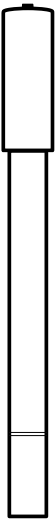
User Guide

Water Hardness Ion Selective Electrode



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This publication supersedes all previous publications on this subject.

Table of Contents

Introduction

This user guide contains information on the preparation, operation and maintenance for the divalent cation ion selective electrode (ISE). General analytical procedures, electrode characteristics and electrode theory are also included in this user guide. Divalent cation electrodes measure water hardness (total calcium plus magnesium) 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. For the most current contact information, visit www.thermo.com/contactwater.

For the latest application and technical resources for Thermo Scientific Orion products, visit www.thermo.com/waterapps.

Divalent Cation Plastic Membrane Half-Cell ISE, Cat. No. 9332BNWP

The divalent cation half-cell electrode must be used with the single junction reference electrode, Cat. No. 900100. The divalent cation half-cell electrode is available with a waterproof BNC connector, Cat. No. 9332BNWP. Electrodes with a waterproof BNC connector can be used on any ISE or mV meter with a BNC connection.

Required Equipment

1. Thermo Scientific Orion ISE meter, such as the 4-Star pH/ISE meter or 5-Star pH/ISE/DO/conductivity meter; equivalent ISE meter; or mV meter with a 0.1 mV resolution.

   Divalent cation electrodes can be used on any ISE or mV meter with a BNC connection. The electrodes can also be used on meters with a variety of inputs when an adapter cable is used. Visit www.thermo.com/water for details.

2. Thermo Scientific Orion divalent cation electrode, Cat. No. 9332BNWP.

3. Single junction reference electrode, Cat. No. 900100.

4. Magnetic stirrer or Thermo Scientific Orion stirrer probe, Cat. No. 096019. The stirrer probe can be used with 3-Star, 4-Star and 5-Star benchtop meters.

5. Volumetric flasks, graduated cylinders and beakers.

6. Distilled or deionized water.

7. Electrode filling solution, Cat. No. 900011.

   ***Note**: Do not use the filling solution that ships with the single junction reference electrode because it contains interferences for divalent cation measurements.*

8. 0.1 M calcium activity standard solution, Cat. No. 922006.

9. 100 ppm calcium as calcium carbonate standard solution, Cat. No. 923206.

10. pH adjustment solutions, 1 M sodium hydroxide and 1 M hydrochloric acid.

Serial Dilutions

Serial dilution is the best method for the preparation of standards. Serial dilution means that an initial standard is diluted, using volumetric glassware, to prepare a second standard solution. The second standard is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.

1. **To prepare a 10^{-2} M standard (1000 ppm as $CaCO_3$ and 401 ppm as Ca^+) –** Pipet 10 mL of the 0.1 M standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

2. **To prepare a 10^{-3} M standard (100 ppm as $CaCO_3$ and 40.1 ppm as Ca^+) –** Pipet 10 mL of the 10^{-2} M standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

3. **To prepare a 10^{-4} M standard (10 ppm as $CaCO_3$ and 4.01 ppm as Ca^+) –** Pipet 10 mL of the 10^{-3} M standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

To prepare standards with a different concentration use the following formula:

$$C_1 * V_1 = C_2 * V_2$$

C_1 = concentration of original standard
V_1 = volume of original standard
C_2 = concentration of standard after dilution
V_2 = volume of standard after dilution

For example, to prepare 100 mL of a 100 ppm calcium carbonate standard from a 10000 ppm calcium carbonate standard:

