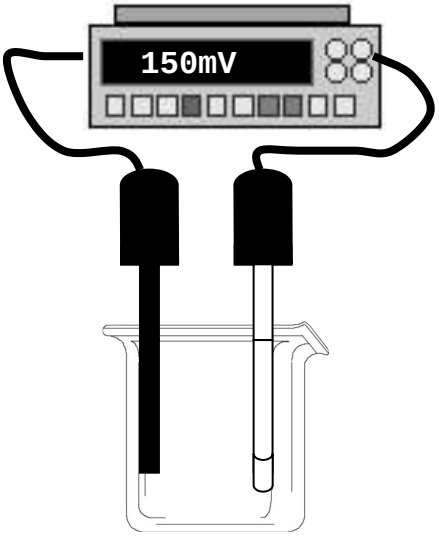
SENTEK

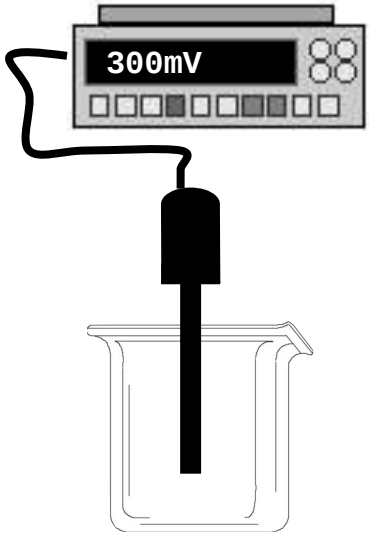
Ion Selective Electrode

OPERATING INSTRUCTIONS

LEAD



Mono/Reference



Combination

SENTEK

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Operating Instructions
Lead Ion Selective Electrode

This Document includes operating instructions for two types of Ion Selective Electrode. A single sensing Half Cell Lead Electrode which requires a separate Reference Electrode, and a Combination Lead 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 Lead ISE

The combination ion selective electrode has a solid state crysytalline membrane with an integral driTEK reference electrode. The electrode is designed for the detection and analysis of Lead 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 10ppm Lead 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 Lead solution for 1 hour.

Should further conditioning be requires rub down the crystal surface with a very fine emery paper until the surface has a grey shiny appearance. Stand electrode in 100ppm Lead solution for 20 minutes.

Specification

Lead 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	0.2 to 20,800 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.	Mercury Silver Copper Cadmium

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 time 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 Lead Ion Selective Electrode

1. Introduction

1.1 Construction

The electrode consists 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 Principles

To measure the activity of lead ions in an aqueous solution, the electrode is placed in the solution and clamped in position. A reference electrode must also be placed in the same solution and both electrodes are then connected to the appropriate input terminals of high impedance mV meter or expanded scale pH meter. A digital readout meter is obviously most convenient and more accurate. A double junction reference electrode should be used since the seepage of chloride ion from the reference will complex the lead ion and cause a steady drift of potential. 1M Kno_3 should be used in the bridge compartment. The potential thus measured is a function of the lead ion activity and any interfering ions present according to the equation:

$$E = E^o + s \log (a_{Pb} + K_{Pb/X}\text{-}a_X)^{2/}x$$

where

S = measured slope of calibration plot in pure lead solvents

a_{Pb}, a_X = activity of lead and interferent ions

$K_{Pb/X}$ = selectivity coefficient

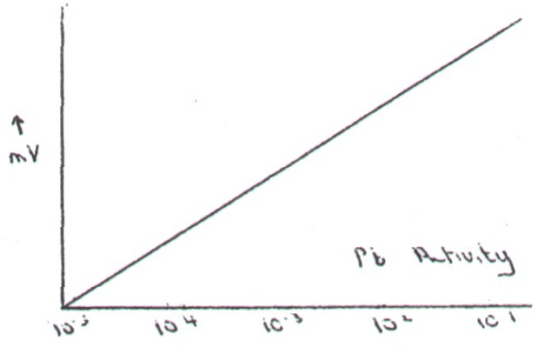
z = ionic strength of interferent ion

E^o = standard potential (constant)

1.3 Selectivity

This electrode will respond to free Pb^{2+} ions in solution in the range 10^{-1}M-10^{-6}M. If the ionic strength of all solutions is maintained constant by the addition of an inert electrolyte, e.g. 0.1M potassium nitrate or acetate buffer, the electrode can be calibrated directly in concentration units.

Daily re-calibration is recommended for analytical use.



Slope of the calibration plot is generally in the region of 29-33 mV/decade

The activity coefficient of lead ions depends upon the ionic strength. The following table can be used to calculate the approximate activity coefficients.

Ionic Strength:	0.001	0.002	0.005	0.01	0.02	0.05	0.10
Activity Pb^{++}:		0.904	0.869	0.805	0.74	0.67	0.55	0.48

1.4 Stability

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

1.5 Selectivity

The only serious interference to the operation of the lead selective electrode arises from the presence of mercuric ions in a test solution. The membrane is only fractionally more sensitive to lead than mercuric ions. The following is a list of the selectivity ratios of other common cations:

		$K_{Pb/Int}$
Calcium	=	3×10^{-4}
Cadmium	=	8×10^{-3}
Copper	=	4×10^{-3}
Iron (Fe^{2+})	=	3.8×10^{-2}
Zinc	=	4×10^{-5}
Sodium	=	1.3×10^{-3}
Mercury (II)	=	0.60

The selectivity ratios will vary slightly with interference concentration. The figures shown are for a concentration of 10^{-1}M.

The presence of certain anions, e.g. Cl^-, Br^-, I^-, S^{2-}, CN^-, OH^- and ammonia also interfere by either precipitating or complexing lead ions and hence reducing the free lead in activity.

pH Range

The electrode will respond to free lead ion in the range pH4-7. Below 4 the electrode responds to hydrogen ion while above 7, the hydroxide formation causes a decreased electrode response.

Response Time

The electrode response time to a step change in lead ion 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 the solution and placed in another of different concentration, it may take up to 20 seconds to regain equilibrium.

The presence of interfering ions does not affect the response time, but in 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 packaging 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 lead nitrate (10^{-1}M) for about two hours or until the electrode potential, when measured against a double junction SCE, 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 lead nitrate solution on a magnetic stirrer. Clamp a reference electrode (a double junction Ag/AgCl or SCE 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 rest solution sequentially for 10^{-2}M, 10^{-3}M and 10^{-4}M lead 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 calibrating and test solutions.

Unknown solutions can now be measured directly. For further details of methods of measurement, 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, washed 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 form 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 lead monitor.

3. Applications and Bibliography

Most of the following reference are concerned with other lead electrode which have been available from time to time, but the applications principles are relevant to this electrode.

1. Titration of oxalate, chromate, tungstate, dihydrogen phosphate, phosphate and ferrocyanide anions with lead nitrate in aqueous medial, methanol, and 1.4 dioxan.

   Analytica Chimica Acta, (1972) 60, 405-412

2. Potentiometric titration of sulphate anion.

   Anal. Chem., 41 (1969), 967

4. Trouble Shooting

4.1 Wildly erratic readings

- i) Air bubble trapped on outside surface of membrane
- ii) Excessively violent stirring

4.2 Steady continuous drift in one direction

i) Poor earthing of the 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 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 re-polishing

ii) Presence of an interfering ion in a constant concentration swamping the selected ions. Check performance with pure lead 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 electrode back to supplier or exchange.