



Van London Co.

"When Accuracy Matters"



Lead Ion Selective Electrode



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GENERAL INSTRUCTIONS

Introduction

The Van London Co. Lead Ion Electrode is used to measure Lead ions in aqueous solutions.

Required Equipment

1. An ion meter
2. Lead Ion Sensing Electrode
3. Polishing Paper to polish dirty or etched Lead 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. Ionic Strength Adjuster (ISA), Cat.# PB2IS01.
3. To prepare this solution from your own laboratory stock, half fill a one liter volumetric flask with distilled water and add 2.30 grams of reagent-grade lead perchlorate, $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$. Swirl the flask to dissolve the solid. Fill the flask to the mark with distilled water, cap, and upend several times to thoroughly mix the solution.
4. Methanol-formaldehyde solution. To prepare this solution from your own laboratory stock, add 3 drops of 37% formaldehyde to 1000 ml of reagent-grade methanol. This solution is used to decrease the solubility and retard oxidation of the membrane.

GENERAL PREPARATION

Electrode Preparation

Remove the rubber cap covering the electrode tip and the rubber insert covering the filling hole of the Electrode Reference Fill Solution #R001015. 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 50 ml of methanol-formaldehyde solution and 50 ml of distilled water and 2 ml of ISA. 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 Lead standard into the solution. Stir moderately. After 1 minute, record the mV reading.
3. Using a pipet, add 10 ml of the 1000 ppm Lead 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 25 ± 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 Lead standard, prepare two Lead 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 50 ml of methanol-formaldehyde solution and 50 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 Lead 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 Lead standard and fix the value in the memory according to the meter manufacturer's instructions.
8. Add 50 ml of methanol-formaldehyde solution and 50 ml of the sample and 2 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 Lead 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.

Use plastic lab-ware for all low level measurements in order to minimize absorption on container walls.

To prevent oxidation of the membrane, always use methanol-formaldehyde solution to mix with all standards and samples.

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 4% 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.

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.

The temperature of the standard solutions and of the sample solutions should be the same and below 80°C.

Interferences should be absent. If they are present, use the procedure found in the **Interference** and **Electrode Response** sections to remove them.

Adjust sample pH with 1M HNO₃ to below pH 7 to avoid precipitation of lead hydroxide, Pb(OH)₂.

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 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. Proper performance can be restored by polishing. See the section entitled **Electrode Response** for proper polishing procedure.

The lead ion electrodes do not respond to anions or to most cations. The electrode membrane is poisoned by solutions containing copper, mercury, and silver. These ions must be absent from the solution.

If the level of ferric or cadmium ion is less than the level of lead ion, no interference occurs. If the level of ferric or cadmium ion is more than the level of lead ion, interferences will be present, resulting in false readings. The ferric ion interference is eliminated by pH adjustment to above pH 4 by the addition of NaOH.

Precipitation and Complexation

Sulfide, phosphate, hydroxide, and other ions precipitate insoluble lead salts. The level of lead ion, the level of the precipitated ion, and the pH of the sample determine formation of a precipitate.

A wide variety of species, including acetate, ammonia, amino acids, citrate, cyanide, and EDTA, form complexes with lead ion. The total lead concentration, the concentration of the complexing species, the solution pH, and the ionic strength all determine the extent of complexation. Complexation reduces the free lead ion concentration and, since the electrode responds only to free lead ions, a false reading results.

Temperature Influences

The electrode response will shift and change slope with change in temperature. Standards and samples should be at the same temperature. A 4% error results with a 1°C temperature change for a 10 ppm solution.

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

For concentrations above 10 ppm Pb^{+2} , 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.

- 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

Lead levels from 0.2 to 20,700 ppm can be measured with the Lead electrode.

The electrodes respond to Lead in the sample as well as to ions dissolved from the membrane at low levels. The electrode membrane shows a very slight water solubility. The detection limit of the electrode is determined by this factor. Plastic lab-ware must be used and the beakers must be covered with Parafilm for low level Lead or determinations or Lead will be lost. Allow a longer stabilization time before taking the meter reading for best results.

pH Effects

Lead reacts with hydroxide ions to form a precipitate in ammonia-free basic solutions. By keeping all solutions slightly acidic, this can be avoided. Adjust the pH of Lead solutions below 8, if necessary, with 1M HNO₃.

Electrode Life

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

Electrode Storage

The Lead electrode may be stored for short periods of time in 10 ppm Lead solution with methanol-formaldehyde solution and 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 <u>Electrode Preparation</u>
	air bubble on membrane	remove air bubble by re-dipping electrode
Noisy or Unstable Reading (readings continuously or	electrode not in solution	put electrode in solution
	insufficient reference filling solution	fill outer body of electrode with proper amount of reference filling solution

randomly changing.)	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 Lead stand with ISA
	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: $10^{-3}\text{M} = 207 \text{ ppm as Pb}^{+2}$
	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:

20,700 to 0.2 ppm

pH Range:

3 to 8

Slope:

25 ± 3 mV between 10 ppm and 100 ppm at 25°C

Temperature Range:

0° to 80°C

Interferences:

Ag^{+1} , Hg^{+2} , Cd^{+2} , Cu^{+2} , Fe^{+2}

Reproducibility:

$\pm 2\%$

Size: 110 mm length
12 mm diameter
1 m cable length
Storage: store electrode in Lead standard with ISA and methanol-formaldehyde solution added

ELECTRODE THEORY

Electrode Operation

The Lead Ion Electrode is composed of a Lead crystal membrane bonded into an epoxy or glass body. When an electrode potential develops across the membrane, the membrane is in contact with a solution containing Lead ions and is capable of measuring free Lead ions. This electrode potential is measured against a constant reference potential, using a pH/mV meter or an ion meter. The level of Lead 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 (-25 mV for Lead)
X = level of Lead 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, γ, by:

$$X = \gamma C_f$$

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
Σ = 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, γ, is constant and the activity, X, is directly proportional to the concentration.