Chloride and Salinity

INTRODUCTION

Chloride

Chloride, in the form of the Cl^- ion, is one of the major inorganic *anions*, or negative ions, in saltwater and freshwater. It originates from the dissociation of salts, such as sodium chloride or calcium chloride, in water.

$$NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq)$$

$$CaCl_2(s) \longrightarrow Ca^{2+}(aq) + 2\ Cl^-(aq)$$

These salts, and their resulting chloride ions, originate from natural minerals, saltwater intrusion into estuaries, and industrial pollution.

Sources of Chloride Ions

- River streambeds with salt-containing minerals
- Runoff from salted roads
- Irrigation water returned to streams
- Mixing of seawater with freshwater
- Chlorinated drinking water
- Water softener regeneration

There are many possible sources of manmade salts that may contribute to elevated chloride readings. Sodium chloride and calcium chloride, used to salt roads, contribute to elevated chloride levels in streams. Chlorinated drinking water and sodium-chloride water softeners often increase chloride levels in wastewater of a community.

In drinking water, the salty taste produced by chloride depends upon the concentration of the chloride ion. Water containing 250 mg/L of chloride may have a detectable salty taste if the chloride came from sodium chloride. The recommended maximum level of chloride in U.S. drinking water is 250 mg/L.

Salinity

Salinity is the total of all non-carbonate salts dissolved in water, usually expressed in parts per thousand (1 ppt = 1000 mg/L). Unlike chloride (Cl^-) concentration, you can think of salinity as a measure of the *total* salt concentration, comprised mostly of Na^+ *and* Cl^- ions. Even though there are smaller quantities of other ions in seawater (e.g., K^+, Mg^{2+}, or SO_4^{2-}), sodium and chloride ions represent about 91% of all seawater ions. Salinity is an important measurement in seawater or in estuaries where freshwater from rivers and streams mixes with salty ocean water. The salinity level in seawater is fairly constant, at about 35 ppt (35,000 mg/L), while brackish estuaries may have salinity levels between 1 and 10 ppt. Since most anions in seawater or brackish water are chloride ions, salinity can be determined from chloride concentration. The following formula is used:

$$\text{salinity (ppt)} = 0.0018066\,5\ Cl^-\ \text{(mg/L)}$$

A Chloride Ion-Selective Electrode can be used to determine the chloride concentration, which is converted to a salinity value using the above formula.

Salinity can also be measured in freshwater. Compared to seawater or brackish water, freshwater has much lower levels of “salt ions” such as Na^+ and Cl^-; in fact, these ions are often lower in concentration than hard-water ions such calcium (Ca^{2+}) and bicarbonate (HCO_3^-). Because salinity readings in freshwater will be significantly lower than in seawater or brackish water, readings are often expressed in mg/L instead of ppt (1 ppt = 1000 mg/L).

Increased salinity levels have been observed in the lower reaches of the Colorado and Rio Grande rivers, due to return of irrigation water (see Table 1). In these arid regions of the United States, water readily evaporates during irrigation, resulting in high concentrations of salt ions in the water returned to the rivers. Salinity is also of interest in bodies of water where seawater mixes with freshwater, since aquatic organisms have varying abilities to survive and thrive at different salinity levels. Saltwater organisms survive in salinity levels up to 40 ppt, yet many freshwater organisms cannot live in salinity levels above 1 ppt.

Expected Levels

Seawater has a chloride ion concentration of about 19,400 mg/L (a salinity of 35.0 ppt). Brackish water in tidal estuaries may have chloride levels between 500 and 5,000 mg/L (salinity of 1 to 10 ppt). Even freshwater streams and lakes have a significant chloride level that can range from 1 to 250 mg/L (salinity of 0.001 to 0.5 ppt).

