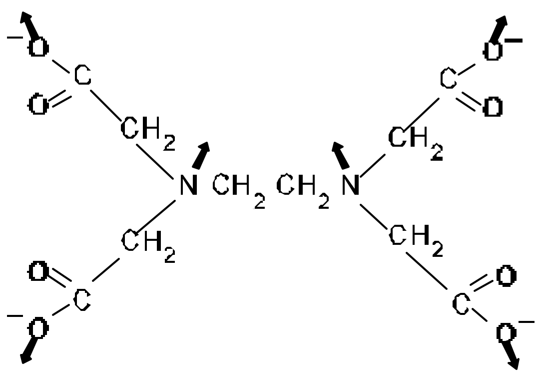
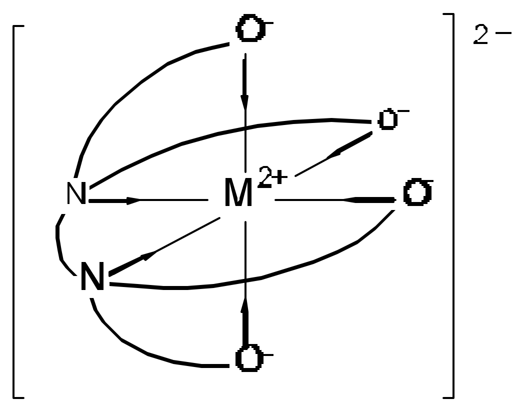
COMPLEXIMETRIC DETERMINATION OF MAGNESIUM OXIDE USING EDTA

DISCUSSION: ***E***thylene***d***iamine***t***etra***a***cetic acid (EDTA), can act as a hexadentate ligand, coordinating to a metal ion simultaneously through six donor sites. In doing so, it engulfs the metal ion forming an extremely stable complex, as shown below. Each ligand donor site is an atom with one or more electron-pairs which can be shared with the metal ion. EDTA serves best as a ligand when it is in the fully ionized state, bearing a 4 ! charge, the result of losing its four ionizable hydrogens. Though EDTA is a weak acid, complex formation drives the ionization process. The structural formula of the tetraanion of EDTA, ethylenediaminetetraacetate, is shown below. Each of the six coordination sites is indicated with an arrow, implying its ability to serve as an electron pair donor, that is, as a Lewis base.



Ethylene**d**iamine**t**etra**a**cetate ($EDTA^{4!}$)



$EDTA^{4!}$ coordinated to M^{2+} engulfing the ion

The tetraanion, $EDTA^{4!}$, for simplicity, is frequently abbreviated as $Y^{4!}$ in chemical equations. Because $EDTA^{4!}$ forms extremely stable complexes, it is a ligand of choice to form complexes with metal ions that do not readily form stable complex ions, such as Mg^{2+}, Ca^{2+}, and Zn^{2+}. In addition, the size of the metal ion can affect the stability of an EDTA complex. Because Ca^{2+} is just a little larger than Mg^{2+}, (having an ionic radius of 1.14 Å versus 0.86 Å for Mg^{2+}) it forms a *more stable* EDTA complex as indicated by its higher formation constant. The size of the "cavity" formed by the EDTA ligand accommodates the larger calcium ion better than the smaller magnesium ion. This fact is used to our advantage in the compleximetric titration of Ca^{2+}, as will be described later.

The formation of a metal-EDTA complex is rapid and occurs, essentially, in a single step. This allows the formation of the complex to be represented in a single (one-step) equation:[1]

$$M^{2+}_{(aq)} + \underset{\text{the dihydrogen EDTA anion}}{H_2Y^{2-}_{(aq)}} \rightarrow \underset{\text{the EDTA-metal complex}}{[MY]^{2-}_{(aq)}} + 2\,H^{+}_{(aq)}$$

High complex stabilities and rapid coordination reactions produce sharp end points when metal ions are titrated with EDTA.

Calmagite and Eriochrome Black T (Erio T®) are coordinating dyes which form weak, but colored, complexes with metal ions. They serve as indicators in compleximetric titrations, since the color they display when coordinated to a metal is different from that when free in solution. Both indicators can be abbreviated as HIn^{2-}.

$$H^{+}_{(aq)} + \underset{\substack{\text{magnesium-indicator complex} \\ \text{(red)}}}{[MgIn]^{-}_{(aq)}} \rightleftharpoons \underset{\substack{\text{compleximetric indicator} \\ \text{(blue)}}}{HIn^{2-}_{(aq)}} + Mg^{2+}_{(aq)}$$

The compleximetric titration of either magnesium or zinc ion proceeds smoothly with an easily observed end point. However, Ca^{+2} is a bit more troublesome. Its titration exhibits a sluggish end point with Calmagite which does not correspond well with the equivalence point. With calcium ion, the replacement of the coordinated indicator with $EDTA^{4-}$ proceeds too slowly to allow a sharp end point. The following equation is typical of this kind of ligand-exchange process. It is *slow* with Ca^{2+} but *fast* with Mg^{2+}.

