibration standard concentrations should bracket the expected sample concentrations.
- The best results are obtained when the concentration of the highest calibration standard is ten to one hundred times the lowest calibration standard concentration. Space additional standards equally within the range.
- If the expected sample concentrations fall within a narrow range (less than one order of magnitude), a ratio of highest to lowest standard concentration of ten should be used.
- This procedure works best with meters that have a concentration mode, blank correction and multiple point calibration features. Refer to the meter user guide for details. The electrode response is very slow in the absence of the ion of interest and a multipoint calibration will be less accurate when zero is included as a standard. Standard concentrations should be selected so the lowest standard value is larger than the blank value and the second lowest standard should be at least twice that of the lowest standard value.
- When using a meter with a mV mode, a calibration curve can be drawn on semi-logarithmic graph paper or the data can be processed using a spreadsheet or graphing program with a non-linear curve fitting feature.
- When using a meter with the autoblack feature, three calibration points are sufficient. If a calibration curve is prepared manually, additional points may be helpful.
- Remember to stir all standards and samples at a uniform rate.
- Review section entitled **Important ISE Measurement Techniques**.

Low Level Measurement Procedure using a Meter with an ISE Mode or mV Mode

1. Prepare the electrode(s) as described in the **Electrode Assembly and Preparation** section.
2. Connect the electrode(s) to the meter and set the meter to the concentration mode (ISE meter) or the mV mode (mV meter).
3. Select a standard solution. Use a 10 ppm calcium as CaCO_3 standard or dilute the 0.1 M calcium standard, Cat. No. 922006, to 10^{-4} M.
4. Prepare a low-level ISA solution by adding 25 mL of ISA, Cat. No. 932011, to a 100 mL volumetric flask and diluting to the mark with distilled water. ***Use this low-level ISA for low-level measurements only.***
5. Measure 100 mL of distilled water into 150 mL beaker. Add 1 mL of the low-level ISA.
6. Rinse the electrode(s) with distilled water, shake them dry, and place the electrode(s) into the beaker. Stir the solution thoroughly.
7. Add increments of the standard to the beaker using the steps outlined in **Table 2**.
8. ***For an ISE meter:*** Refer to the meter user guide for detailed calibration instructions.

For a mV meter: Record the stable millivolt reading after each increment. On semi-logarithmic paper, plot the concentration (log axis) against the millivolt potential (linear axis), see **Figure 4**.

Prepare a new low-level calibration curve with fresh standards each day.

9. Measure 100 mL of the sample into a 150 mL beaker. Add 1 mL of the low-level ISA.

10. Rinse the electrode(s) with distilled water, shake them dry, and place the electrode(s) into the sample. Stir the solution thoroughly.
11. **For an ISE meter:** When the electrode reading stabilizes, the meter will display the sample concentration.

For a mV meter: When the electrode reading stabilizes, the meter will display the sample mV value. Determine the sample concentration corresponding to the measured potential using the low-level calibration curve prepared in step 8.

Table 2: Preparing a Calibration Curve For Low-Level Measurements Using Additions of 10 ppm or 10⁻⁴ M Standard to 100 mL Distilled Water with 1 mL of Low-Level ISA.

Step	Graduated Pipette Size	Added Volume	Concentration	
			ppm Ca ²⁺	Molarity
1	1 mL	0.1 mL	0.01	1.0 x 10 ⁻⁷
2	1 mL	0.1 mL	0.02	2.0 x 10 ⁻⁷
3	1 mL	0.2 mL	0.04	3.9 x 10 ⁻⁷
4	1 mL	0.2 mL	0.06	6.0 x 10 ⁻⁷
5	1 mL	0.4 mL	0.10	9.8 x 10 ⁻⁷
6	2 mL	2.0 mL	0.29	2.9 x 10 ⁻⁶
7	2 mL	2.0 mL	0.47	4.7 x 10 ⁻⁶

Known Addition

Known addition is a convenient technique for measuring samples in the linear response range, greater than 0.4 ppm or 10^{-5} M calcium, because no calibration curve is needed. Use this method to verify the results of a direct measurement or to minimize existing matrix effects. The sample potential is measured before and after addition of a standard solution. Many meters have a known addition algorithms preprogrammed. This programming makes multiple standard additions to the sample, resulting in more precise results. Having the ability to read the sample concentration result directly from these meters provides a great convenience. Accurate measurement requires that the following conditions be met.

For Improved Accuracy:

- Sample concentration should be known to within a factor of three.
- Concentration should approximately double as a result of the addition.
- With double or multiple known addition, the final addition should be 10 to 100 times the sample concentration.
- All samples and standards should be at the same temperature.
- In general, either no complexing agents or a large excess of the complexing agents may be present.
- Standard addition volume should be less than 10% of the sample volume, or standard should be pre-treated with ISA in a 50:1 ratio.
- Dilute samples in a 50:1 ratio of sample to ISA before analysis.
- Review section entitled **Important ISE Measurement Techniques**.

