

**pHoenix Electrode Company**  
**WATER HARDNESS ELECTRODES**  
**INSTRUCTION MANUAL**

**GENERAL INSTRUCTIONS**

**Introduction**

The pHoenix Electrode Company Water Hardness Electrodes are used to quickly, simply, accurately, and economically measure water hardness (total calcium plus magnesium) in aqueous solutions.

**Required Equipment**

1. A pH/mV meter or an ion meter, either line operated or portable.
2. Semi-logarithmic 4-cycle graph paper for preparing calibration curves when using the meter in the mV mode.
3. A magnetic stirrer.
4. The pHoenix Electrode Company Water Hardness Combination Glass Electrode, Cat. No. WHA1502, or the pHoenix Electrode Company Water Hardness Combination Epoxy Electrode, Cat. No. WHA1508.

**Required Solutions**

1. Deionized or distilled water for solution and standard preparation.
2. pHoenix Electrode Company Water Hardness Standard, 0.1M CaCl<sub>2</sub>, Cat. No. WHAAS01. To prepare this standard, add 14.7 grams of reagent-grade calcium chloride (CaCl<sub>2</sub>·2H<sub>2</sub>O) to a 1 liter volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid and fill to the mark with distilled water. Cap the flask and invert several times to mix the solution.
3. pHoenix Electrode Company Water Hardness Standard, 1000 ppm Ca<sup>+2</sup>, Cat. No. WHAAS02. To prepare this standard, add 3.67 grams of reagent-grade calcium chloride (CaCl<sub>2</sub>·2H<sub>2</sub>O) to a 1 liter volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid and fill to the mark with distilled water. Cap the flask and invert several times to mix the solution.
4. pHoenix Electrode Company Water Hardness Standard, 100 ppm Ca<sup>+2</sup> as CaCO<sub>3</sub>. To prepare a 100 ppm stock solution, add 0.15 grams of reagent-grade calcium chloride (CaCl<sub>2</sub>·2H<sub>2</sub>O) to a 1 liter volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid and fill to the mark with distilled water. Cap the flask and invert several times to mix the solution.

5. pHoenix Electrode Company Ionic Strength Adjuster, 4 M KCl, Cat. No. WHAIS01. To prepare the ISA, add 298 grams of reagent-grade potassium chloride (KCl) to a 1000 ml volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid and fill to the mark with distilled water. Cap the flask and invert several times to mix the solution.
6. pHoenix Electrode Company Acid pH Adjustment Solution, 1M HCl. To prepare a 1M HCl solution, add 86 ml of concentrated hydrochloric acid to a 1 liter volumetric flask containing about 500-600 ml of deionized water, swirl the flask to mix the contents, and add water to the mark. Cap the flask and upend it several times to thoroughly mix the contents.
7. pHoenix Electrode Company Alkaline pH Adjustment Solution, 1M NaOH. To prepare a 1M NaOH solution, add 40 grams of sodium hydroxide pellets to a 1 liter volumetric flask containing about 500-600 ml of deionized water, swirl the flask to dissolve the solid, and add water to the mark. Cap the flask and upend it several times to thoroughly mix the contents.

## **GENERAL PREPARATION**

### **Electrode Preparation**

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

Connect the electrode(s) to the proper terminal(s) as recommended by the meter manufacturer.

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

To a 150 ml beaker, add 100 ml of distilled water. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tip(s) into the solution. If drifting or instability is observed, see the **TROUBLESHOOTING** section.

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

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

Determine the difference between the two readings. A difference of  $25 \pm 2\text{mV}$  indicates correct electrode operation, assuming the solution temperature is between  $20^\circ$  and  $25^\circ\text{C}$ . See the **TROUBLESHOOTING** section if the potential change is not within this range.

Slope is defined as the change in potential observed when the concentration changes by a factor of 10.

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

Prepare two standard calcium solutions whose concentrations vary by tenfold. Use either the 0.1M  $\text{Ca}^{+2}$ , 1000 ppm  $\text{Ca}^{+2}$ , or the 100 ppm  $\text{Ca}^{+2}$  (as calcium carbonate) standard stock solutions. Use the serial dilution method for this preparation.

To a 150 ml beaker, add 100 ml of the lower value standard and 2 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip(s) into the solution. Assure that the meter is in the concentration mode.

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

Rinse the electrode(s) with distilled water and blot dry.

To a 150 ml beaker, add 100 ml of the higher value standard and 2 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip(s) into the solution.

