OMEGA ENGINEERING
ISE-8725 AND ISE-8726
INSTRUCTION MANUAL

General Instructions

Introduction:

The Omega Lead Ion Electrodes are used to quickly, simply, accurately, and economically measure lead or sulfate ions in aqueous solutions.

Required Equipment

1. A pH/mV meter or an ion meter, either line operated or portable.
2. Semi-logarithmic 4-cycle graph paper for preparing calibration curves when using the meter in the mv mode.
   Linear graph paper is recommended for low level measurements or lead/sulfate titrations.
3. Magnetic stirrer
4. The ISE-8725 Ion Electrode or ISE-8726 Ion Combination Glass Electrode
5. Double Junction Reference Electrode, PHFS-A250 filling solution in the inner chamber and the PHFS-B250 filling solution in the outer chamber.
6. Lab-ware made of plastic, not glass, for all low level measurements.
7. Polishing paper, to polish dirty or etched electrode membranes.

Required Solutions:

1. Deionized or distilled water for solution and standard preparation
2. Methanol-formaldehyde solution.
3. ISE-8725-R1 Ionic Strength adjuster (IS), 5M $NaClO_4$
4. ISE-8725-S1 Lead Perchlorate Standard 0.1M $Pb(ClO_4)_2$
5. ISE-8725-S2 Lead Perchlorate Standard 1000 ppm $Pb(ClO_4)_2$
6. PB2AS03 Sulfate Standard Solution, 0.1M Na_2SO_4

GENERAL PREPARATION

Electrode Preparation

Remove the rubber caps covering the electrode tips and the rubber insert covering the filling hole of the lead combination ion electrode or the reference electrode. Fill the reference electrode or 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

electrodes to the proper terminals as recommended by the meter manufacturer.

Electrode Slope Check (with pH/mV meter)
(check electrodes each day)

1. To a 150 ml beaker, add 50 ml of methanol-formaldehyde solution and 50 ml of distilled water. Add 2 ml of ISA. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the millivolt mode, lower the electrode tips into the solution.

2. Using a pipet, add 1 ml of 0.1M or 1000 ppm lead standard to the beaker. When the reading has stabilized, record the mV reading.

3. Using a pipet, add 10 ml the same lead standard used above to the beaker. When the reading has stabilized, record the mV reading.

4. Determine the difference between the two readings. The electrode is operating correctly if the millivolt potential has changed by 25±2, assuming the temperature is between 20° and 25°C. See the **TROUBLESHOOTING** sections if the potential change is not within this range.

Slope is defined as the change in potential observed when the concentration changes by a factor of 10.

Electrode Slope Check (with ion meter)
(check electrodes each day)

1. Prepare standard lead solutions whose concentrations vary by tenfold. Use either the 0.1M or 1000 ppm lead standard. Use the serial dilution method for this preparation.

2. To a 150 ml beaker, add 50 ml of methanol-formaldehyde solution and 50 ml of the lower value standard. Add 2 ml of ISA. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution. Assure that the meter is in the concentration mode.

3. Adjust the meter to the concentration of the standard and fix the value in the memory according to the meter manufacturer's instructions.

4. Rinse the electrodes with distilled water and blot dry.

5. To another 150 ml beaker, add 50 ml of methanol-formaldehyde solution and 50 ml of the higher value standard. Add 2 ml of ISA. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution.

6. Ajust the meter to the concentration of the standard and fix the value in the memory.

7. Read the electrode slope according to the meter manufacturer's instructions. Correct electrode operation is indicated by a slope of 90-100%. See the **TROUBLESHOOTING** sections if the slope is not within this range.

MEASUREMENT

Measuring Hints

All samples and standards should be at the same temperature for precise measurement. A difference of 1°C in temperature will result in a 4% measurement error.

Constant, but not violent stirring is necessary for accurate measurement. Magnetic stirrers can generate sufficient heat to change the solution temperature. To counteract this effect, place a piece of insulation material, such as styrofoam sheet, between the stirrer and beaker.

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

Always rinse the electrodes with distilled water and blot dry between measurements. Use a clean, dry tissue to prevent cross-contamination.

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

For samples with high ionic strength, prepare standards whose composition is similar to the sample. Dilute concentrated samples (>0.1M) before measurement.

Use fresh standards for calibration.

Use 2 ml of ISA for each 100 ml of sample or standard.

Always check to see that the membrane is free from air bubbles after immersion into the standard or sample.

