

Cd²⁺

Orion 94-48,
Orion 96-48 ionplus®

Orion Cadmium Electrode

INSTRUCTION MANUAL



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Sure-Flow electrodes are protected by European Patent 278,979 and Canadian Patent 1,286,720.

ionplus electrodes and Optimum Results solutions are protected by US Patent 5,830,338.

ROSS Ultra electrodes have patents pending.

ORION ORP Standard is protected by US Patent 6,350,367.

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This publication supersedes all previous publications on this subject.

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GENERAL INFORMATION

Introduction

The Orion 94-48 Cadmium Half-Cell Electrode and Orion 96-48 Sure-Flow[®] Combination Cadmium Electrode measure cadmium ions in aqueous solutions quickly, simply, accurately, and economically.

The Orion 96-48 offers additional benefits from the Sure-Flow Combination reference design. With this electrode, a separate reference electrode is unnecessary. And measuring small sample volumes is easier than ever. The free-flowing liquid junction assures stable, drift-free potentials. When measuring dirty samples which would clog conventional electrode junctions, the Sure-Flow junction can be opened and flushed clean simply by pressing the cap. The Orion 90-02 Double Junction Reference electrode, when used with Orion 94-48 Cadmium Half-Cell Electrode, also offers the benefits of the Sure-Flow junction design.

General analytical procedures, required solutions, electrode characteristics, and electrode theory are discussed in this manual. Operator instructions for Orion meters are given in the meter instruction manual.

Our Technical Service Chemists can be consulted for assistance and troubleshooting advice. Please refer to **Troubleshooting** for further information.

Required Equipment

Meter — The easiest to use are direct concentration readout specific ion meters (ISE meters), such as Orion EA 940, 920A, 720A, 710A, or 290A. If unavailable, a pH/mV meter with readability to 0.1 mV, such as Orion 420A, 520A, or 525A is recommended.

Reference Electrode	Orion
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For use with Orion 94-48:

Orion 90-02 Double Junction	900200
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Reference Electrode, includes:

Inner Chamber Filling Solution	900002
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Outer Chamber Filling Solution	900003
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For use with Orion 96-48: n/a

The Orion 96-48 Combination Cadmium Electrode does not require a separate reference electrode.

Magnetic Stirrer, Stir Bars — Recommended for laboratory measurements.

Graph Paper — 4 cycle semi-logarithmic paper for preparing calibration curves (for use with pH/mV laboratory meters).

Plastic Labware — For low-level cadmium measurements.

Polishing Strips — Orion 948201. To clean the cadmium sensing element.

Required Solutions

Distilled or Deionized Water –

To prepare all solutions and standards.

Reference Filling Solution	Orion
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Optimum Results™ A (for Orion 96-48 Combination Cadmium Electrode)	900061
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Inner Chamber Filling Solution (for use with Orion 90-02 Reference Electrode)	900002
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Outer Chamber Filling Solution (for use with Orion 90-02 Reference Electrode)	900003
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Standard Solutions	Orion
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0.1 M or 1000 ppm cadmium	Customer Prepared
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EDTA Titrant	Customer Prepared
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Ionic Strength Adjustor (ISA): 5M NaNO₃ To adjust ionic strength of samples and standards	940011
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Customer Prepared Solutions

Cadmium Stock Standard Solutions:

Required Chemicals:

Cadmium Nitrate, reagent grade

Distilled Water

Preparation:

0.1 M Cd(NO₃)₂ • 4H₂O solution: in a 1-liter flask, place 30.8 g of cadmium nitrate. Dissolve the solid, and dilute to volume with distilled water.

1000 ppm Cd²⁺ solution: weigh out 2.74 g of reagent-grade cadmium nitrate in a 1-liter volumetric flask. Dissolve and dilute to volume with distilled water.

EDTA Titrant:

Required Chemicals:

Tetrasodium EDTA (Na₄EDTA), reagent grade

Distilled water

Preparation:

1 M stock solution: place 38.0 g reagent Na₄EDTA in a 100 mL volumetric flask and dissolve in about 75 mL distilled water. Dilute to volume with distilled water.

BEFORE USING THE ELECTRODE

Electrode Preparation

Orion 94-48 Cadmium Electrode

Remove the rubber cap covering the electrode tip.

Orion 90-02 Double Junction Reference Electrode

Fill this reference electrode according to the instructions in the reference electrode instruction manual. Fill the inner chamber with Orion 900002 Filling Solution. Fill the outer chamber with Orion 900003 Filling Solution.

Add filling solution each day before using the electrode. The filling solution level should be at least one inch above the level of sample in the beaker to ensure a proper flow rate. If the filling solution is less than one inch above the sample solution level, electrode potentials may be erratic.

Orion 96-48 Sure-Flow Combination Cadmium Electrode

Orion offers a line of filling solutions designed specifically for your application. Optimum Results™ A (Orion 900061) supplied with this electrode is designed to minimize junction potentials and provide optimum temperature and time response. It can be used for all cadmium measurements.

Add filling solution each day before using the electrode. The filling solution level should be at least one inch above the level of sample in the beaker to ensure a proper flow rate. If the filling solution is less than one inch above the sample solution level, electrode potentials may be erratic.

The electrode is shipped without filling solution in the reference chamber. To fill from the flip-spout bottle:

1. Lift the spout to a vertical position.
2. Insert the spout into the fill hole in the outer sleeve and add a small amount of filling solution to the chamber. Tip the electrode to moisten the O-ring at the top and return electrode to a vertical position.
3. Holding the electrode by the barrel with one hand, use the thumb to push down on the electrode cap, allowing a few drops of filling solution to drain and wet the inner cone.
4. Release sleeve. If sleeve does not return to its original position immediately, check to see if the O-ring is moist enough and repeat steps 2 - 4 until the sleeve has returned to original position. Add filling solution up to the fill hole.

Checking Electrode Operation (Slope)

This procedure measures electrode slope. Slope is defined as the change in millivolts observed with every ten-fold change in concentration. Obtaining the slope value provides the best means for checking electrode performance.

These are general instructions that can be used with most meters to check electrode operation. See individual meter instruction manuals for more specific information.

1. If electrode(s) have been stored dry, prepare the electrode(s) as described in **Electrode Preparation**.
2. Connect the electrode(s) to the meter as described in the meter instruction manual. Non Orion meters may require special adapters. Consult your meter instruction manual.
3. Place 100 mL distilled water into a 150 mL beaker. Add 2 mL ISA, (Orion 940011). Stir thoroughly. Use 0.1 M or 1000 ppm cadmium standard in the following steps.
4. Set the meter to the mV mode.
5. Rinse electrode(s) with distilled water, blot dry, and place in the solution prepared in step 3 above.
6. Select the appropriate standard. Pipet 1 mL of the standard into the beaker. Stir thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.
7. Pipet 10 mL of the same standard into the same beaker. Stir thoroughly. When a stable reading is displayed record the electrode potential in millivolts.
8. The difference between the first and second potential reading is defined as the slope of the electrode. The difference should be in the range of (+) 25-30 mV/decade when the solution temperature is between 20 and 25 °C. If the slope is not within the appropriate range refer to the **Troubleshooting section**.

HELPFUL INFORMATION

Units of Measurement

Cadmium ion can be measured in units of moles per liter, parts per million, or any other convenient unit (see **Table 1**).