Adjust the meter to the concentration of the standard and fix the value in the memory. Read the electrode slope according to the meter manufacturer's instructions. Correct electrode operation is indicated by a slope of 90-100%. See the **TROUBLESHOOTING** section if the slope is not within this range.

## **MEASUREMENT**

### **Measuring Hints**

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

All samples and standards should be at the same temperature for precise measurement, preferably ambient temperature.

Constant, but not violent, stirring is necessary for accurate measurement. Magnetic stirrers can generate sufficient heat to change the solution temperature. To counteract this effect, place a piece of insulating material, such as a styrofoam sheet, between the stirrer and beaker.

Always rinse the electrode tip(s) with distilled water and blot dry with a fresh tissue between readings to prevent solution carryover. Do not wipe or rub the sensing membrane.

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

A slow or sluggish electrode response may indicate surface contamination of the membrane. Soak the electrode tip in distilled water for about 5 minutes to clean the membrane. Rinse the membrane and soak in diluted standard solution for about 5 minutes to restore performance.

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

Dilute concentrated samples (over 0.1M) before measurement.

Recalibrate every few hours for routine measurement.

### **Sample Requirements**

Make sure that the samples and standards are at the same temperature. About a 4% error will be introduced for a 1°C difference in temperature at the  $1.0 \times 10^{-3} \text{M}$  level. Temperature should be less than 40°C.

All samples and standards must be aqueous. They must not contain organic solvents. Adjust the sample solution to between pH 5-10 with NaOH or HCl.

Interferences found in Table 3 should be absent.

### **Units of Measurement**

Water hardness concentrations are measured in units of parts per million as calcium, parts per million as  $\text{CaCO}_3$ , grains of hardness, moles per liter, or any other convenient concentration unit. Table 1 indicates some of the concentration units.

**TABLE 1: Concentration Unit Conversion Factors**

<u>ppm <math>\text{Ca}^{+2}</math></u>	<u>ppm <math>\text{CaCO}_3</math></u>	<u>moles/liter <math>\text{Ca}^{+2}</math></u>	<u>grains/gal</u>
4.01	10.0	$1.0 \times 10^{-4}$	0.6
10.00	24.9	$2.5 \times 10^{-4}$	1.4
70.60	176.0	$1.8 \times 10^{-3}$	10.0

### **MEASUREMENT PROCEDURE**

#### **Direct Measurement**

Direct measurement is a simple procedure for measuring a large number of samples. A single meter reading is all that is required for each sample. The temperature of both sample solution and of standard solutions should be the same.