C_1 = 10000 ppm calcium carbonate

V_1 = unknown

C_2 = 100 ppm calcium carbonate

V_2 = 100 mL

$10000 \text{ ppm} * V_1 = 100 \text{ ppm} * 100 \text{ mL}$

$V_1 = (100 \text{ ppm} * 100 \text{ mL}) / 10000 \text{ ppm} = 1.0 \text{ mL}$

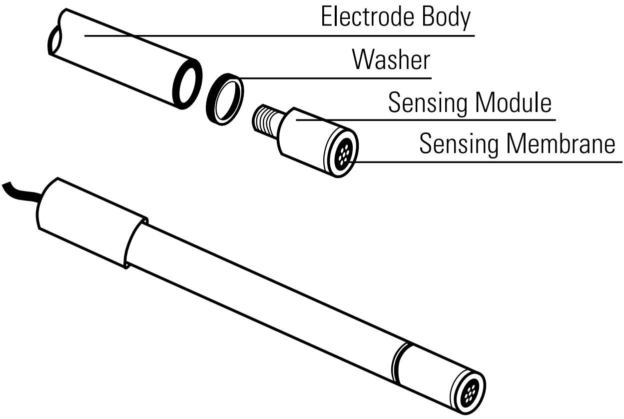
Electrode Setup

Divalent Cation Half-Cell Electrode Preparation

Remove the divalent cation sensing module from the vial and save the vial for electrode storage. Make sure that the rubber electrode washer on the sensing module is in place. See **Figure 1**. Screw the sensing module into the 93 series electrode body until the module is finger-tight. To ensure electrical continuity, shake the electrode down like a clinical thermometer. Rinse the divalent cation module with distilled water and then soak it overnight in a 10^{-2} M or 100 ppm calcium carbonate standard adjusted to pH 7 to 10 with sodium hydroxide (NaOH).

Note: *Do not immerse the electrode past the rubber washer.*

Figure 1
Divalent Cation Half-Cell Electrode



Single Junction Reference Electrode Preparation

Prepare the reference electrode according to the reference electrode user guide. Fill the reference electrode with filling solution, Cat. No. 900011.

Note: *Do not use the filling solution that ships with the 900100 single junction reference electrode because it contains interferences for divalent cation measurements.*

Checking Electrode Operation (Slope)

These are general instructions that can be used with most meters to check the electrode operation. Refer to the meter user guide for more specific information.

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

1. If the electrode has been stored dry, prepare the electrode as described in the **Electrode Preparation** section.

2. Connect the electrode to a meter with a mV mode. Set the meter to the mV mode.

3. Add 100 mL of distilled water to a 150 mL beaker. Stir the solution thoroughly.

4. Rinse the electrode with distilled water and place the electrode into the solution prepared in step 3.

5. Select either a 0.1 M or 100 ppm calcium carbonate standard. Pipet 1 mL of the standard into the beaker and stir the solution thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.

6. Pipet 10 mL of the same standard into the same beaker and stir the solution thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.

7. There should be a 22 to 30 mV difference between the two millivolt readings when the solution temperature is between 20 to 25 °C. If the millivolt potential is not within this range, refer to the **Troubleshooting** section.

Measurement Units

Divalent cation concentration can be measured in moles per liter (M), parts per million (ppm) or any convenient concentration unit.

Table 1
Concentration Unit Conversion Factors

Moles/Liter (M)	ppm as Ca^+	ppm as $CaCO_3$
1.0	40100	100000
10^{-1}	4010	10000
10^{-2}	401	1000
10^{-3}	40.1	100
2.5×10^{-4}	10.0	24.9
10^{-4}	4.01	10

Sample Requirements

All samples must be aqueous and must not contain organic solvents. Contact Technical Support for information on using the electrode for specific applications.

The solution temperature must be less than 50 °C.

Samples and standards should be at the same temperature. A 1 °C difference in temperature for a 10^{-3} M solution will give rise to about a 4% measurement error.

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

Samples must be within a pH range of 7 to 10. The pH of samples outside of this pH range must be adjusted with sodium hydroxide (NaOH) or hydrochloric acid (HCl).