Known Addition Setup

1. Prepare the electrode(s) as described in the **Electrode Assembly and Preparation** section.
2. Connect the electrode(s) to the meter.
3. Prepare a standard solution that, upon addition to the sample, will cause the concentration of the calcium to double. Refer to **Table 3** as a guideline.
4. Determine the slope of the calcium electrode by performing the procedure in the **Checking Electrode Operation (Slope)** section.

Known Addition Using a Meter with a Known Addition Mode

Note: See the meter user guide for more specific information.

1. Set the meter to the known addition mode.
2. Measure 100 mL of the sample and 2 mL of ISA and pour into a 150 mL beaker. Rinse the electrode(s) with distilled water, blot them dry and place the electrode(s) into the sample solution. Stir the solution thoroughly.
3. When a stable reading is displayed, adjust the meter as described in the meter user guide, if required.
4. Pipette the appropriate amount of the standard solution into the beaker. Stir the solution thoroughly.
5. When a stable reading is displayed, record the sample concentration.

Known Addition Using a Meter with a mV Mode

1. Set the meter to the mV millivolt mode.
2. Measure 100 mL of sample and 2 mL of ISA and pour into a 150 mL beaker. Stir the solution thoroughly.
3. Rinse the electrode(s) with distilled water, blot them dry and place the electrode(s) into the beaker. When a stable reading is displayed, record the mV value as E_1 .
4. Pipette the appropriate amount of standard solution into the beaker. See **Table 3**. Stir thoroughly.
5. When a stable reading is displayed, record the mV value as E_2 . Subtract the first reading from the second to find E .
6. Use Table 4 to find the Q value that corresponds to the change in potential, E . To determine the original sample concentration, multiply Q by the concentration of the added standard:

$$C_{\text{sam}} = Q C_{\text{std}}$$

where:

C_{std} = standard concentration

C_{sam} = sample concentration

Q = reading from known addition table

The table of Q values is calculated for a 10% total volume change for electrodes with slopes of 28.8, 29.1, 29.6, and 30.1 mV/decade.

The equation for the calculation of Q for different slopes and volume changes is given below:

$$Q = \frac{p * r}{[(1 + p)10^{\Delta E/S}]^{-1}}$$

where:

ΔE = $E_2 - E_1$

S = slope of the electrode

p = (volume of standard) / (volume of sample & ISA)

r = (volume of sample & ISA) / (volume of sample)

Table 3

Volume of Addition	Concentration of Standard Before Adding ISA
1 mL	100 x sample concentration
5 mL	20 x sample concentration
10 mL *	10 x sample concentration

*Most convenient volume to use, valid for Q tables

If it is more convenient, a simple spreadsheet can be set up to calculate known addition results, using any ratios of sample and addition. A typical worksheet is shown in **Table 4**. The numbers shown are examples, but the formulas and their locations should be copied exactly.

Table 4
Calculating known addition for calcium samples using Lotus, Excel or Quattro Spreadsheet

A	B	C
1	Enter Values	
2	VOL. OF SAMPLE & ISA, ML	51
3	VOL. OF ADDITION, ML	5
4	CONCENTRN. OF ADDITION	10
5	VOL. OF SAMPLE	50
6	INITIAL MV READING	45.3
7	FINAL MV READING	55.5
8	ELECTRODE SLOPE	28.6
9		
10	DERIVED VALUES	
11	DELTA E	+C7-C6
12	p-TERM	+C3/C2
13	ANTILOG TERM	+10^(C11/C8)
14	r TERM	+C2/C5
15	Q TERM	+C12*C14/(((1+C12)*C13)-1)
16	CALCULATED INITIAL CONC. IN SAME UNIT AS ADDITION	+C15*C4

Note: for Excel, use = instead of + at start of formula.

Table 5

Known Addition for an added volume one-tenth the total sample volume. Slopes (in the column headings) are in units of mV/decade.

