User Guide

Cadmium
Ion Selective
Electrode

Thermo
SCIENTIFIC

TABLE OF CONTENTS

GENERAL INFORMATION

Introduction

This user guide contains information on the preparation, operation and maintenance for the cadmium ion selective electrode (ISE). General analytical procedures, electrode characteristics and electrode theory are also included in this user guide. Cadmium electrodes measure free cadmium ions in aqueous solutions quickly, simply, accurately and economically.

Technical Support Chemists can be consulted for assistance and troubleshooting advice. Within the United States call 1.800.225.1480 and 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.

Cadmium ionplus® Sure-Flow® Solid State Combination ISE

The reference and sensing electrodes are built into one electrode, which decreases the amount of required solution and reduces waste. The built-in Sure-Flow reference junction prevents electrode clogging and provides fast and stabile readings. The cadmium ionplus combination ISE is available with a waterproof BNC connector, Cat. No. 9648BNWP.

Cadmium Solid State Half-Cell ISE

The cadmium half-cell electrode must be used with the double junction reference electrode, Cat. No. 900200. The cadmium half-cell is available with a BNC connector, Cat. No. 9448BN or a screw cap connector, Cat. No. 9448SC. Electrodes with a screw cap connector require a separate cable.

Required Equipment

Meter— Thermo Scientific Orion ISE meter, such as the 4-Star pH/ISE meter or 5-Star pH/ISE/DO/conductivity meter. Cadmium electrodes can be used on any ISE meter with a BNC or U.S. standard connection. The electrodes can also be used on meters with a variety of inputs when an adapter cable is used.

Reference Electrode— The 9448BN and 9448SC half-cell cadmium electrodes require the Thermo Scientific Orion double junction reference electrode, Cat. No. 900200. Use the outer chamber filling solution, Cat. No. 900003, and the inner chamber filling solution, Cat. No. 900002, that is supplied with the reference electrode.

Stirrer— Magnetic stirrer or stir probe, Cat. No. 096019. The stir probe can be used with 3-Star, 4-Star and 5-Star benchtop meters.

Labware— Volumetric flasks, graduated cylinders and beakers. Plastic labware is required for low-level cadmium measurements.

Polishing Strips— Cat. No. 948201, To clean the cadmium sensing element.

Required Solutions

Distilled or Deionized Water

Electrode Filling Solution
Use Optimum Results A filling solution with the 9648BNWP combination cadmium electrode.

Use the outer chamber filling solution, Cat. No. 900003, and the inner chamber filling solution, Cat. No. 900002, with the double junction reference electrode that is used with the 9448BN and 9448SC half-cell cadmium electrodes.

0.1 M or 1000 ppm Cadmium Standards– must be prepared by the customer

0.1 M $Cd(NO_3)_2 \cdot 4H_2O$ solution: In a 1 liter flask, place 30.8 g of reagent-grade cadmium nitrate. Dissolve the solid and dilute to volume with distilled water.

1000 ppm Cd^{2+} solution: Weigh out 2.74 g of reagent-grade cadmium nitrate in a 1 liter volumetric flask. Dissolve the solid and dilute to volume with distilled water.

EDTA Titrant– must be prepared by the customer

1 M EDTA stock solution: Place 38.0 g of reagent-grade Na_4EDTA in a 100 mL volumetric flask and dissolve in about 75 mL distilled water. Dilute to volume with distilled water.

Ionic Strength Adjustor (ISA)– Cat. No. 940011. Used to to adjust the ionic strength of samples and standards

BEFORE USING THE ELECTRODE

Electrode Preparation

9448BN and 9448SC Cadmium Half-Cell Electrode– Remove the protective shipping cap from the sensing element and save the cap for storage.

900200 Double Junction Reference Electrode– Prepare the reference electrode according to the reference electrode user guide. Fill the reference electrode with the outer chamber filling solution, Cat. No. 900003, and the inner chamber filling solution, Cat. No. 900002.