Table 1: Chloride and Salinity in Selected Sites

Site (fall season)	Chloride (mg/L)	Salinity (mg/L)	Salinity (ppt)
Columbia River, Newport, WA	1.3	2.3	0.0023
Mississippi River, Memphis, TN	14.1	25.5	0.025
Rio Grande River, San Marcial, NM	56	101	0.101
Rio Grande River, Brownsville, TX	220	397	0.397
Colorado River, State Line, CO-UT	67	121	0.121
Colorado River, Andrade, CA	190	343	0.343

Summary of Methods

Method 1: Chloride Concentration and Salinity (ISE)

A Vernier Chloride Ion-Selective Electrode is used to measure the chloride ion concentration in the water (in mg/L) either on site or after returning to the lab. Salinity can be determined using the relationship, salinity (ppt) = 0.0018066 5 Cl^- (mg/L).

Method 2: Salinity Using a Conductivity Probe (Seawater or Brackish Water)

A Vernier Conductivity Probe is used to measure the salinity value of the water (in ppt). If salinity values exceed 13 ppt, dilution of samples, as described in the procedure, will be necessary. This method uses the assumption that most of the ions in the solution are non-carbonate salt ions (e.g., Na^+, K^+, or Cl^-), and converts the conductivity reading to a salinity value.

Method 1: CHLORIDE CONCENTRATION AND SALINITY (ISE)

Materials Checklist

___ Power Macintosh or Windows PC

___ Vernier computer interface

___ Logger *Pro*

___ Chloride Ion-Selective Electrode

___ wash bottle with distilled water

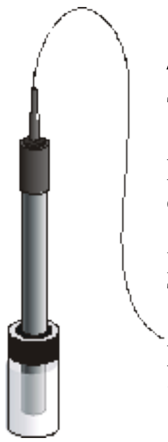
___ Low Standard (10 mg/L Cl^-)

___ High Standard (1000 mg/L Cl^-)

___ Very High Standard (20,000 mg/L Cl^-)

___ tissues

___ small paper or plastic cup (optional)



ISE soaking for travel

Advanced Preparation

The Vernier Chloride Ion-Selective Electrode (ISE) must be soaked in the Chloride High Standard solution (included with the ISE) for approximately 30 minutes. **Important:** Make sure the electrode is not resting on the bottom, and that the small white reference contacts are immersed. Make sure no air bubbles are trapped below the electrode.

If the ISE needs to be transported to the field during the soaking process, use the Short-Term ISE Soaking Bottle. Remove the cap from the bottle and fill it ¾ full with High Standard. Slide the bottle's cap onto the ISE, insert it into the bottle, and tighten. **Important:** Do not leave the ISE soaking for more than 24 hours. Long-term storage should be in the Long-Term ISE Storage Bottle.

Collection and Storage of Samples

1. This test can be conducted on site or in the lab. A 100-mL water sample is required.
2. It is important to obtain the water sample from below the surface of the water and as far away from shore as is safe. If suitable areas of the stream appear to be unreachable, samplers consisting of a rod and container can be constructed for collection. Refer to page Intro-4 of the Introduction of this book for more details.

Testing Procedure

1. Position the computer safely away from the water. Keep water away from the computer at all times.
2. Prepare the computer for data collection by opening "Test 15 Chloride ISE" from the *Water Quality with Computers* experiment files of Logger*Pro*. On the Graph window, the vertical axis has chloride concentration scaled from 0 to 20000 mg/L Cl^-. The horizontal axis has time scaled from 0 to 10 seconds. There is also a Meter window which displays live chloride concentration readings.
3. Prepare the Chloride Ion-Selective Electrode (ISE) for data collection.
   a. The ISE should be soaking in the High Standard. Make sure that it is not resting on the bottom of the container, and that the small white reference contacts are immersed.
   b. Plug the ISE Sensor into Channel 1 of the Vernier interface.
4. You are now ready to calibrate the Calcium ISE.

   First Calibration Point

   a. Choose Calibrate from the Experiment menu and then click .
   b. Type "1000" (the concentration in mg/L Cl^-) in the edit box.
   c. When the displayed voltage reading for Input 1 stabilizes, click .

