

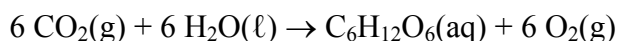
Water Analysis

Background

Water is the most common solvent used in the general chemistry laboratory and is present in nearly all reaction mixtures studied in the typical teaching lab. We tend to take water for granted unless we are investigating physical properties which are conveniently demonstrated with it. The versatility of water in the laboratory only hints at its importance in the larger world.

Exobiologists remind us of the literally "vital" importance of water as they search for other planetary bodies which sport liquid water. Water is essential for life "as we know it" whether one considers the high water content of even the simplest organisms, the speed with which chemical reactions occur in aqueous solution or the ability of water to facilitate ion formation and ion transport.

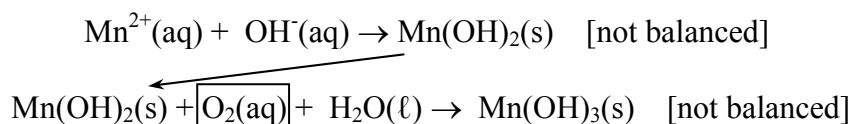
Water is required for photosynthesis:



The production of simple sugars which are used to build up more complex structures is one obvious result of this important process but the oxygen produced as a by-product should not be overlooked. Animal life depends on it. A large part of the photosynthetic oxygen is produced by plant life in the oceans. The careless discharge of waste material (some of it toxic) into the oceans thus represents a real threat not only to marine life but to land animals as well (including humans). Wastes may consume the dissolved oxygen in the sea water (or fresh water bodies) enabling the growth of toxic anaerobic bacteria and preventing fish from obtaining adequate oxygen.

Approximately 4 mg/L or four parts of dissolved oxygen per million parts of water (4 ppm) is the minimum required for life processes in water. The equilibrium concentration of dissolved oxygen in open water, is normally higher than that, 9.2 ppm at 20°C, but the rate of dissolving is dependent on the surface area accessible to the atmosphere and is slow unless the water is deliberately aerated (something done routinely at water treatment plants). In public drinking water the dissolved oxygen level is typically maintained in the range of 8-10 ppm through aeration either during the transit of the water from its original source (lakes, streams, reservoirs, etc.) or during the treatment process as disinfectants are added. In modern laboratories the dissolved oxygen content is typically measured with a selective electrode. After calibration the electrode provides a direct reading of the dissolved O₂ in either ppm or mg/L.

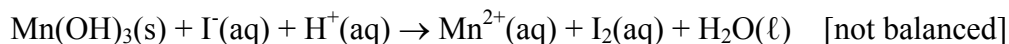
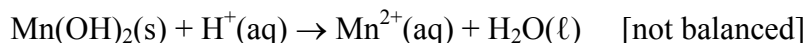
There is also a classic chemical determination for dissolved oxygen in water known as *Winkler's Method*. The water sample is first treated with excess manganese(II) sulfate solution and then with an alkaline solution of potassium iodide. The following reactions are important:



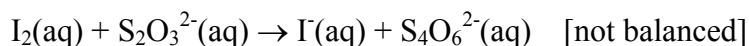
The Mn(OH)₂ initially formed reacts with the dissolved oxygen (boxed). The process is a heterogeneous reaction, involving the combination of a gas with a colloidal solid.

Adapted from: Chemical Principles in the Laboratory, 3rd ed., Robert F. Bryan, Robert S. Boikess and Chloride in natural waters, Lisensky, George; Reynolds, Kelly, *J. Chem Ed.*, 1991, vol. 68, No. 4, p. 334

The amount of Mn(OH)_3 formed is determined by reaction with iodide ion, which is inert in basic solution, but in acidic solution reacts with Mn(OH)_3 to form Mn^{2+} and iodine (excess Mn(OH)_2 is redissolved in the acid):

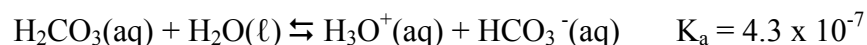
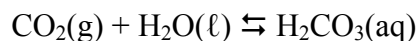


The iodine formed may be titrated against standard thiosulfate solution, using starch as an indicator:



From the stoichiometries of the various equations, the amount of dissolved oxygen can be readily calculated.

