perfectION™ Guidebook

**perfectION™**

# Combination Chloride Electrode

Successful Ion Measurement


METTLER TOLEDO

Contents

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# 1. Introduction

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

**perfectION™ Combination Chloride Electrode**

The reference and sensing electrodes are built into one electrode, which decreases the amount of required solution and reduces waste. The built-in Click & Clear™ reference junction prevents clogging of the diaphragm and provides fast and stable readings.
The perfectION™ Combination Chloride Electrode is available with a BNC connector (P/N 51344706) and a Lemo connector (P/N 51344806) for METTLER TOLEDO titrators.

# 2. Required Equipment

1. METTLER TOLEDO ISE meter, such as the SevenMulti™ benchtop meter or the SevenGo pro™ portable meter, or a METTLER TOLEDO titrator, such as the Tx (T50, T70, T90) Excellence or G20 Compact titrators.

   METTLER TOLEDO combined ISEs can be used on any ISE meter with a BNC connection.
2. perfectION™ combined chloride ion selective electrode
3. Stirrer
4. Volumetric flasks, graduated cylinders, beakers and pipettes
5. Polishing strips to polish a dirty or etched sensing element.
6. Distilled or deionized water
7. Ion Electrolyte B Reference filling solution (P/N 51344751)
8. Chloride standard solution 1000 mg/L (P/N 51344772).
9. Ionic strength adjuster (ISA) for Solid State Ion Selective Electrodes (P/N 51344760). To adjust ionic strength of samples and standards.
10. Chloride oxidazing agent to remove interferences, see the **Use of Chloride oxidazing agent** section.

    ***Preparation note:***
    *Chloride oxidazing agent - Add 15 g of reagent-grade Sodium Bromate ($NaBrO_3$) to a 1000 mL volumetric flask. Add 950 mL of 1 mol/L Nitric Acid ($HNO_3$) and mix the solution thoroughly until the solids are dissolved.*

# 3. Electrode and Measurement Setup

## Electrode Preparation

Remove the protective shipping cap from the sensing element and save the cap for storage. Fill the electrode with Ion Electrolyte B Reference filling solution.

**Electrode Filling Instructions:**

1. Install the flip spout cap on the filling solution bottle and lift the flip spout on the bottle to a vertical position.
2. Insert the spout into the fill hole on the outer body of the electrode and add a small amount of filling solution to the reference chamber. Invert the electrode to moisten the O-ring and return the electrode to the upright position.
3. Hold the electrode body with one hand and use your thumb to push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.
4. Release the electrode cap. If the sleeve does not return to its original position, see if the O-ring is moist and repeat steps 2 through 4 until the sleeve returns to the original position.
5. Add filling solution to the electrode up to the filling hole.

***Note:*** *Add filling solution each day before using the electrode. The filling solution level should be at least 2.5 cm above the level of sample in the beaker to ensure a proper flow rate. The fill hole should always be open when taking measurements.*

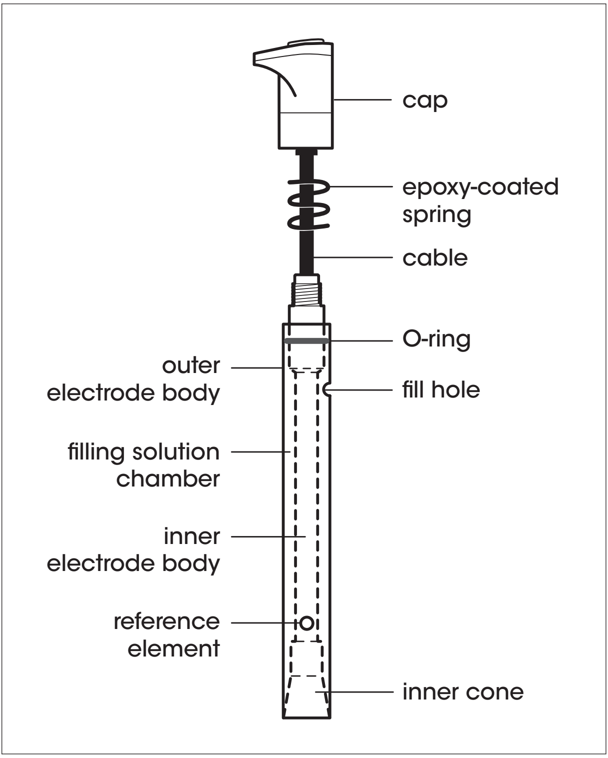


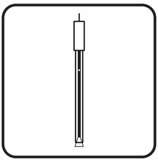

***Figure 1*** *– perfectION™ Chloride combination electrode*

# Checking Electrode Operation (Slope)

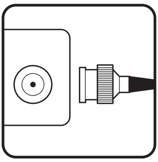
These are general instructions which can be used with most meters to check the electrode operation.

