GENERAL INSTRUCTIONS

Introduction

Cadmium Ion Electrodes are used to quickly, simply, accurately, and economically measure cadmium 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.

3. A magnetic stirrer.

4. ISE-8730
   AND
   ISE-8732

5. Double junction reference electrode with filling solution Part# PHFS-A250 in the inner junction and with filling solution Part# PHFS-B250 in the outer junction.

6. Polishing paper to polish dirty or etched electrode membranes.

Required Solutions

1. Deionized or distilled water for solution and standard preparation.

2. Ionic Strength Adjuster (ISA), 5M NaNO₃.
   To prepare this solution from your own laboratory stock, half fill a one liter volumetric flask with distilled water and add 425 grams reagent-grade sodium nitrate, NaNO₃. Swirl the flask gently to dissolve the solid. Fill to the mark with distilled water, cap, and upend several times to mix the solution.
3. Cadmium Nitrate Standard Solution, 0.1M. To prepare this solution from your own laboratory stock, half fill a one liter volumetric flask with distilled water and add 30.85 grams of reagent-grade Cd(NO₃)₂·4H₂O. Swirl the flask gently to dissolve the solid. Fill to the mark with distilled water, cap, and upend several times to mix the solution.

4. Cadmium Nitrate Standard Solution, 1000 ppm. To prepare this solution from your own laboratory stock, half fill a one liter volumetric flask with distilled water and add 2.74 grams of reagent-grade Cd(NO₃)₂·4H₂O. Swirl the flask gently to dissolve the solid. Fill to the mark with distilled water, cap, and upend several times to mix the solution.

5. EDTA Titrant 1M stock solution for the titration of cadmium. To prepare this solution from your own laboratory stock, add 37.2 grams of reagent-grade Na₂EDTA to a 100 ml volumetric flask about three-fourths full of distilled water. Swirl the flask gently to dissolve the solid. Fill to the mark with distilled water, cap, and upend several times to mix the solution.

GENERAL PREPARATION

Electrode Preparation

Remove the rubber caps covering the electrode tips and the rubber insert covering the filling hole of the cadmium combination 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 a pH/mV meter) (check electrodes each day)

1. To a 150 ml beaker, add 100 ml of distilled water and 2 ml of ISA. Place the beaker on the 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 either the 0.1M or 1000 ppm cadmium standard to the beaker. When the reading has stabilized, record the mV reading.
3. Using a pipet, add 10 ml of the 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 mV potential has changed 27±2 mV, 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 cadmium solutions whose concentrations vary be tenfold. Use either the 0.1M or 1000 ppm standard and the serial dilution method for this preparation.

2. To a 150 ml beaker, add 100 ml of the lower value standard and 2 ml of ISA. Place the beaker on the 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 a 150 ml beaker, add 100 ml of the higher value standard and 2 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution.

6. Adjust 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%. If the slope is not within this range, 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 about a 2% 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 insulating material, such as a styrofoam sheet, between the stirrer and beaker.

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

For samples with high ionic strength, prepare standards whose composition is similar to the sample.

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. Dilute concentrated samples (>0.1M) before measurement.

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 sample solutions and of the standard 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 Interference and Electrode Response sections to remove them.

Adjust sample pH with 1M HNO₃ to below pH 7 to avoid precipitation of cadmium hydroxide, Cd(OH)₂.
Units of Measurement

Cadmium ion concentrations are measured in units of parts per million, moles per liter, equivalents per liter, or any other convenient concentration unit. Table 1 indicates some of these concentration units.

**TABLE 1: Concentration Unit Conversion Factors**

<table>
<thead>
<tr>
<th>ppm Cd$^{2+}$</th>
<th>moles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1124.0</td>
<td>1.0X10$^{-2}$</td>
</tr>
<tr>
<td>112.4</td>
<td>1.0X10$^{-3}$</td>
</tr>
<tr>
<td>11.2</td>
<td>1.0X10$^{-4}$</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 the same by adjustment with ISA. The temperature of both sample solutions and of standard solutions should be the same.

**Direct Measurement of Cadmium (using a pH/mV meter)**

1. By serial dilution prepare three standard solutions from the 0.1M, 1000 ppm or 100 ppm standard. The resultant concentrations should be 10$^{-2}$, 10$^{-3}$, and 10$^{-4}$M or 1000, 100 and 10 ppm standards. Add 2 ml of ISA to each 100 ml of standard. Prepare standards with a composition similar to the samples if the samples have an ionic strength above 0.1M.