ΔE Divalent	Q, Concentration Ratio			
	Slope			
	28.6	29.1	29.6	30.1
2.5	0.2917	0.2957	0.2996	0.3035
2.6	0.2827	0.2867	0.2906	0.2944
2.7	0.2742	0.2781	0.2820	0.2858
2.8	0.2662	0.2700	0.2738	0.2775
2.9	0.2585	0.2623	0.2660	0.2697
3.0	0.2512	0.2550	0.2586	0.2623
3.1	0.2443	0.2480	0.2516	0.2552
3.2	0.2377	0.2413	0.2449	0.2484
3.3	0.2314	0.2349	0.2384	0.2419
3.4	0.2253	0.2288	0.2323	0.2357
3.5	0.2196	0.2230	0.2264	0.2298
3.6	0.2140	0.2174	0.2208	0.2241
3.7	0.2087	0.2121	0.2154	0.2187
3.8	0.2037	0.2070	0.2102	0.2135
3.9	0.1988	0.2020	0.2052	0.2084
4.0	0.1941	0.1973	0.2005	0.2036
4.1	0.1896	0.1927	0.1959	0.1990
4.2	0.1852	0.1884	0.1914	0.1945
4.3	0.1811	0.1841	0.1872	0.1902
4.4	0.1770	0.1801	0.1831	0.1861
4.5	0.1732	0.1762	0.1791	0.1821
4.6	0.1694	0.1724	0.1753	0.1782
4.7	0.1658	0.1687	0.1716	0.1745
4.8	0.1623	0.1652	0.1680	0.1709
4.9	0.1590	0.1618	0.1646	0.1674
5.0	0.1557	0.1585	0.1613	0.1640
5.1	0.1525	0.1553	0.1580	0.1608
5.2	0.1495	0.1522	0.1549	0.1576
5.3	0.1465	0.1492	0.1519	0.1546
5.4	0.1437	0.1463	0.1490	0.1516
5.5	0.1409	0.1435	0.1461	0.1487
5.6	0.1382	0.1408	0.1434	0.1459
5.7	0.1356	0.1382	0.1407	0.1432
5.8	0.1331	0.1356	0.1381	0.1406
5.9	0.1306	0.1331	0.1356	0.1381
6.0	0.1282	0.1307	0.1331	0.1356
6.1	0.1259	0.1283	0.1308	0.1332
6.2	0.1236	0.1260	0.1284	0.1308
6.3	0.1214	0.1238	0.1262	0.1285
6.4	0.1193	0.1217	0.1240	0.1263
6.5	0.1172	0.1195	0.1219	0.1242
6.6	0.1152	0.1175	0.1198	0.1221
6.7	0.1132	0.1155	0.1178	0.1200
6.8	0.1113	0.1136	0.1158	0.1180
6.9	0.1094	0.1117	0.1139	0.1161
7.0	0.1076	0.1098	0.1120	0.1142
7.1	0.1058	0.1080	0.1102	0.1123
7.2	0.1041	0.1063	0.1084	0.1105
7.3	0.1024	0.1045	0.1067	0.1088
7.4	0.1008	0.1029	0.1050	0.1071
7.5	0.0992	0.1012	0.1033	0.1054
7.8	0.0946	0.0966	0.0986	0.1006
8.0	0.0917	0.0936	0.0956	0.0976
8.3	0.0876	0.0895	0.0914	0.0933
8.5	0.0850	0.0869	0.0887	0.0906

ΔE Divalent	Q, Concentration Ratio			
	Slope			
	28.6	29.1	29.6	30.1
8.8	0.0813	0.0831	0.0849	0.0868
9.0	0.0790	0.0808	0.0825	0.0843
9.3	0.0757	0.0774	0.0791	0.0809
9.5	0.0736	0.0753	0.0770	0.0787
9.8	0.0706	0.0722	0.0739	0.0755
10.0	0.0687	0.0703	0.0719	0.0735
10.3	0.0660	0.0675	0.0691	0.0707
10.5	0.0642	0.0658	0.0673	0.0689
10.8	0.0617	0.0633	0.0648	0.0663
11.0	0.0602	0.0617	0.0631	0.0646
11.3	0.0579	0.0593	0.0608	0.0623
11.5	0.0564	0.0579	0.0593	0.0607
11.8	0.0544	0.0558	0.0572	0.0585
12.0	0.0530	0.0544	0.0558	0.0572
12.3	0.0511	0.0525	0.0538	0.0551
12.5	0.0499	0.0512	0.0525	0.0539
12.8	0.0481	0.0494	0.0507	0.0520
13.0	0.0470	0.0483	0.0495	0.0508
13.3	0.0454	0.0466	0.0478	0.0491
13.5	0.0443	0.0455	0.0468	0.0480
13.8	0.0428	0.0440	0.0452	0.0464
14.0	0.0419	0.0430	0.0442	0.0454
14.3	0.0404	0.0416	0.0427	0.0439
14.5	0.0395	0.0407	0.0418	0.0429
14.8	0.0382	0.0393	0.0404	0.0416
15.0	0.0374	0.0385	0.0396	0.0407
15.5	0.0354	0.0365	0.0375	0.0386
16.0	0.0335	0.0345	0.0356	0.0366
16.5	0.0318	0.0328	0.0337	0.0347
17.0	0.0302	0.0311	0.0320	0.0330
17.5	0.0286	0.0295	0.0305	0.0314
18.0	0.0272	0.0281	0.0290	0.0298
18.5	0.0258	0.0267	0.0275	0.0284
19.0	0.0246	0.0254	0.0262	0.0270
19.5	0.0234	0.0242	0.0250	0.0258
20.0	0.0223	0.0230	0.0238	0.0246
20.5	0.0212	0.0219	0.0227	0.0234
21.0	0.0202	0.0209	0.0216	0.0224
21.5	0.0192	0.0199	0.0206	0.0213
22.0	0.0183	0.0190	0.0197	0.0204
22.5	0.0175	0.0181	0.0188	0.0195
23.0	0.0167	0.0173	0.0179	0.0186
23.5	0.0159	0.0165	0.0171	0.0178
24.0	0.0152	0.0158	0.0164	0.0170
24.5	0.0145	0.0151	0.0157	0.0162
25.0	0.0139	0.0144	0.0150	0.0155
25.5	0.0132	0.0138	0.0143	0.0149
26.0	0.0126	0.0132	0.0137	0.0142
26.5	0.0121	0.0126	0.0131	0.0136
27.0	0.0116	0.0120	0.0125	0.0131
27.5	0.0110	0.0115	0.0120	0.0125
28.0	0.0106	0.0110	0.0115	0.0120
28.5	0.0101	0.0106	0.0110	0.0115
29.0	0.0097	0.0101	0.0105	0.0110
29.5	0.0093	0.0097	0.0101	0.0105

