

**COLE-PARMER REPLACEABLE MEMBRANE
BROMIDE ION ELECTRODES
INSTRUCTION MANUAL**

GENERAL INSTRUCTIONS

Introduction

The Cole-Parmer Combination Bromide Electrodes are used to quickly, simply, accurately, and economically measure free bromide ion in aqueous solutions. The primary advantage of combination ion-selective probes with replaceable sensing membranes is that when the sensing membrane fails or loses performance for whatever cause, it can be immediately replaced without discarding any other portion of the combination electrode. This results in time and cost savings.

Another distinct advantage of this replaceable membrane design is that when the sensing membrane fails or loses performance of whatever cause, membrane replacement has no unfortunate side effects on the performance of the reference electrode. There is no side effects on the performance of the reference electrolyte leakage upon replacing the membrane. The membrane replacement assembly is separated from the reference electrolyte/reference junction so that the membrane may be replaced without disturbing the reference electrolyte solution.

Yet another advantage of these ISE probes is the option of interchangeable sensing membranes, where one can select a membrane for a particular analytical ion. A single combination ISE body can be used to measure a variety of analytical ions by simple replacement of the membrane cartridge. This offers benefits in multiple ion analysis whereby an electrode kit containing various replaceable membranes can be made available for the analysis of different ions done on an occasional basis.

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 Cole-Parmer Combination Replaceable Membrane Bromide Electrode, Cat. No. 27506-00.

Required Solutions

- 1) Deionized or distilled water for solution and standard preparation.
- 2) Cole-Parmer Ionic Strength Adjuster (ISA), 5M NaNO₃, Cat. No.27503-51. To prepare this solution from your own laboratory stock, half-fill a 1000 ml volumetric flask with distilled water and add 425 grams of reagent-grade sodium nitrate. Swirl the flask gently to dissolve the solid. Fill to the mark with distilled water, cap, and upend the flask several times to mix the solution.
- 3) Cole-Parmer Bromide Standard, 1000 ppm Br⁻¹, Cat. No. 27503-03. To prepare this solution from your own laboratory 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 black protective cap covering the electrode tip and lower the rubber sleeve 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.

Connecting the Electrode to the Meter

Connect the electrode to the meter according to the meter manufacturer's instructions. No external reference electrode is required. To prevent air entrapment, mount the electrode at a 20° angle from the vertical.

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

A small hole of any size around the membrane seal or breakage of the membrane causes failure of the electrode. It is recommended to check the membrane on every newly assembled electrode.

- 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 millivolt mode, lower the electrode tips into the solution.
- 2) Using a pipet, add 1 ml of the 1000 ppm standard to the beaker. When the reading is stable, record the mV reading.
- 3) Using a pipet, add 10 ml of the same standard used above to the beaker. When the reading has stabilized, record the mV reading.

Determine the difference between the two readings. The electrode is operating correctly if the mV potential has changed by a difference of 57 ± 3 mV, assuming the solution temperature is 25°C. See the **TROUBLESHOOTING** 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 electrodes each day)

A small hole of any size around the membrane seal or breakage of the membrane causes failure of the electrode. It is recommended to check the membrane on every newly assembled electrode.

- 1) Prepare standard bromide solutions whose concentrations vary by tenfold. Use 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 tips 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 electrodes with distilled water and blot dry.
- 5) To another 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 tips 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 **TROUBLESHOOTING** sections if the slope is not within this range.

Changing the Membrane Cartridge (when necessary)

- 1.) Unscrew the bottom cap from the outer body. Remove the old membrane cartridge from the bottom cap by pushing out the cartridge with the tool provided with the electrode.
- 2.) Insert the new membrane cartridge into the bottom cap by pushing in the cartridge using the opposite end of the tool until it seats.

