

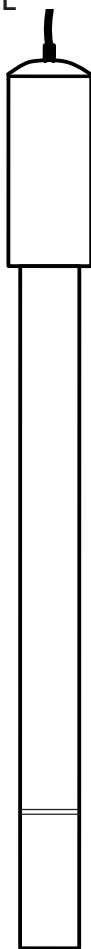
# $\text{ClO}_4^-$

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Orion 93-81

## Orion Perchlorate Electrode or Probe

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 93-81 perchlorate electrode allows perchlorate in aqueous solutions to be measured quickly, 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 given in the meter instruction manual.

The Orion 93-81 perchlorate electrode replaces Orion's 92-81 perchlorate electrode. Most applications in technical journals, Orion Applications Bulletins, or Orion's Analytical Methods Guide that specify use of the 92-81 can be performed with the 93-81 electrode. Please contact The Technical Edge<sup>SM</sup> for Orion Products for more information on specific applications.

Orion Technical Service chemists can be consulted for assistance and troubleshooting advice. Please refer to troubleshooting for information on contacting Orion.

## **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**

Orion 90-02 Double-Junction Reference Electrode

### **Magnetic Stirrer**

Micro-stir bars are recommended for small volume measurements.

### **Graph Paper**

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

## **Packing List**

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One Orion 93-81 Sensing Module

Orion 93-81 Electrode Instruction Manual

Warranty Card

## Required Solutions

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### Distilled or Deionized Water

To prepare all solutions and standards.

### Standard Solutions

#### 0.1M Sodium Perchlorate

Measure 200 mL standard 0.5 M sodium hydroxide into a 500 mL beaker. Titrate to pH 7.00 against 60% perchloric acid using a calibrated pH electrode as the endpoint detector. Transfer to a liter volumetric flask and dilute to volume with distilled water.

***NOTE: Perchloric acid is explosive in contact with reducible substances and is a strong oxidizing agent. Use extreme caution when handling.***

#### 1000 ppm Perchlorate Standard

Transfer 10.0 mL of the 0.1 M Sodium Perchlorate standard to a 100 mL volumetric flask. Dilute to volume with distilled water.

### Ionic Strength Adjuster (ISA)

Orion No. 930711

To keep a constant background of ionic strength in samples and standards

### Reference Electrode (outer chamber) Filling Solution

Add 2 mL of ISA, Orion No. 930711, to 100 mL distilled water. Use this solution to fill the outer chamber of the reference electrode. Do not use the filling solution shipped with the Orion 90-02 reference electrode because it will interfere with your measurements.



# BEFORE USING THE ELECTRODE

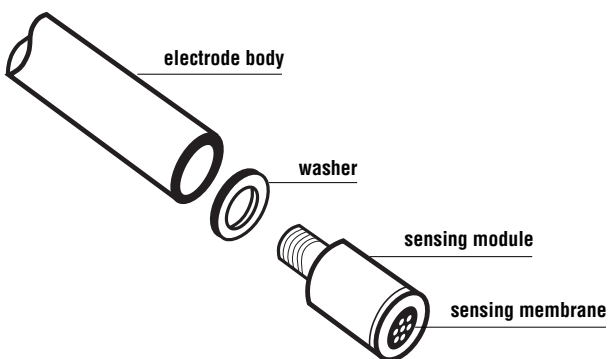
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## Electrode Assembly and Preparation

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### Orion 93-81 Perchlorate Half-Cell Electrode

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



**Figure 1: Orion 93-81 Electrode Assembly**

### Orion 90-02 Double Junction Reference Electrode

Required for use with Orion 93-81 Perchlorate Half-Cell. No assembly is required. Fill the reference electrode according to instructions in the reference electrode instruction manual, using prepared reference electrode filling solution in outer chamber and Orion No. 900002 in inner chamber. *Do not use the outer chamber filling solution shipped with the 90-02 reference electrode because it will interfere with your measurements.*

## Checking Electrode Operation (Slope)

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**NOTE: Check electrodes daily.**

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. Refer to Electrode Assembly and Preparation section before sloping the electrode.
2. Connect electrode(s) to the meter as described in the meter instruction manual.
3. Select either 0.1 M or 1000 ppm of sodium perchlorate standard.
4. Place 100 mL distilled water into a 150mL beaker. Add 2 mL ISA, Orion No. 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.
7. Pipet 1.0 mL of the standard (0.1 M or 1000 ppm) into the beaker. Stir thoroughly.
8. When a stable reading is displayed, record the electrode potential in millivolts.
9. Pipet 10 mL of the same standard into the same beaker. Stir thoroughly.
10. When a stable reading is displayed, record the electrode potential in millivolts.
11. The difference between the first and second potential is defined as the slope of the electrode. The difference should be in the range of 54 to 60 mV/decade when the solution temperature is  $25 \pm 5$  °C. If the slope is not within this range, re-soak the electrode as described under the **Electrode Assembly and Preparation** section. For other troubleshooting techniques, refer to the **Troubleshooting** section.

