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

## GENERAL INSTRUCTIONS

### Introduction

The pHoenix Cyanide Ion Electrodes are used to quickly, simply, accurately, and economically measure cyanide ions in aqueous solutions.

### *IMPORTANT NOTICE*

Acidic cyanide solutions produce hydrogen cyanide (HCN) gas, highly toxic whether breathed or absorbed through the skin.  Use of the proper and recommended ionic strength adjuster (ISA) will keep the solution pH above 10.  If measurements in acidic solution are necessary (decomplexing procedure as given in the section **Complexation**), **THE PROCEDURE MUST BE DONE IN A HOOD**.

Use a pipet bulb when pipeting cyanide solutions, as these solutions are highly toxic.

### 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 Cyanide Ion Electrode, Cat. No. CN01501     (reference electrode necessary), the pHoenix Cyanide Ion Combination Glass Electrode, Cat. No. CN01502, or the pHoenix Cyanide Ion Combination Epoxy Electrode, Cat. No. CN01503.

5.
      The pHoenix Double Junction Reference Electrode, Cat. No. 5731429 (for use with the CN01501) with pHoenix Filling Solution, Cat. No. R001011, in the inner junction and with pHoenix Filling Solution, Cat. No. R001015, in the outer junction.

6.    Lab-ware made of plastic, not glass.

7.
      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 Cyanide Ionic Strength Adjuster (ISA), 10M NaOH, Cat. No. CN0IS01.  To prepare the ISA from your own laboratory stock, fill a 1000 ml beaker with about 900 ml of distilled water.  While gently stirring the solution under a hood, slowly add 400 grams of reagent-grade sodium hydroxide.  Transfer the solution quantitatively to a one liter volumetric flask after the solid NaOH has dissolved and the beaker has cooled.  Dilute to the mark with distilled water, cap, and upend several times to thoroughly mix the solution.  Store in a plastic bottle.

3.
Cyanide Standard, $1X10^{-2}M$.  To prepare this solution from your own laboratory stock, add 10 ml of ISA and about 500 ml of distilled water to a one liter volumetric flask.  Add 0.49 grams of dry, reagent-grade sodium cyanide, NaCN, to the solution and swirl the flask gently to dissolve the solid.  Dilute to the mark with distilled water, cap, and upend the flask several times to thoroughly mix the contents.  Store all standards in plastic bottles and prepare weekly.

4.
Cyanide Standard, 1000 ppm.  To prepare this solution from your own laboratory stock, add 10 ml of ISA and about 500 ml of distilled water to a one liter volumetric flask.  Add 1.88 grams of dry, reagent-grade NaCN and swirl the flask gently to dissolve the solid.  Dilute to the mark with distilled water, cap, and upend the flask several times to thoroughly mix the contents.  Store all standards in plastic bottles and prepare weekly.

## GENERAL PREPARATION

### Electrode Preparation

Remove the rubber caps covering the electrode tips and the rubber insert covering the filling hole of the cyanide combination ion electrode or the reference electrode.  Fill the reference electrode or 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 electrodes to the proper terminals as recommended by the meter manufacturer.

2

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

1.
        To a 150 ml beaker, add 100 ml of distilled water and 1 ml of 10M NaOH 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 $1.0X10^{-2}$M or 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.  After the reading has stabilized, record the mV reading.

4.
        The electrode is operating correctly if the mV potential has changed by 57+2 mV, assuming the solution temperature is between $20^{\circ}$ and $25^{\circ}$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)**

1.
        Prepare standard cyanide solutions whose concentrations vary by tenfold.  Use either the $1.0X10^{-2}$M or the 1000 ppm cyanide standard.  Use the serial dilution method for this preparation.

2.
        To a 150 ml beaker, add 100 ml of the lower value standard and 1 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 a 150 ml beaker, add 100 ml of the higher value standard and 1 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 93-100%. See the **TROUBLESHOOTING** 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 $1^{\circ}C$ 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 the beaker.

