

User Guide

93 Series Chloride
Ion Selective
Electrode



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This publication supersedes all previous publications on this subject.

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Introduction

This user guide contains information on the preparation, operation and maintenance for the 93 series chloride ion selective electrode (ISE). General analytical procedures, electrode characteristics and electrode theory are also included in this user guide. Chloride electrodes measure chloride ions in aqueous solutions quickly, simply, accurately and economically.

Technical Support Chemists can be consulted for assistance and troubleshooting advice. Within the United States call 1.800.225.1480 and 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/contactwater.

For the latest application and technical resources for Thermo Scientific Orion products, visit www.thermo.com/waterapps.

93 Series Chloride Plastic Membrane Module, Cat. No. 931701

The chloride module must be used with the 93 series electrode body and double junction reference electrode, Cat. No. 900200. The 93 series electrode body is available with a waterproof BNC connector, Cat. No. 9300BNWP; U.S. standard connector, Cat. No. 930000; and a screw cap connector, Cat. No. 9300SC. Electrodes with a waterproof BNC connector can be used on any ISE or mV meter with a BNC connection. Electrodes with a screw cap connector require a separate cable.

The 93 series chloride electrode is designed to measure chloride in the range of 1×10^{-5} M to 1 M and can be used in the presence of modest concentrations of sulfide, iodide and cyanide. For concentrated solutions and solutions in which nitrate or sulfate is present, the chloride solid state half-cell ISE, Cat. No. 9417BN or Cat. No. 9417SC, is recommended.

Note: *The 93 series chloride electrode replaces the 92-07 chloride electrode. The 93 series chloride electrode can be used for most procedures in technical journals, applications bulletins or the analytical methods guide that specify the use of the 92-17 chloride electrode.*

Required Equipment

1. Thermo Scientific Orion ISE meter, such as the 4-Star pH/ISE meter or 5-Star pH/ISE/DO/conductivity meter; equivalent ISE meter; or mV meter with a 0.1 mV resolution.
2. Thermo Scientific Orion 93 series chloride module, Cat. No. 931701.
3. 93 Series electrode body, Cat. No. 9300BNWP, Cat. No. 930000 or Cat. No. 9300SC.
4. Double junction reference electrode, Cat. No. 900200.
5. Magnetic stirrer or Thermo Scientific Orion stirrer probe, Cat. No. 096019. The stirrer probe can be used with 3-Star, 4-Star and 5-Star benchtop meters.
6. Volumetric flasks, graduated cylinders and beakers. Plastic labware is recommended for low level chloride analysis.
7. Distilled or deionized water.
8. Double junction reference electrode filling solutions. Use inner chamber filling solution, Cat. No. 900002, and a 0.1 M potassium chloride (KCl) solution for the double junction reference electrode.

To prepare the 0.1 M KCl solution – Add 0.75 grams of reagent-grade KCl to a 100 mL volumetric flask and dilute to the mark with distilled water.

Note: *Do not use the outer chamber filling solution that ships with the double junction reference electrode because it contains interferences for chloride measurements.*

9. 0.1 M NaCl chloride calibration standard, Cat. No. 941706; 1000 ppm chloride calibration standard, Cat. No. 941708; or 100 ppm chloride calibration standard, Cat. No. 941707.

Serial Dilutions

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

1. **To prepare a 10^{-2} M standard (355 ppm as Cl and 585 ppm as NaCl)** – Pipet 10 mL of the 0.1 M standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.
2. **To prepare a 10^{-3} M standard (35.5 ppm as Cl and 58.5 ppm as NaCl)** – Pipet 10 mL of the 10^{-2} M standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.
3. **To prepare a 10^{-4} M standard (3.55 ppm as Cl and 5.85 ppm as NaCl)** – Pipet 10 mL of the 10^{-3} M standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

To prepare standards with a different concentration use the following formula:

$$C_1 * V_1 = C_2 * V_2$$

C_1 = concentration of original standard

V_1 = volume of original standard

C_2 = concentration of standard after dilution

V_2 = volume of standard after dilution

For example, to prepare 100 mL of a 100 ppm chloride standard from a 3550 ppm chloride standard:

$$C_1 = 3550 \text{ ppm chloride}$$

$$V_1 = \text{unknown}$$

$$C_2 = 100 \text{ ppm chloride}$$

$$V_2 = 100 \text{ mL}$$

$$3550 \text{ ppm} * V_1 = 100 \text{ ppm} * 100 \text{ mL}$$

$$V_1 = (100 \text{ ppm} * 100 \text{ mL}) / 3550 \text{ ppm} = 2.82 \text{ mL}$$