Table 1
Concentration Unit Conversion Factors

Moles/Liter	g/L	ppm Cd ²⁺	Avoir. oz. per gallon
1	112.4	112400	15.008
0.0666	7.486	7485.8	1.0
0.01	1.124	1124	0.15008
0.00890	1.0	1000	0.134
0.001	0.112	112.4	0.0150
0.00000890	0.001	1.0	0.000134

Sample Requirements

The epoxy electrode body is resistant to attack by inorganic solutions. The electrode may be used intermittently in solutions containing methanol or ethanol. Consult our Technical Service Chemists for use of the electrode in other organic solvents (See **Assistance**).

Samples and standards should be at the same temperature. A 1 °C difference in temperature will give rise to about a 4% error. Temperature must be less than 100 °C.

Cadmium samples must be below pH 7 to avoid precipitation of Cd(OH)₂. Acidify cadmium samples with 1 M HNO₃ if necessary, if too low hydrogen ion will interfere. See **pH Effects** to determine optimum pH working range for your sample.

GLP Measuring Hints

See **Figure 1**

- Stir all standards and samples at a uniform rate during measurement. Magnetic stirrers may generate sufficient heat to change solution temperature. Place a piece of insulating material such as cork, cardboard, or styrofoam between the stirrer and sample beaker.
- Prepare fresh working standards for calibration daily.
- Always rinse electrode(s) with distilled water between measurements. Shake after rinsing to prevent solution carryover. Blot dry.
- Allow all standards and samples to come to the same temperature for precise measurement.
- The 90-02 reference electrode (when used with the 94-48 Cadmium Half-Cell Electrode) should be submerged to the same depth as the cadmium electrode.
- Concentrated samples (> 0.1 M cadmium) should be diluted before measurement
- Measure under constant lighting, as the sensing element may show an offset or bias if lighting conditions change markedly.
- After immersion in solution, check electrode(s) for any air bubbles on the sensing element and remove by gently tapping the electrode(s).
- For high ionic strength samples, prepare standards with composition similar to that of the sample.

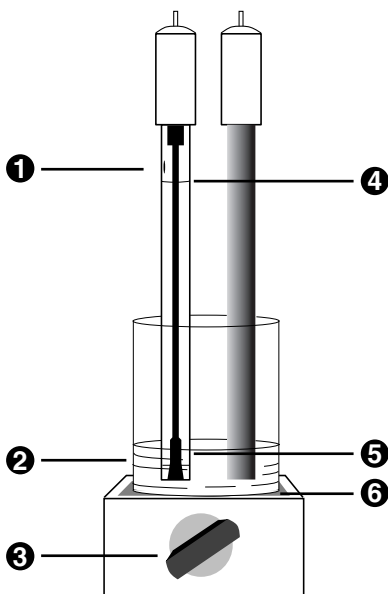


Figure 1: Measuring Hints

1. Filling hole should be uncovered (Orion 90-02 and 96-48).
2. Fresh standard.
3. Stir all samples and standards.
4. Filling solution level must be higher than sample level.
5. Reference junction must be immersed.
6. Place insulation between stirrer and beaker.

CHOOSING THE RIGHT MEASURING TECHNIQUE

A variety of analytical techniques are available to the analyst.

- **Direct Measurement** is a simple procedure for measuring a large number of samples. Only one meter reading is required for each sample. Calibration is performed in a series of standards. The concentration of the samples is determined by comparison to the standards. ISA is added to all solutions to ensure that samples and standards have similar ionic strength and proper pH.
- **Low-Level Measurement** is a similar method to Direct Measurement. This method is recommended when the expected sample concentration is less than 1 ppm or 10^{-5} M Cd^{2+} . A minimum three point calibration is recommended to compensate for the electrode's non-linear response at these concentrations. A special procedure describes the best means of preparing low-level calibration standards.
- **Known Addition** is a useful method for measuring samples, since calibration is not required. This method is recommended when measuring only a few samples, or when samples have a high (> 0.1 M) ionic strength, or a complicated background matrix. Refer to **Theory of Operation** for explanation of these effects. The electrodes are immersed in the sample solution and an aliquot of a standard solution containing the measured species is added to the sample. From the change in potential before and after the addition, the original sample concentration is determined. As in direct calibration, any convenient concentration unit can be used.
- **Titration**s are quantitative analytical techniques for measuring the concentration of a species by incremental addition of a reagent (titrant) that reacts with the sample species. Sensing electrodes can be used for determination of the titration end point. Ion-selective electrodes are useful as end point detectors, because they are unaffected by sample color or turbidity. Titrations are approximately 10 times more precise than direct calibration, but are more time-consuming.
- **Indicator Titration Method** is useful for measuring ionic species where an ion specific electrode does not exist. With this method the electrodes sense a reagent species that has been added to the sample before titration. The cadmium electrode may be used in indicator titrations for many different metal ions.

MEASUREMENT PROCEDURES

Direct Measurement

The following direct measurement procedures are recommended for “high-level” measurements. All samples must be in the electrode’s linear range, greater than 1 ppm or 10^{-5} M Cd^{2+} . A two point calibration is sufficient, though more points can be used if desired. With ISE meters, such as the Orion 920A, 720A, 710A, or 290A, sample concentrations can be read directly from the meter. Refer to the meter instruction manual for calibration details. When using a mV meter, a calibration curve can be prepared on semi-logarithmic graph paper, or a linear regression (against logarithmic concentration values) can be performed at the user’s discretion using a spreadsheet or graphing program.

Measuring Hints

- Standard concentrations should bracket the expected sample concentrations.
- Always add 2 mL ISA per 100 mL of cadmium standard or sample.
- For high ionic strength samples, having an ionic strength of 0.1 M or greater, prepare standards with a composition similar to that of the samples, or measure the samples using the known addition method.
- During calibration, measure the least concentrated standard first, and work up to the most concentrated.
- The best method for preparation of standards is by serial dilution. This procedure involves preparing an initial standard that is diluted, using volumetric glassware, to prepare a second standard solution. The second is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.
- Verify this procedure by measuring a standard of known concentration as an unknown or by spiking a sample with cadmium standard.
- Review section entitled **GLP Measuring Hints**.

Direct Measurement Procedure using ISE Meter

See individual meter instruction manuals for more specific calibration information.

1. Prepare electrode(s) as described in **Electrode Preparation**.
2. Connect electrode(s) to the meter, and adjust the meter to measure concentration.
3. Prepare two standards that bracket the expected sample range and differ in concentration by a factor of ten. Standards can be prepared in any concentration unit to suit the particular analysis requirement. All standards should be at the same temperature as the samples. For details on temperature effects on electrode performance, refer to **Temperature Effects**.
4. Measure 100 mL of each standard and sample into separate 150 mL beakers. Add 2 mL ISA to each beaker.

NOTE: Other solution volumes may be used, as long as the ratio of solution to ISA remains 50:1. Stir thoroughly.

5. Rinse electrode(s) with distilled water, blot dry and place into the beaker containing the most dilute standard. Wait for a stable reading, then calibrate the meter to display the value of the standard as described in the meter instruction manual.
6. Rinse electrode(s) with distilled water, blot dry, and place into the beaker with the next standard. Wait for a stable reading, then adjust the meter to display the value of this standard, as described in the meter instruction manual.
7. Repeat step 6 for all standards, working from the least concentrated to most concentrated standard.
8. Rinse electrode(s) with distilled water, blot dry, and place into sample. The concentration will be displayed on the meter.