9648BNWP Cadmium Combination Electrode– Remove the protective shipping cap from the sensing element and save the cap for storage. Fill the electrode with Optimum Results A filling solution, Cat. No. 900061.

Note: Optimum Results A filling solution minimizes junction potential issues and contamination in the sample. The use of any other filling solution will void the electrode warranty.

Electrode Filling Instructions

1. Lift the flip spout on the filling solution bottle to a vertical position.

2. Insert the spout into the filling hole on the outer body of the electrode and add a small amount of filling solution to the reference chamber. Invert the electrode to moisten the top O-ring and then return the electrode to the upright position.

3. Hold the electrode body with one hand and use your thumb to push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.

4. Release the electrode cap. If the sleeve does not return to its original position, check if the O-ring is moist and repeat steps 2-4 until the sleeve returns to the original position.

5. Add filling solution to the electrode up to the filling hole.

Note: 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. The fill hole should always be open when taking measurements.

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. Refer to the meter user guide for more specific information.

1. If the electrode(s) have been stored dry, prepare the electrode(s) as described in the **Electrode Preparation** section.

2. Connect the electrode(s) to the meter as described in the meter user guide.

3. Place 100 mL of distilled water into a 150 mL beaker and add 2 mL of ISA, Cat. No. 940011. Stir the solution thoroughly.

4. Set the meter to the mV mode.

5. Rinse the electrode(s) with distilled water, blot dry, and place in the solution prepared in step 3.

6. Select either the 0.1 M or 1000 ppm cadmium standard. Pipette 1 mL of the standard into the beaker. Stir the solution thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.

7. Pipette 10 mL of the same standard into the same beaker. Stir the solution 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 to 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 ions 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 Support Chemists for use of the electrode in other organic solvents.

Samples and standards should be at the same temperature. A 1 ˚C difference in temperature will give rise to about a 4% error. Standard and sample temperatures 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 HNO_3 if necessary, but the hydrogen ion will interfere if the pH is too low . See the **pH Effects** section to determine the optimum pH working range for your sample.

GLP Measuring Hints

See **Figure 1**

- Stir all standards and samples at a uniform rate during measurements. 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 the electrode(s) with distilled water between measurements. Shake the electrode(s) after rinsing to prevent solution carryover. Blot the electrode(s) dry.

- Allow all standards and samples to come to the same temperature for precise measurements.

- The double junction reference electrode, Cat. No. 900200, should be submerged to the same depth as the half-cell cadmium electrode, Cat. No. 9448BN or 9448SC.

- 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 significantly.

- After immersing the electrode in solution, check the electrode for any air bubbles on the sensing element and remove air bubbles by gently tapping the electrode.

- For high ionic strength samples, prepare standards with a background composition similar to that of the sample.
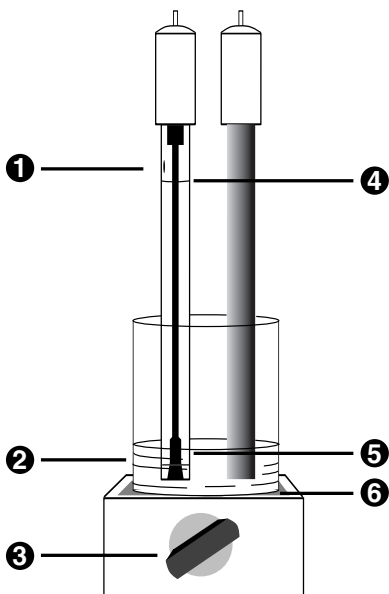
Figure 1: Measuring Hints

1. Filling hole should be uncovered (Cat. No. 900200 and 9648BNWP).

2. Use fresh standards.

3. Stir all samples and standards.

4. The filling solution level must be higher than sample level.

5. The reference junction must be immersed.

6. Place insulation between the 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 using 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, when samples have a high (> 0.1 M) ionic strength, or a complicated background matrix. Refer to the **Theory of Operation** section for an explanation of these effects. The electrode is 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.

