



Orion 93-05

## Orion Fluoroborate Electrode

INSTRUCTION MANUAL



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ORION Series A meters and 900A printer are protected by U.S. patents 5,108,578, 5,198,093 and German patents D334,208 and D346,753.

Sure-Flow electrodes are protected by European Patent 278,979 and Canadian Patent 1,286,720.

ionplus electrodes and Optimum Results solutions are protected by US Patent 5,830,338.

ROSS Ultra electrodes have patents pending.

ORION ORP Standard is protected by US Patent 6,350,367.

ORION Series A conductivity meters are protected by US Patent 5,872,454.

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The specifications, descriptions, drawings, ordering information and part numbers within this document are subject to change without notice.

This publication supersedes all previous publications on this subject.

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# GENERAL INFORMATION

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## Introduction

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The Orion 93-05 Fluoroborate Electrode measures fluoroborate ions in aqueous solutions simply, accurately, and economically.

General analytical procedures, required solutions, electrode characteristics, and electrode theory are discussed in this manual. Operator instructions for Orion meters are outlined in the individual meter's instruction manual.

Consult Thermo Electron's Technical Edge for assistance and troubleshooting advice. Please refer to **Troubleshooting** for information on contacting Thermo.

## Required Equipment

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### Meter

ISE meters, such as Orion EA940, 920A, 720A, 710A, or 290A, offering direct concentration readout for specific ions are the easiest to use. If unavailable, use a pH/mV meter with readability to 0.1 mV, such as Orion 420A, 520A, or 525A.

### Reference Electrode

For use with Model 93-05:

Orion Model 90-02 Double Junction                      Orion 900200

***Note: Do not use the outer chamber filling solution shipped with the reference electrode.***

### Recommended Accessories

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**Plastic labware** is recommended for all fluoroborate measurements since the presence of hydrofluoric acid present in fluoroborate solutions etches glass.

**Magnetic stirrers** are recommended for laboratory measurements for homogeneous mixture.

**Graph paper** 4 cycle semi-logarithmic paper for preparing calibration curves for use with digital pH/mV laboratory meters.

## Required Solutions

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### Distilled or Deionized Water

To prepare all solutions and standards.

### Standards

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#### Orion Ionic Strength Adjustor (ISA)      Orion 930711

To adjust ionic strength of samples and standards.

### Standard Solutions

#### **0.1 M Sodium Fluoroborate**                      **Customer Prepared**

Dissolve 10.98 g. of reagent-grade  $\text{NaBF}_4$  in a 100 mL distilled water and filter. Transfer the filtrate to a 1Liter volumetri flask, and dilute to volume with distilled water. Store the solution in a polyethylene bottle and discard it after a week to avoid errors introduced by hydrolysis of fluoroborate.

#### **1000 ppm Sodium Fluoroborate**                      **Customer Prepared**

To prepare 1000 ppm fluoroborate standard solution, dissolve 16.1 mL of the 0.1 M standard to a 100 mL. volumetric flask. Dilute to volume with distilled water.

#### **Reference Electrode Filling Solution**                      **Customer Prepared** **(outer chamber)**

Add 2 mL of ISA to 100 mL of distilled water. Use this solution to fill the outer chamber of the reference electrode.

# BEFORE USING THE ELECTRODE

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## Electrode Assembly and Preparation

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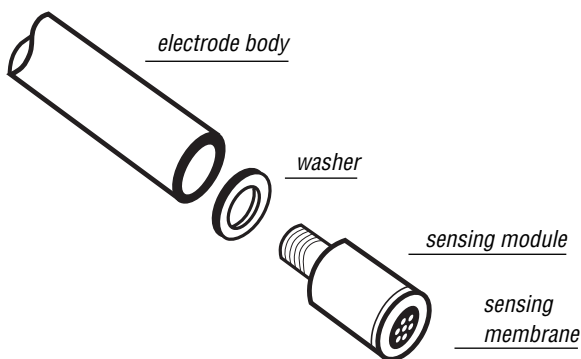
### Orion 93-05 Fluoroborate Half Cell Electrode:

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Remove the sensing module from the vial. Make sure the rubber electrode washer on the sensing module is in place. See Figure 1. Screw the sensing module into the electrode body until finger tight. To ensure electrical continuity, shake down the electrode like a clinical thermometer. Rinse the fluoroborate electrode with distilled water, then soak in distilled water for 10 minutes, then in standard 100 ppm (or  $10^{-2}$  M) fluoroborate solution for 1 to 2 hours prior to initial use.

***Do not immerse the electrode past the rubber electrode washer.***

***See Figure 1.***



**Figure 1**  
***Model 93-05 Electrode Assembly***

### Orion 90-02 Double Junction Reference Electrode:

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Required for use with Orion 93-05 Fluoroborate Half-Cell Electrode. No assembly is required. Fill the reference electrode according to instructions in the reference electrode instruction manual, using Orion 900002 Filling Solution in the inner chamber. ***Do not use the outer chamber filling solution shipped with the 90-02 reference electrode because it will interfere with your fluoroborate measurements.***

***NOTE: Be careful not to touch the sensing membrane during assembly!***

## **Checking Electrode Operation (Slope)**

Use these general instructions to check electrode operation. See individual meter instruction manuals for more specific information.

This procedure measures electrode slope. Slope is defined as the change in millivolts observed with every tenfold (decade) change in concentration. Obtaining the slope value provides the best means for checking electrode operation.

- 1** If electrode(s) has been stored dry, prepare the electrode(s) as described under the section entitled Electrode Assembly and Preparation.
- 2** Connect electrode(s) to the meter as described in the meter instruction manual.
- 3** Select either 0.1 M or 1000 ppm standard solution.
- 4** Place 100 mL distilled water into a 150 mL beaker. Add 2 mL ISA, Orion 930711. Stir thoroughly.
- 5** Set the meter to the mV mode.
- 6** Rinse electrode(s) with distilled water, blot dry, and place in the solution prepared in step 4 above.
- 7** Pipet 1.0 mL of the standard into the beaker. Stir thoroughly.
- 8** When a stable reading is displayed, record the electrode potential in millivolts.
- 9** Pipet 10.0 mL of the same standard into the same beaker. Stir thoroughly.
- 10** When a stable reading is displayed (within 4 to 5 minutes), record the electrode potential in millivolts.
- 11** The difference between the first and second potential reading is defined as the slope of the electrode. The difference should be in the range of 56 to 60 mV/decade when the solution temperature is  $25 \pm 5^\circ\text{C}$ . If the slope is not within this range, resoak the electrode as described under the section entitled Electrode Assembly and Preparation. For other troubleshooting techniques refer to the Troubleshooting section.

## Recommendations for Optimum Results

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### Units of Measurement

Fluoroborate can be measured in units of moles per liter, parts per million, and parts per million as boron or any other convenient unit (see Table 1).

**Table 1**  
*Concentration Unit Conversion Factors*

Moles per Liter	ppm as $\text{BF}_4^-$	ppm as B
$10^{-4}$	8.7	1.1
$10^{-3}$	86.8	10.8
$10^{-2}$	868.0	108.9

### Sample Requirements

Samples must be aqueous and must not contain organic solvents. Consult Thermo Electron's Technical Edge for using the electrode in specific applications.

Sample temperature must be less than 40°C, with samples and standards all at the same temperature. At a 1°C difference in temperature produces about a 2.0 % error. For highly accurate results, use a water bath to control temperature variances.