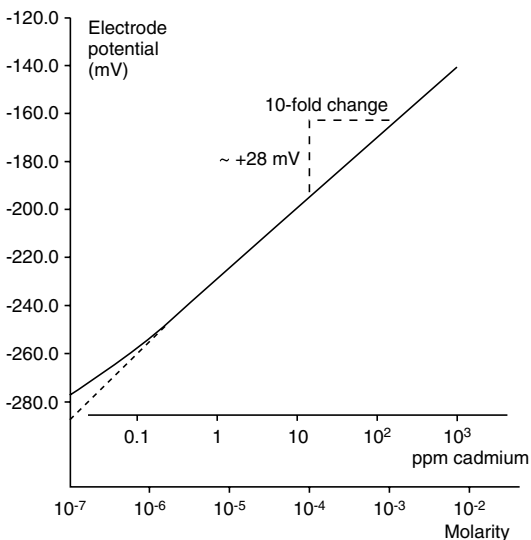


Figure 2: Typical Cadmium Calibration Curve

In the direct measurement procedure, a calibration curve is constructed on semi-logarithmic paper. Electrode potentials of standard solutions are measured and plotted on the linear axis against their concentrations on the log axis. In the linear regions of the curves, only two standards are needed to determine a calibration curve. In nonlinear regions, more points must be taken. The direct measurement procedures in this manual are given for concentrations in the region of linear electrode response. Low-level measurement procedures are given for measurements in the non-linear region. This curve is only used as an example. Actual mV values may differ.

Direct Measurement Procedure using a meter with mV readout

1. Prepare electrode(s) as described in **Electrode Preparation**.
2. Connect electrode(s) to the meter, and adjust the meter to measure mV.
3. Prepare two standards that bracket the expected sample range and differ in concentration by a factor of ten. Standards can be prepared in any concentration unit to suit the particular analysis requirement. All standards should be at the same temperature as the samples. For details on temperature effects on electrode performance, refer to **Temperature Effects**.
4. Measure 100 mL of each standard and sample into separate 150 mL beakers. Add 2 mL ISA to each beaker.

NOTE: Other solution volumes may be used, as long as the ratio of solution to ISA remains 50:1. Stir thoroughly.

5. Rinse electrode(s) with distilled water, blot dry and place into the beaker containing the most dilute standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
6. Rinse electrode(s) with distilled water, blot dry, and place into the beaker with the next standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
7. Repeat step 6 for all standards, working from the least concentrated to most concentrated standard.
8. Using semi-logarithmic graph paper, prepare a calibration curve by plotting the millivolt values on the linear axis and the standard concentration values on the logarithmic axis. See **Figure 2**.
9. Rinse electrode(s) with distilled water, blot dry, and place into sample. When a stable reading is displayed, record the mV value.
10. Using the calibration curve prepared in step 8, determine the unknown sample concentration.

Low-Level Measurements

These procedures are for solutions with a cadmium concentration of less than 1.13 ppm or 10^{-5} M Cd^{2+} , those within the non-linear range of the cadmium electrode. See **Figure 2**. In low-level measurements, at least three standards are required for calibration to compensate for the electrode's non-linearity.

Measuring Hints

- Use plastic labware for low-level cadmium measurements.
- For solutions low in cadmium but high in total ionic strength (greater than 10^{-1} M), perform the same procedure as described below, with one change: prepare a calibration solution with a composition similar to the sample.
- The choice of standard concentrations is important for obtaining the best electrode performance and most rapid analysis time. Here are some guidelines:
 - Ideally, standard concentrations should bracket the expected sample concentrations.
 - When measuring sub-ppm levels with Orion 920A, 720A, 710A, or 290A, take advantage of the autoblack feature. It does not require a zero standard, but can perform blank correction as long as the lowest standard concentration is in the non-linear range of the electrode. Electrodes are very slow in the absence of a measurable concentration and a multipoint calibration generally will be less accurate when "zero" is included as a standard. Standard concentrations should be chosen such that the lowest standard value is larger than the blank value obtained, and the second lowest standard should be at least twice that of the lowest. See your A-Series meter instruction manual for additional information on blank correction.

- If using an ISE meter, such as the Orion EA940, that allows a blank solution value to be entered, it is recommended to do so. A blank solution is prepared with the same dilution water and ISA used when preparing calibration standards. This solution corrects for the curves non-linearity as well as for any background ion contamination that might be present in the standard solutions. When a blank value is entered, it represents the zero point of the curve, and each standard is measured against that blank.
- When not using an ISE meter, a calibration curve can be drawn on semi-logarithmic graph paper, or the data can be processed at the discretion of the user by means of a spreadsheet or graphing program with a non-linear curve fitting feature.
- When using an ISE meter, such as the Orion 920A, 720A, 710A, or 290A, three calibration points are sufficient. If a calibration curve is prepared manually, additional points may be helpful to facilitate drawing the curve.
- Remember to stir all standards and samples at a uniform rate.
- Typical response time for this electrode is approximately 1 minute. Low-level measurements may take longer to stabilize. Wait for 3 minutes or the meter's "ready" signal, whichever takes longer, before calibrating the meter or recording the sample value.
- Review section entitled **GLP Measuring Hints**.

Low-Level Measurement Procedure using ISE Meter

Follow the above procedure entitled **Direct Measurement Procedure using ISE Meter** except substitute low-level ISA. Use at least three calibration standards. Read the **Measuring Hints** section in order to select appropriate standard concentrations. Refer to the meter instruction manual for detailed calibration procedures. If not using an Orion 920A, 720A, 710A, or 290A with the autoblack feature, preparation of a blank solution is recommended to ensure accurate results.

Low-Level Measurement Procedure using a meter with mV readout (see Table 2)

Set Up

1. Prepare electrode(s) as described in Electrode Preparation.
2. Connect electrode(s) to the meter. Set the meter to read mV.
3. Select a standard solution. Use either a 10 ppm cadmium standard or a 10^{-4} M cadmium solution.

To prepare 10 ppm from the 1000 ppm cadmium standard, dilute 10 mL of the 1000 ppm standard to 1 liter with distilled water

To prepare 10^{-4} M from 0.1 M cadmium standard, dilute 1 mL 0.1 M standard to 1 liter with distilled water.

4. Prepare a low-level ISA solution by diluting 20 mL of the cadmium ionic strength adjustor, Orion 940011, to 100 mL with distilled water.

NOTE: use this low-level ISA for low-level measurements only.

Measurement

1. Measure 100 mL distilled water into 150 mL beaker. Add 1 mL low-level ISA.
2. Rinse electrode(s) with distilled water, blot dry, and place into beaker. Stir thoroughly.
3. Add increments of the 10 ppm or 10^{-4} M standard to the beaker using steps outlined in **Table 2**. Record stable millivolt reading after each increment. On semi-logarithmic paper, plot the concentration (log axis) against the millivolt potential (linear axis). See **Figure 2**. Prepare a new calibration curve with fresh standards each day.
4. Measure 100 mL of sample into a beaker. Add 1 mL low-level ISA. Rinse the electrode(s) with distilled water, blot dry, and place into the sample.
5. Stir thoroughly. When a stable reading is displayed, record the mV value.
6. Determine the sample concentration corresponding to the measured potential from the low-level calibration curve.

Table 2**Preparing a Calibration Curve For Low-Level Measurements making 10 ppm cadmium additions:**

Step	Graduated	Added Volume	Concentration ppm
	Pipet Size		
1	1 mL	0.1 mL	0.01
2	1 mL	0.3 mL	0.04
3	1 mL	0.6 mL	0.10
4	2 mL	2.0 mL	0.30

Preparing a Calibration Curve For Low-Level Measurements making 10^{-4} M cadmium additions:

Step	Graduated	Added Volume	Concentration ppm
	Pipet Size		
1	1 mL	0.1 mL	1.0×10^{-7}
2	1 mL	0.3 mL	4.0×10^{-7}
3	1 mL	0.6 mL	1.0×10^{-6}
4	2 mL	2.0 mL	3.0×10^{-6}

Additions of 10 ppm or 10^{-4} M standard to 100 mL distilled water, plus 1 mL low-level ISA

Known Addition

Known addition is a convenient technique for measuring samples in the linear range, greater than 1 ppm Cd^{2+} , because no calibration curve is needed. The sample potential is measured before and after addition of a standard solution. Many meters, such as the Orion 920A, have the known addition algorithms preprogrammed. This programming allows multiple standard additions to be made to the sample, thereby allowing the meter to calculate the electrode slope as well. Having the ability to read the sample concentration directly from the meter is a great convenience and ensures accuracy.

