EXPERIMENT 9: COMPLEXOMETRIC DETERMINATION OF MAGNESIUM WITH EDTA.

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PURPOSE

Determine the percent of MgO in an unknown sample of magnesium sulfate.

THEORY

Most metal ions react with electron-pair donors to form coordination compounds or complexes. The donor species or **ligand**, which acts as a **Lewis base**, must have at least one pair of unshared electrons available for bond formation. The **metal ion** accepts the pair of electrons and acts as a **Lewis acid**. As a coordinate covalent bond is formed in the process, the resulting species is referred to as a **coordination compound**.

Cyanide ion, water, and ammonia are said to be **monodentate ("one-toothed") ligands** because they bind to the metal ion through only one atom. A **multidentate ligand** also called a chelating ligand, binds to the metal ion trough more than one ligand atom. A **chelate** is a cyclic complex formed when two or more donor groups from a single ligand bond to a cation.

Titrimetric methods based upon the formation of a complex (sometimes called complexometric methods) have been used for more than a century. But the truly remarkable growth in their analytical application began in the 1940's with the use of chelates. As titrants, multidentate ligands, particularly those having four or six donor groups, have two advantages over their unidentate counterparts: first, they react with metal ions in a single step process, and second, their reaction with cations is more complete, providing sharper end points. For these reasons, multidentate ligands are ordinarily preferred for complex titrations.

Ethylenediaminetetraacetic acid, EDTA, is by far, the most widely used chelating agent in analytical chemistry. By direct titration, or through an indirect sequence of reactions, virtually every element can be analyzed with EDTA. Its structure is shown in **Figure 1**:

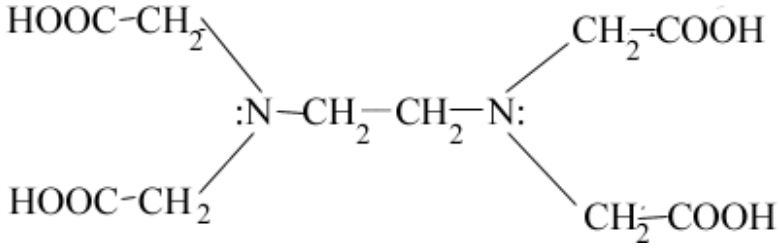

Figure 1: EDTA Structure

True EDTA molecules have six potential sites for bonding a metal ion: the four carboxyl groups and the two amino groups; thus, EDTA is a **hexadentate ligand**. The various EDTA species are often abbreviated H_4Y, H_3Y^-, H_2Y^{2-}, HY^{3-}, and Y^{4-}. Their relative amounts vary as a function of pH. Only at pH values greater than 10 does Y^{4-} become a major component in solution.

The free acid, H_4Y, and the dihydrate of the sodium salt, $Na_2H_2Y{\bullet}2H_2O$, are commercially available in reagent grade quality. Under normal conditions, the dihydrate contains 0.3% moisture in excess of the stoichiometric amount. This excess is sufficiently reproducible to permit the use of a corrected mass of the salt in the direct preparation of a standard solution.

EDTA combines with metal ions in a 1:1 ratio regardless of the charge of the cation. The reaction gives rise to a cage-like structure in which the cation is effectively surrounded and isolated from solvent

molecules. The chelates produced are very stable as a result of the several complexing sites within the molecule. The structure of the complex is shown in Figure 2:
The magnesium titration should be performed at pH values above 9.5 in order to minimize the competition between the metallic and H^+ ions for the ligand. The general reaction may be depicted as:

$$H_xY^{x-4} + Mg^{2+} \rightarrow x\,H^+ + MgY^{2-}$$

EDTA species chelate complex

In this analysis, a metalochromic (metal ion indicator), like eriochrome black T or calmagite, whose color changes when it binds to a metal ion, will be used. For the indicator to be useful in an EDTA titration, it must bind to the metal ion less strongly than EDTA. This indicator is an organic dye that is also an acid-base indicator. Because the color of the free indicator is pH dependent, it can be used only in certain pH ranges. The reaction process may be depicted as follows:

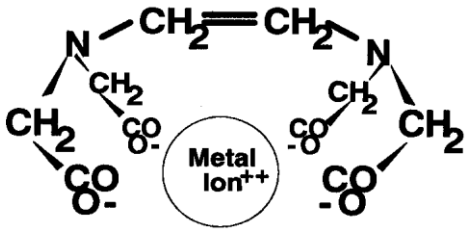

Figure 2: Magnesium-EDTA Complex

MgIn	+	EDTA	→	MgEDTA	+	In
(red)		(colorless)		(colorless)		(blue)

At the beginning of the experiment, a small amount of the indicator (*In*) is added to the colorless solution of Mg^{2+} to form a red *MgIn* complex. As EDTA is added, it first reacts with the free, colorless Mg^{2+}. When the free Mg^{2+} is used up, the last EDTA added before the equivalence point displaces the indicator from the red *MgIn* complex. The change from the red *MgIn* to the blue unbound *In* signals the end point of the titration.