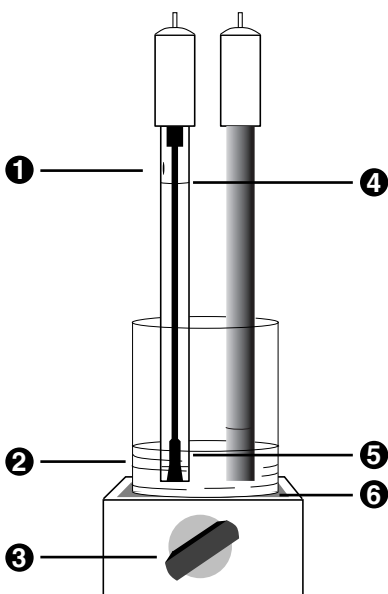
Interferences should be absent. See section entitled Interferences for a list of possible interferences. Electrodes exposed to high interferences will drift for several hours on returning the electrode to fluoroborate standardizing solutions.

Samples must fall in the pH 2 to 12 range. Samples outside this range must be neutralized by adding acid or base. Fluoroborate samples with very high or low pH must be analyzed as soon as possible after preparation to prevent hydrolysis of fluoroborate to  $\text{BF}_3\text{OH}^-$ ,  $\text{BF}_2(\text{OH})_2^-$  and  $\text{BF}(\text{OH})_3^-$ .

Boric acid or borate ion can be analyzed if the boron is converted to fluoroborate by reaction with HF.

### Important ISE Measurement Techniques

- Stir all standards and samples at a uniform rate during measurement. Magnetic stirrers may generate sufficient heat to change solution temperature. Place a piece of insulating material such as cork, cardboard or styrofoam between the stir plate and sample beaker.
- Always use fresh standards for calibration.
- Always rinse electrode(s) with distilled water thoroughly between measurements. Shake electrode after rinsing to prevent solution carryover, then blot dry. Do not wipe or rub the sensing membrane, as you may contaminate and damage the surface.
- Allow all standards and samples to come to room temperature for precise measurements.
- After immersion in solution, check the fluoroborate electrode for any air bubbles on the membrane surface. Remove air bubbles at the electrode surface by gently tapping the electrode.
- The Model 93-05 Fluoroborate Half-Cell Electrode should be submerged approximately half the length of the fluoroborate module. **DO NOT** submerge the electrode above the rubber electrode washer. Submerge the reference electrode to the same depth as the sensing electrode.
- If electrode response is slow, the membrane may contain a surface layer of contaminants. Restore performance by soaking electrodes in distilled water for about 5 minutes, then rinse and soak in a standard solution for about 5 minutes before use.
- For high ionic strength samples, prepare standards with compositions similar to that of the sample.
- Interferences should be removed before measurement. See Interferences section.



**Figure 2 Measuring Hints**

- 1 Filling hole should be uncovered during measurement for Orion 90-02.
- 2 Use fresh standard.
- 3 Stir all samples and standards.
- 4 Filling solution level must be higher than sample level with at least 1 inch above the reference pellet.
- 5 Immerse reference junction.
- 6 Place insulation between stirrer and beaker.

***NOTE: Do not submerge sensing module past rubber electrode washer.***

## Choosing the Right Measuring Technique

- **Direct Measurement** is a simple procedure for measuring a large number of samples. This method requires only one meter reading for each sample. Calibration is performed with a series of standards. The concentration of the samples is determined by comparison to the standards. Addition of ISA to all solutions ensures that samples and standards have similar ionic strength, proper pH, and reduces the effect of interfering ions.
- **Low-Level Measurement** is similar to Direct Measurement. Use this method when the expected sample concentration is less than  $10^{-2}$  M. Using a minimum of three calibration standards compensates for the electrode's non-linear response at low concentrations. This procedure describes the best means of preparing low-level calibration standards.
- **Known Addition** is an alternate method useful when measuring only a few samples, when samples have a high ( $> 0.1$  M) ionic strength, or have a complicated background matrix. Refer to Theory of Operation for an explanation of these effects. The electrodes are immersed in the sample solution and an aliquot of a standard solution is added to the sample. From the change in potential before and after the addition, the original sample concentration is determined. As in direct calibration, any convenient concentration unit can be used.

# MEASUREMENT PROCEDURES

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## Direct Measurement

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The following direct measurement procedures are recommended for "high-level" measurements, when all samples fall within the electrode's linear range, greater than 1.1 ppm as B or  $10^{-4}$  M  $\text{BF}_4^-$ . A two point calibration is sufficient, though more points can be used if desired. Using ISE meters, such as the Orion 920A, 720A, 710A, or 290A, read sample concentrations directly from the meter. Refer to the meter's instruction manual for calibration details. When using a mV meter, prepare a calibration curve on semi-logarithmic graph paper, or a linear regression can be performed at the user's discretion using a spreadsheet or graphing program.

### For Improved Accuracy

- Bracket standard concentrations around the expected sample concentration.
- Always dilute samples and standards in a 50:1 ratio with ISA. For example, 100 mL of sample and 2 mL of ISA.
- Verify this procedure by measuring a standard of known concentration as an unknown or by spiking a sample with standard.
- For high ionic strength samples, having an ionic strength of 0.1 M or greater, prepare standards with a composition similar to that of the samples, measure the samples using the known addition method, or dilute the samples.
- During calibration, measure the least concentrated standard first, and work up to the most concentrated.
- The best method for preparation of standards is serial dilution. This procedure involves preparing an initial standard that is diluted to prepare a second standard solution using volumetric glassware. The second is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.
- Review section entitled Important **ISE Measurement Techniques**.

## **Direct Measurement Procedure using an ISE or a mV meter**

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See individual meter instruction manuals for more specific calibration information.

- 1 Prepare the electrode(s) as described in Electrode Preparation.
- 2 Connect electrode(s) to the meter, and adjust the meter to measure concentration for an ISE meter or mV for a mV meter.
- 3 Prepare at least two standards that bracket the expected sample range and differ in concentration by a factor of ten. Standards can be prepared in any concentration unit to suit the particular analysis requirement. All standards should be at the same temperature as the samples. For details on temperature effects on electrode performance, refer to Temperature Effects.
- 4 Measure 100 mL of each standard and sample into separate 150 mL beakers. Add 2 mL ISA to each standard and sample.

**NOTE: Other solution volumes may be used, as long as the ratio of solution to ISA remains 50:1.**

- 5 For an ISE meter: Rinse electrode(s) with distilled water, shake dry, and place into the beaker containing the most dilute standard. Wait for a stable reading, calibrate the meter to display the value of the standard as described in the meter instruction manual.

For a mV meter: Rinse electrode(s) with distilled water, shake dry, and place into the beaker containing the most dilute standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.

- 6 For an ISE meter: Rinse electrode(s) with distilled water, shake dry, and place into the beaker with the next standard. Wait for a stable reading, then adjust the meter to display the value of the second standard, as described in the meter instruction manual.

For a mV meter: Rinse electrode(s) with distilled water, shake dry, and place into the beaker containing the next standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.

- 7 Repeat step 6 for all standards, working from the least concentrated to most concentrated standard.
- 8 For an ISE meter: Calibration information will be calculated and stored automatically.

- 8** For an ISE meter: Calibration information will be calculated and stored automatically.