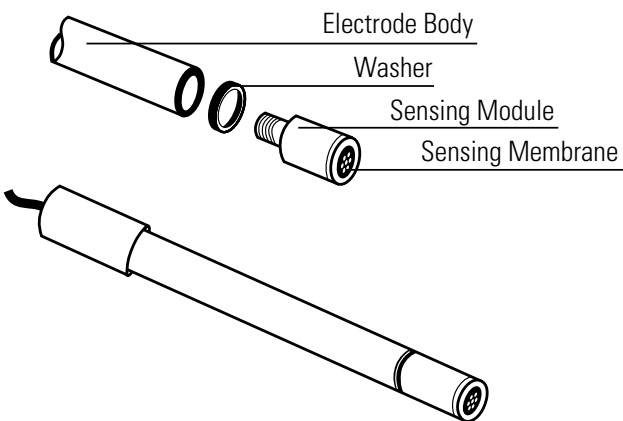
Electrode Setup

Chloride Half-Cell Electrode Preparation

Remove the chloride sensing module from the vial and save the vial for electrode storage. Make sure that the rubber electrode washer on the sensing module is in place. See **Figure 1**. Screw the sensing module into the 93 series electrode body until the module is finger-tight. To ensure electrical continuity, shake the electrode down like a clinical thermometer. Rinse the chloride module with distilled water and then soak it in a 100 ppm or 10^{-2} M chloride standard for 1 to 2 hours prior to use.

Note: Do not immerse the electrode past the rubber washer.

Figure 1
Chloride Half-Cell Electrode



Double Junction Reference Electrode Preparation

Prepare the reference electrode according to the reference electrode user guide. Fill the reference electrode with inner chamber filling solution, Cat. No. 900002, and 0.1 M KCl solution as the outer chamber filling solution. To prepare the 0.1 M KCl solution – add 0.75 grams of reagent-grade KCl to a 100 mL volumetric flask and dilute to the mark with distilled water.

Note: Do not use the outer chamber filling solution that ships with the 900200 double junction reference electrode because it contains interferences for chloride measurements.

Checking Electrode Operation (Slope)

These are general instructions that can be used with most meters to check the electrode operation. Refer to the meter user guide 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 the electrode has been stored dry, prepare the electrode as described in the **Electrode Preparation** section.
2. Connect the electrode to a meter with a mV mode. Set the meter to the mV mode.
3. Add 100 mL of distilled water to a 150 mL beaker. Stir the solution thoroughly.
4. Rinse the electrode with distilled water and place the electrode into the solution prepared in step 3.
5. Select either a 0.1 M or 100 ppm chloride standard. Pipet 1 mL of the standard into the beaker and stir the solution 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 and stir the solution thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.
7. There should be a 54 to 60 mV difference between the two millivolt readings when the solution temperature is between 20 to 25 °C. If the millivolt potential is not within this range, refer to the **Troubleshooting** section.

Measurement Units

Chloride concentration can be measured in moles per liter (M), parts per million (ppm) or any convenient concentration unit.

Table 1
Concentration Unit Conversion Factors

Moles/Liter (M)	ppm as Cl	ppm as NaCl
1.0	35500	58500
10^{-1}	3550	5850
10^{-2}	355	585
10^{-3}	35.5	58.5
10^{-4}	3.55	5.85

Sample Requirements

All samples must be aqueous and must not contain organic solvents. Contact Technical Support for information on using the electrode for specific applications.

The solution temperature must be less than 40 °C.

Samples and standards should be at the same temperature. A 1 °C difference in temperature for a 10^{-3} M chloride solution will give rise to about a 2% measurement error.

Interferences should be absent from all samples. See the **Interferences** section for a list of possible interferences.

Measuring Hints

- Stir all standards and samples at a uniform, moderate rate. Place a piece of insulating material, such as Styrofoam or cardboard, between the magnetic stir plate and beaker to prevent measurement errors from the transfer of heat to the sample.
- Always use freshly prepared standards for calibration.
- Concentrated samples (over 0.1 M) should be diluted before measurement.
- Always rinse the electrode with distilled water between measurements and shake the electrode to remove the water and prevent sample carryover. Do not wipe or rub the electrode sensing module.
- Store the chloride electrode in a 10^{-2} M or 100 ppm chloride standard between measurements.
- The chloride half-cell electrode should be immersed in standards and samples to approximately half the length of the chloride module. Do not immerse the chloride electrode past the electrode washer. Immerse the reference electrode to the same depth as the chloride electrode.
- Allow all standards and samples to reach the same temperature for precise measurements.
- Verify the electrode calibration every two hours by placing the electrode in a fresh aliquot of the least concentrated standard used for calibration. If the value has changed by more than 2%, recalibrate the electrode.
- After immersing the electrode in a solution, check the electrode sensing surface for air bubbles and remove air bubbles by reimmersing the electrode in the solution and gently tapping it.
- For high ionic strength samples, prepare standards with a background composition similar to the sample.
- The double junction reference electrode fill hole must be open during measurements to ensure a uniform flow of filling solution.
- If the electrode response becomes sluggish, the membrane may contain a surface layer of contaminants. See the **Electrode Maintenance** section for cleaning instructions.