2. Place 100 ml of the most dilute solution (1.0X10$^{-4}$M or 10 ppm) in a 150 ml beaker on the magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode lower the electrode tips into the solution. After the reading has stabilized, record the mV reading.

3. Place 100 ml of the mid-range solution (1.0X10$^{-3}$M or 100 ppm) in a 150 ml beaker on the magnetic stirrer and begin stirring at a constant rate. After rinsing the electrodes with distilled water, blot dry and immerse the electrode tips in the solution. After the reading has stabilized, record the mV reading.

4. Place 100 ml of the most concentrated solution (1.0X10$^{-2}$M or 1000 ppm) in a 150 ml beaker on the magnetic stirrer
and begin stirring at a constant rate. After rinsing the electrodes with distilled water, blot dry and immerse the electrode tips in the solution. After the reading has stabilized, record the mV reading.

5. Using the semi-logarithmic graph paper, plot the mV reading (linear axis) against concentration (log axis). Extrapolate the curve down to about $1.0 \times 10^{-5}$ or 1 ppm. A typical calibration curve can be found in Figure 1.

![Figure 1
Typical cadmium electrode calibration curve](image)

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 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 tips with distilled water, blot dry and lower the electrode tips into the solution. After 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 Cadmium (using an ion meter)

1. By serial dilution of the 0.1M or 1000 ppm cadmium standard, prepare two cadmium standards whose concentration is near the expected sample concentration. Measure out 100 ml of each standard into individual 150 ml beakers and add 2 ml of ISA to each.

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. Lower the electrode tips into the solution.

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

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

5. Place the more concentrated solution on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution.

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

7. Place 100 ml of the sample and 2 ml of ISA into a 150 ml beaker. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.

8. Immerse the rinsed, dried electrode tips in the solution and wait for the reading to stabilize. Read the concentration directly from the meter display.

9. The calibration should be checked every two hours. Assuming no change in ambient temperature, immerse the electrode tips in the first cadmium standard. After the
reading has stabilized, compare it to the original reading recorded in Step 3 above. A reading differing by more than ±0.5mV, or a change in ambient temperature will necessitate the repetition of Steps 2-6 above. The meter should be re-calibrated daily.

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

This procedure is recommended for solutions with cadmium concentrations of less than 1.0x10⁻⁵M (1.1 ppm). If the solution is high in ionic strength, but low in cadmium ion, 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 NaNO₃) is added at the rate of 1 ml low level ISA to each 100 ml of solution. The background ionic strength will be 1.0x10⁻²M.

2. Dilute 1 ml of 0.1M standard to one liter to prepare a 1.0x10⁻⁴M 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 of solution for measurements in ppm. Standards should be prepared fresh daily.

3. To a 150 ml beaker add 100 ml of distilled water and 1 ml of low level ISA. 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 in the mV mode.

5. Add increments of the 1.0x10⁻⁴M or 10 ppm standard as given in Table 2 below.

6. After the reading has stabilized, record the mV reading after each addition.

**TABLE 2: Step-wise Calibration for Low Level Cadmium Measurements**

<table>
<thead>
<tr>
<th>Step</th>
<th>Pipet</th>
<th>Added Volume (ml)</th>
<th>Concentration M M</th>
<th>Concentration ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>0.1</td>
<td>0.01</td>
<td>1.0x10⁻⁷</td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>0.1</td>
<td>0.02</td>
<td>2.0x10⁻⁷</td>
</tr>
<tr>
<td>3</td>
<td>A</td>
<td>0.2</td>
<td>0.04</td>
<td>4.0x10⁻⁷</td>
</tr>
<tr>
<td>4</td>
<td>A</td>
<td>0.2</td>
<td>0.06</td>
<td>6.0x10⁻⁷</td>
</tr>
<tr>
<td>5</td>
<td>A</td>
<td>0.4</td>
<td>0.10</td>
<td>9.9x10⁻⁷</td>
</tr>
<tr>
<td>6</td>
<td>B</td>
<td>2.0</td>
<td>0.29</td>
<td>2.9x10⁻⁶</td>
</tr>
<tr>
<td>7</td>
<td>B</td>
<td>2.0</td>
<td>0.48</td>
<td>4.8x10⁻⁶</td>
</tr>
</tbody>
</table>
Pipet A = 1 ml graduated pipet
Pipet B = 2 ml pipet
Solutions: additions of 10 ppm or 1.0×10⁻⁴ 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 with distilled water and blot dry.

