

# CN<sup>-</sup>

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Orion 94-06,  
Orion 96-06 ionplus®

## Orion Cyanide Electrode

INSTRUCTION MANUAL



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ORION Series A meters and 900A printer are protected by U.S. patents 5,108,578, 5,198,093 and German patents D334,208 and D346,753.

Sure-Flow electrodes are protected by European Patent 278,979 and Canadian Patent 1,286,720.

ionplus electrodes and Optimum Results solutions are protected by US Patent 5,830,338.

ROSS Ultra electrodes have patents pending.

ORION ORP Standard is protected by US Patent 6,350,367.

ORION Series A conductivity meters are protected by US Patent 5,872,454.

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The specifications, descriptions, drawings, ordering information and part numbers within this document are subject to change without notice.

This publication supersedes all previous publications on this subject.

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# TOXICOLOGICAL NOTICE

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HCN gas, evolved from acid cyanide solutions, is highly toxic whether breathed or absorbed through the skin. Use the recommended ISA to keep solution pH above 10. If solutions must be made acidic (see **Complexation**), the process must be done in a hood.

Cyanide solutions are also highly toxic. Use a pipet bulb.  
**DO NOT mouth pipet.**

# GENERAL INFORMATION

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## Introduction

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The Orion 94-06 Cyanide Half-Cell Electrode and Orion 96-06 Sure-Flow™ Combination Cyanide Electrode measure cyanide ions in aqueous solutions quickly, simply, accurately, and economically.

The Orion 96-06 offers additional benefits from the Sure-Flow Combination reference design. With this electrode, a separate reference electrode is unnecessary, making it convenient to use with small sample volumes. The free-flowing Sure-Flow junction assures stable, drift-free potentials. When measuring dirty samples which would clog conventional electrode junctions, the Sure-Flow junction can be opened and flushed clean simply by pressing the cap. The Orion 90-02 Double Junction Reference electrode, when used with the 94-06 Cyanide Half-Cell Electrode, also offers the benefits of the Sure-Flow junction design.

General analytical procedures, required solutions, electrode characteristics, and electrode theory are discussed in this manual. Operator instructions for Orion meters are given in the meter instruction manuals.

Thermo Electron Corporation's Technical Edge for Orion Products can be consulted for assistance and troubleshooting advice. Please refer to **Troubleshooting** for information on contacting Thermo Electron Corporation.

## Required Equipment

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**Meter** - The easiest to use are direct concentration readout specific ion meters (ISE meters), such as Orion EA 940, 920A, 720A, 710A, or 290A. If unavailable, a pH/mV meter with readability to 0.1 mV, such as Orion 420A, 520A, or 525A is recommended.

Reference Electrode	Orion
<i>For use with Orion 94-06:</i>	
Orion 90-02 Double Junction Reference Electrode, includes:	
Inner Chamber Filling Solution	900200
Outer Chamber Filling Solution	900002
	900003
<i>For use with Orion 96-16:</i>	
The Orion 96-06 Sure-Flow Combination Cyanide Electrode does not require a separate reference electrode.	n/a

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**Magnetic Stirrer, Stir Bars** - Required for laboratory measurements.

**Graph Paper** - 4 cycle semi-logarithmic paper for preparing calibration curves (for use with pH/mV laboratory meters).

**Plastic Labware** - For low level cyanide measurements

**Polishing Strips** - Orion 948201. To clean the cyanide sensing element.

## Required Solutions

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### Distilled or Deionized Water -

To prepare all solutions and standards.

Reference Filling Solution	Orion
Optimum Results™ B (for Orion 96-06 Combination Cyanide Electrode)	900062
Inner Chamber Filling Solution (for use with Orion 90-02 Reference Electrode)	900002
Outer Chamber Filling Solution (for use with Orion 90-02 Reference Electrode)	900003
<b>Ionic Strength Adjustor (ISA)</b> 10 M NaOH (to adjust solution pH to operating range of electrode and keep a constant background ionic strength)	951011
<b>Stock Cyanide Standard Solutions</b>	(see below)

### Required Chemicals:

Sodium Cyanide, Reagent Grade  
(or Potassium Cyanide, Reagent Grade)

Distilled Water

### Preparation:

10<sup>-2</sup> M cyanide stock standard: put 0.490 g dry, reagent grade NaCN or 0.651 g dry, reagent grade KCN in a 1 liter volumetric flask. Add 10 mL ISA and 500 mL distilled water to dissolve the solid. Add distilled water to bring the volume to one liter.

**1000 ppm cyanide stock standard:** put 1.88 g dry, reagent grade NaCN or 2.50 g dry, reagent grade KCN in a 1 liter volumetric flask. Add 10 mL ISA and 500 mL distilled water to dissolve the solid. Add distilled water to bring the volume to one liter.

Store stock standards in plastic bottles and prepare fresh weekly. Lower concentration working standards used for calibration should be prepared daily.

# BEFORE USING THE ELECTRODE

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## Electrode Preparation

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### **Orion 94-06 – Cyanide Half-Cell Electrode**

Remove the rubber cap covering the electrode tip.

### **Orion 90-02 – Double Junction Reference Electrode**

Fill this reference electrode according to the instructions in the reference electrode instruction manual. Fill the inner chamber with Orion 900002 Filling Solution. Fill the outer chamber with Orion 900003 Filling Solution.

Add filling solution each day before using the electrode. The filling solution level should be at least one inch above the level of sample in the beaker to ensure a proper flow rate. If the filling solution is less than one inch above the sample solution level, electrode potentials may be erratic.

### **Orion 9606 – Sure-Flow Combination Cyanide Electrode**

Orion offers a line of filling solutions designed specifically for your application. Optimum Results™ B (Orion 900062) supplied with this electrode is designed to minimize junction potentials and provide optimum temperature and time response. It can be used for all cyanide measurements.

Add filling solution each day before using the electrode. The filling solution level should be at least one inch above the level of sample in the beaker to ensure a proper flow rate. If the filling solution is less than one inch above the sample solution level, electrode potentials may be erratic.

The electrode is shipped without filling solution in the reference chamber. To fill from the flip-spout bottle:

1. Lift the spout to a vertical position.
2. Insert the spout into the fill hole in the outer sleeve and add a small amount of filling solution to the chamber. Tip the electrode to moisten the O-ring at the top and return electrode to a vertical position.
3. Holding the electrode by the barrel with one hand, use the thumb to push down on the electrode cap, allowing a few drops of filling solution to drain and wet the inner cone.
4. Release sleeve. If sleeve does not return to its original position immediately, check to see if the O-ring is moist enough and repeat steps 2 - 4 until the sleeve has returned to original position. Add filling solution up to the fill hole.

## Checking Electrode Operation (Slope)

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This procedure measures electrode slope. Slope is defined as the change in millivolts observed with every ten-fold change in concentration. Obtaining the slope value provides the best means for checking electrode performance.

These are general instructions that can be used with most meters to check electrode operation. See individual meter instruction manuals for more specific information.

1. If electrode(s) have been stored dry, prepare the electrode(s) as described in **Electrode Preparation**.
2. Connect the electrode(s) to the meter as described in the meter instruction manuals. Non-Orion meters may require special adapters. Consult your meter instruction manual.
3. Place 100 mL distilled water into a 150-mL beaker. Add 1 mL ISA (Orion 951011). Stir thoroughly at a slow to moderate speed.

***NOTE:** Do not create a vortex in the solution. Do not change the position of the electrode during this procedure.*

4. Set the meter to the mV mode.
5. Rinse electrode(s) with distilled water, blot dry, and place in the solution prepared in Step 3 above.
6. Use 0.1 M or 1000 ppm cyanide standard in the following steps. Pipet 1 mL of the standard into the beaker. Stir thoroughly as directed in step 3. When a stable reading is displayed, record the electrode potential in millivolts.
7. Pipet 10 mL of the same standard into the same beaker. Stir thoroughly as directed in step 3. When a stable reading is displayed record the electrode potential in millivolts.
8. The difference between the first and second potential reading is defined as the slope of the electrode. The difference should be in the range of (-) 54-60 mV/ decade when the solution temperature is between 20 and 25 °C. If the slope is not within the appropriate range refer to the **Troubleshooting** section.

# HELPFUL INFORMATION

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## Units of Measurement

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Cyanide ion can be measured in units of moles per liter, parts per million, grams per liter, ounces per gallon, or any other convenient unit (see **Table 1**).

