LEAD ION SELECTIVE ELECTRODE
Always use eye protection and gloves when working with chemicals.
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Introduction

The PASCO Lead Ion Selective Electrode is used to quickly, simply, accurately, and economically measure lead or sulfate ion concentration in aqueous solutions.

Theory

The Lead Ion Electrode is composed of sulfides of lead and silver bonded into an epoxy body. When the electrode membrane is in contact with a solution containing lead ions, an electrode potential develops. This electrode potential is measured against a constant reference potential, using an ISE Amplifier and Science Workshop interface. The level of lead ion, corresponding to the measured potential, is described by the Nernst equation:

$$E = E_0 + S \log X$$

where:

- $E$ = measured electrode potential
- $E_0$ = reference potential (a constant)
- $S$ = electrode slope (-26 mV/decade)
- $X$ = activity 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, $C_f$, by the activity coefficient, $\gamma$, by:

$$X = \gamma C_f$$

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

$$I = \frac{1}{2} \sum C_x Z_x^2$$

where:

- $C_x$ = concentration of ion $X$
- $Z_x$ = charge of ion $X$
- $\sum$ = 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, $\gamma$, 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.
Strongly acidic (pH = 0 – 2) and strongly basic (pH = 12 – 14) solutions are also 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.

**Equipment**

**Included:**
- Lead Ion Selective Electrode
- Lead Ion Selective Electrode fill solution
- pipette for fill solution
- polishing strips

**Additional Required:**

**Required Equipment**
- PASCO CI-6738 ISE (Ion Selective Electrode) Amplifier
- Science Workshop 2.2.5 or higher
- PASCO Science Workshop Computer Interface,
- Semilogarithmic 4-cycle graph paper for preparing calibration curves (Linear graph paper is recommended for low level measurements or lead/sulfate titrations.)
- magnetic stir plate
- Lab-ware made of plastic, not glass, for all low level measurements.

**Required Solutions**

Most of the stock solutions listed in this section may be created as described in the text, or ordered directly from PASCO. The solutions available for order and their respective prices are listed in the “ISE Working Solutions Price List”.

- Deionized or distilled water for solution and standard preparation.
- **Ionic Strength Adjuster (ISA), 5 M NaClO₄**
  To prepare this solution, half fill a one liter volumetric flask with distilled water and add 700 grams of reagent-grade NaClO₄·H₂O. Swirl the flask gently to dissolve the solid. Fill the flask to the mark with distilled water, cap, and upend several times to mix the solution. To each 100 ml of standard or sample, add 2 ml of ISA. The background ionic strength of the resulting solution will be 0.1 M.
- **Lead Perchlorate Standard, 0.1 M Pb(ClO₄)₂**
  To prepare this solution, half fill a one liter volumetric flask with distilled water and add 46.01 grams of reagent-grade lead perchlorate, Pb(ClO₄)₂·3H₂O. Swirl the flask gently to dissolve the solid. Fill the flask to the mark with distilled water, cap, and upend several times to thoroughly mix the solution.
• **Lead Perchlorate Standard, 1000 ppm Pb(ClO$_4$)$_2$**
  
  To prepare this solution, half fill a one liter volumetric flask with distilled water and add 2.30 grams of reagent-grade lead perchlorate, Pb(ClO$_4$)$_2$·3H$_2$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.

• **Methanol-formaldehyde solution.**
  
  The methanol-formaldehyde solution is required when measurements of very low concentrations of lead (on the order of $10^{-6}$ or 0.2 ppm) or sulfite (on the order of $10^{-3}$ or 96 ppm) are to be made. This solution reduces interference to the operation of the electrode caused by the oxidation and solubility of the membrane. This interference will affect the reliability of the low level measurement and titration method. Although not required, methanol-formaldehyde may also be used to improve the repeatability of measurements of greater concentrations.

Whenever the methanol-formaldehyde solution is used, it should be mixed in a 1:1 ratio with the calibration standards and unknown samples.

To prepare this solution, 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.

**Warning:** Use appropriate precautions when handling methanol and formaldehyde. Handle methanol under a vented hood, and use gloves and eye protection when handling formaldehyde.