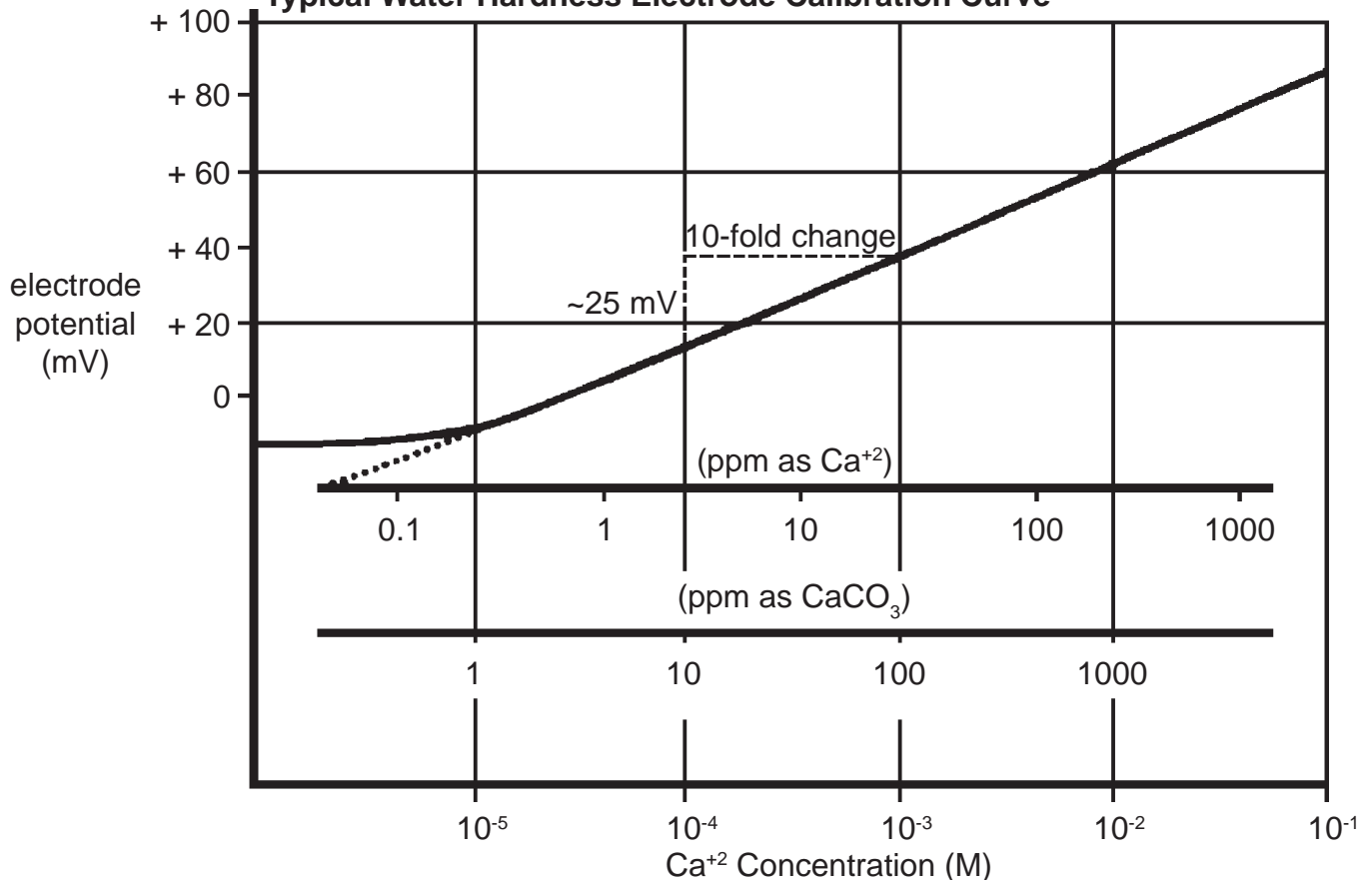
Total calcium plus magnesium ion concentration is determined using the pHoenix Electrode Company Water Hardness Electrodes (WHA1502, WHA1508). The pHoenix Electrode Company Calcium Electrodes (27502-09, 27504-06) measure calcium but not magnesium ion concentrations.

### Direct Measurement of Water Hardness (using a pH/mV meter)

1. By serial dilution of the 0.1M, 1000 ppm, or 100 ppm standard, prepare  $10^{-2}$ ,  $10^{-3}$ , and  $10^{-4}$ M or 100, 10 and 1 ppm standards. Measure out 100 ml of each standard into individual 150 ml beakers. Add 2 ml of ISA to every 100 ml of sample or standard.
2. Place the most dilute solution ( $1.0 \times 10^{-4}$ M or 1 ppm) on the magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tip(s) into the solution. When the reading has stabilized, record the mV reading.
3. Place the mid-range solution ( $1.0 \times 10^{-3}$ M or 10 ppm) on the magnetic stirrer and begin stirring. After rinsing the electrode(s) with distilled water, blot dry, and immerse the electrode tip(s) in the solution. When the reading has stabilized, record the mV reading.
4. Place the most concentrated solution ( $1.0 \times 10^{-2}$ M or 100 ppm) on the magnetic stirrer and begin stirring. After rinsing the electrode(s) with distilled water, blot dry and immerse the electrode tip(s) in the solution. When the reading has stabilized, record the mV reading.
5. Using the semi-logarithmic graph paper, plot the mV reading (linear axis) against the concentration (log axis). A typical calibration curve can be found in Figure 1.

**Figure 1**

**Typical Water Hardness Electrode Calibration Curve**



A calibration curve is constructed on semi- logarithmic paper when using a pH/ mV meter in the direct measurement procedure. The measured electrode potential in mV (linear axis) is plotted against the standard concentration (log axis). In the linear region of the curve, only three standards are necessary to determine a calibration curve. In the non-linear region, additional points must be measured. The direct measurement procedures given are for the linear portion of the curve. The non-linear portion of the curve requires the use of low level procedures.

6. To a clean, dry 150 ml beaker, add 100 ml of sample and 2 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring. Place the electrode tip(s) in the solution. When the reading has stabilized, record the millivolt reading. Determine the concentration directly from the calibration curve.
7. The electrode(s) should be re-calibrated every 1-2 hours. Simply repeat Steps 2-5 above.

