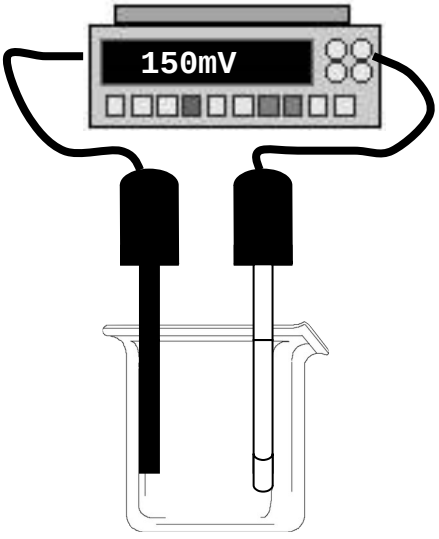
SENTEK

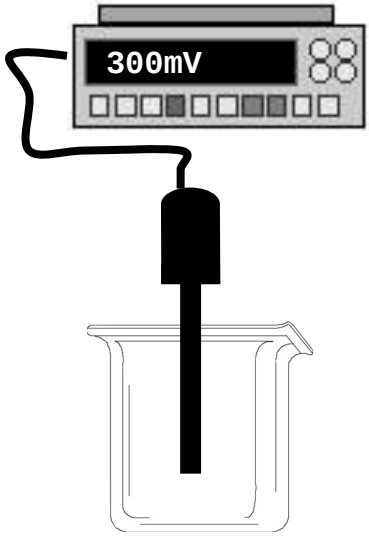
Ion Selective Electrode

OPERATING INSTRUCTIONS

SULPHIDE



Mono/Reference



Combination

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Operating Instructions
Sulphide Ion Selective Electrode

This Document includes operating instructions for two types of Ion Selective Electrode. A single sensing Half Cell Sulphide Electrode which requires a separate Reference Electrode, and a Combination Sulphide 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 Sulphide 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 Sulphide ions in aqueous solutions and is suitable for use in the field in the laboratory and in on line analysers.

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 20 minutes in a 100ppm Sulphide solution (adjusted to pH13-14) is recommended.

The ionic strength of the standards and solutions should be kept constant between all standards and samples. The pH also needs to be controlled and the Sulphide Ions prevented from oxidising. This is achieved by the simple addition of a Sulphide anti oxidant buffer (SAOB). Typical ratio is 1: 1 sample or standard plus SAOB.

SAOB Preparation

To approximately 600ml of distilled Water in a 1000ml beaker add 200 ml of 10 N NaOH, 35g of ascorbic acid and 67g of Di-sodium EDTA. Stir completely until everything dissolves. Dilute to the 1000ml mark with distilled water. Prepare fresh every couple of weeks. Handle with care.

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 Sulphide 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 Sulphide solution for 20 minutes.

Specification

Sulphide is a divalent anion.

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	0.003 to 32,100 ppm
Slope	-24 to -29 mV per decade
Potential Drift	2 mV per 8 hr
Operating pH range	13 to 14
Temperature range	5 to 50 Deg C
Endpoint time	Typically 10 to 30 seconds
Interferences: Ions with coefficients above 0.001.	Silver Mercury

Operating Instructions for Sulphide 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 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

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:

$$E_{(Measured)} = E^{o} \pm \frac{RT}{zT} \ln A_S$$

where:

E^{o} 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
F is the Faraday constant
A_S is the activity of the sulphide ions

This equation can be simplified to:

$$E_m = \text{Constant} \pm S \log A_S$$

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 double-junction reference electrode placed in the same solution. Measurements are made with a high impedance millivolt meter or expanded scale pH meter. A meter with a digital display is obviously more accurate and

most convenient. The electrode potentials encountered with a sulphide electrode are occasionally in the region of -700 to -900mV which means that when smaller, restricted range meters are used, an offset potential source may be needed.

The sulphide 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 sulphide ion activity over the range 10^{o} - 10^{-6}M in aqueous and semi-aqueous solutions. In sulphide-buffered solutions it is possible to extend the measurement range down to 10^{-10}M or better. However in non-buffered media curvature of the calibration plot is observed below 5 x 10^{-6}M sulphide owing to dissolution of membrane material contributing a small amount of sulphide to the test solution.

All sulphide measurements must be made in solutions of pH greater than 12 to prevent association of sulphide ions and protons to form $S^{=}$ and HS^{-} species. This can most easily be done by using 0.1M sodium hydroxide as an ionic strength buffer. Alternatively a buffer known as SAOB can be used. This is Sulphide Anti-Oxidant Buffer which not only sets the pH at a suitable value, but swamps out variations in ionic strengths and prevents aerobic oxidation of sulphide ion. This latter is important at sulphide concentrations below 10^{-4}M. It consists of 80gms NaOH, 320gms sodium salicylate and 72gms ascorbic acid diluted to 1 litre with distilled water.
Sample are diluted 1:3 with this buffer.