Natural water supplies in contact with air also absorb carbon dioxide, producing the weak acid *carbonic acid* in solution. This acid, found only in aqueous solution, interacts with water to form hydrated protons and hydrogen carbonate anions:



Most natural water sources are therefore slightly acidic [typical drinking water: pH 6.0-8.5]. To sustain life, water must remain fairly close to neutral in character. You have seen in other experiments that it takes only a small amount of acid or alkali to alter the pH of unbuffered water. The concern over airborne acidic pollutants and acidic effluents from manufacturing plants is therefore justified. We may not live in a lake or in the rivers but our health is inevitably tied into the larger web of life.

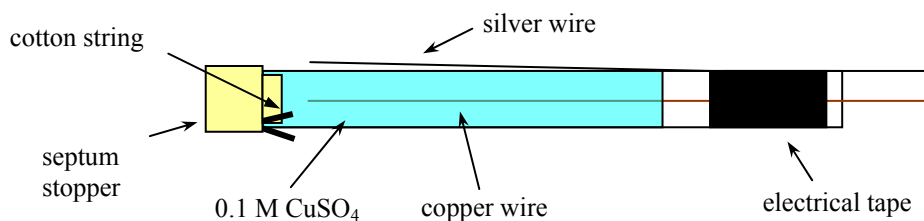
You will test the pH of your water sample by a universal indicator paper, i.e., a paper designed to produce different colors for different pH values throughout the range 1-14.

In addition to the dissolved gases natural waters pick up due to their exposure to the atmosphere, other materials--mostly ions--accumulate in water either because they are leached out from the watercourse itself or because they are added (intentionally or unintentionally) by humans. Chloride ion is a good example. Water flowing over rocky stream beds will dissolve chloride ion and carry it along. Nominal levels of chloride [not *chlorine*] are not harmful and actually have physiological use. The hydrochloric acid in our stomachs must be synthesized by the body and the chloride has to come from somewhere!

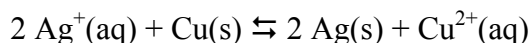
Many manufacturing processes also use either hydrochloric acid or various chloride compounds, and without sufficient treatment effluents from factories can significantly raise the chloride concentration in surrounding water supplies. A much smaller amount of chloride ion is a byproduct of the purification processes used on many domestic drinking water supplies. The most obvious evidence for this is the cloudy white appearance of tap water when used to rinse beakers that held silver nitrate or lead nitrate solutions. Silver and lead chloride are fairly insoluble and even the small amount of chloride present in tap water will cause precipitates to form [typical public drinking water contains about 40 mg/L of Cl^-].

This suggests a technique for determining the amount of chloride ion present in a water sample. Standard solutions of chloride ion can be prepared and excess silver nitrate added to them. The degree of cloudiness is a measure of the amount of chloride ion. This may seem imprecise but there are instrumental techniques (*nephelometry* or *turbidimetry*) based on this simple idea which use the amount of scattered light to determine the concentration of a substance. There is also a classic titration technique which uses chromate ion and silver nitrate as the titrant.

You have seen from earlier work that the concentration of ions in solution will affect the electric potential of a galvanic cell. This is the principle upon which pH electrodes (and many other ion-selective electrodes) operate. It is possible to construct a simple silver-sensitive electrode and use it to determine the chloride content in a water sample. The electrode consists of a $\text{Cu}|\text{Cu}^{2+}$ half cell and a silver wire:



The half-cell is immersed in a water sample so that the silver wire is exposed to the water. When silver nitrate solution is added to the water sample from a buret, the silver ion concentration in the water changes slowly at first because much of the silver is immediately precipitated by any chloride ion present. This results in a gradual increase in the potential of the complete cell in which this reaction occurs:



This is exactly the behavior we would predict with LeChâtelier's principle or the Nernst equation. Titrations performed in this manner, by following the voltage change in a galvanic cell, are called *potentiometric*.