---

**General Preparation**

**Electrode Preparation**

1. Remove the rubber cap covering the electrode tip. Slide the rubber sleeve down away from the filling hole of the Lead Ion Selective Electrode. Fill the electrode with the included filling solution to a level just below the fill hole. Slide the rubber sleeve back over the fill hole (Figure 2a).

2. Connect the Lead Ion Selective Electrode to the ISE Amplifier and insert the DIN connector of the ISE Amplifier into analog channel A or B on a PASCO Computer Interface (Figures 2b and 2c).

**Electrode Slope Check Using Science Workshop** (check electrodes each day)

1. To a 150 ml beaker, add 100 ml of distilled water. Add 2 ml of ISA. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. Start Science Workshop.
select the Ion Selective Electrode sensor, open a Digital display, and begin monitoring data. Lower the electrode tip into the solution.

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

3. Using a pipet, add 10 ml of the same lead standard used above to the beaker. When the reading has stabilized, record the voltage reading indicated in the Digits display.

4. Determine the difference between the two readings. The electrode is operating correctly if the potential has changed by 26 ± 3 mV, assuming the temperature is between 20 °C and 25 °C. See the Troubleshooting sections if the potential change is not within this range.

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

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 a 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.
• For low level concentrations of lead (< $10^{-6}$ or 0.2 ppm) 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 (>0.1 M) 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 and reduce electrode life.
• 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

<table>
<thead>
<tr>
<th>ppm Pb$^{+2}$</th>
<th>M</th>
<th>ppm S$^{4-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.7</td>
<td>1.0 X 10^-4</td>
<td>9.6</td>
</tr>
<tr>
<td>207.0</td>
<td>1.0 X 10^-3</td>
<td>96.0</td>
</tr>
<tr>
<td>2070.0</td>
<td>1.0 X 10^-2</td>
<td>960.0</td>
</tr>
</tbody>
</table>

**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 approximately the same by adjustment with ISA. The temperature of both sample solution and standard solution should be the same.

**Calibration for the Direct Measurement of Lead**

*Note:* A calibration curve is constructed on semilogarithmic paper. The measured electrode potential (linear axis) is plotted against the standard concentration (log axis). In the linear region of the curve, only two standards are necessary to determine a calibration curve. Calibration solutions close to the anticipated value of the “unknown” should be chosen. 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.

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

2. Place 100 ml of the 10^-4 M or 10 ppm standard in a 150 ml beaker. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Add 2 ml of ISA. After assuring that *Science Workshop* is operating, lower the electrode tip into the solution. When the reading has stabilized, record the voltage reading indicated in the Digits display.

3. Place 100 ml of the 10^-3 M or 100 ppm standard in a 150 ml beaker. 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 tip in the solution. When the reading has stabilized, record the voltage reading indicated in the Digits display.
4. Place 100 ml of the $10^{-2}\text{ M}$ or 1000 ppm standard in a 150 ml beaker. 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 tip in the solution. When the reading has stabilized, record the voltage reading indicated in the Digits display.

5. Using the semilogarithmic graph paper, plot the voltage reading (linear axis) against the concentration (log axis). Extrapolate the calibration curve down to about $2.0 \times 10^{-6}\text{ M}$. A typical calibration curve can be found in Figure 3.

6. To a clean, dry, 150 ml beaker, add 100 ml of the sample, and 2 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Rinse the electrode with distilled water, blot dry, and lower the electrode tip into the solution. When the reading has stabilized, record the voltage reading indicated in the Digits display. 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 tip 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.

**Low Level Lead Determination**

This procedure is recommended for solutions with lead concentrations of less than $1.0 \times 10^{-6}\text{ M}$. 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 (1.0 M NaClO₄) is added at the rate of 1 ml low level ISA to each 100 ml of solution. The background ionic strength will be 1.0 X 10⁻² M.

2. Dilute 1 ml of 0.1 M standard to one liter to prepare a 1.0 X 10⁻⁴ 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 lab-ware 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 tip in the solution. Assure that Science Workshop is operating.

