**WATER QUALITY**

**Introduction**

Chloride content in water can be an indication of the human impact on local water supplies. Chloride (Cl\(^-\)) can be found naturally in water supplies (lakes, streams, rivers, etc.) but it is also present in sewage. If a water supply normally contains little chloride, then the presence of higher levels can be an indication of human activity (pollution, recreational activity, land development, etc.). The purpose of this lab is to analyze water samples from the area around Clemson and determine the extent of human activity based on the chloride content. There are several lakes and rivers, and many streams in the Clemson area. Choose a place to obtain a water sample. If you suspect human activity, consider taking several samples (possibly above and below the point of activity) for comparison purposes. Another source of a sample could be a waste water treatment plant. Maps will be available in lab. Using a sticky note, mark on the map where you take your water sample. At the end of lab, the class will review the results of the lab section and reach some conclusions concerning the human impact on the area water supplies.

Remember that chloride (Cl\(^-\)) is not the same as chlorine (Cl\(_2\)). Chlorine is used in small quantities (< 1ppm) to disinfect public water supplies and treat swimming pools (< 5ppm). Although chlorine does produce some chloride, it will be negligible.

Chloride will react with silver ions (Ag\(^+\)) to form an insoluble salt silver chloride (AgCl). Silver nitrate (AgNO\(_3\)) can be used as a soluble source of silver ions.

\[
\text{Cl}^- + \text{AgNO}_3(aq) \rightarrow \text{AgCl(s)} + \text{NO}_3^-(aq)
\]

We will use this reaction to determine the Cl\(^-\) in the collected water samples using a procedure called titration. Refer to SuperChem Lab to understand the basic principles of titration. To a known volume of your water sample, AgNO\(_3\) will slowly be added until just enough has been added to react with all the Cl\(^-\) present in the water sample. During this process, the solution will turn milky due to the formation of the AgCl precipitate. Once all the Cl\(^-\) has reacted, if more AgNO\(_3\) is added, an excess of Ag\(^+\) will be present. An indicator will be used to determine this point when excess Ag\(^+\) is present. Sodium chromate (Na\(_2\)CrO\(_4\)) will be the indicator for this titration. Once all the Cl\(^-\) has reacted with the added Ag\(^+\), the excess Ag\(^+\) will then react with the chromate (CrO\(_4^{2-}\)) which will result in a color change due to the formation of silver chromate (Ag\(_2\)CrO\(_4\)) which is a red precipitate.

\[
2\text{Ag}^+(aq) + \text{CrO}_4^{2-}(aq) \rightarrow \text{Ag}_2\text{CrO}_4(s)
\]

yellow solution \red precipitate
The point when one drop of the $\text{AgNO}_3$ causes the red precipitate to form indicates that enough $\text{AgNO}_3$ has been added to the water sample to react with all the $\text{Cl}^-$. This is referred to as the **endpoint**.

The endpoint for this titration is not dramatic in its color change. It is very gradual and subtle. Therefore some practice will be necessary first to become familiar with the process before the actual water samples are tested.

Knowing the volume of water sample initially used, and the volume and concentration of the $\text{AgNO}_3$ used, the concentration of $\text{Cl}^-$ can be calculated. Concentrations are usually expressed in molarity ($\text{M}$) which is defined as the number of moles of substance dissolved in 1 liter of solution. Concentration in small amounts is often recorded in parts per million (ppm) which can defined as the milligrams per liter of solution.

A titration depends on the accurate measurement of volumes. In this experiment, a bereal pipet will be used to deliver small quantities of water sample and $\text{AgNO}_3$ solution. The pipet will deliver drops of uniform size if the pipet is held in a consistent manner. In this case quantities can then be measured in number of drops. If the molarity ($\text{M}$) of the $\text{AgNO}_3$ is known, then the molarity of $\text{Cl}^-$ can be determined knowing the number of drops of water sample and $\text{AgNO}_3$ solution used. (See explanation in Part V.)

**Procedure**

**I. Water Collection**

Decide where you plan to collect your water sample. Use a suitable container which is clean and dry. Label the container with the exact location of the collection point. If you suspect human activity, collect several samples at various locations. For example if you are collecting near an industrial site on a stream collect 3 samples for comparison purposes: 1) where the site and stream connect, 2) upstream, and 3) downstream. The same can be applied on a lake or pond. Collect samples near suspected human activity and where you suspect no activity.

Using a sticky note, mark on the provided maps the location of your water collection.

**II. Practicing the Titration**

1. Collect the needed equipment: a cell well plate, a stirring rod, 2 bereal pipets (mark one for water sample and one for $\text{AgNO}_3$ solution), a clean, dry beaker with about 10ml of $\text{AgNO}_3$ solution (make note of the molarity), and a clean beaker containing tap water.

2. Place the cell well plate on a piece of white paper for ease in observing the color changes during the titration.
3. Using the water pipet, measure out 10 drops of tap water into one of the cell wells.
4. Add 1 drop of Na$_2$CrO$_4$ indicator solution. The solution will appear yellow-green.
5. Now add the AgNO$_3$ solution slowly to the same cell well. Adding one drop at a time, count the drops and stir after each added drop. (Stirring is very important for thorough mixing and complete reaction.) As each drop is added, a white cloudy haze will appear as the AgNO$_3$ reacts with any Cl$^-$ present in the tap water. With the first drops the solution may momentarily turn a red color but the red color will disappear with stirring. As you approach the endpoint with continued addition and stirring, the solution will start to turn orange in color, even with the stirring. Note the number of drops when you first note the orange tint. Continue adding the AgNO$_3$ solution. A darker orange and eventual red color will form which is due to more Ag$_2$CrO$_4$ being formed.
6. With stirring, add tap water back to the sample until the color returns to a milky yellow-green color. Save for later comparison to collected water samples.

