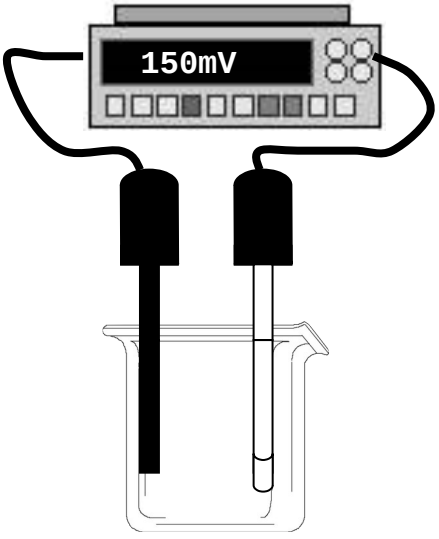
SENTEK

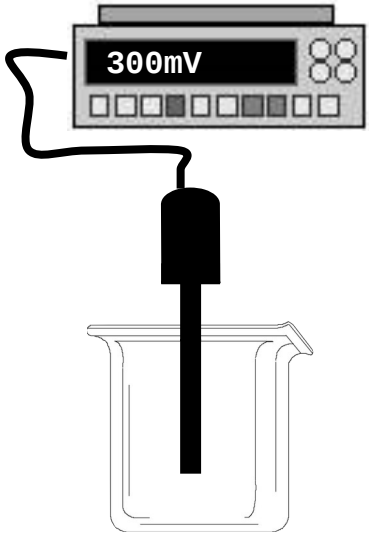
Ion Selective Electrode

OPERATING INSTRUCTIONS

POTASSIUM



Mono/Reference



Combination

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Operating Instructions
Potassium Ion Selective Electrode

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

The combination ion selective electrode has a solid state PVC polymer membrane with an integral driTEK reference electrode. The electrode is designed for the detection and analysis of Potassium 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 Potassium 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). Lithium Acetate 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

Avoid touching the membrane surface.

After use rinse with de-ionised water, 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 Potassium solution for 1 hour.

Rinse with de-ionised water and resume your normal calibration routine.

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	< 10 Meg Ohm
Concentration Range	0.04 to 39,000 ppm
Slope	57 +/- 2 mV per decade
Potential Drift	1 mV per 8 hours
Operating pH range	1 to 9
Temperature range	5 to 50 Deg C
Endpoint time	Typically 10 to 30 seconds
Interferences: Ions with coefficients above 0.001.	Caesium Ammonium

For advice on methodologies and analytical hints and tips contact your local distributor.

Operating Instructions for Potassium Ion Selective Electrode

1. Introduction

1.1 Construction

The electrode consists of an inert fluorocarbon body with a detachable PVC membrane unit, on the end of which is glued the ion-selective membrane. Inside the membrane unit, an internal filling solution makes contact between the membrane and the internal silver/silver chloride reference element. The sensitive membrane consists of liquid ion exchange material immobilised in a poly-(vinyl chloride) matrix. Connection to a millivoltmeter is via a BNC plug, though an alternative plug may be specified.

1.2 Operating Principles

The electrical potential of an ion selective electrode is a function of the activity of certain ions in an aqueous solution. This potential can only be measured against a reference electrode, such as a saturated calomel electrode (SCE), placed in the same solution. Because leakage of KCl form the SCE junction will alter the potassium ion activity of the sample solution, a saturated sodium nitrate salt bridge should be placed between the SCE and sample. Measurements are made with a high impedance millivoltmeter or expanded scale pH meter. A digital readout meter is obviously more accurate and most convenient. The potassium electrode cannot be used in non-aqueous solvents but the presence of up to 40% organic solvents in an aqueous solution can be tolerated. 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 potassium ion activity over the range 10^{0} - 10^{-4}M. The linear detection limit is around 10^{-4}M but careful calibration allows the electrode to be used down to 5 x 10^{-5}M. Curvature of the response is observed at lower concentrations because the solubility of the liquid ion-exchanger, leached from the membrane, contributes a small but significant amount of potassium to the solution being measured. Figure 1 shows a typical calibration plot of the

electrode. Values for the slope of this plot should lie in the range 50-59mV/decade.