## Recommendations for Optimum Results

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### Units of Measurement

Perchlorate can be measured in units of moles per liter, parts per million as perchlorate, parts per million as sodium perchlorate, or any other convenient concentration unit (see **Table 1**).

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

Moles per Liter	ppm as $\text{ClO}_4^-$	ppm as $\text{NaClO}_4$
$10^{-4}$	10.0	12.2
$10^{-3}$	99.5	122.5
$10^{-2}$	995.0	1225.0

### Sample Requirements

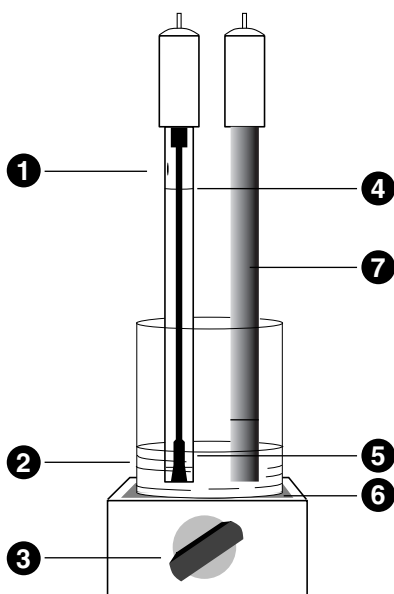
Samples must be aqueous and must not contain organic solvents. Consult Orion's Technical Service Group for using the electrode in specific applications.

Sample temperature must be less than 40 °C with samples and standards all at the same temperature. A 1 °C difference in temperature will give rise to about a 2% error. For highly accurate results, use a water bath to control temperature variances.

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

## Important ISE Measurement Techniques

- Stir all samples and standards at a uniform rate during measurement. For best results, stir at a rate that will not cause a vortex. Magnetic stirrers may generate sufficient heat to change solution temperature. Place a piece of insulating material such as cork, cardboard, or styrofoam between 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 carry over. Do not wipe or rub the sensing membrane, as you may contaminate and damage the surface.
- Store the electrode(s) in  $10^{-3}$  M or 100 ppm perchlorate solution between measurements.
- For long period of time (2~3 days), disassemble the electrode and store the electrode in its vial.
- Allow all standards and samples to come to ambient temperature for precise measurement.
- After immersion in solution, check electrode for any air bubbles on membrane surface. Remove air bubbles at the electrode surface by gently tapping the electrode.
- If electrode response is slow, the membrane may contain a surface layer of contaminant. Restore performance by soaking electrode in distilled water for about five minutes to clean membrane, then rinse and soak in a standard solution for about five minutes before use.
- The Orion 93-81 Perchlorate Half-Cell electrode should be submerged approximately half the length of the module. **DO NOT** submerge the electrode above the rubber electrode washer. Submerge the reference electrode to the same depth as the perchlorate electrode.



**Figure 2: Measuring Hints**

1. Filling hole should be uncovered (Orion 90-02).
2. Use fresh standard.
3. Stir all samples and standards.
4. Filling solution level must be higher than sample level.
5. Reference junction must be immersed.
6. Place insulation between stirrer and beaker.
7. Half-Cell electrode.

***NOTE: Do not submerge perchlorate module past the rubber electrode washer (Orion 93-81).***

## Analytical Procedures

- **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 in 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 effects of interfering ions.
- **Low-Level Measurement** is similar to Direct Measurement. Use this method when the expected sample concentration is less than  $10^{-5}$  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 ionic strength ( $> 0.1$  M), 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 containing the measured species 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.
- **Titration** are quantitative analytical techniques for measuring the concentration of a species by incremental addition of a reagent (titration) that reacts with the sample species. Sensing electrodes can be used to determine the titration end point. Ion selective electrodes are unaffected by sample color or turbidity, making them excellent endpoint detectors. Titration is approximately 10 times more precise than direct calibration, but are more time-consuming.

# 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  $10^{-5}$  M or 1.0 ppm as perchlorate. 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 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 calcium 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 meter or a mV meter**

See individual meter instruction manuals for more specific calibration information.

1. Prepare the electrode(s) as described in **Electrode Assembly and 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 150mL beakers. Add 2mL ISA to each standard and sample. Stir thoroughly.

***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, then 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 least concentrated 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**. When a stable reading is displayed, record the mV value and corresponding standard concentration.

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.