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

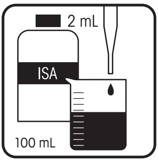
1. If the electrode has been stored dry, prepare the electrode as described in the **Electrode Preparation** section.



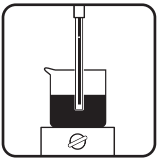
2. Connect the electrode to a meter with a mV mode. Set the meter to the mV mode.



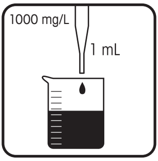
3. Place 100 mL distilled water in a 150 mL beaker and add 2 mL ISA. Stir the solution thoroughly.



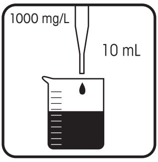

4. Rinse the electrode with distilled water and place the electrode into the solution prepared in step 3.



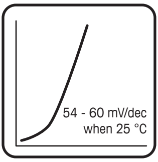
5. Select either 0.1 mol/L chloride standard or 1000 mg/L chloride standard. Pipette 1 mL of the selected standard into the beaker and stir the solution thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.



6. Pipette 10 mL of the same standard into the same beaker and stirr the solution 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 the **Troubleshooting** section.




## Sample Requirements

The epoxy body of the chloride electrode is resistant to damage by inorganic solutions. The electrode may be used intermittently in solutions containing methanol, benzene, or acetone.

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

## Measuring Hints

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*** *– Chloride Concentration Unit Conversion Factors*

| mol/L | mg/L $Cl^-$ | % NaCl |
|---|---|---|
| $10^{-1}$ | 3550 | 0.58% |
| $10^{-2}$ | 355 | 0.058% |
| $10^{-3}$ | 35.5 | 0.0058% |
| $10^{-4}$ | 3.55 | 0.00058% |

- Pipette 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.
- If electrode response is slow, the sensing element may be coated with deposits. Restore performance by polishing the electrode with a polishing strip. 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.
- Start the calibration or measurement with the lowest concentrated standard or sample.

# Electrode Storage and Maintenance

## Electrode Storage

The solution in the chloride combination electrode 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 mol/L 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.

## Disassembly and Cleaning

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 filling solution.

***Note:*** *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 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.

## 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 100 mg/L chloride standard** – Pipette 10 mL of the 1000 mg/L standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.
2. **To prepare a 10 mg/L standard** – Pipette 10 mL of the 100 mg/L standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.
3. **To prepare a 1 mg/L standard** – Pipette 10 mL of the 10 mg/L 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 1 mg/L chloride standard from a 100 mg/L chloride standard:

$C_1$ = 100 mg/L chloride
$V_1$ = unknown
$C_2$ = 1 mg/L chloride
$V_2$ = 100 mL
100 mg/L * $V_1$ = 1 mg/L * 100 mL
$V_1$ = (1 mg/L * 100 mL) / 100 mg/L = 1 mL

To prepare the 1 mg/L chloride standard, pipette 1 mL of the 100 mg/L chloride standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

# 4. Analytical Techniques

A variety of analytical techniques is 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 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** provide a useful method for measuring samples, since 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 (50-100 times) excess of complexing agents. As in direct calibration, any convenient concentration unit can be used.

- **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 electrode(s) 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.

- **Analyte 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 electrode(s) 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.
- **Analyte Subtraction** is used in the measurement of ions for which no ion-selective electrode exists. The electrode(s) are immersed in a reagent solution that 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.

**Titrations** are quantitative analytical techniques 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

## Chloride Combination Electrode Setup

1. Remove the rubber cap covering the electrode tip.
2. Fill the electrode according to instructions in the **Electrode Preparation** section.
3. Connect electrode to the meter.
4. Prepare two standards that bracket the expected sample range and differ in concentration by a factor of ten. Standards can be prepared in any concentration unit to suit the particular analysis requirement. All standards should be at the same temperature as the samples (for details on temperature effects on electrode performance, refer to **Temperature Effects**).

**If using a meter with direct concentration readout capability**
See the meter user guide 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 electrode 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 user guide.
3. Measure 100 mL of the more concentrated standard into a second 150 mL beaker. Add 2 mL ISA. Stir thoroughly.
4. Rinse electrode 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 user guide.
5. Measure 100 mL of the sample into a 150 mL beaker. Add 2 mL ISA. Stir thoroughly. Rinse electrode with distilled water, blot dry and place into sample. The concentration will be displayed on the meter.