Titration

The electrode makes a highly sensitive endpoint detector for titration with EDTA of calcium samples. Titrations are more time-consuming than direct electrode measurement, but the results are more accurate and reproducible. With careful technique, titrations accurate to 0.1% of the total calcium ion concentration of the sample can be performed. The Thermo Scientific Orion 960 Titrator Plus system may be used to automate these titrations.

EDTA complexes with other cations besides calcium ion. Interfering ions whose EDTA complexes are stable only at a certain pH can be eliminated by performing the titration for calcium at about pH 10 but less than pH 11 (adjusting with ammonia). In many cases, other interferences can be eliminated by a suitable choice of sample pH and the addition of masking agents to the sample solution. A comprehensive list of methods is given in:

Handbook of Analytical Chemistry, L. Meites, (ed.) McGraw Hill Book Co., New York, (1st edit.), pp. 3-76, 3-225.

Setup for Titration

1. Prepare the electrode(s) as described in **Electrode Assembly** and **Preparation**.
2. Connect the electrode(s) to the meter.
3. Prepare an EDTA titrant solution 10 - 20 times as concentrated as the sample by dilution of the 1 M stock solution. For a good end point break, the sample concentration should be at least 10^{-3} M in total calcium.

Measurement by Titration

1. Place 100 mL of sample into a 150 mL beaker.
2. Adjust sample pH to 10 with ammonia.
3. Place the electrode(s) into the sample. Stir the solution thoroughly.
4. Using a 10 mL burette, add increments of EDTA and plot electrode potential against mL of EDTA added. The end point is the point of greatest slope (inflection point). See **Figure 5**.
5. Calculate the sample concentration before dilution:

$$C_{\text{sam}} = C_t (V_t/V_{\text{sam}})$$

where:

C_{sam} = sample concentration

C_t = titrant concentration

V_{sam} = sample volume

V_t = titrant volume added at endpoint.

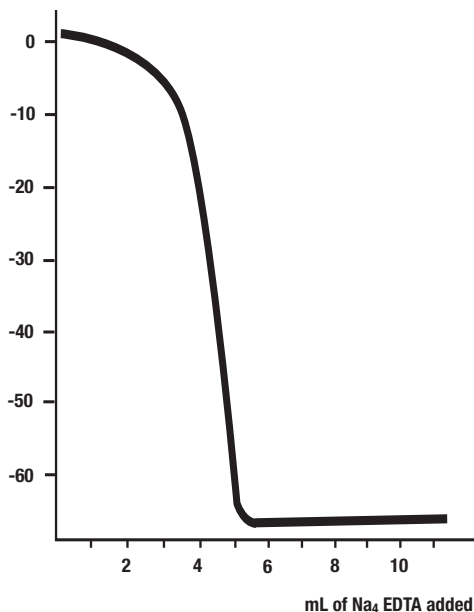


Figure 5

Typical Titration of 100 mL of 5×10^{-3} M CaCl_2
(pH adjusted to ~ 10 with ammonia) with 0.1 M Na_4EDTA

ELECTRODE STORAGE

Calcium Half-Cell Electrode, Cat. No. 9320BN

The calcium sensing module should be kept in the glass vial until used. The assembled electrode can be stored in 10^{-2} M calcium standard. For long periods of time (over 2-3 days), disassemble the calcium electrode, rinse it thoroughly with distilled water, shake it dry and store the module in its vial.

Calcium Combination Electrode, Cat. No. 9720BNWP

The filling solution in the 9720BNWP combination calcium electrode should not be allowed to evaporate and crystallize.

For short periods of time (2-3 days): Store the assembled electrode in a calcium standard with a concentration of about 10^{-2} M.

For storage longer than 2-3 days: Drain the electrode and flush the inside with distilled water. Disassemble the electrode as follows and remove the calcium sensing module:

1. Grasp the outer body sleeve. With your other hand, unscrew the electrode cap. Allow cap and spring assembly to slide down the electrode cable.
2. Push the inner stem of the electrode handle out through the outer electrode sleeve, exposing the sensing module.
3. Rinse the inner stem and module well with distilled water. Gently blot them dry in order not to damage the sensing module.
4. Carefully unscrew the sensing module from the inner stem, ***taking care not to touch the sensing membrane.***
5. Place the calcium sensing module in the glass vial until it is to be used again.
6. Gently dry the inside of the inner stem and O-ring area with a lint-free tissue and reassemble the electrode handle. Store dry.

Single Junction Reference Electrode, Cat. No.

The single junction reference electrode may be stored in a calcium standard between sample measurements (up to 1 hour).

