

Users Guide

Chloride
Electrodes



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This publication supersedes all previous publications on this subject.

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General Information

Introduction

The Orion 9417 Solid State half-cell and Orion 9617 ionplus® Sure-Flow® Combination Chloride Electrodes measure free chloride ions in aqueous solutions 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 outlined in the individual meter instruction manuals.

The Orion ionplus Sure-Flow Combination Chloride Electrode, Orion 9617, was developed specifically for measuring chloride in very small samples with minimal flow.

Thermo Electron Corporation's Technical EdgeSM for Orion Products can be consulted for assistance and troubleshooting advice. Please refer to **Troubleshooting** section for information about contacting Thermo.

Required Equipment

Meter — The easiest to use are direct concentration read-out specific ion meters, such as Orion EA940, 290A, 290Aplus, 710A, 710Aplus, 720A, 720Aplus, 920A, 920Aplus and new Orion Star™ series meters. If unavailable, a pH/mV meter with readability to 0.1 mV is recommended.

Reference Electrode — For Orion 9417: Use an Orion 9002 Double-Junction Reference Electrode. For Orion 9617: None required.

Magnetic Stirrer, Stir Bars — Recommended for laboratory measurements.

Graph Paper — 4-cycle semilogarithmic paper for preparing calibration curves (for use with digital pH/mV laboratory meters).

Polishing Strips — Cat. No. 948201 to polish dirty or etched element.

It is recommended that the 9617/9417 Cl⁻ electrode be polished when the slope of the electrode begins to drop or interferences are suspected.

Required Solutions

Distilled or Deionized Water — To prepare all solutions and standards.

Standard Solutions	Cat. No.
0.1 M Sodium Chloride Standard	941706
100 ppm Chloride Standard	941707
1000 ppm Chloride Standard	941708

Electrode Filling Solutions	Cat. No.
Orion 9417:	
Use with Orion 90-02 Reference Electrode	
• Inner Chamber	900002
• Outer Chamber	900003

Orion 9617:	
Reference Electrode not required	
Optimum Results™ B Reference Electrode Fill Solution	900062
For samples more concentrated than 10^{-2} M (355 ppm Cl ⁻)	900001

Ionic Strength Adjustor (ISA):	
To adjust ionic strength of samples and standards, 5 M NaNO ₃	940011

CISA™:	
To remove interferences, (see Use of CISA)	941709

Using the Electrode

Electrode Preparation

Orion 9417

1. Remove the rubber cap covering the electrode tip.
2. Fill reference electrode Orion 9002 according to instructions in the reference electrode instruction manual. Fill the inner chamber with Cat. No. 900002 and the outer chamber with Cat. No. 900003.

Orion 9617

Filling Solution

The filling solution, Cat. No. 900062, supplied with this electrode is designed to minimize junction potentials and chloride ion contamination of the sample, and can be used for all chloride measurements. Thermo offers an additional filling solution, Cat. No. 900001, designed for use in samples more concentrated than 10^{-2} M chloride. The electrode potential characteristics of the reference electrode portion, when using the Cat. No. 900001 solution, match those of a conventional saturated KCl calomel reference electrode.

NOTE: Use of other filling solutions will void the warranty on the electrode. Use of Cat. No. 900017 Combination Chloride Reference Electrode Filling Solution is acceptable for these electrodes.

Filling Instructions

The electrode is shipped without filling solution in the reference chamber. To fill from the flip-spout bottle:

1. Lift the spout to a vertical position.
2. Insert the spout into the fill hole in the outer sleeve and add a small amount of filling solution to the chamber. Tip the electrode to moisten the O-ring and turn electrode to a vertical position.
3. Holding the electrode by the barrel with one hand, use the thumb to push down on the electrode cap, allowing a few drops of filling solution to drain to wet the inner cone.
4. Release electrode cap and allow sleeve to return to original position.
5. If sleeve does not return to its original position immediately, check to see if the O-ring is moist enough and repeat steps 2-4 until the sleeve has returned to original position. Add filling solution just below the fill hole.

NOTE: Add filling solution each day before using electrode. The filling solution level should be at least one inch above the level of sample in the beaker to ensure a proper flow rate. If the filling solution is less than one inch above the sample solution level, electrode potentials may be erratic.

Checking Electrode Operation (Slope)

These are general instructions which can be used with most meters 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 change in concentration. Obtaining the slope value provides the best means for checking electrode operation.

1. If electrodes have been stored dry, prepare the electrodes as described under the section entitled **Electrode Preparation**.
2. Connect electrodes to the meter by inserting the reference electrode pin-tip connector and the sensing electrode connector into appropriate jacks on the digital pH/mV meter or specific ion meter. Non-Orion meters may require special adapters. Consult your meter instruction manual.
3. Place 100 mL distilled water in a 150 mL beaker. Add 2 mL ISA, Cat. No. 940011. Stir thoroughly. Set the function switch of the meter to the mV mode.
4. Rinse electrodes with distilled water and place in the solution prepared in step 3 above.
5. Select either 0.1 M Chloride standard, Cat. No. 941706, or 1000 ppm Chloride standard, Cat. No. 941708. Pipet 1 mL of the selected standard into the beaker. Stir thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.
6. Pipet 10 mL of the same standard into the same beaker. Stir thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.
7. 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 54-60 mV/decade when the solution temperature is 25 °C. If the difference in potential is not within this range, refer to **Troubleshooting**.