Sample Requirements

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, benzene, or acetonitrile are permitted. Highly polar solvents slowly attack the electrode. Please check with pHoenix Electrode Company before using these electrodes in other organic solvents.

The temperature of the standard solutions and of the sample solutions should be the same and below 80°C. About a 4% error in the slope will occur for each 1°C difference in temperature.

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

Units of Measurement

Lead concentrations are measured in units of ppm as lead, moles per liter, or any other convenient concentration unit. Table 1 indicates some concentration units and conversion factors.

TABLE 1: Concentration Unit Conversion Factors

ppm Pb^{+2}	M	ppm SO_4^{-2}
20.7	$1.0X10^{-4}$	9.6
207.0	$1.0X10^{-3}$	96.0
2070.0	$1.0X10^{-2}$	960.0

MEASUREMENT PROCEDURE

Direct Measurement

Direct measurement is a simple procedure for measuring a large number of samples. A single meter reading is all that is required for each sample. The ionic strength of samples and standards should be made the same by adjustment with ISA. The temperature of both sample solution and standard solution should be the same.

Direct Measurement of Lead (using a pH/mV meter)

1. By serial dilution, prepare 10^{-2}M, 10^{-3}M, and 10^{-4}M or 100 ppm and 10 ppm standards, from the 0.1M or 1000 ppm standards. Prepare standards with a composition similar to the samples if the samples have an ionic strength above 0.1M.

2. Place 50 ml of the 10^{-4}M or 10 ppm standard in a 150 ml beaker and add 50 ml of methanol-formaldehyde solution.

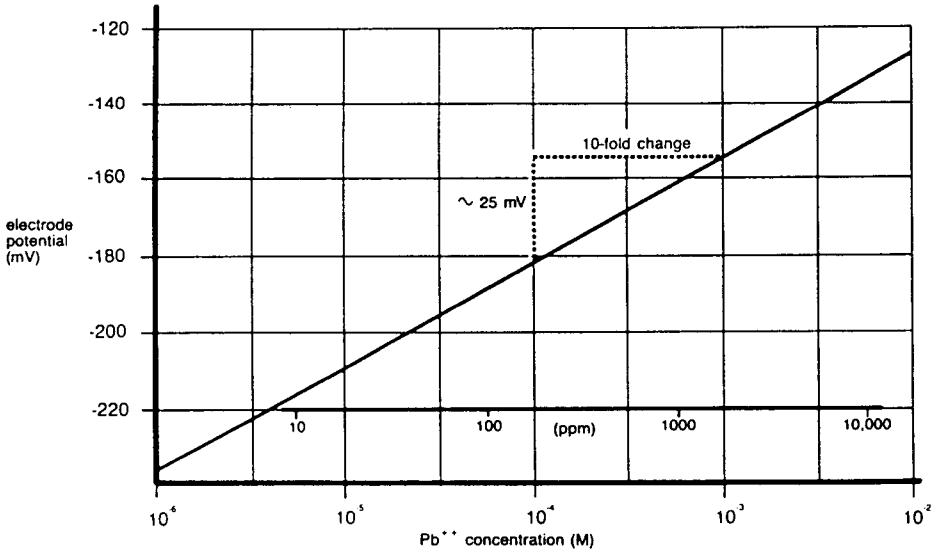
Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Add 2 ml of ISA. After assuring that the meter is in the mV mode, lower the electrode tips into the solution. When the reading has stabilized, record the mV reading.

3. Place 50 ml of the 10^{-3}M or 100 ppm standard in a 150 ml beaker and add 50 ml of methanol-formaldehyde solution. Place the beaker on the magnetic stirrer and begin stirring. Add 2 ml of ISA. After rinsing the electrodes with distilled water, blot dry, and immerse the electrode tips in the solution. When the reading has stabilized, record the mV reading.

4. Place 50 ml of the 10^{-2}M or 1000 ppm standard in a 150 ml beaker and add 50 ml of methanol-formaldehyde solution. Place the beaker on the magnetic stirrer and begin stirring. Add 2 ml of ISA. After rinsing the electrodes with distilled water, blot dry, and immerse the electrode tips in the solution. When the reading has stabilized, record the mV reading.

5. Using the semi-logarithmic graph paper, plot the mV reading (linear axis) against the concentration (log axis). Extrapolate the calibration curve down to about $2.0X10^{-6}$M. A typical calibration curve can be found in Figure 1.