Electrode Storage

Chloride Half-Cell Electrode Storage

The chloride half-cell electrode should be rinsed thoroughly with distilled water and stored in a 10^{-2} M or 100 ppm chloride standard. When storing the electrode for more than three days, rinse the chloride half-cell electrode thoroughly with distilled water, shake the electrode dry, disassemble the electrode and store the sensing module in the glass vial.

Double Junction Reference Electrode Storage

The double junction reference electrode may be stored in a 0.1 M KCl solution between sample measurements and up to one week. The filling solution inside the electrode should not be allowed to evaporate, as crystallization will result.

For storage longer than one week, drain the reference electrode, flush the inside with distilled water and store the electrode dry.

Electrode Maintenance

Double Junction Reference Electrode Flushing

If the area between the electrode outer body and inner cone becomes clogged with sample or precipitate, flush the area with filling solution or distilled water.

1. Hold the electrode body with one hand and use your thumb to push down on the electrode cap to drain all of the filling solution out of the electrode.
2. Fill the electrode with distilled water and then push down on the cap until all the water is drained from the chamber. Repeat this procedure until all of the sample or precipitate is removed from the electrode.
3. Fill the electrode with fresh filling solution up to the fill hole. Push down on the cap to allow a few drops of filling solution to drain out of the electrode and then replenish the lost filling solution.
4. Rinse the electrode with distilled water.

Cleaning the Chloride Sensing Module

If the electrode is exposed to high levels of interfering ions, it may drift and become sluggish in response. When this happens, restore normal performance by soaking the electrode for an hour in distilled water and then soaking the electrode for a few hours a 10^{-2} M or 100 ppm chloride standard. If soaking the electrode does not restore normal electrode performance, replace the chloride sensing module.

Replacing the Chloride Sensing Module

The sensing membrane of plastic membrane electrodes will wear over time, indicated by low slope values, drift, poor reproducibility and loss of response in low level samples. The electrode response can be restored by replacing the sensing module. Each sensing module will last about six months with normal laboratory use, but the actual lifespan of the sensing module will depend on the type of samples that are measured.

For the 93 series chloride half-cell electrode, use the 93 series chloride module, Cat. No. 931701. Rinse the electrode with distilled water, carefully unscrew the sensing module from the electrode and dispose of the old sensing module. Obtain a new chloride module and refer to the **Chloride Half-Cell Electrode Preparation** section for instructions on assembling the electrode.

Analytical Techniques

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

Direct Calibration is a simple procedure for measuring a large number of samples. Only one meter reading is required for each sample. Calibration is performed using a series of standards. The concentration of the samples is determined by comparison to the standards.

Low Level Calibration is similar to the direct calibration technique. This method is recommended when the expected sample concentration is less than 1 ppm or 10^{-4} M chloride. A minimum three point calibration is recommended to compensate for the electrode's non-linear response at these concentrations. A special calibration standard preparation procedure is the best means of preparing low level calibration standards.

Incremental Techniques provide a useful method for measuring samples, since a calibration is not required. 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 to 100 times) excess of complexing agents. As in direct calibration, any convenient concentration unit can be used.

Known Addition is 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 electrode is 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.

Table 2
Recommended Measuring Techniques

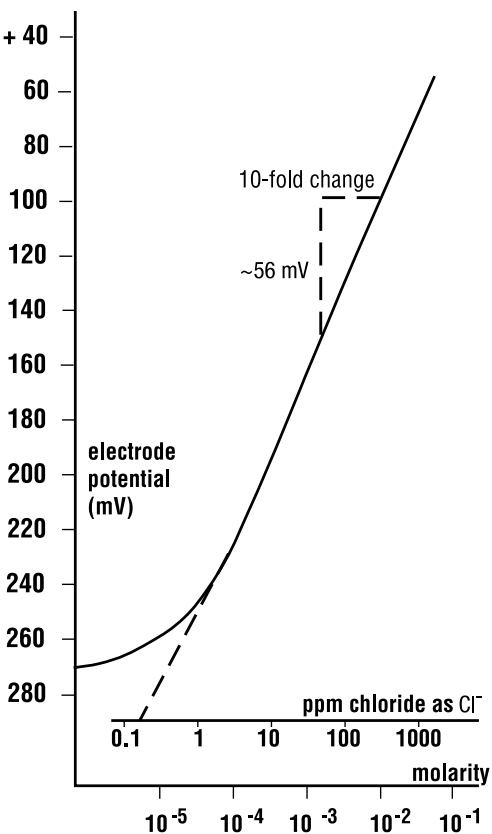
	Direct	Low Level	Known Addition
[Cl] < 1 ppm		✓	
[Cl] > 1 ppm	✓		✓
Occasional Sampling			✓
Small sample volume			✓
Large number of samples	✓	✓	
Field measurement	✓		
Ionic strength greater than 0.1 M	✓		✓

Direct Calibration Technique

Typical Direct Calibration Curve

In the direct calibration procedure, a calibration curve is constructed either in the meter memory or on semi-logarithmic 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 two standards are needed to determine a calibration curve. In non-linear regions, more points must be taken. These direct calibration procedures are given for concentrations in the region of linear electrode response. Low level measurement procedures are given in a following section for measurements in the non-linear electrode region.