9. Measure out 100 ml of the sample into a 150 ml beaker and add 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.

10. Prepare a new low level calibration curve daily. Check the calibration curve every two hours by repeating Steps 3 – 7 above.

Low Level Cadmium Determination (using an ion meter)

1. Using 20 ml of standard ISA, dilute to 100 ml with distilled water. This low level ISA (1.0 M NaNO₃) is added at the rate of 1 ml low level ISA to each 100 ml of solution. The background ionic strength will be 1.0×10⁻² M.

2. Follow the steps given in Direct Measurement of Cadmium (using an ion meter) to the end of Step 6.

3. To a 150 ml beaker, add 100 ml of distilled water and 1 ml of low level ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.

4. 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.

5. Continue with Steps 7–9 in Direct Measurement of Cadmium (using an ion meter), remembering to use the low level ISA described in Step 1 above.

Titration

Titration is a very accurate determination of total cadmium ion concentration. This method makes use of the electrode as an endpoint detector when EDTA is used as a titrant.
Titration of Cadmium

The method outlined in this section makes use of the cadmium ion electrode as a highly sensitive endpoint detector for cadmium-containing samples. The titrant used is EDTA.

EDTA complexes cadmium as well as other cations. The sample pH can be adjusted to pH 10 by adding ammonia to eliminate unwanted ion complexes. Masking agents may be added in some cases.

1. Prepare the stock EDTA titrant as given in the section Required Solutions. Dilute the EDTA to 10 to 20 times as concentrated as the suspected sample concentration. The sample should contain at least 1.0X10^-4 M cadmium for a good detection of the endpoint.

2. Fill a 50 ml buret with the EDTA solution. Pipet 100 ml of the sample into a 150 ml beaker, place the beaker on the magnetic stirrer and begin stirring at a constant rate. Adjust the sample to pH 10 by adding ammonia.

3. Position the buret tip in the beaker, slightly above the liquid level in the beaker and slightly off center. 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 and about 0.1 ml to 0.2 ml increments as the potential begins to change more rapidly. 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 EDTA added against the mV potential on standard coordinate graph paper. (See Figure 2.) The point of greatest potential change is the endpoint.

Figure 2
Typical titration of 100 ml of 5 x 10^-3 M Cd(NO₃)₂ (pH adjusted to 10 with ammonia) with 0.1 M Na₂EDTA
6. The cadmium ion concentration of the sample is calculated as follows:

\[ M_{\text{Cd}^{+2}} = \frac{V_t M_t}{V_{\text{Cd}^{+2}}} \]

where:

- \( M_{\text{Cd}^{+2}} \) = concentration of cadmium ion in the sample (moles/liter)
- \( V_t \) = volume of EDTA added at endpoint
- \( M_t \) = EDTA concentration (moles/liter)
- \( V_{\text{Cd}^{+2}} \) = volume of unknown sample (100 ml)

**ELECTRODE CHARACTERISTICS**

**Reproducibility**

Electrode measurements reproducible to ±2% can be obtained if the electrode is calibrated every hour. 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 cadmium ion electrodes do not respond to anions or 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 ion or lead ion exceeds the level of cadmium ion in the sample, the measurement will be affected. Sodium fluoride added to the sample will eliminate ferric ion.

**Precipitation and Complexation**

Sulfide, carbonate, oxalate, phosphate, hydroxide, and other ions precipitate insoluble cadmium salts. The level of cadmium ion, the level of the precipitating ion, and the pH of the sample determine formation of a precipitate.
A wide variety of species, including acetate, ammonia, bromide, chloride, citrate, cyanide, and EDTA, form complexes with cadmium. The total cadmium concentration, the concentration of the complexing species, the solution pH, and the ionic strength all determine the extent of complexation. Complexation reduces the free cadmium ion concentration and, since the electrode responds only to free cadmium ions, a false reading results.

Temperature Influences

Samples and standards should be at the same temperature, since the electrode potentials are influenced by changes in temperature. A 1°C difference in temperature results in a 4% error at the 1.0X10⁻³M cadmium 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 cadmium ion.

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

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>&quot;S&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>27.10</td>
</tr>
<tr>
<td>10</td>
<td>28.10</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>

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

The temperature range for the pHoenix Cadmium 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 mV potential against the cadmium concentration on semi-logarithmic graph paper results in a straight line with a slope of about 27 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 concentrations of 1.0X10⁻⁶M cadmium. Below 10⁻⁶M, considerably longer response time can be expected. (Refer to Figure 3.)
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 cadmium nitrate solutions is 0.1M. In the presence of other ions, the upper limit of detection is above 1.0x10^{-2}M cadmium, but the possibility of a liquid junction
potential developing at the reference electrode and the "salt extraction effect" are two limiting factors. Some salts may infuse 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 cadmium. Neutral solutions containing free cadmium ions can be measured down to 1.0x10^{-7}M (0.01 ppm). Extreme care must be taken with measurements below 1.0x10^{-5}M (1.1 ppm) to avoid contamination of samples.