Measuring Hints

- Sample concentration should be known within a factor of three.
- Concentration should approximately double as a result of the first standard addition.
- With double or multiple known addition, the final addition should be 10 to 100 times the sample concentration.
- In general, either no complexing agent or a large excess of the complexing agent may be present.
- The ratio of the uncomplexed ion to complexed ion must not be changed by addition of the standard.
- All samples and standards should be at the same temperature.
- Add 2 mL ISA to every 100 mL of sample before analysis.
- Standard addition volume should be no more than 10% of the sample volume, or the standard should be pre-treated with ISA in a 50:1 ratio. See **Table 3**.
- Review section entitled **GLP Measuring Hints**.

Set-up

1. Prepare electrode(s) as described in **Electrode Preparation**.
2. Connect electrode(s) to the meter.
3. Prepare a standard solution that, upon addition to the sample, will cause the concentration of cadmium to double. Refer to **Table 3** as a guideline.
4. Determine the slope of the electrode by performing the procedure under **Checking Electrode Operation (Slope)**.

Known Addition Measurement Procedure using an ISE meter with KA program

See individual meter instruction manual for more specific information.

1. Set the meter to measure in the known addition mode.
2. Measure 100 mL of sample into a beaker. Add 2 mL ISA. Stir thoroughly. Rinse electrode(s) with distilled water, blot dry, and place in sample solution.
3. When a stable reading is displayed, program the meter as described in the meter instruction manual.
4. Pipet the appropriate amount of standard solution into the beaker. Stir thoroughly.
5. When a stable reading is displayed, record the sample concentration.

Table 3
Standard Addition volumes

Volume of Addition	Concentration of Standard
1 mL	100 x sample concentration
5 mL	20 x sample concentration
10 mL*	10 x sample concentration

* Most convenient volume to use.

Known Addition Measurement Procedure using a meter with mV readout

1. Set the meter to millivolt mode.
2. Measure 100 mL of the sample into a 150 mL beaker. Add 2 mL ISA. Stir thoroughly.
3. Rinse electrode(s) with distilled water, blot dry, and place into beaker. When a stable reading is displayed, record the mV value as E_1 .
4. Pipet the appropriate amount of standard solution into the beaker. See **Table 3**. Stir thoroughly.
5. When a stable reading is displayed, record the mV value as E_2 . Subtract the first reading from the second to find ΔE .
6. From Table 5, find the value Q, that corresponds to the change in potential, ΔE . To determine the original sample concentration, multiply Q by the concentration of the added standard:

$$C_{\text{sam}} = Q \cdot C_{\text{std}}$$

where:

C_{std} = standard concentration

C_{sam} = sample concentration

Q = reading from known addition table

The table of Q values is calculated for a 10% volume change for electrodes with slopes 28, 29, 29.6, 30 mV/decade for cadmium. The equation for the calculation of Q for different slopes and volume changes is given below:

$$Q = \frac{p \cdot r}{(1+p)(10^{\Delta E/S})-1}$$

where:

Q = reading from known addition table

ΔE = $E_2 - E_1$

S = slope of the electrode

p = (volume of standard)/(volume of sample & ISA)

r = (volume of sample & ISA) / (volume of sample)

If it is more convenient, a simple spreadsheet can be set up to calculate known addition results, using any ratio of sample to addition. A typical worksheet is shown in **Table 4**. The numbers shown are examples, but the formulas and their locations should be copied exactly.

Table 4

Calculating known addition for cadmium samples using Lotus, Excel, or Quattro Spreadsheet

A	B	C
1		Enter Value
2	Vol. of Sample & ISA, mL:	102
3	Vol. of Addition, mL:	10
4	Concentrn. of Addition:	10
5	Vol. of Sample	100
6	Initial mV Reading	45.3
7	Final mV Reading	63.7
8	Electrode Slope	28.2
9		
10		Derived Values
11	Delta E	+C7 - C6
12	Solution Vol. Ratio	+C3/C2
13	Antilog Term	+10 [^] (C11/C8)
14	Sample Vol. Ratio	+C2/C5
15	Q Term	+C12*C14/{[(1 + C12)*C13]-1}
16	Calculated Initial Conc. in same unit as addition:	+C15*C4

NOTE: for Excel, use = instead of + at start of formula

Table 5 Known Addition Table for an added volume one-tenth the total volume. Slopes, in the column headings, are in units of mV/decade.

ΔE	Q, Concentration Ratio (slope)			
	28.6	29.1	29.6	30.1
Divalent				
2.5	0.2917	0.2957	0.2996	0.3035
2.6	0.2827	0.2867	0.2906	0.2944
2.7	0.2742	0.2781	0.2820	0.2858
2.8	0.2662	0.2700	0.2738	0.2775
2.9	0.2585	0.2623	0.2660	0.2697
3.0	0.2512	0.2550	0.2586	0.2623
3.1	0.2443	0.2480	0.2516	0.2552
3.2	0.2377	0.2413	0.2449	0.2484
3.3	0.2314	0.2349	0.2384	0.2419
3.4	0.2253	0.2288	0.2323	0.2357
3.5	0.2196	0.2230	0.2264	0.2298
3.6	0.2140	0.2174	0.2208	0.2241
3.7	0.2087	0.2121	0.2154	0.2187
3.8	0.2037	0.2070	0.2102	0.2135
3.9	0.1988	0.2020	0.2052	0.2084
4.0	0.1941	0.1973	0.2005	0.2036
4.1	0.1896	0.1927	0.1959	0.1990
4.2	0.1852	0.1884	0.1914	0.1945
4.3	0.1811	0.1841	0.1872	0.1902
4.4	0.1770	0.1801	0.1831	0.1861
4.5	0.1732	0.1762	0.1791	0.1821
4.6	0.1694	0.1724	0.1753	0.1782
4.7	0.1658	0.1687	0.1716	0.1745
4.8	0.1623	0.1652	0.1680	0.1709
4.9	0.1590	0.1618	0.1646	0.1674
5.0	0.1557	0.1585	0.1613	0.1640
5.1	0.1525	0.1553	0.1580	0.1608
5.2	0.1495	0.1522	0.1549	0.1576
5.3	0.1465	0.1492	0.1519	0.1546
5.4	0.1437	0.1463	0.1490	0.1516
5.5	0.1409	0.1435	0.1461	0.1487
5.6	0.1382	0.1408	0.1434	0.1459
5.7	0.1356	0.1382	0.1407	0.1432
5.8	0.1331	0.1356	0.1381	0.1406
5.9	0.1306	0.1331	0.1356	0.1381
6.0	0.1282	0.1307	0.1331	0.1356
6.1	0.1259	0.1283	0.1308	0.1332
6.2	0.1236	0.1260	0.1284	0.1308
6.3	0.1214	0.1238	0.1262	0.1285
6.4	0.1193	0.1217	0.1240	0.1263
6.5	0.1172	0.1195	0.1219	0.1242
6.6	0.1152	0.1175	0.1198	0.1221
6.7	0.1132	0.1155	0.1178	0.1200
6.8	0.1113	0.1136	0.1158	0.1180
6.9	0.1094	0.1117	0.1139	0.1161
7.0	0.1076	0.1098	0.1120	0.1142
7.1	0.1058	0.1080	0.1102	0.1123
7.2	0.1041	0.1063	0.1084	0.1105
7.3	0.1024	0.1045	0.1067	0.1088
7.4	0.1008	0.1029	0.1050	0.1071