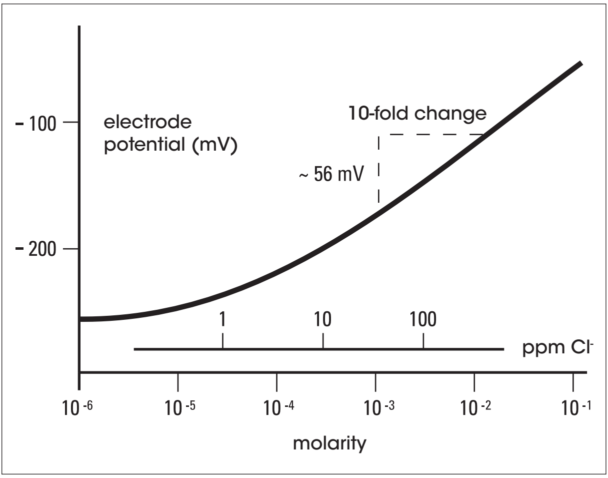



***Figure 2*** *– Typical Chloride Electrode Calibration Curve*

In the direct calibration procedure, a calibration curve is constructed 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 three standards are needed to determine a calibration curve. In non-linear regions, more points must be taken. The direct measurement procedures in the user guide 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 electrode 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 electrode 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 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. Measure 100 mL of sample into a 150 mL beaker. Add 2 mL ISA. Stir thoroughly.
8. Rinse electrode with deionized water, blot dry, and place into the beaker. When a stable reading is displayed, record the mV value.
9. Use the calibration curve prepared in step 6 in order to determine the unknown concentration.

## Low-Level Measurement

These procedures are for low ionic strength solutions with a chloride concentration of less than $10^{-4}$ mol/L. 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.

### Setup

1. Remove the plastic cap covering the electrode tip.
2. Fill electrode with selected filling solution.
   See instructions in the **Electrode Preparation** section.
3. Connect the electrodes to the meter. Set the meter to read mV.
4. Use 1000mg/L or $10^{-2}$ mol/L chloride standard solution.
5. Prepare a low-level ISA solution (1.0 mol/L $NaNO_3$) by diluting 20 mL of ISA 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 with deionized water and place into beaker. Stir thoroughly.
3. Add increments of the 1000 mg/L or $10^{-2}$ mol/L chloride standard to the beaker using steps outlined in **Table 2**. Record stable millivolt reading after each increment. On semi-logarithmic 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 electrode 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 mg/L or 10 -2 mol/L standards to 100 mL distilled water, plus 1 mL low-level ISA*

| Step | Graduated Pipette Size | Added Volume | Concentration mg/L | Molarity |
|---|---|---|---|---|
| **1** | 1 mL | 0.1 mL | 1.0 | $1.0 \times 10^{-5}$ |
| **2** | 1 mL | 0.1 mL | 2.0 | $2.0 \times 10^{-5}$ |
| **3** | 1 mL | 0.2 mL | 4.0 | $4.0 \times 10^{-5}$ |
| **4** | 1 mL | 0.2 mL | 6.0 | $6.0 \times 10^{-5}$ |
| **5** | 1 mL | 0.4 mL | 9.9 | $9.9 \times 10^{-5}$ |
| **6** | 2 mL | 2.0 mL | 29 | $2.9 \times 10^{-4}$ |
| **7** | 2 mL | 2.0 mL | 48 | $4.8 \times 10^{-4}$ |

## 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.

## Setup

1. Remove the plastic cap covering the electrode tip.
2. Fill electrode with selected filling solution.
   See instructions in the **Electrode Preparation** section.
3. Connect the electrode 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 in **Checking Electrode Operation (Slope)**.
6. Rinse electrode 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 the meter user guide 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 electrode with distilled water and place in sample solution. Add 2 mL ISA. Stir thoroughly.
3. When a stable reading is displayed, set the meter as described in the meter user guide.
4. Pipette 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 user guide.

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 electrode with distilled water, blot dry, and place into beaker. When a stable reading is displayed, record the mV value.
4. Pipette the appropriate amount of standard solution into the beaker. Stir thoroughly.
5. When a stable reading is displayed, record the mV value. Subtract the first reading from the second to find $\Delta E$.
6. From **Table 4**, find the value, Q, that corresponds to the change in potential, $\Delta E$. To determine the original sample concentration, multiply Q by the concentration of the added standard:

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

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.