**Table 1**  
**Concentration Unit Conversion Factors**

Moles/Liter	ppm CN <sup>-</sup>	g/L	oz/gal
1	26000	26	3.48
$3.84 \times 10^{-5}$	1	$1 \times 10^{-3}$	$1.34 \times 10^{-4}$
$3.84 \times 10^{-2}$	1000	1	$1.34 \times 10^{-1}$
$2.87 \times 10^{-1}$	7460	7.46	1

## Sample Requirements

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The epoxy electrode body is resistant to all aqueous solutions. The cyanide electrode may be used safely on an intermittent basis in methanol or ethanol. Consult Thermo Electron's Technical Edge for Orion Products (see **Assistance**) for recommendations on use of the electrode in other organic solvents.

Cyanide ion slowly erodes the sensing element. Measurements above 25 ppm or  $10^{-3}$  M cyanide should be done only occasionally (see **Electrode Life**). Dilute samples to below 25 ppm or  $10^{-3}$  M CN<sup>-</sup> if possible. As the electrode is used it may be necessary to polish the sensing element occasionally with polishing strips. See **Electrode Maintenance**.

Samples and standards should be at the same temperature. A 1 °C difference in temperature will produce measurement errors greater than 2%.

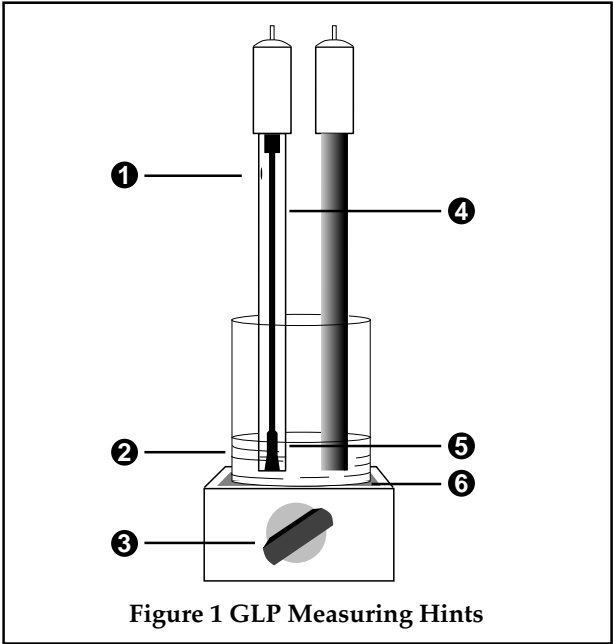
Samples and standards should be above pH 10 so that the cyanide is present as CN<sup>-</sup> rather than as HCN. Use of ISA ensures proper pH.

## GLP Measuring Hints

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See **Figure 1**.

- Stir all standards and samples at a uniform rate during measurement. Stir thoroughly at a slow to moderate speed. Do not create a vortex in the solution. Do not change the position of the electrode while calibrating or measuring samples. Magnetic stirrers may generate sufficient heat to change solution temperature. Place a piece of insulating material such as cork, cardboard, or styrofoam between the stirrer and sample beaker.
- Prepare fresh working standards for calibration daily.
- Always rinse electrode(s) with distilled water between measurements. Shake after rinsing to prevent solution carryover. Blot dry.
- Allow all standards and samples to come to the same temperature for precise measurement.
- The 90-02 reference electrode (when used with the 9406 Cyanide Half-Cell Electrode) should be submerged to the same depth as the cyanide electrode.
- Concentrated samples ( $> 25$  ppm or  $10^{-3}$  M cyanide) should be diluted before measurement.
- After immersion in solution, check electrode(s) for any air bubbles on the sensing element and remove by gently tapping the electrode(s).
- For high ionic strength samples, prepare standards with composition similar to that of the sample.



**Figure 1 GLP Measuring Hints**

- 1 Filling hole should be uncovered  
(Orion 90-02 or 96-06)
- 2 Fresh standard
- 3 Stir all samples and standards
- 4 Filling solution level must be higher than sample level
- 5 Reference junction must be immersed
- 6 Place insulation between stirrer and beaker

# CHOOSING THE RIGHT MEASURING TECHNIQUE

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A variety of analytical techniques are available to the analyst.

**Direct Measurement** is a simple procedure for measuring a large number of samples. Only one meter reading is required for each sample. Calibration is performed in a series of standards. The concentration of the samples is determined by comparison to the standards. ISA is added to all solutions to ensure that samples and standards have similar ionic strength and proper pH.

**Low-Level Measurement** is similar to Direct Measurement. This method is recommended when the expected sample concentration is less than 0.5 ppm or  $2 \times 10^{-5}$  M CN<sup>-</sup>. A minimum three point calibration is recommended to compensate for the electrode's non-linear response at these concentrations. A special procedure describes the best means of preparing low-level calibration standards.

**Known Addition** is a useful method for measuring samples, since calibration is not required. This method is recommended when measuring only a few samples, or when samples have a high ( $> 0.1$  M) ionic strength, or a complicated back-ground matrix. Refer to **Theory of Operation** for explanation of these effects. The electrodes are immersed in the sample solution and an aliquot of a standard solution containing the measured species is added to the sample. From the change in potential before and after the addition, the original sample concentration is determined. As in direct calibration, any convenient concentration unit can be used.

# MEASUREMENT PROCEDURES

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## Direct Measurement

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The following direct measurement procedures are recommended for “high-level” measurements. All samples must be in the electrode’s linear range, greater than 0.5 ppm or  $2 \times 10^{-5}$  M  $\text{CN}^-$ . A two point calibration is sufficient, though more points can be used if desired. With ISE meters, such as the Orion 920A, 720A, 710A, or 290A, sample concentrations can be read directly from the meter. Refer to the meter instruction manual for calibration details. When using a mV meter, a calibration curve can be prepared on semi-logarithmic graph paper, or a linear regression (against logarithmic concentration values) can be performed at the user’s discretion using a spreadsheet or graphing program.

### Measuring Hints

- Standard concentrations should bracket the expected sample concentrations.
- Always add 1 mL ISA per 100 mL of cyanide standard or sample.
- For high ionic strength samples, having an ionic strength of 0.1 M or greater, prepare standards with a composition similar to that of the samples, or measure the samples using the known addition method.
- During calibration, measure the least concentrated standard first, and work up to the most concentrated.
- The best method for preparation of standards is by serial dilution. This procedure involves preparing an initial standard that is diluted, using volumetric glassware, to prepare a second standard solution. The second is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.
- Verify this procedure by measuring a standard of known concentration as an unknown or by spiking a sample with cyanide standard.
- Review section entitled **GLP Measuring Hints**.

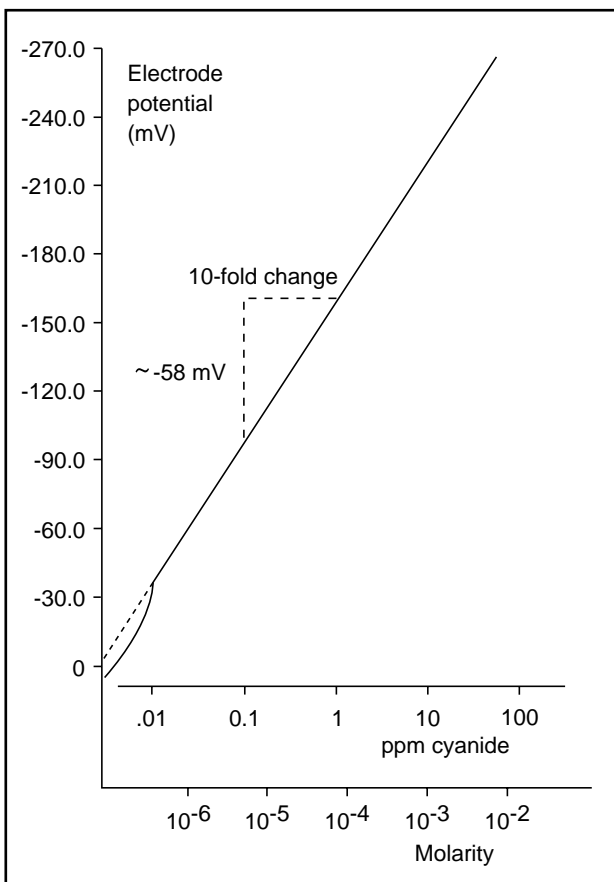
## Direct Measurement Procedure using ISE Meter

See individual meter instruction manuals for more specific calibration information.