For short periods of time (up to one week):

The single junction reference electrode may be stored in its filling solution. Do not allow the solution inside the electrode to evaporate and crystallize.

For long periods of time (over one week):

Drain the reference electrode completely, rinse with distilled water, and store dry.

TROUBLESHOOTING

Troubleshooting Checklist

Symptom– Off-scale or over-range reading

- No electrode filling solution added – Fill the electrode with filling solution up to the fill hole. Refer to the **Electrode Assembly and Preparation** section for details.
- Electrode junction is dry – Push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.
- No reference electrode present – The 9320BN calcium half-cell electrode requires a separate reference electrode, Cat. No. 900100.
- Air bubble on sensing element – Remove air bubble by reimmersing the electrode in solution.
- Electrode not in solution– Immerse the electrode in solution past the reference junction.
- Electrode not properly connected to meter – Unplug and reconnect the electrode to the meter.
- Defective electrode– Refer to the **Troubleshooting Guide** section.
- Defective meter– Check the meter performance. See the meter user guide.

Symptom– Noisy or unstable readings (readings continuously or rapidly changing)

- No electrode filling solution added – Fill the electrode with filling solution up to the fill hole.
- Electrode junction is dry – Push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.
- No reference electrode present – The 9320BN calcium half-cell electrode requires a separate reference electrode, Cat. No. 900100.
- Meter or stir plate not properly grounded – Check the meter and stir plate for proper grounding.
- Air bubble on sensing element – Remove air bubble by reimmersing the electrode in solution.
- ISA not used or incorrect ISA used – ISA must be added to all standards and samples. Use recommended ISA, Cat. No. 932011.

Symptom– Drift (reading slowly changing in one direction)

- No electrode filling solution added – Fill the electrode with filling solution up to the fill hole.
- Electrode junction is dry – Push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.
- Incorrect electrode filling solution used – Refer to the **Electrode Assembly and Preparation** section to verify the correct electrode filling solution.
- Samples and standards at different temperatures – Allow solutions to reach the same temperature.

Symptom– Low slope or no slope

- Electrodes not properly conditioned– Refer to the **Electrode Assembly and Preparation** section.
- Standards contaminated or made incorrectly– Prepare fresh standards.
- ISA not used or incorrect ISA used – ISA must be added to all standards and samples. Use recommended ISA, Cat. No. 932011.
- Electrode exposed to interferences– Refer to the **Troubleshooting Guide** section.

Symptom– Wrong answer, but calibration curve is correct

- Incorrect scaling of semi-logarithmic paper– Plot millivolts on the linear axis and concentration on the log axis.
- Incorrect millivolt sign recorded– Be sure to record the sign (+ or -) of the millivolt values.
- Standards contaminated or made incorrectly– Prepare fresh standards.
- Wrong units used– Apply correct conversion factor:
 $10^{-3} \text{ M} = 40 \text{ ppm as Ca}^{2+} = 100 \text{ ppm as CaCO}_3$
- Complexing agents in sample– Use known addition or titration techniques or a decomplexing procedure.

Troubleshooting Guide

Follow a systematic procedure to isolate the problem. The measuring system can be divided into four components for ease in troubleshooting: meter, electrode, sample/application and technique.

Meter

The meter is the easiest component to eliminate as a possible cause of error. Thermo Scientific Orion meters include an instrument checkout procedure and shorting cap for convenience in troubleshooting. Consult the meter user guide for directions.

Electrode

1. Rinse the electrode thoroughly with distilled water.
2. Verify the electrode performance by performing the procedure in the **Checking Electrode Operation (Slope)** section.
3. If the electrode fails this procedure, soak the calcium electrode as directed in the **Electrode Assembly and Preparation** section. Drain and refill the electrode with fresh filling solution.
4. Repeat the procedure in the **Checking Electrode Operation (Slope)** section.
5. If the electrode fails this procedure again and the half-cell calcium electrode is being used, determine whether the calcium or reference electrode is at fault. To do this, substitute a known working electrode for the electrode in question and repeat the procedure in the **Checking Electrode Operation (Slope)** section.

If the electrode fails this procedure again and the combination calcium electrode is being used, disassemble and reassemble the electrode, taking care not to overtighten the cap. If the electrode still does not perform as described, replace the sensing module and repeat the procedure in the **Checking Electrode Operation (Slope)** section.

6. If the electrode passes the procedure, but measurement problems persist, the sample may contain interferences or complexing agents, or the technique may be in error.
7. Before replacing a faulty electrode, review this user guide and be sure to thoroughly soak the electrode; correctly prepare the electrode; use the proper filling solutions, ISA, and standards; correctly measure the samples and review the **Troubleshooting Checklist** section.

Sample/Application

The quality of results depends greatly upon the quality of the standards. Always prepare fresh standards when problems arise, it could save hours of frustrating troubleshooting! Errors may result from contamination of prepared standards, accuracy of dilution, quality of distilled water, or a mathematical error in calculating the concentrations.

The best method for preparation of standards is serial dilution. The electrode and meter may operate with standards, but not with the sample. In this case, check the sample composition for interferences, incompatibilities or temperature effects.

