

1. Water and Water Pollutants

Objective

In this experiment, three common procedures applied to water resources, to test their fitness for human consumption, will be examined: determination of total dissolved oxygen content, determination of chloride ion content, and determination of calcium ion content.

Introduction

One of humanity's most precious resources is pure water. Most of the mass of the human body consists of water or substances derived from water. An average human can survive without food for several days, or even weeks, but cannot live more than a few days without water. Water, of course, is also needed for many other purposes.

Agriculture, for example, is very dependent on large sources of potable water. If rain does not provide enough water for the growing of crops, water must be provided from some other source through irrigation. The state of California grows much of the fresh vegetables and fruits sold in the United States. Many growing regions of California were originally desert, however, and have been converted into arable farms and orchards by massive irrigation projects.

Industry consumes the major portion of the fresh water used in the United States each day. Oftentimes water used for industrial processes must meet even higher standards than those for human consumption. For example, water is used as a coolant in many situations. Water has a high heat capacity and can absorb and remove a great deal of heat from its surroundings. Power plants use millions of gallons of fresh water daily for this purpose.

To be considered fit for human consumption or for industrial uses, water must meet very high standards. Water must be virtually free of bacterial and viral organisms. For this reason, most drinking water is treated with elemental chlorine (or some chlorine compound that generates Cl_2 *in situ*) to kill such species. Water must be free of suspended solids (sand, silt, or waste material). Water treatment plants contain large filters and settling tanks to remove such solids.

Water must be free of both naturally occurring chemical contaminants and those that have been introduced by humans. For example, water from wells or rivers may contain a large concentration of calcium ion from the leaching of natural minerals. Calcium ion is easily precipitated as calcium carbonate by reaction with carbon dioxide in the air. If water containing large levels of calcium ion were used as a coolant in an industrial process, there is a good chance that the precipitated calcium carbonate would eventually block the pipes used to deliver the water. This happens also in the home, especially in the boilers of home heating systems, or in hot water heaters. Water that contains excessive amounts of calcium ion is said to be *hard*.

Natural sources of water often contain large amounts of sodium chloride. This frequently results from salt, used to treat roadways during the winter, leaching into the groundwater supply. Small amounts of sodium chloride are not harmful, but if the level gets too high, the water becomes unfit for human consumption. Excessive sodium chloride can also be detrimental to industrial processes.

In order to support aquatic life (fish and plants) water must contain not less than a particular minimum amount of dissolved oxygen gas. Fish and underwater plants must obtain oxygen to live. Many pollutants cause the amount of dissolved oxygen gas to decrease substantially below the level needed to support aquatic life. For example, organic wastes (such as sewage) are oxidized by dissolved oxygen (and thereby consume the oxygen).

In this experiment, water samples will be analyzed to determine (1) the amount of available oxygen contained, (2) the concentration of chloride ion they contain, and (3) the level of calcium ion they contain. Although samples of naturally occurring water could be used for this experiment, the samples you will analyze have been prepared so that they contain a known amount of the species under analysis. The methods to be used, however, are essentially the same as would be applied to a sample of water from a well or stream.

“Available” oxygen will be determined by an iodine/thiosulfate method. An excess of potassium iodide will be added to the acidified water sample. Oxygen (or other oxidizing agents) will oxidize a portion of the iodide ion to elemental iodine. The elemental iodine (actually, triiodide ion, I_3^-) thus produced will be determined by titration with standard sodium thiosulfate solution, using starch as indicator.

Chloride ion concentration will be determined by Mohr precipitation titration with standard silver nitrate solution, to a silver chromate endpoint. A small quantity of sparingly soluble calcium carbonate is added to adjust the pH to slightly basic.

Calcium ion concentration will be determined in the sample by titration with standard disodium EDTA solution. A small quantity of the magnesium/EDTA complex is added to sharpen the Eriochrome Black T endpoint, and the sample is buffered at pH 10 with an ammonia/ammonium chloride system.

