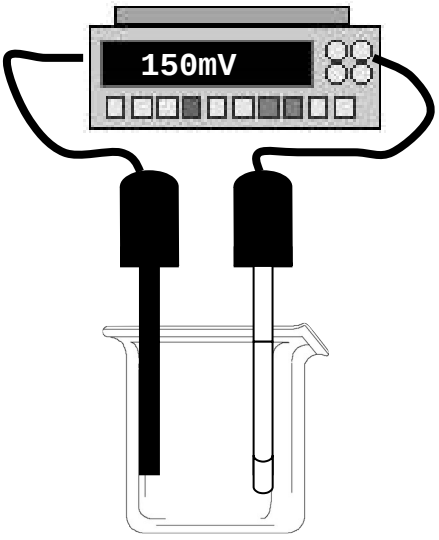
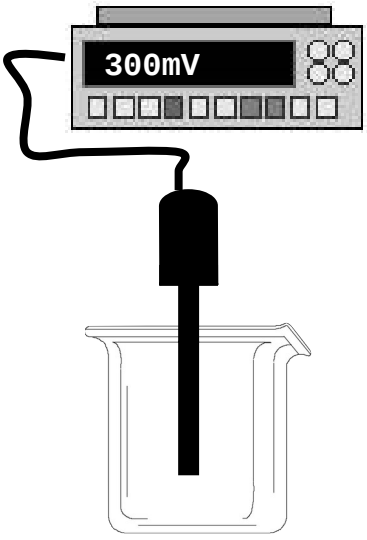
SENTEK

Ion Selective Electrode

OPERATING INSTRUCTIONS



Mono/Reference



Combination

WATER HARDNESS

SENTEK

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Operating Instructions
Water Hardness Ion Selective Electrode

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

The combination ion selective electrode has a solid state PVC polymer membrane with an integral *dri*TEK reference electrode. The electrode is designed for measuring Water Hardness 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 Calcium 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

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 Calcium solution for 1 hour.

Specification

The Water Hardness ISE detects both Calcium and Magnesium Ions to give Total Hardness . If there are no Calcium ions present this ISE may also be used as a Magnesium ISE and Vice Versa.

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	180 mm
Resistance at 25 Deg C	< 2.5 Meg Ohm
Concentration Range	0.00005 to 0.2 mol/l
Slope	24 to 29 mV per decade
Potential Drift	2 mV per day
Operating pH range	2 to 11
Temperature range	5 to 50 Deg C
Endpoint time	Typically 20 to 50 seconds
Interferences. Ions with coefficients above 0.001.	Cadmium Barium Copper

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 Water Hardness 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, 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. 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 water hardness 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 responds to the total uncomplexed ion activity of calcium plus magnesium over the range 10^{-1}M - 10^{-4}M. This represents the linear portion of the calibration curve but careful calibration will allow measurements to be made to 5 x 10^{-5}M. Curvature of the response is observed at lower concentrations because the solubility of the ion exchanger leached from the membrane contributes a small but significant amount of divalent ions to the solution being measured. Figure 1 shows a typical calibration plot of the electrode. values for the slope of this should lie in the range 22-29mV/decade. If the total ionic

strength of all solutions is maintained constant by the addition of a concentrated (approx.10^{-1}M) inert electrolyte.

Daily re-calibration is recommended for analytical use.

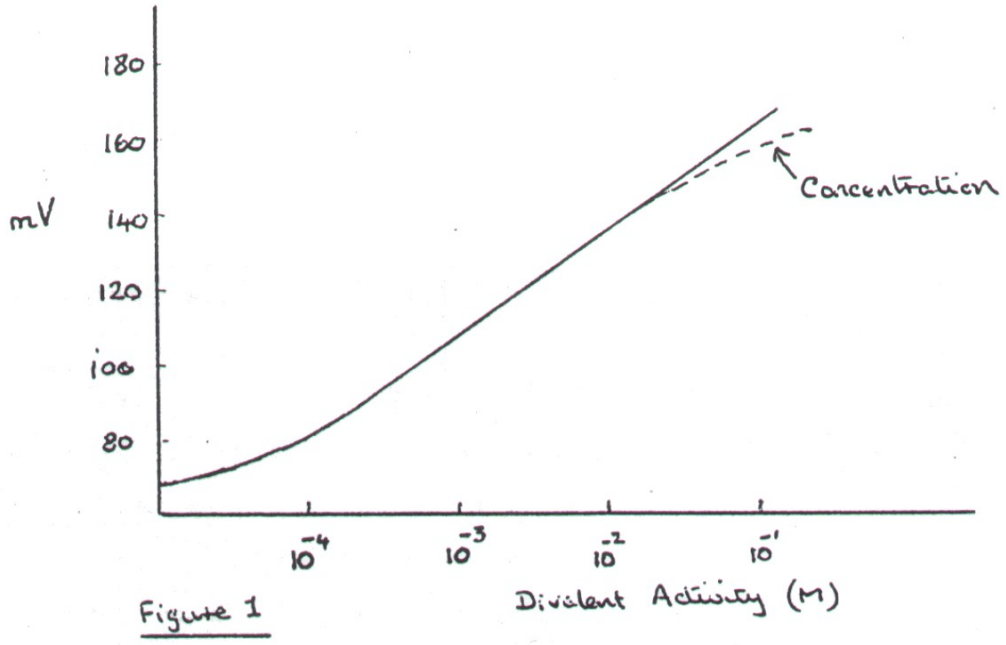

Figure 1

The activity coefficient of divalent ions 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.	0.91	0.81	0.75	0.57	0.49	0.41

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 water hardness electrode is usually in the region of 2-5mV/day.

1.5 Selectivity

The electrode responds approximately uniformly to all divalent cations while the selectivity ratios for common monovalent cations are all around 10^{-2}M or less. Copper, zinc and iron (II) are significant interferences and care should be taken to eliminate these elements from natural waters when hardness measurements are made.

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 be used in the pH range 4.5-8.

1.6 Response Time

When first placed in solution, the electrode may take 10-15 minutes to reach initial equilibrium, depending upon the ionic-strength of the solution. The electrode will respond to a step change in the divalent ion activity in solution in less than one minute. When however, the electrode is removed from one solution and placed in another of different concentration, it may take up to 5 minutes to achieve a new equilibrium.

The presence of some interfering ions, especially Fe^{2+} and Ba^{2+}can cause considerable increase in the response time. After exposure to strong concentrations of such ions, the electrode should be re-conditioned in 10^{-2}M calcium 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 in to 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 tuning it and back-off very slightly to give a flat membrane. Any signs 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 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 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 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 form the electrode suppler.

2.3 Storage

If the electrode is to be used 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.

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 produce rather more 'noise' on the electrode signal than normally found ($\pm$ 0.8mV as opposed to $\pm$ 0.2mV). This can be mitigated by either damping the recorder input signal or using a pulseless pump.

3. Applications and Bibliography

Apart from the direct determination of the Ca and Mg content of a variety o waters the electrode has been used for the determination of magnesium in the absence of calcium.

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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 b 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 from the reference electrode junction leading to continuous changes in the activity coefficients of ions in weaker solutions.
iv) Temperature drift if solutions are not thermosatted, or sample vessel insulated from, for example, stirrer motor.

4.3 Slope of electrode much less than 20mV/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 calcium chloride solutions.