ΔE	Q, Concentration Ratio			
		(slope)		
Divalent	28.6	29.1	29.6	30.1
7.5	0.0992	0.1012	0.1033	0.1054
7.8	0.0946	0.0966	0.0986	0.1006
8.0	0.0917	0.0936	0.0956	0.0976
8.3	0.0876	0.0895	0.0914	0.0933
8.5	0.0850	0.0869	0.0887	0.0906
8.8	0.0813	0.0831	0.0849	0.0868
9.0	0.0790	0.0808	0.0825	0.0843
9.3	0.0757	0.0774	0.0791	0.0809
9.5	0.0736	0.0753	0.0770	0.0787
9.8	0.0706	0.0722	0.0739	0.0755
10.0	0.0687	0.0703	0.0719	0.0735
10.3	0.0660	0.0675	0.0691	0.0707
10.5	0.0642	0.0658	0.0673	0.0689
10.8	0.0617	0.0633	0.0648	0.0663
11.0	0.0602	0.0617	0.0631	0.0646
11.3	0.0579	0.0593	0.0608	0.0623
11.5	0.0564	0.0579	0.0593	0.0607
11.8	0.0544	0.0558	0.0572	0.0585
12.0	0.0530	0.0544	0.0558	0.0572
12.3	0.0511	0.0525	0.0538	0.0551
12.5	0.0499	0.0512	0.0525	0.0539
12.8	0.0481	0.0494	0.0507	0.0520
13.0	0.0470	0.0483	0.0495	0.0508
13.3	0.0454	0.0466	0.0478	0.0491
13.5	0.0443	0.0455	0.0468	0.0480
13.8	0.0428	0.0440	0.0452	0.0464
14.0	0.0419	0.0430	0.0442	0.0454
14.3	0.0404	0.0416	0.0427	0.0439
14.5	0.0395	0.0407	0.0418	0.0429
14.8	0.0382	0.0393	0.0404	0.0416
15.0	0.0374	0.0385	0.0396	0.0407
15.5	0.0354	0.0365	0.0375	0.0386
16.0	0.0335	0.0345	0.0356	0.0366
16.5	0.0318	0.0328	0.0337	0.0347
17.0	0.0302	0.0311	0.0320	0.0330
17.5	0.0286	0.0295	0.0305	0.0314
18.0	0.0272	0.0281	0.0290	0.0298
18.5	0.0258	0.0267	0.0275	0.0284
19.0	0.0246	0.0254	0.0262	0.0270
19.5	0.0234	0.0242	0.0250	0.0258
20.0	0.0223	0.0230	0.0238	0.0246
20.5	0.0212	0.0219	0.0227	0.0234
21.0	0.0202	0.0209	0.0216	0.0224
21.5	0.0192	0.0199	0.0206	0.0213
22.0	0.0183	0.0190	0.0197	0.0204
22.5	0.0175	0.0181	0.0188	0.0195
23.0	0.0167	0.0173	0.0179	0.0186
23.5	0.0159	0.0165	0.0171	0.0178
24.0	0.0152	0.0158	0.0164	0.0170
24.5	0.0145	0.0151	0.0157	0.0162

ΔE	Q, Concentration Ratio (slope)				
	Divalent	28.6	29.1	29.6	30.1
25.0		0.0139	0.0144	0.0150	0.0155
25.5		0.0132	0.0138	0.0143	0.0149
26.0		0.0126	0.0132	0.0137	0.0142
26.5		0.0121	0.0126	0.0131	0.0136
27.0		0.0116	0.0120	0.0125	0.0131
27.5		0.0110	0.0115	0.0120	0.0125
28.0		0.0106	0.0110	0.0115	0.0120
28.5		0.0101	0.0106	0.0110	0.0115
29.0		0.0097	0.0101	0.0105	0.0110
29.5		0.0093	0.0097	0.0101	0.0105
30.5		0.0085	0.0089	0.0093	0.0097
31.5		0.0078	0.0081	0.0085	0.0089
32.0		0.0074	0.0078	0.0082	0.0085
32.5		0.0071	0.0075	0.0078	0.0082
33.0		0.0068	0.0072	0.0075	0.0079
33.5		0.0065	0.0069	0.0072	0.0076
34.0		0.0063	0.0066	0.0069	0.0072
34.5		0.0060	0.0063	0.0066	0.0070
35.0		0.0058	0.0061	0.0064	0.0067
35.5		0.0055	0.0058	0.0061	0.0064
36.0		0.0053	0.0056	0.0059	0.0062
36.5		0.0051	0.0053	0.0056	0.0059
37.0		0.0049	0.0051	0.0054	0.0057
37.5		0.0047	0.0049	0.0052	0.0055
38.0		0.0045	0.0047	0.0050	0.0052
38.5		0.0043	0.0045	0.0048	0.0050
39.0		0.0041	0.0043	0.0046	0.0048
39.5		0.0039	0.0042	0.0044	0.0046
40.0		0.0038	0.0040	0.0042	0.0045
40.5		0.0036	0.0038	0.0041	0.0043
41.0		0.0035	0.0037	0.0039	0.0041
41.5		0.0033	0.0035	0.0037	0.0040
42.0		0.0032	0.0034	0.0036	0.0038
42.5		0.0031	0.0033	0.0035	0.0037
43.0		0.0029	0.0031	0.0033	0.0035
43.5		0.0028	0.0030	0.0032	0.0034
44.0		0.0027	0.0029	0.0031	0.0032
44.5		0.0026	0.0028	0.0029	0.0031
45.0		0.0025	0.0027	0.0028	0.0030
45.5		0.0024	0.0026	0.0027	0.0029
46.0		0.0023	0.0024	0.0026	0.0028

Cadmium Titration

The electrode makes a highly sensitive endpoint detector for titration with EDTA of cadmium samples. Titrations are more time consuming than direct electrode measurement, but results are more accurate and reproducible. With careful technique, titrations accurate to $\pm 0.1\%$ of the total cadmium ion concentration of the sample can be performed. The Orion 960 Autochemistry System may be used to automate these titrations.

EDTA complexes other cations besides cadmium ion. Interferences from other ions, whose EDTA complexes are stable only at low pH, can be eliminated by performing the titration for cadmium ion at a high pH, about pH 10 (adjusted with ammonia). In many cases, other interferences can be eliminated by a suitable choice of sample pH and the addition of masking agents to the sample solution. A comprehensive list of methods is given in: Handbook of Analytical Chemistry, L. Meites, (ed.) McGraw Hill Book Co., New York, (1st edit.), pp. 3-76, 3-225.

Set-up

1. Prepare electrode(s) as described in Electrode Preparation.
2. Connect electrodes to the meter.
3. Prepare an EDTA titrant solution 10 - 20 times as concentrated as the sample by dilution of the 1 M stock solution. For a good endpoint break, the sample concentration should be at least 10^{-4} M in total cadmium.

