

# IOTRODE™

## Ion-Selective Electrode Applications

Bulletin No. 000102

## Free Cyanide Analysis In Water

### INTRODUCTION

The following procedure allows the user to determine free cyanide concentration in water samples. The procedure will not determine cyanide concentrations complexed.

### EQUIPMENT

#### Meter:

pH/Millivolt meter. Readability of 1 mV required; 0.1 mV preferred. Specific ion meter will provide direct readout of final answer or concentration factor. Consult manual for millivolt measurement instructions.

#### Electrodes:

1. Iotrode™ AB160 Cyanide Electrode with polishing kit.
2. Reference electrode (Double Junction Type) Iotrode AB450 (Ag/AgCl internal) or Iotrode AB455 (Calomel Internal)

#### Glassware:

1. 1 ml, 2 ml, and 10 ml pipets
2. 150 ml beakers
3. 100 ml graduated cylinders
4. 100 ml, 1000 ml volumetric flasks
5. Magnetic stirrer and stirbars or glass stirring rods

### REAGENTS

- 1. Ionic Strength Adjustor (ISA):** Dissolve 35.5 grams of disodium hydrogen orthophosphate and 101.1 grams of potassium nitrate in approximately 500 ml of deionized water. Add either 4.4 grams sodium hydroxide or 111 ml of 1N NaOH solution and make up to one liter with deionized water. Store in a polyethylene bottle.
- 2. 1000 ppm Cyanide Standard:** Weigh out 2.50 grams KCN in a 1000 ml volumetric flask. Add 10 ml ISA and 500-600 l deionized water to dissolve the solid KCN. Add deionized water to mark. Store standard in dark plastic bottle and label appropriately. Prepare fresh standard weekly.

**CAUTION:** Do not allow cyanide solutions to become acidic. HCN gas evolved from acid cyanide solutions is highly toxic, whether inhaled or absorbed through the skin.

### ELECTRODE SET-UP

If the electrode is being used for the first time, please follow the instructions for polishing the membrane surface. Plug the sensing electrode into the G.E. or Glass jack of the meter. Fill the inner and outer chambers of the reference electrode with appropriate solutions. Plug the reference electrode into the REF or Reference jack of the meter. Technique Hints:

1. **Stirring:** Electrode response is improved if samples and standardizing solutions are stirred at a fixed rate during measurements. If magnetic stirring is not available, stir solution one minute with a clean glass stirring rod before measuring.
2. **Temperature:** The slope of the sensing electrode and the absolute potential of the reference electrode are temperature dependent. Therefore, samples and standardizing solutions should be at the same temperature.
3. **Cleaning Electrodes:** Rinse both electrodes with a fresh portion of deionized water and blot dry with tissue between all measurements.

### ELECTRODE CALIBRATION

The primary criteria for electrode performance verification is the span test. If 55 millivolts or greater change is observed for a decade change in concentration, the performance is considered satisfactory.

1. Put 100 ml deionized water and 2 ml ISA into a 150 ml beaker. Place the pH meter into the M.V. mode. Place electrodes in the solution to a minimum depth of one inch.
2. Pipet 1 ml of 1000 ppm cyanide standard into the solution. Stir thoroughly. Read stable electrode potential in millivolts and record value as  $E_1$ .
3. Add 10 ml of 1000 ppm cyanide standard and stir thoroughly. Read stable electrode potential in millivolts and record as  $E_2$ . Calculate S by  $E_2 - E_1$ . Assume S value as the slope of the electrode.

**PROCEDURE**

**Sample Preparation:** None.

**Sample Standardization:** Add 100 ml of sample and 2 ml of ISA to a 150 ml beaker. Place electrodes in the solution to a minimum depth of one inch. Read stable electrode potential in millivolts and record as E<sub>3</sub>.

**Standard Addition:** Pipet 1 ml of 1000 ppm cyanide standard into the solution. Stir thoroughly. Read stable electrode potential in millivolts and record value as E<sub>4</sub>. Calculate ΔE by E<sub>4</sub>-E<sub>3</sub>.

Note: If ΔE is more than 30mV, **dilute standard 1:10** with deionized water and divide final concentration by 10. If ΔE is less than 8mV, **dilute fresh sample 1:10** with deionized water and multiply final concentration by 10.

**CALCULATIONS**

To perform the calculation for standard addition, the following factors are needed:

- V<sub>S</sub> = Sample Volume
- V<sub>A</sub> = Volume of standard added
- C\* = Concentration of standard
- ΔE = Change in potential (see procedure section)
- S = Slope of the electrode (see electrode calibration section)

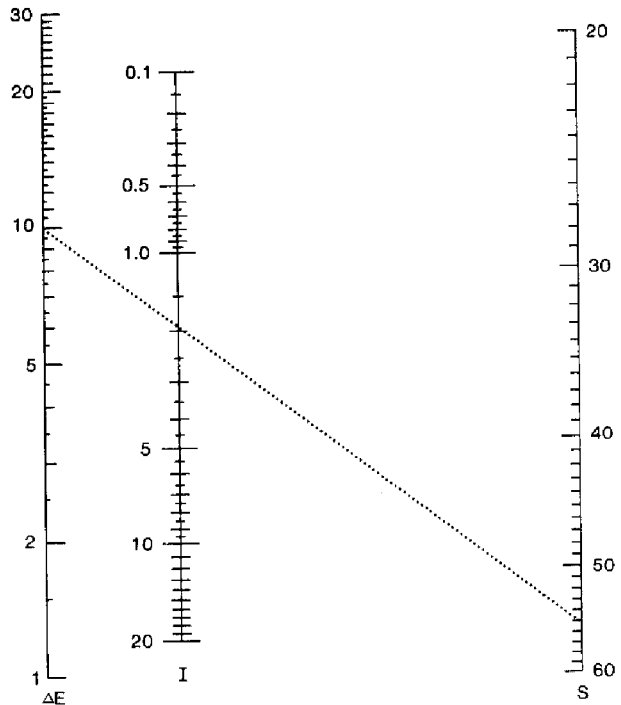
$$\text{Concentration of Sample} = \frac{C^* \left[ \frac{V_a}{V_a + V_s} \right]}{\left[ \text{antilog} \frac{\Delta E}{S} \right] - \left[ \frac{V_s + V_a}{V_s} \right]}$$

Note: If the sample is diluted, multiply sample concentration by appropriate dilution factor.

**REFERENCES:**

Riseman, J.H., Electrode Techniques for Measuring Cyanide in Waste Waters. *Am. Lab.* 4(12):63 (1972).

**Standard Addition Nomograph for use with Iotrode™ Electrodes**



The standard addition nomograph method of calculation is valid when the increment of standard added to the sample is small compared to the volume. Therefore, if more than 1 ml of standard is added, please utilize the mathematical procedure above.

The following data must be known to utilize the nomograph: (See above for description of factors.)

ΔE, S, C\*, and V<sub>S</sub>

Utilizing ΔE and S, draw a straight line to find I on the nomograph.

$$\text{Concentration of Standard} = \frac{I (C^*)}{V_s}$$

The concentration of Standard will be in the same units of concentration as C\*.

- Example: ΔE = 10 mv
- S = 55 mv
- C\* = 1000 ppm
- V<sub>S</sub> = 100 ml
- I = 2.0 (from Nomograph)

$$\text{Sample Concentration} = \frac{(2.0) (1000 \text{ ppm})}{100 \text{ ml}} = 20 \text{ ppm}$$