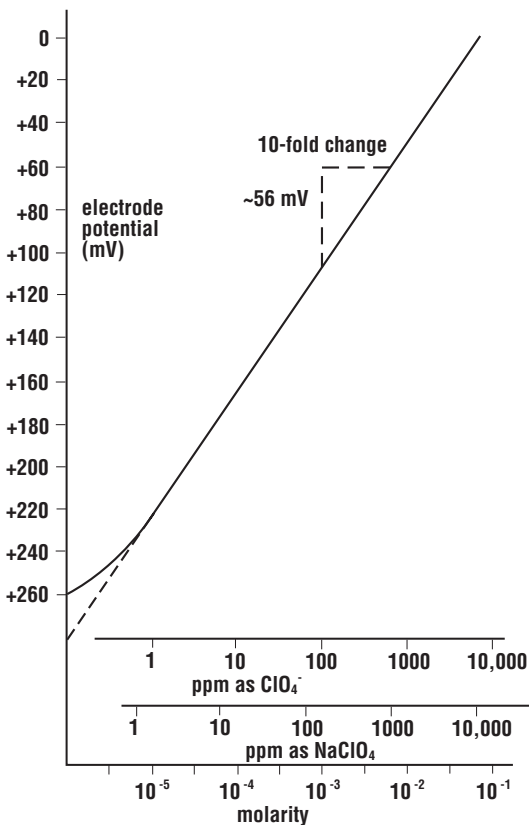
7. Repeat step 6 for all standards, working from the least concentrated to most concentrated standard.

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

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 the electrode(s) with distilled water, shake dry, and place into 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 Perchlorate 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, at least two standards are needed to determine a calibration curve. In non-linear regions, more points must be taken for accuracy. 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 Measurement**

Use this method when measuring solutions with a perchlorate concentration of less than 1.0 ppm or  $10^{-5}$  M, those within the non-linear range of the electrode. Low-level measurements require at least three standards to compensate for the electrode'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 time response at low-levels is faster when it is not also 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 not using an ISE meter, a calibration curve can be drawn on semi-logarithmic graph 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 auto blank 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**.
- Ionic strength of samples must be similar to that of the standards.

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

**NOTE:** *The following procedure is for solutions with ionic strength less than  $10^{-2}$  M. For solutions low in perchlorate but high in ionic strength, perform the same procedure with one change: prepare a calibration solution (step 3) with a composition similar to sample*

1. Prepare electrode(s) as described in Electrode Assembly and Preparation.
2. Connect the electrode(s) to the meter, and adjust the meter to measure concentration for an ISE meter or mV for a mV meter.
3. Select a standard solution. Use either  $10^{-3}$  M of  $\text{ClO}_4^-$  solution by diluting 1 mL of 0.1 M sodium perchlorate standard to 100 mL, or 100 ppm of  $\text{ClO}_4^-$  solution by diluting 10 mL of the 1000 ppm sodium perchlorate standard to 100 mL.
4. Prepare a low-level ISA solution by diluting 20 mL of the Nitrate ISA, Orion No. 930711, to 100 mL with distilled water. Use this low-level ISA for low-level measurements only.
5. Transfer 100 mL of DI water to a 150 mL beaker. Add 1 mL low-level ISA.
6. Rinse the electrode(s) with distilled water and 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. Plot the concentration (log axis) against the millivolt potential (linear axis) on semi-logarithmic paper. See **Figure 3**. Prepare a new low-level calibration curve with fresh standard each day.

9. Measure 100 mL of sample into a 150 mL 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 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 mV Meter**

Step	Graduated Pipet Size	Added volume	Concentration	
			ppm ( $\text{ClO}_4^-$ )	Molarity ( $\text{ClO}_4^-$ )
1	1mL	0.1mL	0.01	$1.0 \times 10^{-6}$
2	1mL	0.1mL	0.02	$2.0 \times 10^{-6}$
3	1mL	0.2mL	0.04	$4.0 \times 10^{-6}$
4	1mL	0.2mL	0.06	$6.0 \times 10^{-6}$
5	1mL	0.4mL	0.10	$9.9 \times 10^{-6}$
6	2mL	2.0mL	0.29	$2.9 \times 10^{-5}$
7	2mL	2.0mL	0.48	$4.8 \times 10^{-5}$

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

## Known Addition Measurement

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Known addition, KA, is convenient technique for measuring samples in the linear response range, greater than 0.1M, because no calibration curve is needed. Use this method to verify the results of a direct measurement to minimize existing matrix effects. The sample potential is measured before and after addition of standard solution. Many meters, such as the Orion 920A and 930Ionalyzer<sup>®</sup>, 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 Improve Accuracy

- Sample concentration should be known to be 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-tested with ISA in a 50:1 ratio.
- Dilute samples in a 50:1 ratio of sample to 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 perchlorate to double. Refer to **Table 3** as a guideline.
4. Determine the slope of the perchlorate electrode by performing the procedure under **Checking Electrode Operation (Slope)**.