Before Analysis

Units of Measurement

Chloride concentration can be measured in units of moles per liter, equivalents per liter, parts per million, or any convenient concentration unit (see **Table 1**).

Table 1
Concentration Unit Conversion Factors

Moles/Liter	ppm Cl ⁻	% NaCl
10 ⁻¹	3550	0.58%
10 ⁻²	355	0.058%
10 ⁻³	35.5	0.0058%
10 ⁻⁴	3.55	0.00058%

Sample Requirements

The epoxy electrode body is resistant to attack by inorganic solutions. The electrode may be used intermittently in solutions containing methanol, benzene, or acetone. Consult Thermo Electron's Technical EdgeSM for Orion Products for use of electrode in specific applications.

Samples and standards should be at the same temperature. Temperature must be less than 100 °C.

Measuring Hints

- Pipet 2 mL ISA per 100 mL of standard or sample.
- 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 stirrer and beaker.
- Verify calibration every two hours by placing electrodes in the first standard solution used for calibration. If the value has changed, recalibrate.
- Always use fresh standards for calibration.

- Always rinse electrodes with deionized water between measurements (see **Electrode Preparation**). Shake after rinsing to prevent solution carryover. ***Do not wipe or rub the sensing element.***
- Allow all standards and samples to come to room temperature for precise measurement.
- After immersion in solution, check electrode for any air bubbles on element surface and remove by redipping electrode into solution.
- For Orion 9417 half-cell and 9617 electrodes: If electrode response is slow, the element may be coated with deposits. Restore performance by polishing with Orion polishing strips, Orion 948201. Cut off 1 inch of the polishing strip and polish the electrode sensing element with a circular motion for about 30 seconds. Rinse and soak in a standard solution for about 5 minutes before use.
- For high ionic strength samples, prepare standards with composition similar to that of the sample.

Analytical Procedures

Analytical Techniques

A variety of analytical techniques is available to the analyst. The following is a description of these techniques.

Direct Calibration

A simple procedure for measuring a large number of samples. Only one meter reading is required for each sample. Calibration is performed in a series of standards. The concentration of the samples is determined by comparison to the standards. ISA is added to all solutions to ensure that samples and standard have similar ionic strength.

Incremental Techniques

A useful method for measuring samples, since calibration is not required. As in direct calibration, any convenient concentration unit can be used. The different incremental techniques are described below. They can be used to measure the total concentration of a specific ion in the presence of a large (50-100 times) excess of complexing agents.

Known Addition is an alternate method useful for measuring dilute samples, checking the results of direct calibration (when no complexing agents are present), or measuring the total concentration of an ion in the presence of an excess complexing agent. 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.

Known Subtraction is useful as a quick version of a titration, or for measuring species for which stable standards do not exist. It is necessary to know the stoichiometric ratio between standard and sample. For known subtraction, an electrode sensing the sample species is used. Stable standards of a species reacting completely with the sample in a reaction of known stoichiometry are necessary.

Analate Addition is often used to measure soluble solid samples, viscous samples, small or very concentrated samples, or to diminish the effects of varying sample temperatures. This method is not suitable for dilute or low concentration samples. Total concentration is measured even in the presence of complexing agents. The electrodes are immersed in a standard solution containing the ion to be measured and an aliquot of the sample is added to the standard. The original sample concentration is determined from the change in potential before and after the addition.

Analate Subtraction is used in the measurement of ions for which no ion-selective electrode exists. The electrodes are immersed in a reagent solution which contains a species that the electrode senses, and that reacts with the sample. It is useful when sample size is small, or samples for which a stable standard is difficult to prepare, and for viscous or very concentrated samples. The method is not suited for very dilute samples. It is also necessary to know the stoichiometric ratio between standard and sample.

Specific instructions for known subtraction, analate addition, and analate subtraction can be found in the Orion meter instruction manuals.

Titration

Titration is a quantitative analytical technique for measuring the concentration of a species by incremental additions of a reagent (titrant) that reacts with the sample species. Sensing electrodes can be used for determination of the titration end point. Ion-selective electrodes are useful as end point detectors, because they are unaffected by sample color or turbidity. Titrations are approximately 10 times more precise than direct calibration, but are more time-consuming.

Direct Calibration

Orion 94-17 Set-up

1. Remove the rubber cap covering the electrode tip.
2. Fill the reference electrode Orion 90-02 according to instructions in the reference electrode instruction manual. Fill the inner chamber with Orion 900002 and the outer chamber with Orion 900003.
3. Connect electrodes to the meter.
4. Prepare two standards which 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**).

Orion 96-17 Set-up

1. Remove the rubber cap covering the electrode tip.
2. Fill the ionplus® Sure-Flow® combination electrode according to instructions in the **Electrode Preparation** section.
3. Connect electrodes to the meter.
4. Prepare two standards which 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**).

If using a meter with direct concentration readout capability

See individual meter instruction manuals for more specific information.

1. Measure 100 mL of the more dilute standard into a 150 mL beaker. Add 2 mL ISA. Stir thoroughly.
2. Rinse electrodes with deionized water, blot dry and place into the beaker. Wait for a stable reading, then calibrate the meter to display the value of the standard as described in the meter instruction manual.