### **Direct Measurement of Water Hardness (using an ion meter)**

1. By serial dilution of the 0.1M, 1000 ppm, or 100 ppm calcium standard, prepare two calcium standards whose concentration is near the expected sample concentration. Measure out 100 ml of each standard into individual 150 ml beakers. Add 2 ml of ISA to each standard or sample.
2. Place the more dilute solution on the magnetic stirrer and begin stirring at a constant rate. Assure that the meter is in the concentration mode.
3. Lower the electrode tip(s) into the solution.
4. Adjust the meter to the concentration of the calcium standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
5. Rinse the electrode tip(s) with distilled water and blot dry.
6. Place the more concentrated solution on the magnetic stirrer and begin stirring at a constant rate.
7. Lower the electrode tip(s) into the solution.
8. Adjust the meter to the concentration of the calcium standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
9. For low level measurements, place the rinsed, dried electrode(s) into a solution containing 100 ml of distilled water and 2 ml of ISA. After stabilization, fix the blank value in the meter according to the meter manufacturer's instructions.
10. Place 100 ml of the sample and 2 ml of ISA in a 150 ml beaker, place it on the magnetic stirrer, and begin stirring.

11. Immerse the electrode tip(s) in the solution and wait for the reading to stabilize. Read the concentration directly from the meter display.
12. The electrode(s) should be re-calibrated every 1-2 hours. Simply repeat Steps 2-8(9) above.

### **Low Level Water Hardness Determination (using a pH/mV meter)**

This procedure is recommended for solutions with ionic strengths less than  $1.0 \times 10^{-2} \text{M}$ . If the solution is high in ionic strength, but low in calcium and magnesium, use the same procedure, but prepare a calibration solution with a composition similar to the sample.

1. Dilute 10 ml of the 0.1M standard to 1000 ml to prepare a  $1.0 \times 10^{-3} \text{M}$  standard solution for measurements in moles per liter. Dilute 10 ml of the 1000 ppm or 1 ml of the 100 ppm standard to 1000 ml to prepare a 10 ppm standard solution for measurements in ppm.
2. Soak the water hardness electrode for at least 1 hour in  $1.0 \times 10^{-3} \text{M}$  or 100 ppm calcium standard solution.
3. To a 150 ml beaker, add 100 ml of distilled water. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.
4. Place the electrode tip(s) in the solution. Assure that the meter is in the mV mode.
5. Add increments of the  $1.0 \times 10^{-3} \text{M}$  or 10 ppm standard as given in Table 2 below.
6. After the reading has stabilized, record the mV reading after each addition.

**TABLE 2: Step-wise Calibration for Low Level Water Hardness Measurements**

<u>Step</u>	<u>Pipet</u>	<u>Added Volume (ml)</u>	<u>Concentration</u>	
			<u>M</u>	<u>ppm</u>
1	A	0.1	$1.0 \times 10^{-6}$	$1.0 \times 10^{-2}$
2	A	0.1	$2.0 \times 10^{-6}$	$2.0 \times 10^{-2}$
3	A	0.2	$4.0 \times 10^{-6}$	$4.0 \times 10^{-2}$
4	A	0.2	$6.0 \times 10^{-6}$	$6.0 \times 10^{-2}$
5	A	0.4	$9.9 \times 10^{-6}$	$1.0 \times 10^{-1}$
6	B	2	$2.9 \times 10^{-5}$	$2.9 \times 10^{-1}$
7	B	2	$4.8 \times 10^{-5}$	$4.8 \times 10^{-1}$

Pipet A = 1 ml graduated pipet

Pipet B = 2 ml pipet

Solutions: additions of  $1.0 \times 10^{-3} \text{M}$  or 10 ppm standard to 100 ml of distilled water.

7. On semi-logarithmic graph paper, plot the mV reading (linear axis) against the concentration (log axis) as in Figure 1.
8. Rinse the electrode(s) in distilled water and blot dry.
9. Measure out 100 ml of the sample into a 150 ml beaker and place the beaker on the magnetic stirrer. Begin stirring. Lower the electrode tip(s) into the solution.
10. After the reading has stabilized, record the mV reading and determine the concentration from the low level calibration curve.
11. Prepare a new low level calibration curve daily. Check the calibration curve every 1-2 hours by repeating Steps 3-7 above.

### **Low Level Water Hardness Determination (using an ion meter)**

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

### **ELECTRODE CHARACTERISTICS**

#### **Reproducibility**

Direct electrode measurements reproducible to  $\pm 4\%$  can be obtained if the electrode is calibrated every hour. Factors such as temperature fluctuations, drift, and noise limit reproducibility. Reproducibility is independent of concentration within the electrode's operating range.

