

**pHOENIX ELECTRODE COMPANY
CHLORIDE ION ELECTRODES
INSTRUCTION MANUAL**

GENERAL INSTRUCTIONS

Introduction

The pHOenix Chloride Ion Electrodes are used to quickly, simply, accurately, and economically measure chloride ions in aqueous solutions.

Required Equipment

1. ApH/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 Chloride Ion Electrode, Cat. No. CL01501, (reference electrode necessary), the pHOenix Chloride Ion Combination Glass Electrode, Cat. No. CL01502, or the pHOenix Chloride Ion Combination Epoxy Electrode, Cat No. CL01503.
5. The pHOenix Double Junction Reference Electrode, Cat. No. 5771429 (for use with the CL01501), with pHOenix Filling Solution, Cat. No. R001011, in the inner junction and with pHOenix Filling Solution, Cat. No. R001015, in the outer junction.
6. pHOenix Polishing Paper, Cat. No. 948201, to polish dirty or etched electrode membranes.

Required Solutions

1. Deionized or distilled water for solution and standard preparation.
2. pHOenix Ionic Strength Adjuster (ISA), 5M NaNO₃, Cat. No. CL0IS01. 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, NaNO₃. Swirl the flask to dissolve the solid. Fill the flask to the mark with distilled water, cap, and invert the flask several times.

mes to mix the contents. ISA is added at the rate of 2 ml of ISA to each 100 ml of standard or sample to adjust the ionic strength to about 0.1M.

3.

pHoenix Electrode Filling Solution, 1M/0.1M KNO₃/KCl, Cat. No. R001046, for the CL01503 chloride combination epoxy electrode. pHoenix Electrode Filling Solution, 1M KNO₃, Cat. No. R001015, for the 5731429 double junction reference electrode or the CL01502 chloride combination glass electrode.

4.

pHoenix Chloride Standard, 0.1M NaCl, Cat. No. CLOAS01. To prepare this solution from your own laboratory stock, add 5.84 grams of reagent-grade sodium chloride, NaCl, to a one liter volumetric flask about half-full of distilled water. Swirl the flask to dissolve the solid. Fill to the mark with distilled water, cap, and upend the flask several times to mix the solution.

5.

pHoenix Chloride Standard, 1000 ppm Cl⁻¹, Cat. No. CLOAS02. To prepare this solution from your own laboratory stock, add 1.65 grams of reagent-grade sodium chloride, NaCl, to a one liter volumetric flask about half-full of distilled water. Swirl the flask to dissolve the solid. Fill to the mark with distilled water, cap, and upend the flask several times to mix the solution.

6.

pHoenix Chloride Standard, 100 ppm Cl⁻¹, Cat. No. CLOAS03. To prepare this solution from your own laboratory stock, add 0.165 grams of reagent-grade sodium chloride, NaCl, to a one liter volumetric flask about half-full of distilled water. Swirl the flask to dissolve the solid. Fill to the mark with distilled water, cap, and upend the flask several times to mix the solution.

GENERAL PREPARATION

Electrode Preparation

Remove the rubber caps covering the electrode tips 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 filling hole. No preparation is required with a sealed reference electrode. Connect the electrodes to the proper terminals of the meter as recommended by the meter manufacturer.

Electrode Slope Check (with pH/mV meter)
(check electrodes 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 tips into the solution.
2. Using a pipet, add 1 ml of 0.1M or 1000 ppm chloride standard to the beaker. When the reading has stabilized, record the millivolt reading.
3. Using a pipet, add 10 ml of the same chloride standard used above to the beaker. When the reading has stabilized, record the millivolt reading.
4. Determine the difference between the two readings. A difference of 56 ± 2 mV indicates correct electrode operation, assuming the solution temperature is between 20° and 25°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)

1. Prepare standard chloride solutions whose concentrations vary by tenfold. Use either the 0.1M or 1000 ppm chloride 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 the 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 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 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** section 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 electrodes 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.

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, ethanol, benzene, and acetonitrile are permitted. Highly polar solvents slowly attack the electrode. Please check with Phoenix Electrode Company before using the electrode in other organic solvents.