3. Measure 100 mL of the more concentrated standard into a second 159 mL beaker. Add 2 mL ISA. Stir thoroughly.
4. Rinse electrodes with deionized water, blot dry, and place into the beaker with the more concentrated 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.
5. Measure 100 mL of the sample into a 150 mL beaker. Add 2 mL ISA. Stir thoroughly. Rinse electrodes with distilled water, blot dry and place into sample. The concentration will be displayed on the meter.

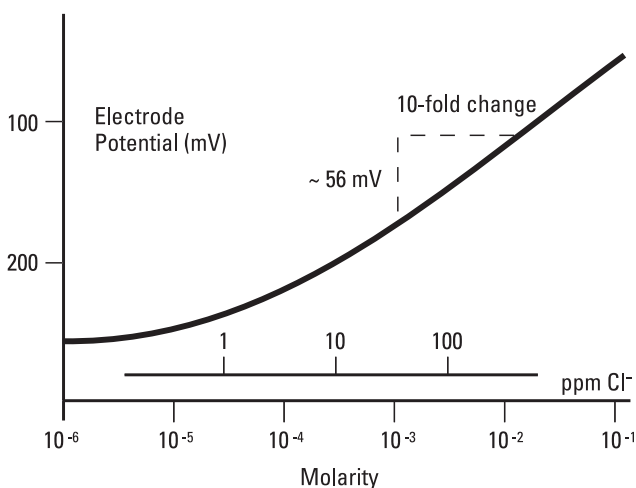


Figure 1 – Typical Chloride Electrode Calibration Curve

In the direct calibration procedure, a calibration curve is constructed on semilogarithmic paper. Electrode potentials of standard solutions are measured and plotted on the linear axis against their concentrations on the log axis. In the linear regions of the curves, only three standards are needed to determine a calibration curve. In non-linear regions, more points must be taken. The direct measurement procedures in the manual are given for concentrations in the region of linear electrode response. Low-level measurement procedures are given for measurements in the non-linear region.

If using a meter with millivolt readout only

1. Adjust the meter to measure mV.
2. Measure 100 mL of the more dilute standard into a 150 mL beaker. Add 2 mL ISA. Stir thoroughly.
3. Rinse electrodes with distilled water, blot dry and place into the beaker. When a stable reading is displayed, record the mV value and corresponding standard concentration.
4. Measure 100 mL of the more concentrated standard into a second 150 mL beaker. Add 2 mL ISA. Stir thoroughly.
5. Rinse electrodes with deionized water, blot dry and place into the second beaker. When a stable reading is displayed, record the mV value and corresponding standard concentration.
6. Using a semilogarithmic graph paper, prepare a calibration curve by plotting the millivolt values on the linear axis, and the standard concentration values on the logarithmic axis.
7. Measure 100 mL of sample into a 150 mL beaker. Add 2 mL ISA. Stir thoroughly.
8. Rinse electrodes with deionized water, blot dry, and place into the beaker. When a stable reading is displayed, record the mV value.
9. Using the calibration curve prepared in Step 6, determine the unknown concentration.

Low-Level Measurement

These procedures are for low ionic strength solutions with a chloride concentration of less than 10^{-4} M. For solutions low in chloride but high in total ionic strength, perform the same procedure with one change – prepare a calibration solution with a composition similar to the sample. Accurate measurement requires that the following conditions be met.

- Adequate time must be allowed for electrode stabilization. Longer response time will be needed at low levels.
- Stir all standards and samples at a uniform rate.

For meters with only a millivolt scale, without special low-level procedures, or without blank correction, prepare a calibration curve as outlined below.

Set-up

1. Remove the plastic cap covering the electrode tip.
- 2a. **Orion 9417:** Fill the reference electrode Orion 9002 according to instructions in the reference electrode instruction manual. Fill the inner chamber with Cat. No. 900002 and the outer chamber with Cat. No. 900003.
- 2b. **Orion 9617:** Fill electrode with selected filling solution. See instructions in **Electrode Preparation** section.
3. Connect the electrodes to the meter. Set the meter to read mV.
4. Select a standard solution. Use either 1000 ppm NaCl, standard Cat. No. 941708, or dilute the 0.1 M Chloride Standard, Cat. No. 941706, to 10^{-2} M.
5. Prepare a low-level ISA solution (1.0 M NaNO_3) by diluting 20 mL of ISA, Cat. No. 940011, to 100 mL with distilled water. Use this low-level ISA solution for low-level measurements only.

Measurement

1. Measure 100 mL distilled water into a 150 mL beaker. Add 1 mL low-level ISA.
2. Rinse the electrode(s) with deionized water and place into beaker. Stir thoroughly.
3. Add increments of the 1000 ppm or 10^{-2} M chloride standard to the beaker using steps outlined in **Table 2**. Record stable millivolt reading after each increment. On semilogarithmic paper, plot the concentration (log axis) against the millivolt potential (linear axis). See **Figure 2**. Prepare a new calibration curve with fresh standards each day.
4. Measure 100 mL of sample into a beaker. Rinse the electrodes with distilled water, blot dry, and place into sample. Add 1 mL low-level ISA to 100 mL sample.
5. Stir thoroughly. When a stable reading is displayed, record the mV value.
6. Determine the sample concentration corresponding to the measured potential from the low-level calibration curve.

Table 2
Serial Calibration For Low-Level Measurements

Additions of 1000 ppm or 10^{-2} M standards to 100 mL distilled water, plus 1 mL low-level ISA.