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

See individual meter instruction manuals for more specific information.

1. Set up the meter to measure in the known addition mode.
2. Measure 100 mL of the sample into a beaker. Add 2 mL ISA, Orion No. 930711. 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 100 mL of the sample into a 150 mL beaker. Add 2 mL ISA. Stir thoroughly.
3. Rinse electrode(s) with distilled water, shake dry and place into beaker.
4. When a stable reading is displayed, record the mV value as  $E_1$ .
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  $E_2$ . 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:

$\Delta E$  =  $E_2 - E_1$

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**

<b>A</b>	<b>B</b>	<b>C</b>
<b>1</b>	Enter Value	
<b>2</b>	Vol. Of Sample & ISA, mL	102
<b>3</b>	Vol of Addition, mL	10
<b>4</b>	Concentration of Addition	10
<b>5</b>	Vol of Sample	100
<b>6</b>	Initial mV reading	45.3
<b>7</b>	Final mV reading	63.7
<b>8</b>	Electrode Slope	59.2
<b>9</b>		
<b>10</b>		Derived Values
<b>11</b>	Delta E	= C7-C6
<b>12</b>	p Term	= C3/C2
<b>13</b>	Antilog Term	= 10^(C11/C8)
<b>14</b>	r Term	= C2/C5
<b>15</b>	Q Term	= (C12*C14)/{(1+C12)*C13}-1}
<b>16</b>	calculated initial concentration in same unit addition	= C15*C4

**NOTE: This is an example of excel spreadsheet.**

**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			
	Monovalent	57.2	58.2	59.2
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
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

$\Delta E$	Q, Concentration Ratio			
	Monovalent	Slope		
	57.2	58.2	59.2	60.1
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
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

$\Delta E$	Q, Concentration Ratio			
	Monovalent	Slope		
	57.2	58.2	59.2	60.1
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 93-81 Perchlorate Half-Cell**

Orion 93-81 perchlorate sensing module should be kept in the glass vial until it is to be used. The assembled electrode can be stored in  $10^{-2}$  M perchlorate solution for a short period of time (2-3 days). 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**

Orion 90-02 Reference Electrode may be stored in air between sample measurements (up to 1 hours). For short period of time (up to 1 week), the reference electrode 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 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  Air bubble on membrane Calibration control not turned far enough
Noisy or unstable readings (readings continuously or rapidly changing)	Defective meter Module not installed properly Air bubble on membrane Wrong reference electrode ISA Meter or stirrer improperly grounded
Drift (Reading slowly changing in one direction)	Samples and standards at different temperatures Electrode exposed to interference Incorrect reference filling solution
Low slope or No slope	Standards contaminated or incorrectly made ISA not used Standard used as ISA Defective sensing module Electrode exposed to interferences
“Wrong Answer” (But calibration curve is OK)	Incorrect scaling of semi-log paper  Incorrect sign Incorrect standards Wrong units used  Complexing agents in sample

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## Solution

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Check meter with shorting strap (See meter instruction manual)  
Check electrode operation  
Unplug electrodes and reset  
Check electrode assembly  
Hold cap and lift outer sleeve to expel a few drops of filling solution  
Be sure reference electrode is filled  
Remove air bubble by gently tapping electrode  
Continue turning the calibration control. It provides 10 turns of coarse calibration range, and is more difficult to turn after the 270° fine tuning range has been exceeded.

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Check meter with shorting strap  
Check **Before Using the Electrode** section  
Remove air bubble by gently tapping electrode  
Do not use calomel or Ag/AgCl (frit-or-fiber-type) reference electrode  
Use recommended ISA  
Check meter and stirrer for grounding

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Allow solutions to come to room temperature before measurement  
Soak electrode in perchlorate standard  
Use recommended filling solution

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Prepare fresh standards  
Use recommended ISA  
Use ISA!  
Check electrode operation  
Soak electrode in perchlorate standard

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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  
Be sure to note sign of millivolt value correctly  
Prepare fresh standards  
Apply correct conversion factor:  
 $10^{-3} \text{ M} = 99.5 \text{ ppm as } \text{ClO}_4^- = 122.5 \text{ ppm as } \text{NaClO}_4$   
Use known addition, or a decomplexing procedure

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For additional information on blank correction with your A-Series meter, see your meter operations manual.