The temperature of the standard solutions and of the sample solutions should be the same and below 50°C.

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

The pH range for the chloride ion electrode is 2-12. Neutralize samples outside this range with acid or base to bring them in range.

Units of Measurement

Chloride concentrations are measured in units of parts per million, equivalents per liter, 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 Cl⁻¹</u> | <u>moles/liter Cl⁻¹</u> |
|----------------------------|------------------------------------|
| 354.50 | 1.0X10 ⁻² |
| 35.45 | 1.0X10 ⁻³ |
| 3.55 | 1.0X10 ⁻⁴ |

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 chloride solution. The temperature of both sample solution and of standard solutions should be the same.

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

1. By serial dilution of the 0.1M or 1000 ppm standards, prepare 10⁻², 10⁻³, and 10⁻⁴M or 100 and 10 ppm chloride standards. Add 2 ml of ISA per 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 (1.0x10⁻⁴M 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 tips into the solution. When the reading has stabilized,

record the mV reading.

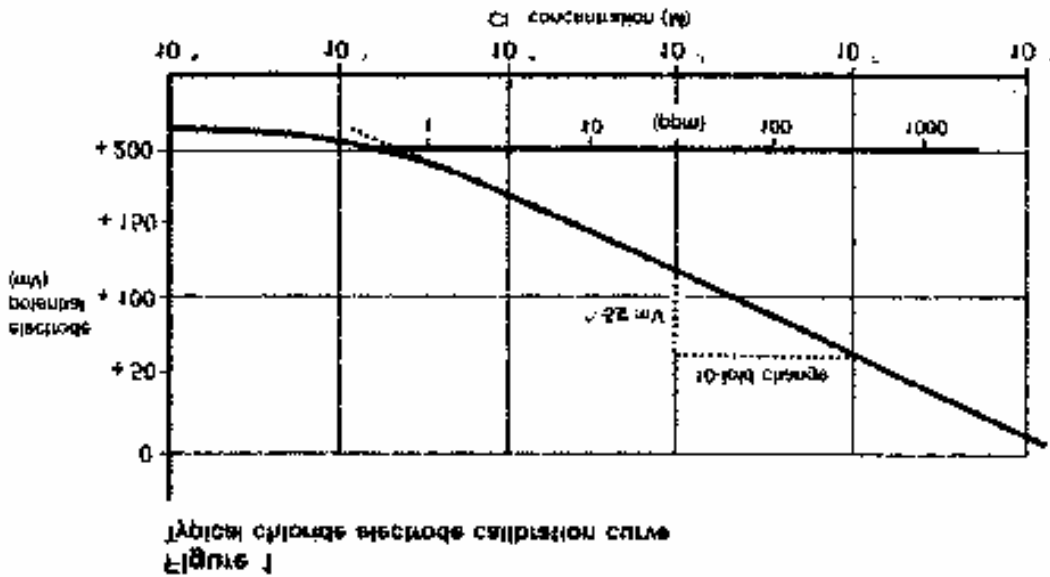
3.

Place the mid-range solution ($1.0 \times 10^{-3} \text{M}$ or 100 ppm) on the magnetic stirrer and begin stirring. After rinsing the electrodes with 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 ($1.0 \times 10^{-2} \text{M}$ or 1000 ppm) on the magnetic stirrer and begin stirring. After rinsing the electrodes with distilled water, blot dry and immerse the electrode tips in the solution. When the reading has stabilized, record the mV reading.

Using the 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 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 sample and 2 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring. Place the electrode tips 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 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 Step 2-5 above. A new calibration curve should be prepared daily.

Direct Measurement of Chloride (using a ion meter)

1. By serial dilution of the 0.1M or 1000 ppm chloride standard, prepare two chloride 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.

3. Lower the electrode tips into the solution.

4. Adjust the meter to the concentration of the chloride standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.

5. Rinse the electrodes 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 tips into the solution.

8. Adjust the meter to the concentration of the chloride 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 electrodes into the 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 tips 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 tips in the first chloride 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 Chloride Determination (using a pH/mV meter)

Use the following low level chloride measurement procedure in the non-linear portion of the calibration curve. (See Figure 1). This procedure is recommended for solutions containing less than $1.0 \times 10^{-4} \text{M}$.