1. Prepare electrode(s) as described in **Electrode Preparation**.
2. Connect electrode(s) to the meter, and adjust the meter to measure concentration.
3. Prepare two standards that bracket the expected sample range and differ in concentration by a factor of ten. Standards can be prepared in any concentration unit to suit the particular analysis requirement. All standards should be at the same temperature as the samples. For details on temperature effects on electrode performance, refer to **Temperature Effects**.
4. Measure 100 mL of each standard and sample into separate 150 mL beakers. Add 1 mL ISA to each beaker.

***NOTE:** Other solution volumes may be used, as long as the ratio of solution to ISA remains 100:1. Stir thoroughly.*

5. Rinse electrode(s) with distilled water, blot dry and place into the beaker containing the most dilute standard. Wait for a stable reading, then calibrate the meter to display the value of the standard as described in the meter instruction manual.
6. Rinse electrode(s) with distilled water, blot dry, and place into the beaker with the next standard. Wait for a stable reading, then adjust the meter to display the value of this standard, as described in the meter instruction manual.
7. Repeat step 6 for all standards, working from the least concentrated to most concentrated standard.
8. Rinse electrode(s) with distilled water, blot dry, and place into sample. The concentration will be displayed on the meter.



**Figure 2**  
**Typical Cyanide Electrode Calibration Curve**

*In the direct measurement procedure, a calibration curve is constructed on semi-logarithmic paper. Electrode potentials of standard solutions are measured and plotted on the linear axis against their concentrations on the log axis. In the linear regions of the curves, only two standards are needed to determine a calibration curve. In nonlinear regions, more points must be taken. The direct measurement procedures in this manual are given for concentrations in the region of linear electrode response. Low-level measurement procedures are given for measurements in the non-linear region. This curve is only used as an example. Actual mV values may differ.*

## Direct Measurement Procedure using a meter with mV readout

1. Prepare electrode(s) as described in Electrode Preparation.
2. Connect electrode(s) to the meter, and adjust the meter measure mV.
3. Prepare two standards that bracket the expected sample range and differ in concentration by a factor of ten. Standards can be prepared in any concentration unit to suit the particular analysis requirement. All standards should be at the same temperature as the samples. For details on temperature effects on electrode performance, refer to **Temperature Effects**.
4. Measure 100 mL of each standard and sample into separate 150 mL beakers. Add 1 mL ISA to each beaker.

***NOTE:** Other solution volumes may be used, as long as the ratio of solution to ISA remains 100:1. Stir thoroughly.*

5. Rinse electrode(s) with distilled water, blot dry and place into the beaker containing the most dilute standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
6. Rinse electrode(s) with distilled water, blot dry, and place into the beaker with the next standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
7. Repeat step 6 for all standards, working from the least concentrated to most concentrated standard.
8. Using semi-logarithmic graph paper, prepare a calibration curve by plotting the millivolt values on the linear axis and the standard concentration values on the logarithmic axis. See **Figure 2**.
9. Rinse electrode(s) with distilled water, blot dry, and place into sample. When a stable reading is displayed, record the mV value.
10. Using the calibration curve prepared in step 8, determine the unknown sample concentration.

## Low-Level Measurements

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These procedures are for solutions with a cyanide concentration of less than 0.5 ppm or  $2 \times 10^{-5}$  M  $\text{CN}^-$ , those within the non-linear range of the cyanide electrode. See **Figure 2**. For more accurate measurements below these levels, an electrode indicator technique using the silver/sulfide electrode (Orion 9616), may be preferable. Call or write the Thermo's Technical Edge for Orion Products for more information (see **Assistance**). In low-level measurements, at least three standards are required for calibration to compensate for the electrode's non-linearity.

### Measuring Hints

- Use plastic labware for low-level cyanide measurements.
- For solutions low in cyanide but high in total ionic strength (greater than  $10^{-1}$  M), perform the same procedure with one change: prepare a calibration solution with a composition similar to the sample.
- The choice of standard concentrations is important for obtaining the best electrode performance and most rapid analysis time. Here are some guidelines:
  - Ideally, standard concentrations should bracket the expected sample concentrations.
  - When measuring sub-ppm levels with Orion 920A, 720A, 710A, or 290A, take advantage of the autoblack feature. It does not require a zero standard, but can perform blank correction as long as the lowest standard concentration is in the non-linear range of the electrode. Electrodes are very slow in the absence of a measurable concentration and a multipoint calibration generally will be less accurate when "zero" is included as a standard. Standard concentrations should be chosen such that the lowest standard value is larger than the blank value obtained, and the second lowest standard should be at least twice that of the lowest. See your A-Series meter instruction manuals for additional information on blank correction.
  - If using an ISE meter, such as the Orion EA 940, that allows a blank solution value to be entered, it is recommended to do so. A blank solution is prepared with the same dilution water and ISA used when preparing calibration standards. This solution corrects for the curves non-linearity as well as for any background ion contamination that might be present in the standard solutions. When a blank value is entered, it represents the zero point of the curve, and each standard is measured against that blank.

- When not using an ISE meter, a calibration curve can be drawn on semi-logarithmic graph paper, or the data can be processed at the discretion of the user by means of a spreadsheet or graphing program with a non-linear curve fitting feature.
  - When using ISE meters, such as Orion 920A, 720A, 710A, or 290A, three calibration points are sufficient. If a calibration curve is prepared manually, additional points may be helpful to facilitate drawing the curve.
- Remember to stir all standards and samples at a uniform rate. Stir thoroughly at a slow to moderate speed. Do not create a vortex in the solution. Do not change the position of the electrode while calibrating or measuring samples.
  - Typical response time for this electrode is approximately 1 minute. Low-level measurements may take longer to stabilize. Wait for 3 minutes or the meter's "ready" signal, *whichever takes longer*, before calibrating the meter or recording the sample value.
  - Review section entitled **GLP Measuring Hints**.

### **Low-Level Measurement Procedure using ISE Meter**

Follow the above procedure entitled **Direct Measurement Procedure using ISE Meter**. Use at least three calibration standards. Read the **Measuring Hints** section on pg. 19 in order to select appropriate standard concentrations. Refer to the meter instruction manual for detailed calibration procedures. If not using an Orion 920A, 720A, 710A, or 290A with the autoblack feature, preparation of a blank solution is recommended to ensure accurate results.

### **Low-Level Measurement Procedure using a meter with mV readout (see Table 2)**

#### **Set Up**

1. Prepare electrode(s) as described in **Electrode Preparation**.
2. Connect electrode(s) to the meter. Set the meter to read mV.
3. Select a standard solution. Use either a 10 ppm cyanide standard or a  $10^{-3}$  M cyanide solution.

## Measurement

1. Measure 100 mL distilled water into 150 mL beaker. Add 1 mL ISA.
2. Rinse electrode(s) with distilled water, blot dry, and place into beaker. Stir thoroughly.
3. Add increments of the 10 ppm or  $10^{-3}$  M standard to the beaker using steps outlined in **Table 2**. Record stable millivolt reading after each increment. On semi-logarithmic paper, plot the concentration (log axis) against the millivolt potential (linear axis). See **Figure 2**. Prepare a new calibration curve with fresh standards each day.
4. Measure 100 mL of sample into a beaker. Add 1 mL ISA. Rinse the electrode(s) with distilled water, blot dry, and place into the sample.
5. Stir thoroughly. When a stable reading is displayed, record the mV value.
6. Determine the sample concentration corresponding to the measured potential from the low-level calibration curve.

**Table 2**  
**Preparing a Calibration Curve For Low-Level Measurements**  
**making 10 ppm cyanide additions**

Step	Graduated Pipet Size	Added Volume	Concentration ppm
1	1 mL	0.1 mL	0.01
2	1 mL	0.4 mL	0.05
3	1 mL	0.8 mL	0.13
4	2 mL	2.0 mL	0.32

**Preparing a Calibration Curve For Low-Level**  
**Measurements making  $10^{-3}$  M cyanide additions**

Step	Graduated Pipet Size	Added Volume	Concentration Molarity
1	1 mL	0.1 mL	$1.0 \times 10^{-6}$
2	1 mL	0.4 mL	$5.0 \times 10^{-6}$
3	1 mL	1.0 mL	$1.5 \times 10^{-5}$
4	2 mL	2.0 mL	$3.4 \times 10^{-5}$

## Known Addition

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Known addition is a convenient technique for measuring samples in the linear range, greater than 0.5 ppm or  $2 \times 10^{-5}$  M  $\text{CN}^-$ , because no calibration curve is needed. The sample potential is measured before and after addition of a standard solution. Many meters, such as the Orion 920A, have the known addition algorithms preprogrammed. This programming allows multiple standard additions to be made to the sample, thereby allowing the meter to calculate the electrode slope as well. Having the ability to read the sample concentration directly from the meter is a great convenience and ensures accuracy.