MEASUREMENT

Measuring Hints

- 1) All samples and standards should be at the same temperature for precise measurement. A difference of 1°C in temperature will result in about a 2% measurement error.
- 2) 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.
- 3) Always rinse the electrodes with distilled water and blot dry between measurements. Use a clean, dry tissue to prevent cross contamination.
- 4) For samples with high ionic strength, prepare standards whose composition is similar to the sample. Dilute concentrated samples (>0.1M) before measurement.
- 5) Use fresh standards for calibration.
- 6) Use 2 ml of ISA for each 100 ml of sample or standard.
- 7) 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 Cole-Parmer Scientific 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.

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.

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

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⁻¹</u>
1.0X10 ⁻⁴	8.0
1.0X10 ⁻³	79.9
1.0X10 ⁻²	799.0
1.0X10 ⁻¹	7,990.0

MEASUREMENT PROCEDURE

Direct Measurement

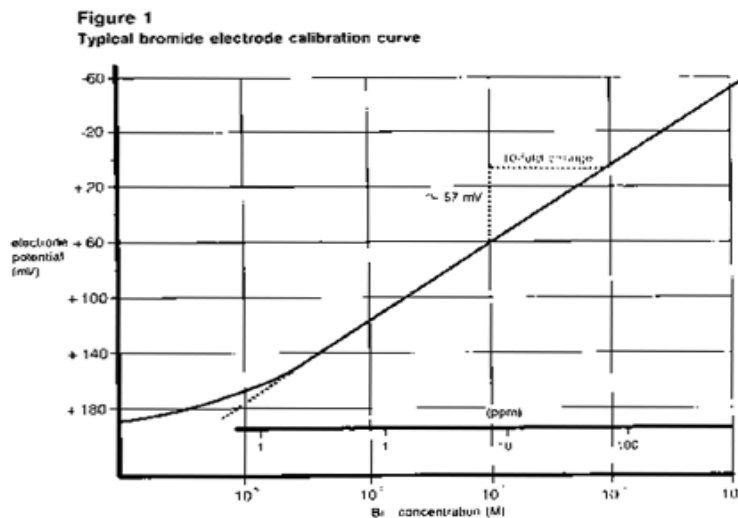
Direct measurement is a simple procedure for measuring a large number of samples. A single meter reading is all that is required for each sample. The ionic strength of samples and standards should be made the same by adjustment with ISA for all bromide solutions. The temperature of both sample solutions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

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

- 1.) By serial dilution prepare three standard solutions from the 1000 ppm standard. The resultant concentrations should be 1000, 100 and 10 ppm bromide standards. Add 2 ml of ISA to each 100 ml of 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 ppm) in a 150 ml beaker on the magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode,

lower the electrode tips into the solution. When the reading has stabilized, record the mV reading.

- 3) Place the mid-range solution (100 ppm) in a 150 ml beaker on the magnetic stirrer and begin stirring at a constant rate. After rinsing the electrodes in distilled water, blot dry and immerse the electrode tips in the solution. When the reading has stabilized, record the mV reading.
- 4) Place the most concentrated solution (1000 ppm) in a 150 ml beaker on the magnetic stirrer and begin stirring at a constant rate. After rinsing the electrodes in distilled water, blot dry and immerse the electrode tips 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 ppm. A typical calibration curve for bromide can be found in Figure 1.



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 at a constant rate. Rinse the electrode tips with distilled water, blot dry and lower the electrode tips into the

solution. After the reading has stabilized, record the mV reading. Using the calibration curve, determine the sample concentration.

7. The calibration should be checked every two hours. Assuming no change in ambient temperature, immerse the electrode tips in the mid-range 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 1000 ppm cadmium standard, prepare two cadmium standards whose concentration is near the expected sample concentration. Measure out 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. Lower the electrode tips into the solution.
3. Adjust the meter to the concentration of the cadmium standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
4. Rinse the electrodes with distilled water and blot dry.
5. Place the more concentrated solution on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution.
6. Adjust the meter to the concentration of the bromide standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
7. Place 100 ml of the sample and 2 ml of ISA into a 150 ml beaker. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.
8. Immerse the rinsed, dried electrode tips in the solution and wait for the reading to stabilize. Read the concentration directly from the meter display.
9. The calibration should be checked every two hours. Assuming no change in ambient temperature, immerse the electrode tips in the first bromide 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 ambient

temperature will necessitate the repetition of Steps 2-6 above. The meter should be re-calibrated daily.