Measuring Hints

- Soak new modules overnight in a 10^{-2} M or 100 ppm calcium carbonate standard adjusted to pH 7 to 10 with sodium hydroxide (NaOH).
- Adjust the pH of samples to between pH 7 and 10 with sodium hydroxide (NaOH) or hydrochloric acid (HCl).
- Stir all standards and samples at a uniform, moderate rate. Place a piece of insulating material, such as Styrofoam or cardboard, between the magnetic stir plate and beaker to prevent measurement errors from the transfer of heat to the sample.
- Always use freshly prepared standards for calibration.
- Concentrated samples (over 0.1 M) should be diluted before measurement.
- Always rinse the electrode with distilled water between measurements and shake the electrode to remove the water and prevent sample carryover. Do not wipe or rub the electrode sensing module.
- Store the divalent cation electrode in a 10^{-2} M or 100 ppm calcium carbonate standard between measurements.
- The divalent cation half-cell electrode should be immersed in standards and samples to approximately half the length of the divalent cation module. Do not immerse the divalent cation electrode past the electrode washer. Immerse the reference electrode to the same depth as the divalent cation electrode.
- Allow all standards and samples to reach the same temperature for precise measurements.
- Verify the electrode calibration every two hours by placing the electrode in a fresh aliquot of the least concentrated standard used for calibration. If the value has changed by more than 2%, recalibrate the electrode.
- After immersing the electrode in a solution, check the electrode sensing surface for air bubbles and remove air bubbles by reimmersing the electrode in the solution and gently tapping it.
- For high ionic strength samples, prepare standards with a background composition similar to the sample.
- The single junction reference electrode fill hole must be open during measurements to ensure a uniform flow of filling solution.
- If the electrode response becomes sluggish, the membrane may contain a surface layer of contaminants. See the **Electrode Maintenance** section for cleaning instructions.

Electrode Storage

Divalent Cation Half-Cell Electrode Storage

The divalent cation half-cell electrode should be rinsed thoroughly with distilled water and stored a 10^{-2} M or 100 ppm calcium carbonate standard. When storing the electrode for more than three days, rinse the divalent cation half-cell electrode thoroughly with distilled water, shake the electrode dry, disassemble the electrode and store the sensing module in the glass vial.

Single Junction Reference Electrode Storage

The single junction reference electrode may be stored in a 0.1 M KCl solution between sample measurements and up to one week. The filling solution inside the electrode should not be allowed to evaporate, as crystallization will result.

For storage longer than one week, drain the reference electrode, flush the inside with distilled water and store the electrode dry.

Electrode Maintenance

Single Junction Reference Electrode Flushing

If the area between the electrode outer body and inner cone becomes clogged with sample or precipitate, flush the area with filling solution or distilled water.

1. Hold the electrode body with one hand and use your thumb to push down on the electrode cap to drain all of the filling solution out of the electrode.

2. Fill the electrode with distilled water and then push down on the cap until all the water is drained from the chamber. Repeat this procedure until all of the sample or precipitate is removed from the electrode.

3. Fill the electrode with fresh filling solution up to the fill hole. Push down on the cap to allow a few drops of filling solution to drain out of the electrode and then replenish the lost filling solution.

4. Rinse the electrode with distilled water.

Cleaning the Divalent Cation Sensing Module

If the electrode is exposed to high levels of interfering ions, it may drift and become sluggish in response. When this happens, restore normal performance by soaking the electrode for an hour in distilled water and then soaking the electrode for a few hours a 10^{-2} M or 100 ppm calcium carbonate standard. If soaking the electrode does not restore normal electrode performance, replace the divalent cation sensing module.

Replacing the Divalent Cation Sensing Module

The sensing membrane of plastic membrane electrodes will wear over time, indicated by low slope values, drift, poor reproducibility and loss of response in low level samples. The electrode response can be restored by replacing the sensing module. Each sensing module will last about six months with normal laboratory use, but the actual lifespan of the sensing module will depend on the type of samples that are measured.

For the divalent cation half-cell electrode, use the divalent cation module, Cat. No. 933201. Rinse the electrode with distilled water, carefully unscrew the sensing module from the electrode and dispose of the old sensing module. Obtain a new divalent cation module and refer to the **Divalent Cation Half-Cell Electrode Preparation** section for instructions on assembling the electrode.