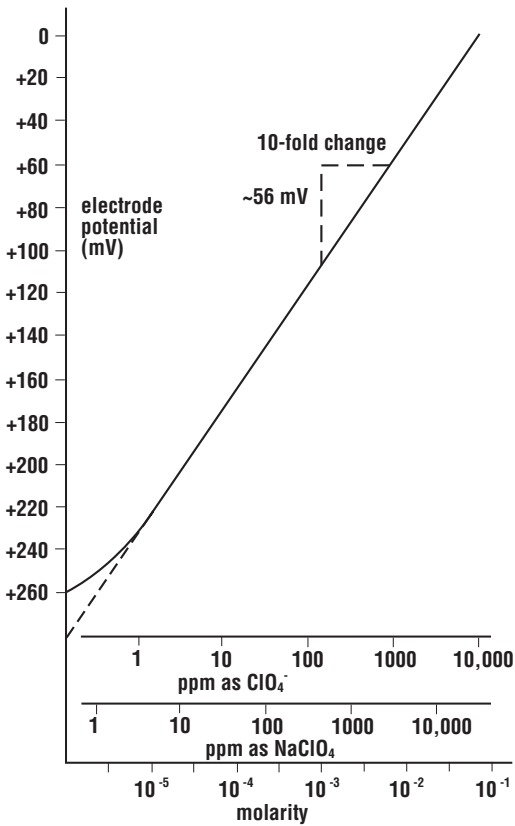
For a mV meter: Using semi-logarithmic graph paper, prepare a calibration curve by plotting the millivolt values on the linear axis and the standard concentration values on the logarithmic axis.

**See Figure 3.**

- 9** Rinse electrode(s) with distilled water, shake dry, and place into the sample.

- 10** For an ISE meter: When the electrode stabilizes, the meter will display the sample concentration.

For a mV meter: When the electrode stabilizes, the meter will display the mV value for the sample. Using the calibration curve prepared in step 8, determine the unknown sample concentration.



**Figure 3 Typical Fluoroborate Electrode Calibration Curve**

During the direct measurement procedure, a calibration curve is constructed automatically by the ISE meter. Alternately, a calibration curve may be plotted by hand using semi-logarithmic paper. Measured electrode potentials of standard solutions are plotted on the linear axis against their concentrations on the log axis. In the linear regions of the curves, only two standards are needed to determine a calibration curve. In non-linear regions, more points must be taken for accurate results. The direct measurement procedures in the manual are given for concentrations in the region of linear electrode response. When measuring in the non-linear region follow the low-level measurement procedure. This curve serves as an example only. Actual mV values may differ.

## **Low-Level Measurements By Direct Measurements**

Use this method when measuring solutions with fluoroborate concentration of less than  $10^{-2}$  M of the  $\text{BF}_4^-$ , those within the non-linear range of the fluoroborate electrode. Low-level measurements require at least three standards to compensate for the electrodes's non-linearity.

### **For Improved Accuracy**

- If some samples have low-level concentrations, and some have higher concentrations, dilute the higher concentrations down to the low-level range. The electrode's response time at low-levels is faster when it is not exposed to high concentrations.
- The choice of calibration standard concentrations is important for obtaining the best electrode performance and most rapid analysis time. Here are some guidelines:

Ideally, calibration standard concentrations should bracket the expected sample concentrations.

The best results are obtained when the concentration of the highest calibration standard is ten to one hundred times the lowest calibration standard concentration. Space additional standards equally within the range.

If the expected sample concentrations fall within a narrow range (less than one order of magnitude), a ratio of highest to lowest standard concentration of ten should be used.

When measuring sub-ppm levels with Orion 920A, 720A, 710A, or 290A, take advantage of the autoblack feature. It does not require a zero standard, but can perform blank correction as long as the lowest standard concentration is in the non-linear range of the electrode. Electrodes are very slow in the absence of a measurable concentration and a multipoint calibration generally will be less accurate when "zero" is included as a standard. Standard concentrations should be chosen such that the lowest standard value is larger than the blank value obtained, and the second lowest standard should be at least twice that of the lowest. See your A Series meter instruction manual for additional information on blank correction.

When not using an ISE meter, a calibration curve can be drawn on semi-logarithmic graph paper or the data can be processed by means of a spreadsheet or graphing program with a non-linear curve fitting feature.

When using the Orion 920A, 720A, 710A or 290A, with the autoblack feature, three calibration points are sufficient. If a calibration curve is prepared manually, additional points may be helpful to facilitate drawing the curve.

- Remember to stir all standards and samples at a uniform rate.
- Review section entitled **Important ISE Measurement Techniques**.

### **Low-Level Measurement Procedure using an ISE or a mV meter**

- 1** Prepare electrode(s) as described in Electrode Preparation.
- 2** Connect electrode(s) to the meter. Set the meter to read mV.
- 3** Select a standard solution. Use either a 10 ppm or a  $10^{-4}$  M fluoroborate standard. To prepare 10 ppm from the 1000 ppm standard, dilute 1 mL of the 1000 ppm standard to 100 mL with distilled water. To prepare  $10^{-4}$  M from 0.1 M standard, dilute 1 mL 0.1 M standard to 1 Liter with distilled water.
- 4** Prepare a low-level ISA solution by diluting 20 mL of the nitrate ionic strength adjustor, Orion 930711 ISA, to 100 mL with distilled water. Use this low-level ISA for low-level measurements only.
- 5** Measure 100 mL distilled water into 150 mL beaker. Add 1 mL low-level ISA.
- 6** Rinse the electrode(s) with distilled water, place into beaker. Stir thoroughly.
- 7** Add increments of the standard to the beaker using steps outlined in **Table 2**.
- 8** For an ISE meter: Follow meter instruction manual for detailed calibration instructions For a mV meter: Record stable millivolt reading after each increment. On semi-logarithmic paper, plot the concentration (log axis) against the millivolt potential (linear axis), see Figure 3. Prepare a new low-level calibration curve with fresh standards each day.
- 9** Measure 100 mL of sample into a beaker. Add 1 mL of low-level ISA.

**10** Rinse the electrode(s) with distilled water, shake dry, and place into the sample. Stir thoroughly.

**11** For an ISE meter: When the electrode stabilizes, the meter will display the sample concentration.

For a mV meter: When the electrode stabilizes, the meter will display the sample mV value. Determine the sample concentration corresponding to the measured potential using the low-level calibration curve prepared in step 8.

**Table 2**  
**Preparing a Calibration Curve For Low-Level Measurements**  
**Using a Meter with mV Readout**

<b>Step</b>	<b>Graduated Pipet Size</b>	<b>Added Volume</b>	<b>Concentration ppm (<math>\text{BF}_4^-</math>)</b>	<b>Concentration Molarity (<math>\text{BF}_4^-</math>)</b>
1	1 mL	0.1 mL	0.01	$1.0 \times 10^{-6}$
2	1 mL	0.1 mL	0.02	$2.0 \times 10^{-6}$
3	1 mL	0.2 mL	0.04	$3.9 \times 10^{-6}$
4	1 mL	0.2 mL	0.06	$5.9 \times 10^{-6}$
5	1 mL	0.4 mL	0.10	$9.8 \times 10^{-6}$
6	2 mL	2.0 mL	0.29	$2.9 \times 10^{-5}$
7	2 mL	2.0 mL	0.48	$4.7 \times 10^{-5}$

Additions of 100 ppm or  $10^{-3}$  M as  $\text{BF}_4^-$  standards to 100 mL distilled water, plus 1 mL low-level ISA.

