Van London Co.

"When Accuracy Matters"

Chloride Ion Selective Electrode

www.VanLondon.com
info@VanLondon.com

Toll Free (800) 522-7920
Local (832) 456-6641

GENERAL INSTRUCTIONS

Introduction
The Van London Co. Chloride Ion Selective Electrode is used to measure dissolved chloride ion in aqueous solutions.

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

Required Solutions
1. Deionized or distilled water for solution preparation.
2. Van London Co. Chloride Standard, 1000 ppm Cl^{-1}, Cat. #CLOAS02.
3. Van London Co. Ionic Strength Adjuster (ISA), 5M $NaNO_3$, Cat. #CLOIS01.
4. Chloride 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 re-dipping probe.
2. Using a pipet, add 1 ml of 1000 ppm chloride standard into the solution. Stir moderately. After 1 minute, record the mV reading.
3. Using a pipet, add 10 ml of the 1000 ppm chloride 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 56±3 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 chloride standard, prepare two chloride 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 chloride 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 chloride 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 chloride 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 $1^{o}C$ 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 Co. 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 chloride ion electrode is 2-12. Neutralize samples outside this range with acid or base to bring them in range.

ELECTRODE CHARACTERISTICS

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

Interferences
A surface layer of silver metal may be formed by strongly reducing solutions. A layer of silver salt may be

deposited on the membrane if high levels of ions forming very insoluble salts are present in the sample. Performance may be restored by polishing. See the section **Electrode Response** for proper polishing procedure.

Though measurements can be made in solutions containing oxidizing agents such as MnO_4^{-1}, mercury ions must not be present in the samples.

The maximum allowable ratio of interfering ion to chloride ion is given in Table 1. This ratio is expressed as the ratio of the interfering ion molarity to the chloride 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 Chloride Ion**

Interferences	$\dfrac{\text{Interfering Ion (M)}}{\text{Chloride Ion (M)}}$
$OH^{-1(1)}$	80
$NH_3^{(2)}$	1.2×10^{-1}
$S_2O_3^{-2(2)}$	1.0×10^{-2}
$Br^{-1(3)}$	3.0×10^{-3}
$S^{-2(4)}$	1.0×10^{-6}
$I^{-1(3)}$	5.0×10^{-7}
$CN^{-1(4)}$	2.0×10^{-7}

1. Acidify with 1M HNO_3 to pH 4 to remove hydroxide interference.
2. These substances represent complexing species whose maximum level can be exceeded without electrode damage. Value shown represents a 1% error.
3. Add CISA to solutions containing mixed halides to remove interferences. See the procedure below.
4. Add CISA or a solution of Ni^{+2} to remove sulfide or cyanide interferences.

Removal of Various Interferences with CISA
CISA is an oxidizing agent which will oxidize up to a 100-fold excess of CN^{-1} over Cl^{-1}, 100 ppm NH_3, 100 ppm Br^{-1} or I^{-1}, or 500 ppm S^{-2}. Chloride measurement interferences may be removed by using CISA. The reagents used to prepare CISA are strong oxidizing agents and should be handled in a fume hood.

To prepare CISA, add approximately 800 ml of distilled water to a 1 liter volumetric flask. Add 15.1 grams of $NaBrO_3$ to the flask and swirl to dissolve the solid. Slowly add 75 ml of concentrated nitric acid (70% w/w or 15.9N), mix, and dilute to the mark with distilled water.

To use CISA, mix equal amounts of CISA and sample. Solutions should be allowed to stand for ten minutes before measuring. Since chloride will be oxidized upon prolonged standing, all standards or samples mixed with CISA should be discarded after measuring. A fresh mixture of CISA and standard should be prepared for each calibration. After adding CISA, follow the procedures for direct measurement.

Complexation
Total concentration (C_t) consists of free ions (C_f) and complexed or bound ions (C_c) in solution:

$$C_t = C_f + C_c$$

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

4

Chloride ions complex with some metal ions. Table 2 lists the levels of complexing metals causing a 10% error at 3.5 ppm chloride.

TABLE 2: **Levels of Complexing Agents Causing a 10% Error at 3.5 ppm Chloride**

Ion	Concentration
Bi^{+3}	80 ppm
Cd^{+2}	200 ppm
Mn^{+2}	1100 ppm
Pb^{+2}	400 ppm
Sn^{+2}	700 ppm
Tl^{+3}	8 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 $1^{\circ}C$ temperature change for a 10 ppm solution.

The electrode can be used at temperatures from 0° - $80^{\circ}C$. 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 chloride concentration results in a straight line with a slope of 56 ± 3 mV between 10 ppm and 100 ppm at $25^{\circ}C$.

For chloride concentrations above 10 ppm Cl^{-1}, the electrode exhibits good time response (95% of total mV reading in 30 seconds 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

Chloride concentration down to 1.8 ppm chloride can be measured in neutral solutions. Since sample contamination can be a factor in low level chloride measurements, care must be taken in making determinations below 2 ppm. The upper limit of detection is a saturated chloride solution.

pH Effects

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

Electrode Life

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

Electrode Storage
The chloride electrode may be stored for short periods of time in 10 ppm chloride solution with ISA added.   For longer storage (longer than two weeks), rinse and dry the sensing pellet and cover the membrane tip with any protective cap shipped with the electrode. The reference portion of the combination electrode (or the outer chamber of the reference electrode) should be drained of filling solution, if refillable, and the rubber insert placed over the filling hole.

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

Symptom	Possible Causes	Next Step
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 **Electrode Preparation**
	air bubble on membrane	remove air bubble by re-dippingelectrode
	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 chloride 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: $10^{-3}M = 35$ ppm as Cl^{-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 1.8 ppm
pH Range:	2 to 12
Slope:	56 ± 3 mV between 10 ppm and 100 ppm at 25°C
Temperature Range:	0° to 80°C
Interferences:	S^{-2}, Br^{-1}, I^{-1}, CN^{-1}
Reproducibility:	$\pm 2\%$
Size:	110 mm length
	12 mm diameter
	1 m cable length
Storage:	store electrode in chloride standard with ISA added

ELECTRODE THEORY

Electrode Operation
The Chloride Ion Electrodes are composed of a glass or an epoxy body and a silver chloride/silver sulfide membrane. When the membrane is in contact with a solution containing chloride 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 chloride 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 chloride 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:

$$I = 1/2\ \acute{O}\ C_x Z_x{}^2$$

where: C_x = concentration of ion X
     Z_x = charge of ion X
     $\acute{O}$ = 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.