Measurement

1. Place 50 mL of sample into a 150 mL beaker and adjust the pH of the sample to about pH 10 with NH_4OH . Place electrode(s) in the sample. Stir thoroughly.
2. Using a 10 mL burette, add increments of titrant and plot electrode potential against mL of titrant added. The end point is the point of greatest slope (inflection point). See **Figure 3**.
3. Calculate the sample concentration before dilution:

$$C_{\text{sam}} = C_t (V_t/V_{\text{sam}})$$

where:

C_{sam} = sample concentration

C_t = titrant concentration

V_{sam} = sample volume

V_t = titrant volume added at endpoint.

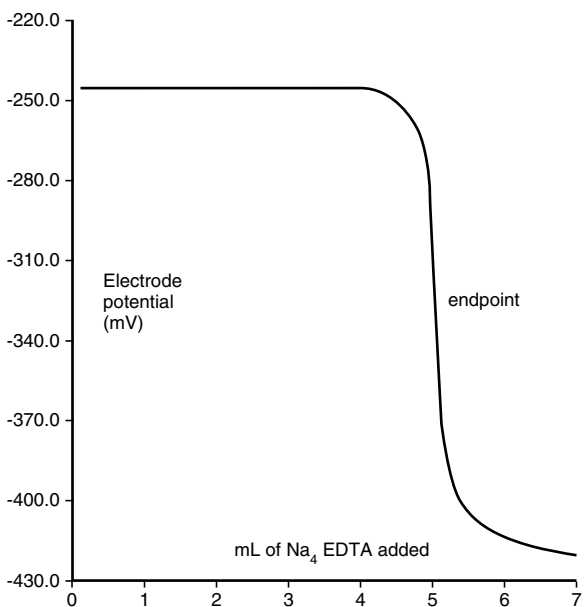


Figure 3: Typical Titration of 100 mL of 5×10^{-3} M $\text{Cd}(\text{NO}_3)_2$ (pH Adjusted to ~10 with Ammonia) with 0.1 M Na_4EDTA

Indicator Titrations

The cadmium electrode can be substituted for the cupric electrode to detect the end point in titrations of other metal ions. A small amount of cadmium complex is added to the sample, and a complexometric titration is done. The end point volume of titrant is used to calculate the sample concentration. The minimum level of sample ion that can be determined by indicator titration is above 10^{-4} M. Titrations of barium, calcium, cobalt (+2), magnesium, manganese (+2), nickel, and strontium are possible. For more information refer to *Chelometric Indicator Titrations with the Solid-State Cupric Ion Selective Electrode*, Ross J.W., and Frant, M.S.; *Anal. Chem.*, 1969 41(13), 1900.

ELECTRODE STORAGE

Orion 94-48 Cadmium Half-Cell Electrode

The Orion 94-48 Cadmium Half-Cell Electrode should be rinsed thoroughly and stored in distilled water or in the air at all times. When storing for long periods of time, replace the cap to protect the sensing element and store dry.

Orion 96-48 Sure-Flow Combination Cadmium Electrode

The solution in the Orion 96-48 Combination Cadmium Electrode should not be allowed to evaporate, causing crystallization.

For short periods of time (up to one week):

Store the electrode in distilled water.

For storage longer than one week:

Drain the electrode, flush the inside with distilled water and store dry with the cap on to protect the sensing element.

Orion 90-02 Double Junction Reference Electrode

The Orion 90-02 Reference Electrode may be stored in air between sample measurements (up to two hours).

For short periods of time (up to one week):

90-02 should be stored in filling solution. Distilled water is also an acceptable storage solution. The solutions inside the electrode should not be allowed to evaporate causing crystallization.

For storage longer than one week:

Drain both chambers of the reference electrode, flush the inside with distilled water, and store dry.

ELECTRODE MAINTENANCE

Cadmium Electrode Cleaning Procedure

Place a drop of liquid dish detergent on a moist cloth or tissue and gently rub over the sensing element. Rinse with distilled water.

Cadmium Electrode Polishing Procedure

To be used when electrode becomes sluggish or drifts and above cleaning procedure does not improve electrode response.

1. Cut off a 1-inch length of the polishing strip, Orion 948201
2. Hold electrode with the sensing element facing upwards.
3. Place a few drops of distilled water on the sensing element surface.
4. With the frosted side down, place the polishing strip on the sensing element using light finger pressure.
5. Rotate the electrode for about 30 seconds.
6. Rinse and soak in a 1 ppm or 10^{-5} M cadmium standard solution for about two minutes before use.

Disassembly And Cleaning of 96-48 Sure-Flow Combination Cadmium Electrode

Disassembly is not normally required or recommended. When the area between the electrode sleeve and inner cone becomes clogged with sample or precipitate from filling solution, the chamber can be cleaned by flushing out with filling solution. (Hold the electrode by the cap with one hand and push the outer sleeve of the electrode up into the cap to drain the chamber.) If the chamber is not completely clean, repeat the procedure. Refill with the appropriate filling solution.

If a more thorough cleaning is required, the electrode can be disassembled using the following instructions:

1. Rinse the outer body under warm running water.
2. Hold the electrode body by the cap with one hand and push the outer sleeve of the electrode up into the cap to drain the chamber.
3. Unscrew the cap, slide the cap and epoxy-coated spring up along the cable.
4. Hold the outer sleeve with one hand and firmly push down on the threaded portion with the thumb and forefinger to separate the inner body from the sleeve.
5. Grasp the cone with a clean tissue and withdraw the body from the sleeve with a gentle twisting motion. Note: Do not touch the AgCl pellet above the cone as it may cause damage to the pellet. Rinse the outside of the electrode body and the entire sleeve with distilled water. Allow to air dry.

Reassemble

1. Moisten the O-ring on the electrode body with a drop of filling solution. Insert screw-thread end of the electrode body into the tapered, ground end of sleeve.
2. Push body into sleeve with a gentle twisting motion until bottom surface of inner cone is flush with the tapered end of the sleeve.
3. Place the spring on the electrode body and screw on the cap. Refill with filling solution. The electrode is now ready for use.

TROUBLESHOOTING

Troubleshooting Checklist

Symptom	Possible Causes
Off-scale or Over-range reading	Defective meter Defective electrode Electrodes not plugged in properly Reference electrode junction is dry Reference electrode chamber not filled Air bubble on electrode Electrodes not in solution
Noisy or unstable readings (readings continuously or rapidly changing)	Defective meter Meter or stirrer improperly grounded Air bubble on electrode or rapidly Wrong reference electrode changing)ISA not used
Drift (Reading slowly changing in one direction)	Samples and standards at different temperatures Sensing element dirty or etched Incorrect reference filling solution
Low slope or No slope	Electrodes not properly conditioned Standards contaminated or incorrectly made ISA not used Standard used as ISA Electrode exposed to interferences
“Wrong Answer” (But calibration curve is OK)	Incorrect scaling of semilog paper Incorrect sign Incorrect standards Wrong units used Complexing agents in sample

Solution

Check meter with shorting strap (See meter instruction manual)

Refer to **Troubleshooting Guide**

Unplug electrodes and reset

Hold reference electrode and push cap to expel a few drops of filling solution

Be sure reference electrode chamber is filled. See **Electrode Preparation**

Remove air bubble on electrode by gently tapping it

Put electrodes in solution

Check meter with shorting strap (See meter instruction manual)

Check meter and stirrer for grounding

Check **Using the Electrode**

Remove air bubble on electrode by gently tapping it

Use appropriate reference electrode. See **Required Equipment**

Do not use calomel or Ag/AgCl (frit-or fiber-type) reference electrode

Use recommended ISA, Orion 940011

Allow solutions to come to room temperature before measurement

Polish sensing element (see **Electrode Maintenance**)

Use recommended filling solution. See **Required Solutions**

Prepare fresh standards

Use recommended ISA, Orion 940011

Use ISA!