Figure 1
Typical lead electrode calibration curve



A calibration curve is constructed on semi-logarithmic paper when using a pH/mV meter in the millivolt mode. The measured electrode potential in mV (linear axis) is plotted against the standard concentration (log axis). In the linear region of the curve, only three standards are necessary to determine a calibration curve. In the non-linear region, additional points must be measured. The direct measurement procedures given are for the linear portion of the curve. The non-linear portion of the curve requires the use of low level procedures.

6. To a clean, dry, 150 ml beaker, add 50 ml of the sample, 50 ml of methanol-formaldehyde solution, and 2 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Rinse the electrodes with distilled water, blot dry, and lower the electrode tips into the solution. When the reading has stabilized, record the mV reading. Using the calibration curve determine the sample concentration.

7. The calibration should be checked every two hours. Assuming no change in ambient temperature, immerse the electrode tips in the mid-range standard. After the reading has stabilized, compare it to the original reading recorded in Step 3 above. A reading differing by more than 0.5 mV or a change in the ambient temperature will necessitate the repetition of Steps 2-5 above. A new calibration curve should be prepared daily.

Direct Measurement of Lead (using an ion meter)

1. By serial dilution of the 0.1M or 1000 ppm lead standard, prepare two lead standards whose concentration is near the expected sample concentration. Measure out 50 ml of each standard into individual 150 ml beakers. Add 50 ml of methanol-formaldehyde solution and 2 ml of ISA to each beaker.

2. Place the more dilute solution on the magnetic stirrer and begin stirring at a constant rate. Assure that the meter is in the concentration mode.

3. Lower the electrode tips into the solution.

4. Adjust the meter to the concentration of the lead standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.

5. Rinse the electrodes with distilled water and blot dry.

6. Place the more concentrated solution on the magnetic stirrer and begin stirring at a constant rate.

7. Lower the electrode tips into the solution.

8. Adjust the meter to the concentration of the lead standard and fix the value in the memory according to the manufacturer's instructions after stabilization of the reading.

9. Place 50 ml of the sample, 50 ml of methanol-formaldehyde solution, and 2 ml of ISA into a 150 ml beaker. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.

10. After rinsing the electrodes, blot dry, and lower the electrode tips into the solution. After stabilization, read the concentration directly from the meter display.

11. The calibration should be checked every two hours. Assuming no change in ambient temperature, immerse the electrode tips in the more dilute standard. After the reading has stabilized, compare it to the original reading recorded in Step 4 above. A reading differing by more than 0.5 units or a change in ambient temperature will necessitate repetition of Steps 2-8 (2-9) above. The meter should be re-calibrated daily.

Low Level Lead Determination (using a pH/mV meter)

This procedure is recommended for solutions with lead concentrations of less than $1.0X10^{-6}M$. If the solution is high in ionic strength, but low in lead ion concentration, use the same procedure, but prepare a calibration solution with a composition similar to the sample.

1. Using 20 ml of standard ISA, dilute to 100 ml with distilled water. This low level ISA (1.0M $NaClO_4$) is added at the rate of 1 ml low level ISA to each 100 ml of solution. The background ionic strength will be $1.0X10^{-2}M$.

2. Dilute 1 ml of 0.1M standard to one liter to prepare a $1.0X10^{-4}M$ solution for measurements in moles per liter. Prepare a 10 ppm standard solution by diluting 1 ml of the 1000 ppm standard to 100 ml for measurements in ppm. Standards should be prepared fresh daily. Plastic labware is recommended to avoid absorption of lead on the beaker walls.

3. Add 50 ml of distilled water, 50 ml of methanol-formaldehyde solution, and 1 ml of low level ISA to a 150 ml plastic beaker. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.

4. Place the electrode tips in the solution. Assure that the meter is in the mV mode.

5. Add increments of the $1.0X10^{-4}$M or 10 ppm standard as given in Table 2 below.

6. After the reading has stabilized, record the mV reading.

TABLE 2: Step-wise Calibration For Low Level Lead Measurements

STEP	PIPET	ADDED VOLUME (ml)	CONCENTRATION ppm	CONCENTRATION M
1	A	0.1	$1.0X10^{-2}$	$1.0X10^{-7}$
2	A	0.1	$2.0X10^{-2}$	$2.0X10^{-7}$
3	A	0.2	$4.0X10^{-2}$	$4.0X10^{-7}$
4	A	0.2	$6.0X10^{-2}$	$6.0X10^{-7}$
5	A	0.4	$1.0X10^{-1}$	$9.9X10^{-7}$
6	B	2.0	$2.9X10^{-1}$	$2.9X10^{-6}$
7	B	2.0	$4.8X10^{-1}$	$4.8X10^{-6}$