Step	Graduated Pipet Size	Added Volume	Concentration	
			ppm	Molarity
1	1 mL	0.1 mL	1.0	1.0×10^{-5}
2	1 mL	0.1 mL	2.0	2.0×10^{-5}
3	1 mL	0.2 mL	4.0	4.0×10^{-5}
4	1 mL	0.2 mL	6.0	6.0×10^{-5}
5	1 mL	0.4 mL	9.9	9.9×10^{-5}
6	2 mL	2.0 mL	29	2.9×10^{-4}
7	2 mL	2.0 mL	48	4.8×10^{-4}

Known Addition

Known addition is a convenient technique for measuring samples because no calibration curve is needed. It can be used to verify the results of a direct calibration or to measure the total concentration of an ion in the presence of a large excess of a complexing agent. The sample potential is measured before and after addition of a standard solution. Accurate measurement requires that the following conditions be met:

- Concentration should approximately double as a result of the addition.
- Sample concentration should be known to within a factor of three.
- In general, either no complexing agent or a large excess of the complexing agent may be present.
- The ratio of the uncomplexed ion to complexed ion must not be changed by addition of the standard.
- All samples and standards should be at the same temperature.

Set-up

1. Remove the plastic cap covering the electrode tip.
- 2a. **Orion 9417:** Fill the reference electrode Orion 9002 according to the instructions in the reference electrode instruction manual. Fill the inner chamber with Cat. No. 900002 and the outer chamber with Cat. No. 900003.
- 2b. **Orion 9617:** Fill electrode with selected filling solution. See instructions in **Electrode Preparation** section.
3. Connect the electrodes to the meter.
4. Prepare a standard solution which, upon addition to the sample, will cause the concentration of the chloride ion to double. Refer to **Table 3** as a guideline (Sample volume 100 mL).
5. Determine the slope of the electrode by performing the procedure under Checking **Electrode Operation (Slope)**.
6. Rinse electrodes between solutions with deionized water.

Table 3

Volume of addition	Concentration of Standard
1 mL	100 x sample concentration
5 mL	20 x sample concentration
10 mL*	10 x sample concentration

* Most convenient volume to use.

If using an instrument with direct known addition readout capability

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. Rinse electrodes with distilled water and place in sample solution. Add 2 mL ISA. Stir thoroughly.
3. When a stable reading is displayed, calibrate the meter as described in the meter instruction manual.
4. Pipet the appropriate amount of the standard solution into the beaker. Stir thoroughly.
5. When a stable reading is displayed, record the sample concentration.

Analysis using a meter with millivolt readout only

Use this procedure when no instructions for Known Addition are available in the meter instruction manual.

1. Set the meter to relative millivolt mode.
2. Measure 100 mL of sample into a 150 mL beaker. Add 2 mL ISA. Stir thoroughly.
3. Rinse electrodes with distilled water, blot dry, and place into beaker. When a stable reading is displayed, set the reading to 000.0 by turning the calibration control. If the reading cannot be set to 000.0, record the mV value.
4. Pipet the appropriate amount of standard solution into the beaker. Stir thoroughly.
5. When a stable reading is displayed, record the mV value. If the meter could not be zeroed in Step 3, subtract the first reading from the second to find ΔE .

6. From **Table 4**, find the value, Q, that corresponds to the change in potential, ΔE . To determine the original sample concentration, multiply Q by the concentration of the added standard:

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

where:

C_{std} = standard concentration

C_{sam} = sample concentration

Q = reading from known addition table

The table of Q values is calculated for a 10% volume change for electrodes with slope of 58 mV. The equation for the calculation of Q for different slopes and volume changes is given below.

$$Q = \frac{P}{[(1 + p)10^{\Delta E/S}] - 1}$$

where:

Q = reading from known addition table

ΔE = $E_2 - E_1$

S = slope of the electrode

$p = \frac{\text{volume of standard}}{\text{volume of sample}}$

Table 4
Known Addition Values for Q vs. ΔE at 25 °C for 10% Volume Addition. Slope (in the column headings) are units of mV/decade

ΔE	Q1 Concentration Ratio				
	Monovalent	(57.2)	(58.2)	(59.2)	(60.1)
5.0		0.2894	0.2933	0.2972	0.3011
5.2		0.2806	0.2844	0.2883	0.2921
5.4		0.2722	0.2760	0.2798	0.2835
5.6		0.2642	0.2680	0.2717	0.2754
5.8		0.2567	0.2604	0.2640	0.2677
6.0		0.2495	0.2531	0.2567	0.2603
6.2		0.2426	0.2462	0.2498	0.2533
6.4		0.2361	0.2396	0.2431	0.2466
6.6		0.2298	0.2333	0.2368	0.2402
6.8		0.2239	0.2273	0.2307	0.2341
7.0		0.2181	0.2215	0.2249	0.2282
7.2		0.2127	0.2160	0.2193	0.2226
7.4		0.2074	0.2107	0.2140	0.2172
7.6		0.2024	0.2056	0.2088	0.2120
7.8		0.1975	0.2007	0.2039	0.2071
8.0		0.1929	0.1961	0.1992	0.2023
8.2		0.1884	0.1915	0.1946	0.1977
8.4		0.1841	0.1872	0.1902	0.1933
8.6		0.1800	0.1830	0.1860	0.1890
8.8		0.1760	0.1790	0.1820	0.1849
9.0		0.1722	0.1751	0.1780	0.1809
9.2		0.1685	0.1714	0.1742	0.1771
9.4		0.1649	0.1677	0.1706	0.1734
9.6		0.1614	0.1642	0.1671	0.1698
9.8		0.1581	0.1609	0.1636	0.1664
10.0		0.1548	0.1576	0.1603	0.1631
10.2		0.1517	0.1544	0.1571	0.1598
10.4		0.1487	0.1514	0.1540	0.1567
10.6		0.1458	0.1484	0.1510	0.1537
10.8		0.1429	0.1455	0.1481	0.1507
11.0		0.1402	0.1427	0.1453	0.1479
11.2		0.1375	0.1400	0.1426	0.1451
11.4		0.1349	0.1374	0.1399	0.1424
11.6		0.1324	0.1349	0.1373	0.1398
11.8		0.1299	0.1324	0.1348	0.1373

