

## **GENERAL INSTRUCTIONS**

### **Introduction**

The Van London-pHoenix Company Cyanide Ion Selective Electrode is used to measure dissolved cyanide ion 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. An ion meter
2. Cyanide Ion Sensing Electrode
3. Polishing Paper to polish dirty or etched Cyanide electrode crystals
4. Plastic syringe, pipets, volumetric flasks, 150 ml beakers

### **Required Solutions**

1. Deionized or distilled water for solution preparation.
2. Cyanide Ionic Strength Adjuster (ISA), 10M NaOH. 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, 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.
4. Cyanide Electrode Reference Fill Solution, Cat. #R001015.

## **GENERAL PREPARATION**

### **Electrode Preparation**

Remove the rubber cap covering the electrode tip and the rubber insert covering the filling hole of the reference electrode. Fill the combination electrode with the filling solution shipped with the electrode to a level just below the fill hole. No preparation is required with a sealed reference electrode. Connect the electrode to the proper terminals of the meter as recommended by the meter manufacturer. Store the black shipping cap for later use.

### **Electrode Slope Check (for Ion meters which display mV)**

1. To a clean, dry, 150 ml beaker, add 100 ml of distilled water and 2 ml of ISA 1. After assuring that the meter is in the millivolt mode, lower the electrode tip into the solution. Stir moderately. Remove air bubbles on the dark gray membrane by redipping probe.
2. Using a pipet, add 1 ml of 1000 ppm Cyanide standard into the solution. Stir moderately. After 1 minute, record the mV reading.
3. Using a pipet, add 10 ml of the 1000 ppm Cyanide standard to the beaker. Stir moderately. After 1 minute, record the mV reading.

4. Determine the difference between the two readings. The electrode is operating correctly if a slope difference of 52-59 mV is found, assuming the solution temperature is 25°C. Slope is defined as the change in mV observed when the concentration changes by a factor of 10.

#### **Measurement using an Ion Meter (in the Concentration Mode)**

1. By serial dilution of the 1000 ppm Cyanide standard, prepare two cyanide standards whose concentration is near the expected sample concentration. (e.g 10 ppm and 100 ppm) For example, to make a 100 ppm standard, pipet 10 ml of the 1000 ppm standard into a 100 ml volumetric flask and dilute to volume with deionized water. Next to make a 10 ppm standard, pipet 10 ml of the newly-made 100 ppm standard into a 100 ml volumetric flask and dilute to volume with deionized water. A 1 ppm standard is made by further dilution of the 10 ppm standard. Measure out 100 ml of each standard into individual 150 ml beakers.
2. Assure that the meter is in the concentration mode and set for a 2-point calibration.
3. Lower the electrode tip into the least concentrated solution. Begin stirring at a constant rate. Add 2 ml of ISA to the solution and continue stirring.
4. After 1 minute, adjust the meter to the concentration of the more dilute cyanide standard and fix the value in the memory according to the meter manufacturer's instructions.
5. Rinse the electrode tip with distilled water and blot dry.
6. Lower the electrode tip into the more concentrated solution. Begin stirring at a constant rate. Add 2 ml of ISA to the solution and continue stirring.
7. After 1 minute, adjust the meter to the concentration of the more concentrated cyanide standard and fix the value in the memory according to the meter manufacturer's instructions.
8. Add 100 ml of the sample and 10 ml of ISA in a 150 ml beaker. Lower the electrode tip into the solution. Begin stirring at a constant rate. Ensure that the meter is in sample mode.
9. After 1 minute, read the concentration directly from the meter display.
10. The electrode should be re-calibrated every 2-3 hours. Simply repeat Steps 2-7 above.

#### **Measuring Hints**

As Cyanide electrodes are used or stored for long periods, they will experience some deterioration in performance and slope errors will increase. By using the meter's calibration controls this error can be corrected. If an electrode is able to be calibrated and is stable and responsive, it is still a functional electrode and may be used in service even though it no longer meets "new" electrode specifications.

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

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

Constant, but not violent, stirring is necessary for accurate measurement.

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

When making low level measurements (below 0.3 ppm), use only plastic lab-ware and cover the beaker with Parafilm to avoid loss of cyanide. When making high cyanide measurements (above 260 ppm), samples should be diluted before measurements. Measurements above 26 ppm should be done infrequently, as cyanide ion slowly erodes the membrane.

A slow or sluggish electrode response may indicate surface contamination of the membrane. Use a moistened polishing strip to lightly scrub the membrane surface, then soak in deionized water for five minutes to restore proper performance.

Use fresh standards for calibration. Re-calibrate every few hours for routine measurement.

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 Van London-pHoenix Electrode Company before using the electrode in other organic solvents.

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 Cyanide ion electrode is 11-13. Proper pH is ensured if ISA is used. The pH should be above 11 so that cyanide is present as  $\text{CN}^{-1}$  rather than as HCN in all standards and samples.

## **ELECTRODE CHARACTERISTICS**

### **Reproducibility**

Electrode measurements reproducible to  $\pm 2\%$  can be obtained if the electrode is calibrated every hour. Factors such as temperature fluctuation, drift, and noise limit reproducibility.