Pipet A = 1 ml graduated pipet
Pipet B = 2 ml pipet
Solutions: additions of 10 ppm or $1.0X10^{-4}$M standard to 100 ml of solution prepared in Step 3 above

7. On semi-logarithmic graph paper, plot the mV reading (linear axis) against the concentration (log axis) as in Figure 1.

8. Rinse the electrodes and blot dry.

9. Measure out 50 ml of the sample into a 150 ml plastic beaker. Add 50 ml of methanol-formaldehyde solution and 1 ml of low level ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution. After the reading has stabilized, record the mV reading and determine the concentration from the low level calibration curve. Prepare a new low level calibration curve daily. Check the calibration curve every two hours by repeating Steps 3- 7 above.

Low Level Lead Determination (using an ion meter)

1. Using 20 ml of standard ISA, dilute to 100 ml with distilled water. This low level (1.0M $NaClO_4$) is added at a the rate of 1 ml low level ISA to each 100 ml of solution. The background ionic strength will be $1.0X10^{-2}M$.

2. Follow the steps given in **Direct Measurement of Lead (using an ion meter)** to the end of Step 8. Use plastic lab-ware to avoid adsorption of lead on the beaker walls.

3. Add 50 ml of distilled water, 50 ml of methanol-formaldehyde, and 1 ml of low level ISA to a 150 ml plastic beaker. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution. When the reading has stabilized, fix the blank value in the meter according to the meter manufacturer's instructions.

4. Place 50 ml of the sample, 50 ml of methanol-formaldehyde solution, and 1 ml of low level ISA in a 150 ml plastic beaker. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution. When the reading has stabilized, read the sample concentration directly from the meter display.

5. The calibration should be checked every two hours. Assuming no change in ambient temperature, immerse the electrode tips in the more dilute standard. After the reading has stabilized, compare it to the original reading recorded in Step 3 above. If the reading differs by more than ±0.5 units, or the temperature has changed from ambient, recalibrate the electrode.

Titration

Titration is a very accurate determination of total lead or sulfate ion concentration. This method makes use of the electrode as an endpoint detector. The endpoint break is enhanced by the use of methanol-formaldehyde solution added to samples to reduce the solubility of the product formed during titration.

Titration of Lead

The method outlined in this section makes use of the lead ion electrode as a highly sensitive endpoint detector for lead-containing sample. The titrant used is EDTA. The sample concentrations should be above $1.0X10^{-3}M$ lead ion. If the samples contain lower lead concentrations, the titration will not be as accurate and the EDTA titrant must be diluted correspondingly.

EDTA complexes lead as well as other cations. The sample pH can be adjusted to eliminate unwanted ion complexes. Masking agents may be added in some cases.

1. Prepare a 0.01M EDTA titrant by adding 3.772 grams of reagent-grade $Na_2EDTA \cdot 2H_2O$ to a 1 liter volumetric flask containing 500 ml of methanol-formaldehyde solution. Swirl the flask gently to dissolve the solid. Fill the flask to the mark with distilled water, cap, and upend the flask several times to mix the solution.

2. Fill a 50 ml buret with the EDTA solution. Pipet 50 ml of the sample into a 150 ml beaker and add 50 ml of methanol-formaldehyde solution. Place the beaker on a magnetic stirrer, and begin stirring at a constant rate.

3. Position the electrode tips in the solution about halfway between the center of the beaker and the beaker wall.

4. Begin adding the EDTA in 0.5 ml to 1.0 ml increments, followed by smaller increments down to about 0.1 ml to 0.2 ml increments as the potential change increases. Record the mV potential after each addition. Continue the additions several milliliters past the endpoint until little change is noted in the mV reading even when adding 0.5-1.0 increments.