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

When making low level measurements (below $1X10^{-5}M$), use only plastic lab-ware and cover the beaker with Parafilm to avoid loss of cyanide. When making high cyanide measurements (above $1X10^{-3}M$), samples should be diluted before measurements.

Use fresh standards for calibration.

Use 1 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 epoxy body electrode. Please check with pHoenix Electrode Company before using the electrode in other 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 **Interferences** and **Electrode Response** sections to remove them.

Measurements above $1X10^{-3}M$ should be done infrequently, as cyanide ion slowly erodes the membrane. (See section on **Electrode Life**.) It may be necessary to polish the membrane occasionally with polishing paper or jeweller's rouge as the electrode is used. Samples should be diluted below $1X10^{-3}M$ if possible.

Proper pH is ensured if ISA is used. The pH should be above 10 so that cyanide is present as $CN^{-1}$ rather than as HCN in all standards and samples.

**Units of Measurement**

Cyanide ions can be measured in units of ppm, moles per liter, or any other convenient concentration unit. Table 1 indicates some concentration units and conversion factors.

**TABLE 1: Concentration Unit Conversion Factors**

| ppm $CN^-$ | moles/liter |
|---|---|
| 26.00 | $1.0X10^{-3}$ |
| 10.00 | $3.8X10^{-4}$ |
| 2.60 | $1.0X10^{-4}$ |
| 1.00 | $3.8X10^{-5}$ |
| 0.26 | $1.0X10^{-5}$ |

**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. The temperature of both sam

ple solutions and standard solutions should be the same.

**Direct Measurement of Cyanide (using a pH/mV meter)**

1.
By serial dilution, prepare $10^{-3}$, $10^{-4}$, and $10^{-5}$M or 10, 1 and 0.1 ppm standards for the cyanide ion from the 0.01M ppm or 1000 ppm standards. Prepare standards with a composition similar to the samples if the samples have an ionic strength above 0.1M.

2.
Place 100 ml of the most dilute standard solution in a 150 ml plastic beaker. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Add 1 ml of 10M NaOH (ISA). After assuring that the meter is in the mV mode, lower the electrode tips into the solution. After the reading has stabilized, record the mV reading.

3.
Place 100 ml of the mid-range solution in a 150 ml plastic beaker. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Add one ml of 10M NaOH (ISA). After rinsing the electrodes with distilled water, blot dry, and lower the electrode tips into the solution. After the reading has stabilized, record the mV reading.

4.
Place 100 ml of the most concentrated standard solution in a 150 ml plastic beaker. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Add 1 ml of 10M NaOH (ISA). After rinsing the electrodes with distilled water, blot dry, and lower the electrode tips into the solution. After the reading has stabilized, record the mV reading.

5.
Using the semi-logarithmic graph paper, plot the mV reading (linear axis) against the concentration (log axis). Extrapolate the curve down to about $1.0 \times 10^{-5}$M. 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 plastic beaker, add 100 ml of the sample and 1 ml of 10M NaOH (ISA). Place the beaker on the magnetic stirrer and begin stirring. Rinse the electrodes with distilled water, blot dry, and lower the electrode tips into the solution. When the reading has stabilized, record the mV reading. Using the calibration curve, determine the sample concentration.

7.

    The calibration should be checked every 2 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 Steps 2-5 above. A new calibration curve should be prepared daily.

**Direct Measurement of Cyanide (using an ion meter)**

1.

    By serial dilution of the $1.0 \times 10^{-2}$M or 1000 ppm cyanide standard, prepare two standards whose concentration is near the expected sample concentration. Measure 100 ml of each standard into individual 150 ml beakers and add 1 ml of 10M NaOH (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 cyanide 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 cyanide 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 (below $8X10^{-6}$M or 0.2 ppm), place the rinsed, dried electrodes into a solution containing 100 ml of distilled water and 1 ml ISA. After stabilization, fix the blank value in the meter according to the meter manufacturer's instruction.