Low Level Bromide Determination (using a pH/mV meter)

This procedure is recommended for solutions with bromide concentrations of less than 1.1 ppm. If the solution is high in ionic strength, but low in bromide ion, use the same procedure, but prepare a calibration solution with a composition similar to the sample.

1. Using 20 ml of standard ISA, dilute to 100 ml with distilled water. This low level ISA (1.0M NaNO₃) is added at the rate of 1 ml low level ISA to each 100 ml of solution. The background ionic strength will be 1.0X10⁻²M.
2. Prepare a 10 ppm standard solution by diluting 1 ml of the 1000 ppm standard to 100 ml of solution for measurements in ppm. Standards should be prepared fresh daily.
3. To a 150 ml beaker add 100 ml of distilled water and 1 ml of low level ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.
4. Place the electrode tips in the solution. Assure that the meter in the mV mode.
5. Add increments of the 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 Bromide Measurements

<u>Step</u>	<u>Pipet</u>	<u>Added Volume (ml)</u>	<u>Concentration</u>	
			<u>ppm</u>	<u>M</u>
1	A	0.1	0.01	1.0X10 ⁻⁷
2	A	0.1	0.02	2.0X10 ⁻⁷
3	A	0.2	0.04	4.0X10 ⁻⁷
4	A	0.2	0.06	6.0X10 ⁻⁷
5	A	0.4	0.10	9.9X10 ⁻⁷
6	B	2.0	0.29	2.9X10 ⁻⁶
7	B	2.0	0.48	4.8X10 ⁻⁶

Pipet A = 1 ml graduated pipet

Pipet B = 2 ml pipet

Solutions: additions of 10 ppm standard to 100 ml of solution prepared in Step 3 above.

7. On semi-logarithmic graph paper, plot the mV reading (linear axis) against the concentration (log axis) as in Figure 1.

8. Rinse the electrodes with distilled water and blot dry.
9. Measure out 100 ml of the sample into a 150 ml beaker and add 1 ml of low level ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips 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 3 - 7 above.

Low Level Bromide Determination (using an ion meter)

1. Using 20 ml of standard ISA, dilute to 100 ml with distilled water. This low level ISA (1.0M NaNO₃) is added at the rate of 1 ml low level ISA to each 100 ml of solution. The background ionic strength will be $1.0 \times 10^{-2} \text{M}$.
2. Follow the steps given in **Direct Measurement of Bromide (using an ion meter)** to the end of Step 6.
3. To a 150 ml beaker, add 100 ml of distilled water and 1 ml of low level ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.
4. Lower the electrode tips into the solution. When the reading has stabilized, fix the blank value in the meter according to the meter manufacturer's instructions.
5. Continue with Steps 7-9 in **Direct Measurement of Bromide (using an ion meter)**, remembering to use the low level ISA described in Step 1 above.

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 surface layer of silver metal may be formed by strongly reducing solutions. A layer of silver salt may be deposited on the membrane if high levels of ions forming very insoluble salts are present in the sample. Proper performance can be restored by polishing. See the section entitled **Electrode Response** for proper polishing procedure.

The bromide ion electrodes do not respond to anions or most cations. The electrode membrane is poisoned by solutions containing copper, mercury, and silver. These ions must be absent from the solution.