1. Using 20 ml of standard ISA, dilute to 100 ml with distilled water. This low level ISA (1.0M 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 10 ml of 0.1M standard to 100 ml to prepare a $1.0 \times 10^{-2} \text{M}$ standard solution for measurements in moles per liter. Use the 1000 ppm standard for measurements in ppm. Standards should be prepared fresh daily.
3. Add 1 ml of the low level ISA to a 100 ml volumetric flask and fill to the mark with distilled water. Pour this solution into a 150 ml beaker and place the beaker on the magnetic stirrer. Begin stirring at a constant rate.

4. Place the electrode tips in the solution. Assure that the meter is in the mV mode.
5. Add increments of the $1.0 \times 10^{-2} \text{M}$ or 1000 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 Chloride 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 | 1.0×10^{-5} | 1.0 |
| 2 | A | 0.1 | 2.0×10^{-5} | 2.0 |
| 3 | A | 0.2 | 4.0×10^{-5} | 4.0 |
| 4 | A | 0.2 | 6.0×10^{-5} | 6.0 |
| 5 | A | 0.4 | 9.9×10^{-5} | 9.9 |
| 6 | B | 2.0 | 2.9×10^{-4} | 29.0 |
| 7 | B | 2.0 | 4.8×10^{-4} | 48.0 |

Pipet A = 1 ml graduated pipet

Pipet B = 2 ml pipet

Solutions: additions of 1000 ppm or $1.0 \times 10^{-2} \text{M}$ standard to 100 ml of ISA 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 electrodes in distilled water and blot dry.
9. Measure out 100 ml of the 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 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 t

he calibration curve every two hours by repeating Steps 2-7.

Low Level Chloride Determination (using an ion meter)

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

ELECTRODE CHARACTERISTICS

Reproducibility

Electrode measurements reproducible to +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. Performance may be restored by polishing. See the section **Electrode Response** for proper polishing procedure.

Though measurements can be made in solutions containing oxidizing agents such as MnO_4^- , mercury ions must not be present in the samples.

The maximum allowable ratio of interfering ion to chloride ion is given in Table 3. This ratio is expressed as the ratio of the interfering ion molarity to the chloride 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 Chloride Ion

| <u>Interferences</u> | <u>Interfering Ion (M)</u> <u>Chloride Ion (M)</u> |
|--------------------------------|---|
| $\text{OH}^{-1(1)}$ | 80 |
| $\text{NH}_3^{(2)}$ | 1.2×10^{-1} |
| $\text{S}_2\text{O}_3^{-2(2)}$ | 1.0×10^{-2} |
| $\text{Br}^{-1(3)}$ | 3.0×10^{-3} |
| $\text{S}^{-2(4)}$ | 1.0×10^{-6} |
| $\text{I}^{-1(3)}$ | 5.0×10^{-7} |

$\text{CN}^{-1(4)}$

2.0×10^{-7}

1. Acidify with 1M HNO_3 to pH 4 to remove hydroxide interference.
2. These substances represent complexing species whose maximum level can be exceeded without electrode damage. Value shown represents a 1% error.
3. Add CISA to solutions containing mixed halides to remove interferences. See the procedure below.
4. Add CISA or a solution of Ni^{+2} to remove sulfide or cyanide interferences.

Removal of Various Interferences with CISA

CISA is an oxidizing agent which will oxidize up to a 100-fold excess of CN^{-1} over Cl^{-1} , 100 ppm NH_3 , 100 ppm Br^{-1} or I^{-1} , or 500 ppm S^{-2} . Chloride measurement interferences may be removed by using CISA. The reagents used to prepare CISA are strong oxidizing agents and should be handled in a fume hood.

To prepare CISA, add approximately 800 ml of distilled water to a 1 liter volumetric flask. Add 15.1 grams of NaBrO_3 to the flask and swirl to dissolve the solid. Slowly add 75 ml of concentrated nitric acid (70% w/w or 15.9N), mix, and dilute to the mark with distilled water.