Refer to **Troubleshooting Guide**

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 value correctly

Prepare fresh standards

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

Use known addition or titration techniques, or a decomplexing procedure

For additional information on blank correction with your A-Series meter, see your meter operations manual.

Troubleshooting Guide

The most important principle in troubleshooting is to isolate the components of the system and check each in turn. The components of the system are: 1) Meter 2) Electrodes 3) Standard 4) Sample and 5) Technique.

See also **GLP Measuring Hints** section.

Meter

The meter is the easiest component to eliminate as a possible cause of error. Orion meters are provided with an instrument checkout procedure in the instruction manual and a shorting cap for convenience in troubleshooting. Consult the manual for complete instructions and verify that the instrument operates as indicated and is stable in all steps.

Electrodes

1. Rinse electrode(s) thoroughly with distilled water.
2. Determine electrode slope. See **Check Electrode Operation**.
3. If electrode fails this procedure, prepare electrode(s) as directed in Electrode Preparation. Clean electrode(s) as described in Electrode Maintenance.
4. Repeat step 2, Checking Electrode Operation.
- 5a. For the 94-48 Cadmium Half-Cell Electrode:
If the electrodes still do not perform as described, determine whether the cadmium or reference electrode is at fault. To do this, substitute a known working electrode for the electrode in question and repeat the slope check.
- 5b. For the 96-48 Sure-Flow Combination Cadmium Electrode:
If the electrode still does not perform as described replace the electrode.
6. If the stability and slope check out properly, but measurement problems persist, the sample may contain interferences or complexing agents, or the technique may be in error. See **Standard, Sample, and Technique** sections.

7. Before replacing a “faulty” electrode, or if another electrode is not available for test purposes, review the instruction manual and be sure to:
- Clean the electrode thoroughly
 - Prepare the electrode properly
 - Use proper filling solution, ISA, and standards
 - Measure correctly
 - Review **Troubleshooting Checklist**

Standard

The quality of results depends greatly upon the quality of the standards. ALWAYS prepare fresh standards when problems arise – it could save hours of frustrating troubleshooting! Error may result from contamination of prepared standards, quality distilled water, or a numerical error in calculating the concentrations.

The best method for preparation of standards is by serial dilution. This means that an initial standard is diluted, using volumetric glassware, to prepare a second standard solution. The second is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.

Sample

If the electrodes work properly in standards but not in sample, look for possible interferences, complexing agents, or substances that could affect response or physically damage the sensing electrode or the reference electrode. If possible, determine the composition of the samples and check for problems. See **Sample Requirements**, **Interferences**, and **pH Requirements**.

Technique

Check the method of analysis for compatibility with your sample. Direct measurement may not always be the method of choice. If a large amount of complexing agents is present, or if the sample has a high ionic strength, known addition may be best. If working at low levels, be sure to follow the low-level measurement technique. Also, be sure that the expected concentration of the ion of interest is within the electrode’s limits of detection. If problems persist, review operational procedures and instruction manuals to be sure that proper technique has been followed. Read **Measuring Hints**, **Analytical Procedures**, and **Electrode Characteristics**.

Assistance

For the most current warranty information, visit www.thermo.com.

After troubleshooting all components of your measurement system, contact The Technical EdgeSM for Orion products. Within the United States call 1.800.225.1480, outside the United States call 978.232.6000 or fax 978.232.6031. In Europe, the Middle East and Africa, contact your local authorized dealer. For the most current contact information, visit www.thermo.com.

ELECTRODE CHARACTERISTICS

Electrode Response

The electrode potential plotted against cadmium concentration on semi-logarithmic paper results in a straight line until concentration reaches 10^{-6} M, with a slope of about (+) 25 to 30 mV per decade (see **Figure 4**). The electrode exhibits good time response (99% response to one minute or less) for concentrations above 10^{-6} M. Below this value response times vary from 2 to 5 minutes.

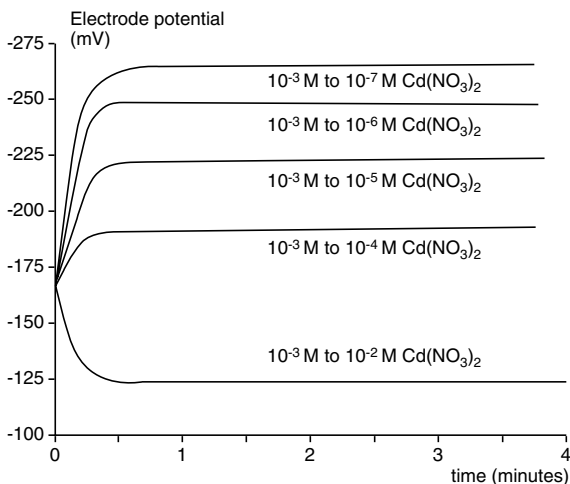


Figure 4: Typical Electrode Response to Step Changes in $\text{Cd}(\text{NO}_3)_2$ Concentration

Reproducibility

Reproducibility is limited by factors such as temperature fluctuations, drift and noise. Within the electrode operating range, reproducibility is independent of concentration. With calibration every hour, direct electrode measurements reproducible to $\pm 4\%$ can be obtained.

Temperature Effects

Since the electrode potentials are affected by changes in temperature, samples and standard solutions should be within $\pm 1\text{ }^{\circ}\text{C}$ ($\pm 2\text{ }^{\circ}\text{F}$) of each other. At the 10^{-3} M level, a $1\text{ }^{\circ}\text{C}$ difference in temperature results in a 4% error. The absolute potential of the reference electrode changes slowly with temperature because of the solubility equilibria on which the electrode depends. The slope of the electrode also varies with temperature, as indicated by the “S” in the Nernst equation, see **Theory of Operation**. Theoretical values of the slope at different temperatures are given in **Table 6**. If temperature changes occur, meter and electrodes should be recalibrated.

The electrode can be used at temperatures from 0° to $100\text{ }^{\circ}\text{C}$, provided that temperature equilibrium has occurred. For use at temperatures substantially different from room temperature, calibration standards should be at the same temperature as samples. The electrode should be used only intermittently at temperatures above $80\text{ }^{\circ}\text{C}$.

Table 6
Theoretical Values of Electrode Slope vs. Temperature

$^{\circ}\text{C}$	Slope (Cd^{2+})
0	27.1
10	28.1
20	29.1
25	29.6
30	30.1
40	31.1
50	32.1

If sample temperatures vary, use of the Orion 96-48 Sure-Flow Combination Cadmium Electrode is recommended. The Optimum Results™ A Filling Solution, provided with this electrode, will minimize junction potentials and provide optimum temperature and time response. Optimum Results A produces an isopotential point of $1.7 \times 10^{-3}\text{ M Cd}^{2+}$.

The isopotential point is the concentration at which the potential of the electrode does not vary with temperature. Since the isopotential point of this electrode is known, the Orion 96-48 may be used on meters that allow automatic temperature compensation for ISE, such as the Orion EA 940 and 920A. By programming in the isopotential point, and placing an ATC probe into the sample, any time the temperature changes, the meter will automatically adjust the slope of the calibration curve, resulting in more accurate measurement results.

Interferences

Mercury and silver ion poison the cadmium electrode sensing element and must be absent from the sample solution. Exposure to either of these species at levels greater than 10^{-7} M will require polishing of the electrode surface. Ferric ion affects the sensing element only if the ferric ion level is greater than one tenth of cadmium ion level (ferric ion can be eliminated from the sample simply by adding sodium fluoride and adjust to pH 4 - 6). Lead ion affects the membrane surface if the level of ion exceeds the level of cadmium ion present in sample. Copper ions may also be an interference.