5. Add increments of the 1.0 X 10⁻⁴ M or 10 ppm standard as given in Table 2 below.

<table>
<thead>
<tr>
<th>Step</th>
<th>Pipet</th>
<th>Added Volume (ml)</th>
<th>Concentration ppm</th>
<th>Concentration M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 A</td>
<td>0.1</td>
<td>1.0 X 10⁻²</td>
<td>1.0 X 10⁻²</td>
<td></td>
</tr>
<tr>
<td>2 A</td>
<td>0.1</td>
<td>2.0 X 10⁻²</td>
<td>2.0 X 10⁻²</td>
<td></td>
</tr>
<tr>
<td>3 A</td>
<td>0.2</td>
<td>4.0 X 10⁻²</td>
<td>4.0 X 10⁻²</td>
<td></td>
</tr>
<tr>
<td>4 A</td>
<td>0.2</td>
<td>6.0 X 10⁻²</td>
<td>6.0 X 10⁻²</td>
<td></td>
</tr>
<tr>
<td>5 A</td>
<td>0.4</td>
<td>1.0 X 10⁻¹</td>
<td>9.9 X 10⁻¹</td>
<td></td>
</tr>
<tr>
<td>6 B</td>
<td>2.0</td>
<td>2.9 X 10⁻¹</td>
<td>2.9 X 10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>7 B</td>
<td>2.0</td>
<td>4.8 X 10⁻¹</td>
<td>4.8 X 10⁻⁶</td>
<td></td>
</tr>
</tbody>
</table>

Pipet A = 1 ml graduated pipet
Pipet B = 2 ml pipet

Solutions: additions of 10 ppm or 1.0 X 10⁻⁴ M standard to 100 ml of solution prepared in step 3 above

6. After the reading has stabilized, record the voltage reading indicated in the Digits display.

7. On semilogarithmic graph paper, plot the voltage reading on the Digits display (linear axis) against the concentration (log axis) as in Figure 3.

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 tip into the solution. After the reading has stabilized, record the voltage reading indicated in the Digits display 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.
**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 (ethylenediamine tetraacetate). The sample concentrations should be above $1.0 \times 10^{-3}$ 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 0.01 M EDTA titrant by adding 3.772 grams of reagent-grade $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ 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 electrode potential after each addition. Continue the additions several milliliters past the endpoint until little change is noted in the voltage reading indicated in the Digits display, even when adding 0.5–1.0 ml increments.

5. Plot the milliliters of EDTA added against the electrode 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:

$$M_{\text{Pb}}^{+2} = \frac{V_\text{t}M_\text{t}}{V_{\text{Pb}}^{+2}}$$

where:
- $M_{\text{Pb}}^{+2}$ = concentration of lead ion in the sample (moles/liter)
- $V_\text{t}$ = volume of EDTA added at endpoint
- $M_\text{t}$ = EDTA concentration (moles/liter)
- $V_{\text{Pb}}^{+2}$ = 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.
Interferences:

If present in amounts in excess of the following,

\[
\begin{align*}
\text{NO}_3^- & > 50 \times \text{SO}_4^{2-} \\
\text{Cl}^- & > 50 \times \text{SO}_4^{2-} \\
\text{HCO}_3^- & > 100 \times \text{SO}_4^{2-} \text{ at pH 4,}
\end{align*}
\]

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

The titrant is lead standard, 0.1 M, 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 0.01 M lead perchlorate titrant by pipeting 100 ml of the 0.1 M 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 electrode potential after each addition. Continue the additions several milliliters past the endpoint until little change is noted in the voltage reading indicated in the Digits display even when adding 0.5 –1.0 ml increments.

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

![Figure 4](image-url)

_{Typical titration of 100 ml of 10^{-3} M Na_2SO_4 with 10^{-1} M Pb(ClO_4)_2_}
Electrode Characteristics

Reproducibility

Electrode measurements reproducible to ±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.

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

\[ M_{SO_4}^{-2} = \frac{V_Mt}{V_{SO_4}} \]

where:

- \( M_{SO_4}^{-2} \) = concentration of sulfate ion in the unknown (moles/liter)
- \( V_t \) = volume of lead added at endpoint
- \( M_t \) = lead concentration (moles/liter)
- \( V_{SO_4} \) = volume of unknown sample (50 ml)
**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 1.0 \( \times 10^{-3} \) 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 calculated values for the “S” factor in the Nernst equation for the lead ion. If changes in temperature occur, the electrodes should be recalibrated.

