

**pHoenix Electrode Company  
Bromide Ion Electrodes  
Instruction Manual**

**GENERAL INSTRUCTIONS**

**Introduction**

The pHoenix Electrode Company Bromide Ion Electrodes are used to quickly, simply, accurately, and economically measure free bromide ion 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 Bromide Ion Combination Glass Electrode, Cat. No. BR01502, or the pHoenix Electrode Company Bromide Ion Combination Epoxy Electrode, Cat. No. BR01508.
5. pHoenix Electrode Company Filling Solution, Cat. No. R001015, for the BR01502 and BR01508 electrodes.
6. Polishing paper or jeweller's rouge to polish dirty or etched electrode membranes.

**Required Solutions**

1. Deionized or distilled water for solution and standard preparation.
2. pHoenix Electrode Company Ionic Strength Adjuster ISA), 5M NaNO<sub>3</sub>, Cat. No. BROIS01. To prepare ISA from your own stock, half fill a 1000 ml volumetric flask with distilled water and add 425 grams of reagent grade sodium nitrate. Swirl the flask to dissolve the solid. Fill the flask to the mark with distilled water, cap, and upend the flask several times to mix the solution.

3. pHOenix Electrode Company Bromide Standard, 1000 ppm Br<sup>-1</sup>, Cat. No. BROAS02. To prepare this solution from your own stock, half fill a one liter volumetric flask with distilled water and add 1.29 grams of reagent grade NaBr. Swirl the flask gently to dissolve the solid. Fill the flask to the mark with distilled water, cap, and upend several times to mix the solution.

## **GENERAL PREPARATION**

### **Electrode Preparation**

Remove the rubber cap covering the electrode tip and the rubber insert covering the filling hole of the combination electrode. Fill the combination electrode with the filling solution shipped with the electrode to a level just below the fill hole. No preparation is required with a sealed reference electrode. Connect the electrode to the proper terminal(s) as recommended by the meter manufacturer.

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

1. To a 150 ml beaker, add 100 ml of distilled water and 2 ml of ISA. 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 into the solution.
2. Using a pipet, add 1 ml of either the 0.1M or the 1000 ppm standard to the beaker. When the reading is stable, record the millivolt reading.
3. Using a pipet, add 10 ml of the same standard to the beaker. When the reading has stabilized, record the millivolt reading.
4. Determine the difference between the two readings. A difference of 57±3 mV indicates correct electrode operation, assuming the solution temperature is 25°C. See the **TROUBLESHOOTING GUIDE** and **TROUBLESHOOTING HINTS** sections 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 an ion meter)**  
**(check electrode each day)**

1. Prepare standard bromide solutions whose concentrations vary by tenfold. Use either the 0.1M or the 1000 ppm bromide standard. Use the serial dilution method for this preparation.
2. To a 150 ml beaker, add 100 ml of the lower value standard and 2 ml of ISA. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip into the solution. Assure that the meter is in the concentration mode.
3. Adjust the meter to the concentration of the standard and fix the value in the memory according to the meter manufacturer's instructions.
4. Rinse the electrode with distilled water and blot dry.
5. To a 150 ml beaker, add 100 ml of the higher value standard and 2 ml of ISA. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip into the solution.
6. Adjust the meter to the concentration of the standard and fix the value in the memory.
7. Read the electrode slope according to the meter manufacturer's instructions. Correct electrode operation is indicated by a slope of 90-100%. See the TRUBLESHOOTING GUIDE and TRUBLESHOOTING HINTS sections if the slope is not within this range.

**MEASUREMENT**

**Measuring Hints**

All samples and standards should be at the same temperature for precise measurement. A difference of 1 degree C in temperature will result in about a 2% measurement error.

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 styrofoam sheet, between the stirrer and beaker.

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

For samples with high ionic strength, prepare standards whose composition is similar to the sample. Dilute concentrated samples (>0.1M) before measurement.

Use fresh standards for calibration.

Use 2 ml of ISA for each 100 ml of sample or standard.

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

### **Sample Requirements**

All samples must be aqueous and not contain organics which can dissolve the epoxy electrode body and/or the cement bonding the sensing crystal to the electrode body. Infrequent measurements in solutions containing methanol, benzene, or acetonitrile are permitted. Highly polar solvents slowly attack the electrode. Please check with pHoenix Electrode Company Company before using these electrodes in other organic solvents.