Second Calibration Point

d. If you are testing a **freshwater** sample, place the tip of the electrode into the Low Standard (10 mg/L Cl^-). If you are testing a **seawater-** or **brackish-water** sample, place the tip of the electrode into the Very High Standard (20,000 mg/L Cl^-). Be sure that the electrode is not resting on the bottom of the bottle and that the small white reference contacts are immersed. Make sure no air bubbles are trapped below the electrode.

e. After briefly swirling the solution, hold the ISE still and wait approximately 30 seconds for the voltage reading displayed on the computer screen to stabilize.

f. Enter "10" (the concentration of the Low Standard) or "20,000" (the concentration of the Very High Standard), depending on which one you used.

g. When the displayed voltage reading for Input 1 stabilizes, click Keep, then click OK.

5. You are now ready to collect chloride concentration data.

   a. Rinse the ISE with distilled water and gently blot it dry.

   b. Place the tip of the probe into the stream at Site 1, or into a cup with sample water from the stream. Make sure the ISE is not resting on the bottom and that the small white reference contacts are immersed. Make sure that no air bubbles are trapped below the ISE.

   c. After briefly swirling the solution, hold the ISE still and wait approximately 30 seconds.

   d. If the chloride concentration value appears stable, simply record it on the Data & Calculations sheet and proceed to Step 7.

6. If the chloride concentration value displayed in the Meter window is fluctuating, determine the *mean* (or average) value. To do this:

   a. Click Collect to begin a 10-second sampling run. **Important:** Leave the probe tip submerged for the 10 seconds that data is being collected.

   b. When the sampling run is complete, click on the Statistics button, , to display the statistics box on the graph.

   c. Record the mean chloride concentration value on the Data & Calculations sheet.

7. Return to Step 5 to obtain a second reading.

8. Determine the salinity value of your sample (in ppt). Use this formula to calculate the salinity, based on the chloride concentration, Cl^-

$$\text{salinity (ppt)} = 0.0018066 \; 5 \; Cl^- \text{ (mg/L)}$$

   Record this value in the Data & Calculations table (round to the nearest 0.1 mg/L Cl^-).

DATA & CALCULATIONS

Method 1: Chloride Concentration and Salinity (ISE)

Stream or lake: ______________________________ Time of day: ______________________________

Site name: ______________________________ Student name: ______________________________

Site number: ______________________________ Student name: ______________________________

Date: ______________________________________ Student name: ___________________________

Column	A	B
Reading	Chloride (mg/L Cl^-)	Salinity (ppt)
1		
2		
Average		

Column Procedure:

A. Record the chloride concentration value (in mg/L Cl^-) from the computer.
B. Calculate salinity, using the formula:

salinity (ppt) = 0.0018066 5 Cl^- (mg/L).

Field Observations (e.g., weather, geography, vegetation along stream)_____________________________

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Test Completed: _______________ Date: ______

Method 2: SALINITY USING A CONDUCTIVITY PROBE

Materials Checklist

___ Power Macintosh or Windows PC
___ Vernier computer interface
___ Logger *Pro*
___ Vernier Conductivity Probe
___ 100-mL graduated cylinder
___ 500-mL bottle with lid
___ wash bottle with distilled water
___ tissues or paper towels
___ 5 ppt salinity standard
___ 10 ppt salinity standard
___ small paper or plastic cup (optional)

Collection and Storage of Samples

1. This test can be conducted on site or in the lab. A 100-mL water sample is required.

2. It is important to obtain the water sample from below the surface of the water and as far away from shore as is safe. If suitable areas of the stream appear to be unreachable, samplers consisting of a rod and container can be constructed for collection. Refer to page Intro-4 of the Introduction of this book for more details.