Daily re-calibration is recommended for analytical use.

Figure 1 shows a typical calibration plot for the sulphide electrode in 0.1M sodium hydroxide solution. Values of the slope should be in the range 25-29mV/decade. Since the latter keeps the ionic strength constant the electrode is behaving directly as a concentration probe.

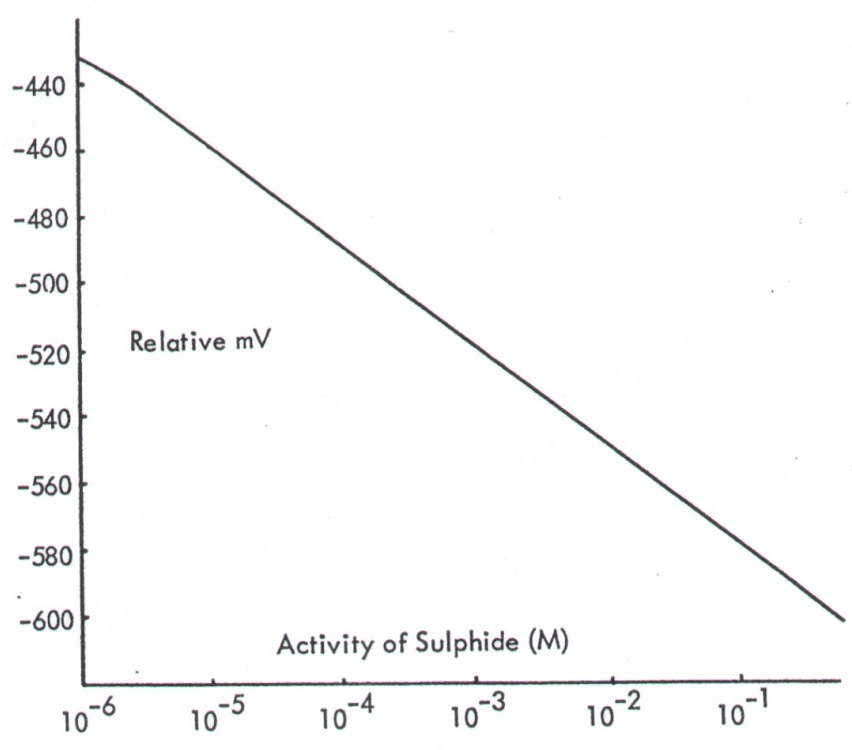

Figure 1

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

Ionic Strength	0.001	0.005	0.01	0.05	0.1	0.2
Activity Coeff. (f)	0.903	0.805	0.744	0.55	0.465	0.38

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

$$\text{Ionic Strength} = \tfrac{1}{2} \Sigma C_i Z_i^2$$

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 :

$$\text{Activity } (A_i) = \text{Concentration } (C_i) \times \text{Activity Coefficient (f)}$$

1.4 Stability

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

1.5 Selectivity

The sulphide electrode is free from all interference's apart from mercuric ions. The level of mercuric ions should be below 10^{-7}M.

1.6 Response Time

The electrode will respond to a step change in sulphide ion activity in solution in milliseconds. When, however, the electrode is removed from the one solution and placed in another of different sulphide concentrations, it may take up to 10 seconds to achieve a new equilibrium. The presence of other cations has no appreciable effect on response time.

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 transparent membrane which forms the sensing end of the electrode. Clamp the electrode with its sensing end in a solution of sodium sulphide in SAOB (10^{-1}M) for about an hour or until the electrode potential, when measured against a double junction, 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 sulphide solution on a magnetic stirrer. Clamp a reference electrode (a double junction reference electrode is quite adequate) 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 sulphide solutions and plot the calibration curve, washing and drying the electrode between solution.

Unknown solutions can now be measured directly. For further details of method 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 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 down-stream of the electrode. The combination of this electrode with a sample and pumping system can result in a versatile and low-cost continuous sulphide monitor.

3. Applications and Bibliography

The sulphide electrode has been widely used to determine sulphur containing organic compounds. It has found application in the determination of sulphides as environmental pollutants and in waste waters, while its used in the pulp and paper industry has been well documented.

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Sulphide in Soils

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See also Orion Research Inc. Applications
Bulletin Nos. 3 and 12

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.

4.3 Slope of electrode much less then 50mV/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 sulphide 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 for exchange.