- **Titrations** 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.

Cadmium Ion Selective Electrode User Guide

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, sample concentrations can be read directly from the meter. Refer to the meter user guide 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 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 standard.

- The best method for preparation of standards is 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 the **GLP Measuring Hints** section.

Direct Calibration Using a Meter with an ISE Mode

Note: See the meter user guide for more specific information.

1. Measure 100 mL of the less concentrated standard and 2 mL of ISA and pour into a 150 mL beaker. Stir the solution thoroughly.

2. Rinse the electrode(s) with distilled water, blot them dry and place the electrode(s) into the beaker with the less concentrated standard. Wait for a stable reading and then adjust the meter to display the value of the standard, as described in the meter user guide.

3. Measure 100 mL of the more concentrated standard and 2 mL of ISA and pour into a second 150 mL beaker. Stir the solution thoroughly.

4. Rinse the electrode(s) with distilled water, blot them dry and place the electrode(s) into the beaker with the more concentrated standard. Wait for a stable reading and then adjust the meter to display the value of the second standard, as described in the meter user guide.

5. Record the resulting slope value. The slope should be between 25 to 30 mV when the standards are between 20-25 °C.

6. Measure 100 mL of the sample and 2 mL of ISA and pour into a clean 150 mL beaker. Stir the solution thoroughly.

7. Rinse the electrodes with distilled water, blot them dry and place the electrodes into the sample. The concentration of the sample will be displayed on the meter.
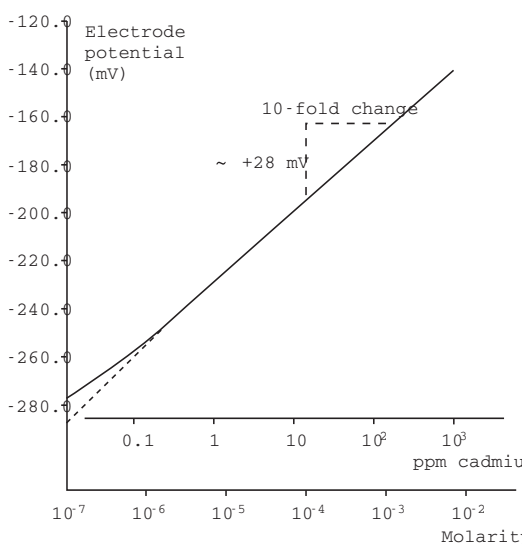
Figure 2: Typical Cadmium Calibration Curve

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 Calibration Using a Meter with a Millivolt Mode

1. Set the meter to the mV measuring mode.

2. Measure 100 mL of the less concentrated standard and 2 mL of ISA and pour into a 150 mL beaker. Stir the solution thoroughly.

3. Rinse the electrode(s) with distilled water, blot them dry and place the electrode(s) into the beaker with the less concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.

4. Measure 100 mL of the more concentrated standard and 2 mL of ISA and pour into a second 150 mL beaker. Stir the solution thoroughly.

5. Rinse the electrode(s) with distilled water, blot them dry and place the electrode(s) into the beaker with the more concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.

6. 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.

7. Measure 100 mL of the sample and 2 mL of ISA and pour into a clean 150 mL beaker. Stir the solution thoroughly.

8. Rinse the electrode(s) with distilled water, blot them dry and place the electrode(s) into the beaker. When a stable reading is displayed, record the mV value.

9. Using the calibration curve prepared in step 6, determine the unknown concentration of the sample.

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-linear response.

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 background 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 a Thermo Scientific Orion meter, use the blank correction 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 of the ion of interest and a multipoint calibration generally will be less accurate when a zero point is included as a standard. Standard concentrations should be selected 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. Refer to the meter user guide for additional information on blank correction.

- If using an ISE meter 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 using a mV meter, a calibration curve can be drawn on semi-logarithmic graph paper, or the data can be processed using a spreadsheet or graphing program with a non-linear curve fitting feature.