Figure 2
Typical Direct Calibration Curve



Direct Calibration Overview

The following direct measurement procedures are recommended for moderate to high level measurements. Samples must be in the linear range of the electrode – greater than 1 ppm or 10^{-4} M chloride. A two point calibration is sufficient, although more points can be used. When using an ISE meter, sample concentrations can be read directly from the meter. When using a mV meter, a calibration curve can be prepared on semi-logarithmic graph paper, or a linear regression (against logarithmic concentration values) can be performed using a spreadsheet or graphing program.

Calibration Hints

- Standard concentrations should bracket the expected sample concentrations.
- For high ionic strength samples that have an ionic strength of 0.1 M or greater, prepare standards with a background composition similar to that of the samples, or measure the samples using the known addition method.
- During calibration, measure the least concentrated standard first, and work up to the most concentrated standard.

Direct Calibration Setup

1. Prepare the electrode as described in the **Electrode Preparation** section.
2. Connect the electrode to the 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. See the **Serial Dilution** section for instructions on how to prepare standards. All standards should be at the same temperature as the samples. For details on temperature effects on electrode performance, refer to the **Temperature Effects** section.

Direct Calibration Procedure Using a Meter with an ISE Mode

Note: See the meter user guide for more specific information.

1. Add 100 mL of the less concentrated standard to a 150 mL beaker and stir the solution thoroughly.
2. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the less concentrated standard. Wait for a stable reading and adjust the meter to display the value of the standard, as described in the meter user guide.
3. Add 100 mL of the more concentrated standard to a second 150 mL beaker and stir the solution thoroughly.
4. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the more concentrated standard. Wait for a stable reading and adjust the meter to display the value of the second standard, as described in the meter user guide.
5. Record the resulting slope value. The slope should be between 54 and 60 mV when the standards are between 20 and 25 °C.
6. Add 100 mL of sample to a clean 150 mL beaker and stir the solution thoroughly.
7. Rinse the electrode with distilled water, blot it dry and place it into the sample. The concentration of the sample will be displayed on the meter.

Direct Calibration Procedure Using a Meter with a mV Mode

Note: See the meter user guide for more specific information.

1. Set the meter to the mV mode.
2. Add 100 mL of the less concentrated standard to a 150 mL beaker and stir the solution thoroughly.
3. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the less concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
4. Add 100 mL of the more concentrated standard to a second 150 mL beaker and stir the solution thoroughly.
5. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the more concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
6. 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.
7. Add 100 mL of sample to a clean 150 mL beaker and stir the solution thoroughly.
8. Rinse the electrode with distilled water, blot it dry and place it 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 of the sample.

Low Level Calibration Technique

These procedures are for solutions that have a chloride concentration of less than 1 ppm or 10^{-4} M chloride. For solutions low in chloride but high in total ionic strength (greater than 10^{-1} M), perform the same procedure by preparing a calibrating solution with a composition similar to the sample.

Accurate results require that the following conditions be met:

- Prepare at least three calibration standards that bracket the expected sample concentration.
- Plastic labware is recommended for all low level chloride measurements.
- Adequate time must be allowed for electrode stabilization. Longer response time will be needed at low level measurements.
- Stir all standards and samples at a uniform rate.

Low Level Setup

1. Prepare the electrode as described in the **Electrode Preparation** section.
2. Connect the electrode to the meter. Set the meter to the mV mode.
3. Select a standard solution. Use either a 10 ppm or 10^{-3} M chloride standard.

Low Level Calibration and Measurement

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

Table 3
Calibration Curve For Low Level Calibrations

Additions of standard to 100 mL distilled water.

Step	Pipet Size	Volume Added	Concentration ppm	M
1	1 mL	0.1 mL	0.01	1.0×10^{-6}
2	1 mL	0.1 mL	0.02	2.0×10^{-6}
3	1 mL	0.2 mL	0.04	3.9×10^{-6}
4	1 mL	0.2 mL	0.06	6.0×10^{-6}
5	1 mL	0.4 mL	0.10	9.8×10^{-6}
6	2 mL	2.0 mL	0.29	2.9×10^{-5}
7	2 mL	2.0 mL	0.48	4.8×10^{-5}

Known Addition Technique

Known addition is a convenient technique for measuring samples in the linear range of the electrode (greater than 1 ppm or 10^{-4} M chloride) because no calibration curve is required. 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 results require 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.
- 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.
- With double or multiple known addition, the final addition should be 10 to 100 times the sample concentration.