## **Known Addition Measurement**

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Known addition, KA, is a convenient technique for measuring samples in the linear response range because no calibration curve is needed. Use this method to verify the results of a direct measurement or to minimize existing matrix effects. The sample potential is measured before and after addition of a standard solution. Many meters, such as the Orion 920A and 930 Ionalyzer(s), have the known addition algorithms pre-programmed. This programming makes multiple standard additions to the sample, resulting in more precise results. These direct-reading meters provide a great convenience. Accurate measurement requires that the following conditions be met.

### **For Improved Accuracy**

- Sample concentration should be known to within a factor of three.
- Concentration should approximately double as a result of the addition.
- With double or multiple known addition, the final addition should be 10 to 100 times the sample concentration.
- All samples and standards should be at the same temperature.
- In general, either no complexing agents or a large excess of the complexing agents may be present.
- Standard addition volume should be less than 10% of the sample volume, or standard should be pre-treated with ISA in a 50:1 ratio.
- Dilute samples in a 50:1 ratio with ISA before analysis.
- Review section entitled Important ISE Measurement Techniques.

### **Set-up for Known Addition with all meters**

- 1** Prepare electrode(s) as described in Electrode Preparation.
- 2** Connect electrode(s) to the meter.
- 3** Prepare a standard solution that, upon addition to the sample, will cause the concentration of the standard to double. Refer to Table 3 as a guideline.
- 4** Determine the slope of the electrode by performing the procedure under Checking Electrode Operation (Slope).

## **Known Addition Measurement Procedure using an ISE meter with KA program**

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See individual meter instruction manuals for more specific information.

- 1** Set up the meter to measure in the known addition mode.
- 2** Measure 50 mL of the sample into a beaker. Add 1 mL ISA and stir thoroughly.
- 3** Rinse electrode(s) with distilled water, shake dry, and place into sample solution.
- 4** When a stable reading is displayed, program the meter as described in the meter instruction manual.
- 5** Pipet the appropriate amount of the standard solution into the beaker. Stir thoroughly.
- 6** When a stable reading is displayed, record the sample concentration.

### Known Addition Measurement Procedure using a mV meter

- 1 Set the meter to millivolt mode.
- 2 Measure 50 mL of the sample into a 150 mL beaker. Add 1 mL ISA.
- 3 Rinse electrode(s) with distilled water, blot dry and place into sample solution.
- 4 When a stable reading is displayed, record the mV value as E1.
- 5 Pipet the appropriate amount of standard solution into the beaker. See **Table 3**. Stir thoroughly.
- 6 When a stable reading is displayed, record the mV value as E2. Subtract the first reading from the second to find  $\Delta E$ .
- 7 From Table 5, or by calculation, find the Q value that corresponds to the change in potential,  $\Delta E$ . To determine the original sample concentration, multiply Q by the concentration of the added standard:

$$C_{\text{sam}} = QC_{\text{std}}$$

where:  $C_{\text{std}}$  = standard concentration

$C_{\text{sam}}$  = sample concentration

Q = reading from known addition table

The table of Q values is calculated for a 10% total volume change for electrodes with slopes of 57.2, 58.2, 59.2, and 60.1 mV/decade.

The equation for the calculation of Q for different slopes and volume changes is given below:

$$Q = \frac{p * r}{((1 + p)10^{\Delta E/S}) - 1}$$

where:  $\Delta E$  = E2 - E1

S = slope of the electrode

p = (volume of standard) /  
(volume of sample & ISA)

r = (volume of sample & ISA) /  
(volume of sample)

**Table 3**

<b>Volume of Addition</b>	<b>Concentration of Standard Before Adding ISA</b>
1 mL	100 x sample concentration
5 mL	20 x sample concentration
10 mL*	10 x sample concentration

\*Most convenient volume to use, valid for Q Tables

If it is more convenient, a simple spreadsheet can be set up to calculate known addition results, using any ratios of sample and addition. A typical worksheet is shown in **Table 4**. The numbers shown are examples, but the formulas and their locations should be copied exactly.

**Table 4**

**Calculating known addition for fluoroborate samples using Lotus, Excel or Quattro Spreadsheet**

<b>A</b>	<b>B</b>	<b>C</b>
<b>1</b>		<b>Enter Values</b>
<b>2</b>	<b>VOL. OF SAMPLE &amp; ISA, ML.</b>	<b>51</b>
<b>3</b>	<b>VOL. OF ADDITION, ML</b>	<b>10</b>
<b>4</b>	<b>CONCENTRN. OF ADDITION</b>	<b>10</b>
<b>5</b>	<b>VOL. OF SAMPLE</b>	<b>50</b>
<b>6</b>	<b>INITIAL MV READING<sup>45</sup>.</b>	<b>3</b>
<b>7</b>	<b>FINAL MV READING<sup>63</sup>.</b>	<b>7</b>
<b>8</b>	<b>ELECTRODE SLOPE<sup>59</sup>.</b>	<b>2</b>
<b>9</b>		
<b>10</b>	<b>DERIVED VALUES</b>	
<b>11</b>	<b>DELTA E</b>	<b>+C7-C6</b>
<b>12</b>	<b>p TERM</b>	<b>+C3/C2</b>
<b>13</b>	<b>ANTILOG TERM</b>	<b>+10^(C11/C8)</b>
<b>14r</b>	<b>TERM</b>	<b>+C2/C5</b>
<b>15Q</b>	<b>TERM</b>	<b>+C12*C14/(((1+C12)*C13)-1)</b>
<b>16</b>	<b>CALCULATED INITIAL CONC. IN SAME UNIT AS ADDITION</b>	<b>+C15*C4</b>

**NOTE: for Excel, use = instead of + at start of formula**

**Table 5**  
**Known Addition for an added volume one-tenth the sample**  
**volume. Slopes (in the column headings) are in units of**  
**mV/decade.**

$\Delta E$	Q, Concentration Ratio			
	Slope			
Monovalent	57.2	58.2	59.2	60.1
5.0	0.2917	0.2957	0.2996	0.3031
5.2	0.2827	0.2867	0.2906	0.2940
5.4	0.2742	0.2781	0.2820	0.2854
5.6	0.2662	0.2700	0.2738	0.2772
5.8	0.2585	0.2623	0.2660	0.2693
6.0	0.2512	0.2550	0.2586	0.2619
6.2	0.2443	0.2480	0.2516	0.2548
6.4	0.2377	0.2413	0.2449	0.2480
6.6	0.2314	0.2349	0.2384	0.2416
6.8	0.2253	0.2288	0.2323	0.2354
7.0	0.2196	0.2230	0.2264	0.2295
7.2	0.2140	0.2174	0.2208	0.2238
7.4	0.2087	0.2121	0.2154	0.2184
7.6	0.2037	0.2070	0.2102	0.2131
7.8	0.1988	0.2020	0.2052	0.2081
8.0	0.1941	0.1973	0.2005	0.2033
8.2	0.1896	0.1927	0.1959	0.1987
8.4	0.1852	0.1884	0.1914	0.1942
8.6	0.1811	0.1841	0.1872	0.1899
8.8	0.1770	0.1801	0.1831	0.1858
9.0	0.1732	0.1762	0.1791	0.1818
9.2	0.1694	0.1724	0.1753	0.1779
9.4	0.1658	0.1687	0.1716	0.1742
9.6	0.1623	0.1652	0.1680	0.1706
9.8	0.1590	0.1618	0.1646	0.1671
10.0	0.1557	0.1585	0.1613	0.1638
10.2	0.1525	0.1553	0.1580	0.1605
10.4	0.1495	0.1522	0.1549	0.1573
10.6	0.1465	0.1492	0.1519	0.1543
10.8	0.1437	0.1463	0.1490	0.1513
11.0	0.1409	0.1435	0.1461	0.1485
11.2	0.1382	0.1408	0.1434	0.1457
11.4	0.1356	0.1382	0.1407	0.1430
11.6	0.1331	0.1356	0.1381	0.1404
11.8	0.1306	0.1331	0.1356	0.1378
12.0	0.1282	0.1307	0.1331	0.1353
12.2	0.1259	0.1283	0.1308	0.1329
12.4	0.1236	0.1260	0.1284	0.1306
12.6	0.1214	0.1238	0.1262	0.1283
12.8	0.1193	0.1217	0.1240	0.1261
13.0	0.1172	0.1195	0.1219	0.1239
13.2	0.1152	0.1175	0.1198	0.1218
13.4	0.1132	0.1155	0.1178	0.1198
13.6	0.1113	0.1136	0.1158	0.1178
13.8	0.1094	0.1117	0.1139	0.1159