10.

   After rinsing the electrodes and blotting dry, place the electrode tips into 100 ml of the sample and 1 ml of ISA. After stabilization, read the concentration directly from the meter display.

11.

   The calibration should be checked every 2 hours. Assuming no change in ambient temperature, place the electrode tips in the first cyanide 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 Step 2-10 above. The meter should be re-calibrated daily.

**Low-Level Cyanide Measurements (using a pH/mV meter)**

Use the following low level cyanide measurement procedure in the non-linear portion of the calibration curve (below $8X10^{-6}$M or 0.2 ppm). (See Figure 1.) A more accurate electrode indicator technique, such as titration, using a silver/sulfide ion electrode, may be preferred below these levels.

1.

   By serial dilution, prepare 100 ml of $1.0X10^{-3}$M or 10 ppm cyanide standard from the $1.0X10^{-2}$M or 1000 ppm cyanide standard.

2.

   Using a 150 ml plastic beaker, add 100 ml of distilled water and 1 ml 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 mV mode.

3.

   Increments of the standard should be added to the beaker according to the steps outlined in Table 2 below. After the reading stabilizes, record the mV reading for each addition.

**TABLE 2:** Low Level Measurement Calibration Curve

| Step | Pipet | Added Volume (ml) | Concentration ppm | M |
|------|-------|-------------------|-------------------|---|
| 1 | A | 0.1 | 0.01 | $1.0 \times 10^{-6}$ |
| 2 | A | 0.1 | 0.02 | $2.0 \times 10^{-6}$ |
| 3 | A | 0.2 | 0.04 | $4.0 \times 10^{-6}$ |
| 4 | A | 0.2 | 0.06 | $6.0 \times 10^{-6}$ |
| 5 | A | 0.4 | 0.10 | $9.9 \times 10^{-6}$ |
| 6 | B | 2.0 | 0.29 | $2.9 \times 10^{-5}$ |
| 7 | B | 2.0 | 0.48 | $4.8 \times 10^{-5}$ |

Pipet A = 1 ml graduated pipet
Pipet B = 2 ml pipet
Solutions: additions of $1.0 \times 10^{-3}$M or 10 ppm standard to 100 ml
          of distilled water and 1 ml ISA

4.
    On semi-logarithmic paper, plot the concentration (log axis) against the millivolt reading (linear axis) as in Figure 1. Reserve the final solution for checking the electrode each hour.

5.
    To a 150 ml plastic beaker, add 100 ml of sample and 1 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. After rinsing the electrodes, blot dry and lower the electrode tips into the solution. After stabilization of the reading, read the mV potential and determine the concentration from the calibration curve. A new low level calibration curve should be prepared daily using fresh standards.

## 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 layer of silver metal may form on the electrode surface in the presence of strongly reducing solutions, such as photographic developer. Ions forming very insoluble silver salts will cause the electrodes to malfunction if present in solution at sufficiently high levels to form a layer of silver salt on the membrane surface. Electrode performance can be restored by polishing if the surface of the

sensing element becomes contaminated.  See the section **Electrode Re sponse** for proper polishing procedure.
Solutions containing oxidizing agents such as $Fe^{+3}$, $Cu^{+2}$, and $MnO_4^-$ will not affect electrode performance.  All samples must be free of mercury.