Known Addition Setup

1. Prepare the electrode as described in the **Electrode Preparation** section.
2. Connect the electrode to the meter.
3. Prepare a standard solution that will cause the chloride concentration of the sample to double when added to the sample solution. Refer to **Table 4** for guidelines.
4. Determine the electrode slope by performing the procedure in the **Checking Electrode Operation (Slope)** section.
5. Rinse the electrode with distilled water.

Table 4
Guideline For Known Addition

Volume of Addition	Concentration of Standard
1 mL	100 times sample concentration
5 mL	20 times sample concentration
10 mL*	10 times sample concentration

* Most convenient volume to use

Known Addition Using a Meter with a Known Addition Mode

Note: See the meter user guide for more specific information.

1. Set the meter to measure in the known addition mode.
2. Measure 100 mL of the sample and pour the solution into a beaker. Rinse the electrode with distilled water and place it into the sample solution. Stir the solution thoroughly.
3. When a stable reading is displayed, set the meter as described in the meter user guide, if required.
4. Pipet the appropriate amount of the standard solution into the beaker. Stir the solution thoroughly.
5. When a stable reading is displayed, record the sample concentration.

Known Addition Using a Meter with a Millivolt Mode

1. Set the meter to the relative millivolt mode. If a relative millivolt mode is not available, use the millivolt mode.
2. Measure 100 mL of sample and pour the solution into a 150 mL beaker. Stir the solution thoroughly.
3. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker. When a stable reading is displayed, set the meter to read 0.0 mV. If the reading cannot be adjusted to 0.0 mV, record the actual mV value.
4. Pipet the appropriate amount of standard solution into the beaker. Stir the solution thoroughly.
5. When a stable reading is displayed, record the mV value. If the meter could not be set to 0.0 mV in step 3, subtract the first reading from the second reading to calculate ΔE .
6. Use **Table 6** to find the Q value that corresponds to the change in potential, ΔE . To determine the original sample concentration, multiply Q by the concentration of the added standard:

$$C_{\text{sample}} = Q * C_{\text{standard}}$$

C_{standard} = standard concentration

C_{sample} = sample concentration

Q = value from **Table 6**

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

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

Q = value from **Table 6**

$\Delta E = E_2 - E_1$

S = slope of the electrode

p = volume of standard / volume of sample

r = volume of sample / volume of sample

Calculating Known Addition for Samples using Lotus, Excel, or Quattro Spreadsheets

If it is more convenient, a simple spreadsheet can be set up to calculate the known addition results, using any ratio of sample to addition. A typical worksheet is shown in **Table 5**. The numbers shown are examples, but the formulas and their locations should be copied exactly.

Table 5
Known Addition Calculations using Lotus, Excel, or Quattro Spreadsheets

A	B	C
1		Enter Value
2	Volume of sample (mL)	100
3	Volume of addition (mL)	10
4	Concentration of addition	10
5	Volume of sample	100
6	Initial mV reading	45.3
7	Final mV reading	63.7
8	Electrode slope	58.2
9		
10		Derived Values
11	Delta E	+C7 - C6
12	Solution volume ratio	+C3/C2
13	Antilog term	+10 [^] (C11/C8)
14	Sample volume ratio	+C2/C5
15	Q term	+C12*C14/ (((1+C12)*C13)-1)
16	Calculated initial concentration in same units as addition	+C15*C4

Note: For Excel, use = instead of + at start of formulas.