5. Plot the milliliters of EDTA added against the mV potential on standard coordinate graph paper. The point of greatest potential change is the endpoint. The lead ion concentration from the unknown is calculated as follows:

$$M_{Pb}^{+2} = \frac{V_t \, M_t}{V_{Pb}^{+2}}$$

where:

M_{Pb}^{+2} = concentration of lead ion in the sample (moles/liter)
V_t = volume of EDTA added at endpoint
M_t = EDTA concentration (moles/liter)
V_{Pb}^{+2} = volume of unknown sample (50 ml)

Titration of Sulfate

Titrations of sulfate ion with lead perchlorate make use of the lead ion electrode as a sensitive endpoint detector. Sulfate determinations by the gravimetric or turbidimetric methods are more complicated and more time consuming than titration. Titration offers the same or greater precision in solutions as dilute as 10^{-4}M or 10 ppm sulfate ion.

If present in amounts in excess of the following,

NO_3^- $\rangle$ 50 X SO_4^{-2}

Cl^- $\rangle$ 50 X SO_4^{-2}

HCO_3^- $\rangle$ 100 X SO_4^{-2} at pH 4,

the above ions will interfere with the titration. Phosphate and calcium must be absent.

The titrant is pHoenix Lead Standard, 0.1M, Cat. No. PB2AS01, and should be diluted to the proper range for the expected concentration of the unknown. The methanol-formaldehyde solution is used to dilute the unknown 1:1 before performing the titration.

The concentration of lead perchlorate titrant should be about 10 times greater than the expected sulfate ion concentration of the unknown. Unknowns containing about 10^{-3}M sulfate ion are ideal for this titration method. If the sulfate samples are more dilute, the lead perchlorate titrant should be correspondingly more dilute.

1. Prepare 0.01M lead perchlorate titrant by pipeting 100 ml of the 0.1M lead standard into a one liter volumetric flask. Fill to the mark with distilled water, cap, and upend several times to thoroughly mix the contents.

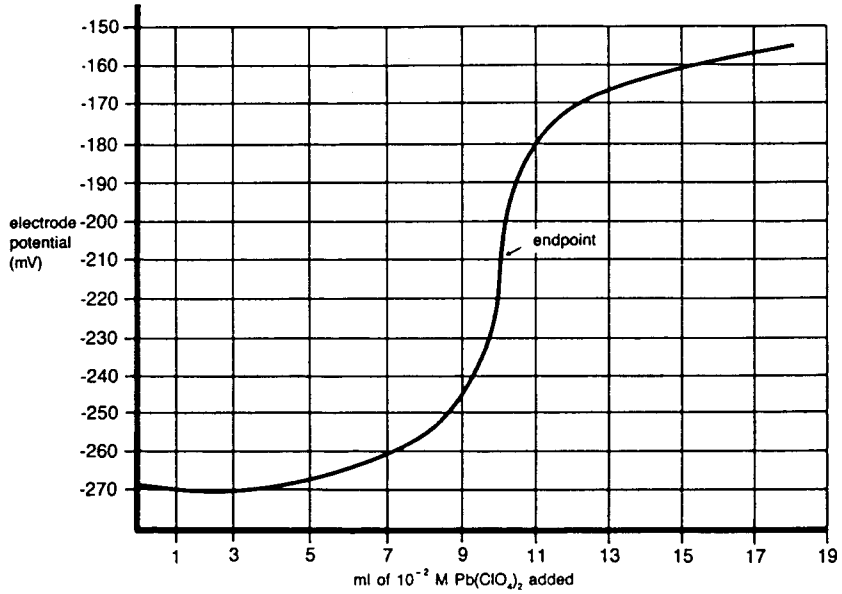
2. Into a 150 ml beaker, pipet 50 ml of sample and 50 ml of methanol-formaldehyde solution. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.

3. Fill a 50 ml burette with the lead perchlorate titrant. Position the electrode tips in the solution about halfway between the center of the beaker and the beaker wall.

4. Begin adding the titrant in 0.5 ml to 1.0 ml increments, followed by smaller increments down to about 0.1 ml to 0.2 ml increments as the potential change increases. Record the mV potential after each addition. Continue the additions several milliliters past the endpoint until little change is noted in the mV reading even when adding 0.5 - 1.0 ml increments.

5. Plot the milliliters of lead perchlorate added against the mV potential on standard coordinate graph paper. The point of greatest potential change is the endpoint. (See Figure 4.)