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## 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: 1) Meter 2) Electrode(s) 3) Standard 4) Samples 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 perchlorate 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. If the electrodes still do not perform as described, determine whether the perchlorate 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 problem arise-it could save hours of frustrating troubleshooting! Error may result from contamination of prepares 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 standard 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 limit detection. If problem persist, review operational procedures and instruction manuals to be sure that proper technique has been followed. Read **Important ISE Measurement Technique** and **Measurement Procedures**.

## **Assistance**

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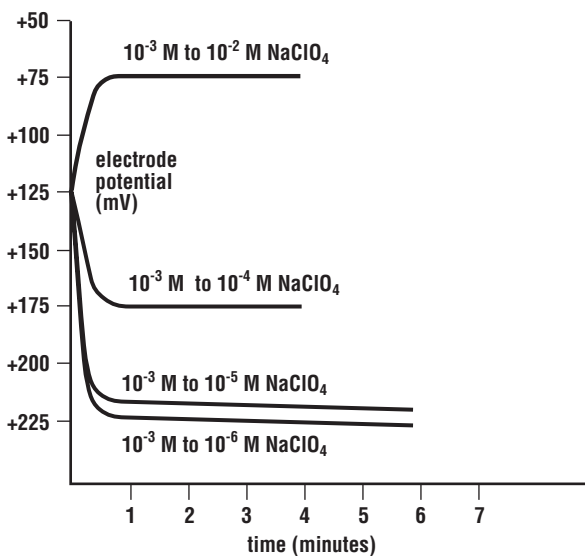
After troubleshooting all components of your measurement system, contact The Technical Edge<sup>SM</sup> for Orion products. Within the United States call 1.800.225.1480, outside the United States call 978.232.6000 or fax 978.232.6031. In Europe, the Middle East and Africa, contact your local authorized 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 semilogarithmic paper results in a straight line with a slope of about 56 mV per decade. See **Figure 2**.

The electrode exhibits good time response (99% response in one minute or less) for perchlorate concentrations above  $10^{-5}$  M. Below this value, response times vary from two to five 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 NaClO<sub>4</sub>

## Limits of Detection

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In pure sodium perchlorate solutions, the upper limit of detection is 1 M. When other ions are present, the upper limit of detection is above  $10^{-1}$  M perchlorate, but is influenced by two factors — the possibility of a liquid junction potential developing at the reference electrode and the “salt extraction effect”. 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 four or five intermediate points, or dilute the sample.

The lower limit of detection is determined by the slight water solubility of the ion exchanger from the sensing module, which causes deviation from theoretical response. **Figure 3** shows the theoretical response at low levels of sodium perchlorate compared to the actual response. If perchlorate measurements are made below  $10^{-5}$  M  $\text{ClO}_4^-$  (1 ppm as  $\text{ClO}_4^-$ ), 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’s 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  $\pm 1\text{ }^{\circ}\text{C}$  ( $\pm 2\text{ }^{\circ}\text{F}$ ) of each other. At the  $10^{-3}\text{ M}$  level, a  $1\text{ }^{\circ}\text{C}$  difference in temperature results in a 2% 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 perchlorate electrode also varies with temperature, as indicated by the factor "S" in the NERNST equation. Values of the Nernst factor for perchlorate ion are given in **Table 5**. If temperature change occur, meter and electrodes should be recalibrated.

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

**Table 5**  
**Values of Theoretical Electrode Slope vs. Temperature**

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

**Table 6**

Levels of possible interferences causing a 10% error at various levels of sodium perchlorate with a background ionic strength of 0.12 M ammonium sulfate. See **Interferences** for a description of the letters that precede each ion.

**Interferences**

(moles per liter)	$10^{-4}$ M	$10^{-3}$ M	$10^{-2}$ M $\text{ClO}_4^-$
(b) $\text{I}^-$	$2 \times 10^{-4}$	$2 \times 10^{-3}$	$2 \times 10^{-2}$
(d) $\text{ClO}_3^-$	$2 \times 10^{-3}$	$2 \times 10^{-2}$	0.2
(b) $\text{CN}^-$	$4 \times 10^{-3}$	$4 \times 10^{-2}$	0.4
(b) $\text{Br}^-$	$4 \times 10^{-3}$	$4 \times 10^{-2}$	0.4
(c) $\text{NO}_2^-$	$5 \times 10^{-3}$	$5 \times 10^{-2}$	0.5
(d) $\text{NO}_3^-$	$5 \times 10^{-3}$	$5 \times 10^{-2}$	0.5
(a) $\text{HCO}_3^-$	0.2	2.0	20
(a) $\text{CO}_3^{=}$	0.2	2.0	20
(b) $\text{Cl}^-$	0.2	2.0	20
(b) $\text{H}_2\text{PO}_4^-$	0.2	2.0	20
(b) $\text{HPO}_4^{=}$	0.2	2.0	20
(b) $\text{PO}_4^{3-}$	0.2	2.0	20
(e) $\text{OAC}^-$	0.2	2.0	20
(d) $\text{F}^-$	0.2	2.0	20
(b) $\text{SO}_4^{=}$	0.2	2.0	20