$\Delta E$	Q, Concentration Ratio			
	Slope			
Monovalent	57.2	58.2	59.2	60.1
14.0	0.1076	0.1098	0.1120	0.1140
14.2	0.1058	0.1080	0.1102	0.1121
14.4	0.1041	0.1063	0.1084	0.1103
14.6	0.1024	0.1045	0.1067	0.1086
14.8	0.1008	0.1029	0.1050	0.1069
15.0	0.0992	0.1012	0.1033	0.1052
15.5	0.0953	0.0973	0.0994	0.1012
16.0	0.0917	0.0936	0.0956	0.0974
16.5	0.0882	0.0902	0.0921	0.0938
17.0	0.0850	0.0869	0.0887	0.0904
17.5	0.0819	0.0837	0.0856	0.0872
18.0	0.0790	0.0808	0.0825	0.0841
18.5	0.0762	0.0779	0.0797	0.0813
19.0	0.0736	0.0753	0.0770	0.0785
19.5	0.0711	0.0727	0.0744	0.0759
20.0	0.0687	0.0703	0.0719	0.0734
20.5	0.0664	0.0680	0.0696	0.0710
21.0	0.0642	0.0658	0.0673	0.0687
21.5	0.0621	0.0637	0.0652	0.0666
22.0	0.0602	0.0617	0.0631	0.0645
22.5	0.0583	0.0597	0.0612	0.0625
23.0	0.0564	0.0579	0.0593	0.0606
23.5	0.0547	0.0561	0.0575	0.0588
24.0	0.0530	0.0544	0.0558	0.0570
24.5	0.0514	0.0528	0.0541	0.0553
25.0	0.0499	0.0512	0.0525	0.0537
25.5	0.0484	0.0497	0.0510	0.0522
26.0	0.0470	0.0483	0.0495	0.0507
26.5	0.0456	0.0469	0.0481	0.0492
27.0	0.0443	0.0455	0.0468	0.0479
27.5	0.0431	0.0443	0.0455	0.0465
28.0	0.0419	0.0430	0.0442	0.0452
28.5	0.0407	0.0418	0.0430	0.0440
29.0	0.0395	0.0407	0.0418	0.0428
29.5	0.0385	0.0396	0.0407	0.0417
30.0	0.0374	0.0385	0.0396	0.0406
30.5	0.0364	0.0375	0.0385	0.0395
31.0	0.0354	0.0365	0.0375	0.0384
31.5	0.0345	0.0355	0.0365	0.0374
32.0	0.0335	0.0345	0.0356	0.0365
32.5	0.0327	0.0336	0.0346	0.0355
33.0	0.0318	0.0328	0.0337	0.0346
33.5	0.0310	0.0319	0.0329	0.0337
34.0	0.0302	0.0311	0.0320	0.0329
34.5	0.0294	0.0303	0.0312	0.0321

$\Delta E$	Q, Concentration Ratio			
	Slope			
Monovalent	57.2	58.2	59.2	60.1
35.0	0.0286	0.0295	0.0305	0.0313
35.5	0.0279	0.0288	0.0297	0.0305
36.0	0.0272	0.0281	0.0290	0.0298
36.5	0.0265	0.0274	0.0282	0.0290
37.0	0.0258	0.0267	0.0275	0.0283
37.5	0.0252	0.0260	0.0269	0.0276
38.0	0.0246	0.0254	0.0262	0.0270
38.5	0.0240	0.0248	0.0256	0.0263
39.0	0.0234	0.0242	0.0250	0.0257
39.5	0.0228	0.0236	0.0244	0.0251
40.0	0.0223	0.0230	0.0238	0.0245
40.5	0.0217	0.0225	0.0232	0.0239
41.0	0.0212	0.0219	0.0227	0.0234
41.5	0.0207	0.0214	0.0221	0.0228
42.0	0.0202	0.0209	0.0216	0.0223
42.5	0.0197	0.0204	0.0211	0.0218
43.0	0.0192	0.0199	0.0206	0.0213
43.5	0.0188	0.0195	0.0202	0.0208
44.0	0.0183	0.0190	0.0197	0.0203
44.5	0.0179	0.0186	0.0192	0.0198
45.0	0.0175	0.0181	0.0188	0.0194
45.5	0.0171	0.0177	0.0184	0.0190
46.0	0.0167	0.0173	0.0179	0.0185
46.5	0.0163	0.0169	0.0175	0.0181
47.0	0.0159	0.0165	0.0171	0.0177
47.5	0.0156	0.0162	0.0168	0.0173
48.0	0.0152	0.0158	0.0164	0.0169
48.5	0.0148	0.0154	0.0160	0.0166
49.0	0.0145	0.0151	0.0157	0.0162
49.5	0.0142	0.0147	0.0153	0.0158
50.0	0.0139	0.0144	0.0150	0.0155
50.5	0.0135	0.0141	0.0146	0.0151
51.0	0.0132	0.0138	0.0143	0.0148
51.5	0.0129	0.0135	0.0140	0.0145
52.0	0.0126	0.0132	0.0137	0.0142
52.5	0.0124	0.0129	0.0134	0.0139
53.0	0.0121	0.0126	0.0131	0.0136
53.5	0.0118	0.0123	0.0128	0.0133
54.0	0.0116	0.0120	0.0125	0.0130
54.5	0.0113	0.0118	0.0123	0.0127
55.0	0.0110	0.0115	0.0120	0.0125
55.5	0.0108	0.0113	0.0118	0.0122
56.0	0.0106	0.0110	0.0115	0.0119
56.5	0.0103	0.0108	0.0113	0.0117
57.0	0.0101	0.0106	0.0110	0.0114
57.5	0.0099	0.0103	0.0108	0.0112
58.0	0.0097	0.0101	0.0105	0.0110
58.5	0.0095	0.0099	0.0103	0.0107
59.0	0.0093	0.0097	0.0101	0.0105
59.5	0.0091	0.0095	0.0099	0.0103
60.0	0.0089	0.0093	0.0097	0.0101



# ELECTRODE STORAGE

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## **Orion 93-05 Fluoroborate Half-Cell Electrode**

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The fluoroborate sensing module should be kept in the glass vial until used. The assembled electrode can be stored in  $10^{-2}$  M fluoroborate standard for short periods of time. For long periods of time (over 2-3 days), disassemble the electrode, rinse thoroughly with distilled water, blot dry, and store the module in its vial. Be sure to rinse and refill a stored reference electrode before attempting measurements.