To use CISA, mix equal amounts of CISA and sample. Solutions should be allowed to stand for ten minutes before measuring. Since chloride will be oxidized upon prolonged standing, all standards or samples mixed with CISA should be discarded after measuring. A fresh mixture of CISA and standard should be prepared for each calibration. After adding CISA, follow the procedures for direct measurement.

Complexation

Total concentration (C_t) consists of free ions (C_f) and complexed or bound ions (C_c) in solution:

$$C_t = C_f + C_c$$

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

Chloride ions complex with some metal ions. Table 4 lists the levels of complexing metals causing a 10% error at $1.0 \times 10^{-4}\text{M}$ chloride.

TABLE 4: Levels of Complexing Agents Causing a 10% Error at $1.0 \times 10^{-4} \text{M}$ Chloride

| <u>Ion</u> | <u>Concentration</u> |
|------------------|--|
| Bi^{+3} | $4.0 \times 10^{-4} \text{M}$ (80 ppm) |
| Cd^{+2} | $2.0 \times 10^{-3} \text{M}$ (200 ppm) |
| Mn^{+2} | $2.0 \times 10^{-2} \text{M}$ (1100 ppm) |
| Pb^{+2} | $2.0 \times 10^{-3} \text{M}$ (400 ppm) |
| Sn^{+2} | $6.0 \times 10^{-3} \text{M}$ (700 ppm) |
| Tl^{+3} | $4.0 \times 10^{-5} \text{M}$ (8 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. 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 5 gives values for the "S" factor in the Nernst equation for the chloride ion.

TABLE 5: Temperature vs. Values for the Electrode Slope

| <u>Temp. ($^\circ\text{C}$)</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 electrodes should be re-calibrated.

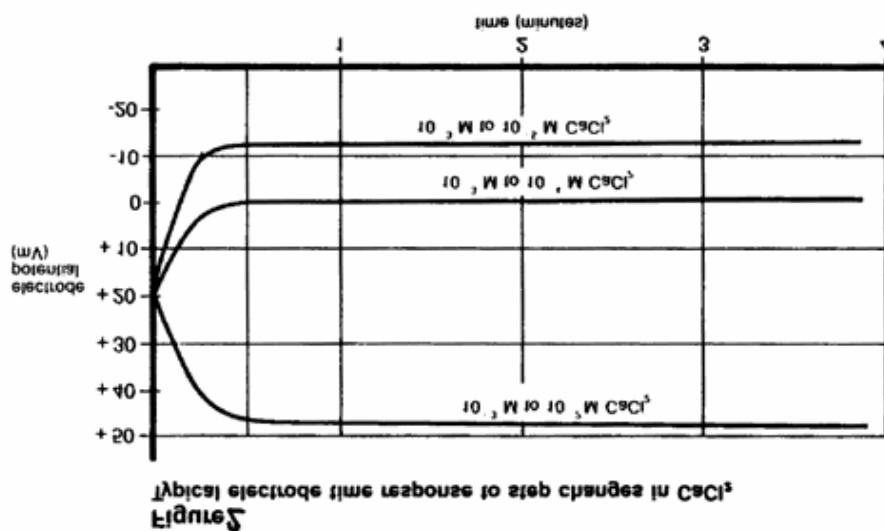
The temperature range for the Phoenix Chloride Ion Electrodes is 0° to -80°C , provided that temperature equilibrium has occurred. If the temperature varies substantially from room temperature, equilibrium times up to one hour are recommended.

Electrode Response

Plotting the electrode mV potential against the chloride concentration on semi-logarithmic paper results in a straight line with a slope of about 56 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 hi

ghly 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 chloride solutions is 1 M. In the presence of other ions, the upper limit of detection is above 1.0×10^{-1} M chloride, 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 1.0×10^{-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 chloride. Chloride measurements below 10^{-4} M CL^{-1} should employ low level procedures.

pH Effects

Hydroxide ion interferes with measurements of low levels of chloride 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 chloride measurements can be made without more than a 10% error due to hydroxide ion interference.