**Interferences**

(ppm)	1 ppm	10 ppm	100 ppm $\text{ClO}_4^-$
(b) $\text{I}^-$	2	25	253
(d) $\text{ClO}_3^-$	17	166	1660
(b) $\text{CN}^-$	10	104	1040
(b) $\text{Br}^-$	32	320	3200
(c) $\text{NO}_2^-$	23	230	2300
(d) $\text{NO}_3^-$	31	310	3100
(a) $\text{HCO}_3^-$	1,220	12,200	122,000
(a) $\text{CO}_3^{=}$	1,200	12,000	120,000
(b) $\text{Cl}^-$	700	7,000	70,000
(b) $\text{H}_2\text{PO}_4^-$	1,940	19,400	194,000
(b) $\text{HPO}_4^{=}$	1,920	19,200	192,000
(b) $\text{PO}_4^{3-}$	1,900	19,000	190,000
(e) $\text{OAC}^-$	1,460	14,600	146,000
(d) $\text{F}^-$	380	3,800	38,000
(b) $\text{SO}_4^{=}$	1,920	19,200	192,000

## Interferences

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Some other anions, if present at high enough levels, are electrode interferences and will cause measurement errors or electrode malfunction. **Table 6** indicates levels of common anions that will cause 10% error at three levels of perchlorate. The top half of the table shows interference levels in moles per liter at  $10^{-4}$ ,  $10^{-3}$ , and  $10^{-2}$  M concentrations of perchlorate. The bottom half of the table shows interference levels in ppm at 100, 10, and 1 ppm perchlorate.

In many samples, anions listed in **Table 6** are absent or insignificantly low. Many of the interferences can be removed by the following procedures (letters refer to letters in **Table 6**):

- 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 removed 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 sulfamic acid per 100 mL sample(s).
- d) These interferences cannot be removed very readily.
- e) Many organic (carboxylic) anions also interfere with the perchlorate 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 requires similar treatment of standards as well as samples.***

In cases where interferences are not removed and the electrode is exposed to high levels of interfering ions, it may become drifty and sluggish in response. When this happens, restore normal performance by soaking for an hour in distilled water, then for a few hours in perchlorate standard solution.

### Electrode Storage

The sensing module should be kept in the glass vial until it is ready to use. The assembled electrode can be stored in  $10^{-3}$  M perchlorate solution between measurement. For long periods of time (over two to three days), disassemble the electrode, rinse and store the module dry in its vial. Be sure to rinse and refill a stored reference electrode before attempting measurements.

## Electrode Life

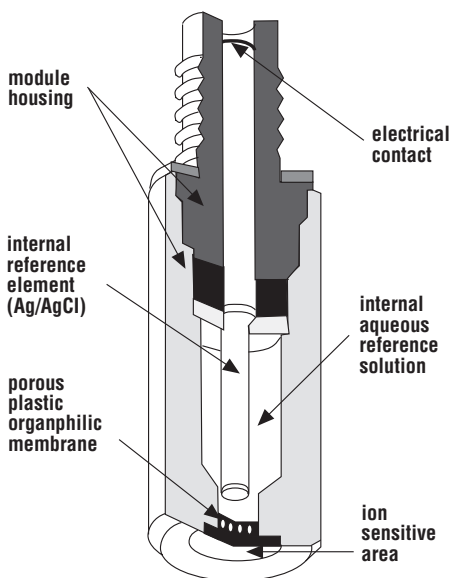
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Each sensing module should last at least six months in normal laboratory use. In time, electrode slope will decrease and readings will start to drift, indicating that the module should be changed. Before replacement, refer to the **Troubleshooting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

## Theory of Operation

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The perchlorate 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 perchlorate ion-selective ion exchanger. See **Figure 5**.



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

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

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

Where:

- E = measured electrode potential
- $E_0$  = reference potential (a constant)
- A = perchlorate ion level in solution
- S = electrode slope (about 56 mV per decade)

The level of perchlorate ion, A, is the activity or “effective concentration” of free perchlorate ion in solution. The total perchlorate concentration  $C_t$  includes some bound or complexed ions as well as free ions. The electrode responds only to free ions, whose concentration is:

$$C_f = C_t - C_b$$

Where  $C_b$  is the concentration of perchlorate ions in all bound or complexed forms. Fortunately, perchlorate ions form very few stable complexes, so that the free ion concentration ( $C_f$ ) may be taken as equal to the total perchlorate ion concentration ( $C_t$ ).