Figure 4
Typical titration of 100 ml of 10^{-3} M Na_2SO_4 with 10^{-2} M $Pb(ClO_4)_2$



6. The sulfate ion concentration from the unknown is calculated as follows:

$$M_{SO4}^{-2} = \frac{V_t \, M_t}{V_{SO4}^{-2}}$$

where:

M_{SO4}^{-2} = concentration of sulfate ion in the unknown (moles/liter)
V_t = volume of lead added at endpoint
M_t = lead concentration (moles/liter)
V_{SO4}^{-2} = volume of unknown sample (50 ml)

ELECTRODE CHARACTERISTICS

Reproducibility

Electrode measurements reproducible to $\pm 2\%$ can be obtained if the electrode is calibrated frequently. Factors such as temperature fluctuations, drift, and noise limit reproducibility. Reproducibility is independent of concentration within the electrode's operating range.

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

Samples and standards should be within ±1°C of each other, since electrode potentials are influenced by changes in temperature. A 1°C difference in temperature results in a 4% error at $1.0X10^{-3}M$ lead ion concentration. Because of the solubility equilibria on which the electrode depends, the absolute potential of the reference electrode changes slowly with temperature. The slope of the electrode, as indicated by the factor "S" in the Nernst equation, also varies with temperature. Table 3 gives values for the "S" factor in the Nernst equation for the lead ion.

TABLE 3: Temperature vs. Values for the Electrode Slope

Temp(°C)	S
0	27.10
10	28.09
20	29.08
25	29.58
30	30.07
40	31.07
50	32.06

If changes in temperature occur, the electrodes should be re-calibrated.

The temperature range for the pHoenix Lead Ion Electrode is 0°-80°C, provided that temperature equilibrium has occurred. If the temperature varies substantially from room temperature, equilibrium times up to one hour are recommended.

Electrode Response

Plotting the electrode mV potential against the lead concentration on semi-logarithmic paper results in a straight line with a slope of about 25 mV per decade. (Refer to Figure 1.)

The time needed to reach 99% of the stable electrode potential reading, the electrode response time, varies from several seconds in highly concentrated solutions to several minutes near the detection limit.

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.

5. If using jeweller's rouge, place a cotton ball on the table top and flatten it using the bottom of a beaker.

6. Put 1-2 drops of distilled or deionized water in the center of the cotton pad.

7. Add a small amount of jeweller's rouge to the damp cotton.

8. Continue with Steps 3 and 4 above.

Limits of Detection

The upper limit of detection in pure lead perchlorate solutions is 0.1M. In the presence of other ions, the upper limit of detection is above $1.0x10^{-2}$M lead, but two factors influence this upper limit. Both the possibility of a liquid junction potential developing at the reference electrode and the salt extraction effect influence this upper limit. Some salts may extract into the electrode membrane at high salt concentrations, causing deviation from the theoretical response. Either dilute samples between 0.1M and $1.0x10^{-2}$M or calibrate the electrode at 4 or 5 intermediate points.

The lower limit of detection is influenced by the slight water solubility of the electrode pellet. Refer to Figure 1 for a comparison of the theoretical response to the actual response at low levels of lead ion. Neutral solutions containing free lead ions can be measured down to $1.0X10^{-6}$M (0.2 ppm). Extreme care must be taken with measurements below $1.0X10^{-5}$M (2.0 ppm) to avoid adsorption of lead ions in the sample onto container walls.