Technique

If trouble persists, review operating procedures. Review calibration and measurement sections to be sure proper technique has been followed. Verify that the expected concentration of the ion of interest is within the limit of detection of the electrode.

Check the method of analysis for compatibility with your sample. Direct measurement may not always be the method of choice. If a large amount of complexing agents are present, known addition may be the best method. If the sample is viscous, alternate addition may solve the problem. If working with low-level samples, follow the procedure in the **Low-Level Measurement** section.

Assistance

After troubleshooting all components of your measurement system, contact Technical Support. Within the United States call 1.800.225.1480 and outside the United States call 978.232.6000 or fax 978.232.6031. In Europe, the Middle East and Africa, contact your local authorized dealer. For the most current contact information, visit www.thermo.com/water.

Warranty

For the most current warranty information, visit www.thermo.com/water.

ELECTRODE CHARACTERISTICS

Electrode Response

The electrode potential plotted against concentration on semi-logarithmic paper results in a straight line with a slope of about 25 to 30 mV per decade until concentration reaches 10^{-5} M. See **Figure 4**.

The electrode exhibits good time response (99% in one minute or less) for calcium concentrations above 10^{-5} M Ca^{2+} . Below this value response times vary from 2 to 5 minutes. See **Figure 6**.

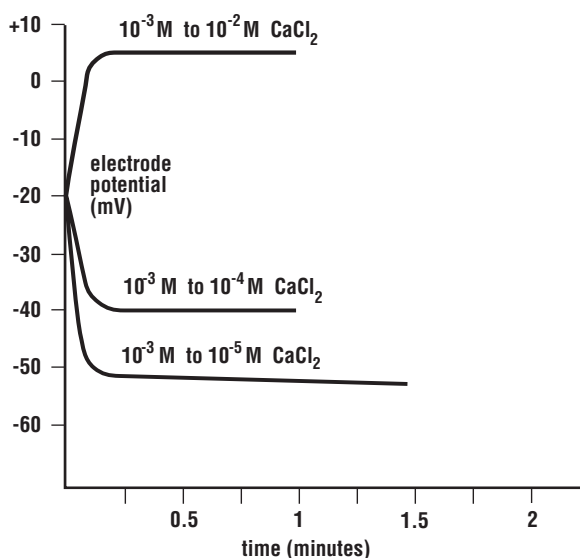


Figure 6
Typical Electrode Response to CaCl_2

Limits of Detection

In pure calcium chloride solutions, the upper limit of detection is 1 M. When possible, dilute the sample into the linear range of the electrode. If this is not possible, the possibility of a liquid junction potential at the reference electrode and the “salt extraction effect”, need to be considered. At high salt concentrations, some salts may be extracted into the electrode membrane, causing deviation from theoretical response. To measure samples between 10^{-1} and 1 M, calibrate the electrode at 4 or 5 intermediate points, or dilute the sample.

The lower limit of detection is determined by the slight water solubility of the ion exchanger, which causes deviation from theoretical response. **Figure 4** shows the theoretical response at low levels of calcium chloride compared to the actual response. If calcium measurements are made below 10^{-5} M (0.4 ppm as Ca^{2+}), a low-level measurement procedure is recommended.

Reproducibility

Reproducibility is limited by factors such as temperature fluctuations, drift, and noise. Within the electrode operating range, reproducibility is independent of concentration. With calibration every hour, direct electrode measurements reproducible to $\pm 4\%$ can be obtained.

Temperature Effects

Since electrode potentials are affected by changes in temperature, samples and standard solutions should be within $\pm 1^{\circ}\text{C}$ ($\pm 2^{\circ}\text{F}$) of each other. At the 10^{-3} M level, a 1°C difference in temperature results in a 4% error (Cat. No. 9320BN) and 1.2% error (Cat. No. 9720BNWP). The absolute potential of the reference electrode changes slowly with temperature because of the solubility equilibria on which the electrode depends. The slope of the calcium electrode also varies with temperature, as indicated by the factor S in the Nernst equation. Values for the change in slope for calcium ion are given in **Table 6**. If temperature changes occur, the meter and electrodes should be recalibrated. The electrode can be used at temperatures from 0 to 40°C , provided that temperature equilibrium has occurred. For use at temperatures substantially different from room temperature, equilibration times of up to one hour are recommended.

The isopotential concentration, C_{iso} , for the 9720BNWP calcium combination electrode is approximately 0.027 M.

Table 6
Values of Electrode Slope vs. Temperature

T° C	S	T° C	S
0	27.10	25	29.58
10	28.10	30	30.07
20	29.08	40	31.07

Interferences

Cations, if present at high enough levels, are electrode interferences and will cause measurement errors. **Table 7** indicates levels of common cations that will cause 10% errors at different concentrations of calcium.

If the electrode is exposed to high levels of interfering ions, it may become drift and sluggish in response. When this happens, restore normal performance by soaking for an hour in distilled water, then for a few hours in calcium standard solution.