The temperature of the sample solutions and of the standard solutions should be the same and below 80°C.

Interferences should be absent. If they are present, use the procedure found in the **Interference** and **Electrode Response** sections to remove them.

The pH range for the bromide ion electrode is 2-14. Neutralize samples outside this range with acid or base to bring them in range.

### **Units of Measurement**

Bromide ions can be measured in units of moles/liter, parts/million, or any other convenient concentration unit. Table 1 indicates some of the concentration units.

**TABLE 1:** Concentration Unit Conversion Factors

<u>moles/liter</u>	<u>ppm Br<sup>-1</sup></u>
1.0X10 <sup>-4</sup>	8.0
1.0X10 <sup>-3</sup>	79.9
1.0X10 <sup>-2</sup>	799.0
1.0X10 <sup>-1</sup>	7,990.0

## **MEASUREMENT PROCEDURES**

### **Direct Measurement**

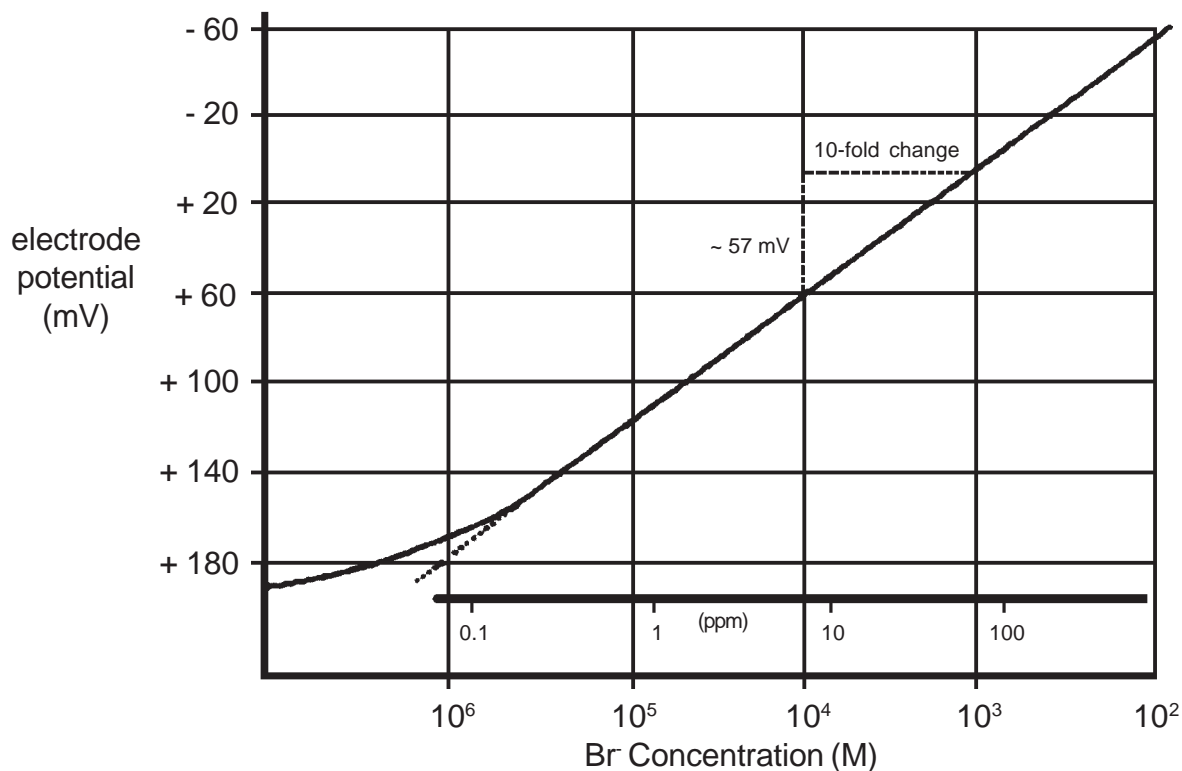
A simple procedure for measuring a large number of samples. A single meter reading is all that is required for each sample. The ionic strength of samples and standards should be made the same by adjustment with ISA for all bromide solutions. The temperature of both sample solutions and of standard solutions should be the same.