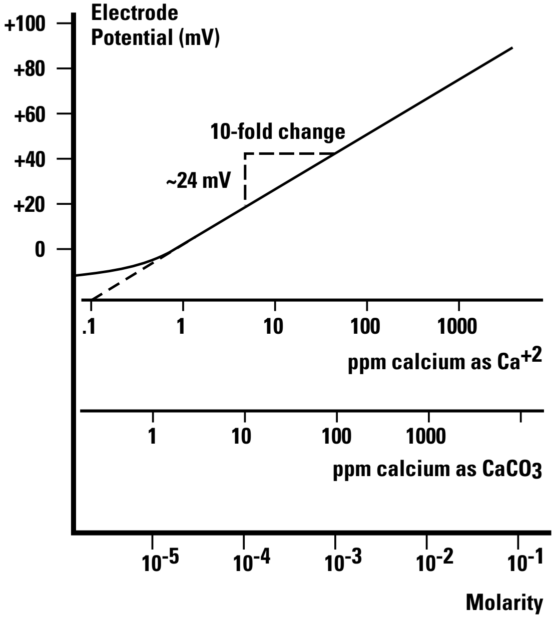
Direct Calibration Technique

Direct calibration is a simple procedure for measuring a large number of samples. Only one meter reading is required for each sample. Calibration is performed using a series of standards. The concentration of the samples is determined by comparison to the standards.

Typical Direct Calibration Curve

In the direct calibration procedure, a calibration curve is constructed either in the meter memory or on semi-logarithmic paper. Electrode potentials of standard solutions are measured and 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. These direct calibration procedures are given for concentrations in the region of linear electrode response.

Figure 2
Typical Direct Calibration Curve



Direct Calibration Overview

Direct measurement determines the concentration of the total calcium plus magnesium ion concentration (water hardness). The Thermo Scientific Orion calcium electrode, Cat. No. 9720BNWP, measures calcium in the presence of magnesium. A two point calibration is sufficient, although more points can be used. When using an ISE meter, sample concentrations can be read directly from the meter. When using a mV meter, a calibration curve can be prepared on semi-logarithmic graph paper, or a linear regression (against logarithmic concentration values) can be performed using a spreadsheet or graphing program.

Calibration Hints

- Standard concentrations should bracket the expected sample concentrations.

- For high ionic strength samples that have an ionic strength of 0.1 M or greater, prepare standards with a background composition similar to that of the samples, or measure the samples using the known addition method.

- During calibration, measure the least concentrated standard first, and work up to the most concentrated standard.

Direct Calibration Setup

1. Prepare the electrode as described in the **Electrode Preparation** section. Soak the divalent cation electrode for at least one hour in a 10^{-2} M or 100 ppm calcium carbonate standard adjusted to pH 7 to 10 with sodium hydroxide (NaOH).

2. Connect the electrode to the meter.

3. Prepare at least two standards that bracket the expected sample range and differ in concentration by a factor of ten. Standards can be prepared in any concentration unit to suit the particular analysis requirement. See the **Serial Dilution** section for instructions on how to prepare standards. All standards should be at the same temperature as the samples. For details on temperature effects on electrode performance, refer to the **Temperature Effects** section.

Direct Calibration Procedure Using a Meter with an ISE Mode

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

1. Add 100 mL of the less concentrated standard to a 150 mL beaker and stir the solution thoroughly.

2. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the less concentrated standard. Wait for a stable reading and adjust the meter to display the value of the standard, as described in the meter user guide.

3. Add 100 mL of the more concentrated standard to a second 150 mL beaker and stir the solution thoroughly.

4. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the more concentrated standard. Wait for a stable reading and 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 22 and 30 mV when the standards are between 20 and 25 °C.

6. Add 100 mL of sample to a clean 150 mL beaker and stir the solution thoroughly.

7. Rinse the electrode with distilled water, blot it dry and place it into the sample. The concentration of the sample will be displayed on the meter.