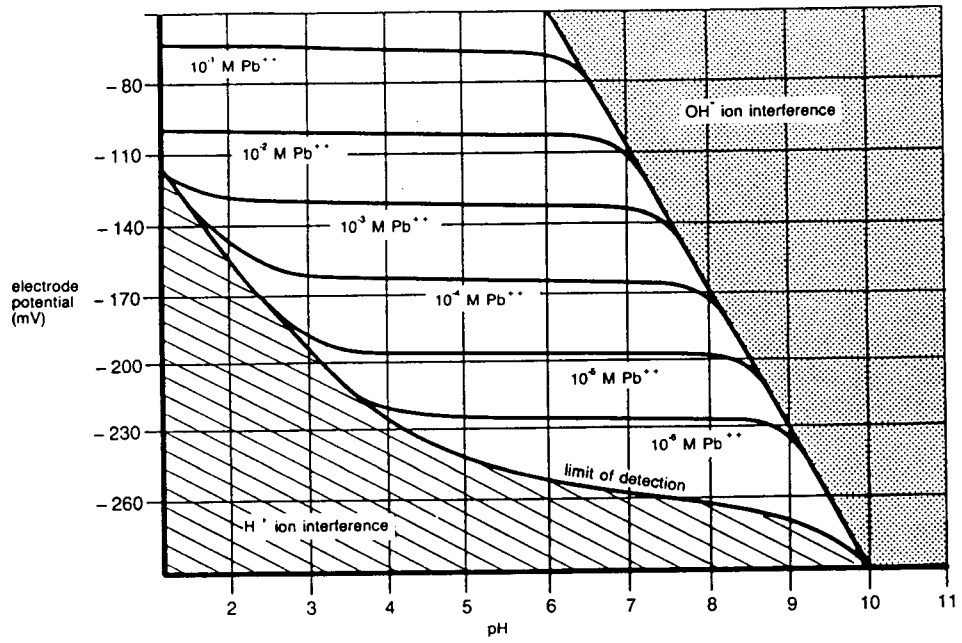
pH Effects

Figure 2 shows the electrode response to lead ion in solution at various pH levels. Hydrogen ion interferes with low lead ion measurements. The minimum pH at which lead ion concentrations can be measured without interference is given by the shaded area to the left in Figure 2.

At a high pH, free lead ion precipitates with hydroxide ion, thereby reducing the lead ion concentration. The maximum pH at which the lead concentrations can be measured without interference from hydroxide is given by the shaded area to the right in Figure 2. Within this shaded area, lead combines with hydroxide to form $Pb(OH)_2$. Since only free lead concentration can be measured with the lead ion electrodes, a false reading results.

Figure 2

Electrode potential behavior versus solution pH in pure $Pb(ClO_4)_2$ solutions at 25°C



Electrode Life

The lead electrode will last six months 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.

Electrode Storage

The lead electrode may be stored for short periods of time in 1.0×10^{-2}M lead solution. 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.

ELECTRODE THEORY

Electrode Operation

The pHoenix Lead Ion Electrodes are composed of sulfides of lead and silver 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. This electrode potential is measured against a constant reference potential, using a pH/mV meter or an ion meter. The level of lead ion, 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/decade)
X = level of lead ions in solution

The activity, X, represents the effective concentration of free lead ion in the solution. Both bound, C_b, and free, C_f, lead ions are included in the total lead ion concentration, C_t. The lead ion electrode will only respond to free lead ions, the concentration of which is:

$$C_f = C_t - C_b$$

The activity is related to the free lead ion concentration, Cf, by the activity coefficient, γ, by:

$$X = \gamma C_f$$

Activity coefficients vary, depending on total ionic strength, I, defined as:

$$I = \tfrac{1}{2} \Sigma C_x Z_x^2$$

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.

The lead ion activity coefficients depend, to some extent, on the anions present. Pure lead nitrate and lead perchlorate solutions do not display the same activity coefficient, even though both solutions have the same total ionic strength.

To adjust the background ionic strength to a high and constant value, ionic strength adjuster (ISA) is added to samples and standards. The recommended ISA solution for the lead electrodes is sodium perchlorate, $NaClO_4$. Solutions other than this may be used as ionic strength adjusters as long as ions that they contain do not interfere with the electrode's response to lead ions.

The reference electrode must also be considered. When two solutions of different composition are brought into contact with one another, liquid junction potentials arise. Millivolt

potentials occur from the inter-diffusion of ions in the two solutions. Electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions, since ions diffuse at different rates. When making measurements, it is important to remember that this potential be the same when the reference is in the standardizing solution as well as in the sample solution or the change in liquid junction potential will appear as an error in the measured electrode potential.

The composition of the liquid junction filling solution in the reference electrode is most important. The speed with which the positive and negative ions in the filling solution diffuse into the sample should be equitransferent. No junction potential can result if the rate at which positive and negative charge carried into the sample is equal.

Strongly acidic (pH = 0 - 2) and strongly basic (pH = 12 - 14) solutions are particularly troublesome to measure. The high mobility of hydrogen and hydroxide ions in samples make it impossible to mask their effect on the junction potential with any concentration of an equitransferent salt. One must either calibrate the electrodes in the same pH range as the sample or use a known increment method for ion measurement.

TROUBLESHOOTING GUIDE

The goal of troubleshooting is the isolation of a problem through checking each of the system components in turn: the meter, the glass-ware, the electrodes, the standards and reagents, the sample, and the technique.

Meter

The meter may be checked by following the check-out procedure in the instrument instruction manual.

Glass-ware/Plastic-ware

Clean glass-ware is essential for good measurement. Be sure to wash the glass-ware/plastic-ware well with a mild detergent and rinse very well with distilled or deionized water. Clean glass-ware will drain without leaving water droplets behind.