#### **Interferences**

Table 3 lists some common cations that, if present in high enough levels, will cause electrode interferences and measurement errors or electrode drift when using the water hardness electrodes.

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



**TABLE 3: Concentration of Possible Interferences Causing a 10% Error at Various Levels of Calcium and/or Magnesium.**

<u>Interferences</u> (moles/liter)	<u>10<sup>-2</sup>M</u>	<u>10<sup>-3</sup>M</u>	<u>10<sup>-4</sup>M</u>
Zn <sup>+2</sup>	3.0x10 <sup>-4</sup>	3.0x10 <sup>-5</sup>	3.0x10 <sup>-6</sup>
Ba <sup>+2</sup>	6.0x10 <sup>-3</sup>	6.0x10 <sup>-4</sup>	6.0x10 <sup>-5</sup>
K <sup>+1</sup>	3.0x10 <sup>-1</sup>	1.0x10 <sup>-1</sup>	3.0x10 <sup>-2</sup>
Na <sup>+1</sup>	8.0x10 <sup>-2</sup>	3.0x10 <sup>-2</sup>	8.0x10 <sup>-3</sup>
Ni <sup>+2</sup>	1.0x10 <sup>-3</sup>	1.0x10 <sup>-4</sup>	1.0x10 <sup>-5</sup>
Cu <sup>+2</sup>	3.0x10 <sup>-4</sup>	3.0x10 <sup>-5</sup>	3.0x10 <sup>-6</sup>
Fe <sup>+2</sup>	6.0x10 <sup>-4</sup>	6.0x10 <sup>-5</sup>	6.0x10 <sup>-6</sup>
Sr <sup>+2</sup>	4.0x10 <sup>-3</sup>	4.0x10 <sup>-4</sup>	4.0x10 <sup>-5</sup>

### Complexation

Sulfate, bicarbonate, and carbonate are the most common species that complex calcium and/or magnesium ions. The level of calcium/magnesium ions, the level of the complexing ion, the pH of the solution, and the total ionic strength of the solution determine the extent of the complexation. Complexation reduces the free calcium/magnesium ion concentration and, since the electrode responds only to free calcium/magnesium ions, a false reading results.

### Temperature Influences

Samples and standards should be at the same temperature, since electrode potentials are influenced by changes in temperature. A 1°C difference in temperature results in a 4% error at the 1.0x10<sup>-3</sup>M level.

Provided that temperature equilibria has occurred, the water hardness electrodes can be used at temperatures from 0°-40°C. Room temperature measurements are recommended, since measurements at temperatures quite different from room temperature may require equilibrium times up to one hour.

Table 4 indicates the variation of theoretical slope with temperature.

