

Chelometric Titration :

The Determination of Water Hardness and Water Filtration

Things for the lab notebook and to be included in the lab report:

1. Write the equation for the titration of Ca^{+2} with EDTA. -
2. Write the equations for the endpoint color change of Eriochrome Black T (EBT) with Mg^{+2}
3. Report the water hardness as ppm CaCO_3 of a 50 ml water sample that required 32.50 ml of 0.01 M EDTA to reach the end point of the titration.

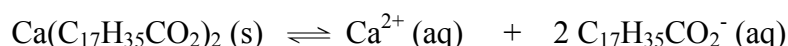
INTRODUCTION

Many metal cations form complexes in solution with substances containing a pair of unshared electrons. A ligand is a molecule (or ion) which possesses at least one position at which it can attach itself to a metal ion. Ammonia is a common example. It can attach itself to the water insoluble AgCl and convert it to the water soluble form $[\text{Ag}(\text{NH}_3)]^{2+}$. The NH_3 molecule has a single point of coordination which is through its nitrogen atom. For this reason it is referred to as a unidentate (or one "toothed") ligand.

Other ligands can attach themselves to many different places: bidentate (two "toothed"), tridentate (three "toothed"), tetradentate (four "toothed"), and hexadentate (six "toothed") ligands are not uncommon. When the number of attachment points increases, the ligand effectively wraps itself around and "claws" itself to the ion. When this happens, the complexing agent is called a chelate (pronounced key-late), which is derived from the Greek word for claw or hoof, representing the characteristics of the metal-ligand complex. A very widely used complexing reagent for this type of titration reaction is ethylenediaminetetraacetic acid (EDTA). For solubility reasons the disodium salt will be used in this experiment. EDTA complexes with the ions contributing to water hardness in a one-to-one stoichiometry. Even though a ligand may attach itself to the metal ion many different places within the complex it does not affect the overall stoichiometry, which is what we really need to know to carry out the calculations. In the case of EDTA it is not known with certainty whether it

attaches itself to the hard water metal ions at either four or six positions but it does not really matter because regardless of the number of points of attachment the stoichiometry is known to be one-to-one between the metal ion and the EDT A. The procedure described below fulfills all of the requirements for a volumetric titration and is widely used for the routine determination of water hardness.

A water supply is considered hard when the amount of Ca^{+2} , Mg^{+2} , and/or Fe^{+3} ions becomes too high for its intended use. Soft water does not contain any significant amounts of these ions. Around the globe, water hardness varies quite a bit. In the Midwest section of the United States it is typically harder than on the East Coast while in areas such as Australia the water is so soft (has very little Ca^{+2} , Mg^{+2} , and/or Fe^{+3} ions) that it rarely needs conditioning. People with medical intolerance to hard water may need to have a water treatment cartridge installed on their water supply to remove the hard water ions. We have all experienced the problems of hard water when using soaps. When you take a shower and use a bar of soap, you will notice a scum or "ring" around the bathtub or the walls of the shower, which is a direct result of the formation of the insoluble calcium (or other hard water metal ion) salts of the fatty acids that occurred when the soap solution came in contact with the hard water ions. Using sodium stearate as a typical soap molecule, it dissolves in water to form sodium and stearate ions. When hard water is used, the calcium ion reacts with the stearate ion and forms the slightly soluble compound calcium stearate, which has a solubility product constant (K_{sp}) associated with it so that an equilibrium condition is established. The equation for the dissolving of calcium stearate in water is:



Obviously, this soap scum would cause many problems if soap is used to wash your hair, clean your clothes, or wash dishes because the scum could deposit itself and remain on the object being cleaned. The Fe^{+3} salts in particular are what contribute to laundered clothes looking dingy or off color if soap is used. For applications such as these, soap is replaced by a detergent, which is more expensive than soaps so their use has been restricted to applications where the problems of the soap scum warrant the additional expense. Detergents became very popular because they do not have the typical "scum" problems associated with soaps. The Ca^{+2} , Mg^{+2} , and/or Fe^{+3} salts of detergents are water soluble and are then efficiently removed from the cleaning system by merely rinsing with water.

For reasons such as these, it becomes necessary to readily determine just how hard a

water supply is and whether it may need conditioning to reduce the hardness. It is not necessary to measure each ion contributing to the water hardness separately. Instead, all hard water ions are determined collectively and reported as an "apparent hardness" assuming that all of the hardness is derived from CaCO_3 . This is done more for convenience than any other reason. It really does not matter whether the hard water ions are Ca^{+2} , Mg^{+2} , and/or Fe^{+3} because they all contribute to the problem. The only significant point is that any or all of them exist in solution and therefore make the water hard. To keep the reporting units consistent from one location to another, a uniform standard has been adopted by mutually agreeing to report water hardness as parts per million (ppm) of CaCO_3 which is equivalent to mg CaCO_3 per kg of water.

In the titration we are going to perform, the indicator is itself also a chelating agent. For Ca^{+2} , Mg^{+2} , and/or Fe^{+3} analysis Eriochrome Black T (EBT), which has 3 ionizable protons (represented as H_3In), is used as the indicator. The color of the indicator complexed with Mg^{+2} in solution is red. As EDTA is added the free metal cation is complexed first because the Mg-EDTA complex is more stable than the $\text{Mg}(\text{In})^-$. After the free metal cation is used up, the metal is displaced from the indicator and complexed to the EDTA which causes a color change from red to blue (which is the color of uncomplexed indicator). The first time through this may be a little tricky. As the titration progresses, the color will change from red to a reddish-purple, then finally to blue. You want to continue until you see the distinct blue color.

