



Iodide Ion Selective Electrode



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## **GENERAL INSTRUCTIONS**

### **Introduction**

The Van London-pHoenix Company Iodide Ion Selective Electrode is used to measure dissolved iodide ion in aqueous solutions.

### **Required Equipment**

1. An ion meter
2. Iodide Ion Sensing Electrode
3. Polishing Paper to polish dirty or etched Iodide electrode crystals
4. Plastic syringe, pipets, volumetric flasks, 150 ml beakers

### **Required Solutions**

1. Deionized or distilled water for solution preparation.
2. Van London-pHoenix Ionic Strength Adjuster (ISA), Cat.# IOOIS01.
3. Van London-pHoenix Company Iodide Standard, 1000 ppm I<sup>-1</sup>, Cat.# IOOAS02.
4. Iodide 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 Iodide standard into the solution. Stir moderately. After 1 minute, record the mV reading.
3. Using a pipet, add 10 ml of the 1000 ppm Iodide 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 Iodide standard, prepare two Iodide 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 iodide 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 iodide 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 Iodide 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.

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.

Dilute concentrated samples (over 5000 ppm) before measurement.

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 Iodide ion electrode is 0-14.

## **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 iodide ion is given in Table 1. This ratio is expressed as the ratio of the interfering ion molarity to the iodide 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 Iodide Ion**

<u>Interference</u>	<u>Maximum Ratio</u>
$\text{Cl}^{-1}$ (1)	$1.0 \times 10^6$
$\text{S}_2\text{O}_3^{-2}$ (2)	$1.0 \times 10^5$
$\text{Br}^{-1}$ (1)	$5.0 \times 10^3$
$\text{CN}^{-1}$ (3)	$4.0 \times 10^{-1}$
$\text{S}^{-2}$ (3)	$1.0 \times 10^{-6}$

- (1) Gran's plot titration can be used to measure mixed halides in solution.
- (2) These substances represent complexing species whose maximum level can be exceeded without electrode damage. Values shown represents a 1% error.
- (3) Add  $\text{Ni}^{+2}$  to remove sulfide or cyanide interferences.

As an example of Table 1's use when using the iodide ion electrode:

What is the maximum level of iodide tolerable in a sample whose iodide concentration is  $10^{-4}\text{M}$ ?

Using Table 1, the maximum ratio is:

$$\frac{[\text{Br}^{-1}]}{[\text{I}^{-1}]} = 5 \times 10^3$$

or  $[\text{Br}^{-1}] = 5 \times 10^3 [\text{I}^{-1}]$

$$= 5 \times 10^3 (1 \times 10^{-4})$$

$$[\text{Br}^{-1}] = 5 \times 10^{-1} \text{M maximum bromide concentration for no interference}$$

### **Complexation**

Total concentration (Ct) consists of free ions (Cf) and complexed or bound ions (Cc) 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.

Iodide ions complex with some metal ions. Table 2 lists the levels of complexing metals causing a 20% error.

**TABLE 2: Levels of Complexing Agents Causing a 20% Error at 13 ppm Iodide**

<u>Ion</u>	<u>Concentration</u>
$\text{Bi}^{+3}$	4 ppm
$\text{Cd}^{+2}$	50 ppm
$\text{Pb}^{+2}$	1000 ppm

### **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 Iodide concentration results in a straight line with a slope of about 56 mV between 10 ppm and 100 ppm at 25°C.

For Iodide concentrations above 10 ppm I<sup>-1</sup>, 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**

Iodide concentration down to 0.006 ppm Iodide can be measured in neutral solutions. Since sample contamination can be a factor in low level Iodide measurements, care must be taken in making determinations below 1 ppm. The upper limit of detection is a saturated Iodide solution.

### **pH Effects**

Hydroxide ion interferes with measurements of low levels of Iodide although the electrode can be used over a reasonable pH range.

### **Electrode Life**

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

### **Electrode Storage**

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

<u>Symptom</u>	<u>Possible Causes</u>	<u>Next Step</u>
Out of Range Reading	defective meter	check meter with shorting strap (see meter instruction manual)
	defective electrode	check electrode operation
	electrode not plugged in properly	unplug electrode from meter and reseat
	electrode reference chamber not filled	fill reference chamber as instructed in <b><u>Electrode Preparation</u></b>
	air bubble on membrane	remove air bubble by re-dipping electrode
	electrode not in solution	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 Iodide standard
	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: $10^{-3}M = 127 \text{ ppm as } I^{-1}$
	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:	saturated solutions to 0.006 ppm
pH Range:	0 to 14
Slope:	53 – 59 mV between 10 ppm and 100 ppm at 25°C
Temperature Range:	0° to 80°C
Interferences:	$S^{-2}$ , $CN^{-1}$ , $NH_3$
Reproducibility:	± 2%
Size:	110 mm length 12 mm diameter 1 m cable length
Storage:	store electrode in Iodide standard with ISA added

### **ELECTRODE THEORY**

#### **Electrode Operation**

The Iodide 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 iodide 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 iodide ions, corresponding to the measured potential, is described by the Nernst equation:

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

where: E = measured electrode potential  
 $E_o$  = reference potential (a constant)  
S = electrode slope (.56 mV/decade)  
X = level of iodide ions in solution

The activity, X, represents the effective concentration of the ions in solution. The activity is related to the free ion concentration,  $C_f$ , 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:  $C_x$  = concentration of ion X  
 $Z_x$  = charge of ion X  
 $\sum O$  = sum of all of the types of  
ions in the solution

In the case of high and constant ionic strength relative to the sensed ion concentration, the activity coefficient,  $\tilde{a}$ , is constant and the activity, X, is directly proportional to the concentration.