When the level of interferences in samples is constant, it is sometimes possible to measure calcium accurately when interference levels are higher than those in **Table 7**. For example, calcium can be measured in sea water by using synthetic ocean water for calibration. Contact our Technical Support Chemists for more information.

pH Effects

Although the electrode can be used over a wide pH range, hydrogen ion interferes with measurements of low levels of calcium ion. Refer to **Table 7** to determine the minimum pH at which low level calcium measurements can be made without more than a 10% error due to hydrogen ion interference.

At high pH, sufficient hydroxide ion is present to form a precipitate with a portion of the calcium ion. This reaction reduces the level of free calcium ion in the sample. Since the electrode responds only to free, unbound calcium ion, it does not detect that portion of the sample calcium precipitated by hydroxide ion. Precipitation can be avoided by adjusting pH of sample and standards to below pH 11 with 1 M HCl when necessary.

Electrode Life

Each sensing module should last at least six months in normal laboratory use. In time, the electrode slope will decrease and readings will start to drift, indicating that the module should be changed. Before replacement, refer to the **Troubleshooting Checklist** section to make sure that the difficulties are caused by the sensing module.

Moles/Liter	10 ⁻⁴ M	10 ⁻³ M	10 ⁻² M Ca ²⁺
Pb ⁺⁺	1.0 x 10 ⁻⁶	1.0 x 10 ⁻⁵	1.0 x 10 ⁻⁴
Hg ⁺⁺	4.0 x 10 ⁻⁴	4.0 x 10 ⁻³	4.0 x 10 ⁻²
H ⁺	4.0 x 10 ⁻⁴	4.0 x 10 ⁻³	4.0 x 10 ⁻²
Sr ⁺⁺	6.0 x 10 ⁻⁴	6.0 x 10 ⁻³	6.0 x 10 ⁻²
Fe ⁺⁺	2.0 x 10 ⁻³	2.0 x 10 ⁻²	0.2
Cu ⁺⁺	4.0 x 10 ⁻³	4.0 x 10 ⁻²	0.4
Ni ⁺⁺	5.0 x 10 ⁻³	5.0 x 10 ⁻²	0.5
NH ₄ ⁺	2.0 x 10 ⁻²	0.2	2.0
Na ⁺	2.0 x 10 ⁻²	0.2	2.0
*Tris ⁺	3.0 x 10 ⁻²	0.3	3.0
Li ⁺	3.0 x 10 ⁻²	0.3	3.0
K ⁺	4.0 x 10 ⁻²	0.4	4.0
Ba ⁺⁺	7.0 x 10 ⁻²	0.7	7.0
Zn ⁺⁺	0.1	1.0	10
Mg ⁺⁺	0.1	1.0	10

* Tris is the cation of tris(hydroxymethyl) aminomethane.

Interferences

ppm	1 ppm as CaCO ₃	10 ppm as CaCO ₃	100 ppm as CaCO ₃
Pb ⁺⁺	0.2	2	20
Hg ⁺⁺	80	800	8,000
H ⁺	3.4 pH	2.4 pH	1.4 pH
Sr ⁺⁺	52	520	5,200
Fe ⁺⁺	111	1,110	11,100
Cu ⁺⁺	254	2,540	25,400
Ni ⁺⁺	294	2,940	29,400
NH ₄ ⁺	340	3,400	34,000
Na ⁺	460	4,600	46,000
*Tris ⁺	3,630	36,300	363,000
Li ⁺	208	2,080	20,800
K ⁺	1,564	15,640	156,000
Ba ⁺⁺	9,614	96,140	96,140
Zn ⁺⁺	6,537	65,370	653,700
Mg ⁺⁺	2,430	24,300	243,000

* Tris is the cation of tris(hydroxymethyl) aminomethane.

Complexation and Precipitation

The electrode responds to the “free” calcium in solution, and not to calcium which is bound or complexed. Certain calcium compounds are relatively insoluble. Among them, in the order of least soluble first, are calcium oxalate, carbonate, fluoride, phosphate and sulfate. For example, in a 40 ppm calcium solution, as little as 10 ppm of fluoride would cause part of the calcium to precipitate as calcium fluoride. About 650 ppm of sulfate would cause the precipitation of calcium at concentrations above about 400 ppm. These solubilities are affected by pH, with the solubility increasing in more acidic solutions. Calcium carbonate precipitation can be avoided completely by operating at pHs less than 7 and with the total carbonate and bicarbonate concentration kept below 3×10^{-3} M (280 ppm).

Calcium forms soluble complexes with certain inorganic species, such as hydroxide, bicarbonate and polyphosphates. It also forms complexes with some organic anions, such as citrate, tartrate, and EDTA. The extent of complexation increases with increasing calcium concentration and more alkaline pH, and will vary with the sample ionic strength. When it is desired to measure the total calcium concentration in the presence of complexing agents, this can often be done by adding a large excess of complexing agent, and then measuring by known addition.