- Three calibration points are generally 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 3 minutes or until the meter's ready signal is given, whichever takes longer, before calibrating the meter or recording the sample value.

- Review the **GLP Measuring Hints** section.

Low-Level Measurement Procedure Using a Meter with an ISE Mode

Follow the procedure in the **Direct Calibration Using a Meter with an ISE Mode** section and substitute the low-level ISA. Refer to the meter user guide for detailed calibration procedures.

Prepare a low-level ISA solution by adding 20 mL of the ISA, Cat. No. 940011, to a 100 mL volumetric flask and diluting to volume with with distilled water.

Use at least three calibration standards.

Low-Level Measurement Procedure Using a Meter with a mV Mode

1. Prepare the electrode(s) as described in the **Electrode Preparation** section.

2. Connect the electrode(s) to the meter. Set the meter to the mV mode.

3. Select either a 10 ppm cadmium standard or a 10^{-4} M cadmium standard.

    To prepare a 10 ppm standard from the 1000 ppm cadmium standard, add 10 mL of the 1000 ppm standard to a 1 liter volumetric flask and dilute to volume with distilled water.

    To prepare a 10^{-4} M standard from the 0.1 M cadmium standard, add 1 mL of the 0.1 M standard to a 1 liter volumetric flask and dilute to volume with distilled water.

4. Prepare a low-level ISA solution by adding 20 mL of the ISA, Cat. No. 940011, to a 100 mL volumetric flask and diluting to volume with with distilled water.

    Note: Use the low-level ISA for low-level measurements only.

5. Measure 100 mL of distilled water into 150 mL beaker. Add 1 mL of low-level ISA.

6. Rinse the electrode(s) with distilled water, blot them dry and place the electrode(s) into the beaker. Stir the solution thoroughly.

7. Add increments of the 10 ppm or 10^{-4} M standard to the beaker using the steps outlined in **Table 2**. Record the 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 daily.

8. Measure 100 mL of the sample into a beaker. Add 1 mL of low-level ISA. Rinse the electrode(s) with distilled water, blot them dry and place the electrode(s) into the sample.

9. Stir the solution thoroughly. When a stable reading is displayed, record the mV value.

10. Determine the sample concentration corresponding to the measured potential from the low-level calibration curve.

Table 2
Preparing a Low-Level Calibration Curve Using the 10 ppm
Standard:

Step	Graduated Pipette Size	Pipette Added Volume	Concentration ppm
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 Low-Level Calibration Curve Using the 10^{-4} M Standard:

Step	Graduated Pipette Size	Pipette Added Volume	Concentration M
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. Some meters 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 convenient and ensures accuracy.

Measuring Hints

- Sample concentration should be known within a factor of three.

- The solution 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 the **GLP Measuring Hints** section.

Setup

1. Prepare the electrode(s) as described in the **Electrode Preparation** section.

2. Connect the 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 in the **Checking Electrode Operation (Slope)** section.

Known Addition Using a Meter with a Known Addition Mode

Refer to the meter user guide for more specific information.

1. Set the meter to the known addition mode.

2. Measure 100 mL of sample into a beaker. Add 2 mL of ISA. Stir the solution thoroughly. Rinse the electrode(s) with distilled water, blot them dry, and place them in the sample solution.

3. When a stable reading is displayed, set the meter as described in the meter user guide, if required.

4. Pipette the appropriate amount of standard solution into the beaker. Stir the solution 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 Using a Meter with a mV Mode

1. Set the meter to the mV mode.

2. Measure 100 mL of the sample into a 150 mL beaker. Add 2 mL of ISA. Stir the solution thoroughly.

3. Rinse the electrode(s) with distilled water, blot them dry, and place the electrode(s) into beaker. When a stable reading is displayed, record the mV value as E_1.