The temperature range for the Lead Ion Electrode is 0 °C–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 potential against the lead concentration on semilogarithmic paper results in a straight line with a slope of about 26 mV per decade. (Refer to Figure 3.)

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.

**Limits of Detection**

The upper limit of detection in pure lead perchlorate solutions is 0.1 M. In the presence of other ions, the upper limit of detection is above 1.0 \( \times 10^{-2} \) M of lead. However, 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 0.1 M and 1.0 \( \times 10^{-3} \) 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 3 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 1.0 \( \times 10^{-6} \) (0.2 ppm). Extreme care must be taken with measurements below 1.0 \( \times 10^{-5} \) (2.0 ppm) to avoid adsorption of lead ions in the sample onto container walls.

**pH Effects**

Figure 5 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 5.

---

**TABLE 3: Temperature vs. Theoretical Values for the Electrode Slope**

<table>
<thead>
<tr>
<th>Temp ( °C)</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>27.10</td>
</tr>
<tr>
<td>10</td>
<td>28.09</td>
</tr>
<tr>
<td>20</td>
<td>29.08</td>
</tr>
<tr>
<td>25</td>
<td>29.58</td>
</tr>
<tr>
<td>30</td>
<td>30.07</td>
</tr>
<tr>
<td>40</td>
<td>31.07</td>
</tr>
<tr>
<td>50</td>
<td>32.06</td>
</tr>
</tbody>
</table>
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 5. 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.

**Electrode Life**

The lead electrode will last six months in normal daily laboratory use. On-line continuous 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.

**Maintenance**

**Electrode Storage**

The lead electrode may be stored for short periods of time in 1.0 X 10$^{-2}$ M lead solution. For longer storage (longer than two weeks), rinse and dry the sensing pellet and cover the membrane tip with the protective cap shipped with the electrode. The electrode should be drained of filling solution and the rubber shield placed over the filling hole.

**Polishing the Membrane:**

1. If using cotton 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 cotton paper 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 cotton polishing paper 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 jewellers 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 jewellers rouge to the damp cotton.

8. Continue with steps 3 and 4 above.

**Specifications**

<table>
<thead>
<tr>
<th>Specification</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration Range</td>
<td>$10^{-1}$ M to $10^{-6}$ M Pb$^{2+}$</td>
</tr>
<tr>
<td></td>
<td>(20,700 to 0.2 ppm Pb$^{2+}$)</td>
</tr>
<tr>
<td>pH Range</td>
<td>3 to 8</td>
</tr>
<tr>
<td>Temperature Range</td>
<td>0 °C – 80 °C</td>
</tr>
<tr>
<td>Resistance</td>
<td>$&lt; 1$ mohm</td>
</tr>
<tr>
<td>Reproducibility</td>
<td>+/- 2%</td>
</tr>
<tr>
<td>Samples</td>
<td>aqueous solutions only no organic solvents</td>
</tr>
<tr>
<td>Size</td>
<td>110 mm length</td>
</tr>
<tr>
<td></td>
<td>12 mm diameter</td>
</tr>
<tr>
<td></td>
<td>cable length = 1 m</td>
</tr>
</tbody>
</table>

**Troubleshooting Guide**

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

**Glassware/Plastic-ware**

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

**Electrode**

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 electrode still fails to respond as expected, substitute another lead ion electrode that is known to be in good working order for the questionable 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 following.)
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 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, particularly the General Preparation and Electrode Characteristics sections.