**TABLE 4: Temperature vs Value for the Electrode Slope**

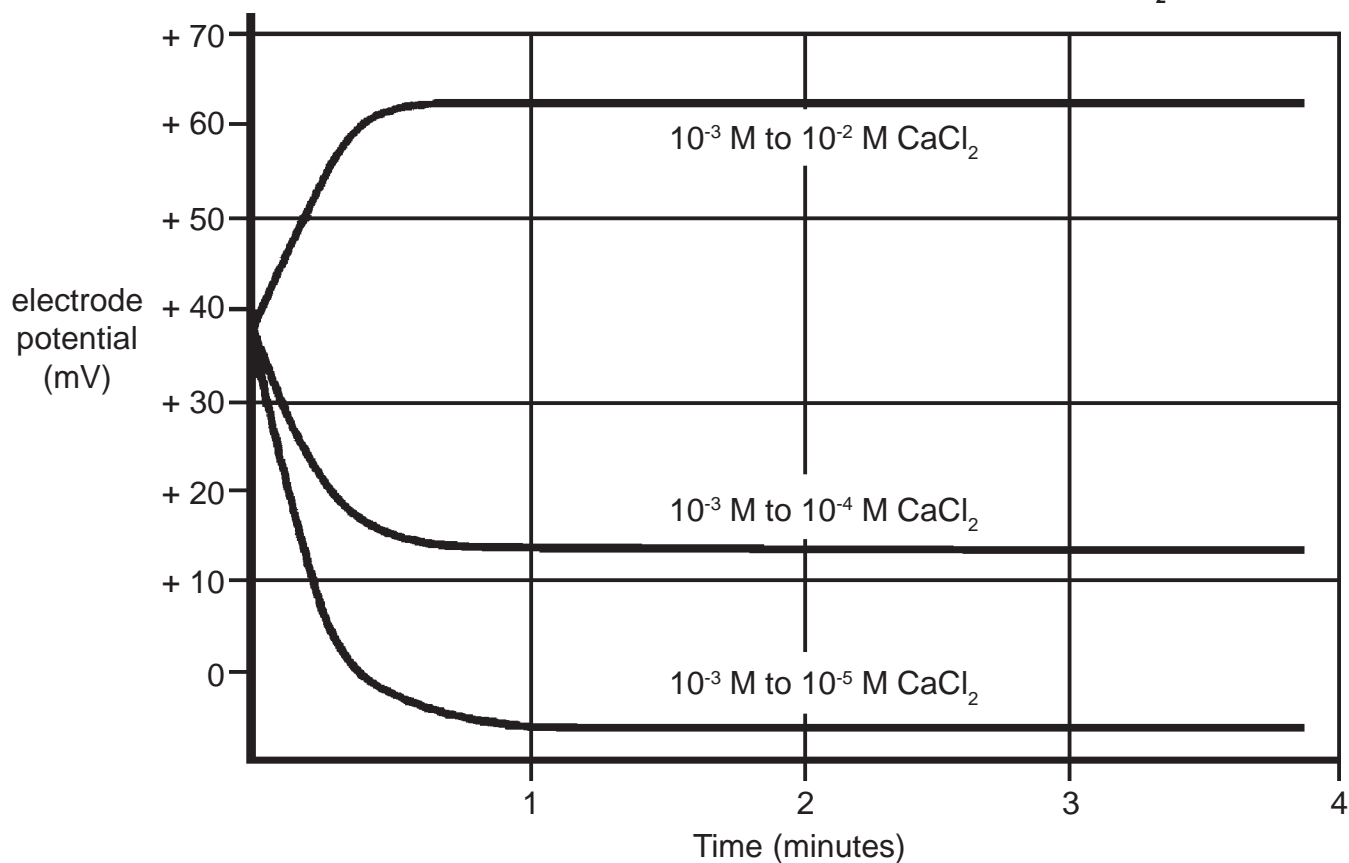
<u>Temp (°C)</u>	<u>“S”</u>
0	27.10
10	28.10
20	29.08
25	29.58
30	30.07
40	31.07

## Electrode Response

Plotting the electrode mV potential against the calcium/magnesium concentration on semi-logarithmic paper results in a straight line with a slope of about 25 mV per decade. (Refer to Figure 1.)

The time needed to reach 99% of the stable electrode potential reading, the electrode response time, varies from one minute or less for calcium/magnesium concentration above  $1.0 \times 10^{-4} \text{M}$  to several minutes near the detection limit. (Refer to Figure 2.)

**Figure 2**  
Typical Electrode Time Response to Step Changes in  $\text{CaCl}_2$



## Limits of Detection

The upper limit of detection is 1M in pure calcium/magnesium chloride solutions. The upper limit of detection is above  $1.0 \times 10^{-1} \text{M}$  when other ions are present, but the possibility of a liquid junction potential developing at the reference electrode and the “salt extraction effect” are two limiting factors. Some salts may be extracted into the electrode membrane at high salt concentrations causing deviation from theoretical response. Calibrate the electrode at four or five intermediate points, or dilute the sample, to measure samples between  $1.0 \times 10^{-1} \text{M}$  and 1M.

The slight water solubility of the ion exchanger in the sensing module, which causes deviation from theoretical response, determines the lower limit of detection. The theoretical response at low levels of calcium/magnesium chloride compared to actual response is shown in Figure 1.

To avoid formation of  $\text{CaSO}_4$  and  $\text{MgSO}_4$ , the sulfate concentrations must be less than  $5 \times 10^{-4} \text{M}$  (50 ppm). To avoid formation of  $\text{CaCO}_3$  or formation of the  $\text{CaHCO}_3^+$  complex, the pH of the solution should be less than 7, and the total carbonate/bicarbonate concentration should be less than  $3 \times 10^{-3} \text{M}$  (280 ppm carbonate).

### **pH Effects**

The water hardness electrode has an operating pH range of 5-10. Use at other pH values can adversely affect the membrane. Hydrogen ion interferes with measurements of low levels of calcium/magnesium. Hydroxide ion will complex calcium and/or magnesium ions.