SAFETY PRECAUTIONS

- **Wear safety glasses at all times while in the laboratory.**
- **Use a rubber safety bulb when transferring solutions with a pipet. Do *not* pipet by mouth.**
- **Sulfuric acid is dangerous to the skin. Wash immediately if spilled and inform the instructor.**
- **Silver nitrate and iodine/iodide solutions will stain the skin. Nitrates are strong oxidizing agents and are toxic. Wash after handling.**

- **Chromium compounds are toxic. Wash hands after use. Dispose as directed by the instructor.**
- **Ammonia is a respiratory irritant and heart stimulant. Confine the pouring of the ammonia buffer to the exhaust hood.**

Apparatus/Reagents Required

Burets, 25-mL pipets and safety bulb, 0.0500 *M* standard silver nitrate solution, 0.0500 *M* standard disodium EDTA (Na_2EDTA) solution, 0.0500 *M* standard sodium thiosulfate solution, potassium iodide, starch indicator solution, 0.035 *M* sodium chromate indicator solution, pH 10.6 6.0 *M* ammonia/ammonium chloride buffer, Eriochrome Black T indicator solution, calcium carbonate, 0.01 *M* Mg/EDTA solution, 6 *M* sulfuric acid

Procedure

Record all data and observations directly in your notebook in ink.

A. Determination of Dissolved Oxygen in Water

Clean out two 250-mL Erlenmeyer flasks and rinse with distilled water. Label the flasks as samples 1 and 2.

Clean out the buret and the 25-mL pipet with soap and water. Rinse with several portions of tap water, followed by several portions of distilled water. Rinse the buret with several portions of standard 0.0500 *M* sodium thiosulfate solution (discard the rinsings), and then fill the buret with the sodium thiosulfate solution.

Obtain a sample of water for oxygen analysis. Record the identification number of the sample. Using a rubber safety bulb, pipet 25 mL of the water sample into each of the two Erlenmeyer flasks.

Add 2 g (roughly measured) of potassium iodide and 10 mL of 6 *M* sulfuric acid (*Caution!*) to sample 1. Iodide ion will reduce any oxidizing agents present (available oxygen) and will itself be oxidized to elemental iodine, I_2 . A brown solution (of iodine) will result if the water sample contains available oxygen. Elemental iodine can be titrated with standard sodium thiosulfate solution.

Record the initial reading of sodium thiosulfate in the buret to the nearest 0.02 mL. Begin adding sodium thiosulfate to sample 1, swirling the flask during the addition. The brown color of the elemental iodine will begin to fade. Stop adding sodium thiosulfate when the sample reaches a *light yellow* color.

The disappearance of brown color from an iodine solution gives an indistinct endpoint. Starch forms an intense blue/black color with even a small amount of iodine. It is much easier to see the sudden complete disappearance of the blue/black color of the starch/iodine complex.

Add 2–3 mL of starch solution to the sample. A deep blue or black color will result. Continue adding sodium thiosulfate from the buret drop by drop until the starch/iodine color just disappears. Record the final buret volume to the nearest 0.02 mL.

Repeat the titration with sample 2, adding potassium iodide and sulfuric acid before titrating, and adding starch just before the endpoint is reached. From the concentration of the sodium thiosulfate solution and from the volume used in the titration, calculate the concentration of available oxygen in the water sample.

B. Determination of Chloride Ion in Water

Clean out two 250-mL Erlenmeyer flasks and rinse with distilled water. Label the flasks as samples 1 and 2. Clean out the buret and the 25-mL pipet with soap and water. Rinse with several portions of tap water, followed by several portions of distilled water. Rinse the buret with several portions of standard 0.0500 M silver nitrate solution (*Caution!*) and discard the rinsings. Then fill the buret with the silver nitrate solution.

Obtain a sample of water for chloride analysis. Record the identification number of the sample. Using a rubber safety bulb, pipet 25 mL of the water sample into each of the two Erlenmeyer flasks. Add 3–5 drops of sodium chromate indicator solution (*Caution!*) to each of the sample flasks. The sample will be yellow at this point. Silver chromate, which has a red color, will form during the titration. The endpoint is the *first* appearance of the red color.

