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EDTA determination of water hardness using calmagite

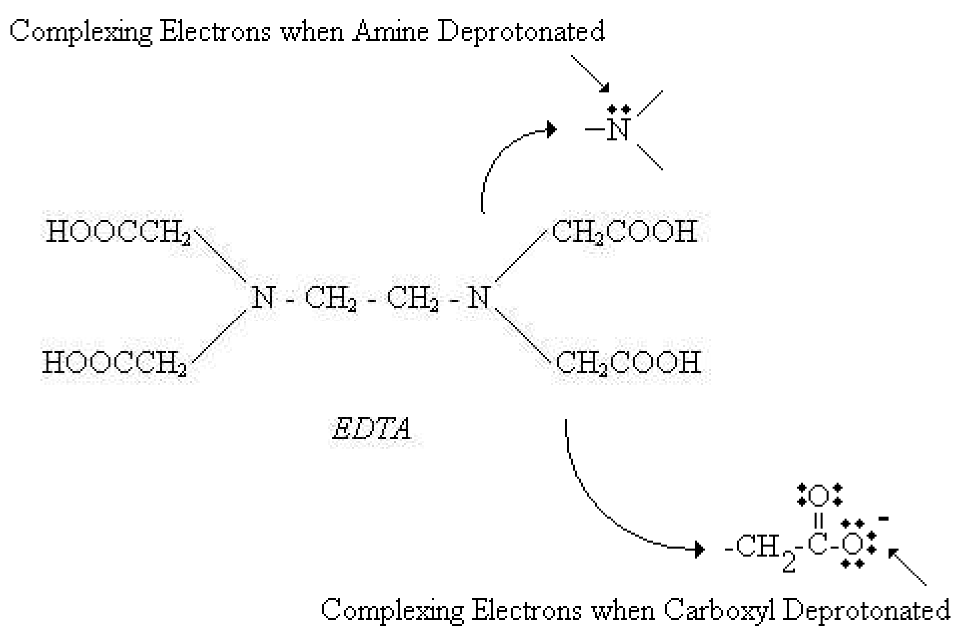
Introduction:

Most metal ions react with electron-pair donors to form coordination compounds or complexes. The donor species, or ligand, must have at least one pair of unshared electrons available for bond formation. Water, ammonia, and halide ions are common inorganic ligands. The number of covalent bonds that a cation tends to form with electron donors is its coordination number. A ligand that attaches to a metal ion through more than one donor atom is said to be multidentate or a chelating ligand and the complex formed usually called chelate.

Complexometric titration is a form of volumetric analysis in which the formation of a colored complex is used to indicate the end point of a titration. Complexometric titrations are particularly useful for the determination of a mixture of different metal ions in solution. An indicator capable of producing a color change at the end point is usually used.

In theory, any complexation reaction can be used as a volumetric technique provided that:
1. The reaction reaches equilibrium rapidly after each portion of titrant is added.
2. Interfering situations do not arise. For instance, the stepwise formation of several different complexes of the metal ion with the titrant, resulting in the presence of more than one complex in solution during the titration process.
3. A complexometric indicator capable of locating equivalence point with fair accuracy is available.
In practice, the use of EDTA as a titrant is well established.

EDTA, ethylenediaminetetraacetic acid a hexadentate ligand (H_4Y), has four carboxyl groups and two amine groups that can act as electron pair donors, or Lewis bases. The metal ion is usually held in a (1:1) complex with the EDTA molecule.



EDTA is the most important chelating agent in analytical chemistry, its used for the determination of the metal ion contents in different samples.

In this experiment, we will analyze an unknown drinking water samples for their total hardness. Calcium, along with Magnesium, is one of the major cations present in Tap Water. The concentration of Calcium plus Magnesium is generally referred to as the "total hardness" of the water. While both metals are nutrients that are needed for good human health, high concentrations of these cations (Ca^{2+} and Mg^{2+}) in water can cause deposits to form in bathrooms and kitchens, and cause the formation of "soap scum." Therefore, very "hard" water is undesirable for use as Tap Water.

EDTA is usually standardized against a standard solution of calcium (II) ion prepared by dissolving reagent grade calcium carbonate in hydrochloric acid and boiling to remove most of the carbonic acid as carbon dioxide.

$$CaCO_3(s) + 2H^+ \leftrightarrow Ca2^+ + H_2O + CO_2 \quad \text{Equation 1}$$

The titration in equation 2 is performed by buffering the solution at pH 10. This permits the calcium-EDTA chelates to form stoichiometrically, along with a sharp indicator change. The breakup of the wine-red magnesium-Calmagite chelate (equation 3) coincide with the equivalence point.

$$2H_2Y^{2-} + Ca^{2+} + Mg^{2+} \leftrightarrow CaY^{2-} + MgY^{2-} + 4H^+ \quad \text{Equation 2}$$

$$H_2Y^{2-} + \underset{\text{(wine-red)}}{MgIndic^-} \leftrightarrow MgY^{2-} + \underset{\text{(blue)}}{HIndic^{2-}} + H^+ \quad \text{Equation 3}$$

Precaution are necessary to prevent traces of metal ions, such as iron (III), copper (II), and aluminum (III), from irreversibly forming complexes with the Calmagite and preventing a sharp color change. The ammonia pH 10 buffer is always added before the indicator to tie up iron (III) and aluminum (III) in unreactive forms.