## **Orion 90-02 Double Junction Reference Electrode**

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Orion 90-02 Reference Electrode may be stored in air between sample measurements (up to 1 hour). For short periods of time (up to one week), Orion 90-02 may be stored in its filling solution or distilled water. Do not allow the solution inside the electrode to evaporate and crystallize. For long periods of time (over one week), drain the reference electrode completely, rinse with distilled water, and store dry.

# TROUBLESHOOTING

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## Troubleshooting Checklist

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Symptom	Possible Causes
Off-scale or Over-range reading	Defective meter Defective sensing module Electrodes not plugged in properly Module not installed properly Reference electrode junction is dry No reference electrode (Orion 93-05) Reference electrode chamber not filled (Orion 90-02) Interior of membrane not thoroughly wetted Air bubble on membrane Electrodes not in solution
Noisy or unstable readings (readings continuously or rapidly changing)	Defective meter Meter or stirrer improperly grounded Module not installed properly Air bubble on membrane Interior of membrane not thoroughly wetted Wrong reference electrode  ISA not used
Drift (Reading slowly changing in one direction)	Samples and standards at different temperatures Membrane may contain a surface layer of contaminants Incorrect Reference Filling Solution Electrode exposed to interferences
Low slope or No slope	Electrodes not properly conditioned Standards contaminated or incorrectly made ISA Standard used as ISA  Defective sensing module Electrode exposed to interferences
"Wrong Answer" (But calibration curve is OK)	Incorrect scaling of semilog paper  Incorrect standards Incorrect sign Wrong units used

## Solution

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Check meter with shorting strap (See meter instruction manual)  
Refer to Troubleshooting Guide  
Unplug electrodes and reset  
Check electrode assembly  
Through the reference junction, expel a few drops of filling solution  
Use Orion Orion 90-02 reference electrode  
Be sure reference electrode is filled with correct solution .  
Tap module gently or shake down like a clinical thermometer  
Remove air bubble on electrode by gently tapping it  
Put electrodes in solution

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Check meter with shorting strap (See meter instruction manual)  
Check meter and stirrer for grounding  
Check Before Using the Electrode  
Remove air bubble by gently tapping electrode  
Tap module gently or shake down like a clinical thermometer  
Use Orion 90-02 Double Junction Reference Electrode (with Orion 93-05 Fluoroborate Electrode) Do not use calomel or Ag/AgCl (frit- or fiber-type) reference electrode  
Use recommended ISA, Orion 930711

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Allow solutions to come to room temperature before measurement  
Rinse electrode with distilled water and soak in standard ( $10^{-2}$  M) for 1hr.  
Use recommended filling solution.  
See Electrode Assembly and Preparation. See Interferences Section.

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See Electrode Assembly and Preparation. Prepare fresh standards  
Use recommended ISA, Orion 930711  
Reassemble electrode. See Electrode Assembly and Preparation

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Refer to Troubleshooting Guide  
See Interferences.

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Plot millivolts on the linear axis. On the log axis, be sure concentration numbers within each decade are increasing with increasing concentration  
Prepare fresh standards  
Be sure to note sign of millivolt value correctly  
Apply correct conversion factor:  $10^{-3}$  M = 86.8 ppm as  $\text{BF}_4^-$  = 10.8ppm as B

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For additional information on blank correction with your meter, see meter instruction manual.

## Troubleshooting Guide

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The most important principle in troubleshooting is to isolate the components of the system and check each in turn. The components of the system are: 1) Meter 2) Electrode(s) 3) Standard 4) Sample and 5) Technique.

See also **Important ISE Measurement Techniques and For Improved Accuracy** sections.

### Meter

The meter is the easiest component to eliminate as a possible cause of error. Orion meters are provided with an instrument checkout procedure in the instruction manual and a shorting cap for convenience in troubleshooting. Consult the manual for complete instructions and verify that the instrument operates as indicated and is stable in all steps.

### Electrode(s)

- 1 Rinse electrode(s) thoroughly with distilled water.
- 2 Check electrode operation (slope), see **Checking Electrode Operation**.
- 3 If electrode fails this procedure, re-soak module electrode as directed in **Electrode Assembly and Preparation**.

Clean Orion 90-02 reference electrode as described in reference electrode instruction manual.

- 4 Repeat step 2.

- 5 For the 93-05 Fluoroborate Half-Cell Electrode:

If the electrodes still do not perform as described, determine whether the sensing electrode or reference electrode is at fault. To do this, substitute a known working electrode for the electrode in question and repeat the slope check.

- 6 If the stability and slope check out properly, but measurement problems persist, the sample may contain interferences or complexing agents, or the technique may be in error. See **Standard, Sample, and Technique** sections below.

**7** Before replacing a "faulty" electrode, or if another electrode is not available for test purposes, review the instruction manual and be sure to:

- Clean the electrode thoroughly
- Prepare the electrode properly
- Use proper filling solution, ISA, and standards
- Measure correctly
- Review Troubleshooting Checklist

### **Standard**

The quality of results depends greatly upon the quality of the standards. ALWAYS prepare fresh standards when problems arise - it could save hours of frustrating troubleshooting! Error may result from contamination of prepared standards, quality of dilution, distilled water, or a numerical error in calculating the concentrations.

The best method for preparation of standards is serial dilution. This procedure involves preparing an initial standard that is diluted to prepare a second standard solution using volumetric glassware. The second is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.

### **Sample**

If the electrodes work properly in standards but not in the sample, look for possible interferences, complexing agents, or substances that could affect response or physically damage the sensing electrode or the reference electrode. If possible, determine the composition of the samples and check for problems. See **Sample Requirements, Interferences, and Specifications**.

### **Technique**

Check the method of analysis for compatibility with your sample. Direct measurement may not always be the method of choice. If the ionic strength varies markedly from sample to sample, known addition may be best. If working at low levels, be sure to follow the low-level measurement technique. Also, be sure that the expected concentration of the ion of interest is within the electrode's limits of detection. If problems persist, review operational procedures and instruction manuals to be sure that proper technique has been followed. Read **Important ISE Measurement Techniques and Measurement Procedures**.

## Assistance

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**For the most current warranty information, visit [www.thermo.com](http://www.thermo.com).**

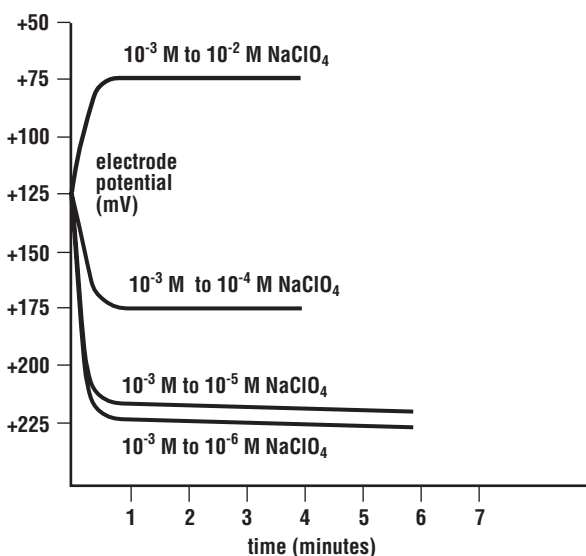
After troubleshooting all components of your measurement system, contact The Technical Edge<sup>SM</sup> for Orion products. Within the United States call 1.800.225.1480, outside the United States call 978.232.6000 or fax 978.232.6031. In Europe, the Middle East and Africa, contact your local authorized dealer. For the most current contact information, visit [www.thermo.com](http://www.thermo.com).