As additional silver nitrate is added, the amount of free chloride in the mixture becomes very small until there is essentially none. Now added silver ions are not removed as AgCl and the concentration of silver rises more rapidly. This corresponds to a more rapid increase in the potential of the cell. A plot of voltage vs. mL of AgNO_3 in fact yields a typical s-curve and the equivalence point can be determined graphically from a derivative plot. *At the equivalence point the moles of Ag^+ added are equal to the moles of Cl^- present in the sample.*

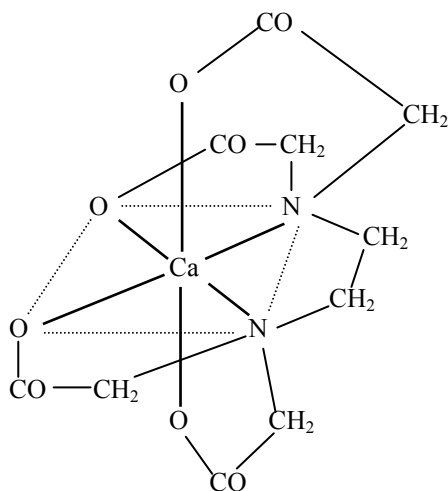
Natural water supplies contain varying amounts of dissolved cations reflecting the nature of the ground over which the water has passed or is stored. Small amounts of Na^+ and K^+ are common and of little concern. Both are important in biochemical processes. Less benign in some situations are Ca^{2+} , Mg^{2+} , and Fe^{3+} ions because of their tendency to precipitate as insoluble salts, particularly carbonates, phosphates, and hydroxides. Deposits of these materials cause damage in domestic water heaters and pipes (CaCO_3 is actually *less* soluble in hot water). They also contribute to "scale" formation on plumbing fixtures and shower doors.

Magnesium and calcium in particular present additional problems because they combine with the anionic component of some soaps and detergents to form insoluble precipitates--the familiar scum in the sink or washing machine. Soaps are sodium or potassium salts of aliphatic fatty acids. These binary salts are soluble, but the ternary calcium or magnesium salts are not.

Water with a high concentration of Mg^{2+} and Ca^{2+} is referred to as "hard" water, and the degree of hardness is linked to the concentrations of these two cations [typical public drinking water: 60-150 mg $CaCO_3/L$]. Water with a low concentration of these ions is referred to as being "soft". Domestic water is "softened" by exchanging sodium ions for the calcium and magnesium ions.

The hardness of a water sample can be determined by titration of the alkaline earth cations with ethylenediaminetetracetic acid (EDTA), a complexing agent. The acid itself is practically insoluble in water so it is typical to use the disodium salt of EDTA (" Na_2H_2Y ").

As a complexing agent EDTA has the potential to bind at 6 sites (we say it is *hexadentate*--i.e., six-toothed) and its capacity to do so is somewhat determined by pH. In strongly basic solution (pH 10), the remaining two protons on the " H_2Y^{2-} " form are displaced and the Y^{4-} ion complexes 1:1 with magnesium and/or calcium ions.



The titration is monitored by using another complexing agent, eriochrome black T (EBT), as an indicator. EBT will also form 1:1 complexes with calcium and magnesium ions. But EBT-Mg complexes are more stable than EDTA-Mg complexes, whereas EBT-Ca complexes are less stable than EDTA-Ca complexes. In addition, the EBT-Mg complex is a wine-red color while everything else is either colorless or blue (uncomplexed EBT is blue as well).

The accurate determination of total hardness (i.e., $Mg + Ca$) using EDTA/EBT depends on sharpening the transition from the wine-red color of the EBT-Mg complex to the blue color of uncomplexed EBT. To ensure a sufficient amount of magnesium for this purpose, a very small amount is added to the EDTA titrant just in case the water sample itself has none (or very little).