4. Pipette the appropriate amount of standard solution into the beaker. See **Table 3**. Stir the solution thoroughly..

5. When a stable reading is displayed, record the mV value as E_2. Subtract the first reading from the second to find E.

6. From **Table 5**, find the Q value that corresponds to the change in potential, E. To determine the original sample concentration, multiply Q by the concentration of the added standard:

    $$C_{sam} = Q * C_{std}$$

    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:

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

where:
Q = reading from known addition table
E = $E_2 - E_1$
S = slope of the electrode
p = (volume of standard)/(volume of sample and ISA)
r = (volume of sample and 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)			
Divalent	28.6	29.1	29.6	30.1
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

∆E	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

∆E	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 cadmium 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 ± 0.1% of the total cadmium ion concentration of the sample can be performed. The 960 titrator 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 the Handbook of Analytical Chemistry, L. Meites, (ed.) McGraw Hill Book Co., New York, (1st edit.), pp. 3-76, 3-225.

Setup

1. Prepare the electrode(s) as described in the **Electrode Preparation** section.

2. Connect the electrode(s) to the meter.

3. Prepare an EDTA titrant solution 10 to 20 times as concentrated as the sample by dilution of the 1 M stock solution. For a good end point 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 the electrode(s) in the sample. Stir the solutions thoroughly.

2. Using a 10 mL burette, add increments of titrant and plot the 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:

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

   where:
   C_{sam} = sample concentration
   C_t = titrant concentration
   V_{sam} = sample volume
   V_t = titrant volume added at endpoint.
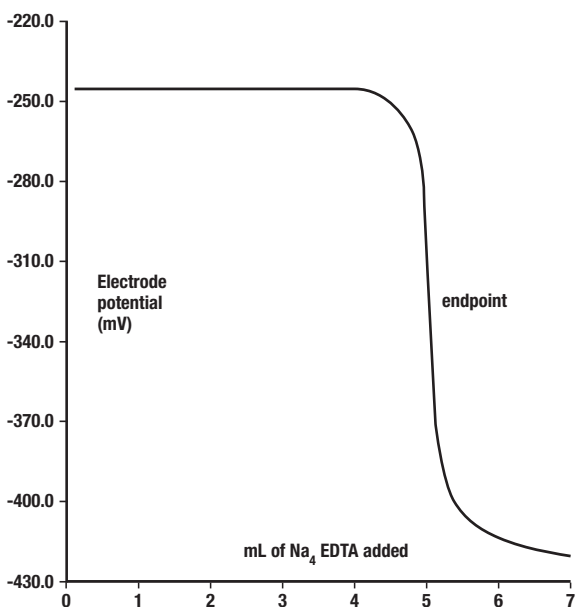
Figure 3: Typical Titration of 100 mL of 5 x 10^{-3} M Cd(NO$_3$)$_2$ (pH Adjusted to ~10 with ammonia) with 0.1 M Na$_4$EDTA

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

9448BN and 9448SC Half-Cell Cadmium Electrode
The half-cell cadmium electrode should be rinsed thoroughly and stored in distilled water at all times. When storing the electrode for long periods of time, replace the cap to protect the sensing element and store the electrode dry.

9648BNWP Combination Cadmium Electrode
The filling solution in the 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 the electrode dry with the cap on to protect the sensing element.

900200 Double Junction Reference Electrode
The double junction reference electrode may be stored in distilled water between sample measurements (up to two hours).

For short periods of time (up to one week):
The double junction reference electrode should be stored in its 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 of the electrode with distilled water and store it 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. Thoroughly rinse the electrode with distilled water.

Polishing the Sensing Surface of the Cadmium Combination Electrodes and Cadmium Half-Cell Electrodes
The sensing surface of solid state electrodes can wear over time, which causes drift, poor reproducibility and loss of response in low-level samples. The electrode can be restored by polishing the sensing surface with a polishing strip, Cat. No. 948201.

1. Cut off an inch length of the polishing strip.

2. Hold the electrode with the sensing surface facing up.

3. Place a few drops of distilled water on the sensing surface.

4. With the frosted side of the polishing strip facing down, use light finger pressure to place the polishing strip on top of the sensing surface.