### Measuring Hints

- Sample concentration should be known within a factor of three.
- Concentration should approximately double as a result of the first standard addition.
- With double or multiple known addition, the final addition should be 10 to 100 times the sample concentration.
- All samples and standards should be at the same temperature.
- Add 1 mL ISA to every 100 mL of sample before analysis.
- Standard addition volume should be no more than 10% of the sample volume, or standard should be pre-treated with ISA in a 100:1 ratio. See **Table 3**.
- Review section entitled **GLP Measuring Hints**.

## Set-up

1. Prepare electrode(s) as described in **Electrode Preparation**.
2. Connect electrode(s) to the meter.
3. Prepare a standard solution that, upon addition to the sample, will cause the concentration of cyanide to double. Add 1 mL ISA to each 100 mL of standard. Refer to **Table 3** as a guideline.
4. Determine the slope of the electrode by performing the procedure under **Checking Electrode Operation (Slope)**.

## Known Addition Measurement Procedure using an ISE meter with KA program

See individual meter instruction manuals for more specific information.

1. Set the meter to measure in the known addition mode.
2. Measure 100 mL of sample into a beaker. Add 1 mL ISA. Stir thoroughly. Rinse electrode(s) with distilled water, blot dry, and place in sample solution.
3. When a stable reading is displayed, program the meter as described in the meter instruction manual.
4. Pipet the appropriate amount of standard solution into the beaker. Stir thoroughly.
5. When a stable reading is displayed, record the sample concentration.

**Table 3**  
**Standard Addition volumes**

<b>Volume of Addition</b>	<b>Concentration of Standard</b>
1 mL	100 x sample concentration
5 mL	20 x sample concentration
10 mL*	10 x sample concentration

\* Most convenient volume to use.

## Known Addition Measurement Procedure using a meter with mV readout

See individual meter instruction manual for more specific information.

1. Set the meter to millivolt mode.
2. Measure 100 mL of the sample into a 150 mL beaker. Add 1 mL ISA. Stir thoroughly.
3. Rinse electrode(s) with distilled water, blot dry, and place into beaker. When a stable reading is displayed, record the mV value as  $E_1$ .
4. Pipet the appropriate amount of standard solution into the beaker. See **Table 3**. Stir thoroughly.
5. When a stable reading is displayed, record the mV value as  $E_2$ . Subtract the first reading from the second to find DE.
6. From **Table 5**, find the value Q, that corresponds to the change in potential, DE. To determine the original sample concentration, multiply Q by the concentration of the added standard:

$$C_{sam} = Q * C_{std}$$

where:

C<sub>std</sub> = standard concentration

C<sub>sam</sub> = sample concentration

Q = reading from known addition table

The table of Q values is calculated for a 10% volume change for electrodes with slopes of -57, -58, -59, -60 mV/decade for cyanide. The equation for the calculation of Q for different slopes and volume changes is given below:

$$Q = \frac{p * r}{(1+p)10DE/S - 1}$$

where:

Q = reading from known addition table

DE =  $E_2 - E_1$

S = slope of the electrode

p = (volume of standard) / (volume of sample & ISA)

r = (volume of sample & ISA) / (volume of sample)

If it is more convenient, a simple spreadsheet can be set up to calculate known addition results, using any ratio of sample to addition. A typical worksheet is shown in **Table 4**. The numbers shown are examples, but the formulas and their locations should be copied exactly.

**Table 4**  
**Calculating known addition for cyanide using Lotus, Excel, or Quattro Spreadsheet**

A	B	C
1		Enter Value
2	Vol. of Sample & ISA, mL:	101
3	Vol. of Addition, mL:	10
4	Concentrn. of Addition:	10
5	Vol. of Sample	100
6	Initial mV Reading	- 45.3
7	Final mV Reading	- 63.7
8	Electrode Slope	- 59.2
9		
10		Derived Values
11	Delta E	+ C7 - C6
12	Solution Vol. Ratio	+ C3/C2
13	Antilog Term	+ 10 <sup>^</sup> (C11/C8)
14	Sample Vol. Ratio	+ C2/C5
15	Q Term	+ C12*C14/{[(1+C12)*C13]-1}
16	Calculated Initial Conc.in same units as addition:	+ C15*C4

**NOTE:** for Excel, use = instead of + at start of formula

**Table 5**

**Known Addition Table for an added volume one-tenth the total volume. Slopes, in the column headings, are in units of mV/decade.**

$\Delta E$	Q, Concentration Ratio			
	(slope) 57.2	58.2	59.2	60.1
5.0	0.2917	0.2957	0.2996	0.3031
5.2	0.2827	0.2867	0.2906	0.2940
5.4	0.2742	0.2781	0.2820	0.2854
5.6	0.2662	0.2700	0.2738	0.2772
5.8	0.2585	0.2623	0.2660	0.2693
6.0	0.2512	0.2550	0.2586	0.2619
6.2	0.2443	0.2480	0.2516	0.2548
6.4	0.2377	0.2413	0.2449	0.2480
6.6	0.2314	0.2349	0.2384	0.2416
6.8	0.2253	0.2288	0.2323	0.2354
7.0	0.2196	0.2230	0.2264	0.2295
7.2	0.2140	0.2174	0.2208	0.2238
7.4	0.2087	0.2121	0.2154	0.2184
7.6	0.2037	0.2070	0.2102	0.2131
7.8	0.1988	0.2020	0.2052	0.2081
8.0	0.1941	0.1973	0.2005	0.2033
8.2	0.1896	0.1927	0.1959	0.1987
8.4	0.1852	0.1884	0.1914	0.1942
8.6	0.1811	0.1841	0.1872	0.1899
8.8	0.1770	0.1801	0.1831	0.1858
9.0	0.1732	0.1762	0.1791	0.1818
9.2	0.1694	0.1724	0.1753	0.1779
9.4	0.1658	0.1687	0.1716	0.1742
9.6	0.1623	0.1652	0.1680	0.1706
9.8	0.1590	0.1618	0.1646	0.1671
10.0	0.1557	0.1585	0.1613	0.1638
10.2	0.1525	0.1553	0.1580	0.1605
10.4	0.1495	0.1522	0.1549	0.1573
10.6	0.1465	0.1492	0.1519	0.1543
10.8	0.1437	0.1463	0.1490	0.1513
11.0	0.1409	0.1435	0.1461	0.1485
11.2	0.1382	0.1408	0.1434	0.1457
11.4	0.1356	0.1382	0.1407	0.1430
11.6	0.1331	0.1356	0.1381	0.1404
11.8	0.1306	0.1331	0.1356	0.1378
12.0	0.1282	0.1307	0.1331	0.1353
12.2	0.1259	0.1283	0.1308	0.1329
12.4	0.1236	0.1260	0.1284	0.1306
12.6	0.1214	0.1238	0.1262	0.1283
12.8	0.1193	0.1217	0.1240	0.1261
13.0	0.1172	0.1195	0.1219	0.1239
13.2	0.1152	0.1175	0.1198	0.1218
13.4	0.1132	0.1155	0.1178	0.1198
13.6	0.1113	0.1136	0.1158	0.1178
13.8	0.1094	0.1117	0.1139	0.1159
14.0	0.1076	0.1098	0.1120	0.1140
14.2	0.1058	0.1080	0.1102	0.1121
14.4	0.1041	0.1063	0.1084	0.1103
14.6	0.1024	0.1045	0.1067	0.1086
14.8	0.1008	0.1029	0.1050	0.1069

Table 5 (continued)