### **Direct Measurement of Bromide (using a standard pH/mV meter)**

1. By serial dilution of the 0.1M or 1000 ppm standards, prepare 10<sup>-2</sup>, 10<sup>-3</sup>, and 10<sup>-4</sup>M or 100 and 10 ppm bromide standards. Add 2 ml of ISA per 100 ml of each standard. Prepare standards with a composition similar to the samples if the samples have an ionic strength above 0.1M.
2. Place the most dilute solution (10<sup>-4</sup>M or 10 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 into the solution. When the reading has stabilized, record the mV reading.
3. Place the midrange solution (10<sup>-3</sup>M or 100 ppm) on the magnetic stirrer and begin stirring at a constant rate. After rinsing the electrode in distilled water, blot dry and immerse the electrode tip in the solution. When the reading has stabilized, record the mV reading.
4. Place the most concentrated solution (10<sup>-2</sup>M or 1000 ppm) on the magnetic stirrer and begin stirring at a constant rate. After rinsing the electrode in distilled water, blot dry and immerse the electrode tip in the solution. When the reading has stabilized, record the mV reading.

5. Using semi-logarithmic graph paper, plot the mV reading (linear axis) against the concentration (log axis). Extrapolate the curve down to about  $1.0 \times 10^{-5} \text{M}$  or 1 ppm. A typical calibration curve for bromide can be found in Figure 1.

Figure 1  
Typical Bromide Electrode Calibration Curve



A calibration curve is constructed on semi-logarithmic paper when using a pH/mV meter in the millivolt mode. 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 the sample and 2 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring. Place the electrode tip in the solution. When the reading has stabilized, record the mV reading. Determine the concentration directly from the calibration curve.
7. The calibration should be checked every two hours. Assuming no change in ambient temperature, place the electrode tip in the midrange standard. After the reading has stabilized, compare it to the original reading recorded in Step 3 above. A reading differing by more than 0.5 mV or a change in the ambient temperature will necessitate the repetition of Steps 2-5 above. A new calibration curve should be prepared daily.

#### **Direct Measurement of Bromide (using an ion meter)**

1. By serial dilution of the 0.1M or 1000 ppm bromide standards, prepare two standards whose concentration is near the expected sample concentration. Measure 100 ml of each standard into individual 150 ml beakers and add 2 ml of ISA to each.
2. Place the more dilute solution on the magnetic stirrer and begin stirring at a constant rate. Assure that the meter is in the concentration mode.
3. Lower the electrode tip into the solution.
4. Adjust the meter to the concentration of the standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
5. Rinse the electrode 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 into the solution.
8. Adjust the meter to the concentration of the standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.

9. For low level bromide measurements, place the rinsed dried electrode into a solution containing 100 ml of distilled water and 2 ml of ISA. After stabilization, fix the blank value into 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 in the solution and wait for the reading to stabilize. Read the concentration directly from the meter display.
12. The calibration should be checked every two hours. Assuming no change in ambient temperature, place the electrode tip in the first bromide standard. After the reading has stabilized, compare it to the original reading in Step 4 above. A reading differing by more than 0.5 mV or a change in the ambient temperature will necessitate the repetition of Steps 2-8(9) above. The meter should be re-calibrated daily.

#### **Low Level Bromide Determinations (using a standard pH/mV meter)**

Use the following low level bromide measurement procedure in the non-linear portion of the calibration curve. See Figure 1. This procedure is recommended for solutions containing less than  $2.0 \times 10^{-6} \text{M}$  (0.2ppm).

1. Using 20 ml of the standard ISA, dilute to 100 ml with distilled water. This low level ( $1.0 \text{M NaNO}_3$ ) is added at the rate of 1 ml low level ISA to each 100 ml of sample. The background ionic strength will be  $1.0 \times 10^{-2} \text{M}$ .
2. Dilute 1 ml of 0.1M standard to 1000 ml to prepare a  $1.0 \times 10^{-4} \text{M}$  standard solution for measurements in moles per liter. Dilute 10 ml of 1000 ppm standard to 1000 ml to prepare a 10 ppm standard solution for measurements in ppm.
3. Add 100 ml of distilled water to a 150 ml beaker. Add 1 ml of low level ISA, place the beaker on the magnetic stirrer, and begin stirring at a constant rate.



4. Place the rinsed, dried electrode tip in the solution and assure that the meter is in the mV mode.
5. Add increments of the  $1.0 \times 10^{-4} \text{M}$  or 10 ppm standard as given in Table 2 below.
6. After the reading has stabilized, record the mV reading after each addition. Electrode response time is much longer at these levels. Allow adequate time for the electrode to stabilize.