Table 6**Q Values for a 10% volume change and 59 mV/decade slope**

ΔE	Q	ΔE	Q	ΔE	Q	ΔE	Q
5.0	0.297	10.0	0.160	20.0	0.0716	30.0	0.0394
5.1	0.293	10.2	0.157	20.2	0.0707	30.2	0.0390
5.2	0.288	10.4	0.154	20.4	0.0698	30.4	0.0386
5.3	0.284	10.6	0.151	20.6	0.0689	30.6	0.0382
5.4	0.280	10.8	0.148	20.8	0.0680	30.8	0.0378
5.5	0.276	11.0	0.145	21.0	0.0671	31.0	0.0374
5.6	0.272	11.2	0.143	21.2	0.0662	31.2	0.0370
5.7	0.268	11.4	0.140	21.4	0.0654	31.4	0.0366
5.8	0.264	11.6	0.137	21.6	0.0645	31.6	0.0362
5.9	0.260	11.8	0.135	21.8	0.0637	31.8	0.0358
6.0	0.257	12.0	0.133	22.0	0.0629	32.0	0.0354
6.1	0.253	12.2	0.130	22.2	0.0621	32.2	0.0351
6.2	0.250	12.4	0.128	22.4	0.0613	32.4	0.0347
6.3	0.247	12.6	0.126	22.6	0.0606	32.6	0.0343
6.4	0.243	12.8	0.123	22.8	0.0598	32.8	0.0340
6.5	0.240	13.0	0.121	23.0	0.0591	33.0	0.0336
6.6	0.237	13.2	0.119	23.2	0.0584	33.2	0.0333
6.7	0.234	13.4	0.117	23.4	0.0576	33.4	0.0329
6.8	0.231	13.6	0.115	23.6	0.0569	33.6	0.0326
6.9	0.228	13.8	0.113	23.8	0.0563	33.8	0.0323
7.0	0.225	14.0	0.112	24.0	0.0556	34.0	0.0319
7.1	0.222	14.2	0.110	24.2	0.0549	34.2	0.0316
7.2	0.219	14.4	0.108	24.4	0.0543	34.4	0.0313
7.3	0.217	14.6	0.106	24.6	0.0536	34.6	0.0310
7.4	0.214	14.8	0.105	24.8	0.0530	34.8	0.0307
7.5	0.212	15.0	0.103	25.0	0.0523	35.0	0.0304
7.6	0.209	15.2	0.1013	25.2	0.0517	36.0	0.0289
7.7	0.207	15.4	0.0997	25.4	0.0511	37.0	0.0275
7.8	0.204	15.6	0.0982	25.6	0.0505	38.0	0.0261
7.9	0.202	15.8	0.0967	25.8	0.0499	39.0	0.0249
8.0	0.199	16.0	0.0952	26.0	0.0494	40.0	0.0237
8.1	0.197	16.2	0.0938	26.2	0.0488	41.0	0.0226
8.2	0.195	16.4	0.0924	26.4	0.0482	42.0	0.0216
8.3	0.193	16.6	0.0910	26.6	0.0477	43.0	0.0206
8.4	0.190	16.8	0.0897	26.8	0.0471	44.0	0.0196
8.5	0.188	17.0	0.0884	27.0	0.0466	45.0	0.0187
8.6	0.186	17.2	0.0871	27.2	0.0461	46.0	0.0179
8.7	0.184	17.4	0.0858	27.4	0.0456	47.0	0.0171
8.8	0.182	17.6	0.0846	27.6	0.0450	48.0	0.0163
8.9	0.180	17.8	0.0834	27.8	0.0445	49.0	0.0156
9.0	0.178	18.0	0.0822	28.0	0.0440	50.0	0.0149
9.1	0.176	18.2	0.0811	28.2	0.0435	51.0	0.0143
9.2	0.174	18.4	0.0799	28.4	0.0431	52.0	0.0137
9.3	0.173	18.6	0.0788	28.6	0.0426	53.0	0.0131
9.4	0.171	18.8	0.0777	28.8	0.0421	54.0	0.0125
9.5	0.169	19.0	0.0767	29.0	0.0417	55.0	0.0120
9.6	0.167	19.2	0.0756	29.2	0.0412	56.0	0.0115
9.7	0.165	19.4	0.0746	29.4	0.0408	57.0	0.0110
9.8	0.164	19.6	0.0736	29.6	0.0403	58.0	0.0105
9.9	0.162	19.8	0.0726	29.8	0.0399	59.0	0.0101

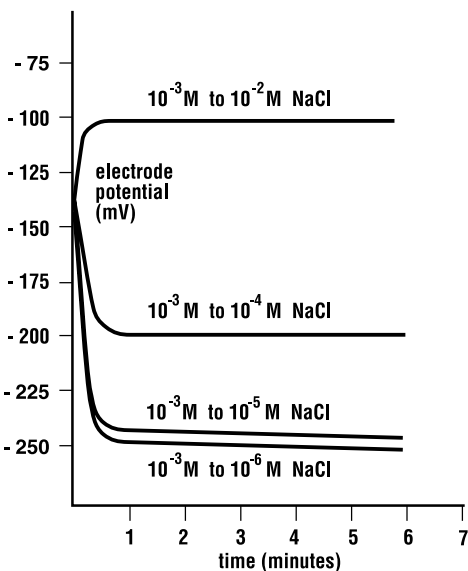
Electrode Characteristics

Electrode Response

The electrode potential plotted against concentration on semi-logarithmic paper results in a straight line with a slope of about 54 to 60 mV per decade change in concentration.

The time response of the electrode (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.

Figure 3
Typical Electrode Response to NaCl Concentration



Reproducibility

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

Limits of Detection

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

The lower limit of detection is determined by the slight water solubility of the ion exchanger, which causes deviation from theoretical response. **Figure 2** shows the theoretical response at low levels of chloride compared to the actual response. If chloride measurements are made below 10^{-4} M or 1 ppm, a low level measurement procedure is recommended.

Electrode Life

Each sensing module will last approximately six months with normal laboratory use, but the actual lifespan of the sensing module will depend on the type of samples that the electrode is used in. Refer to the **Electrode Maintenance** section for instructions on changing the sensing module. In time, the electrode slope will decrease and readings will start to drift, indicating that the module should be changed. Before replacement, refer to the **Troubleshooting** section to make sure that the difficulties are caused by the sensing module.