Electrodes

The electrodes may be checked by using the procedure found in the sections entitled **Electrode Slope Check**.

1. Be sure to use distilled or deionized water when following the procedures given in **Electrode Slope Check.**

2. If the electrode fails to respond as expected, see the sections **Measuring Hints** and **Electrode Response.** Repeat the slope check.

3. If the electrodes still fail to respond as expected, substitute another lead ion electrode that is known to be in good working order for the questionable electrode. If the problem persists and you are using an electrode pair, try the same routine with a working reference electrode.

4. If the problem persists, the reagent may be of poor quality, interferences in the sample may be present or the technique may be faulty. (See **Standards & Reagents**, **Sample**, and **Technique** sections below.)

5. If another electrode is not available for test purposes, or if the electrode in use is suspect, review the instruction manual and be sure to:

   - Clean and rinse the electrodes thoroughly.
   - Prepare the electrodes properly.
   - Use the proper filling solution.
   - Adjust the pH and the ionic strength of the solution by the use of the proper ISA.
   - Measure correctly and accurately.
   - Review TROUBLESHOOTING HINTS.

Standards & Reagents

Whenever problems arise with the measuring procedure that has been used successfully in the past, be sure to check the reagent solutions. If in doubt about the credibility of any of the reagents, prepare them again. Errors may result from contamination of the ISA, incorrect dilution of the standards, poor quality distilled/deionized water, or a simple mathematical miscalculation.

Sample

Look for possible interferences, complexing agents, or substances which could affect the response or physically damage the sensing electrode (or the reference electrode) if the electrodes work perfectly in the standard, but not in the sample.

Try to determine the composition of the samples prior to testing to eliminate a problem before it starts. (See **Measuring Hints**, **Sample Requirements**, and **Interferences.**)

Technique

Be sure that the electrode's limit of detection has not been exceeded. Be sure that the analysis method is clearly understood and is compatible with the sample.

Refer to the instruction manual again. Reread **GENERAL PREPARATION** and **ELECTRODE CHARACTERISTICS**.

TROUBLESHOOTING HINTS

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
	electrodes not plugged in properly	unplug electrodes & reseat electrodes
	reference electrode not filled	be sure reference electrode is filled
	air bubble on membrane	remove bubble by re-dipping electrode
	electrodes not in solution	put electrodes in solution
Noisy or Unstable Readings (readings continuously or rapidly changing)	defective meter	check meter with shorting strap
	air bubble on membrane	remove bubble by re-dipping electrode
	electrode exposed to interferences	soak electrode in lead standard
	defective electrode	replace electrode
	ISA not used	use recommended ISA

	meter or stirrer not grounded	ground meter or stirrer
Drift (reading slowly changing in one direction)	samples and standards at different temperatures	allow solutions to come to room temperature before measurement
	complexing agents in sample	check section entitled **Precipitation and Complexation**
	incorrect reference filling solution	use recommended filling solution
	membrane dirty or oxidized	polish membrane; use methanol-formaldehyde solution
Low Slope or No Slope	standards contaminated or incorrectly made	prepare fresh standards
	standard used as ISA	use ISA
	ISA not used	use recommended ISA
	membrane dirty or oxidized	polish membrane; use methanol-formaldehyde solution
	air bubble on membrane	remove bubble by re-dipping probe
"Incorrect Answer" (but calibration curve is good)	incorrect scaling of semi-log paper	plot millivolts on the linear axis. On the log axis, be sure concentration numbers within each decade are increasing with increasing concentration
	incorrect sign	be sure to note sign of millivolt reading correctly
	incorrect standards	prepare fresh standards

wrong units used	apply correct conversion factor: $10^{-3}M$ = 207 ppm Pb^{+2} = 96 ppm SO_4^{-2}
complexing agents in sample	check section entitled **Precipitation and Complexation**; use titration methods

SPECIFICATIONS

Concentration Range:	10^{-1}M to 10^{-6}M Pb^{+2} (20,700 to 0.2 ppm Pb^{+2})
pH Range:	3 to 8
Temperature Range:	0° - 80°C
Resistance:	< 1 Mohm
Reproducibility:	+/- 2%
Samples:	aqueous solutions only; no organic solvents
Size:	110 mm length 12 mm diameter 1 m cable length
Storage:	store in lead solution

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