**TABLE 2:** Stepwise Calibration for Low Level Bromide Measurements

<u>Step</u>	<u>Pipet</u>	<u>Added</u>	<u>Concentration</u>	
		<u>Volume (ml)</u>	<u>M</u>	<u>ppm</u>
1	A	0.1	$1.0 \times 10^{-7}$	0.01
2	A	0.1	$2.0 \times 10^{-7}$	0.02
3	A	0.2	$4.0 \times 10^{-7}$	0.04
4	A	0.2	$6.0 \times 10^{-7}$	0.06
5	A	0.4	$9.9 \times 10^{-7}$	0.99
6	B	2.0	$2.9 \times 10^{-6}$	2.90
7	B	2.0	$4.8 \times 10^{-6}$	4.80

Pipet A = 1 ml graduated pipet

Pipet B = 2 ml pipet

Solutions: additions of  $1.0 \times 10^{-4} \text{M}$  or 10 ppm standard to 100 ml of solution as prepared in Step 3 above.

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

## ELECTRODE CHARACTERISTICS

### **Reproducibility**

Electrode measurements reproducible to  $\pm 2\%$  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**

A layer of silver may form on the electrode surface in the presence of strongly reducing solutions. Insoluble salts of silver may be deposited on the membrane, causing electrode malfunction if high levels of ions forming these salts are present in the sample. Proper performance can be restored by polishing. See the section **Electrode Response** for proper polishing procedure.

Solutions containing oxidizing agents such as  $\text{MnO}_4^{-1}$ ,  $\text{Fe}^{+3}$ , and  $\text{Cu}^{+2}$ , may be measured without problem. All samples must be free of mercury.

The maximum allowable ratio of interfering ion to bromide ion is given in Table 3. This ratio is expressed as the ratio of the interfering ion molarity to the bromide molarity. Readings will be in error if this ratio is exceeded. Neither accuracy of the measurement nor surface of the electrode membrane will be affected if the ratio is less than that listed in the table.

**TABLE 3: Maximum Allowable Ratio of Interfering Ion to Bromide Ion**

<u>Interference</u>		<u>Maximum Ratio for Bromide</u>
$\text{OH}^{-1}$	(2)	30000
$\text{Cl}^{-1}$	(1)	400
$\text{S}_2\text{O}_3^{-2}$	(3)	20
$\text{NH}_3$	(3)	2
$\text{I}^{-1}$	(1)	$2.0 \times 10^{-4}$
$\text{CN}^{-1}$	(4)	$8.0 \times 10^{-5}$
$\text{S}^{-2}$	(4)	$1.0 \times 10^{-6}$

- 1) Gran's plot titration can be used to measure mixed halides in solution.
- 2) Acidify with 1M HNO<sub>3</sub> to pH 4 to remove hydroxide interference.
- 3) These substances represent complexing species whose maximum level can be exceeded without electrode damage. Values shown represents a 1% error.
- 4) Add Ni<sup>+2</sup> to remove sulfide or cyanide interferences.

As an example of Table 3's use when using the bromide ion electrode:

What is the maximum level of iodide tolerable in a sample whose bromide concentration is 10<sup>-2</sup>M?

Using Table 3, the maximum ratio is:

$$\frac{[I^{-1}]}{[Br^{-1}]} = 2 \times 10^{-4}$$

or  $[I^{-1}] = 2 \times 10^{-4} [Br^{-1}]$

$$[I^{-1}] = 2 \times 10^{-4} (1 \times 10^{-2})$$

$$[I^{-1}] = 2 \times 10^{-6} \text{M maximum iodide concentration for no interference}$$

### Complexation

Total concentration (Ct) consists of free ions (Cf) and complexed or bound ions (Cc) in solutions:

$$Ct = Cf + Cc$$

Since the electrode only responds to free ions, any complexing agent in the solution reduces the measured concentration of ions.

Bromide ions complex with some metal ions. Table 5 lists the levels of complexing metals causing a 20% error at 1.0X10<sup>-4</sup>M bromide.