**pH Effects**

Figure 4 shows how the electrode responds to cadmium ion in solution at various pH levels. Hydrogen ion interferes with low cadmium ion measurements. The minimum pH at which cadmium ion concentrations can be measured without interference is given by the solid line "limit of detection" above the shaded area in Figure 4.

At a high pH, free cadmium ion precipitates with hydroxide ion, thereby reducing the cadmium ion concentration. The maximum pH at which cadmium concentration can be measured without interference from hydroxide is given by a dashed line to the left of the dotted area on Figure 4. Within this dotted area, cadmium combines with hydroxide to form Cd(OH)₂. Since only free cadmium concentration can be measured with the cadmium ion electrodes, a false reading results.
Electrode Life

The Phoenix Cadmium 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 cadmium electrode may be stored for short periods of time in 1.0x10^{-2}M cadmium 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 Cadmium Ion Electrode consists of sulfides of cadmium and other metals bonded into an epoxy or glass body. When an electrode potential develops across the membrane, the membrane is in contact with a solution containing cadmium ions. The electrode potential is measured against a constant reference potential, using a standard pH/mV meter. The level of cadmium ions, 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 (-27mV/decade)
- \( X \) = level of cadmium ions in solution

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

\[ C_f = C_t + C_b \]

The activity, \( X \), represents the effective concentration of the ions in solution. The activity is related to the free cadmium ion by the activity coefficient, \( \gamma \), by:

\[ X = \gamma C_f \]
Activity coefficients vary, depending on total ionic strength, $I$, defined as:

$$I = \frac{1}{2} \Sigma c_x z_x^2$$

where:

- $c_x$ = concentration of ion X
- $z_x$ = charge of ion X
- $\Sigma$ = sum of all 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.

To adjust the background ionic strength to a high and constant value, ionic strength adjuster is added to samples and standards. The recommended ISA solution for the cadmium electrodes is sodium nitrate, NaNO$_3$. 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 cadmium ions. Samples with high ionic strength (greater than 0.1M) do not need ISA added and standards for these solutions should be prepared with a composition similar to the samples.

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 as nearly equal as possible, that is, the filling solution 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 equitranferent salt. One must either calibrate
the electrode 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
glassware, 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

Clean glass-ware is essential for good measurement. Be sure to
wash the glass-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 cadmium 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 standard and reagent solutions. If in doubt about the credibility of any of the solutions prepare them again. Errors may result from contamination of the ISA, incorrect dilution, 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

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<th>Possible Causes</th>
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<td>Noisy or Unstable Readings (readings continuously or rapidly changing)</td>
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<td>remove bubble by re-dipping electrode</td>
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<td>use recommended ISA</td>
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<td>samples and standards at different temperatures</td>
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<td>check section entitled Precipitation and Complexation</td>
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<td>ISA not used</td>
<td>use recommended ISA</td>
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</table>
standard used as ISA electrode exposed to complexing agents

air bubble on membrane

"Incorrect Answer" (but calibration curve is good)

incorrect scaling of semi-log paper

incorrect sign

incorrect standards

wrong units used

complexing agents in sample

use ISA

check section entitled Precipitation and Complexation

remove bubble by redipping probe

plot millivolts on the linear axis. On the log axis, be sure concentration numbers within each decade are increasing with increasing concentration.

be sure to note sign of millivolt number correctly

prepare fresh standards

apply correct conversion factor: 
$10^{-3}M = 112$ ppm as Cd$^{2+}$

check section entitled Precipitation and Complexation; use titration
**SPECIFICATIONS**

Concentration Range: $1.0 \times 10^{-1} \text{M}$ to $1.0 \times 10^{-7} \text{M}$  
(11,200 to 0.01 ppm)

pH Range: 2 to 12

Temperature Range: $0^\circ$-$80^\circ$C

Resistance: $<1$ Mohm

Reproducibility: $\pm 2\%$

Samples: aqueous solutions only; no organic solvents

Size: 110 mm length  
12 mm diameter  
1 m cable length

Storage: store in cadmium solution