The maximum allowable ratio of interfering ions to cyanide ions is given in Table 3.  The ratio is expressed as the ratio of the interfering ion concentration in moles per liter to the sample cyanide concentration in moles per liter.  Readings will be in error if this ratio is exceeded.  Neither the 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 Cyanide Ion**

| Interferences | Maximum Ratio |
|---|---|
| $Cl^{-1}$ | $1X10^6$ |
| $Br^{-1}$ | $5X10^3$ |
| $I^{-1}$ | $1X10^{-1}$ |
| $S^{-2}$ | must be absent |

When using the cyanide ion electrode, an example of the use of Table 3 follows:

What is the maximum level of bromide allowable in a sample whose cyanide concentration is $1X10^{-5}$M?
Using Table 3, the maximum ratio is:

$$\frac{[Br^{-1}]}{[CN^{-1}]} = 5X10^3$$

$$[Br^{-1}] = 5X10^3 \ [CN^{-1}]$$
$$= (5X10^3)(1X10^{-5})$$
$$[Br^{-1}] = 5X10^{-2}M = \text{maximum bromide concentration for no interference}$$

**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.

Hydrogen ions and many metal ions form complexes with cyanide ions.  The presence of any complexing agent lowers the measured concentration.  Since the electrode measures only free cyanide ions, use of

10M NaOH (ISA) is essential, since it eliminates complexation by hydrogen.

EDTA can be used to break up cyanide complexes formed with many metal ions, including cadmium, copper, nickel, and zinc. To a sample whose cyanide concentration is not more than 10 ppm, or about $1X10^{-3}M$, add acetic acid to make the sample solution's    pH~4. Add EDTA (disodium) to about 0.02M (or about 0.76 grams $Na_2$ EDTA per 100 ml sample.) In a hood, heat the mixture to about $50^{\circ}C$ for about five minutes to speed up the decomplexation. After cooling the solution, add 10M NaOH (ISA) until the pH~13. The cyanide remains free long enough for concentration measurements to be made, since EDTA complexes of the metals break up very slowly.

This method will not work for silver, mercury, gold, or cobalt, since they will bind the cyanide too strongly.

**Temperature Influences**

Samples and standards should be within $\pm1^{\circ}C$ of each other, since electrode potentials are influenced by changes in temperature. A $1^{\circ}C$ difference in temperature results in a 2% error at the $1.0X10^{-3}M$ concentration level. Because of the solubility equilibria on which the electrode depends, the absolute potential of the reference electrode (or reference portion of the combination 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 cyanide ion.

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

| Temp.($^{\circ}C$) | "S" |
|---|---|
| 0 | 54.20 |
| 10 | 56.18 |
| 20 | 58.17 |
| 25 | 59.16 |
| 30 | 60.15 |
| 40 | 62.13 |
| 50 | 64.11 |

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

The temperature range for the pHoenix Cyanide Ion Electrodes is $0^{\circ}$-$80^{\circ}C$, 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 cyanide 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.

Rinse the electrode surface with distilled water and soak the electrode tip in $1 \times 10^{-4}$M or 1 ppm standard solution for about two minutes before use.

**Limits of Detection**

Cyanide levels from $5X10^{-6}M$ to $1X10^{-2}M$ cyanide can be measured with the cyanide electrodes. However, since cyanide ion attacks the electrode membrane, measurements above $1X10^{-3}M$ should be done only intermittently.

The electrodes respond to cyanide in the sample as well as to ions dissolved from the membrane at low levels. The electrode membrane shows a very slight water solubility. The detection limit of the electrode is determined by this factor. Figure 1 shows the theoretical linear response -- the dashed line -- in comparison with the actual response (solid line). The low-level procedure is recommended if measurements are to be made in the non-linear region below $8X10^{-6}M$.

Plastic lab-ware must be used and the beakers must be covered with Parafilm for low level cyanide determinations or cyanide will be lost. Allow a longer stabilization time before taking the meter reading for best results.

**pH Effects**

The cyanide electrode can be used over the pH range 11 to 13. It is necessary to adjust the sample pH to above 11 using the recommended ISA to convert all cyanic acid species in solution to cyanide.