# ELECTRODE CHARACTERISTICS

## Electrode Response

The electrode potential plotted against concentration on semi-logarithmic paper results in a straight line with a slope of about 54 to 60 mV per decade until concentration reaches  $10^{-4}$  M  $\text{BF}_4^-$ . See **Figure 3**.

The electrode exhibits good time response (98% in one minute or less) for  $\text{BF}_4^-$  concentrations above  $10^{-5}$  M. Below this value response times vary from 2 to 5 minutes. See **Figure 4**. Response time is more rapid when going from dilute to concentrated solutions than in the other direction.



**Figure 4** Typical Electrode Response to Step Changes in  $\text{NaBF}_4$

## Limits of Detection

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In pure sodium fluoroborate solutions, the upper limit of detection is 1 M. When possible, dilute the sample to the linear working range of the electrode. If this is not possible, the possibility of a liquid junction potential developing at the reference electrode and the "salt extraction effect" need to be considered. At high salt concentrations, some salts may be extracted into the electrode membrane, causing deviation from theoretical response. To measure samples between  $10^{-1}$  and 1 M, calibrate the electrode at 4 or 5 intermediate points, or dilute the sample.

The lower limit of detection is determined by the slight water solubility of the ion exchanger, which causes deviation from theoretical response. Figure 4 shows the theoretical response at low levels of sodium fluoroborate compared to the actual response. If fluoroborate measurements are made below  $10^{-5}$  M  $\text{BF}_4^-$  (0.11 ppm as B or 0.87 ppm as  $\text{BF}_4^-$ ), a low-level measurement procedure is recommended.

## Reproducibility

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Reproducibility is limited by factors such as temperature fluctuations, drift, and noise. Within the electrode operating range, reproducibility is independent of concentration. With calibration every hour, direct electrode measurements reproducible to  $\pm 2\%$  can be obtained.

## Temperature Effects

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Since electrode potentials are affected by changes in temperature, samples and standard solutions should be within  $\pm 1^\circ\text{C}$  ( $\pm 2^\circ\text{F}$ ) of each other. At the  $10^{-3}$  M level, a  $1^\circ\text{C}$  difference in temperature results in a 1.5% error. The absolute potential of the reference electrode changes slowly with temperature because of the solubility equilibria on which the electrode depends. The slope of the fluoroborate electrode also varies with temperature, as indicated by the factor "S" in the Nernst equation. Values for the change in slope for fluoroborate ion are given in **Table 6**.

If temperature changes occur, meter and electrodes should be recalibrated.

The electrode can be used at temperatures from 0 to  $40^\circ\text{C}$ , provided that temperature equilibrium has occurred. For use at temperatures substantially different from room temperature, equilibrium times of up to one hour are recommended.

**Table 6**  
**Values of Electrode Slope vs. Temperature**

<b>T °C</b>	<b>S</b>	<b>T °C</b>	<b>S</b>
0	54.20	30	60.15
10	56.18	40	62.13
20	58.16	50	64.11
25	59.16		

## Interferences

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Some anions, if present at high enough levels, are electrode interferences and will cause measurement errors. **Table 7** indicates levels of common anions that will cause 10% error at various concentrations of sodium fluoroborate.

In many samples anions listed in **Table 7** are absent or insignificantly low. Many of the interferences can be removed or minimized by the following procedures (letters refer to letters in parenthesis in **Table 7**):

- a. Carbonate and bicarbonate can be removed by acidifying the sample to pH 4.5 with sulfuric acid, converting the ions to carbon dioxide.
- b. These interferences can be minimized by precipitation with silver. Dissolve 0.5 g. silver sulfate per 100 mL sample(s) to effect removal.
- c. Nitrite can be removed by adding 0.3 g. sufficient sulfamic acid to 100 mL sample(s).
- d. These interferences cannot be removed readily.
- e. Many organic (carboxylic) anions also interfere with the fluoroborate electrode. These anions can be removed by using a 1 M ISA containing aluminum sulfate, instead of ammonium sulfate.

**NOTE: Use of any of the above procedures require similar treatment of standards as well as samples.**

If the electrode is exposed to high levels of interfering ions, it may become drift and sluggish in response. When this happens, restore normal performance as outlined in **Troubleshooting**.

When the level of interferences in samples is constant, it is sometimes possible to measure fluoroborate accurately when interference levels are higher than those in **Table 7**. Call or write Thermo Electron's Technical Edge for more information. See section entitled **Assistance**.

## Electrode Life

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Each sensing module should last at least three months in normal laboratory use. In time, electrode slope will decrease and readings will start to drift, indicating that the module should be changed. Before replacement, refer to **Troubleshooting Checklist**, to make sure that the difficulties are caused by the sensing module.

**Table 7**  
**Levels of Possible Interferences Causing a 10% Error**  
**Interferences**

<b>Moles/Liter</b>	<b>10<sup>-4</sup>M</b>	<b>10<sup>-3</sup>M</b>	<b>10<sup>-2</sup>M BF<sub>4</sub><sup>-</sup></b>
(d) ClO <sub>4</sub> <sup>-</sup>	5 x 10 <sup>-8</sup>	5 x 10 <sup>-7</sup>	5 x 10 <sup>-6</sup>
(b) I <sup>-</sup>	5 x 10 <sup>-7</sup>	5 x 10 <sup>-6</sup>	5 x 10 <sup>-5</sup>
(d) ClO <sub>3</sub> <sup>-</sup>	5 x 10 <sup>-6</sup>	5 x 10 <sup>-5</sup>	5 x 10 <sup>-4</sup>
(b) CN <sup>-</sup>	5 x 10 <sup>-5</sup>	5 x 10 <sup>-4</sup>	5 x 10 <sup>-3</sup>
(b) Br <sup>-</sup>	1 x 10 <sup>-4</sup>	1 x 10 <sup>-3</sup>	1 x 10 <sup>-2</sup>
(c) NO <sub>2</sub> <sup>-</sup>	1 x 10 <sup>-4</sup>	1 x 10 <sup>-3</sup>	1 x 10 <sup>-2</sup>
(d) NO <sub>3</sub> <sup>-</sup>	5 x 10 <sup>-4</sup>	5 x 10 <sup>-3</sup>	5 x 10 <sup>-2</sup>
(a) HCO <sub>3</sub> <sup>-</sup>	3 x 10 <sup>-3</sup>	3 x 10 <sup>-2</sup>	0.3
(a) CO <sub>3</sub> <sup>2-</sup>	3 x 10 <sup>-3</sup>	5 x 10 <sup>-2</sup>	0.3
(b) Cl <sup>-</sup>	5 x 10 <sup>-3</sup>	8 x 10 <sup>-2</sup>	0.5
(b) H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	8 x 10 <sup>-3</sup>	8 x 10 <sup>-2</sup>	0.8
(b) HPO <sub>4</sub> <sup>2-</sup>	8 x 10 <sup>-3</sup>	8 x 10 <sup>-2</sup>	0.8
(b) PO <sub>4</sub> <sup>3-</sup>	8 x 10 <sup>-3</sup>	0.2	0.8
(e) OA <sub>c</sub> <sup>-</sup>	2 x 10 <sup>-2</sup>	0.2	2
(d) F <sup>-</sup>	6 x 10 <sup>-2</sup>	0.6	6
(b) SO <sub>4</sub> <sup>2-</sup>	0.1	1.0	10