ΔE Monovalent	Q1 Concentration Ratio			
	(57.2)	(58.2)	(59.2)	(60.1)
12.0	0.1276	0.1300	0.1324	0.1348
12.2	0.1253	0.1277	0.1301	0.1324
12.4	0.1230	0.1254	0.1278	0.1301
12.6	0.1208	0.1232	0.1255	0.1278
12.8	0.1187	0.1210	0.1233	0.1256
13.0	0.1167	0.1189	0.1212	0.1235
13.2	0.1146	0.1169	0.1192	0.1214
13.4	0.1127	0.1149	0.1172	0.1194
13.6	0.1108	0.1130	0.1152	0.1174
13.8	0.1089	0.1111	0.1133	0.1155
14.0	0.1071	0.1093	0.1114	0.1136
14.2	0.1053	0.1075	0.1096	0.1118
14.4	0.1036	0.1057	0.1079	0.1100
14.6	0.1019	0.1040	0.1061	0.1082
14.8	0.1003	0.1024	0.1045	0.1065
15.0	0.0987	0.1008	0.1028	0.1048
15.5	0.0949	0.0969	0.0989	0.1009
16.0	0.0913	0.0932	0.0951	0.0971
16.5	0.0878	0.0897	0.0916	0.0935
17.0	0.0846	0.0865	0.0883	0.0901
17.5	0.0815	0.0833	0.0852	0.0870
18.0	0.0786	0.0804	0.0822	0.0839
18.5	0.0759	0.0776	0.0793	0.0810
19.0	0.0733	0.0749	0.0766	0.0783
19.5	0.0708	0.0724	0.0740	0.0757
20.0	0.0684	0.0700	0.0716	0.0732
20.5	0.0661	0.0677	0.0693	0.0708
21.0	0.0640	0.0655	0.0670	0.0686
21.5	0.0619	0.0634	0.0649	0.0664
22.0	0.0599	0.0614	0.0629	0.0643
22.5	0.0580	0.0595	0.0609	0.0624
23.0	0.0562	0.0576	0.0590	0.0605
23.5	0.0545	0.0559	0.0573	0.0586
24.0	0.0528	0.0542	0.0555	0.0569
24.5	0.0512	0.0526	0.0539	0.0552
25.0	0.0497	0.0510	0.0523	0.0536
25.5	0.0482	0.0495	0.0508	0.0521
26.0	0.0468	0.0481	0.0493	0.0506
26.5	0.0455	0.0467	0.0479	0.0491
27.0	0.0442	0.0454	0.0466	0.0478
27.5	0.0429	0.0441	0.0453	0.0464

ΔE Monovalent	Q1 Concentration Ratio			
	(57.2)	(58.2)	(59.2)	(60.1)
28.0	0.0417	0.0428	0.0440	0.0452
28.5	0.0405	0.0417	0.0428	0.0439
29.0	0.0394	0.0405	0.0416	0.0427
29.5	0.0383	0.0394	0.0405	0.0416
30.0	0.0373	0.0383	0.0394	0.0405
31.0	0.0353	0.0363	0.0373	0.0384
32.0	0.0334	0.0344	0.0354	0.0364
33.0	0.0317	0.0326	0.0336	0.0346
34.0	0.0300	0.0310	0.0319	0.0328
35.0	0.0285	0.0294	0.0303	0.0312
36.0	0.0271	0.0280	0.0288	0.0297
37.0	0.0257	0.0266	0.0274	0.0283
38.0	0.0245	0.0253	0.0261	0.0269
39.0	0.0233	0.0241	0.0249	0.0257
40.0	0.0222	0.0229	0.0237	0.0245
41.0	0.0211	0.0218	0.0226	0.0233
42.0	0.0201	0.0208	0.0215	0.0223
43.0	0.0192	0.0199	0.0205	0.0212
44.0	0.0183	0.0189	0.0196	0.0203
45.0	0.0174	0.0181	0.0187	0.0194
46.0	0.0166	0.0172	0.0179	0.0185
47.0	0.0159	0.0165	0.0171	0.0177
48.0	0.0151	0.0157	0.0163	0.0169
49.0	0.0145	0.0150	0.0156	0.0162
50.0	0.0138	0.0144	0.0149	0.0155
51.0	0.0132	0.0137	0.0143	0.0148
52.0	0.0126	0.0131	0.0136	0.0142
53.0	0.0120	0.0125	0.0131	0.0136
54.0	0.0115	0.0120	0.0125	0.0130
55.0	0.0110	0.0115	0.0120	0.0124
56.0	0.0105	0.0110	0.0115	0.0119
57.0	0.0101	0.0105	0.0110	0.0114
58.0	0.0096	0.0101	0.0105	0.0109
59.0	0.0092	0.0096	0.0101	0.0105
60.0	0.0088	0.0092	0.0096	0.0101

Electrode Storage

Orion 9417

The Orion 9417 should be rinsed thoroughly and stored dry in air at all times. When storing for long periods of time, replace the protective cap to protect the sensing element.