The maximum allowable ratio is 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 the 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>
OH ⁻¹ (2)	30000
Cl ⁻¹ (1)	400
S ₂ O ₃ ⁻² (3)	20
NH ₃ (3)	2
I ⁻¹ (1)	2.0X10 ⁻⁴
CN ⁻¹ (4)	8.0X10 ⁻⁵
S-2 (4)	1.0X10 ⁻⁶

- 1.) Gran's pilot titration can be used to measure mixed halides in solution.
- 2.) Acidify with 1M HNO₃ to pH 4 to remove hydroxide interferences.
- 3.) These substances represent complexing species whose maximum level can be exceeded without electrode damage. Values shown represents a 1% error.
- 4.) Add Ni⁺² to remove sulfide or cyanide interferences.

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

What is the maximum level of iodide tolerable in a sample whose bromide concentration is 10^{-2}M ?

Using Table 3, the maximum ratio is:

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

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

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

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

Precipitation and Complexation

Sulfide, carbonate, oxalate, phosphate, hydroxide, and other ions precipitate insoluble bromide salts. The level of bromide ion, the level of the precipitating ion, and the pH of the sample determine formation of a precipitate.

A wide variety of species, including acetate, ammonia, bromide, chloride, citrate, cyanide, and EDTA, form complexes with bromide. The total bromide concentration, the concentration of the complexing species, the solution pH, and the ionic strength all determine the extent of complexation. Complexation reduces the free bromide ion concentration and, since the electrode responds only to free bromide ions, a false reading results.

Temperature Influences

Samples and standards should be at the same temperature, since the electrode potentials are influenced by changes in temperature. A 1°C difference in temperature results in a 4% error at the $1.0 \times 10^{-3}\text{M}$ bromide concentration. Because of the solubility equilibria on which the electrode depends, the absolute potential of the reference electrode changes slowly with temperature. The slope of the electrode, as indicated by the factor "S" in the Nernst equation, also varies with temperature. Table 4 gives values for 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	27.10
10	28.10
20	29.08
25	29.58
30	30.07
40	31.07
50	32.06

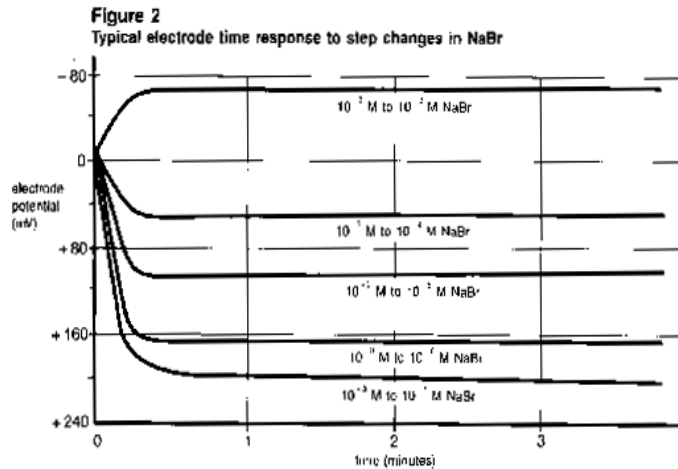
If changes in temperature occur, the electrodes should be re-calibrated.

The temperature range for the Cole-Parmer Replaceable Membrane Bromide Ion Electrode is 0°-80°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 mV potential against the Bromide concentration on semi-logarithmic graph paper results in a straight line with a slope of about 27 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 concentrations of $1.0 \times 10^{-6} \text{M}$ Bromide. Below 10^{-6}M , considerably longer response time can be expected (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. Unscrew the small cap from the outer body and remove the membrane cartridge from the small cap. 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. Insert the membrane cartridge back into place, and re-assemble the electrode.
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 Bromide nitrate solutions is 0.1M. In the presence of other ions, the upper limit of detection is above 1.0×10^{-2} M Bromide, 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 infuse into the electrode membrane at high salt concentrations causing deviation from the theoretical response. Either dilute samples between 0.1M and 1.0×10^{-2} 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. Neutral solutions containing free Bromide ions can be measured down to 0.01 ppm. Extreme care must be taken with measurements below 1.1 ppm to avoid contamination of samples.

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 Cole-Parmer Replaceable Membrane 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 membrane cartridge replacement is required.