If the electrode is exposed to high levels of interfering ions, it may become unstable and sluggish in response. When this happens, restore normal performance by polishing (see **Electrode Maintenance**).

pH Effects

The electrode response to cadmium ion in solutions at various pH is shown in Figure 5. Although the electrode can be used over a wide pH range, hydrogen ion interferes with measurements of low levels of cadmium ion. The edge of the shaded area to the left in **Figure 5** indicates the minimum pH at which low level cadmium measurements can be made without hydrogen ion interference.

At high solution pH, sufficient hydroxide ion is present to form a precipitate with a portion of the cadmium ion, reducing the level of free cadmium ion in the sample. As shown in **Figure 5**, $\text{Cd}(\text{OH})_2$ forms at a higher pH in dilute solutions than in concentrated solutions. Since the electrode responds only to free, unbound cadmium ion, it does not detect that portion of the cadmium precipitated by hydroxide ion. Precipitation can be avoided by adjusting the pH of sample and standards to below 7.

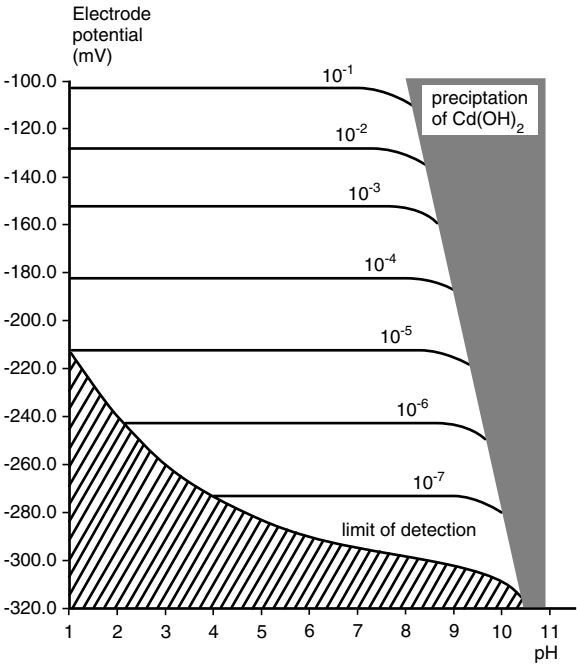


Figure 5: Electrode Potential Behavior vs. Solution pH in Pure Cd(NO₃)₂ Solutions at 25 °C

Complexation

Cadmium forms complexes with a wide variety of species including acetate, ammonia, bromide, chloride, citrate, cyanide, and EDTA. The extent of complexation depends on the concentration of cadmium and complexing agent, and pH. Since the electrode only responds to free cadmium ions, complexation reduces the measured concentration. In a large excess (50 to 100 times) of a complexing agent, total cadmium concentration can be measured by known addition.

Soluble cadmium salts are precipitated by sulfide, carbonate, oxalate, phosphate, hydroxide, and other ions. The formation of a precipitate depends on the level of cadmium ion, the level of the precipitating ion in the sample solution, and the solution pH.

Theory of Operation

The cadmium electrode includes a cadmium sensing element bonded into an epoxy body. When the sensing element is in contact with a solution containing cadmium ions an electrode potential develops across the sensing element. This potential, which depends on the level of free cadmium ion in solution, is measured against a constant reference potential with a pH/mV meter or specific ion meter. The measured potential, corresponding to the level of cadmium ion in solution, is described by the Nernst equation:

$$E = E_0 + S \log (A)$$

where:

E = measured electrode potential

E₀ = reference potential (a constant)

A = level of cadmium ion in solution

S = electrode slope (about 28 mV per decade for cadmium)

$$S = \frac{2.3 R T nF}{nF}$$

where:

R & F are constants

T = temperature degrees K

n = ionic charge

The ionic level, A, is the activity or “effective concentration”. The cadmium ion activity is related to free-ion concentration, C_i, by the activity coefficient, y:

$$A = y \cdot C_i$$

Ionic activity coefficients are variable and largely depend on total ionic strength. The ionic strength of a solution is determined by all of the ions present. It is calculated by multiplying the concentration of each individual ion by the square of its charge, adding all these values up, and then dividing by two.

Ionic strength is defined as:

$$I = 1/2 \sum (C_i Z_i^2)$$

where:

C_i = concentration of ion i

Z_i = charge of ion i

Σ = symbolizes the sum of all the types of ions in solution

If the background ionic strength is high and constant relative to the sensed-ion concentration, the activity coefficient is constant and activity is directly proportional to concentration. Ionic strength adjustor (ISA) is added to all standards and samples so that the background ionic strength is high and constant relative to variable concentrations of cadmium. For cadmium, the recommended ISA is NaNO_3 . Other solutions can be used as long as they do not contain ions that would interfere with the electrode's response to cadmium. If samples have a high ionic strength (above 0.1 M), standards should be prepared with a composition similar to the samples.

Reference electrode conditions must also be considered. Liquid-junction potentials arise any time two solutions of different composition are brought into contact. The potential results from the interdiffusion of ions in the two solutions. Since ions diffuse at different rates, electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions. In making electrode measurements, it is important that this potential be the same in the standardizing solution as in the sample solution; otherwise, the change in liquid-junction potential will appear as an error in the measured electrode potential.

Optimum Results™ filling solutions are specifically designed to meet all reference electrode conditions. The filling solution is equitransferent. Therefore, the speed with which the positive and negative ions in the filling solution diffuse into the sample is as nearly equal as possible. If the rate at which positive and negative charge is carried into the sample solution is equal, then minimum junction potential can result.

ORDERING INFORMATION

Orion	Description
9448BN	Cadmium Solid-State Epoxy Electrode, BNC Connector
944800	Cadmium Solid-State Epoxy Electrode, U.S. Std. Connector
9448SC	Cadmium Solid-State Epoxy Electrode, Screw Cap Connector. Requires separate cable
9648BN	Sure-Flow® Cadmium Combination Solid-State Epoxy Electrode, BNC Connector
964800	Sure-Flow Cadmium Combination Solid State Epoxy Electrode, U.S. Std. Connector
900200	Double-Junction Sure-Flow Reference Electrode
900002	Double-Junction, Inner Chamber Fill Solution, 5 x 60 mL bottle
900003	Double-Junction, Outer Chamber Fill Solution, 5 x 60 mL bottle
900061	Optimum Results™ A Filling Solution for 96-48 Combination Cadmium Electrode, 5 x 60 mL bottle
940011	ISA, 5M NaNO ₃ , 475 mL
948201	Polishing Strips, pk of twenty-four 6" strips

SPECIFICATIONS

Concentration Range:

10^{-7} to 0.1 M (0.01 to 11,200 ppm)

pH Range:

2 to 12 pH units

Temperature Range:

0 ° to 80 °C continuous use

80 ° to 100 °C intermittent use

Electrode Resistance:

Less than 1 megohm

Reproducibility:

± 4%

Size:

Electrode Length: 110 mm (excluding cap)

Diameter: For 94-48 12 mm

For 96-48 13 mm

Cap Diameter: 16 mm

Cable Length: 1 M

Environmental Instruments

Water Analysis

North America

166 Cummings Center
Beverly, MA 01915 USA
Tel: 978-232-6000
Dom. Fax: 978-232-6015
Int'l. Fax: 978-232-6031

Europe

12-16 Sedgeway Business Park
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Wanchai, Hong Kong
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