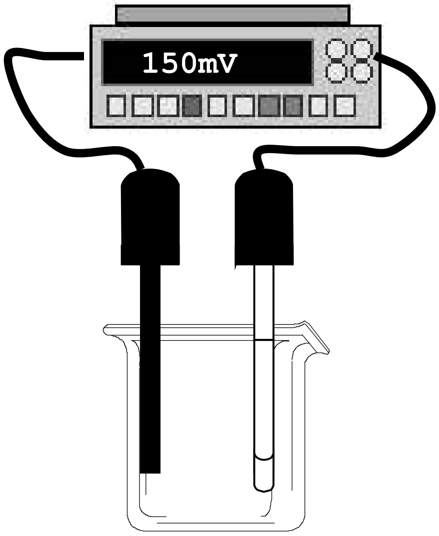
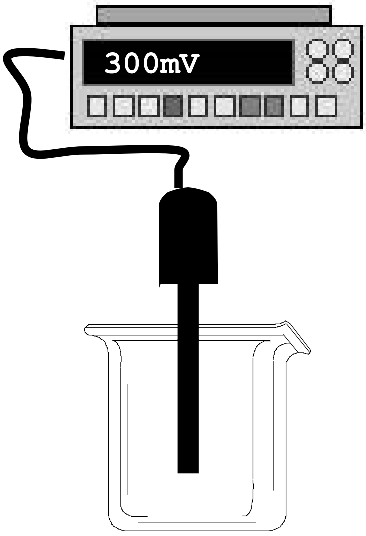
# SENTEK

# Ion Selective Electrode
# OPERATING INSTRUCTIONS

## FLUORIDE



Mono/Reference



Combination

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# Operating Instructions
# Fluoride Ion Selective Electrode

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

## Introduction

The Fluoride ion selective electrode is a combination sensor, which does not require a separate reference electrode.
The electrode is designed for the detection and analysis of fluoride ions in aqueous solutions and is ideal for both field and laboratory use.

## Installation

1. Remove the black protective cap and keep in a safe place.
2. Connect the electrode to a suitable pH, millivolt or ion meter.
3. Immerse the electrode in the weakest calibration standard to be used for 10 minutes.
4. Rinse the electrode tip with distilled or de-ionised water prior to all measurements.

## Operation

1. Start calibration from the lowest concentration standard.
2. Rinse electrode tip with distilled water between readings.
3. Ensure the slope is -57mV ± 3mV @ 20 °C
4. The electrode need not be immersed in more than 1 cm for an accurate result, but it may be completely immersed if required e.g. when field monitoring from boats, banks or bridges.
5. Avoid strongly acidic or alkaline solutions, detergents or PVC solvents.
6. To prolong the life of the electrode ensure that it is not left in sample solutions for longer than is necessary after a result is obtained.

## Storage

Place the black electrode protection cap over the membrane. If appropriate, the electrode can be stored in its box.

**NOTE: The electrode once used can be left dry. Upon re-use the electrode tip must be immersed in a 100ppm fluoride solution.**

## Specification

| | |
|---|---|
| Slope: | -57mV/dec |
| Range: | 0.2-1900ppm |
| pH Range: | 4-8 |
| Reproducibility: | 2% |
| Potential Drift: | 0.5mV/8Hrs |
| Selectivity coefficients: (max. level for a 10% error at 0.001M Fluoride) | Hydroxide 0.0001M |

# Operating Instructions for Fluoride Electrode
## Specifications

**Range**: The Fluoride Electrode responds to uncomplexed fluoride ion activity over the range 1M-1x 10-6M. Linear detection limit is about 5x10-6M

**Interference's:** The only serious interference's to the performance of the Fluoride Electrode are those ions which cause complexation of Fluoride in the measuring solution and from hydroxyl ions.

| Interference's | Level at which interference occurs |
|---|---|
| OH- | K /OH = 10-1 |
| A13+ | Form complexes with F- |
| Fe3+ | Should be preferentially complexed |
| La3+ | |

**pH Range:** The Fluoride Electrode should be used in the pH range 4-9 to eliminate OH- interference.

**Response Time:** The electrode will respond to a step change in the fluoride ion activity in solution in less than 4s. When, however, the electrode is removed from one solution and placed in another of different fluoride concentration, it may take up to 30s to equilibrate.

**Temperature Range:** 0-80 Deg. C

**Stability:** The long term drift in Eo 1-2mV/day

## Section 1

Recommended Equipment
Meter: For fast results in direct concentration units, use a good quality Ion Analyser or a pH/mV Meter with a resolution of 0.1mV.
Reference: Single Junction Calomel
Electrode
Magnetic Stirrer
Anglepoise Stand

Required Solutions
Reference electrode filling solution
3M KCl
Standard solutions
0.1M NaF
1000ppm NaF
Ionic Strength Adjustment Buffer (ISAB)
TISAB
NB: Only highest quality de-ionised water should be used when preparing solutions and standards

## Section 2

### Activity Coefficients

The activity coefficient of fluoride ion depends upon the ionic strength of the solution.

