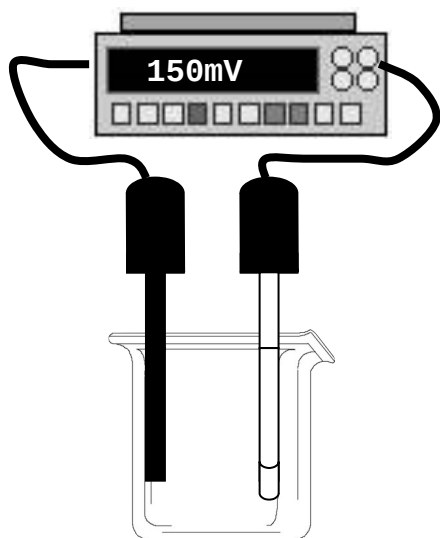
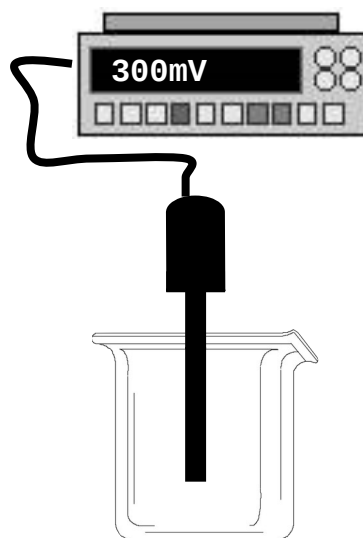


SENTEK

Ion Selective Electrode OPERATING INSTRUCTIONS



Mono/Reference



Combination

SENTEK

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Operating Instructions

Cadmium Ion Selective Electrode

This Document includes operating instructions for two types of Ion Selective Electrode. A single sensing Half Cell Cadmium Electrode which requires a separate Reference Electrode, and a Combination Cadmium Electrode which has the Reference built into the outer shaft.

For extremely low level work the Half Cell plus Reference Electrode should be used. For general applications the Combination is more convenient.

Depending on the type of ISE chosen you will need to disregard some information for instance if you have the Combination Electrode then disregard any comments about reference electrodes.

A quick guide is included with a more involved section following.

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Quick Guide to Cadmium

ISE

The combination ion selective electrode has a solid state crystalline membrane with an integral driTEK reference electrode. The electrode is designed for the detection and analysis of Cadmium ions in aqueous solutions and is suitable for use in the field in the laboratory and in on line analyzers.

Installation

Connect the ISE to the mV or ion meter.

Remove the black protective cap and keep it in a safe place.

The ISE can be used immediately but pre soaking for 5 minutes in a 100ppm Cadmium solution is recommended.

The ionic strength of the standards and solutions should be kept constant between all standards and samples. This is achieved by the simple addition of an Ionic strength adjustment buffer (ISAB). Potassium Nitrate is ideal. A typical addition would be 1 ml of 1 molar ISAB to 100 ml of standard and sample.

For low level measurements below around 50ppm in relatively pure samples no ISAB is needed.

No temperature correction is necessary however standards and samples should be measured at the same temperature.

Begin calibration from the lowest concentration standard to avoid cross contamination. Calibration should cover the anticipated range of the samples.

Rinse tip with de-ionised water between measurements.

Avoid strongly acidic or alkaline samples, strong detergents and organic solvents.

Storage and Maintenance

After use rinse with de-ionised water, wipe clean with a tissue or lint free cloth, replace protective cap and store dry in its box.

If performance becomes sluggish, rinse with dilute detergent, rinse with de-ionised water and immerse the tip in a 1000ppm Cadmium solution for 1 hour.

Should further conditioning be required rub down the crystal surface with a very fine emery paper until the surface has a grey shiny

appearance. Stand electrode in 100ppm Cadmium solution for 20 minutes.

Specification

Cadmium is a divalent Cation.

Refer to the table below for the full specification

Parameter	Specification
Overall length	155 mm
Body Diameter	12 mm
Cap Diameter	16mm
Connector	BNC
Cable length	1000 mm
Resistance at 25 Deg C	< 2.5 Meg Ohm
Concentration Range	0.1 to 11,200 ppm
Slope	24 to 29 mV per decade
Potential Drift	2 mV per day
Operating pH range	3 to 7
Temperature range	5 to 50 Deg C
Endpoint time	Typically 20 to 50 seconds
Interferences: Ions with coefficients above 0.001.	Copper Mercury Silver

Recommendations for successful analysis

The combination ISE's can be used with any pH/mV meter or Ion meter. If the meter does not have a BNC socket and you have a BNC electrode please contact your distributor who will arrange to have the correct plug fitted. Adapters are also available if the same electrode has to be used on more than one meter.