$\Delta E$	Q, Concentration Ratio			
	(slope) 57.2	58.2	59.2	60.1
15.0	0.0992	0.1012	0.1033	0.1052
15.5	0.0953	0.0973	0.0994	0.1012
16.0	0.0917	0.0936	0.0956	0.0974
16.5	0.0882	0.0902	0.0921	0.0938
17.0	0.0850	0.0869	0.0887	0.0904
17.5	0.0819	0.0837	0.0856	0.0872
18.0	0.0790	0.0808	0.0825	0.0841
18.5	0.0762	0.0779	0.0797	0.0813
19.0	0.0736	0.0753	0.0770	0.0785
19.5	0.0711	0.0727	0.0744	0.0759
20.0	0.0687	0.0703	0.0719	0.0734
20.5	0.0664	0.0680	0.0696	0.0710
21.0	0.0642	0.0658	0.0673	0.0687
21.5	0.0621	0.0637	0.0652	0.0666
22.0	0.0602	0.0617	0.0631	0.0645
22.5	0.0583	0.0597	0.0612	0.0625
23.0	0.0564	0.0579	0.0593	0.0606
23.5	0.0547	0.0561	0.0575	0.0588
24.0	0.0530	0.0544	0.0558	0.0570
24.5	0.0514	0.0528	0.0541	0.0553
25.0	0.0499	0.0512	0.0525	0.0537
25.5	0.0484	0.0497	0.0510	0.0522
26.0	0.0470	0.0483	0.0495	0.0507
26.5	0.0456	0.0469	0.0481	0.0492
27.0	0.0443	0.0455	0.0468	0.0479
27.5	0.0431	0.0443	0.0455	0.0465
28.0	0.0419	0.0430	0.0442	0.0452
28.5	0.0407	0.0418	0.0430	0.0440
29.0	0.0395	0.0407	0.0418	0.0428
29.5	0.0385	0.0396	0.0407	0.0417
30.0	0.0374	0.0385	0.0396	0.0406
30.5	0.0364	0.0375	0.0385	0.0395
31.0	0.0354	0.0365	0.0375	0.0384
31.5	0.0345	0.0355	0.0365	0.0374
32.0	0.0335	0.0345	0.0356	0.0365
32.5	0.0327	0.0336	0.0346	0.0355
33.0	0.0318	0.0328	0.0337	0.0346
33.5	0.0310	0.0319	0.0329	0.0337
34.0	0.0302	0.0311	0.0320	0.0329
34.5	0.0294	0.0303	0.0312	0.0321
35.0	0.0286	0.0295	0.0305	0.0313
35.5	0.0279	0.0288	0.0297	0.0305
36.0	0.0272	0.0281	0.0290	0.0298
36.5	0.0265	0.0274	0.0282	0.0290
37.0	0.0258	0.0267	0.0275	0.0283
37.5	0.0252	0.0260	0.0269	0.0276
38.0	0.0246	0.0254	0.0262	0.0270
38.5	0.0240	0.0248	0.0256	0.0263
39.0	0.0234	0.0242	0.0250	0.0257
39.5	0.0228	0.0236	0.0244	0.0251

Table 5 (continued)

$\Delta E$	Q, Concentration Ratio			
	(slope) 57.2	58.2	59.2	60.1
40.0	0.0223	0.0230	0.0238	0.0245
40.5	0.0217	0.0225	0.0232	0.0239
41.0	0.0212	0.0219	0.0227	0.0234
41.5	0.0207	0.0214	0.0221	0.0228
42.0	0.0202	0.0209	0.0216	0.0223
42.5	0.0197	0.0204	0.0211	0.0218
43.0	0.0192	0.0199	0.0206	0.0213
43.5	0.0188	0.0195	0.0202	0.0208
44.0	0.0183	0.0190	0.0197	0.0203
44.5	0.0179	0.0186	0.0192	0.0198
45.0	0.0175	0.0181	0.0188	0.0194
45.5	0.0171	0.0177	0.0184	0.0190
46.0	0.0167	0.0173	0.0179	0.0185
46.5	0.0163	0.0169	0.0175	0.0181
47.0	0.0159	0.0165	0.0171	0.0177
47.5	0.0156	0.0162	0.0168	0.0173
48.0	0.0152	0.0158	0.0164	0.0169
48.5	0.0148	0.0154	0.0160	0.0166
49.0	0.0145	0.0151	0.0157	0.0162
49.5	0.0142	0.0147	0.0153	0.0158
50.0	0.0139	0.0144	0.0150	0.0155
50.5	0.0135	0.0141	0.0146	0.0151
51.0	0.0132	0.0138	0.0143	0.0148
51.5	0.0129	0.0135	0.0140	0.0145
52.0	0.0126	0.0132	0.0137	0.0142
52.5	0.0124	0.0129	0.0134	0.0139
53.0	0.0121	0.0126	0.0131	0.0136
53.5	0.0118	0.0123	0.0128	0.0133
54.0	0.0116	0.0120	0.0125	0.0130
54.5	0.0113	0.0118	0.0123	0.0127
55.0	0.0110	0.0115	0.0120	0.0125
55.5	0.0108	0.0113	0.0118	0.0122
56.0	0.0106	0.0110	0.0115	0.0119
56.5	0.0103	0.0108	0.0113	0.0117
57.0	0.0101	0.0106	0.0110	0.0114
57.5	0.0099	0.0103	0.0108	0.0112
58.0	0.0097	0.0101	0.0105	0.0110
58.5	0.0095	0.0099	0.0103	0.0107
59.0	0.0093	0.0097	0.0101	0.0105
59.5	0.0091	0.0095	0.0099	0.0103
60.0	0.0089	0.0093	0.0097	0.0101

# ELECTRODE STORAGE

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## **Orion 94-06 Cyanide Half-Cell Electrode**

Orion 94-06 Cyanide Half-Cell Electrode should be rinsed thoroughly and stored in distilled water or in the air. When storing for long periods of time, replace the cap to protect the sensing element and store dry.

## **Orion 96-06 Sure-Flow Combination Cyanide Electrode**

The solution in the Orion 9606 Combination Cyanide Electrode should not be allowed to evaporate, causing crystallization.

### **For short periods of time (up to one week):**

Store the electrode in distilled water.

### **For storage longer than one week:**

Drain the electrode, flush the inside with distilled water and store dry with the cap on to protect the sensing element.

## **Orion 90-02 Double Junction Reference Electrode**

Orion 90-02 Reference Electrode may be stored in air between sample measurements (up to two hours).

### **For short periods of time (up to one week):**

90-02 should be stored in filling solution. Distilled water is also an acceptable storage solution. The solutions inside the electrode should not be allowed to evaporate causing crystallization.

### **For storage longer than one week:**

Drain both chambers of the reference electrode, flush the inside with distilled water, and store dry.

# ELECTRODE MAINTENANCE

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## Cyanide Electrode Polishing Procedure

To be used when electrode becomes sluggish or drifty

1. Cut off a 1-inch length of the polishing strip, Orion 948201
2. Hold electrode with the sensing element facing upwards.
3. Place a few drops of distilled water on the sensing element surface.
4. With the frosted side down, place the polishing strip on the sensing element using light finger pressure.
5. Rotate the electrode for about 30 seconds.
6. Rinse and soak in a 1 ppm or  $10^{-5}$  M  $\text{CN}^-$  standard solution for about two minutes before use.

## Disassembly And Cleaning of 96-06 Sure-Flow Combination Cyanide Electrode

Disassembly is not normally required or recommended. When the area between the electrode sleeve and inner cone becomes clogged with sample or precipitate from the filling solution, the chamber can be cleaned by flushing out with filling solution. (Hold the electrode by the cap with one hand and push the outer sleeve of the electrode up into the cap to drain the chamber.) If the chamber is not completely clean, repeat the procedure. Refill with the appropriate filling solution.

If a more thorough cleaning is required, the electrode can be disassembled using the following instructions:

1. Rinse the outer body under warm running water.
2. Hold the electrode body by the cap with one hand and push the outer sleeve of the electrode up into the cap to drain the chamber.
3. Unscrew the cap, slide the cap and epoxy-coated spring up along the cable.
4. Hold the outer sleeve with one hand and firmly push down on the threaded portion with the thumb and forefinger to separate the inner body from the sleeve.
5. Grasp the cone with a clean tissue and withdraw the body from the sleeve with a gentle twisting motion.