Temperature Effects

Since electrode potentials are affected by changes in temperature, samples and standard solutions should be within ± 1 °C (± 2 °F) of each other. At the 10^{-3} M level, a 1 °C difference in temperature results in errors greater than 2 %. 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 electrode also varies with temperature, as indicated by the factor S in the Nernst equation. Theoretical values of the slope at different temperatures are given in **Table 7**. If the temperature changes, the meter and electrode should be recalibrated.

The electrode can be used at temperatures from 0 to 40 °C, provided that temperature equilibrium has occurred. For use at temperatures substantially different from room temperature, calibration standards should be at the same temperature as samples.

Table 7
Theoretical Slope vs. Temperature Values

Temperature (°C)	Slope (mV)
0	54.20
10	56.18
20	58.16
25	59.16
30	60.15
40	62.13

Interferences

Some anions, if present at high enough levels, are electrode interferences and will cause measurement errors. **Table 8** indicates levels of common ions that will cause 10% errors at different concentrations of chloride.

If the electrode is exposed to high levels of interfering ions, it may drift and become sluggish in response. When this happens, restore normal performance by soaking the electrode for an hour in distilled water and then soaking the electrode for a few hours a 10^{-2} M or 100 ppm chloride standard. If soaking the electrode does not restore normal electrode performance, refer to the **Electrode Maintenance** section for instructions on how to replace the sensing module.

Table 8
Chloride Electrode Interferences

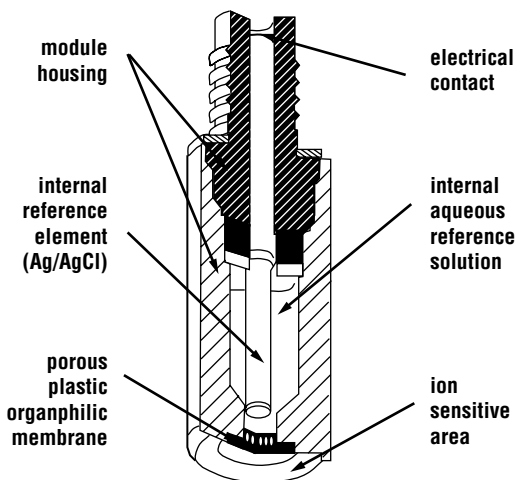
Interferences Moles/Liter	10^{-4} M Chloride	10^{-3} M Chloride	10^{-2} M Chloride
ClO_4^-	1.0×10^{-7}	1.0×10^{-6}	1.0×10^{-5}
I ⁻	5.0×10^{-6}	5.0×10^{-5}	5.0×10^{-4}
NO_3^-	5.0×10^{-6}	5.0×10^{-5}	5.0×10^{-4}
OH ⁻	1.0×10^{-5}	1.0×10^{-4}	1.0×10^{-3}
SO_4^-	2.0×10^{-5}	2.0×10^{-4}	2.0×10^{-3}
Br	1.0×10^{-4}	1.0×10^{-3}	1.0×10^{-2}
HCO_3^-	1.0×10^{-4}	1.0×10^{-3}	1.0×10^{-2}
OAC ⁻	3.0×10^{-4}	3.0×10^{-3}	3.0×10^{-2}
F ⁻	7.0×10^{-4}	7.0×10^{-3}	7.0×10^{-2}

Interferences ppm	1 ppm Chloride	10 ppm Chloride	100 ppm Chloride
ClO_4^-	3.0×10^{-3}	3.0×10^{-2}	0.3
I ⁻	0.2	1.8	18
NO_3^-	9.0×10^{-2}	0.9	9.0
OH ⁻	5.0×10^{-2}	0.5	5.0
SO_4^-	0.5	5.4	54
Br	2.2	23	225
HCO_3^-	1.7	17	170
OAC ⁻	5.0	50	500
F ⁻	3.8	38	375

Theory of Operation

The chloride electrode consists of a replaceable, pretested sensing module connected to an epoxy body. The sensing module contains a liquid internal filling solution in contact with a gelled organophilic membrane that contains a chloride selective ion exchanger.

Figure 4
Example of an Ion Sensing Module



When the module is in contact with a solution containing chloride ions, an electrode potential develops across the module. 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 ISE (concentration) meter. The measured potential corresponding to the level of chloride ion in solution is described by the Nernst equation.

$$E = E_o + S * \log (A)$$

E = measured electrode potential

E_o = reference potential (a constant)

A = chloride ion activity level in solution

S = electrode slope (about 56 mV per decade)

$$S = (2.3 RT) / nF$$

R and F are constants, T = temperature in degrees K and

n = ionic charge

The level of chloride ions, A , is the activity or “effective concentration” of free chloride ions 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. The ionic strength of a solution is determined by all of the ions present. It is calculated by multiplying the concentration of each individual ion by the square of its charge, adding all these values up and then dividing by two.

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

C_i = concentration of ion i

Z_i = charge of ion i

\sum symbolizes the sum of all the types of ions in solutions

If 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.

If samples have a high ionic strength (above 0.1 M), standards should be prepared with a composition similar to the samples.