Meters with a 0.1 mV resolution are recommended whilst dedicated Ion meters will provide direct concentration readouts saving time and effort in constructing calibration curves and performing calculations. Your distributor can advise on the most suitable meter.

Magnetic stirrer/stirrer bars are recommended for laboratory analysis. Please operate at the lowest constant speed available.

Semi-logarithmic (4-cycle) graph paper is required for preparing calibration curves when you are using a mV meter.

Required Solutions

Distilled or de-ionised water will be required to prepare Standards, ISABs and to rinse the electrode between measurements.

1000ppm Stock Standard solution. Used for preparation of Standards.
(Prepared by customer)

ISAB. Used to adjust the Ionic strength of all standards and samples.
Typical addition is 1 ml of 4 Molar ISAB to 50ml of all standards and samples.

Operation

1. Connect the electrode to the meter being used for analysis
2. Prepare a series (at least 2) of standards that bracket the expected sample concentration. This is best done by serial dilution of the stock solution. Ideally standards should be a decade in concentration apart e.g. 1, 10, and 100ppm.
3. Dispense 50 ml of each standard into analytically clean beakers (100 to 150 ml size is perfect)
4. Add ISAB/TISAB in the appropriate ratio. As a guide with sample concentrations in the 1 to 1000ppm range 1ml of a 4 Molar ISAB to 50 ml sample is satisfactory. For TISAB(Fluoride analysis only) please read the label.
5. Rinse the electrode with de-ionised water and blot dry with a lint free cloth and place in the lowest standard. When the reading is stable record the mV value.
6. Repeat step 6 for all subsequent standards proceeding from lowest to highest.
7. Plot a calibration curve on semi log paper using mV values on the linear Axis and concentration on the log scale.
8. Rinse the electrode in de-ionised water and blot dry. Place the electrode in the sample and record the stable mV value.
9. Using the calibration curve determine the unknown sample concentration.

Hints and tips

1. Ensure that the temperature of all standards and samples are the same to reduce errors.
2. Using a magnetic stirrer for laboratory analysis is recommended but not essential. It is however important to have the stirrer set on a low constant speed which must be reproducible for all measurements.
3. Prior to sample measurement ensure that the electrode is thoroughly rinsed with de-ionised water. It is worth performing this rinse twice given the possibility of carryover being greatest in high concentration solutions.
4. Prepare standards by serial dilution.
5. Make sure your electrode is conditioned by leaving the tip in the lowest concentration standard for 1 hour prior to analysis.

Methods of Analysis

We have described direct potentiometry above. This method is simplified by using a direct reading ion meter. There are several other methods, which are useful.

Known Addition: An incremental technique where the potential of the sample solution is measured followed by addition of a small volume of a higher concentration standard solution. The new potential is measured and from difference in the two values, and using the known electrode slope, the unknown concentration is determined.

This method is ideal for samples whose matrix is not entirely clean or aqueous. In these instances comparisons with clean standards is not appropriate thereby making direct potentiometry unsuitable. Known addition works because both standard and sample are measured in the same matrix.

Typical sample volume is 50 ml, typical standard volume is 5 ml. The standard should be approximately 100 times the sample concentration for accurate analysis.

Sample Addition: An incremental technique where the potential of a dilute standard solution is measured followed by the addition of a small volume of more concentrated sample. The new potential is recorded and the difference noted. Using this value (and the predetermined electrode slope) the unknown concentration is determined.

This method is ideal for dirty or viscous samples with an awkward matrix. The sample however needs to be relatively concentrated i.e. at least 100 times the Electrodes linear detection limit. The analysis does have the benefit of only requiring a small volume.

The sample matrix is basically broken down by dilution with the standard and therefore analysis is carried out in the same media.

End Point Titration: Flow Plus combination ISE's are ideal end point indicators and will produce a significant potential change at the equivalence point. The Ion in question must be contained in the titrand or the titrant and must therefore be in excess or absence at the end point.