If trouble still persists, call PASCO Technical Support.
# Troubleshooting Hints

<table>
<thead>
<tr>
<th>Symptom</th>
<th>Possible Causes</th>
<th>Next Step</th>
</tr>
</thead>
<tbody>
<tr>
<td>Out of Range Reading</td>
<td>defective electrode</td>
<td>check electrode operation</td>
</tr>
<tr>
<td></td>
<td>electrodes not plugged in</td>
<td>unplug electrodes and reseat electrodes</td>
</tr>
<tr>
<td>properly</td>
<td>reference electrode not filled</td>
<td>be sure reference electrode is filled</td>
</tr>
<tr>
<td></td>
<td>air bubble on membrane</td>
<td>remove bubble by re-dipping electrode</td>
</tr>
<tr>
<td></td>
<td>electrodes not in solution</td>
<td>put electrodes in solution</td>
</tr>
<tr>
<td>Noisy or Unstable Readings (readings</td>
<td>air bubble on membrane</td>
<td>remove bubble by re-dipping electrode</td>
</tr>
<tr>
<td>continuously or rapidly changing)</td>
<td>electrode exposed to interferences</td>
<td>soak electrode in lead standard</td>
</tr>
<tr>
<td></td>
<td>defective electrode</td>
<td>replace electrode</td>
</tr>
<tr>
<td></td>
<td>ISA not used</td>
<td>use recommended ISA</td>
</tr>
<tr>
<td></td>
<td>stirrer not grounded</td>
<td>ground stirrer</td>
</tr>
<tr>
<td>Drift (reading slowly changing in one</td>
<td>samples end standards at different</td>
<td>allow solution to come to room temperature</td>
</tr>
<tr>
<td>direction)</td>
<td>temperatures</td>
<td>before measurement</td>
</tr>
<tr>
<td></td>
<td>complexing agents in sample</td>
<td>check section entitled **Precipitation and</td>
</tr>
<tr>
<td></td>
<td>incorrect reference filling solution</td>
<td><em>Complexation</em></td>
</tr>
<tr>
<td></td>
<td>membrane dirty or oxidized</td>
<td>use recommended filling solution</td>
</tr>
<tr>
<td></td>
<td></td>
<td>polish membrane; use methanol-formaldehyde</td>
</tr>
<tr>
<td></td>
<td></td>
<td>solution</td>
</tr>
<tr>
<td>Low Slope or No Slope</td>
<td>standards contaminated or incorrectly made</td>
<td>prepare fresh standards</td>
</tr>
<tr>
<td></td>
<td>standard used as ISA</td>
<td>use ISA</td>
</tr>
<tr>
<td></td>
<td>ISA not used</td>
<td>use recommended ISA</td>
</tr>
<tr>
<td></td>
<td>membrane dirty or oxidized</td>
<td>polish membrane; use methanol-formaldehyde</td>
</tr>
<tr>
<td></td>
<td>air bubble on membrane</td>
<td>remove bubble by re-dipping probe</td>
</tr>
<tr>
<td>Symptom</td>
<td>Possible Causes</td>
<td>Next Step</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>-------------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>“Incorrect Answer” calibration curve is good</td>
<td>incorrect scaling of semilog paper plot voltage potential on the linear axis. (but On the log axis, be sure concentration numbers within each decade are increasing with increasing concentration.</td>
<td>be sure to note sign of millivolt reading correctly</td>
</tr>
<tr>
<td>incorrect sign</td>
<td></td>
<td>be sure to note sign of millivolt reading correctly</td>
</tr>
<tr>
<td>incorrect standards</td>
<td></td>
<td>prepare fresh standards</td>
</tr>
<tr>
<td>wrong units used</td>
<td></td>
<td>apply correct conversion factor: $10^{-3} \text{ M} = 207 \text{ ppm} \text{ Pb}^{2+} = 96 \text{ ppm} \text{ SO}_4^{2-}$</td>
</tr>
<tr>
<td>complexing agents in sample</td>
<td></td>
<td>check section entitled <em>Precipitation and Complexation</em>; use titration methods</td>
</tr>
</tbody>
</table>
Feedback
If you have any comments about the product or manual, please let us know. If you have any suggestions on alternate experiments or find a problem in the manual, please tell us. PASCO appreciates any customer feedback. Your input helps us evaluate and improve our product.

To Reach PASCO
For technical support, call us at 1-800-772-8700 (toll-free within the U.S.) or (916) 786-3800.

fax: (916) 786-3292

e-mail: techsupp@pasco.com

web: www.pasco.com

Contacting Technical Support
Before you call the PASCO Technical Support staff, it would be helpful to prepare the following information:

➤ If your problem is with the PASCO apparatus, note:
  - Title and model number (usually listed on the label);
  - Approximate age of apparatus;
  - A detailed description of the problem/sequence of events (in case you can’t call PASCO right away, you won’t lose valuable data);
  - If possible, have the apparatus within reach when calling to facilitate description of individual parts.

➤ If your problem relates to the instruction manual, note:
  - Part number and revision (listed by month and year on the front cover);
  - Have the manual at hand to discuss your questions.