When EBT is added to the pH 10 buffered water sample the wine-red color of the EBT-Mg complex is evident. During the titration EDTA complexes any calcium ions in the sample and continues to do so in preference to magnesium ions (which are bound to the EBT) until all the calcium ions are complexed. At that point excess EDTA added will abstract magnesium ions from the EBT-Mg complex. As the complex comes apart the wine-red color gives way to the blue of uncomplexed EBT. This is the end-point of the titration. The color change can be difficult to judge without prior experience and for that reason you will standardize the EDTA solution with a known concentration of Ca^{2+} before analyzing the actual water sample.

YOU WILL NEED ABOUT 250 mL OF WATER FOR THIS EXPERIMENT. BRING SOME FROM HOME OR YOUR FAVORITE LOCAL SUPPLY. A BOTTLE WILL BE PROVIDED FOR THIS PURPOSE.

COLLECT YOUR SAMPLE IN SUCH A WAY AS TO MINIMIZE THE AMOUNT OF AIR CONTACT. IF YOU HAVE A FAUCET AERATOR, REMOVE IT FIRST BEFORE FILLING THE BOTTLE, AND THEN LET THE WATER COME OUT ONLY IN A SLOW STREAM, NOT A GUSHER. IF YOU HAVE A DOMESTIC WATER SOFTENING UNIT, BE SURE TO COLLECT WATER FROM A TAP NOT CONNECTED TO IT (E.G., AN OUTDOOR HOSE CONNECTION).

The Experiment

There are four parts to this experiment:

- determining the pH of the water sample
- determining the dissolved oxygen content of the water sample
- determining the Cl^- concentration of the water sample
- determining the total hardness of the water sample

The following non-locker materials will be provided:

- pH indicator paper
- 25 mL Erlenmeyer flask w/stopper
- 2.6 M MnSO_4
- 0.90 M KI/12.5 M NaOH mixture
- concentrated H_2SO_4 [fume hood]
- 0.00050 M $\text{Na}_2\text{S}_2\text{O}_3$
- starch indicator
- 200 mL Berzelius-style beaker w/black paper shield
- approx. 0.004 M AgNO_3 [record exact concentration]
- 0.10 M CuSO_4
- pre-cut glass tubes, electrode wire pairs, electrical tape, etc.
- CBL voltage probe (0 to +5 V)
- 0.10 g CaCO_3 /L standard solution
- EBT indicator
- EDTA solution
- four 125 mL Erlenmeyer flasks
- pH 10 $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer [fume hood]

The Chemicals

Manganese(II) sulfate is a pale red/pink powder which is slightly efflorescent. It is soluble in 1 part cold water. It has been used in dyeing, for red glazes on porcelain, in fertilizers and feeds.

Potassium iodide is a white solid, slightly deliquescent, and prone to oxidation in air. It is used in the manufacture of photographic emulsions, and in table salt and some drinking water to help prevent iodine deficiency disease.

Sodium hydroxide is commonly known as lye or caustic soda. It is a very hygroscopic white solid (absorbs water from the air rapidly) and also absorbs CO_2 . It is very corrosive to vegetable and animal matter and aluminum metal, especially in the presence of moisture. Dissolving NaOH in water generates considerable heat.

Besides its use in the laboratory, sodium hydroxide is used in commercial drain cleaner preparations, to treat cellulose in the manufacture of rayon and cellophane and in the manufacture of some soaps. It is corrosive to all tissues and can be detected on skin by the "slimy" feeling associated with bases. It should be rinsed off thoroughly upon contact. It can damage delicate eye tissues and cause blindness.

Sulfuric acid is a clear, colorless, oily liquid in concentrated form (98%). It is highly corrosive and has a high affinity for water, abstracting it from wood, paper, sugar, etc., leaving a carbon residue behind. Dilution of concentrated sulfuric acid generates a tremendous amount of heat. Here in the lab your instructor prepares the dilute sulfuric acid you use by pouring the concentrated acid slowly over ICE while stirring! Even so, the resulting solution is very warm. As with all acid dilutions, acid is added to water, not the reverse, since the heat generated can boil the water at the point of contact and cause spattering.

