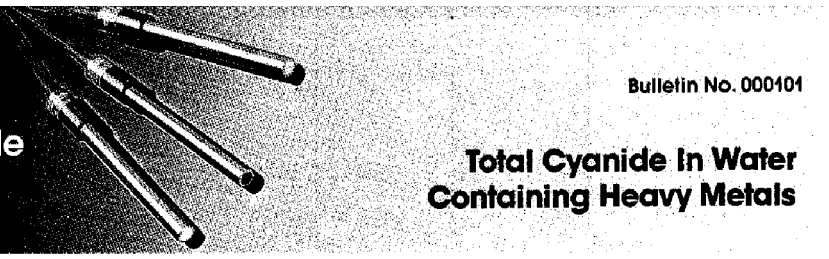
IOTRODE™
Ion-Selective Electrode Applications



Bulletin No. 000101

Total Cyanide In Water Containing Heavy Metals

INTRODUCTION

Cyanide forms complexes with many types of metal ions. Cyanide electrodes however, respond only to free cyanide ions. The following method allows the user to temporarily break down the complexes and measure total cyanide concentration.

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
6. Hot plate adjusted to 50° C

REAGENTS

1. Ionic Strength Adjustor (ISA) — 10 M NaOH: Prepare solution by dissolving 40 grams NaOH in 100 ml of deionized water.

2. 1000 ppm Cyanide Standard: — Weigh out 2.50 grams KCN in a 1000 ml volumetric flask. Add 10 ml ISA and 500-600 ml deionized water to dissolve the solid KCN. Add deionized water to mark. Store standard in dark plastic bottle properly labeled. 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.

3. Reference Electrode Outer Junction Solution: 10 grams KNO_3/100 ml deionized water.

4. EDTA Decomplexing Solution: Dissolve 7.44 grams disodium ethylenediamine tetraacetic acid dihydrate (EDTA) in 900 ml of deionized water and adjust to pH 4 by adding glacial acetic acid dropwise. Follow pH change with a pH electrode. Make up to 1000 ml with deionized water and store in polyethylene bottle.

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 80 ml deionized water, 10 ml ISA and 10 ml EDTA solution 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.

Note: If the slope value is below 55 mV, check electrode set-up and repolish sensing electrode.

PROCEDURE

Sample Preparation: Add 100 ml sample solution into a 150 ml beaker and place in a fume hood. Add 10 ml EDTA solution and heat on a hot plate to 50°C. Heat for exactly 5 minutes and remove from hot plate. Add 10 ml of ISA, stir thoroughly and allow solution to cool to room temperature (preferably in a room temperature water bath for approximately 20 minutes).

Sample Standardization: Using 120 ml of prepared sample, place electrodes in the 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_3.

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_4. Calculate ΔE by E_4-E_3.
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

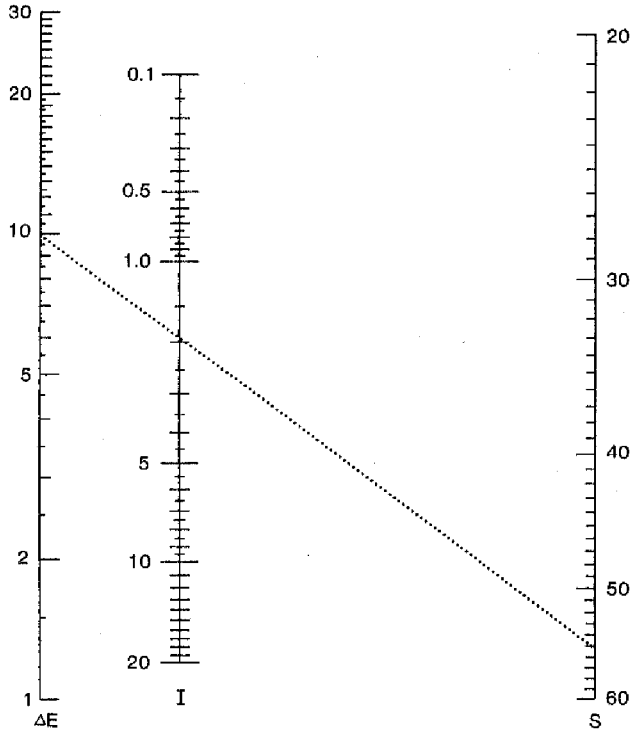
To perform the calculation for standard addition, the following factors are needed:

V_S = Sample Volume
V_a = 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.

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_S

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

$$\text{Concentration of Sample} = \frac{(I)\,(C^*)}{V_S}$$

The concentration of Sample will be in the same units of concentration as C^*.

Example: ΔE = 10 mv
S = 55 mv
C^* = 1000 ppm
V_S = 100 ml
I = 2.0 (from Nomograph)

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

$$= 20\text{ ppm}$$

REFERENCES:

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