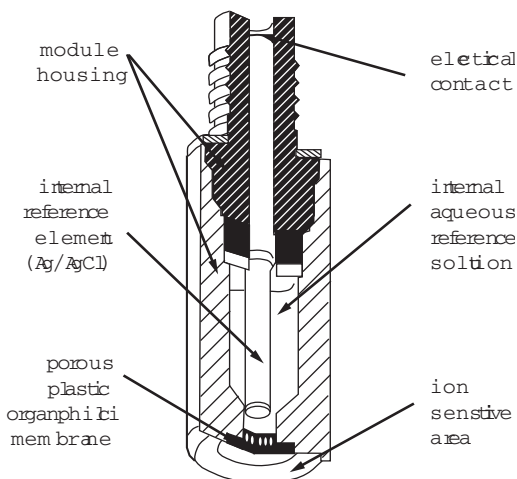


Figure 7
Example of Ion Sensing Module

Theory of Operation

The calcium electrode consists of an electrode body and a replaceable pretested sensing module. The sensing module contains a liquid internal filling solution in contact with a gelled organophilic membrane containing a calcium selective ion exchanger. See **Figure 7**.

When the membrane is in contact with a calcium solution, an electrode potential develops across the membrane. This potential, which depends on the level of free calcium ion in solution, is measured against a constant reference potential with a pH/mV meter or specific ion meter. The measured potential corresponding to the level of calcium ion in solution is described by the Nernst equation:

$$E = E_0 + S \log (A)$$

where:

E = measured electrode potential

E_0 = reference potential (a constant)

A = calcium ion level in solution

S = electrode slope (about 27 mV per decade)

The level of calcium ion, A , is the activity or “effective concentration” of free calcium ion in solution. The total calcium concentration, C_t , includes some bound or complexed ions as well as free ions, whose concentration is:

$$C_t = C_f + C_b$$

where:

C_b = concentration of calcium ions in all bound or complexed forms

C_f = concentration of free calcium ions

The calcium ion activity is related to free calcium ion concentration by the activity coefficient:

$$A = \gamma C_f$$

Ionic activity coefficients are variable and largely depend on total ionic strength. Ionic strength is defined as:

$$\text{Ionic strength} = 1/2 \sum (C_i Z_i^2)$$

C_i = concentration of ion i

Z_i = charge of ion i

If the background ionic strength is high and constant relative to the sensed ion concentration, the activity coefficient is constant and activity is directly proportional to concentration.

Ionic strength adjustor (ISA) is added to all calcium standards and samples so that the background ionic strength is high and constant relative to variable concentrations of calcium ion. For the calcium electrode, NaCl is the recommended ISA. Other solutions can be used as long as they do not contain ions that would interfere with the electrode's response to calcium ion.

Reference electrode conditions must also be considered. Liquid junction potentials arise any time two solutions of different composition are brought into contact. The potential results from the interdiffusion of ions in the two solutions. Since ions diffuse at different rates, the electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions. In making electrode measurements, it is important that this potential be the same when the reference electrode is in the standard solution as well as in the sample solution; otherwise, the change in liquid junction potential will appear as an error in the measured specific ion electrode potential.

The most important variable which analysts have under their control is the composition of the liquid junction filling solution. The filling solution should be equitransferent. That is, the speed with which the positive and negative ions in the filling solution diffuse into the sample should be as nearly equal as possible. If the rate at which positive and negative charge is carried into the sample solution is equal, then no junction potential can result.

ORDERING INFORMATION

Cat. No.	Description
9720BNWP	Calcium ionplus Sure-Flow combination electrode, waterproof BNC connector
9320BN	Calcium half-cell electrode, BNC connector
900100	Single junction reference electrode, pin tip connector
900011	Filling solution for single junction reference electrode, 5 x 60 mL
900061	Optimum Results A filling solution for calcium combination electrode, 5 x 60 mL
922006	0.1 M calcium standard, 475 mL
923206	100 ppm as CaCO ₃ calcium standard, 475 mL
932011	Calcium ISA solution, 475 mL
972001	Sensing module for 9720BNWP calcium combination electrode
932001	Sensing module for 9320BN calcium half-cell electrode
9700BNWP	Replacement electrode handle for calcium combination electrode, waterproof BNC connector
9300BNWP	Replacement electrode handle for calcium half-cell electrode, waterproof BNC connector

SPECIFICATIONS

Concentration Range

5×10^{-7} M to 1 M Ca^{2+}

0.02 to 40,100 ppm as Ca^{2+} or 0.05 to 100,000 ppm as CaCO_3

pH Range

2.5 to 11 pH

Low-level measurements may be influenced by hydrogen or hydroxide ion interferences.

Temperature Range

0 to 40°C

Electrode Resistance

0.1 to 4 megohms

Reproducibility

$\pm 4\%$

Sample

Aqueous solutions only

Module Life

Six months under normal laboratory conditions

Size (9720BNWP)

Electrode Length: 110 mm (excluding cap)

Cap Length: 30 mm

Electrode Diameter: 13 mm

Cap Diameter: 16 mm

Cable Length: 1 meter

Size (9320BN)

Electrode Length: 135 mm (excluding cap)

Cap Length: 30 mm

Electrode Diameter: 12 mm

Cap Diameter: 16 mm

Cable Length: 1 meter

254806-001 Rev.A

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Water Analysis Instruments

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