Sulfuric acid is used to make fertilizers, explosives, dyes, parchment paper, and glue. It is used, in concentrated form, in automobile batteries as the electrolyte. It is corrosive to all body tissues and contact with eyes may result in total blindness. Ingestion may cause death. Frequent skin contact with dilute solutions may cause dermatitis.

Sodium thiosulfate (photographer's "hypo") is most commonly obtained as a pentahydrate in colorless, odorless crystals or granules. It melts at 48°C and has a tendency to form supersaturated solutions. The compound dissolves silver halides and many other salts of silver. It is used as a fixer in photography, for extraction of silver from ores, as a mordant in dyeing and printing textiles and in the manufacture of leather. The compound has relatively low toxicity. Large doses orally cause purging.

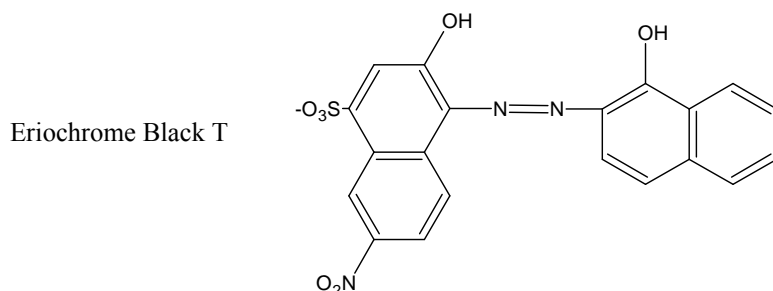
Silver nitrate forms colorless, transparent crystals. It is stable and not darkened by light in pure air but darkens in the presence of organic matter and H_2S . It decomposes at low red heat into metallic silver. It is used in photography and the manufacture of mirrors, silver plating, indelible inks, hair dyes, etching ivory and as an important reagent in analytical chemistry.

It has been used as a topical antiseptic in a 0.1 to 10% solution. However, it is caustic and irritating to skin. Silver nitrate stains skin and clothing. These stains will wear off skin in a few days to a week but clothing is generally ruined. Swallowing silver nitrate can cause severe gastroenteritis that may end fatally.

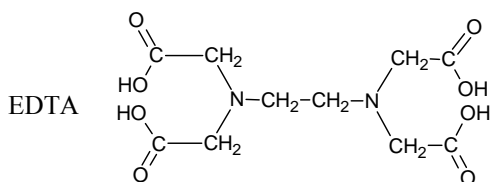
Copper(II) sulfate is available in both anhydrous form (pale blue to white) and the more common pentahydrate blue crystals (*blue vitriol*). It slowly effloresces in air, losing 2 waters at 30°C, 2 more at 110°C and becoming anhydrous at 250°C. It is very soluble in water and methanol. The pentahydrate is used as an agricultural fungicide and bactericide as well as an herbicide (readily available at your local hardware store to kill roots in sewer pipes). It has many other uses in the dye, tanning, plating and photography industries. Copper is a trace nutrient but is toxic when ingested in sufficient quantities.

Calcium carbonate is found in limestone, marble and chalk deposits but the commercial substance is manufactured chemically. It is a white, odorless, tasteless powder, practically insoluble in water. The compound is used in the manufacture of paint, rubber, plastics, paper, and in foods and pharmaceuticals. The solution used in this experiment was prepared by dissolving a sample of the solid in dilute HCl and diluting to volume.

Eriochrome Black T, $C_{20}H_{12}N_3NaO_7S$, or C.I. Mordant Black 11, 3-hydroxy-4-[(1-hydroxy-2-naphthyl)azo]-7-nitro-1-naphthalenesulfonic acid sodium salt, is a brownish-black powder with a slight metallic sheen. It is soluble in hot water. Indicator solutions are prepared according to a variety of recipes. Solutions have limited shelf-life. It can be used to dye wool and in analytical chemistry as a metal ion indicator in the determination of total water hardness with EDTA as a titrant.



Na_2EDTA , $C_{10}H_{14}N_2Na_2O_8$, or ethylenediaminetetraacetic acid disodium salt, is very slightly soluble in water and exhibits the characteristics of a weak acid, including displacing CO_2 from carbonates and reacting with metals to form hydrogen. It is used as a sequestering agent, in particular as a chelating agent which combines with calcium, etc.