The following table can be used to calculate the approximate activity coefficients at various strengths.

| Ionic Strength | 0.001 | 0.005 | 0.01 | 0.05 | 0.1 | 0.2 |
|---|---|---|---|---|---|---|
| Activity Coeff. | 0.97 | 0.95 | 0.914 | 0.82 | 0.77 | 0.64 |

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

$$\text{Ionic Strength} = 1/2 \nexists C Z^2$$

Where C is the concentration of species i, Zi 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 Above, then the activity of the ion of interest is found from :

Activity (Ai) = Concentration (Ci) x Activity Coeff. (f)

If the total ionic strength of all solutions is kept constant by the addition of a solution of high ionic strength that does not react or interfere with standards or samples, then the electrode can be calibrated in concentration units without considering the effects of activity (see. p.5)

## Section 3

### Setting Up

The Sensing Electrode

1. Inspect the electrode for damage, particularly to the highly polished membrane which forms the sensing end of the electrode.
2. Place in the special electrode holder and lower into a solution of 0.1M NaF.
3. Soak for two hours or until the electrode potential remains stable when measured against a single junction reference electrode (overnight soaking is recommended).
4. The electrode is now ready for use.

The Reference Electrode

The reference electrode should be prepared as indicated in the reference electrode instruction manual.

Points to remember:

1. Remove protective teat from the end of reference electrode.
2. The fill hole should be uncovered during use.

The Standard Solutions

10-1M and 1000ppm NaF solutions are available from SENTEK Limited.

To Prepare Calibration Standards (M)

1. Pipette 50ml 10-1M into 500ml volumetric flask and make up to the mark with de-ionised water.
   =10-2M
2. Pipette 10ml of 10-2M standard prepared in 1, into 100ml volumetric flask and make up to the mark with de-ionised water.
   =10-3M

3.Pipette 10ml of 10-3M standard prepared in 2, into 100ml volumetric flask and make up to the mark with de-ionised water.

=10-4M

For standards of 1000; 100; 10 and 1 ppm, follow procedure 1 to 3 above and use the 1000ppm standard as stock solution.

This process of preparation of a series of standards is known as "Serial Dilution".

### The Ionic Strength Adjustments Buffer (ISAB)

This is a solution of high ionic strength added to dilute samples and standards before measurement, the purpose of which is to:

1. Ensure that that background ionic strength of all solutions is kept constant.
2. Minimise the differences in ionic strength between samples and standards.
3. Adjust the pH to the correct value for measurement.
4. In the case of fluoride, this solution also preferentially complexes those ions that would otherwise complex with fluoride.

The ISAB for the Fluoride Electrode is known as TISAB, and can be supplied by SENTEK Limited (see p.2), or prepared according to the following compositions.

| | |
|---|---|
| 57ml/litre | Glacial Acetic Acid |
| 58 g/litre | Sodium Chloride |
| 0.2 g/litre | CDTA |

adjusted to pH 5.5 with 4M Sodium Hydroxide.

## A Note About Interference's

An interference is defined as any species (apart from the ion being measured) which affects the measured potential of the sensing electrode/reference electrode pair.

Interference's can be:

1. Species that give a similar response to the ion being measured.
2. Species that interact with the membrane.
3. Species that interact with the ion being measured so decreasing its activity.

The level at which interference occurs for different ions is given on p.1.

## Section 4

## Calibration and Making a Measurement

General Hints for Accurate Results.

a) Temperature

ALWAYS ensure that standards and samples are kept at the same temperature and that the temperature remains constant.

b) Stirring

It is preferable to stir standards and samples. Stir such that no vortex is visible.

If using a magnetic stirrer it is a good policy to place a piece of insulating material between the plate and the beaker to eliminate any temperature effects arising from the stirrer itself.

Some samples are impossible to stir consistently. If this is the case it may be better not to stir but remember to treat any standards in the same way.

## Calibration and Measurement Using a pH/mV Meter.

Set the mode or function switch on meter to mV.

1. Prepare standards and electrodes as described in Section 3. Pipette 50ml of 10-1M standard into a beaker and add (accurately) 50.0ml of TISAB. Repeat for each of 10-2, 10-3, and 10-4M standards.
2. Connect the Fluoride Electrode and Reference electrode to meter and place in the special electrode holder in a vertical position.3. Place electrodes in the 10-1M standard. Wait for a stable reading and record mV value.
3. Raise electrodes from the solution, rinse with de-ionised water, blot with a tissue and place in the 10-2M standard. Wait for a stable reading and record mV value.
4. Repeat this process sequentially for 10-3M and 10-4M fluoride solutions and plot the calibration curve of mV readings against the corresponding standard solution concentration (fig.1)
5. Pipette 50ml of sample into a beaker and add (accurately) 50.0ml of TISAB. Rinse the electrode with de-ionised water, blot with a tissue and place in sample. Wait for a stable reading, record mV value and read concentration from the graph.