Electrode Life

The chloride 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 Chloride Electrodes may be stored for short periods of time in 1.0×10^{-2} M chloride 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 pHoenix Chloride Ion Electrodes are composed of a glass or an epoxy body and a silver chloride/silver sulfide membrane. When the membrane is in contact with a solution containing chloride ions, an electrode potential develops across the membrane. This electrode potential is measured against a constant reference potential, using a pH/mV meter or an ion meter. The level of chloride 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 (.56 mV/decade)
- X = level of chloride 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, a, by:

$$X = aC_f$$

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

$$I = 1/2 \sum C_x Z_x^2$$

where:

- C_x = concentration of ion X
- Z_x = charge of ion X
- \sum = 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, 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 chloride is 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 chloride 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

g 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 electrodes, 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 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.

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 chloride 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 **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 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 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**.

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 |
| | electrodes not plugged in properly | unplug electrodes and reseat |
| | reference electrode not filled | be sure reference electrode is filled |
| | air bubble on membrane | remove bubble by re-dipping electrode |
| | electrodes not in solution | put electrodes in solution |
| Noisy or Unstable Readings (readings continuously or rapidly changing) | defective meter | check meter with shorting strap |
| | air bubble on membrane | remove 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 chloride 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 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 Complexation |
| | air bubble on membrane | remove bubble by re-dipping probe |
| "Incorrect Answer" (but calibration | incorrect scaling of the linear axis. On the log axis, be | plot millivolts on semi-log paper (curve is good) 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: $1.0 \times 10^{-3} \text{M} = 35.5 \text{ ppm}$ as Cl^- |
| | complexing agents in sample | check section entitled Complexation |

SPECIFICATIONS

Concentration Range: 1M to 5.0×10^{-5} M (35,500 to 1.8 ppm)
pH Range: 2 to 12
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 chloride solution

ORDERING INFORMATION

| <u>P/N</u> | <u>DESCRIPTION</u> |
|------------|---|
| CL01501 | Chloride Ion Electrode, mono (reference electrode necessary), epoxy body |
| CL01502 | Chloride Ion Electrode, combination, glass body |
| CL01503 | Chloride Ion Electrode, combination, epoxy body |
| 5731429 | Reference Electrode, double junction, sleeve, epoxy body, for use with the CL01501 |
| CL0AS01 | Chloride Standard, 0.1M NaCl |
| CL0AS02 | Chloride Standard, 1000 ppm NaCl |
| CL0AS03 | Chloride Standard, 100 ppm NaCl |
| CL0IS01 | Chloride Ionic Strength Adjuster (ISA), 5 M NaNO ₃ |
| R001011 | Reference Electrode Filling Solution, 4M KCl/AgCl, for the 5731429 inner chamber |
| R001015 | Reference Electrode Filling Solution, 1M KNO ₃ , for the 5731429 outer chamber and CL01502 electrode |
| R001046 | Electrode Filling Solution, 1M KNO ₃ /0.1M KCl, for the CL01503 electrode |
| 948201 | Polishing Paper for the Chloride Ion Electrodes |

INDEX

| | |
|---|----|
| General Instructions | 1 |
| Introduction | 1 |
| required equipment | 1 |
| required solutions | 1 |
| General Preparation | 2 |
| electrode preparation | 2 |
| electrode slope check (with pH/mV meter) | 2 |
| electrode slope check (with ion meter) | 3 |
| Measurement | 4 |
| measuring hints | 4 |
| sample requirements | 4 |
| units of measurement | 4 |
| Measurement Procedure | 5 |
| direct measurement | 5 |
| direct measurement of chloride (using a pH/mV meter) | 5 |
| direct measurement of chloride (using an ion meter) | 6 |
| low level chloride determination (using a pH/mV meter) | 8 |
| low level chloride determination (using an ion meter) | 9 |
| Electrode Characteristics | 9 |
| Reproducibility | 9 |
| Interferences | 9 |
| removal of various interferences with cisa | 10 |
| complexation | 11 |
| temperature influences | 11 |
| electrode response | 12 |
| limits of detection | 13 |
| pH effects | 13 |
| electrode life | 13 |
| electrode storage | 14 |
| Electrode Theory | 14 |
| electrode operation | 14 |
| Troubleshooting Guide | 15 |
| Troubleshooting Hints | 17 |
| Specifications | 20 |
| Ordering Information | 20 |
| Index | 21 |