Direct Calibration Procedure Using a Meter with a mV Mode

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

1. Set the meter to the mV mode.

2. Add 100 mL of the less concentrated standard to a 150 mL beaker and stir the solution thoroughly.

3. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the less concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.

4. Add 100 mL of the more concentrated standard to a second 150 mL beaker and stir the solution thoroughly.

5. Rinse the electrode with distilled water, blot it dry and place it 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. Add 100 mL of sample to a clean 150 mL beaker and stir the solution thoroughly.

8. Rinse the electrode with distilled water, blot it dry and place it 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.

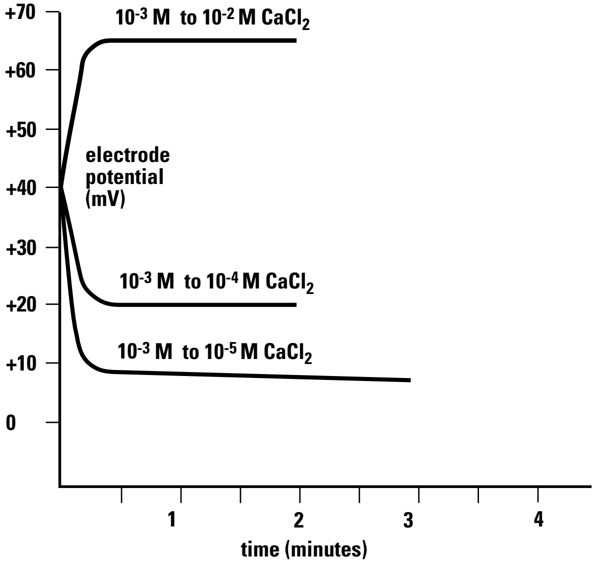
Electrode Characteristics

Electrode Response

The electrode potential plotted against concentration on semi-logarithmic paper results in a straight line with a slope of about 22 to 30 mV per decade change in concentration.

The time response of the electrode (the time required to reach 99% of the stable potential reading) varies from several seconds in concentrated solutions to several minutes near the limit of detection. The electrode exhibits good time response for concentrations above 5 x 10^{-5} M. Below this value response times are considerably longer and response is no longer linear.

Figure 3
Typical Electrode Response to $CaCl_2$ Concentration



Reproducibility

Reproducibility is limited by factors such as temperature fluctuations, drift and noise. Within the operating range of the electrode, reproducibility is independent of concentration. With hourly calibrations, direct electrode measurements reproducible to ± 4% can be obtained.

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 samples are not diluted, the possibility of a liquid reference junction potential and the salt extraction effect, need to be considered. At high salt concentrations, 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 2** shows the theoretical response at low levels of divalent cation compared to the actual response.

Electrode Life

Each sensing module will last approximately six months with normal laboratory use, but the actual lifespan of the sensing module will depend on the type of samples that the electrode is used in. Refer to the **Electrode Maintenance** section for instructions on changing the sensing module. 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** section to make sure that the difficulties are caused by the sensing module.

Temperature Effects

Since electrode potentials are affected by changes in temperature, samples and standard solutions should be within ± 1 °C (± 2 °F) of each other. At the 10^{-3} M level, a 1 °C difference in temperature results in errors greater than 4%. 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 electrode also varies with temperature, as indicated by the factor S in the Nernst equation. Theoretical values of the slope at different temperatures are given in **Table 2**. If the temperature changes, the meter and electrode 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, calibration standards should be at the same temperature as samples.

Table 2
Theoretical Slope vs. Temperature Values

Temperature (°C)	Slope (mV)
0	27.10
10	28.10
20	29.08
25	29.58
30	30.07
40	31.07

Interferences

Some cations, if present at high enough levels, are electrode interferences and will cause measurement errors. **Table 3** indicates levels of common ions that will cause 10% errors at different concentrations of divalent cation.