***NOTE:** Do not touch the AgCl pellet above the cone as it may cause damage to the pellet. Rinse the outside of the electrode body and the entire sleeve with distilled water. Allow to air dry.*

### **Reassemble**

1. Moisten the O-ring on the electrode body with a drop of filling solution. Insert screw-thread end of the electrode body into the tapered, ground end of sleeve.
2. Push body into the sleeve with a gentle twisting motion until bottom surface of inner cone is flush with the tapered end of the sleeve.
3. Place the spring on the electrode body and screw on the cap. Refill with filling solution. The electrode is now ready for use.

# TROUBLESHOOTING

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## Troubleshooting Checklist

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Symptom	Possible Causes
Off-scale or Over-range reading	Defective meter
	Defective electrode
	Electrodes not plugged in properly
	Reference electrode junction is dry
	Reference electrode chamber not filled
	Air bubble on electrode
	Electrodes not in solution
Noisy or unstable readings (readings continuously or rapidly changing)	Defective meter
	Meter or stirrer improperly grounded
	Air bubble on electrode
	Wrong reference electrode
	ISA not used
Drift (Reading slowly changing in one direction)	Samples and standards at different temperatures
	Sensing element dirty or etched
	Incorrect reference filling solution

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## Solution

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Check meter with shorting strap (See meter instruction manual)

Refer to **Troubleshooting Guide**

Unplug electrodes and reseal

Hold reference electrode and push cap to expel a few drops of filling solution

Be sure reference electrode chamber is filled.  
See **Electrode Preparation**.

Remove air bubble on electrode by gently tapping it.

Put electrodes in solution

Check meter with shorting strap (See meter instruction manual)

Check meter and stirrer for grounding

Check **Using the Electrode**

Remove air bubble on electrode by gently tapping it.

Use appropriate reference electrode. See **Required Equipment**.

Do not use calomel or Ag/AgCl (frit-or fiber-type) reference electrode

Use recommended ISA

Allow solutions to come to room temperature before measurement

Polish sensing element (see **Electrode Maintenance**)

Use recommended filling solution. See **Electrode Preparation**.

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## Troubleshooting Checklist (con't)

Symptom	Possible Causes
Low slope or No slope	Electrodes not properly conditioned  Standards contaminated or incorrectly made  ISA not used  Standard used as ISA  Electrode exposed to interferences
High Slope	Stirring solution too rapidly
"Wrong Answer" (But calibration curve is OK)	Incorrect scaling of semilog paper  Incorrect sign  Incorrect standards  Wrong units used  Complexing agents in sample

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## Solution

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Prepare fresh standards

Use recommended ISA

Use ISA!

Refer to **Troubleshooting Guide**

Stir sample at slow to moderate speed

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

Be sure to note sign of millivolt value correctly

Prepare fresh standards

Apply correct conversion factor:  $10^{-3} \text{ M} = 26.0 \text{ ppm CN}^-$

Use known addition

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## Troubleshooting Guide

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The most important principle in troubleshooting is to isolate the components of the system and check each in turn. The components of the system are: 1) Meter 2) Electrodes 3) Standard 4) Sample and 5) Technique.

See also **GLP Measuring Hints** section.

### Meter

The meter is the easiest component to eliminate as a possible cause of error. Orion meters are provided with an instrument checkout procedure in the instruction manual and a shorting cap for convenience in troubleshooting. Consult the manual for complete instructions and verify that the instrument operates as indicated and is stable in all steps.

### Electrodes

1. Rinse electrode(s) thoroughly with distilled water.
2. Determine electrode slope, see **Checking Electrode Operation**.
3. If electrode fails this procedure, prepare electrode(s) as directed in **Electrode Preparation**. Clean electrode(s) as described in **Electrode Maintenance**.
4. Repeat step 2, **Checking Electrode Operation**.
- 5a. *For the 94-06 Cyanide Half-Cell Electrode:*  
If the electrodes still do not perform as described, determine whether the cyanide or reference electrode is at fault. To do this, substitute a known working electrode for the electrode in question and repeat the slope check.
- 5b. *For the 96-06 Sure-Flow Combination Cyanide Electrode:*  
If the electrode still does not perform as described replace the electrode.
6. If the stability and slope check out properly, but measurement problems persist, the sample may contain interferences or complexing agents, or the technique may be in error. See **Standard, Sample, and Technique** sections.

7. Before replacing a “faulty” electrode, or if another electrode is not available for test purposes, review the instruction manual and be sure to:
- Clean the electrode thoroughly
  - Prepare the electrode properly
  - Use proper filling solution, ISA, and standards
  - Measure correctly
  - Review **Troubleshooting Checklist**

## Standard

The quality of results depends greatly upon the quality of the standards. ALWAYS prepare fresh standards when problems arise – it could save hours of frustrating troubleshooting! Error may result from contamination of prepared standards, quality of distilled water, or a numerical error in calculating the concentrations.

The best method for preparation of standards is by serial dilution. This means that an initial standard is diluted, using volumetric glassware, to prepare a second standard solution. The second is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.

## Sample

If the electrodes work properly in standards but not in sample, look for possible interferences, complexing agents, or substances that could affect response or physically damage the sensing electrode or the reference electrode. If possible, determine the composition of the samples and check for problems. See **Sample Requirements, Interferences, and pH Requirements**.

## Technique

Check the method of analysis for compatibility with your sample. Direct measurement may not always be the method of choice. If a large amount of complexing agents is present, or if the sample has a high ionic strength, known addition may be best. If working at low levels, be sure to follow the low-level measurement technique. Also, be sure that the expected concentration of the ion of interest is within the electrode’s limits of detection. If problems persist, review operational procedures and instruction manuals to be sure that proper technique has been followed. Read **Measuring Hints, Analytical Procedures, and Electrode Characteristics**.

## **Assistance**

After troubleshooting all components of your measurement system, contact The Technical Edge<sup>SM</sup> for Orion products. Within the United States call 1.800.225.1480, outside the United States call 978.232.6000 or fax 978.232.6031. In Europe, the Middle East and Africa, contact your local authorized dealer. For the most current contact information, visit [www.thermo.com](http://www.thermo.com).

For the most current warranty information, visit [www.thermo.com](http://www.thermo.com).

# ELECTRODE CHARACTERISTICS

## Electrode Response

The electrode potential plotted against cyanide concentration on semi-logarithmic paper results in a straight line with a slope of about (-) 54 to 60 mV per decade with moderate stirring (see **Figure 2**). The electrode exhibits good time response (99% response to one minute or less) for concentrations above  $10^{-5}$  M. Below this value response times vary from 2 to 5 minutes.

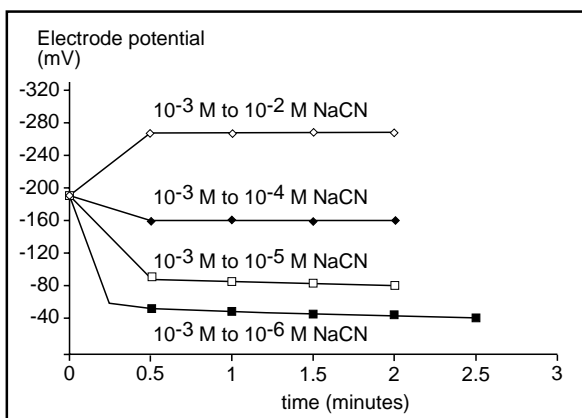


Figure 3 Typical Electrode Response

## Reproducibility

Reproducibility is limited by factors such as temperature fluctuations, drift and noise. Within the electrode operating range, reproducibility is independent of concentration. With calibration every hour, direct electrode measurements are reproducible to  $\pm 2\%$ .

## Temperature Effects

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Since the electrode potentials are affected by changes in temperature, samples and standard solutions should be within  $\pm 1$  °C ( $\pm 2$  °F) of each other. At the  $10^{-3}$  M level, a 1 °C difference in temperature results in errors greater than 2%. The absolute potential of the reference electrode changes slowly with temperature because of the solubility equilibria on which the electrode depends. The slope of the electrode also varies with temperature, as indicated by the "S" in the Nernst equation, see **Theory of Operation**. Theoretical values of the slope at different temperatures are given in **Table 6**. If temperature changes occur, meter and electrodes should be recalibrated.

The electrode can be used at temperatures from 0° to 80 °C, provided that temperature equilibrium has occurred. For use at temperatures substantially different from room temperature, calibration standards should be at the same temperature as samples. Electrode life is significantly shorter when used above 80 °C.