5. Rotate the electrode for about 30 seconds.

6. Rinse the electrode with distilled water and then soak the electrode in a 1 ppm or 10^{-5} M cadmium standard for about ten minutes.

Flushing the 9644BNWP Cadmium Combination Electrode and 900200 Double Junction Reference Electrode
If the area between the electrode sleeve and inner cone becomes clogged with sample or precipitate, flush the area with filling solution or distilled water.

1. Hold the electrode body with one hand and use your thumb to push down on the electrode cap to drain the chamber. Push down on the cap until all the filling solution is drained from the chamber.

2. Fill the electrode with distilled water and then push down on the cap until all the water is drained from the chamber.

3. Fill the electrode with fresh filling solution up to the fill hole. Push down on the cap to allow a few drops of filling solution to drain out of the electrode and then refill any lost filling solution.

Disassembling the Cadmium Combination Electrode
Note: Disassembly is usually not required and should not be done unless a thorough cleaning is required.

1. Tip the electrode so the filling solution moistens the O-ring on the electrode body. Hold the electrode body with one hand and use your thumb to push down on the electrode cap to drain the chamber.

2. Unscrew the cap counter clock-wise and then slide the cap and the spring up the cable.

3. 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.

4. Grasp the cone with a clean, lint-free tissue and withdraw the body from the sleeve using a gentle twisting motion. Do not touch the pellet above the cone, it will damage to the pellet. Rinse the outside of the electrode body and the entire sleeve with distilled water. Allow it to air dry.

Reassembling the Cadmium Combination Electrode
1. Moisten the O-ring on the electrode body with a drop of filling solution. Insert the screw-thread end of the electrode body into the tapered, ground end of the sleeve.

2. Push the body into the sleeve using a gentle twisting motion until the bottom surface of the inner cone is flush with the tapered end of the sleeve.

3. Place the spring onto the electrode body and screw on the cap. Refill the electrode with filling solution.

TROUBLESHOOTING

Troubleshooting Checklist

Symptom– Off-scale or over-range reading

- No electrode filling solution added – Fill the electrode with filling solution up to the fill hole. Refer to the **Electrode Preparation** section for details.

- Electrode junction is dry – Push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.

- No reference electrode present – The 9448BN and 9448SC cadmium half-cell electrodes require a separate reference electrode, Cat. No. 900200.

- Air bubble on sensing element – Remove air bubble by reimmersing the electrode in solution.

- Electrode not in solution– Immerse the electrode in solution past the reference junction.

- Electrode not properly connected to meter – Unplug and reconnect the electrode to the meter.

- Defective electrode– Refer to the **Troubleshooting Guide** section.

- Defective meter– Check the meter performance. See the meter user guide.

Symptom– Noisy or unstable readings (readings continuously or rapidly changing)

- No electrode filling solution added – Fill the electrode with filling solution up to the fill hole.

- Electrode junction is dry – Push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.

- No reference electrode present – The cadmium half-cell electrodes require a separate reference electrode, Cat. No. 900200.

- Meter or stir plate not properly grounded – Check the meter and stir plate for proper grounding.

- Air bubble on sensing element – Remove air bubble by reimmersing the electrode in solution.

- ISA not used or incorrect ISA used – ISA must be added to all standards and samples. Use recommended ISA, Cat. No. 940011.

Symptom– Drift (reading slowly changing in one direction)

- No electrode filling solution added – Fill the electrode with filling solution up to the fill hole.

- Electrode junction is dry – Push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.

- Incorrect electrode filling solution used – Refer to the **Electrode Preparation** section to verify the correct electrode filling solution.

- Samples and standards at different temperatures – Allow solutions to reach the same temperature.

- Sensing element dirty or etched– Polish the sensing element. See the **Electrode Maintenance** section.