If the electrode is exposed to high levels of interfering ions, it may drift and become sluggish in response. When this happens, restore normal performance by soaking the electrode for an hour in distilled water and then soaking the electrode for a few hours a 10^{-2} M or 100 ppm calcium carbonate standard. If soaking the electrode does not restore normal electrode performance, refer to the **Electrode Maintenance** section for instructions on how to replace the sensing module.

Table 3
Divalent Cation Electrode Interferences

Interferences Moles/Liter	10^{-4} M Calcium Carbonate	10^{-3} M Calcium Carbonate	10^{-2} M Calcium Carbonate
Na^+	8×10^{-3}	3×10^{-2}	8×10^{-2}
K^+	3×10^{-2}	0.1	0.3
Cu^{+2}	3×10^{-6}	3×10^{-5}	3×10^{-4}
Zn^{+2}	3×10^{-6}	3×10^{-5}	3×10^{-4}
Fe^{+2}	6×10^{-6}	6×10^{-5}	6×10^{-4}
Ni^{+2}	1×10^{-5}	1×10^{-4}	1×10^{-2}
Sr^{+2}	4×10^{-5}	4×10^{-4}	4×10^{-3}
Ba^{+2}	6×10^{-5}	6×10^{-4}	6×10^{-3}

Complexation and Precipitation

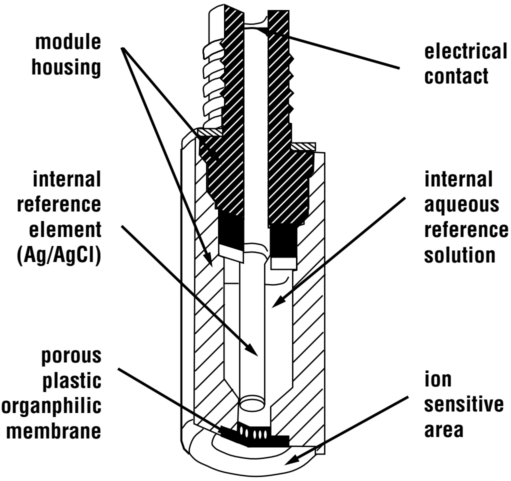
Calcium and magnesium form complexes with a wide variety of species including hydroxide, sulfate, bicarbonate, and carbonate. The extent of complexation depends on the concentration of the complexing agent, the total calcium and magnesium ion concentration, the pH of the solution, and the total ionic strength of the solution. Since the electrode responds only to free ions, complexation reduces the measured concentration.

Sulfate concentrations must be less than 5×10^{-4} M (50 ppm) to avoid formation of $CaSO_4$ and $MgSO_4$. To avoid precipitation of $CaCO_3^+$, the pH of the solution should be approximately 7 and the total carbonate and bicarbonate concentration should be less than 3×10^{-3} M (280 ppm carbonate).

Theory of Operation

The divalent cation electrode consists of a replaceable sensing module connected to an epoxy body. The sensing module contains a liquid internal filling solution in contact with a gelled organophilic membrane that contains a divalent cation selective ion exchanger.

Figure 4
Example of an Ion Sensing Module



When the module is in contact with a solution containing calcium and magnesium ions, an electrode potential develops across the module. This potential, which depends on the level of free calcium and magnesium ions in solution, is measured against a constant reference potential with a digital pH/mV meter or ISE (concentration) meter. The measured potential corresponding to the level of divalent cation ion in solution is described by the Nernst equation.

$$\mathbf{E = E_o + S * \log (A)}$$

E = measured electrode potential
E_o = reference potential (a constant)
A = divalent cation ion activity level in solution
S = electrode slope (about 24 mV per decade)
$S = (2.3\ R\,T) / nF$
R and F are constants, T = temperature in degrees K and
n = ionic charge

The level of calcium and magnesium ions, A, is the activity or "effective concentration" of free calcium and magnesium ions in solution. The calcium and magnesium ion activity is related to free calcium and magnesium ion concentration, C_f, by the activity coefficient, y.

$$\mathbf{A = y * C_f}$$

Ionic activity coefficients are variable and largely depend on total ionic strength. The ionic strength of a solution is determined by all of the ions present. It is calculated by multiplying the concentration of each individual ion by the square of its charge, adding all these values up and then dividing by two.