**Table 6**  
**Theoretical Values of Electrode**  
**Slope vs. Temperature**

°C	Slope (CN <sup>-</sup> )
0	- 54.2
10	- 56.2
20	- 58.2
25	- 59.2
30	- 60.1
40	- 62.1
50	- 64.1

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## Interferences

---

The electrode will malfunction if the ions listed in **Table 7**, which form insoluble silver salts, are present at sufficiently high concentrations to form a layer of the salt on the sensing element surface. In addition, the electrode must not be placed in strong reducing solutions, such as photographic developer, which form a layer of silver metal on the electrode sensing element. If the surface of the sensing element becomes contaminated, restore performance by polishing.

**Table 7** gives the maximum allowable concentration of the more common interfering ions expressed as the ratio of the interfering ion concentration in moles per liter to the sample cyanide concentration in moles per liter. If the ratio is exceeded, the electrode will malfunction. See **Table 1** for conversion factors from moles per liter to ppm.

**Table 7**

Interferences	Maximum Ratio (moles/L)
Cl <sup>-</sup>	10 <sup>6</sup>
I <sup>-</sup>	0.1
Br <sup>-</sup>	5 x 10 <sup>3</sup>
S <sup>2-</sup>	must be absent

For example:

What is the maximum level of iodide tolerable in a sample whose cyanide concentration is 10<sup>-4</sup> M? From **Table 7** the maximum ratio is:

$$\frac{[I^-]}{[CN^-]} = 0.1$$

$$[I^-] = 0.1 [CN^-]$$

$$= 0.1 \times 10^{-4}$$

$$= 10^{-5} \text{ M maximum iodide concentration}$$

## Limits of Detection

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Although the electrode responds to cyanide levels from  $8 \times 10^{-6}$  M to  $10^{-2}$  M, cyanide ion attacks the sensing element. Measurements above  $10^{-3}$  M should be done only intermittently.

The lower limit of detection is determined by the very slight water solubility of the sensing element. At low levels the electrode responds to cyanide in the sample as well as to ions dissolved from the sensing element. The discrepancy between the theoretical linear response in comparison with the actual response (full line) curves is due to the response to dissolved ions from the sensing element.

For low levels, care must be taken not to lose cyanide. Use plastic labware. Cover beakers with Parafilm. Allow longer stabilization time prior to reading meter to assure best results.

## Complexation

---

The electrode is strongly selective for cyanide, and will detect not only free cyanide ions, but cyanide in certain weak complexes with metals. The response depends on the stability of the metal-cyanide complex. Thus, for a zinc or cadmium complex, if the solution is diluted to between  $10^{-2}$  and  $10^{-5}$  M in cyanide, the electrode will give the total cyanide present, regardless of the amount of the zinc or cadmium in the solution. Stronger complexes, like copper, silver or gold, give only the free cyanide.

Many metal ions, such as copper and nickel, complex cyanide strongly. These can be broken up with EDTA. To a sample whose cyanide concentration is not more than 10 ppm, or about  $10^{-3}$  M (dilute more concentrated samples), add enough acetic acid to make the sample solution pH 4, then add tetrasodium EDTA to a level of 0.02 M (0.76 g  $\text{Na}_4$  EDTA per 100 mL sample). Heat in a hood to about  $50^\circ\text{C}$  for five minutes to speed up the decomplexing. Cool the solution. Add 10 M NaOH ISA to raise the pH to 13. EDTA complexes of the metals break up very slowly so that the cyanide remains free long enough for concentration measurements to be made.

## Electrode Life

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Because the sensing element is dissolved by cyanide ion, the electrode lifetime will be adversely affected by exposure to high levels of  $CN^-$ . Measurements above the  $10^{-3}$  M level should be done only intermittently.

## Theory of Operation

---

The cyanide electrode consists of a solid sensing element containing a mixture of inorganic silver compounds bonded into the tip of an epoxy electrode body. When the sensing element is in contact with a cyanide solution, silver ions dissolve from the membrane surface. Silver ions within the sensing element move to the surface to replace the dissolved ions, setting up a potential difference that depends on the cyanide level in the solution. This potential is measured against a constant reference potential with a mV meter or ISE meter. The measured potential, corresponding to the level of cyanide in solution, is described by the Nernst equation:

$$E = E_0 + S \log (A)$$

where:

- E = measured electrode potential
- $E_0$  = reference potential (a constant)
- A = level of cyanide ion in solution
- S = electrode slope (about -57 mV per decade for cyanide)

$$S = \frac{2.3 R T}{nF}$$

- where:
- R & F are constants
  - T = temperature degrees K
  - n = ionic charge

The ionic level,  $A$ , is the activity or "effective concentration". The cyanide ion activity is related to free-ion concentration,  $C_f$ , by the activity coefficient,  $y$ :

$$A = y \cdot C_f$$

Ionic activity coefficients are variable and largely depend on total ionic strength. The ionic strength of a solution is determined by all of the ions present. It is calculated by multiplying the concentration of each individual ion by the square of its charge, adding all these values up, and then dividing by two.

Mathematically, ionic strength is defined as:

$$I = \frac{1}{2} \sum (C_i Z_i^2)$$

where:

$C_i$	=	concentration of ion $i$
$Z_i$	=	charge of ion $i$
$\sum$	=	symbolizes the sum of all the types of ions in solution.

If the background ionic strength is high and constant relative to the ion concentration, the activity coefficient is constant and activity is directly proportional to concentration. Ionic strength adjuster (ISA) is added to all standards and samples so that the background ionic strength is high and constant relative to variable concentrations of cyanide. For cyanide the recommended ISA is 10 M NaOH. Other solutions can be used as long as they do not contain ions that would interfere with the electrode's response to cyanide. If samples have a high ionic strength (above 0.1 M), standards should be prepared with a composition similar to the samples.

Reference electrode conditions must also be considered. Liquid-junction potentials arise any time two solutions of different composition are brought into contact. The potential results from the interdiffusion of ions in the two solutions. Since ions diffuse at different rates, electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions. In making electrode measurements, it is important that this potential be the same in the standardizing solution as in the sample solution; otherwise, the change in liquid-junction potential will appear as an error in the measured electrode potential.

Optimum Results™ filling solutions are specifically designed to meet all reference electrode conditions. The filling solution is equitransferent. Therefore, the speed with which the positive and negative ions in the filling solution diffuse into the sample is as nearly equal as possible. If the rate at which positive and negative charge is carried into the sample solution is equal, then minimum junction potential can result.

# WARRANTY

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For the most current warranty information, visit [www.thermo.com](http://www.thermo.com).

The Thermo Electron Corporation, Orion products warranty covers failures due to manufacturer's workmanship or material defects from the date of purchase by the user. User should return the warranty card and retain proof of purchase. Warranty is void if product has been abused, misused, or repairs attempted by unauthorized persons.

Warranties herein are for product sold/installed by Thermo or its authorized dealers.

Any product sold by a U.S. or Canadian distributor must be returned to Thermo for any warranty work. Please contact our Technical Service department for further information. A Return Authorization Number must be obtained from The Technical EDGE<sup>SM</sup> For Orion Products before returning any product for in-warranty repair or replacement.

In the event of failure within the warranty period, Thermo will at the company's option, repair or replace product not conforming to this warranty. There may be additional charges, including freight, for warranty service performed in some countries. For service, call Thermo or its authorized dealer outside the United States and Canada. Thermo reserves the right to ask for proof of purchase, such as the original invoice or packing slip.

Field Service is available on Orion BOD AutoEZ<sup>TM</sup>, EZ Flash<sup>®</sup> GC Accessory and TEA Analyzer<sup>®</sup>. Contact our Field Service department for details on quotations, service, other field service-related activities.

The following products are warranted to be free from defects in material and workmanship in the period listed below from the date of purchase from the user or from the date of shipment from Thermo, whichever is earlier, provided use is in accordance with the operating limitations and maintenance procedures in the instruction manual and when not having been subjected to accident, alteration, misuse, abuse or breakage of electrodes:

**Thirty-six months from date of purchase by the user (or forty-two months from date of shipment from Thermo)**

- Waterproof Meters (Orion 630, 635, 830A, 835A, 260A, 261S, 265A, 266S, 130A, 131S, 135A, 136S, 1230, 142 and 842), Conductivity Meters (Orion 105Aplus™, 115Aplus™, 125Aplus™, 145Aplus™, 150Aplus™ and 162A), PerpHect® pH/ISE Meters (Orion 310, 320, 330, 350, 370) pH/ISE Meters (Orion 210Aplus™, 230Aplus™, 250Aplus™, 290Aplus™, 410Aplus™, 420Aplus™, 520Aplus™, 525Aplus™, 710Aplus™, 720Aplus™ and 920Aplus™), pHuture MMS™ Meters (Orion 535A and 555A), pH/Conductivity Meter (Orion 550A), Dissolved Oxygen Meters (Orion 805Aplus™, 810Aplus™, 850Aplus™ and 862A).