III. Analysis of Tap Water
As discovered in the previous section, the endpoint is not a dramatic color change. Tap water will first be tested to become comfortable with the color changes.
1. To four different cell wells, add 20 drops of tap water and 1 drop of Na$_2$CrO$_4$ indicator. Be consistent in delivery of the drops. (Hold the pipet in a vertical position or a constant angle to ensure uniform delivery of the drops. Avoid air bubbles in the pipet during sample delivery.)
2. Next add the AgNO$_3$ solution. Stir after each drop addition and keep track of the number of added drops. Stop the addition when the last drop creates a permanent orange color change in the cell well. Refer to the sample created and saved in Part II. The endpoint desired will be one drop away from this color.
3. Continue to run numerous tap water samples (at least four). If a mistake is made, just discard that sample and try another one. Record all trials but note reasons if a mistake or other problem is encountered with a trial. It is acceptable practice to omit these values when doing final calculations.
4. Record the number of drops of AgNO$_3$ needed to arrive at the endpoint for each sample.

IV. Analysis of Water Samples
1. Rinse out the water pipet with a portion of the collected water sample.
2. Repeat the procedure in Part III with the collected water sample. Start by using sample sizes of about 20 drops. This can be increased or decreased in subsequent trials if the Cl$^-$ content is found to be very low or very high. Results will be more accurate if the recorded number of AgNO$_3$ drops to reach the endpoint is not small (<5 drops). Also it is not desirable to count a large number of drops. Both scenerios can be avoided by controlling the initial sample size. Be sure and accurately record the sample sizes used for each trial.
3. Perform several trials of the water sample (minimum of four).
4. Repeat for other collected water samples if more than one location is being tested by the group.

V. Calculations
As can be seen in the introduction, 1 mole of Cl\(^-\) reacts with 1 mole of Ag\(^+\) to form the AgCl white solid. At the endpoint, when the reaction is complete, there are equal number of moles of Cl\(^-\) and Ag\(^+\). By definition molarity is the number of moles of substance per liter of solution. Using these concepts, the following formula may be derived:

1. Moles Cl\(^-\) = moles of Ag\(^+\)
2. Molarity = number of moles of substance/liter of solution.
   Rearranging terms, this becomes:
   \[(\text{Molarity})(\text{liter of solution}) = \text{moles of substance}\]
   Abbreviated this becomes \((M)(V) = \text{moles of substance}\)
3. Using the equation obtained in number 2 above, the equation in number 1 can be rewritten as:
   \[(M \text{ of the Cl}^-)(V \text{ of the Cl}^-) = (M \text{ of AgNO}_3)(V \text{ of AgNO}_3)\]
4. In this experiment V (volume) was measured in number of drops.
   The equation in number 3 can be rewritten as:
   \[(M \text{ of the Cl}^-)(\text{drops of the Cl}^-) = (M \text{ of AgNO}_3)(\text{drops of AgNO}_3)\]

Knowing the drops of Cl\(^-\) and AgNO\(_3\) and the M of AgNO\(_3\), the M of Cl\(^-\) can be calculated.

Perform the following calculations first for the tap water samples and then for the collected water samples.

1. Look at the number of AgNO\(_3\) drops for each trial and discard any trials that seem out of line with the others or that are deemed to be in error. Take the remaining trials and calculate the average number of drops of AgNO\(_3\) used to reach the endpoint.
2. Using this average and the equation in number 4 above, calculate the molarity (M) of the Cl\(^-\) in the tap water (and then in the collected water sample(s)).
3. Knowing the molarity of Cl\(^-\), the ppm can be calculated using the following formula:
   \[(M \text{ of Cl}^-) = \text{Moles of Cl}^-/\text{liter of solution}\]
   Therefore:
   \[(\text{Moles of Cl}^-/\text{liter of solution})(35,500\text{mg Cl}^-/1\text{ mole Cl}^-) = \text{mg Cl}^-/\text{liter of solution} = \text{ppm of Cl}^-\]
4. Turn in results to the TA.

Questions
1. During the experiment, care must be taken that all the drops hit the bottom of the cell well, not the sides. Why?
2. If consistent AgNO\(_3\) was added to all trials to change the indicator color to a deeper orange –red, would this affect your results? Explain.
3. Why is it helpful to do multiple trials of the same sample?
4. Review results obtained from your lab section. What impact does the surroundings have on the natural water sources in the Clemson area?
5. What could be some of the non-industrial sources of chloride in the natural water sources?
6. Do you consider chloride to be a serious water pollutant? Why/why not?
### Tap Water Data

Average number of AgNO3 drops

Concentration of Chloride mole/liter

Concentration of Chloride ppm

### Collected Water Sample Data

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Average number of AgNO3 drops

Concentration of Chloride mole/liter

Concentration of Chloride ppm

Use additional tables if additional water samples are tested.