## Calibration Using a Direct Readout Concentration Meter

Set the mode or function switch on meter to "Concentration".

1. Prepare standards and electrodes as described in Section 3. Select two standards such that their concentrations bracket the expected sample concentration and are a decade apart. For each standard, pipette 50.0ml into a clean beaker and add (accurately) 50.0ml of TISAB.
2. Connect the Fluoride Electrode and Reference Electrode to meter and place in the special electrode holder in a vertical position.
3. Lower electrodes into standard of highest concentration. Wait for a stable reading and enter correct value in the concentration units in which you wish to work.
4. Remove electrodes, rinse with de-ionised water, blot with a tissue and place in second standard. Wait for a stable reading and enter the correct value in concentration units.
5. Pipette 50.0ml of sample into a beaker and add (accurately) 50.0ml TISAB. Rinse the electrodes with de-ionised water, blot with a tissue and place in the sample.

Wait for a stable reading and read the concentration of the sample directly from the display in concentration units.

## Checking the Electrode Slope

This can be done using either of the meter types above.
Set the mode switch on the meter to "mV".

1. Select two standards solutions whose concentrations are one decade apart. For each standard, pipette 50.0ml into a clean beaker and add (accurately) 50.0ml of TISAB.
2. Place the Fluoride Electrode and Reference Electrode in the first standard Wait for a stable reading and record mV value.
3. Remove electrodes, rinse with de-ionised water, blot with a tissue and place in the second standard. Wait for a stable reading and record mV value.
4. The difference between the two recorded mV values should be 57+/-2mV. (If slope is too low see section 5).

## Section 5

| Problem | Possible Cause (s) | Solution |
|---|---|---|
| Wildly Erratic Readings | Air Bubbles trapped on out side surface of membranes.<br>Poor connections inside electrode plug<br>Meter or stirrer not grounded properly<br>Excessively violent stirring<br>Reference Electrode junction blocked<br>Defective meter | Check outside of membrane and tap electrode to release.<br>Open plug and check wiring<br>Ground meter or stirrer<br>Reduce stirrer speed<br>Clean Junction (see Section 6)<br>Check meter with shorting plug |
| Steady continuous drift in one direction | Membrane leaking<br>Excessive leakage from reference electrode junction<br>Temperature drift | Replace electrode<br>Replace Reference electrode<br>Thermostat all solutions or allow to some to room temp before measurement |
| Electrode slope less than 55mV/Decade | Presence of an interfering ion in a constant concentrating, swamping the selected ions. | Check performance with fresh standards and ISAB. (See. p.4 and p.7) |

| | | |
|---|---|---|
| | Electrode aged | Replace electrode |
| Problem | Possible Cause (s) | Solution |
| Over range reading | Air bubble trapped on inside of membrane | Shake electrode (with membrane facing downwards) to release air bubble |
| | Reference electrode not filled | Fill reference electrode with correct solution |
| | Poor connections inside electrode plugs | Open plugs and check wiring |
| | Defective meter | Check meter with shorting plug. |

# Section 6

## Storage and Maintenance

The Fluoride Electrode
Storage/Short Term: Rinse with distilled water, dry and clamp in air.
Long Term: Rinse with distilled water, dry and return to the electrode box.
Maintenance: The factors which reduce membrane life are damage to the membrane surface and hydrolysis of adhesives used to mount the membrane in position.
Do not store in solution.
Inspect the membrane surface for scratches on a regular basis. SENTEK can re-polish a damage membrane (if scratches are not too deep). An occasional polish with a tissue or soft cloth will help keep the membrane shiny.
Check the slope of the electrode on a regular basis. (see p.9). If the slope is less then 55mV/Decade, it is probably necessary to replace the electrode but first check other possible causes of low slop given in Section 5.

### The Reference Electrode

(Always refer to the reference electrode instruction manual)
Storage/Short Term: Overnight the reference can be left soaking in a solution of 2M KCl.
Long Term: For periods of storage of longer than two days replace the electrode storage teat containing 3M KCl and return electrode to the electrode reference box.
Maintenance: To ensure good results the internal filling solution should be replaced at least every six months. (More often s necessary).
Always ensure that the level of internal filling solution covers the internal element.
Top up the electrode via the side filling hole when needed.

If the external filling solution becomes contaminated by influx of extraneous solutions through the liquid junction: Remove external filling solution using a hypodermic syringe, rinse the chamber with de-ionised water followed by 3M KCl and then refill with 3M KCl.
If the inner element becomes contaminated the electrode should be discarded.

The major cause of reference electrode failure is junction blockage. The following steps can be taken to unclog a reference junction.

1. Replace filling solution and soak overnight in filling solution.
2. Force filling solution through the junction by applying pressure to the filling hole, or vacuum to the junction.
3. Soak junction for 10 minutes in dilute filling solution heated to 50°C maximum.