PRELABORATORY EXERCISE

1. Why should the unknown magnesium sample be dried above 100°C for three hours?
2. What is the primary standard used?
3. What kind of reaction takes place between the magnesium and the EDTA?
4. At what pH condition is the titration performed? Why?
5. What indicator is used in the analysis? What is its color change?

APPARATUS AND MATERIALS

250 mL volumetric flask
25 mL volumetric pipet
50 mL buret
3-250 mL Erlenmayer flasks
Eriochrome Black T or **calmagite** indicator **(as solid)**

The following solutions <u>will be available in the laboratory</u>:

- Buffer solution pH 10: 57 mL of concentrated NH_3 and 7 g NH_4Cl in 100 mL of solution

EXPERIMENTAL

1. You will be using the disodium salt of EDTA (M.W. = 372.24 g/mole). It has been dried for 1 week at 80°C to drive off any superficial moisture. It is in the TA desiccator. Be sure to return it to the desiccator when you are through with it. Weigh carefully about 0.9 g of EDTA (record to the nearest 0.1 mg). Quantitatively transfer the solid into a 250 mL volumetric flask then add 2-3 mL of pH 10 ammonia buffer. Fill the flask about halfway to the mark with deionized water and swirl to dissolve. This process can take up to 15 minutes. Once dissolved, dilute to the mark and then cap and invert the flask at least 6 times to get a uniform solution. Keep the solution capped.

2. Dry the unknown magnesium sulfate sample for 3 hours at 150 ^{o}C. **(Note: Besides humidity, water of hydration should also be removed).** Cool in the desiccator.

3. Weigh accurately a **1.6 g** sample into a 150 mL beaker. Note: You will get the sample from your TA.

4. Transfer quantitatively into a clean 250 mL volumetric flask. Fill to the mark with distilled water and shake to mix the solution.

5. Using a 25.00 mL pipet, deliver 3 aliquots of the unknown solution into each of three properly labeled 250 mL Erlenmayer flasks. Add 20 ml of distilled water and 10 mL of the buffer solution pH 10 to each.

6. Fill the buret with the standard EDTA solution provided by the instructor. Record its concentration.

7. Heat one of the aliquots between 60 and 80^{o}C. Add a very small amount of the solid indicator, just before the titration. The solution will turn into an intense red color. Titrate with the EDTA solution until the color changes to blue.

Note: The color changes slowly in the vicinity of the end point. Care must be taken to avoid overtitration. If necessary, a small amount of methyl red may be added to the solution as an inert dye to alter colors. In this case, the original solution is red, then changes to yellow, and finally turns into green at the end point.

8. Repeat step 6 with the other two aliquots.

CALCULATIONS

1. Calculate the concentration of your standard EDTA solution.
2. Using the volume of EDTA required for each titration, calculate the moles of MgO present on each aliquot. Remember: the EDTA to Mg and the Mg to MgO stoichiometric ratios are both 1:1.

   Moles EDTA = $(V*M)_{EDTA}$ = moles Mg^{2+} = moles MgO

3. Calculate the grams of MgO (FW = 40.31) present on each aliquot.
4. Remember that only 25.00 ml aliquots of the magnesium solution were titrated, while the original unknown sample was diluted to a total volume of 250.00 mL. Accounting for the dilution (volumetric difference) between the aliguot and the original sample determine the grams of MgO in the original sample.
5. Divide the MgO from each trial by the mass of unknown magnesium sulfate sample and determine the individual %MgO for each trial.
6. Determine the average % MgO, and the relative standard deviation in parts per thousand.

QUESTIONS

1. What are the sources of error in this experiment?
2. What would happen if tap water is used instead of distilled water to dilute your sample?
3. Why does the rate of the reaction decrease near the end point?
4. Explain why the change from red to blue in the experiment occurs suddenly at the equivalence point instead of gradually throughout the entire titration.
5. What would happen if you add an excess of indicator?
6. A 100.00 mL sample of 0.050 M Ca^{2+} solution buffered to pH 9.0, was titrated with 0.050 M ^{ED}TA:
   a. What is the stoichiometry of the reaction?
      a. What is the equivalence volume in milliliters?
7. What is meant by water hardness?
8. Describe what is done in a complexometric titration.