Symptom– Low slope or no slope

- Electrodes not properly conditioned– Refer to the **Electrode Preparation** section.

- Standards contaminated or made incorrectly– Prepare fresh standards.

- ISA not used or incorrect ISA used – ISA must be added to all standards and samples. Use recommended ISA, Cat. No. 940011.

- Electrode exposed to interferences– Refer to the **Troubleshooting Guide** section.

Symptom– Wrong answer, but calibration curve is correct

- Incorrect scaling of semi-logarithmic paper– Plot millivolts on the linear axis and concentration on the log axis.

- Incorrect millivolt sign recorded– Be sure to record the sign (+ or -) of the millivolt values.

- Standards contaminated or made incorrectly– Prepare fresh standards.

- Wrong units used– Apply correct conversion factor:
  10^{-3} M = 112 ppm as Cd^{2+}

- Complexing agents in sample– Use known addition or titration techniques or a decomplexing procedure.

Troubleshooting Guide

Follow a systematic procedure to isolate the problem. The measuring system can be divided into four components for ease in troubleshooting: meter, electrode, sample/application and technique.

Meter

The meter is the easiest component to eliminate as a possible cause of error. Thermo Scientific Orion meters include an instrument checkout procedure and shorting cap for convenience in troubleshooting. Consult the meter user guide for directions.

Electrode

1. Rinse the electrode thoroughly with distilled water.

2. Verify the electrode performance by performing the procedure in the **Checking Electrode Operation (Slope)** section.

3. If the electrode fails this procedure, review the **Measuring Hints** section. Clean the electrode thoroughly as directed in the **Electrode Maintenance** section. Drain and refill the electrode with fresh filling solution.

4. Repeat the procedure in the **Checking Electrode Operation (Slope)** section.

5. If the electrode fails this procedure again and the half-cell cadmium electrode is being used, 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 procedure in the **Checking Electrode Operation (Slope)** section.

6. If the electrode passes the procedure, but measurement problems persist, the sample may contain interferences or complexing agents, or the technique may be in error.

7. Before replacing a faulty electrode, review this user guide and be sure to thoroughly clean the electrode; correctly prepare the electrode; use the proper filling solutions, ISA, and standards; correctly measure the samples and review the **Troubleshooting Checklist** section.

Sample/Application

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! Errors may result from contamination of prepared standards, accuracy of dilution, quality of distilled water, or a mathematical error in calculating the concentrations.

The best method for preparation of standards is serial dilution. The electrode and meter may operate with standards, but not with the sample. In this case, check the sample composition for interferences, incompatibilities or temperature effects. Refer to the **Sample Requirements**, **Interferences**, **pH Requirements**, **Measuring Hints**, **Analytical Procedures**, and **Electrode Characteristics** sections.

Technique

If trouble persists, review operating procedures. Review calibration and measurement sections to be sure proper technique has been followed. Verify that the expected concentration of the ion of interest is within the limit of detection of the electrode.

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 are present, known addition may be the best method. If the sample is viscous, analate addition may solve the problem. If working with low-level samples, follow the procedure in the **Low-Level Measurement** section.

Assistance

After troubleshooting all components of your measurement system, contact Technical Support. Within the United States call 1.800.225.1480 and 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/water.

Warranty

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

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.
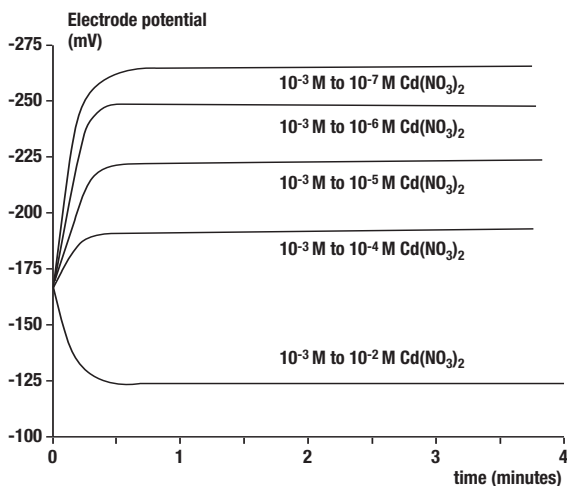

Figure 4: Typical Electrode Response to Step Changes in $Cd(NO_3)_2$ Concentration

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 ± 4% can be obtained.