The perchlorate ion activity is related to free perchlorate ion concentration by the activity coefficient,  $\gamma$  :

$$A = \gamma C_f$$

Ionic activity coefficients are variable and largely depend on total ionic strength.

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

Where:

- $C_i$  = concentration of ion i
- $Z_i$  = 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 adjuster (ISA) is added to all perchlorate standards and samples so that the background ionic strength is high and constant relative to variable concentrations of perchlorate ion. For the perchlorate 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 perchlorate ion.

Reference electrode condition must also be considered. Liquid junction potentials arise any time when 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 rates, 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 the analyst has under his 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.

However, there are a few samples where no filling solution adequately fulfills the condition stated above. Particularly troublesome are samples containing high levels of strong acids (pH 0-2) or strong bases (pH 12-14). The high mobility of hydrogen and hydroxide ions in samples makes it impossible to "swamp out" their effect on the junction potential with any concentration of an equitransferent salt. For these solutions, it is recommended to: calibrate in the same pH range as the sample; or, use a known increment method for ion measurement. For more information, call Technical Services at Orion Research, Inc.

# WARRANTY

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

The Thermo Electron Corporation, Orion products warranty covers failures due to manufacturer's workmanship or material defects from the date of purchase by the user. User should return the warranty card and retain proof of purchase. Warranty is void if product has been abused, misused, or repairs attempted by unauthorized persons.

Warranties herein are for product sold/installed by Thermo or its authorized dealers.

Any product sold by a U.S. or Canadian distributor must be returned to Thermo for any warranty work. Please contact our Technical Service department for further information. A Return Authorization Number must be obtained from The Technical EDGE<sup>SM</sup> for Orion Products before returning any product for in-warranty repair or replacement.

In the event of failure within the warranty period, Thermo will at the company's option, repair or replace product not conforming to this warranty. There may be additional charges, including freight, for warranty service performed in some countries. For service, call Thermo or its authorized dealer outside the United States and Canada. Thermo reserves the right to ask for proof of purchase, such as the original invoice or packing slip.

Field Service is available on Orion BOD AutoEZ<sup>TM</sup>, EZ Flash<sup>®</sup> GC Accessory and TEA Analyzer<sup>®</sup>. Contact our Field Service department for details on quotations, service and other field service-related activities.

The following products are warranted to be free from defects in material and workmanship in the period listed below from the date of purchase from the user or from the date of shipment from Thermo, whichever is earlier, provided use is in accordance with the operating limitations and maintenance procedures in the instruction manual and when not having been subjected to accident, alteration, misuse, abuse or breakage of electrodes:

## **Thirty-six months from date of purchase by the user (or forty-two months from date of shipment from Thermo)**

- Waterproof Meters (Orion 630, 635, 830A, 835A, 260A, 261S, 265A, 266S, 130A, 131S, 135A and 136S), Conductivity Meters (Orion 105Aplus, 115Aplus, 125Aplus, 145Aplus, 150Aplus and 162A), PerpHect<sup>®</sup> pH/ISE Meters (Orion 310, 320, 330, 350, 370) pH/ISE Meters (Orion 210Aplus, 230Aplus, 250Aplus, 290Aplus, 410Aplus, 420Aplus, 520Aplus, 525Aplus, 710Aplus, 720Aplus and 920Aplus), pHuture MMS<sup>TM</sup> Meters (Orion 535A and 555A), pH/Conductivity Meter (Orion 550A), Dissolved Oxygen Meters

(Orion 805Aplus, 810Aplus, 850Aplus and 862A).

**Twenty-four months from date of purchase by the user (or thirty-six months from date of shipment from Thermo)**

- Orion ROSS Ultra® Electrodes, Orion AQUAfast® IV Colorimeters, Orion AQUAfast® IV Turbidimeter, Orion 925 Flash Titrator™, Series 100 DuraProbe™ Conductivity Cells and Series 800 Dissolved Oxygen Probes.

