

Hard Water Ion Concentration in Natural or Drinking Water

If you've ever lived in a place with a hard water supply, you've probably noticed a white scale build up around faucets and at the bottom of tea kettles. This is a mineral deposit, which is the result of hardness ions in the water precipitating out. Hardness specifically refers to the concentration of calcium and magnesium cations, which are introduced when groundwater passes through mineral-rich deposits such as limestone (which is made of calcium carbonate) or gypsum (which is calcium sulfate dihydrate).

Surface water (which comes from sources like lakes and rivers) and atmospheric water, on the other hand, are examples of "soft" water – that is, they tend to have lower concentrations of calcium and magnesium. The hardness of tap water therefore varies depending on the local water source, which is part of why water tastes differently in different cities.

Although hard water can taste unpleasant, it does not pose a health risk. In fact, calcium and magnesium ions are both essential nutrients. These ions are essential for many enzymes to perform their biological function and for cells. For example, an IV of calcium gluconate is given to help stabilize cardiac cells.

In order to determine the hardness of your water or IV solution sample, you will titrate a sample of water, in the presence of an indicator, with EDTA.

The indicator used in this titration is called Calmagite (CAL). CAL appears blue on its own. However, when CAL encounters free calcium or magnesium ions in solution, it forms the wine-red complex $M(CAL)^{2+}$.

We can write the equation for the metal complexing with Calmagite indicator as follows:



As EDTA is titrated into the sample, it will chelate the metal ions from the indicator to form the more stable complex, as shown in Figure 1. When all of the hardness ions have complexed with EDTA the solution will turn blue, since there will be no more free calcium or magnesium ions for the indicator to form a complex with.

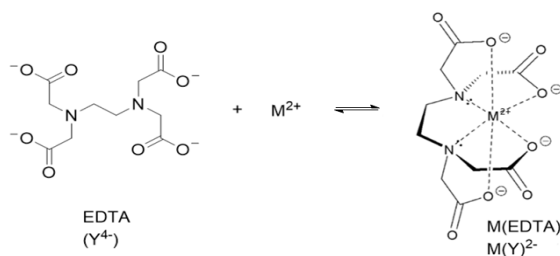
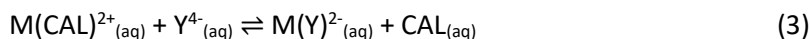


Figure 2. Complex formed by EDTA with a metal ion in the 2+ oxidation state, such as calcium or magnesium.

We can simplify the equation for the metal complexing with EDTA as follows:



Thus, the overall equation for the titration can be written as:



The formation constant, or K_f , for EDTA with ions in the 2+ oxidation state is extremely high (5.01×10^{10} with calcium and 4.90×10^8 with magnesium) compared to the formation constant for Calmagite with the same ions (4.4×10^3 with calcium, for example).¹ This explains why the $M(Y)^{2-}$ complex is strongly favored over the $M(CAL)^+$ complex.

This week, the titration will be monitored using spectrophotometry, allowing for a more precise determination of the equivalence point.

More About EDTA

Ethylenediaminetetraacetic acid, or EDTA, is a type of molecule known as a chelating agent, meaning it has the ability to bind to metal ions through two or more bonds, forming a stable and water-soluble complex. The verb “chelate” comes from the Ancient Greek word for claw (χηλή, khēlē), owing to the pincer-like behavior of these molecules. EDTA in particular is a hexadentate chelator, meaning it forms six bonds with a metal ion such as calcium or magnesium. EDTA is used in medicine to treat mercury and lead poisoning (among other things) by forming a stable complex with the metals which can then be flushed from the body.

¹ <https://www.chem.uci.edu/~unicorn/M3LC/handouts/Week7/calmagite.pdf>

Procedure

Measure 2.0 mL of your water sample using a micropipette and place into a cuvette with several drops of CAL indicator and mix by inversion. Add 0.5 mL pH 10 buffer. Test the pH of your sample with alkacid paper. Set the spectrophotometer to measure absorbance at 610 nm, and blank with a sample of your water (without indicator). Titrate your sample of water with 0.00500 M EDTA. First use increments of 50-100 microliters of EDTA, mixing by inversion and recording the absorbance between each addition. When the absorbance first shows a significant increase, reduce your increments to 10 microliters. When the absorbance stops increasing, take another three to four measurements in 15 microliter increments. Plot your data as absorbance versus volume of EDTA. Determine the volume and moles of EDTA required to reach the endpoint of the titration. Use this information to determine the hardness ion concentration of your sample in ppm.

Writing Your Report

Calculations

1. Determine the total hardness ion (molarity) in mol hardness ions/L water
2. Calculate the concentration of hardness ions in ppm (parts per million)

Results

Include an annotated plot from your titration.

Report the concentration of hardness ions in mol/L and ppm.

Questions

1. Suppose the pH was not adjusted to 10 and instead was a pH of 2, how would this affect the titration?
2. If the concentration of calcium ion in water was 5.00×10^{-3} M and the concentration of carbonate ion was 4.00×10^{-4} M, would a precipitate form? (You will need to look up the K_{sp} value for calcium carbonate). Make sure to show all your work.