Ion Selective Electrode
OPERATING INSTRUCTIONS

Mono/Reference
Combination

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Operating Instructions
Calcium Ion Selective Electrode

This Document includes operating instructions for two types of Ion Selective Electrode. A single sensing Half Cell Calcium Electrode which requires a separate Reference Electrode, and a Combination Calcium 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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1. Introduction

1.1 Construction

The electrode consists of an inert fluorocarbon body with a solid state PVC membrane unit. The sensitive membrane consists of liquid ion exchange material immobilised in a poly-(vinyl chloride) matrix. Connection to a millivoltmeter is via coaxial cable and BNC plug. As an alternative, other plugs 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. 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 calcium 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 principals 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 calcium ion activity over the range $10^{-5}$ - $5 \times 10^{-4}$M. The linear detection limit is around $10^{-5}$M but careful calibration allows the electrode to be used down to $5 \times 10^{-6}$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 calcium to the solution being measured. Figure 1 shows a typical calibration plot of the electrode. Values for the slope of the plot should lie in the range 24-29mV/decade.

If the total ionic strength of all solutions is maintained constant by the addition of a concentrated (ca. $10^{-3}$M) inert electrolyte, such as potassium nitrate or sodium fluoride, the electrode can be calibrated directly in concentration units.
Daily re-calibration is recommended for analytical use.

![Graph showing the relationship between Millivolts and Activity of Calcium.](image)

The activity coefficient of calcium 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.

<table>
<thead>
<tr>
<th>Ionic Strength</th>
<th>0.001</th>
<th>0.005</th>
<th>0.01</th>
<th>0.05</th>
<th>0.1</th>
<th>0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activity coeff.</td>
<td>0.905</td>
<td>0.809</td>
<td>0.749</td>
<td>0.57</td>
<td>0.485</td>
<td>0.405</td>
</tr>
</tbody>
</table>

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

\[
\text{Ionic Strength} = \frac{1}{2} \sum_{i=1}^{N} C_i Z_i^2
\]

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 calcium electrode is usually in the region of 1-2mV/day.
1.5 Selectivity

The calcium electrode is free from any really major interference with the exception of zinc ions. Relative selectivity ratios for several interfering ions are given in the table below:

<table>
<thead>
<tr>
<th>Interfering Ion</th>
<th>Selectivity Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(^{2+})</td>
<td>2.5 \times 10^4</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>3 \times 10^3</td>
</tr>
<tr>
<td>Pb(^{2+})</td>
<td>0.1</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>1.0</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>0.8</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>1.45 \times 10^4</td>
</tr>
<tr>
<td>K(^+)</td>
<td>less than 10^6</td>
</tr>
</tbody>
</table>

The selectivity ratios vary with interferent activity and according to method of measurement. These figures should be used as a guide only. The electrode should be used in the pH range 4-9.

1.6 Response Time

The electrode will respond to a step change in the calcium ion activity in solution in less than 10 seconds. When however, the electrode is removed from one solution and placed in another of different calcium concentration, it may take up to 30 seconds to achieve a new equilibrium.

The presence of some interfering ions, especially Mg\(^{2+}\), Zn\(^{2+}\), and Sr\(^{2+}\), can cause considerable increase in the response time. After exposure to strong concentrations of such ions, the electrode should be reconditioned in 10^{-5}M calcium solution or about an hour.

2. Operating and Handling

2.1 Initial Setting Up

On receipt of the electrode remove it from its packaging and inspect for damage, particularly to the delicate membrane, which forms the sensing end of the electrode. The electrode is now ready for use.

2.2 Making a Measurement

The electrode should first be calibrated as follows. Clamp the electrode vertical in a position such that the membrane is immersed in a beaker of 10^{-5}M calcium 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 single junction Ag/AgCl or S.C.E. is quite adequate) so that its end is immersed in the same solution and connect both electrodes to a pH or millivoltmeter. Record the potential when it becomes steady. Change the test solution sequentially for 10^{-5}M, 10^{-6}M and
$10^{-4}$M calcium solutions and plot the calibration curve, washing and drying the electrode between 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

If the electrode is to beused within a week or so, it can be merely removed from the test solution, washed and dried and be clamped in a vertical position in the air. 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 twelve 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 produce rather more 'noise' on the electrode signal than normally found ($\pm 0.8$ mV as opposed to $\pm 0.2$ mV). This can be mitigated by either damping the recorder input signal or using a pulseless pump.

3. Applications and Bibliography

The calcium electrode has been used extensively for the measurement of inorganic calcium in aqueous systems. Applications such as titration's, complexometric studies and activity coefficient determinations are now commonplace and references can be found in almost any journal. The increasingly widespread use of calcium electrode in physiological and biological fluids has been a result of the many research papers published in this field. Continuous flow measurements of ionised calcium in blood and serum have provided a new simple and rapid method for the routine determination of free/bound calcium ratios, which are of significant physiological importance.

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

Calcium in Tap Water

G. J. Moody et al., Analyst, 95 (1970) 910
Calcium in Sea Water

M. E. Thompson, Science, 153 (1966) 867
M. E. Thompson and J. W. Ross, Science, 154 (1966) 1643

Calcium in Detergents

R. W. Cummins, Detergent Age, March 1698, P.22

Calcium in Soil Extracts

K. L. Cheng et al., Microchem J., 18 (1973) 256

Calcium in Milk


Calcium in Serum

D. S. Bernstein, Endocrinol., 85 (1969) 589
I. C. Radale et al., Clin. Chem., 17 (1971) 1002