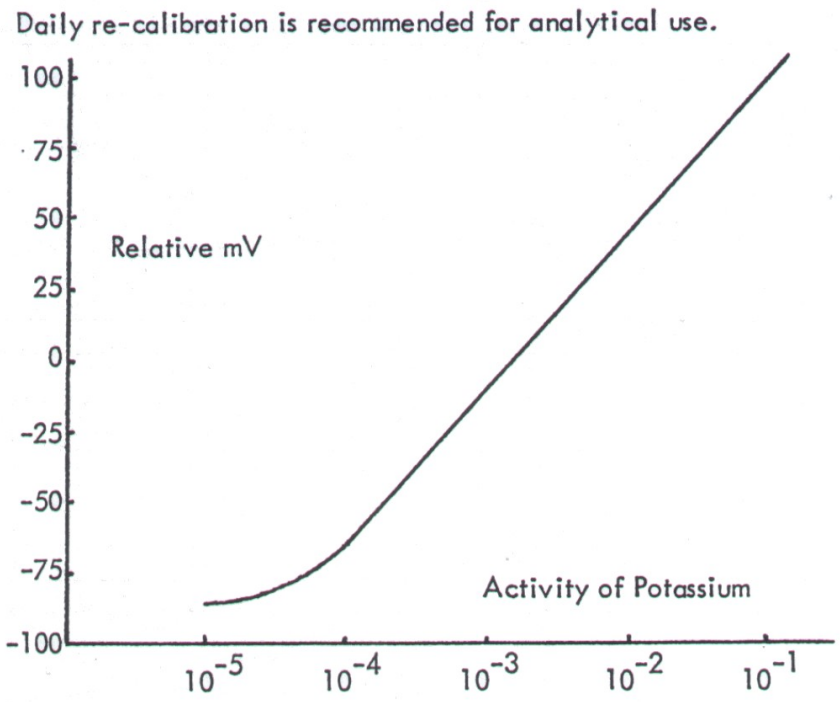

Figure 1

The activity coefficient of potassium ion 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	0.005	0.01	0.05	0.1	0.2
Activity Coeff.	0.975	0.945	0.925	0.85	0.805	0.755

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 the E_o value of the potassium electrode is usually in the region of 1-2mV/day.

1.5 Selectivity

The selectivity of the potassium electrode can be altered quite dramatically, by changing the composition of the membrane. In its normally supplied form, the parameters are chosen to give the greatest possible selectivity for potassium over sodium, which in this case is around 400.

The following is a list of some typical selectivity ratios found with this electrode:

Li^+	2.1×10^{-3}	Ca^{2+}	2.5×10^{-3}
Na^+	2.6×10^{-3}	Mg^{2+}	1.9×10^{-3}
Rb^+	1.9		
Cs^+	0.38		
NH_4	0.30		

The selectivity ratios vary with interferent activity and according to the method of measurement. These figures should be used as a guide only.

The electrode should b used in the pH range 4-9.

1.6 Response Time

When first placed in a solution of potassium, the electrode may take 5-10 minutes to reach initial equilibrium, depending upon the ionic-strength of the solution. The electrode will respond to a step change in the potassium ion activity in solution in less than one minute. When however, the electrode is removed from one solution and placed in another of different potassium concentration, it may take up to 5 minutes to achieve a new equilibrium.

The presence of some interfering ions, especially Na^+ and NH^{4+} can cause considerable increase in the response time. After exposure to strong concentrations of such ions, the electrode should be reconditioned in 10^{-2}M potassium solution for about an hour.