Operating Instructions for Cadmium Ion Selective Electrode

1. Introduction

1.1 Construction

The electrode consist of an inert polymer body on the end of which is mounted the sensitive membrane. All connections in the electrode are solid-state contacts, there being no liquids of any type inside the body. The high state of surface finish of the membrane is an essential feature for maximum sensitivity and performance. The low-noise shielded cable terminates in a BNC, though an alternative plug may be specified.

1.2 Operating Instructions

The electrical potential of an ion selective electrode is a function of the logarithm of the activity of the ion to be measured. The relationship is given by the Nernst Equation:

$$E_{\text{(Measured)}} = \frac{RT}{zF} \ln A_{\text{Cd}}$$

where

E^0 is a constant characteristic of the electrode

R is the Universal Gas Constant

T is the Absolute Temperature

Z is the charge of the ion (2 in the case of Cadmium)

F is the Faraday constant

A_{Cd} is the activity of the Cadmium ions

This equation can be simplified to:

$$E_m = \text{Constant} \pm S \log A_{\text{Cd}}$$

where S is the slope of the calibration curve. The measured potential E_m can only be measured against a reference electrode, such as a saturated calomel electrode (SCE), placed in the same solution. A double junction reference electrode is also suitable for use with the Cadmium electrode.

Measurements are made with a high impedance millivoltmeter or expanded scale pH meter. A meter with digital display is obviously more accurate and most convenient. The cadmium electrode can be used in solutions containing high proportion of organic solvents without ill-effect. For further discussion on the principles of ISE measurements, the user is referred to the Technical Bulletin, which is available on demand.

1.3 Sensitivity

The electrode will respond to uncomplexed cadmium ion activity over the range 10^{-1} - 10^{-6} M. The linear detection limit is around 10^{-7} M. Curvature of the response is observed at lower concentrations because the solubility of the membrane material, dissolved from the membrane, contributes a small but significant amount of cadmium to the solution being measured. Figure 1 shows a typical calibration plot of the electrode. Values for the slope of strength of this plot should lie in the range 25-30mV/decade. If the total ionic strength of all solutions is maintained constant by the addition of a concentrated (approx. 10^{-1} M) inert electrolyte such as sodium nitrate, the electrode can be calibrated directly in concentration units.

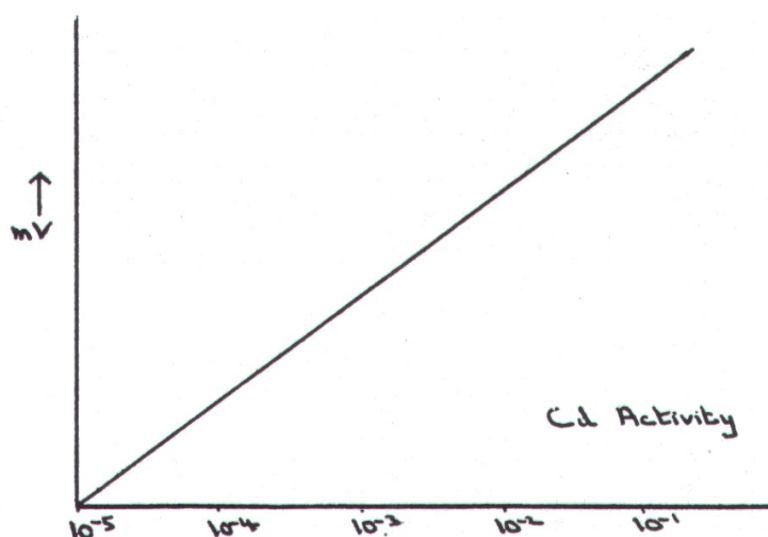


Figure 1

The activity coefficient of cadmium depends upon the ionic strength of the solution. The following table can be used to calculate the approximate activity coefficients at various ionic strengths.

Ionic Strength	0.001	0.002	0.005	0.01	0.02	0.05	0.10
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Activity Coeff. (f) 0.904 0.869 0.805 0.74 0.67 0.55 0.48

The ionic strength of the solution to be tested can be calculated from the formula:

$$\text{Ionic Strength} = \frac{1}{2} \sum C_i Z_i^2$$

where C_i is the concentration of species i and Z_i is its charge, and all species, cations and anions, must be taken into account.

Once the ionic strength is calculated and the activity coefficient found from Table 1 then the activity of the ion of interest is found from:

$$\text{Activity (A}_i\text{)} = \text{Concentration (C}_i\text{)} \times \text{Activity Coefficient (f)}$$

1.4 Stability

The long-term drift in E_0 value of the cadmium electrode is usually in the region of 2-4 mV/day.