Electrode Storage

The Cole-Parmer Replaceable Membrane Bromide electrode 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 (or the outer chamber of the reference electrode) should be drained of filling solution, if refillable, and the rubber insert placed over the filling hole.

ELECTRODE THEORY

Electrode Operation

The Cole-Parmer Replaceable Membrane Bromide Ion Electrode consists of sulfides of Bromide and other metals bonded into an epoxy or glass body. When an electrode potential develops across the membrane, the membrane is in contact with a solution containing Bromide ions. The electrode potential is measured against a constant reference potential, using a standard pH/mV meter. The level of Bromide 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 (~27mV/decade)
 X = level of Bromide ions in solution

The activity, X, represents the effective concentration of free Bromide ions in solution. Both bound, C_b, and free, C_f, Bromide ions are included in the total Bromide ion concentration, C_t. The Bromide ion electrode will only respond to free Bromide ions, the concentration of which is:

$$C_f = C_t + C_b$$

The activity, X, represents the effective concentration of the ions in solution. The activity is related to the free Bromide ion by the activity coefficient, γ , by:

$$X = \gamma C_f$$

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

Σ = 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, γ , 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 solution for the Bromide electrodes is sodium nitrate, 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 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 inter-diffusion 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 as nearly equal as possible, that is, the filling solution 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 electrode 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 electrodes, the standards and reagents, the sample, and the technique.

Meter

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

Glass-ware

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

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 sections **Measuring Hints** and **Electrode Response**. Repeat the slope check.
3. If the electrodes still fail to respond as expected, substitute another Bromide ion electrode that is known to be in good working order for the questionable 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 **Standards & 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 electrodes thoroughly.
 - Prepare the electrodes 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**.

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 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 electrodes 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 is compatible with the sample.

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

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
	electrodes not plugged in properly	unplug electrodes and reseal
	reference electrode not filled	be sure reference electrode is filled
	air bubble on membrane	remove bubble by redipping electrode
Noisy or Unstable	electrodes not in solution defective meter	put electrodes in solution check meter with

Readings (readings continuously or rapidly changing)

air bubble on membrane

shorting strap

remove bubble by re-dipping electrode

electrode exposed to interferences

soak electrode in Bromide standard

defective electrode

replace membrane

ISA not used

use recommended ISA

meter or stirrer not grounded

ground meter or stirrer

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 **Precipitation and Complexation**

incorrect reference filling solution

use recommended filling solution

Low Slope or No Slope

standards contaminated or incorrectly made

prepare fresh standards

ISA not used

use recommended ISA

standard used as ISA

use ISA

electrode exposed to complexing agents

check section entitled **Precipitation and Complexation**

air bubble on membrane

remove bubble by redipping probe

"Incorrect Answer"
(but calibration
good)

incorrect scaling
of semi-log paper

plot millivolts on
the linear axis. On curve is
the log axis, be sure
concentration numbers within
each decade are increasing
with increasing
concentration.

incorrect sign
of millivolt number

be sure to note sign
correctly

incorrect standards

prepare fresh standards

wrong units used

apply correct
conversion factor:
 $10^{-3}\text{M} = 112 \text{ ppm as Cd}^{+2}$

complexing agents
in sample

check section
entitled **Precipitation
and Complexation**

SPECIFICATIONS

Concentration Range:

$1.0 \times 10^{-1}\text{M}$ to $1.0 \times 10^{-7}\text{M}$
(11,200 to 0.01 ppm)

pH Range:

2 to 12

Temperature Range:

0° - 80°C

Resistance:

<1 Mohm

Reproducibility:

$\pm 2\%$

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
27506-00	Combination Bromide Ion Electrode, epoxy body, replaceable membrane
27503-03	Bromide Standard, 1000 ppm NaBr
27503-51	Ionic Strength Adjuster (ISA), 5M NaNO ₃
27506-50	Replaceable Membrane Kit containing 3 membrane cartridges, o-rings and reference fill solution

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