Orion 9617

The solution in the Orion 9617 should not be allowed to evaporate, causing crystallization. For short periods of time, between sample measurements, and up to one week, store the electrode in 0.01 M chloride standard.

For storage longer than one week or for an indefinite period, drain the electrode. Flush the inside with distilled water and store dry with the protective cap to protect the sensing element.

Orion 9002

The Orion 9002 reference electrode may be stored in air between sample measurements (up to two hours). For short periods of time (up to one week) the Orion 9002 should be stored in its filling solution. Chloride standard (0.01 M) and distilled water are also acceptable storage solutions. The solutions inside the electrode should not be allowed to evaporate causing crystallization.

For periods of time over one week, drain the electrode, flush the inside with distilled water, and store dry.

Disassembly and Cleaning of Orion 9617

When the area between the electrode sleeve and inner cone becomes clogged with sample or precipitate from filling solution, the chamber can be cleaned by flushing out with filling solution. (Hold the electrode body and push down on the cap to drain the chamber.) If the chamber is not completely clean, repeat the procedure. Refill with Orion Filling Solution, Cat. No. 900062, 900017 or 900001.

Disassembly is not normally required or recommended. If a more thorough cleaning is required, the electrode can be disassembled using the following instructions:

1. Tip the electrode so that the filling solution moistens the dark green O-ring on the electrode body. Hold the electrode body and push down on the cap to drain the chamber.
2. Unscrew the cap, slide the cap and epoxy-coated spring up along the cable.
3. Hold the outer sleeve with one hand, and firmly push down on the threaded portion with the thumb and forefinger to separate the inner body from the sleeve.
4. Grasp the cone with a clean tissue and withdraw the body from the sleeve with a gentle twisting motion. **Do not touch the AgCl pellet above the cone.** Rinse the outside of the electrode body and entire sleeve with distilled water. Allow to air dry.

Reassembly

1. Moisten the O-ring on the electrode body with a drop of filling solution. Insert the screw-thread end of the electrode body into the tapered, ground end of sleeve.
2. Push body into sleeve with a gentle twisting motion until bottom surface of inner cone is flush with the tapered end of the sleeve.
3. Place the spring on the electrode body, and screw on the cap. Follow the filling instructions in the **Electrode Preparation** section. The electrode is now ready for use.

Troubleshooting

Troubleshooting Checklist

Symptom	Possible Causes
Off-scale or Over-range reading	Defective meter
	Electrodes not plugged in properly
	Reference electrode junction is dry
	No reference electrode
	Reference electrode not filled
	Air bubble on element
	Electrodes not in solution
Static electricity	
Noisy or unstable readings (readings continuously or rapidly changing)	Defective meter
	Meter or stirrer improperly grounded
	Air bubble on sensing element
	Wrong reference electrode
ISA not used	
Drift (Reading slowly changing in one direction)	Samples and standards at different temperatures
	Sensing element dirty or etched
	Incorrect reference filling solution
Low slope or No slope	Standards contaminated or incorrectly made
	ISA not used
	Standard used as ISA
	Defective electrode
Sensing element dirty or etched	
"Wrong Answer" (But calibration curve is OK)	Incorrect scaling of semilog paper
	Incorrect sign
	Incorrect standards
	Wrong units used
	Complexing agents in sample
Interferences	

Next Step

Perform meter checkout procedure (see meter instruction manual)

Unplug electrodes and reset

Hold reference electrode and push cap to expel a few drops of filling solution

Use Cat. No. 900200 Reference Electrode with Orion 9417

Be sure reference electrode is filled with correct fill solution

Remove bubble by redipping electrode in solution

Put electrodes in solution

Wipe plastic parts of meter with detergent solution

Check meter with shorting strap (see meter instruction manual)

Check meter and stirrer for grounding

Remove bubble by redipping electrode in solution

Do not use calomel or Ag/AgCl single junction reference electrode

Use recommended ISA, Orion 940011

Allow solutions to come to the room temperature before measurement

Polish sensing element (see **Measuring Hints**)

Use recommended filling solutions, in Orion 9617 or Cat. No. 900002 and 900003 in Orion 9002

Prepare fresh standards

Use recommended ISA, Cat. No. 940011

Use ISA!

Refer to **Troubleshooting**

Polish sensing element (see **Measuring Hints**)

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} M = 35.5 ppm as Cl^-

Use known addition or titration techniques, or a decomplexing procedure

Remove by using CISA™ (See **Use of CISA**)

Troubleshooting Guide

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) Electrodes, (3) Standard, (4) Sample, and (5) Technique.

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 strap for convenience in troubleshooting. Consult the manual for complete instructions and verify that the instrument operates as indicated and is stable in all steps.