EBT cannot be used to indicate the titration of Ca^{+2} alone because it forms too weak a complex with the indicator and therefore does not give a sharp endpoint. Therefore a very small amount of Mg^{+2} is added as Mg-EDTA for a sharper endpoint. This small amount has an insignificant effect on the final result.

The total water hardness determination is done at pH of around 10, using an ammonia-ammonium chloride buffer. This is done because if the pH is too high the hard water metal ion hydroxide(s) may precipitate, causing the reaction with EDTA to be slow. Also, EBT is a weak acid and its color can depend on the pH, because the different ionized species have different colors. This change in color could complicate or cloud the endpoint detection.

EXPERIMENTAL PROCEDURE

PRELIMINARY STEPS

1. If a standardized solution of the Na_2EDTA titrant is not provided, you will need to prepare one from solid Na_2EDTA which has been dried for at least one hour in an oven set to at least 110°C . Using an analytical balance, transfer about 2.0 grams (weighed to within 0.0001 gram) of dry solid Na_2EDTA to a 500 volumetric flask. Fill the flask about halfway with water and swirl the mixture to dissolve the solid. It may not all dissolve at first since it is not very water soluble. The solubility can be enhanced by adding one or two pellets of NaOH to the solution. Dilute to the 500 ml mark. The solution will be approximately 0.01 M.

TITRATION PROCEDURE

1. Obtain a water sample from your instructor. Using either a pipet or volumetric flask, transfer exactly 100 ml of the sample into a 250 ml Erlenmeyer flask, add 2 ml of the ammonia/ammonium chloride buffer solution, 0.5 ml of the Mg-EDTA solution, and five drops of EBT indicator solution. Do not use too much indicator or you could make the endpoint detection more difficult. The volumes of buffer and Mg-EDTA are not critical and will not be used in any calculations so they can be added from a graduated cylinder. The buffer should be added before the indicator, so that any small amounts of Fe^{+3} present will not react with the indicator.
2. This step is to be done only if your instructor indicates it is necessary. If the sample contains high levels of Fe^{+3} a violet endpoint color may be seen instead of a blue one. The interference can be eliminated by adding a few crystals of KCN . CAUTION: KCN is poisonous and must not come in contact with an acid since it will release the deadly gas HCN . Add this only after the alkaline buffer is added. After the titration, add about 1 gram (qualitative measure) of $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ to convert CN^- to $[\text{Fe}(\text{CN})_6]^{-4}$ before disposing of the solution.
3. Add a stir bar to the flask and place it on a sheet of white paper on top of a magnetic stirrer. The white paper will help show the endpoint color change more clearly. Titrate the sample using your standardized Na_2EDTA solution. The endpoint color change is from wine red to blue. The first

time through, you may not be familiar with the change and accidentally overshoot the endpoint. If this happens, you will need to repeat the analysis. The reaction is slower near the end point, and the titrant must be added slowly and the solution stirred thoroughly.

4. If your water sample was fairly soft and you used less than about 20 ml of the EDTA titrant, adjust the sample size to require at least 20 ml and repeat the analysis. When you are done you should have three "good runs" using an acceptable volume of titrant.
5. Now pass your water sample (enough for three more runs) through the Brita water filter.
6. Perform the titration again (three more runs) on the filtered sample.

TREATMENT OF THE DATA

1. If you had to prepare your own standard Na_2EDTA solution, determine its exact molarity from your mass of Na_2EDTA and total volume of solution.

The molar mass of Na_2EDTA is $372.24 \text{ g mol}^{-1}$

2. Using the volume of Na_2EDTA titrant and its molarity, calculate the moles of Na_2EDTA used.

This is the same as the number of moles of Ca^{+2} present since the titrant and the metal ion(s) react in a one-to-one stoichiometry.

3. Using the moles of Ca^{+2} above and the molar mass of CaCO_3 calculate the number of mg of CaCO_3 in the water sample. This, of course, assumes that all of the Na_2EDTA reacted with Ca^{+2} , which is the standard reporting method for water hardness.

4. Take the density of the water sample to be 1.00 gram/ml and calculate the water hardness in ppm of CaCO_3 which is equivalent to mg CaCO_3/kg (or mg per liter) of water. Report the mean value and its 95% confidence limit.

5. Calculate the water hardness of the filtered water in ppm as the mean and its 95% confidence limit.
6. Include in the report how Brita and other water filtration units work. An important component of these filtration systems is ion-exchange resin. What is it, are there different types? How do they work.? Rationalize your data with this background knowledge in mind.

QUESTIONS

1. When Mg-EDTA is added to a sample to compensate for a lack of Mg^{+2} , why is no blank correction necessary?
2. Report the minimum pH for an effective titration of the following metal ions with EDTA.
 - a. Ca^{+2}
 - b. Fe^{+2}
 - c. Ga^{+3}

Why do different metal ions have different minimum pH requirements for titration?