2. Operation and Handling

2.1 Initial Filling and Setting-Up

On receipt of the electrode remove it from its packing and inspect for damage, particularly to the delicate, transparent membrane, which forms the sensing end of the electrode. Unscrew the sensor unit and introduce a few ml of the Internal Filling Solution supplied. Remove air bubbles from inside the unit by tapping or pushing a blunt instrument of suitable diameter down into the unit, placing a finger over the membrane to feel when the instrument makes contact and avoiding rupturing the membrane. Fill the membrane unit to overflowing with solution and screw it slowly back onto the electrode body. After the first few turns observe the surface of the membrane as the unit is screwed up and when the membrane begins to bulge, stop turning it and back-off very slightly to give a flat membrane. Any sign of solution seeping around the membrane indicates a damaged membrane unit and a replacement should be used.

The electrode is now 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 potassium solution placed on a magnetic stirrer. Ensure that the liquid level does not come above the membrane unit/electrode body junction. Clamp a reference electrode (a double junction Ag/AgCl or SCE with 1M sodium nitrate in the bridge) so that its end is immersed in the same solution and connect both electrodes to a pH or milivolt meter. Record the potential when it becomes steady. Change the test solution sequentially for 10^{-2}M, 10^{-3}M and 10^{-4}M potassium solutions and plot the calibration curve, washing and drying the electrode between solutions.

Unknown solutions can 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

If the electrode is to be used within a week or so, it can merely removed from the test solution, washed and dried and be clamped in a vertical

position in the air. For longer storage, the internal filling solution should be emptied and the unit stored dry. There is in principle no limit to the storage time but gradual oxidation of the membrane will, however, cause it to harden and lose its response. Shelf life, in its dry state, is better than six months.

2.4 Flow Through Configuration

A conversion kit 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 flexible nature of the membrane causes the pump pulses to product rather more 'noise' on the electrode signal than normally found (+ 0.8mV as opposed to +0.2mV). This can be mitigated by either damping the recorder input signal or using a pulseless pump.

3. Applications and Bibliography

The potassium electrode has been used extensively for the measurement of inorganic potassium in aqueous systems. The application of the electrode to biological fluids has also been described.

The following is a selected list of some of the more interesting applications of the potassium electrode.

Potassium in Serum and Other Biological Fluids

1. M. S. Frant and J. W. Ross, Science, 167, (1970) 987
2. D. S. Miyada, K. Inami and G. Matsuyama, Clin. Chem., 17 (1971) 27
3. P. Hnik et al., Brain Research, 40 (1972) 559
4. L. A. R. Pioda et al., Clin Chim. Acta., 29 (1970) 289
5. W. M. Wise, M. J. Kurey and G. Baum, Clin. Chem., 16 (1970) 103
6. R. N. Khuri et al., Pfluegers Arch., 322 (1971) 39
7. F. Schneeweiss and R. L'Orange, Z. Naturforsch. B., 26 (1971) 624

Potassium Activity Measurements

1. H. Z. Trutnovsky, S. Klin, Chem. Klin, Biochem., 9 (1971) 341
2. J. N. Butler, R. Huston, Anal. Chem., 42 (1970) 676
3. G. A. Richnitz and M. S. Mohan, Science 168 (1970) 1460

Potassium in Soil

A. Banin, D. Shabed, Agrochimica, 15 (1971) 238

Potassium in Sea Water

T. Anfalt and D. Jagner, Anal. Chim. Acta., 66 (1973) 152

4. Trouble Shooting

4.1. Wildly erratic readings

i) Air bubble trapped either inside membrane unit or outside on the surface of the membrane.

ii) Wrong filling solution used.

iii) Excessively violent stirring.

4.2. Steady continuous drift in one direction

i) Check membrane for leaks. This can be done by wiping the face of the membrane dry and screwing the membrane unit up a little tighter and observing whether any fluid escapes. Replace membrane.

ii) Poor earthing of the mV meter.

iii) Excessive leaking form the reference electrode junction leading to continuous changes in the activity coefficients of ions in weaker solutions.

iv) Temperature drift if solutions are not thermostatted, or sample vessel insulated from. For example, stirrer motor.

v) Not using a double junction reference electrode.

4.3. Slope of electrode much less than 50mV/decade

i) Membrane unit old and in need of replacing.

ii) Presence of an interfering ion in a constant concentration, swamping the selected ions - check performance with pure potassium chloride solutions.