Reference electrode conditions 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, 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 is the same when the reference is in the standardizing solution as well as in the same solution; otherwise, the change in liquid junction potential will appear as an error in the measured specific ion electrode potential.

The most important variable that 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 nearly as 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.

Troubleshooting

Follow a systematic procedure to isolate the problem. The measuring system can be divided into four components for ease in troubleshooting: meter, electrode, sample/application and technique.

Meter

The meter is the easiest component to eliminate as a possible cause of error. Thermo Scientific Orion meters include an instrument checkout procedure and shorting cap for convenience in troubleshooting. Consult the meter user guide for directions.

Electrode

1. Rinse the electrode thoroughly with distilled water.
2. Verify the electrode performance by performing the procedure in the **Checking Electrode Operation (Slope)** section.
3. If the electrode fails this procedure, review the **Measuring Hints** section. Clean the electrode thoroughly as directed in the **Electrode Maintenance** section. Drain and refill the reference electrode with fresh filling solution.
4. Repeat the procedure in the **Checking Electrode Operation (Slope)** section.
5. If the electrode fails this procedure again, 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 procedure in the **Checking Electrode Operation (Slope)** section.
6. If the electrode passes the procedure, but measurement problems persist, the sample may contain interferences or complexing agents, or the technique may be in error.
7. Before replacing a faulty electrode, review this user guide and be sure to thoroughly clean the electrode, correctly prepare the electrode, use the proper filling solution and standards, correctly measure the samples and review the **Troubleshooting Checklist** section.

Sample/Application

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! Errors 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 serial dilution. Refer to the **Serial Dilution** section. The electrode and meter may operate with standards, but not with the sample. In this case, check the sample composition for interferences, incompatibilities or temperature effects. Refer to the **Sample Requirements, Temperature Effects and Interferences** sections.

Technique

If trouble persists, review operating procedures. Review calibration and measurement sections to be sure proper technique has been followed. Verify that the expected concentration of the ion of interest is within the limit of detection of the electrode.

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 are present, known addition may be the best method. If working with low level samples, follow the procedure in the **Low Level Calibration Technique** section.

Assistance

After troubleshooting all components of your measurement system, contact Technical Support. Within the United States call 1.800.225.1480 and 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/contactwater.

For the latest application and technical resources for Thermo Scientific Orion products, visit www.thermo.com/waterapps.

Warranty

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

Troubleshooting Checklist

- No electrode filling solution added –
Fill the reference electrode with filling solution up to the fill hole. Refer to the **Electrode Preparation** section for details.
- Incorrect electrode filling solution used –
Refer to the **Electrode Preparation** section to verify that the correct electrode filling solution was used.
- Electrode junction is dry –
Push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.
- No reference electrode present –
The chloride half-cell electrode require a separate reference electrode, Cat. No. 900200.
- Electrode is clogged or dirty –
Refer to the **Electrode Maintenance** section for electrode cleaning and flushing instructions.
- Sensing module is not installed properly, dirty or defective –
Refer to the **Electrode Preparation** section and verify that the electrode was assembled correctly. Refer to the **Electrode Maintenance** section for instructions on installing a new sensing module.
- Standards are contaminated or made incorrectly –
Prepare fresh standards. Refer to the **Serial Dilution, Measurement Hints** and **Analytical Techniques** sections.
- Samples and standards at different temperatures –
Allow solutions to reach the same temperature.
- Air bubble on sensing module –
Remove air bubble by reimmersing the electrode in solution.
- Electrode not properly connected to meter –
Unplug and reconnect the electrode to the meter.
- Meter or stir plate not properly grounded –
Check the meter and stir plate for proper grounding.
- Static electricity present –
Wipe plastic parts on the meter with a detergent solution.
- Defective meter –
Check the meter performance. See the meter user guide.

Ordering Information

Cat. No.	Description
931701	93 series chloride sensing module
9300BNWP	Electrode body for the 93 series chloride sensing module, waterproof BNC connector
930000	Electrode body for the 93 series chloride sensing module, U.S. standard connector
9300SC	Electrode body for the 93 series chloride sensing module, screw cap connector
900200	Double junction reference electrode, pin tip connector
900002	Inner chamber filling solution for the double junction reference electrode, 5 x 60 mL bottles
941706	0.1 M NaCl chloride calibration standard
941708	1000 ppm chloride calibration standard
941707	100 ppm chloride calibration standard

Specifications

Concentration Range

5×10^{-6} M to 1 M (0.18 ppm to 35,000 ppm)

pH Range

3.5 to 9

Temperature Range

0 to 40 °C

Electrode Resistance

1 to 5 megohms

Reproducibility

± 2%

Size – Assembled Chloride Half-Cell Electrode

Body Diameter: 12 mm

Body Length: 110 mm

Cap Diameter: 16 mm

Cable Length: 1 meter

** Specifications are subject to change without notice*

Thermo Fisher Scientific

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Water Analysis Instruments



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