Electrodes

1. Rinse electrodes thoroughly with distilled water.
2. Check electrode operation (slope).
3. If electrode fails this procedure. For Orion 9417: polish the chloride electrode as directed in **Measuring Hints**. Clean reference electrode as described in reference electrode instruction manual.
4. Repeat step 2, **Checking Electrode Operation**.
5. If the electrodes still do not perform as described, determine whether the chloride or reference electrode is at fault. To do this, substitute a known working electrode for the electrode in question and repeat the slope check. When testing combination electrodes, test each half of the electrode separately.
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.
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 solutions, 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, accuracy of dilution, quality of distilled water, or a mathematical error in calculating the concentrations.

The best method for preparation of standards is by serial dilution. This means that an initial standard is diluted, using volumetric glassware, to prepare a second standard solution. 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 sample, look for possible interferences, complexing agents, or substances which 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 pH Requirements**.

Technique

Check the method of analysis for compatibility with your sample. Direct measurement may not always be the method of choice. If a large amount of complexing agents is present, known addition may be best. If the sample is viscous, analate addition may solve the problem. 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. Reread **Measuring Hints** and **Analytical Procedures**.

Electrode Characteristics

Electrode Response

The electrode potential plotted against concentration on semilogarithmic paper results in a straight line with a slope of about 54-60 mV per decade. See **Figure 1**.

The time response of the electrode, that is, the time required to reach 99% of the stable potential reading, varies from several seconds in concentrated solutions to several minutes near the limit of detection. See **Figure 2**.

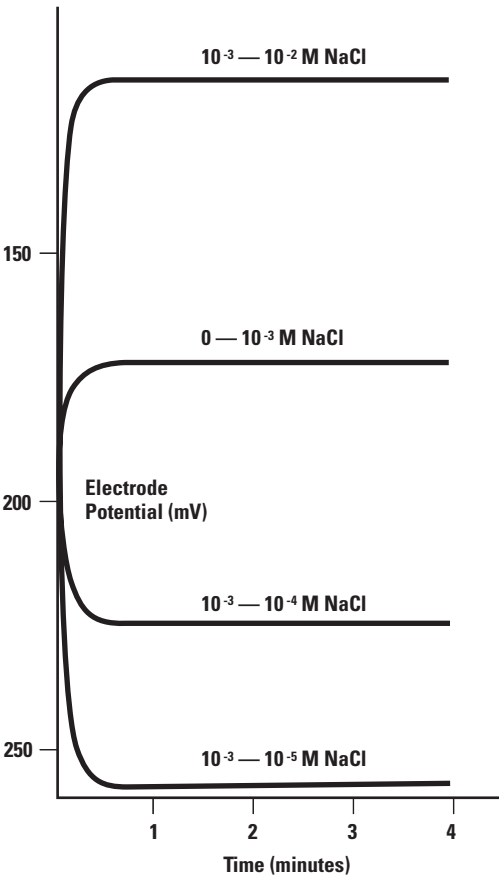


Figure 2 — Typical Electrode Response to Step Changes in NaCl

Reproducibility

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

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} 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 chloride electrode also varies with temperature, as indicated by the factor "S" in the Nernst equation. Values of the Nernst factor for chloride ion are given in **Table 5**. If temperature changes occur, meter and electrodes should be recalibrated.

The electrode can be used at temperatures from 0-100 $^{\circ}\text{C}$, provided that temperature equilibrium has occurred. For use at temperatures substantially different from room temperature, equilibrium times of up to one hour are recommended. The electrode must be used only intermittently at solution temperatures above 80 $^{\circ}\text{C}$.

Table 5
Values of Theoretical Electrode Slope vs. Temperature

T $^{\circ}\text{C}$	S	T $^{\circ}\text{C}$	S
0	54.2	30	60.1
10	56.2	40	62.1
20	58.2	50	64.1
25	59.2		

Interferences

High levels of ions which form very insoluble salts of silver may deposit a layer of salt on the membrane, causing electrode malfunction. In addition, strongly reducing solutions may form a surface layer of silver. In either case, restore performance by polishing, or rinse thoroughly and fill new filling solution.

Mercury must be absent from samples.

Measurements can be made in solutions containing oxidizing agents such as Cu^{++} , Fe^{+++} , and MnO_4^- .

Table 6 gives the maximum allowable concentration of the more common interfering ions, expressed as the ratio of the interfering ion molarity to the sample chloride molarity. If the ratio is exceeded, readings will be in error. If the ratio is less than that listed in the table, neither accuracy of the measurement nor surface of the electrode membrane will be affected. To convert molarity to ppm, see **Table 1**.

Table 6
Maximum Allowable Ratio of Interfering Ion to Chloride

Interference	Maximum Allowable Ratio Interference Chloride
(a) OH^-	80
(b) Br^-	3×10^{-3}
(b) I^-	5×10^{-7}
(c) $\text{S}^{=}$	10^{-6}
(c) CN^-	2×10^{-7}
(d) NH_3	0.12
(d) $\text{S}_2\text{O}_3^{=}$	0.01

- (a) Hydroxide interference can be removed by acidifying to pH 4 with 1 M HNO_3 .
- (b) Mixed halides in solution can be measured using CISA™ to remove interferences or by a Gran's Plot titration. A procedure for using CISA can be found below. Write or call Thermo's The Technical EdgeSM for Orion Products for information.
- (c) Sulfide and cyanide may be removed by adding a nickel (+2) solution or by using CISA.
- (d) Represents a complexing species. Maximum level can be exceeded without electrode damage. Value shown is for 1% error.