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

C_i = concentration of ion i
Z_i = charge of ion i
$\sum$ symbolizes the sum of all the types of ions in solutions

If 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.

If samples have a high ionic strength (above 0.1 M), standards should be prepared with a composition similar to the samples.

Reference electrode conditions must also be considered. Liquid junction potentials arise any time when 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 is the same when the reference is in the standardizing solution as well as in the same solution; otherwise, the change in liquid junction potential will appear as an error in the measured specific ion electrode potential.

The most important variable that 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 nearly as 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.

Troubleshooting

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, review the **Measuring Hints** section. Clean the electrode thoroughly as directed in the **Electrode Maintenance** section. Drain and refill the reference electrode with fresh filling solution.

4. Repeat the procedure in the **Checking Electrode Operation (Slope)** section.

5. It the electrode fails this procedure again, determine whether the divalent cation 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.

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 clean the electrode; correctly prepare the electrode; use the proper filling solution 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. Refer to the **Serial Dilution** section. 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. Refer to the **Sample Requirements**, **Temperature Effects** and **Interferences** sections.

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.

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/contactwater.

For the latest application and technical resources for Thermo Scientific Orion products, visit www.thermo.com/waterapps.

Warranty

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

Troubleshooting Checklist

- No electrode filling solution added –
  Fill the reference electrode with filling solution up to the fill hole. Refer to the **Electrode Preparation** section for details.

- Incorrect electrode filling solution used –
  Refer to the **Electrode Preparation** section to verify that the correct electrode filling solution was used.

- 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 divalent cation half-cell electrode require a separate reference electrode, Cat. No. 900100.

- Electrode is clogged or dirty –
  Refer to the **Electrode Maintenance** section for electrode cleaning and flushing instructions.

- Sensing module is not installed properly, dirty or defective –
  Refer to the **Electrode Preparation** section and verify that the electrode was assembled correctly. Refer to the **Electrode Maintenance** section for instructions on installing a new sensing module.

- Standards are contaminated or made incorrectly –
  Prepare fresh standards. Refer to the **Serial Dilution**, **Measurement Hints** and **Analytical Techniques** sections.

- Sample not in the correct pH range of pH 7 to 10 –
  Add sodium hydroxide (NaOH) or hydrochloric acid (HCl) to the sample until the sample pH is between 7 and 10. Make sure to account for the dilution factor of adding sodium hydroxide (NaOH) or hydrochloric acid (HCl) to the sample.

- Samples and standards at different temperatures –
  Allow solutions to reach the same temperature.

- Air bubble on sensing module –
  Remove air bubble by reimmersing the electrode in solution.

- Electrode not properly connected to meter –
  Unplug and reconnect the electrode to the meter.

- Meter or stir plate not properly grounded –
  Check the meter and stir plate for proper grounding.

- Static electricity present –
  Wipe plastic parts on the meter with a detergent solution.

- Defective meter –
  Check the meter performance. See the meter user guide.

Ordering Information

Cat. No.	Description
9332BNWP	Divalent cation half-cell electrode, waterproof BNC connector (requires separate reference electrode)
900100	Single junction reference electrode, pin tip connector
900011	Filling solution for the single junction reference electrode, 5 x 60 mL bottles
922006	0.1 M calcium activity standard solution, 475 mL bottle
923206	100 ppm calcium as calcium carbonate standard solution, 475 mL bottle
933201	Replacement divalent cation sensing module

Specifications

Concentration Range

6×10^{-6} M to 1 M

pH Range

7 to 10

Temperature Range

0 to 50 °C

Electrode Resistance

Less than 10 megohms

Reproducibility

± 4%

Size – Divalent Cation Half-Cell Electrode

Body Diameter: 12 mm

Body Length: 105 mm

Cap Diameter: 16 mm

Cable Length: 1 meter

* *Specifications are subject to change without notice*

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