### **Interferences**

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

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

The maximum allowable ratio of interfering ion to Cyanide ion is given in Table 1. This ratio is expressed as the ratio of the interfering ion molarity to the Cyanide 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 1: Maximum Allowable Ratio of Interfering Ion to Cyanide Ion**

<u>Interferences</u>	<u>Maximum Ratio</u>
$\text{Cl}^{-1}$	$1 \times 10^6$
$\text{Br}^{-1}$	$5 \times 10^3$
$\text{I}^{-1}$	$1 \times 10^{-1}$
$\text{S}^{-2}$	must be absent

When using the cyanide ion electrode, an example of the use of Table 1 follows:

What is the maximum level of bromide allowable in a sample whose cyanide concentration is  $1 \times 10^{-5} \text{M}$ ?

$$\begin{aligned}
 [\text{Br}^{-1}] &= 5 \times 10^3 [\text{CN}^{-1}] \\
 &= (5 \times 10^3)(1 \times 10^{-5}) \\
 [\text{Br}^{-1}] &= 5 \times 10^{-2} \text{M} = \text{maximum bromide concentration for no} \\
 &\quad \text{interference}
 \end{aligned}$$

### **Complexation**

Total concentration,  $C_t$ , consists of free ions,  $C_f$ , and complexed or bound ions,  $C_c$ , in solutions:

$$C_t = C_f + C_c$$

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

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, add acetic acid to make the sample solution's pH~4. Add EDTA (disodium) to about 0.02M (or about 0.76 grams  $\text{Na}_2\text{EDTA}$  per 100 ml sample.) In a hood, heat the mixture to about 50°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**

The electrode response will shift and change slope with change in temperature. Standards and samples should be at the same temperature. A 2% error results with a 1°C temperature change for a 10 ppm solution.

The electrode can be used at temperatures from 0° - 80°C. Room temperature measurements are recommended, since measurements at temperatures quite different from room temperature may require equilibrium times up to one hour.

### **Electrode Response**

Plotting the electrode mV potential against the cyanide concentration results in a straight line with a slope of about 56 mV per decade.

For Cyanide concentrations above 10 ppm  $\text{CN}^{-1}$ , the electrode exhibits good time response (95% of total mV reading in one minute or less). Response times are longer below this value.

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.

### **Limits of Detection**

Cyanide levels from 0.13 ppm to 260 ppm cyanide can be measured with the Cyanide electrodes. However, since cyanide ion attacks the electrode membrane, measurements above 26 ppm 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. 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 one year 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.

Since Cyanide electrodes have a limited shelf life, it is important to have a backup electrode which is in working condition when required.

### **Electrode Storage**

The Cyanide electrode may be stored for short periods of time in 10 ppm 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.

### **TROUBLESHOOTING HINTS**

\*Remember to remove the black protective shipping cap on the bottom of the electrode and expose the fill hole underneath the electrode cap. Fill the electrode with the Reference Filling Solution shipped with the electrode to a level just below the fill hole.

#### **Symptom**

Out of Range Reading

#### **Possible Causes**

defective meter

defective electrode

electrode not plugged  
in properly

electrode reference  
chamber not filled

air bubble on membrane

electrode not in solution

#### **Next Step**

check meter with shorting strap (see meter  
Instruction manual)

check electrode operation

unplug electrode from meter and reset

fill reference chamber as instructed in  
**Electrode Preparation**

remove air bubble by re-dipping electrode

put electrode in solution

Noisy or Unstable Reading (readings continuously or randomly changing)	insufficient reference filling solution	fill outer body of electrode with proper amount of reference filling solution
	defective meter	check meter with shorting strap (see meter instruction manual)
	defective electrode	check electrode operation
	air bubble on membrane	remove air bubble by re-dipping electrode
	meter or stirrer improperly grounded	check meter and stirrer for grounding
Drift (reading slowly changing in one direction)	electrode exposed to interferences	soak electrode in cyanide stand with ISA
	incorrect reference filling solution	refill outer body of electrode using filling solution shipped with electrode
	total sample level of dissolved species above 1M	dilute sample
	membrane failure (wet, perforation, discoloration)	replace electrode
	samples and standards at different temperatures	allow samples and standards to come to same temperature before measurement
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
	membrane failure (wet, perforation, discoloration)	replace electrode
"Incorrect Answer" but calibration curve is good)	incorrect standards	prepare fresh standards
	wrong units used	apply correct conversion factor: $10^{-3}\text{M} = 26 \text{ ppm as CN}^{-1}$
	ISA added to standards and not samples	add same proportions of ISA to standards and samples
	sample carryover	rinse electrodes thoroughly between samples

## **SPECIFICATIONS**

Concentration Range:	260 to 0.13 ppm
pH Range:	11 to 13
Slope:	53 – 59 mV between 10 ppm and 100 ppm at 25°C
Temperature Range:	0° to 80°C
Interferences:	S <sup>-2</sup> , I <sup>-1</sup> , Br <sup>-1</sup>
Reproducibility:	± 2%
Size:	110 mm length 12 mm diameter 1 m cable length
Storage:	store electrode in Cyanide standard with ISA added

## **ELECTRODE THEORY**

### **Electrode Operation**

The Van London-pHoenix Cyanide Ion Electrodes are composed of a glass or an epoxy body and a silver iodide/silver sulfide membrane. When the membrane is in contact with a solution containing cyanide 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 cyanide ions, corresponding to the measured potential, is described by the Nernst equation:

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

where: E = measured electrode potential  
E<sub>o</sub> = reference potential (a constant)  
S = electrode slope (.56 mV/decade)  
X = level of cyanide 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<sub>f</sub>, by the activity coefficient,  $\tilde{a}$ , by:

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

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

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

where: C<sub>x</sub> = concentration of ion X  
Z<sub>x</sub> = 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,  $\tilde{a}$ , is constant and the activity, X, is directly proportional to the concentration.