Starch (soluble starch, *amylopectrin*) is a white, odorless, tasteless powder which is soluble in water when heated. It is frequently used in the lab as an indicator for iodometric analysis since it forms an intense blue-to-black complex with I_2 but not with I^- .

Ammonium chloride (once commonly known as "sal ammoniac") is a white crystalline or granular solid with a cooling, saline taste. It sublimes without melting, is very soluble in water and dissolves with significant cooling. It is used as a soldering flux, in ordinary dry cells and for slowing the melting of snow on ski slopes.

Ammonia is a gas at room temperature. Laboratory solutions of aqueous ammonia have sometimes been erroneously called "ammonium hydroxide" although there is little evidence for the existence of that compound. Aqueous solutions of ammonia are basic.

Ammonia gas can be manufactured from industrial gases associated with the processing of "coke", a spongy form of carbon obtained from processing coal and essential in steel-making. In the Haber-Bosch process nitrogen and hydrogen from these industrial gas mixtures are combined at high temperature and pressure in the presence of a catalyst to form ammonia. The gas and its aqueous solutions are colorless with a very pungent odor (lower limit of human perception: 0.04 g/m^3). Mixtures of ammonia gas and air can explode when ignited under favorable conditions. At room temperature ammonia is soluble to the extent of 31% in water, only 16% in methanol. It is used in the manufacture of nitric acid, explosives, fertilizers and in refrigeration. In anhydrous liquid form it is a good solvent for many elements and compounds, notably the alkali metals which yield blue solutions when dissolved in liquid ammonia.

Inhalation of the concentrated vapor causes swelling in the respiratory tract, spasms and asphyxia.

Technique Discussion

Checking the acidity of your water sample is the simplest procedure and might as well be done first before there is any chance of trace contamination. Remember that indicator paper is NEVER dipped into a solution (dyes leach out.....). A clean stirring rod is dipped into the solution and then touched to a piece of indicator paper.

A 25 mL sample of the water is used for the dissolved oxygen determination. After the water is transferred into the 25 mL Erlenmeyer flask, 20 drops of MnSO_4 and 20 drops of the KI/NaOH solution [caution: use different beral pipets for these!!!! They react!!!!] are used to "fix" the dissolved oxygen so that no additional oxygen which might be inadvertently introduced during handling, stirring, pouring, etc. will react in the titration. The solution should be stoppered and inverted a few times to mix thoroughly.

The $\text{Mn}(\text{OH})_3$ precipitate is then dissolved with 10-20 drops of concentrated H_2SO_4 (fume hood). Stopper and invert to mix. If all of the precipitate does not dissolve, a few additional drops of acid may be added, followed by further mixing. Large excesses of acid should be avoided but all of the precipitate must be dissolved. Precipitates which stand for long periods of time seem to be more difficult to dissolve.

10 mL of the acidified mixture is then placed in a 100 mL beaker and titrated to a starch endpoint with 0.00050 M $\text{Na}_2\text{S}_2\text{O}_3$ solution. As with all iodometric/starch titrations, some of the iodine should be discharged before adding the starch. The solution should be pale yellow before sufficient starch is added to give a definite blue color. At the endpoint the sample should look like plain water. Because the decrease in blue color is gradual it may help to place a beaker of water next to the titration beaker in order to judge when the endpoint has been reached. Repeat the titration with a second 10 mL sample only if problems are encountered with the first sample.

To construct the electrode for the chloride determination, obtain a short length of glass tubing, a small septum stopper, and a copper/silver wire pair. Clean the wires with a steel wool pad. The bare copper wire is inserted into the glass tube and the silver wire remains outside (you can fasten the silver wire to the glass tube with a small rubber band if you like). Insert the wire as far into the tube as it will go and secure it with a piece of electrical tape. Insert a short length of cotton string in the other end of the tube and then place the stopper firmly in the same end. Fold over the collar of the stopper. The Cu wire should not touch the string inside the tube. The final assembly should resemble the diagram shown in the **Background** discussion.