1.5 Selectivity

High levels of lead and ferric ion interfere with the operation of the cadmium electrode. Other cations which may interfere are Ag^+ , Hg^{2+} and Cu^{2+} and these should not be present in concentrations of more than 10^{-7}M .

If the membrane has been in contact with any of the above interferent and has become discoloured, original performance can often be regained by gentle polishing.

The electrode can be used over the pH range 3-7.

1.6 Response Time

The electrode response time to a step change in cadmium activity in solution is extremely rapid, with 95% of the potential change completed in 200 msec. Equilibrium is reached in less than 2 seconds. When, however, the electrode is removed from solution and placed in another of different concentration, it may take up to 20 seconds to regain equilibrium.

The presence of interfering ion does not affect the response time, but in the solutions of very low ionic strength, i.e. with no ionic strength buffer, the response time may be extended to several minutes.

2. Operation and Handling

2.1 Initial Setting-Up

On receipt of the electrode remove it from its packing and inspect for damage, particularly to the highly polished membrane which forms the sensing end of the electrode. Clamp the electrode with its sensing end in a solution of cadmium nitrate (10^{-1}M) for about two hours or until the electrode potential, when measured against a standard calomel electrode, remains constant. Overnight soaking is recommended. After this conditioning the electrode is ready for use.

2.2 Making a Measurement

The electrode should first be calibrated as follows. Clamp the electrode in a vertical position such that the membrane is immersed in a beaker of 10^{-1}M cadmium nitrate solution on a magnetic stirrer. Clamp a reference electrode (a standard calomel electrode may be used) so that its end is immersed in the same solution and connect both electrodes to a pH or millivolt meter. Record the potential when it becomes steady. Change the test solution sequentially for 10^{-2}M , 10^{-3}M and 10^{-4}M cadmium solutions and plot the calibration curve, washing and drying the electrode between solutions. If an ionic strength adjusting buffer is used add equal volumes of 0.1M buffer to all calibrations and test solutions.

Unknown solutions can now be measured directly. For further details of methods of measurements, the user is referred to Technical Bulletin E1 available from the electrode supplier.

2.3 Storage and Maintenance

When the electrode is no longer needed it can be merely removed from the test solution, wash and dried and be clamped in the air or returned to its packing container. There is in principle no limit to the storage time. The membrane should be protected from scratching and abrasion during storage. The only maintenance required is an occasional polish with a tissue or soft cloth to keep the membrane surface shiny.

2.4 Flow Through Configuration

A Flow-Through version is available to enable continuous flow-through measurements to be made. The reference contact can be made at any point in the solution stream joined to the flow cell by a continuous stream of liquid usually downstream of the electrode. The combination of this electrode with a sampler and pumping system can result in a versatile and low-cost continuous cadmium monitor.

3. Typical Applications and Bibliography

The cadmium electrode has a wide range of applications. Apart from being used as a direct method to measure cadmium it can be used for direct or indirect titrations with EDTA to measure metal ions for example Zinc and Nickel. Very few papers have been published in the cadmium electrode but most of the standard analytical chemistry text books contain useful applications.

- e.g. 1) D. Midgley and K. Torrance
 Potentiometric Water Analysis
- 2) P. L. Bailey
 Analysis with Ion Selective Electrodes

4. Trouble Shooting

- 4.1 Wildly erratic reading
- i) Air bubbles trapped on outside surface of membrane
 - ii) Excessively violent stirring
- 4.2 Steady continuous drift in one direction
- i) Poor earthing of mV meter.
 - ii) Excessive leaking from the reference electrode junction leading to continuous changes in the activity coefficients of ions in weaker solutions.
 - iii) Temperature drift if solutions are not thermostatted, or sample vessel insulated from, for example, stirrer motor.
 - iv) Not using a double-junction reference electrode or salt bridge.
- 4.3 Slope of electrode much less than 25mV/decade.
- i) Membrane old and in need of replacing or repolishing.

ii) Presence of an interfering ion in a constant concentration swamping the selected ions. Check performance with pure cadmium nitrate solutions.

4.4 Totally incomprehensible results may arise from leakage of solution into electrode via the membrane/body seal. If all fails to cure a problem please ship the electrode back to supplier for exchange.