Record the initial volume of silver nitrate in the buret to the nearest 0.02 mL. Add an amount of solid calcium carbonate about the size of a pea to sample 1. Start adding silver nitrate from the buret to sample 1 slowly, swirling the flask during the addition. A white precipitate of silver chloride will begin to form as the silver nitrate is added. (The precipitate may appear yellow because of the chromate ion present in the sample.) Eventually, red streaks will begin to appear as silver chromate begins to form (as the concentration of chloride ion decreases). Add silver nitrate solution from the buret until one drop causes a permanent red color of silver chromate to appear.

Record the final volume of silver nitrate solution in the buret to the nearest 0.02 mL.

Repeat the titration with sample 2. From the volume of standard silver nitrate used to titrate the sample, and the concentration of the silver nitrate, calculate the concentration of chloride ion present in the water sample.

C. Determination of Calcium Ion in a Water Sample

Clean out two 250-mL Erlenmeyer flasks and rinse with distilled water. Label the flasks as samples 1 and 2. Clean out the buret and the 25-mL pipet with soap and water. Rinse with several portions of tap water, followed by several portions of distilled water. Rinse the buret with several portions of standard 0.0500 M Na₂EDTA solution (discard the rinsings); then fill the buret with the Na₂EDTA solution.

Obtain a sample of water for calcium analysis. Record the identification number of the sample. Using a rubber safety bulb, pipet 25 mL of the water sample into each of the two Erlenmeyer flasks. Take the two flasks to the exhaust hood, and add 20 mL of ammonia/ammonium chloride buffer (*Caution!*) to each flask.

Record the initial volume of standard Na_2EDTA solution in the buret to the nearest 0.02 mL. To sample 1, add 10 mL of the Mg/EDTA solution (which promotes a sharper color change at the endpoint) and 5–6 drops of Eriochrome Black T indicator solution. The sample should be red at this point.

Begin titrating with standard EDTA solution from the buret. The red color of the initial solution will gradually change to purple/gray as the blue calcium/EDTA complex forms. The endpoint is signaled by the disappearance of the initial red/purple color, and the appearance of the *pure blue* color of the calcium/EDTA complex.

Record the final volume of Na_2EDTA in the buret to the nearest 0.02 mL.

Repeat the process with sample 2. From the volume of Na_2EDTA used to titrate the sample and the concentration of the Na_2EDTA , calculate the concentration of calcium ion in the water sample.

Water and Water Pollutants

Date: Student name:
Course: Team members:
Section:
Instructor:

Results/Observations

A. Available Oxygen Determination

Concentration of $\text{Na}_2\text{S}_2\text{O}_3$ standard solution

	Sample 1	Sample 2
Initial buret reading
Final buret reading
Volume thiosulfate used
Moles thiosulfate used
Volume of water sample
Concentration of sample
Mean concentration of sample	Code number

B. Chloride Determination

Concentration of standard AgNO_3 solution

	Sample 1	Sample 2
Initial buret reading
Final buret reading
Volume AgNO_3 used
Moles AgNO_3 used
Volume of water sample
Concentration of sample
Mean concentration of sample	Code number

C. Calcium Determination

Concentration of Na₂EDTA solution

	Sample 1	Sample 2
Initial buret reading
Final buret reading
Volume Na ₂ EDTA used
Moles Na ₂ EDTA used
Volume of water sample
Concentration of sample
Mean concentration of sample	Code number	

Questions

1. Elemental iodine is volatile: It undergoes substantial sublimation even at room temperature. For this reason, the iodine in Part A was generated by adding KI to the samples one at a time. What error in the determination of available oxygen would be introduced if a portion of the iodine generated had vaporized prior to the titration?

2. Why was it necessary to add a small amount of magnesium/EDTA complex to the calcium samples before titrating?

3. How do pollutants such as sewage lower the dissolved oxygen content of water sources?