Use of CISA™

Interferences to the chloride measurement may be minimized by addition of CISA, an oxidizing agent which will oxidize up to 500 mg/L S^{2-} , 100 mg/L Br^- or I^- , 100 mg/L NH_3 , or a 100-fold excess of CN^- over Cl^- . Chloride can be measured in the presence of other halides without the need for a Gran's Plot titration. Since the reagents used are strong oxidizing agents, solutions should be handled in a well-ventilated area, preferably under a hood.

CISA:

Orion 941709, 1 M HNO_3 and 0.1 M $NaBrO_3$.

Procedure: 1:1 ratio, **example:** 50 mL of CISA to 50 mL of standard and 50 mL of sample. Mix CISA in equal quantities with both standards and samples. Allow solutions to stand ten minutes before measuring. Standards mixed with CISA should be discarded after measuring since chloride will be oxidized upon prolonged standing. Prepare a fresh mixture of standard and CISA for each calibration. Follow procedures in the **Direct Measurement** section after adding CISA.

Complexation and Precipitation

Chloride ion forms complexes with some metal ions. Since the electrode responds only to free chloride ions, the presence of any complexing agents lowers the measured concentration.

Table 7 lists the levels of complexing metals causing a 10% error at 10^{-4} M chloride.

Total concentration in the presence of a large excess (by a factor of at least 50-100) of complexing agent can be measured by the known addition method previously described.

Table 7

Levels of Complexing Agents Causing a 10% Error at 10^{-4} M Chloride

Bi^{+++}	4×10^{-4} M (80 ppm)
Cd^{++}	2×10^{-3} M (200 ppm)
Mn^{++}	2×10^{-2} M (1100 ppm)
Pb^{++}	2×10^{-3} M (400 ppm)
Sn^{++}	6×10^{-3} M (700 ppm)
Tl^{+++}	4×10^{-5} M (8 ppm)

Electrode Life

Each electrode should last at least one year in normal laboratory use. In time, electrode slope will decrease and readings will start to drift, indicating that the electrode should be replaced. Before replacement, refer to Troubleshooting Checklist section, to verify that the symptoms are caused by the electrode.

Theory of Operation

The chloride electrode consists of a sensing element bonded into an epoxy body. When the sensing element is in contact with a solution containing chloride ions, an electrode potential develops across the sensing element. This potential, which depends on the level of free chloride ion in 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 chloride ion in solution is described by the Nernst equation:

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

where:

- E = measured electrode potential
- E_0 = reference potential (a constant)
- A = chloride ion activity level in solution
- S = electrode slope (about 57 mV per decade)

The level of chloride ion, A, is the activity or “effective concentration” of free chloride ion in solution. The chloride ion activity is related to free chloride ion concentration, C_f , by the activity coefficient, γ :

$$A = \gamma C_f$$

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_i = concentration of ion i
- Z_i = charge of ion i
- and Σ symbolizes the sum of all the types of ions in solution.

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 all chloride standards and samples so that the background ionic strength is high and constant relative to variable concentrations of chloride ions. For the chloride electrode, NaNO_3 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 chloride ion. If samples have a high ionic strength (above 0.1 M), standards must be prepared with a composition similar to the samples.

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 rates, 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.

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 The Technical EdgeSM for Orion Products. See **Assistance**.

Assistance

After troubleshooting all components of your measurement system, contact The Technical EdgeSM 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.

Warranty

For the most current warranty information, visit www.thermo.com/water.

Ordering Information

Electrodes

Orion Electrodes are available with a variety of connectors. For more information, consult your Orion pH Electrode Catalog and price list or your local Orion Distributor.

Cat. No.	Description
900200	Orion 9002 Double-Junction Reference Electrode
900001	Filling Solution for Orion 9617 Combination Chloride Electrode (samples more concentrated than 10^{-2} M)
900002	Inner Chamber Fill Solution, for Orion 9002 Double-Junction Reference Electrode used with Orion 9417
900003	Outer Chamber Fill Solution, for Orion 9002 Double-Junction Reference Electrode used with Orion 9417
900017	Filling Solution for Orion 9617 Combination Chloride Electrode
900062	Optium Result™ Reference Electrode Filling Solution for Orion 9617

Cat. No.	Accessories
941706	0.1 M Sodium Chloride Standard Solution
941707	100 ppm Chloride Standard Solution
941708	1000 ppm Chloride Standard Solution
940011	5 M NaNO ₃ Ionic Strength Adjustor, (ISA)
941709	CISA™ (Chloride Ionic Strength Adjustor)
948201	Polishing Strips

Specifications

Concentration Range

1 M to 5×10^{-5} M
35,500 to 1.8 ppm

pH Range

2 - 12 pH

Temperature Range

0 to 100 °C for Orion 9417
10 to 100 °C for Orion 9617

Electrode Resistance

Less than 1.0 megohm

Reproducibility

$\pm 2\%$

Minimum Sample Size

3 mL in a 50 mL beaker

Size

Electrode Length: 110 mm
Diameter: Orion 9417: 12 mm
 Orion 9617: 13 mm
Cap Diameter: 16 mm
Cable Length: 1 M

Specifications subject to change without notice.

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