**TABLE 5: Levels of Complexing Agents Causing a 20% Error at 1.0X10<sup>-4</sup>M Bromide**

<u>Ion</u>	<u>Concentration</u>
Bi <sup>+3</sup>	4.0x10 <sup>-4</sup> M (80 ppm)
Cd <sup>+2</sup>	2.0x10 <sup>-3</sup> M (200 ppm)
Pb <sup>+2</sup>	8.0x10 <sup>-3</sup> M (1600 ppm)
Sn <sup>+2</sup>	2.0x10 <sup>-2</sup> M (2400 ppm)
Tl <sup>+3</sup>	2.0x10 <sup>-5</sup> M (4 ppm)

### Temperature Influences

Samples and standards should be within  $\pm 1^{\circ}\text{C}$  of each other, since electrode potentials are influenced by changes in temperature. A  $1^{\circ}\text{C}$  difference in temperature results in a 2% error at the  $1.0 \times 10^{-3}\text{M}$  concentration level. Because of solubility equilibria on which the electrode depends, the absolute potential of the reference electrode changes slowly with the temperature. The slope of the electrode, as indicated by the factor "S" in the Nernst equation, also varies with temperature. Table 4 gives values of the "S" factor in the Nernst equation for the bromide ion.

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

<u>Temp (°C)</u>	<u>"S"</u>
0	54.2
10	56.2
20	58.2
25	59.2
30	60.1
40	62.1
50	64.1

If changes in temperature occur, the electrode should be re-calibrated.

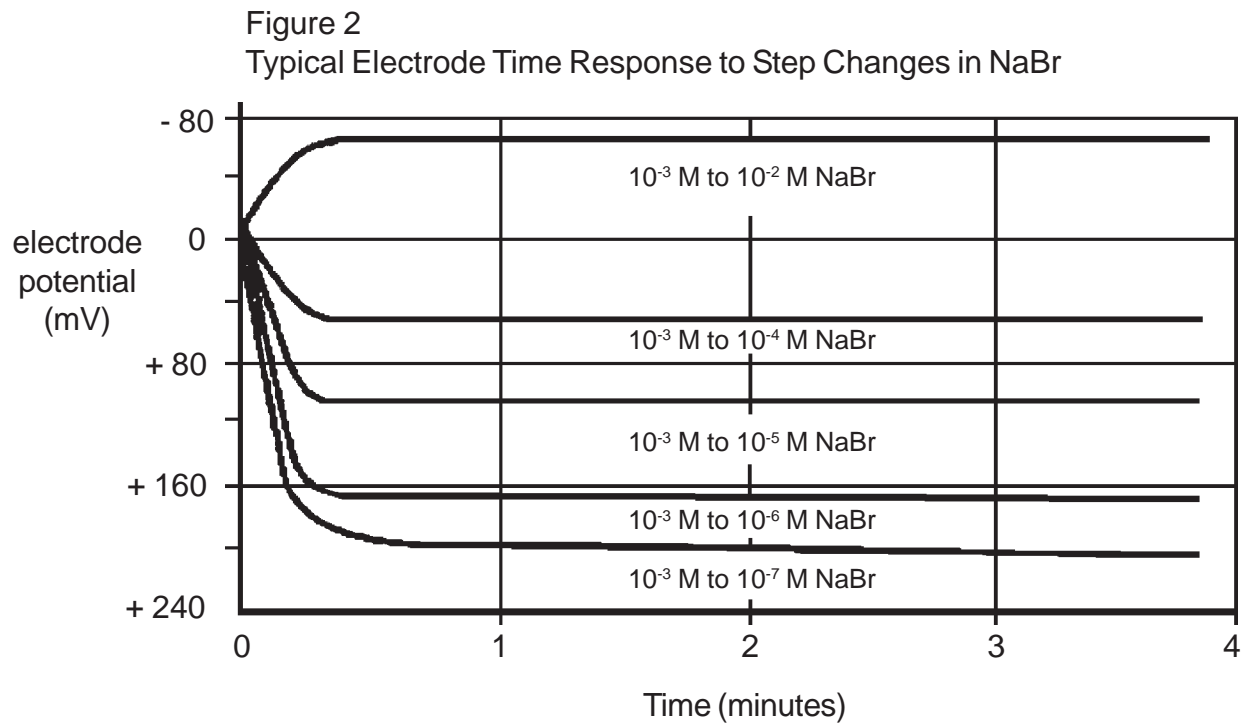
The temperature range of the pHoenix Electrode Company Bromide Ion Electrodes is  $0^{\circ}\text{-}80^{\circ}\text{C}$ , provided that temperature equilibrium has occurred.