**Note: Letters in parentheses refer to comments in the Interferences section.**

<b>Interferences</b>	<b>1 ppm</b>	<b>10 ppm</b>	<b>100 ppm Boron</b>
(d) ClO <sub>4</sub> <sup>-</sup>	5 x 10 <sup>-3</sup>	5 x 10 <sup>-2</sup>	0.5
(b) I <sup>-</sup>	6 x 10 <sup>-2</sup>	0.6	6
(d) ClO <sub>3</sub> <sup>-</sup>	0.4	3	30
(b) CN <sup>-</sup>	1	12	120
(b) Br <sup>-</sup>	7	74	740
(c) NO <sub>2</sub> <sup>-</sup>	4	42	420
(d) NO <sub>3</sub> <sup>-</sup>	28	287	2870
(a) HCO <sub>3</sub> <sup>-</sup>	169	1,694	16,940
(a) CO <sub>3</sub> <sup>2-</sup>	166	1,667	16,670
(b) Cl <sup>-</sup>	164	1,641	16,410
(b) H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	718	7,185	71,850
(b) HPO <sub>4</sub> <sup>2-</sup>	710	7,105	71,050
(b) PO <sub>4</sub> <sup>3-</sup>	702	7,025	70,250
(e) OA <sub>c</sub> <sup>-</sup>	1,130	11,300	113,000
(d) F <sup>-</sup>	1,060	10,600	106,000
(b) SO <sub>4</sub> <sup>2-</sup>	8,900	89,000	890,000

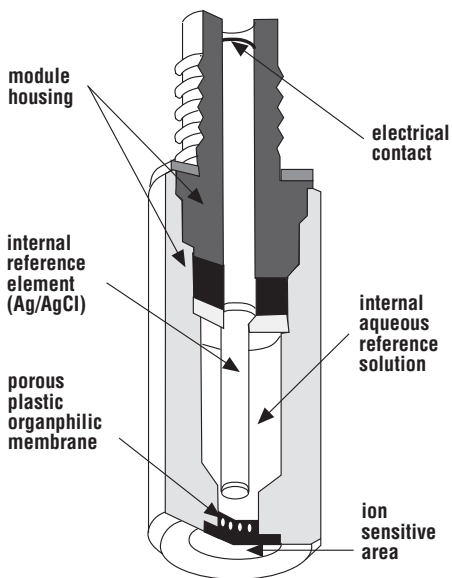
**Note: Letters in parentheses refer to comments in the Interferences section.**

## Theory of Operation

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The fluoroborate electrode consists of an electrode body and a replaceable pretested sensing module. The sensing module contains a liquid internal filling solution in contact with a gelled organophilic membrane containing a fluoroborate ion-selective ion exchanger.

**See Figure 5.**



**Figure 5**  
**Construction of Electrode Sensing Module**

When the membrane is in contact with a nitrate solution, an electrode potential develops across the membrane. This potential, which depends on the level of free nitrate ion in solution, is measured against a constant reference potential with a pH/mV meter or specific ion meter. The measured potential corresponding to the level of nitrate ion in solution is described by the Nernst equation:

$$E = E_0 - S \log (A)$$

**where:**

- E = measured electrode potential
- E<sub>0</sub> = reference potential (a constant)
- A = fluoroborate ion level in solution
- S = electrode slope (about 56 mV per decade)

The level of fluoroborate ion, A, is the activity or "effective concentration" of free fluoroborate ion in solution. The total fluoroborate concentration, C<sub>t</sub>, includes some bound or complexed ions as well as free ions, whose concentration is:

$$C_t = C_f - C_b$$

**where:**

- C<sub>b</sub> = concentration of fluoroborate ions in all bound or complexed forms
- C<sub>f</sub> = concentration of free fluoroborate ions

The fluoroborate ion activity is related to free fluoroborate ion concentration by the activity coefficient:

$$A = \gamma C_f$$

Ionic activity coefficients are variable and largely depend on total ionic strength. Ionic strength is defined as:

$$\text{Ionic strength} = 1/2 \sum (C_i Z_i^2)$$

**where:**

- C<sub>i</sub> = concentration of ion (i)
- Z<sub>i</sub> = charge of ion (i)

If the background ionic strength is high and constant relative to the sensed ion concentration, the activity coefficient is constant and activity is directly proportional to concentration.

Ionic strength adjustor (ISA) is added to fluoroborate standards and samples so that the background ionic strength is high and constant relative to variable concentrations of fluoroborate ion. For the fluoroborate electrode,  $(\text{NH}_4)_2\text{SO}_4$  is the recommended ISA. Other solutions can be used as long as they do not contain ions that would interfere with the electrode's response to fluoroborate ion.

Reference electrode conditions must also be considered. Liquid junction potentials arise any time two solutions of different composition are brought into contact. The potential results from the interdiffusion of ions in the two solutions. Since ions diffuse at different rate, the electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions. In making electrode

measurements, it is important that this potential be the same when the reference is in the standardizing solution as well as in the sample solution; otherwise, the change in liquid junction potential will appear as an error in the measured specific ion electrode potential.

The most important variable which analysts have under their control is the composition of the liquid junction filling solution. The filling solution should be equitransferent. That is, the speed with which the positive and negative ions in the filling solution diffuse into the sample should be as nearly equal as possible. If the rate at which positive and negative charge is carried into the sample solution is equal, then no junction potential can result.

# ORDERING INFORMATION

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<b>Orion</b>	<b>Description</b>
<b>9305BN</b>	Orion 93-05 Fluoroborate Electrode with BNC connector
<b>930501</b>	Replacement Fluoroborate Electrode Module for Orion 93-05
<b>930500</b>	Fluoroborate Electrode with Two Sensing Modules with US Std. connector
<b>090032</b>	BNC Electrode to U.S. Standard Meter Adapter
<b>900200</b>	Orion 90-02 Double Junction Sure-Flow® Reference Electrode
<b>900002</b>	Inner Chamber Filling Solution for Orion 90-02 Reference Electrode, 5 x 60 mL bottles
<b>930711</b>	Nitrate Ionic Strength Adjustor Solution, 475 mL
<b>9300BN</b>	Replacement Electrode Body with BNC connector
<b>930000</b>	Replacement Electrode Body with U.S. Standard connector

# SPECIFICATIONS

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**Concentration range:**

7 x 10<sup>-6</sup> M to 1 M BF<sub>4</sub><sup>-</sup>

0.09 to 10,800 ppm as B

**pH range:**

2.5 to 11 pH

Low-level measurements may be influenced by hydrogen or hydroxide ion interferences

**Temperature range:**

0 to 40°C

**Electrode resistance:**

1 to 5 megohms

**Reproducibility:**

± 2%

**Sample:**

Aqueous solutions only

**Module life:**

Three months under normal laboratory conditions

**Size:**

Electrode Length (Body with Module)	135 mm
Cap Length	30 mm
Cap Diameter	16 mm
Electrode Diameter	12 mm
Cable Length	1 meter
Maximum Immersion Depth	22 mm

## **Environmental Instruments**

### Water Analysis

#### **North America**

166 Cummings Center  
Beverly, MA 01915 USA  
Tel: 978-232-6000  
Dom. Fax: 978-232-6015  
Int'l. Fax: 978-232-6031

#### **Europe**

12-16 Sedgeway Business Park  
Witchford, Cambridgeshire  
England, CB6 2HY  
Tel: 44-1353-666111  
Fax: 44-1353-666001

#### **Far East**

Room 904, Federal Building  
369 Lockhart Road  
Wanchai, Hong Kong  
Tel: 852-2836-0981  
Fax: 852-2834-5160

#### **Customer Support**

Toll Free: 800-225-1480  
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