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

where:

Q = reading from known addition table
$\Delta E = E_2 - E_1$
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** | **Q 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 | Q1 Concentration Ratio | | | |
|---|---|---|---|---|
| **Monovalent** | **(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 | Q1 Concentration Ratio | | | |
|---|---|---|---|---|
| **Monovalent** | **(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 |

# 5. Electrode Characteristics

## Electrode Response

The electrode potential plotted against concentration on semi-logarithmic paper results in a straight line with a slope of about 54-60 mV per decade. See **Figure 2**.

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 3**.

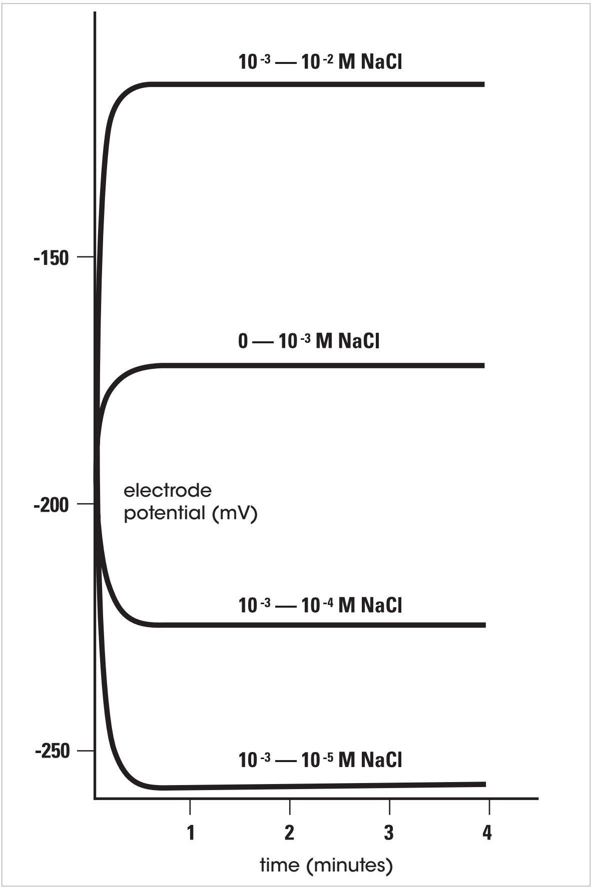



***Figure 3*** *– Typical Electrode Response to Step Changes in NaCl*

## 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 ± 2% can be obtained.

## 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 $10^{-3}$ mol/L level, a 1 °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 0-80 °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 °C.

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

| T °C | S | T °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 $Cu^{2+}$, $Fe^{3+}$, 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 mg/L, see **Table 1** in section **Measuring Hints**.

***Table 6*** *– Maximum Allowable Ratio of Interfering Ion to Chloride*

| Interference | Maximum Allowable Ratio Interference Chloride |
|---|---|
| (a) $OH^-$ | 80 |
| (b) $Br^-$ | $3 \times 10^{-3}$ |
| (b) $I^-$ | $5 \times 10^{-7}$ |
| (c) $S^{2-}$ | $10^{-6}$ |
| (c) $CN^-$ | $2 \times 10^{-7}$ |
| (d) $NH_3$ | 0.12 |
| (d) $S_2O_3^{2-}$ | 0.01 |

(a) Hydroxide interference can be removed by acidifying to pH 4 with 1 mol/L $HNO_3$.

(b) Mixed halides in solution can be measured using Chloride oxidazing agent to remove interferences or by a Gran's Plot titration. A procedure for using Chloride oxidazing agent can be found below.

(c) Sulfide and cyanide may be removed by adding a nickel (+2) solution or by using Chloride oxidazing agent.

(d) Represents a complexing species. Maximum level can be exceeded without electrode damage. Value shown is for 1% error.

## Use of Chloride oxidazing agent

Interferences to the chloride measurement may be minimized by addition of Chloride oxidazing agent, that 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.