If the temperature varies substantially from room temperature, equilibrium times up to one hour are recommended.

## Electrode Response

Plotting the electrode mV potential against the bromide concentration on semi-logarithmic paper results in a straight line with a slope of about 57 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 several seconds in highly concentrated solutions to several minutes near the detection limit. Refer to Figure 2.



A drifting potential reading or a decrease in electrode slope may mean that the electrode membrane needs polishing.

To polish the membrane:

1. If using polishing paper, cut off a 1-2" piece and place it face up on the lab bench.
2. Put a few drops of distilled or deionized water in the center of the paper.

3. Holding the paper (cotton) steady with one hand, bring the membrane of the electrode down perpendicular to the paper and, with a slight swirling motion, gently polish the tip of the electrode against the surface of the polishing paper (cotton) for a few seconds.
4. Rinse the electrode surface with distilled or deionized water and soak the electrode tip in standard solution for about five minutes before use.
5. If using jeweller's rouge, place a cotton ball on the table top and flatten it using the bottom of a beaker.
6. Put 1-2 drops of distilled or deionized water in the center of the cotton pad.
7. Add a small amount of jeweller's rouge to the damp cotton.
8. Continue with Steps 3 and 4 above.

### **Limits of Detection**

The upper limit of detection in pure sodium bromide solutions is 1M. In the presence of other ions, the upper limit of detection is above  $1.0 \times 10^{-1}$ M bromide, but two factors influence this upper limit. Both the possibility of a liquid junction potential developing at the reference electrode and the salt extraction effect influence this upper limit. Some salts may extract into the electrode membrane at high salt concentrations, causing deviation from the theoretical response. Either dilute samples between 1M and  $1.0 \times 10^{-1}$ M or calibrate the electrode at 4 or 5 intermediate points.

The lower limit of detection is influenced by the slight water solubility of the electrode pellet. Refer to Figure 1 for a comparison of the theoretical response to the actual response at low levels of bromide. Bromide measurements below  $10^{-4}$ M  $\text{Br}^{-1}$  should employ low level procedures.

### **pH Effects**

Hydroxide ion interferes with measurements of low levels of bromide although the electrode can be used over a reasonable pH range. Table 3 should be used to determine the minimum pH at which low level bromide measurements can be made without more than a 10% error due to hydroxide ion interference.

## **Electrode Life**

The bromide electrode will last six months in normal laboratory use. On-line measurements 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 Bromide Electrodes may be stored for short periods of time in  $1.0 \times 10^{-2} \text{M}$  bromide solution. For longer storage (longer than two weeks), rinse and dry the sensing pellet and cover the membrane tip with any protective cap shipped with the electrode. The reference portion of the combination electrode should be drained of filling solution, if refillable, and the rubber insert placed over the filling hole.

## **ELECTRODE THEORY**

### **Electrode Operation**

The pHOenix Electrode Company Bromide Ion Electrodes are composed of a sensing membrane bonded into a glass or an epoxy body. The membrane is composed of silver bromide/silver sulfide. When an electrode potential develops across the membrane, the electrode is in contact with solution containing bromide ions and is capable of measuring free bromide ions. This electrode potential is measured against a constant reference potential, using a standard pH/mV meter or an ion meter. The level of the bromide ions, corresponding to the measured potential, is described by the Nernst equation:

$$E = E_0 - S \log X$$

where:

- E = measured electrode potential
- $E_0$  = measured potential (a constant)
- S = electrode slope (~57mV)
- X = level of bromide ions in solution

The activity, X, represents the effective concentration of the ions in solution. 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 of ion x

$\Sigma$  = sum of all 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 is added to samples and standards. The recommended ISA for bromide ions is  $\text{NaNO}_3$ . Solutions other than this may be used as ionic strength adjusters as long as ions that they contain do not interfere with the electrode's response to the bromide ions. Samples with high ionic strength (greater than 0.1M) do not need ISA added and standards for these solutions should be prepared with a composition similar to the samples.

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 in the two solutions. Electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions, since ions diffuse at different rates. When making measurements, it is important to remember that this potential be the same when the reference is in the standardizing solution as well as in the sample solution or the change in liquid junction potential will appear as an error in the measured electrode potential.

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



Strongly acidic (pH=0-2) and strongly basic (pH=12-14) solutions are particularly troublesome to measure. The high mobility of hydrogen and hydroxide ions in samples make it impossible to mask their effect on the junction potential with any concentration of an equitransferent salt. One must either calibrate the electrodes in the same pH range as the sample or use a known increment method for ion measurement.