### **Electrode Life**

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

### **Electrode Storage**

The pHoenix Electrode Company Water Hardness Electrodes may be stored in  $1.0 \times 10^{-2} \text{M}$  calcium standard for short periods of time. For storage over two weeks, rinse and dry the water hardness membrane and cover the tip with any protective cap shipped with the electrode(s). The reference portion of the combination electrode (or the outer chamber of the reference electrode) should be drained of filling solution, if refillable, and the rubber insert should be placed over the filling hole.

## **ELECTRODE THEORY**

### **Electrode Operation**

The pHoenix Electrode Company Water Hardness Electrode consists of an electrode body containing an ion exchanger in a sensing module. This sensing module contains a liquid internal filling solution in contact with a gelled organophilic membrane containing a calcium/magnesium selective ion exchanger.

An electrode potential develops across the membrane when the membrane is in contact with a calcium/magnesium solution. Measurement of this potential against a constant reference potential with a digital pH/mV meter or with a specific ion meter depends on the level of free calcium and magnesium ion in solution. The level of calcium and magnesium ions, corresponding to the measured potential, is described by the Nernst equation:

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

where:	E	= measured electrode potential
	$E_o$	= reference potential (a constant)
	S	= electrode slope (~26 mV/decade)
	X	= level of calcium and magnesium ions in solution

The activity,  $X$ , represents the effective concentration of the ions in solution. Total calcium/magnesium concentration,  $C_t$ , includes free calcium/magnesium ions,  $C_f$ , plus bound or complexed calcium/magnesium ions,  $C_b$ . Since the water hardness electrodes only respond to free ion, the free ion concentration is:

$$C_f = C_t - C_b$$

The activity is related to the free ion concentration,  $C_f$ , by the activity coefficient,  $\tilde{a}$ , by:

$$X = \tilde{a} C_f$$

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

$$I = \frac{1}{2} \sum C_x Z_x^2$$

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

In the case of high and constant ionic strength relative to the sensed ion concentration, the activity coefficient,  $\tilde{a}$ , is constant and the activity,  $X$ , is directly proportional to the concentration.

To adjust the background ionic strength to a high and constant value, ionic strength adjuster (ISA) is added to samples and standards. The recommended ISA for water hardness is potassium chloride, KCl. Solutions other than this may be used as long as ions that they contain do not interfere with the electrode's response to calcium/magnesium ions.

The reference electrode must also be considered. When two solutions of different composition are brought into contact with one another, liquid junction potentials arise. Millivolt potentials occur from the interdiffusion of ions into the two solutions. Electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions, since ions diffuse at different rates. When making measurements, it is important to remember that this potential be the same when the reference is in the standardizing solution as well as in the sample solution or the change in liquid junction potential will appear as an error in the measured electrode potential.

The composition of the liquid junction filling solution in the reference electrode is most important. The speed with which the positive and negative ions in the filling solution diffuse into the sample should be equitransferent. No junction potential can result if the rate at which positive and negative charge carried into the sample is equal.

## **TROUBLESHOOTING GUIDE**

The goal of troubleshooting is the isolation of a problem through checking each of the system components in turn: the meter, the glassware, the electrode(s), the standards & reagents, the sample, and the technique.

### **Meter**

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

## **Glassware**

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

## **Electrodes**

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

1. Be sure to use distilled or deionized water when following the procedures given in **Electrode Slope Check**.
2. If the electrode fails to respond as expected, see the section **Measuring Hints**. Repeat the slope check.
3. If the electrode(s) still fail to respond as expected, substitute another water hardness electrode that is known to be in good working order for the questionable electrode. If the problem persists and you are using an electrode pair, try the same routine with a working reference electrode.
4. If the problem persists, the standards and/or reagents may be of poor quality, interferences in the sample may be present or the technique may be faulty. (See **Standards & Reagents**, **Sample**, and **Technique** sections.)
5. If another electrode is not available for test purposes, or if the electrode in use is suspect, review the instruction manual and be sure to:
  - Clean and rinse the electrode(s) thoroughly.
  - Prepare the electrode(s) properly.
  - Use the proper filling solution.
  - Adjust the pH of the solution according to the method being used for the analysis.
  - Measure correctly and accurately.
  - Review **TROUBLESHOOTING HINTS**.

## **Standards & Reagents**

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

## **Sample**

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

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

## **Technique**

Be sure that the electrodes' limit of detection has not been exceeded. Be sure that the analysis method is clearly understood and is compatible with the sample.

Refer to the instruction manual again. Reread **GENERAL PREPARATION** and **ELECTRODE CHARACTERISTICS**.