Temperature Effects

Since the electrode potentials are affected by changes in temperature, samples and standard solutions should be within ± 1 ˚C (± 2 ˚F) of each other. At the 10^{-3} M level, a 1 ˚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 the **Theory of Operation** section. Theoretical values of the slope at different temperatures are given in **Table 6**. If temperature changes occur, the meter and electrodes should be recalibrated.

The electrode can be used at temperatures from 0˚ to 100 ˚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. T he electrode should be used only intermittently at temperatures above 80 ˚C.

Table 6
Theoretical Values of Electrode Slope vs. Temperature

°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 combination cadmium electrode, Cat. No. 9648BNWP, is recommended. The Optimum Results A filling solution that is provided with this electrode will minimize junction potentials and provide optimum temperature and time response. Optimum Results A produces an isopotential point of 1.7×10^{-3} 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 9648BNWP may be used on meters that allow automatic temperature compensation for ISE. 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 by 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. Refer to the **Electrode Maintenance** section.

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**, $Cd(OH)_2$ 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.
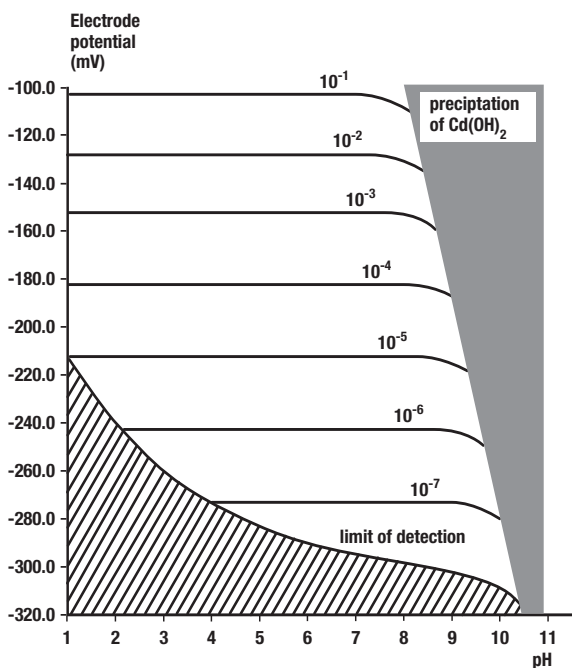
Figure 5: Electrode Potential Behavior vs, Solution pH
in Pure Cd(NO$_3$)$_2$ Solutions at 25 °C

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
E_0 = 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 and 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_f, by the activity coefficient, y:

$$A = y * C_f$$

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:

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

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 background 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

Cat. No.	Description
9648BNWP	Cadmium ionplus Sure-Flow combination electrode, waterproof BNC connector
9448BN	Cadmium half-cell electrode, BNC connector (requires separate reference electrode)
9448SC	Cadmium half-cell electrode, screw cap connector (requires separate cable and reference electrode)
900200	Double junction reference electrode, pin tip connector
900002	Inner chamber filling solution for double junction reference electrode, 5 x 60 mL
900003	Outer chamber filling solution for double junction reference electrode, 5 x 60 mL
900061	Optimum Results A filling solution for combination cadmium electrode, 5 x 60 mL
940011	ISA, 475 mL
948201	Polishing strips

SPECIFICATIONS

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

pH Range:
2 to 12 pH

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 (9648BNWP): 13 mm
Diameter (9448BN and 9448SC): 12 mm
Cap Diameter: 16 mm
Cable Length: 1 meter

254805-001   Rev.A

Thermo
SCIENTIFIC