**Twelve months from date of purchase by the user (or eighteen months from date of shipment from Thermo)**

- Laboratory pH Meters, (Orion 301, 611 and 940), SensorLink®, pHuture™ pH Meters (Orion 610 and 620), Sage® Pumps, Cahn® Balances, 930 Ionalyzer®, 950 ROSS™ FAST QC™ Titrator, 960 Titrator PLUS®, Karl Fischer Titrators, Autosamplers, Liquid Handling Devices, Liquid Handling Automation Workstations (Orion AS2000, AS2500 and AS4000), Pumps (Orion SP201, SP201-HR, SP201-S, Peristaltic and Rinse), pHuture® Conversion Box, Wine Master®, 607 Switchbox, rf link™, AQUAfast® II Colorimeters, Vacuum Degasser and Flowmeter.
- Orion EZ Flash® GC Accessory, Orion TEA Analyzer® 610 and 510 excluding consumable items carry twelve months warranty only.
- Orion Ion Selective Electrodes, ionplus® Electrodes, ROSS™ Electrodes, Sure-Flow® Electrodes, PerpHecT® Electrodes, AquaPro Professional Electrodes, No Cal™ pH electrodes, Standard Line pH Electrodes, Tris pH Electrodes, KNIpHE® electrode, ORP Triode™ (Orion 9180BN), pHuture™ pH Probes (Orion 616500) and pHuture MMS™ Quatrode™ and Triode™ (Orion 616600 and 617900), Orion 97-08 DO Probe, Series 100 Conventional Conductivity Cells, temperature probes and compensators (except those products noted).
- Orion 93 and 97 ionplus Series sensing modules are warranted to give six months of operation if placed in service before the date indicated on the package, except 93-07 and 97-07 Nitrate modules are warranted to give ninety days of operation if placed in service before the date indicated on the package.

**Six months from date of purchase by the user (or twelve months from date of shipment from Thermo)**

- Orion Flash Titration™ Probe (Orion 092518), pHuture™ Electrode (Orion 615700), pHuture MMS™ Pentrode™ (Orion 617500), Quatrode™ (Orion 617800) and Triode™ (Orion 615800), Low

Maintenance Triode™ (Orion 9107BN), ORP Low Maintenance Triode™ (Orion 9179BN), and PerpHecT® Low Maintenance Triode™ (Orion 9207BN), Waterproof Triode™ (Orion 9107WP, 9107WL, 9109WL and 9109WP), QuiKcheK® Meters and Micro Electrodes.

**Three months from date of purchase by the user (or six months from date of shipment from Thermo)**

- Economy Line Electrodes, Orion 91-05, 91-06, 91-15, 91-16, 91-25, 91-26, 91-35, 91-36, 92-06. Warranty also includes failure for any reason (excluding breakage), except abuse, provided the electrode is not used in solutions containing silver, sulfide, perchlorate, or hydrofluoric acid; or in solutions more than one (1) Molar in strong acid or base at temperatures above 50 °C.

**“Out-of-Box” Warranty - Should any of the following products fail to work when first used, contact Thermo immediately for replacement.**

- Orion Solutions, Standards, Reagents, Cables, Ferrules, Tubing, Line adapters, Printers, Software, Cases, Stands, Probe Membranes, AQUAfast® Test Strips, EZ Flash® columns, Liquid Handling Probes, Adapter Plates and Racks and general accessories.

For products in the catalog not listed in this warranty statement, please visit our website at: [www.thermo.com](http://www.thermo.com).

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# ORDERING INFORMATION

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<b>Orion No.</b>	<b>Description</b>
938101	Replacement Sensing Module for Perchlorate Electrode Orion 93-81
9300BN	Replacement Electrode Body with BNC Connector
930000	Replacement Electrode Body with US Standard Connector
900200	Double Junction Sure-Flow® Reference Electrode
930711	Nitrate ISA, 2 M Ammonium Sulfate Solution, 475 mL
090032	BNC Electrode to US Standard Adapter
900002	Double-Junction, Inner Chamber Filling Solution, 5 x 60 mL Bottle



# SPECIFICATIONS

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<b>Concentration range:</b>	7 x 10 <sup>-6</sup> M to 1 M as ClO <sub>4</sub> <sup>-</sup> 0.70 to 99,500 ppm as ClO <sub>4</sub> <sup>-</sup>
<b>pH range:</b>	2.5 to 11 pH
<b>Temperature range;</b>	0 to 40 °C
<b>Electrode resistance:</b>	1 to 5 megohms
<b>Reproducibility:</b>	± 2%
<b>Sample:</b>	Aqueous solutions only
<b>Minimum sample Size:</b>	3 mL in a 50 mL beaker,
<b>Storage:</b>	Store in perchlorate standard
<b>Module life:</b>	Six months under normal laboratory conditions
<b>Size:</b>	Electrode length: 105 mm Diameter: 12 mm Cap diameter: 16 mm Cap length: 30 mm Cable length: 1 meter

# NOTES

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## **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  
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### **Customer Support**

Toll Free: 800-225-1480  
[www.thermo.com](http://www.thermo.com)  
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Int'l. e-mail: [intcs1@thermoorion.com](mailto:intcs1@thermoorion.com)

**For updated contact information, visit [www.thermo.com](http://www.thermo.com)**

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