The distilled water should be tested for appreciable concentrations of these ions, and deionized if necessary. Titration flasks should be scrupulously cleaned to remove traces of these ions also.

Reagents:

- To be prepared by the technician:
  1. pH 10 ammonia buffer.
  2. Dilute, aqueous solution of Calmagite.
- To be prepared by the students:
  1. **EDTA solution:** Prepare 0.01 M EDTA titrant by dissolving about 1.9 g of the reagent grade disodium salt ($Na_2H_2Y.2H_2O$, molecular weight 372 g/mole) in 500 ml of distilled water. Add about 0.5 g of sodium hydroxide and about 0.1 g of magnesium chloride $MgCl_2.6H_2O$. Mix well. Store in a Pyrex bottle.
     Note: Magnesium (II) is added to the titrant as magnesium chloride to ensure a sharp end point, since calcium (II) does not form a strong enough chelate with the indicator.
  2. **Calcium (II) standard solution:**Prepare a standard 0.0100 M calcium (II) solution by weighing 0.500 g ±0.2 mg of 99 + % calcium carbonate into 20 ml of distilled water in a 250-ml beaker. pipet about 1 ml of concentrated hydrochloric acid down the side of the beaker, and place a watch glass directly on the top of the beaker, raise it on glass hooks, and evaporate the solution to a volume of about 2 ml to expel most of the carbon dioxide. Add 50 ml of distilled water, transfer the solution to a 500 ml volumetric flask, and dilute it to the mark.

Procedure:

1. Pipet exactly 20 ml of 0.0100 M calcium (II) solution into each of three clean 250-ml flasks, and add about 1-ml of the pH 10 ammonia buffer to each flask. Add enough Calmagite indicator to the first flask to give a wine-red color.
   Notes: possible air oxidation makes it advisable to add the indicator just before titrating. Avoid adding too much indicator because the end point color change will be too gradual.
2. Titrate with 0.01 M EDTA from a 50-ml buret until a color change from wine-red through purple to clear blue is observed. The color change is somewhat slow, so titrant must be added slowly near the end point. Repeat the titration for the remaining two samples. Calculate the molarity of the EDTA, using the 0.0100 molarity of the calcium (II) solution.
3. Determine the hardness of the unknown hard water by pipetting exactly 50 ml of the sample into each of three clean 250-ml flasks. Add 1 ml of ammonia buffer and Calmagite indicator to the first sample and titrate with 0.01 M EDTA from 50-ml buret to a clear blue end point.

Data and calculations:

Name: ___________________________________ID:_________________

Partner's name:________ __________________Date: ______________________

General observations

Color of the solution before adding Calmagite indicator. **……………………….…………**

Color of the solutionafter adding Calmagite indicator. **…………………………………**

Data and results

Part I: Preparation and standardization of EDTA

Mass of calcium carbonate **……………………….…………………..g**

Molecular weight of calcium carbonate. **……………………….…………………..g/mol**

Moles of Ca(II) **……………………….…………………..mol**

Molar Concentration of Ca(II) **……………………….…………………..M**

	Trail #1	Trail #2	Trail #3
Initial volume of EDTA (ml)	………………	………………	………………
Final volume of EDTA (ml)	………………	………………	………………
Net volume of EDTA (ml)	………………	………………	………………
EDTA average volume (ml)		………………	

Molar Concentration of EDTA ………………………………………. M

Sample calculations:

Calculate the average molar concentration of EDTA using the following equation:

At the end point: # moles of Ca(II) = # moles of EDTA

$$V_{Ca(II)}(ml) \times M_{Ca(II)} = V_{EDTA}(ml) \times M_{EDTA}$$

Part II: Determination of Total Hardness of water

Volume of water sample **…………………………..…………………..ml**

	Trail #1	Trail #2	Trail #3
Initial volume of EDTA (ml)	………………	………………	………………
Final volume of EDTA (ml)	………………	………………	………………

Net volume of EDTA (ml) ……………… ……………… ………………

Sample calculation:

Calculate the total hardness (ppm) as if it is $CaCO_3$ using the following equation:

$$\text{Total Hardness} = \frac{V_{EDTA}\,(L) \times \text{avg. } M_{EDTA} \times 100.09\,(g\backslash mol) \times 1000}{V_{sample}\,(L)}$$