## **TROUBLESHOOTING GUIDE**

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

### **Meter**

The meter may be checked by following the checkout procedure in the instrument instruction manual.

### **Glassware**

Clean glassware is essential for good measurement. Be sure to wash the glassware well with a mild detergent and rinse very well with distilled or deionized water. Clean glassware will drain without leaving water droplets behind.

### **Electrode**

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 sections **Measuring Hints** and **Electrode Response**. Repeat the slope check.
3. If the electrode still fails to respond as expected, substitute another bromide ion 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 reagent may be of poor quality, interferences in the sample may be present or the technique may be faulty. See **Reagents**, **Sample**, and **Technique** sections below.
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 thoroughly.
  - Prepare the electrode properly.
  - Use the proper filling solution.
  - Adjust the pH and the ionic strength of the solution by the use of the proper ISA.
  - Measure correctly and accurately.
  - Review **TROUBLESHOOTING HINTS**.

## **Reagents**

Whenever problems arise with the measuring procedure that has been used successfully in the past, be sure to check the reagent solutions. If in doubt about the credibility of any of the reagents, prepare them again. Errors may result from contamination of the ISA, incorrect dilution, 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 electrode's limit of detection has not been exceeded.

Be sure that the analysis method is clearly understood and that Good Laboratory Practice has been followed.

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

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

## TROUBLESHOOTING HINTS

Symptom	Possible Causes	Next Step
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 reseal
	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
	ISA not used	use recommended ISA
	meter or stirrer not grounded	ground meter or stirrer
	defective electrode	replace electrode
	electrode exposed to interferences	soak electrode in bromide standard
Drift (reading slowly changing in one direction)	samples and standards at different temperatures	allow solutions to come to room temperature before measurement
	electrode exposed to complexing agents	check section entitled <b>Complexation</b>
	incorrect reference filling solution	use recommended filling solution
Low Slope or No Slope	standards contaminated or incorrectly made	prepare fresh standards
	ISA not used	use recommended ISA
	standard used as ISA	use ISA

Symptom	Possible Causes	Next Step
	electrode exposed to complexing agents	check section entitled <b>Complexation</b>
	air bubble on membrane	remove bubble by re-dipping electrode
“Incorrect Answer” (but calibration 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: $1.0 \times 10^{-3} \text{M} = 79.9 \text{ ppm as Br}^-$
	complexing agents in sample	check section entitled <b>Complexation</b>

### **SPECIFICATIONS**

Concentration Range:	1M to $5.0 \times 10^{-6} \text{M}$ Bromide 79,900 ppm to 0.4 ppm Bromide
pH Range:	2 to 14
Temperature Range:	0°- 80°C
Resistance:	<1 Mohm
Reproducibility:	+/-2%
Samples:	aqueous solutions only; no organic solvents
Size:	110 mm length 12 mm diameter 1 m cable length
Storage:	Store in bromide solution

## ORDERING INFORMATION

P/N	DESCRIPTION
BRO1502	Bromide Ion Electrode, combination, glass body
BRO1508	Bromide Ion Electrode, combination, epoxy body
BROAS01	Bromide Standard, 0.1M NaBr
BROAS02	Bromide Standard, 1000 ppm NaBr
BROIS01	Ionic Strength Adjuster (ISA), 5M NaNO <sub>3</sub>
R001015	Electrode Filling Solution, 1M KNO <sub>3</sub> , for the BRO1502 and BRO1508 electrode(s)

## 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 standard 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> .....	5
direct measurement.....	5
direct measurement of bromide (using a standard pH/mV meter).....	5
direct measurement of bromide (using an ion meter).....	7
low level bromide determination (using a standard pH/mV meter).....	8

<b>Electrode Characteristics</b> .....	10
reproducibility.....	10
interferences.....	10
complexation.....	11
temperature influences.....	12
electrode response.....	13
limits of detection.....	14
pH effects.....	14
electrode life.....	15
electrode storage.....	15
<b>Electrode Theory</b> .....	15
electrode operation.....	15
<b>Troubleshooting Guide</b> .....	17
<b>Troubleshooting Hints</b> .....	20
<b>Specifications</b> .....	21
<b>Ordering Information</b> .....	22
<b>Table of Contents</b> .....	22