**Electrode Life**

The cyanide 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 cyanide electrode may be stored for short periods of time in $1.0x10^{-4}M$ cyanide solution with ISA added. 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 Cyanide Ion Electrodes consist of a solid membrane containing a mixture of inorganic silver compounds bonded into the tip of a glass or epoxy electrode body.  An electrode potential develops across the membrane when the electrode is in contact with solution containing cyanide ions and is capable of measuring free cyanide ions.  This potential is measured against a constant reference potential, using a standard pH/mV meter or an ion meter.  The Nernst equation describes the level of cyanide ions in solution corresponding to the measured potential:

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

where:
  $E$ = measured electrode potential
  $E_o$ = reference potential (a constant)
  $S$ = electrode slope (~57 mV/decade)
  $X$ = level of cyanide ions in solution

The activity, X, represents the effective concentration of free cyanide ions in the solution.  Total cyanide concentration, Ct, may include some bound as well as free cyanide ions.  Since the electrode only responds to free ions, the concentration of the free ions, Cf, is found by:

$$Cf = Ct - Cb$$

where Cb represents the concentration of all bound or complexed cyanide ions.

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

$$X = a\ C_f$$

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

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

where:
$C_x$ = concentration of ion X
$Z_x$ = charge of ion X
$O$ = 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.

All samples and standards containing cyanide ions have ionic strength adjuster (ISA) added so that the background ionic strength is high and constant relative to variable concentrations of cyanide. The recommended ISA for the cyanide electrode is sodium hydroxide, NaOH, though other basic solutions can be used as long as they do not contain ions that would interfere with the electrode's response to cyanide.

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 equitransferent. No junction potential can result if the rate at which positive and negative charge carried into the sample is equal.

## TROUBLESHOOTING GUIDE

The goal of troubleshooting is the isolation of a problem through checking each of the system components in turn: the meter, the plastic-ware, 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.

### Plastic-ware

Clean plastic-ware is essential for good measurement. Be sure to wash the plastic-ware well with a mild detergent and rinse very well with distilled or deionized water.

### 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 cyanide 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 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 w
hich could affect the response or physically damage the sensing ele
ctrode (or the reference electrode) if the electrodes work perfectl
y 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**, **Sampl
e Requirements**, and **Interferences**.)

**Technique**

Be sure that the electrode's limit of detection has not been exceed
ed.  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 |
| | electrode exposed to interferences | soak electrode in cyanide standard |
| | ISA not used | use recommended ISA |
| | meter or stirrer not grounded | ground meter or stirrer |
| | defective electrode | replace electrode |
| 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 curve is good) | incorrect scaling of semi-log paper | plot millivolts on the linear axis. On the log axis, be sure concentration numbers within each decade are |

18

|                        | 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: $10^{-3}M = 26.0$ ppm $CN^-$ |
| complexing agents in sample | check section entitled **Complexation** |

## SPECIFICATIONS

Concentration Range:        $1X10^{-2}M$ to $5X10^{-6}M$
260 to 0.1 ppm

pH Range:        11-13

Temperature Range:        $0^{\circ}-80^{\circ}C$

Resistance:        <1 Mohms

Reproducibility:        $\pm 2\%$

Size:        110 mm length
12 mm diameter
1 m cable length

Storage:        store in cyanide standard with ISA added

## ORDERING INFORMATION

P/N        DESCRIPTION

CN01501        Cyanide Ion Electrode, mono (reference electrode necessary), epoxy body

CN01502        Cyanide Ion Electrode, combination, glass body

CN01503        Cyanide Ion Electrode, combination, epoxy body

5731429        Reference Electrode, double junction, sleeve, epoxy body, for use with the CN01501

CN0IS01        Ionic Strength Adjuster (ISA), 10M NaOH

R001011        Electrode Filling Solution, 4M KCl/AgCl, 125 ml, for the 5731429 inner chamber

R001015        Electrode Filling Solution, 1M $KNO_3$, 125 ml, for the 5731429 outer chamber and the CN01502 electrode

R001046        Electrode Filling Solution, 1M $KNO_3$/0.1M KCl, 125 ml, for the CN01503 electrode

948201        Polishing Paper for the Cyanide Ion Electrodes

## TABLE OF CONTENTS