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

## **TROUBLESHOOTING HINTS**

<b>Symptom</b>	<b>Possible Causes</b>	<b>Next Step</b>
Out of Range Reading	defective meter	check meter with shorting strap (see meter instruction manual)
	defective electrode	check electrode operation
	electrode not plugged in properly	unplug electrode and reseat
	reference electrode not filled	be sure reference electrode is filled
	air bubble on membrane	remove air bubble by re-dipping electrode
	electrode not in solution	put electrode in solution
Noisy or Unstable Readings (readings continuously or rapidly changing)	defective meter	check meter with shorting strap
	air bubble on membrane	remove air bubble by re-dipping electrode
	outer filling solution too low	fill electrode to level just below fill hole
	meter or stirrer not grounded	ground meter or stirrer
	defective electrode	replace electrode
Drift (reading slowly changing in one direction)	electrode exposed to interferences	soak electrode in water hardness standard
	samples and standards at different temperatures	allow solutions to come to room temperature before measurement
	electrode exposed to interferences	soak electrode in water hardness standard
	incorrect reference filling solution	use recommended filling solution
	incorrect pH	adjust tp pH 5-10 with NaOH or HCl

## **TROUBLESHOOTING HINTS**

<b>Symptom</b>	<b>Possible Causes</b>	<b>Next Step</b>
Low Slope or No Slope	standards contaminated or incorrectly made	prepare fresh standards
	defective electrode	check electrode operation
	air bubble on membrane	remove bubble by re-dipping probe
	electrode exposed to interferences	soak electrode in water hardness standard
	standard used as ISA	use ISA
“Incorrect Answer” (but calibration curve is good)	incorrect scaling of semi-log paper	plot millivolts on the linear axis. On the log axis, be sure concentration numbers within each decade are increasing with increasing concentration
	incorrect sign	be sure to note sign of millivolt number correctly
	incorrect standards	prepare fresh standards
	wrong units used	apply correct conversion factor: $1.0 \times 10^{-3} \text{ M} = 40 \text{ ppm Ca}^{+2} = 100 \text{ ppm as CaCO}_3$
	sample carryover	rinse electrodes thoroughly between samples



## **SPECIFICATIONS**

Concentration Range:	1M to $1 \times 10^{-5}$ M
pH Range:	5 to 10
Temperature Range:	0° to 40°C
Resistance:	100 megaohms
Reproducibility:	±4%
Samples:	aqueous solutions only no organic solvents
Size:	110 mm length 12 mm diameter 1 m cable length
Storage:	electrode should be stored in dilute water hardness standard

## **ORDERING INFORMATION**

P/N	DESCRIPTION
WHA1502	Water Hardness Electrode, combination, glass body
WHA1508	Water Hardness Electrode, combination, epoxy body
WHAAS01	Water Hardness Standard, 0.1M CaCl <sub>2</sub>
WHAAS02	Water Hardness Standard, 1000 ppm Ca <sup>+2</sup>
WHAIS01	Water Hardness ISA (Ionic Strength Adjustor), 4 M KCl
R001013	Electrode Filling Solution, 4 M KCl, for both the WHA1502 and WHA1508 combination electrodes

## **TABLE OF CONTENTS**

<b>General Instructions</b> .....	1
introduction.....	1
required equipment.....	1
required solutions.....	1
<b>General Preparation</b> .....	2
electrode preparation.....	2
electrode slope check (with pH/mV meter).....	2
electrode slope check (with ion meter).....	3
<b>Measurement</b> .....	3
measuring hints.....	3
sample requirements.....	4
units of measurement.....	4
<b>Measurement Procedure</b> .....	4
direct measurement.....	4
direct measurement of water hardness (using a pH/mV meter).....	5
direct measurement of water hardness (using an ion meter).....	6
low level water hardness determination (using a pH/mV meter).....	7
low level water hardness determination (using an ion meter).....	8
<b>Electrode Characteristics</b> .....	8
reproducibility.....	8
interferences.....	8
complexation.....	9
temperature influences.....	9
electrode response.....	10
limits of detection.....	10
pH effects.....	11
electrode life.....	11
electrode storage.....	11
<b>Electrode Theory</b> .....	11
electrode operation.....	11
<b>Troubleshooting Guide</b> .....	12
<b>Troubleshooting Hints</b> .....	15
<b>Specifications</b> .....	17
<b>Ordering Information</b> .....	17
<b>Table of Contents</b> .....	18