**Chloride oxidazing agent**

***Preparation note:***
*Chloride oxidazing agent - Add 15 g of reagent-grade Sodium Bromate ($NaBrO_3$) to a 1000 mL volumetric flask. Add 950 mL of 1 mol/L Nitric Acid ($HNO_3$) and mix the solution thoroughly until the solids are dissolved.*

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

## 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 $10^{-4}$ mol/L 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 $10^{-4}$ mol/L Chloride*

| | |
|---|---|
| $Bi^{3+}$ | $4 \times 10^{-4}$ mol/L (80 mg/L) |
| $Cd^{2+}$ | $2 \times 10^{-3}$ mol/L (200 mg/L) |
| $Mn^{2+}$ | $2 \times 10^{-2}$ mol/L (1100 mg/L) |
| $Pb^{2+}$ | $2 \times 10^{-3}$ mol/L (400 mg/L) |
| $Sn^{2+}$ | $6 \times 10^{-3}$ mol/L (700 mg/L) |
| $Tl^{3+}$ | $4 \times 10^{-5}$ mol/L (8 mg/L) |

# 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:

$$\mathbf{E = E_0 + S \log (A)}$$

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, g:

$$\mathbf{A = g\, C_f}$$

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

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

where:
$C_i$ = concentration of ion i
$Z_i$ = charge of ion i
and ∑ 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 the 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 mol/L), 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 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 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.

# 6. Troubleshooting

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

**Meter/Titrator**

The meter/titrator is the easiest component to eliminate as a possible cause of error. Consult the meter/titrator user guide for complete instructions and verify that the instrument operates as indicated and is stable in all steps.

**Electrode**

1. Rinse electrode thoroughly with distilled water.
2. Perform the procedure in the **Checking Electrode Operation (Slope)** section.
3. If electrode fails this procedure, polish the chloride electrode as directed in **Measuring Hints**.
4. Repeat the procedure in the **Checking Electrode Operation (Slope**) section.
5. 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.
6. Before replacing a faulty electrode, or if another electrode is not available for test purposes, review the user guide 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, analyte 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 user guides to be sure that proper technique has been followed. Reread **Measuring Hints** and **Analytical Techniques**.

# Troubleshooting Checklist

| Symptom | Possible Causes |
| --- | --- |
| Off-scale or Over-range reading | Defective meter/titrator<br>Electrodes not plugged in properly |
| | Electrode not filled |
| | Air bubble on element |
| | Electrode not in solution |
| | Static electricity |
| Noisy or unstable readings (readings continuously or rapidly changing) | Defective meter/titrator |
| | Meter/Titrator or stirrer improperly grounded |
| | Air bubble on sensing element |
| | 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 |
| | 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 |
|---|
| See meter/titrator user guide<br>Unplug electrode and reset |
| Be sure the electrode is filled with the correct reference filling solution |
| Remove bubble by redipping electrode in solution |
| Put electrode in solution |
| Wipe plastic parts of meter/titrator with detergent solution |
| See meter/titrator user guide |
| Check meter/titrator and stirrer for grounding |
| Remove bubble by redipping electrode in solution |
| Use recommended ISA |
| Allow solutions to come to the room temperature before measurement |
| Polish sensing element (see **Measuring Hints**) |
| Use recommended reference filling solutions |
| Prepare fresh standards |
| Use recommended 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: $10^{-3}$ mol/L = 35.5 mg/L as $Cl^-$ |
| Use known addition or titration techniques, or a decomplexing procedure |
| Remove by using Chloride oxidazing agent (See **Use of Chloride oxidazing agent**) |

# 7. Ordering Information

| Parts | Order No. |
|---|---|
| Combined Chloride electrode with BNC connector perfectION™ comb $Cl^-$: | **51344706** |
| Combined Chloride electrode with Lemo connector perfectION™ comb $Cl^-$ Lemo: | **51344806** |
| Ion Electrolyte B: | **51344751** |
| Chloride Standard Solution 1000 mg/L: | **51344772** |
| ISA solid state ISE: | **51344760** |
| Removable cone: | **00022986** |

# 8. Electrode Specifications

**Membrane type**

solid state

**Concentration Range**

1 mol/L to 5 x 10-5 mol/L
35'500 to 1.8 mg/L

**pH Range**

pH 2 to 12

**Temperature Range**

0 to 80°C

**Electrode Resistance**

Less than 1 MΩ

**Reproducibility**

± 2%

**Minimum Sample Size**

3 mL in a 50 mL beaker

**Size**

| | |
|---|---|
| Electrode Length: | 110 mm |
| Diameter: | 13 mm |
| Cap Diameter: | 16 mm |
| Cable Length: | 1.2 m |

* Specifications subject to change without notice.

**www.mt.com**
For more information

**Mettler-Toledo AG**
Analytical
Sonnenbergstrasse 74
CH-8603 Schwerzenbach
Switzerland
Phone ++41 (0)44 806 77 11
Fax ++41 (0)44 806 73 50
Internet: www.mt.com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