When you are ready to use the electrode, place enough 0.1 M CuSO₄ inside the glass tube to immerse the bare copper wire.

50 mL of the water sample is added to a tall 200 mL beaker wrapped with black paper. Place the electrode in the water. Keep the water from entering the top of the tube and diluting the copper solution. *Be sure the silver wire is actually in the water before you start.* Attach the wire leads to the CBL voltage probe, matching the colors of the leads with the small pieces of colored insulation on the wire ends. This ensures that the silver is connected to the + terminal. **Be sure to bring your TI-83/84 calculator to lab and have the HCHEM.8XG programs in memory.** Set up the calculator to measure VOLTAGE (0 to +5 V) VS. USER X (volume) and use the GRAPHICAL option. YMAX and YMIN can be 0.4 and 0.09, respectively. XMAX and XMIN should be 50 and 0.

Standard 0.004 M AgNO₃ solution (note exact concentration on bottle!) is added slowly from a buret while monitoring the voltage. Chloride ion contents vary. Time can be saved by taking an initial voltage reading of your sample [once you enter the actual data-collection part of the program the CBL displays the voltage from the electrode continuously until you take a reading]. It is not necessary to begin recording data until the voltage is around 0.09 volts. If your cell gives less than this, add silver nitrate from the buret in a slow stream (while stirring) until the cell voltage approaches 0.09 V. At that point record the volume of AgNO₃ added and the voltage. **[if the initial voltage is higher than 0.09 notify the instructor before continuing]**

AgNO₃ is added in 0.5 mL increments once the minimum voltage is obtained, recording the voltage after each addition. There should be a gradual increase, then a marked increase, and then a gradual flattening out, just as in an acid/base titration but perhaps not so dramatic. Data should be taken at least 2 mL past the endpoint.

The EDTA solution for the water hardness determination must be standardized before the actual water sample can be titrated. The color change at the endpoint is often difficult to judge. Until the endpoint is near there is practically no change in the solution. It then becomes a sort of indigo color. At this point you should halt and allow the solution to mix before completing (there may be additional change on mixing). The final color at the endpoint is blue with no trace of purple. You might want to save your first titration for a reference.

The standardization should be done in triplicate using 10 mL of the CaCO₃ solution in a clean, dry 125 mL Erlenmeyer flask. 5 drops of EBT indicator and 2 mL of the buffer are added [**CAUTION: the buffer contains a high concentration of ammonia**]. The buret for delivering the EDTA must be rinsed with a small amount of EDTA (discard) before using. EDTA is an excellent ion scavenger and any impurities left in the buret after cleaning will change the concentration of the EDTA and give spurious results. The CaCO₃ samples should be titrated to the color of the "color standard" mixture.

A 10 mL volume should be sufficient for the water sample titration. 5 drops of EBT and 2 mL of buffer are also required. A duplicate titration is recommended, but not required.

The Report

Your initial calculations should include:

1. The moles thiosulfate used in dissolved O₂ titration [may be mean or single value]
2. The equivalent moles of I₂, Mn(OH)₃, and O₂
3. The mass of O₂ in mg
4. The total dissolved oxygen content expressed as parts per million by mass (mg/L)
5. The volume of EDTA solution needed to titrate 1 mg CaCO₃
[the standard solution is 0.10 mg CaCO₃/mL]
6. The hardness of the water expressed as mg CaCO₃/L [may be mean or a single value]
7. A graph of your potentiometric titration data (voltage or E vs. mL AgNO₃)
8. A table of ΔE , ΔV , $\Delta E/\Delta V$ and \bar{V} (average mL AgNO₃) for your titration
(near the endpoint region only)
9. A graph of $\Delta E/\Delta V$ vs. \bar{V} (first derivative plot)
10. The Cl⁻ concentration for your water sample expressed in mg/L

Your conclusion to this experiment should include the balanced equations needed to complete the calculations and a summary table for all of the tests done. There should be a brief discussion of any results that seem abnormal. Be sure to include the source of your water sample.