**Twenty-four months from date of purchase by the user (or thirty-six months from date of shipment from Thermo)**

- Orion ROSS Ultra® Electrodes, AQUAfast® IV Colorimeters, AQUAfast® IV Turbidimeter, Orion 925 Flash Titrator™, Series 100 DuraProbe™ Conductivity Cells and Series 800 Dissolved Oxygen Probes.

**Twelve months from date of purchase by the user (or eighteen months from date of shipment from Thermo)**

- Laboratory pH Meters, (Orion 301, 611 and 940), SensorLink®, pHuture™ pH Meters (Orion 610 and 620), Smart Chek™ meters, Sage® Pumps, Cahn® Balances, 930 Ionalyzer®, 950 ROSS™ FAST QC™ Titrator, 960 Titrator PLUS®, Karl Fischer Titrators, Autosamplers, Liquid Handling Devices, Liquid Handling Automation Workstations (Orion AS2000, AS2500 and AS4000), Pumps (Orion SP201, SP201-HR, SP201-S, Peristaltic and Rinse), pHuture® Conversion Box, Wine Master®, 607 Switchbox, rf link™, AQUAfast® II Colorimeters, Vacuum Degasser and Flowmeter.
- Orion EZ Flash® GC Accessory, Orion TEA Analyzer® 610 and 510 excluding consumable items carry twelve months warranty only.

- Orion Ion Selective Electrodes, ionplus® Electrodes, ROSS™ Electrodes, Sure-Flow® Electrodes, PerpHecT® Electrodes, AquaPro Professional Electrodes, No Cal™ pH electrodes, Standard Line pH Electrodes, Tris pH Electrodes, KNiPHE® electrode, ORP Triode™ (Orion 9180BN), pHuture™ pH Probes (Orion 616500) and pHuture MMS™ Quatrode™ and Triode™ (Orion 616600 and 617900), Orion 97-08 DO Probe, Series 100 Conventional Conductivity Cells, temperature probes and compensators (except those products noted).
- Orion 93 and 97 ionplus Series sensing modules are warranted to give six months of operation if placed in service before the date indicated on the package, except 93-07 and 97-07 Nitrate modules are warranted to give ninety days of operation if placed in service before the date indicated on the package.

**Six months from date of purchase by the user (or twelve months from date of shipment from Thermo)**

- Orion Flash Titration™ Probe (Orion 092518), pHuture™ Electrode (Orion 615700), pHuture MMS™ Pentrode™ (Orion 617500), Quatrode™ (Orion 617800) and Triode™ (Orion 615800), Low Maintenance Triode™ (Orion 9107BN), ORP Low Maintenance Triode™ (Orion 9179BN), and PerpHecT® Low Maintenance Triode™ (Orion 9207BN), Waterproof Triode™ (Orion 9107WP, 9107WL, 9109WL and 9109WP), QuiKcheK® Meters and Micro Electrodes.

**Three months from date of purchase by the user (or six months from date of shipment from Thermo)**

- Economy Line Electrodes, Orion 91-05, 91-06, 91-15, 91-16, 91-25, 91-26, 91-35, 91-36, 92-06. Warranty also includes failure for any reason (excluding breakage), except abuse, provided the electrode is not used in solutions containing silver, sulfide, perchlorate, or hydrofluoric acid; or in solutions more than one (1) Molar in strong acid or base at temperatures above 50 °C.

**“Out-of-Box” Warranty - Should any of the following products fail to work when first used, contact Thermo immediately for replacement.**

- Orion Solutions, Standards, Reagents, Cables, Ferrules, Tubing, Line adapters, Printers, Software, Cases, Stands, Probe Membranes, AQUAfast® Test Strips, EZ Flash® columns, Liquid Handling Probes, Adapter Plates and Racks and general accessories.

For products in the catalog not listed in this warranty statement, please visit our website at: [www.thermo.com](http://www.thermo.com)

THE WARRANTIES DESCRIBED ABOVE ARE EXCLUSIVE AND IN LIEU OF ALL OTHER WARRANTIES WHETHER STATUTORY, EXPRESS OR IMPLIED INCLUDING, BUT NOT LIMITED TO, ANY IMPLIED WARRANTY OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE AND ALL WARRANTIES ARISING FROM THE COURSE OF DEALING OR USAGE OF TRADE. THE BUYER'S SOLE AND EXCLUSIVE REMEDY IS FOR REPAIR OR REPLACEMENT OF THE NON-CONFORMING PRODUCT OR PART THEREOF, OR REFUND OF THE PURCHASE PRICE, BUT IN NO EVENT SHALL THERMO (ITS CONTRACTORS AND SUPPLIERS OF ANY TIER) BE LIABLE TO THE BUYER OR ANY PERSON FOR ANY SPECIAL, INDIRECT, INCIDENTAL, OR CONSEQUENTIAL DAMAGES WHETHER THE CLAIMS ARE BASED IN CONTRACT, IN TORT (INCLUDING NEGLIGENCE), OR OTHERWISE WITH RESPECT TO OR ARISING OUT OF THE PRODUCT FURNISHED HEREUNDER.

REPRESENTATION AND WARRANTIES MADE BY ANY PERSON, INCLUDING ITS AUTHORIZED DEALERS, REPRESENTATIVES AND EMPLOYEES OF THERMO WHICH ALTER OR ARE IN ADDITION TO THE TERMS OF THIS WARRANTY SHALL NOT BE BINDING UPON THERMO UNLESS IN WRITING AND SIGNED BY ONE OF ITS OFFICERS.

## ORDERING INFORMATION

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Orion	Description
9406BN	Cyanide Solid-State Epoxy Electrode, BNC Connector
940600	Cyanide Solid-State Epoxy Electrode, U.S. Std. Connector
9406SC	Cyanide Solid-State Epoxy Electrode, Screw Cap Connector. Requires separate cable
9606BN	Sure-Flow™ Cyanide Combination Solid-State Epoxy Electrode, BNC Connector
960600	Sure-Flow Cyanide Combination Solid State Epoxy Electrode, U.S. Std. Connector
900200	Double-Junction Sure-Flow Reference Electrode
900002	Double-Junction, Inner Chamber Fill Solution, 5 x 60 mL bottle
900003	Double-Junction, Outer Chamber Fill solution, 5 x 60 mL bottle
900062	Optimum Results™ B Filling Solution for 9606 Combination Cyanide Electrode, 5 x 60 mL bottle
951011	Ionic Strength Adjustor, 10 M NaOH, 475 mL
984201	Polishing Strips, pk of twenty-four 6" strips

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# SPECIFICATIONS

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**Concentration Range:**

$8 \times 10^{-6}$  to  $10^{-2}$  M (0.2 to 260 ppm)

**pH Range:**

0 to 14 (sample pH range 10-14 recommended)

**Temperature Range:**

0 - 80 °C

**Electrode Resistance:**

Less than 30 megohms

**Reproducibility:**

± 2%

**Size:**

Length: 110 mm (excluding cap)

Diameter: 9406      12 mm

                  9606      13 mm

Cap Diameter: 16 mm

Cable Length: 1 M

Distributed by Thermo Electron.

## **Environmental Instruments**

Water Analysis

### **North America**

166 Cummings Center  
Beverly, MA 01915 USA  
Tel: 978-232-6000  
Dom. Fax: 978-232-6015  
Int'l. Fax: 978-232-6031

### **Europe**

12-16 Sedgeway Business Park  
Witchford, Cambridgeshire  
England, CB6 2HY  
Tel: 44-1353-666111  
Fax: 44-1353-666001

### **Far East**

Room 904, Federal Building  
369 Lockhart Road  
Wanchai, Hong Kong  
Tel: 852-2836-0981  
Fax: 852-2834-5160

### **Customer Support**

Toll Free: 800-225-1480  
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**For updated contact information, visit [www.thermo.com](http://www.thermo.com)**

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