Testing Procedure

1. Position the computer safely away from the water. Keep water away from the computer at all times.

2. Prepare the computer for data collection by opening "Test 15 Salinity Conductivity" from the *Water Quality with Computers* experiment files of Logger*Pro*. On the Graph window, the vertical axis has salinity concentration scaled from 0 to 13 ppt. The horizontal axis has time scaled from 0 to 10 seconds. There is also a Meter window which displays live chloride concentration readings.

3. Prepare the Conductivity Probe for data collection.
   a. Plug the Conductivity Probe into Channel 1 of the Vernier interface.
   b. Set the switch on the probe box to the 0-20000 µS range (0-13 ppt salinity).

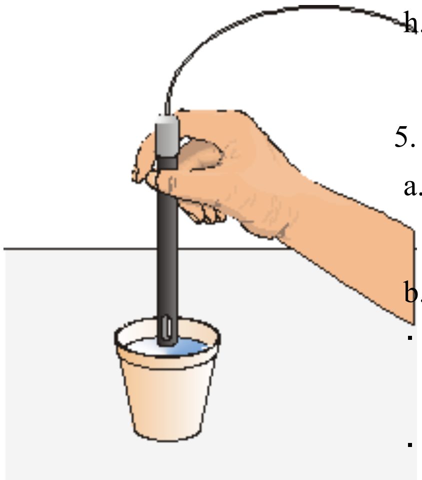
4. You are now ready to calibrate the Conductivity Probe.
   - If your instructor directs you to use the calibration stored in the experiment file, then proceed to Step 5.
   - If your instructor directs you to perform a new calibration for the Conductivity Probe, follow this procedure:

   First Calibration Point

   a. Choose Calibrate from the Experiment menu and then click Perform Now.
   b. Perform the first calibration point by placing the Conductivity Probe into the 5 ppt salinity standard. The hole near the tip of the probe should be covered completely.
   c. Type "5" (the salinity value) in the edit box.
   d. When the displayed voltage reading for Input 1 stabilizes, click Keep.

   Second Calibration Point

   e. Place the Conductivity Probe into the 10 ppt salinity standard solution. The hole near the tip of the probe should be covered completely.
   f. Type "10" (the salinity value) in the edit box.
   g. When the displayed voltage reading for Input 1 stabilizes, click Keep, then click OK.



h. Rinse the electrode with distilled water and gently blot it dry with a tissue.

5. You are now ready to collect salinity concentration data.
   a. Place the tip of the electrode into a cup with sample water from the body of water you are testing. The hole near the tip of the probe should be covered completely.
   b. Monitor the salinity concentration value in the Meter window.
      - If the value is less than 13 ppt (the upper range of the Conductivity Probe), record this value on the Data & Calculations sheet. If you did a ¼ dilution of the sample, be sure to multiply this value by 4!
      - If the salinity value is greater than 13 ppt, go to Step 7.

6. Repeat Step 5 to obtain a second reading.

7. If your salinity value is greater than 13 ppt, then the sample had a salinity value that is beyond the upper range of the Conductivity Probe. You will need to dilute the sample to a salinity value that is within the range of the probe. To do this,
   a. Use a graduated cylinder to add 100 mL of the water sample to a 500-mL bottle.
   b. Add 300 mL of distilled water to the sample in the bottle, screw the lid on, and shake it well.
   c. **Important:** The sample has been diluted by a factor of 100/400 or ¼. Any salinity measurements made on this sample will have to be multiplied by a factor of 4 to account for this dilution.
   d. Repeat Step 5 to obtain a second reading.

DATA & CALCULATIONS

Method 2: Salinity Using a Conductivity Probe

Stream or lake: ______________________ Time of day: ______________________

Site name: ______________________ Student name: ______________________

Site number: ______________________ Student name: ______________________

Date: ______________________ Student name: ______________________

Column	A
Reading	Salinity (ppt)
1	
2	

Average	

Column Procedure:

A. Record the salinity concentration as determined by interpolation of the calibration curve.

Field Observations (e.g., weather, geography, vegetation along stream)______________________________

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Test Completed: ________________ Date: ______