$$\underset{\text{(red)}}{[Ca(In)]^{-}_{(aq)}} + H_2Y^{2-}_{(aq)} \rightarrow [CaY]^{2-}_{(aq)} + \underset{\text{(blue)}}{In^{3-}_{(aq)}}$$

This problem is alleviated by adding a small amount of Mg^{2+} to the EDTA solution, the titrant, to form $[MgY]^{2-}$. As the titrant is added to the calcium ion solution, two things happen: First, as the EDTA enters the solution it quickly forms a complex with Ca^{2+}.

$$Ca^{2+}_{(aq)} + H_2Y^{2-}_{(aq)} \rightarrow [CaY]^{2-}_{(aq)} + 2\,H^{+}_{(aq)}$$

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1 The actual form of the EDTA anion, Y^{4-}, HY^{3-}, H_2Y^{2-} or H_3Y^{-}, will depend upon the pH of the solution it is in.

Second, as the magnesium-EDTA complex enters the solution (simultaneously with the uncomplexed EDTA), the following reaction quickly occurs between the magnesium-EDTA complex and Ca^{2+}. Remember, $[CaY]^{2-}$ is more stable than the magnesium complex, $[MgY]^{2-}$ which drives the ligand-exchange reaction to the right.

$$Ca^{2+}{}_{(aq)} + [MgY]^{2-}{}_{(aq)} \rightarrow [CaY]^{2-}{}_{(aq)} + Mg^{2+}{}_{(aq)}$$

You might think initially that adding another complexing metal ion, Mg^{2+}, to the solution would introduce an error, giving a Ca^{2+} content greater than the true value. But, this is not a problem. For each Mg^{2+} released into the solution, one very stable CaY^{2-} is formed, *and removed from further reaction*. In its place is the magnesium ion which can now complex with EDTA just as would the calcium ion. So, for each Ca^{2+} taken out, one Mg^{2+} takes its place. Near the end of the titration when all the calcium ion is tied up as the EDTA complex, only Mg^{2+} (coordinated to the indicator dye) is left to react with EDTA. Since Mg^{2+} exchanges the dye for EDTA more rapidly, it allows a much sharper end point to be observed than would have been observed with Ca^{2+}. The reaction at the end point, which now coincides with the equivalence point is then

$$\underset{\text{red}}{[MgIn]^{-}{}_{(aq)}} + H_2Y^{2-}{}_{(aq)} = [MgY]^{2-}{}_{(aq)} + \underset{\text{blue}}{HIn^{2-}{}_{(aq)}} + H^{+}{}_{(aq)}$$

and the color change from *red to blue* occurs quickly, signaling the end of the titration. Since the stoichiometric ratio of EDTA to metal ion is 1 to 1, the number of mole of EDTA added in the titrant equals the number of mole of metal ion.

REAGENTS:

0.025 M EDTA (approximate) Weigh approximately 7.5 g of disodiumdihydrogenethylenediaminetetraacetate dihydrate, $Na_2H_2EDTA \cdot 2\,H_2O$, (FW = 372) into a one-liter glass stoppered bottle or large acid bottle. Add to this approximately 0.3 g $MgCl_2 \cdot 6\,H_2O$ and 1 g NaOH (about 8 to 10 pellets). The NaOH will increase the pH of the solution from 5 to 10, increasing the solubility of Na_2H_2EDTA. Add 750 mL of deionized water to this mixture and shake until *all is dissolved*. Continue shaking for five minutes to insure homogeneity. Check the pH of the solution with universal pH paper and, if the pH is not 10, add more NaOH. Once pH 10 is achieved, add two additional pellets of NaOH to bring the pH to approximately 11.

0.02 M $CaCO_3$ Standard Dry a sample of primary-standard $CaCO_3$ for 1 to 2 hours at 110°C. Cool in a desiccator for 40 minutes. Weigh out accurately (to four decimal places) about 0.5 g of $CaCO_3$ and quantitatively transfer the mass to a *calibrated* 250.0 mL volumetric flask using a powder funnel.

> NOTE: You may assume that a "class-A" volumetric flask is calibrated, but if you are not certain of this, or do not have a class-A flask, one may be calibrated as follows: Using a clean class-A volumetric 50-mL pipet, carefully transfer 5 aliquots of tap water to the clean and dry 250 mL volumetric flask. Mark the location of the meniscus with fine line drawn on a label if different from the etched line. When filled to this mark, an aliquot taken with the *same* 50 mL pipet will constitute one-fifth of the total sample.

Use 5 to 10 mL of deionized water to rinse any residual $CaCO_3$ from the funnel into the flask, making certain that the entire mass of $CaCO_3$ is on the flask bottom. Slowly add up to 4 mL of concentrated HCl (the less the better) to dissolve the solid. Swirl the flask periodically. If the solid is slow to dissolve, warm the flask in a water bath, but do not heat the flask directly. Do not stopper the flask until the $CaCO_3$ is completely dissolved. Dilute the resulting solution to volume with deionized water and ensure the solution is homogeneous by thoroughly shaking and inverting the stoppered flask. Calculate the molarity of $CaCO_3$ to the fifth decimal place, that is, to four significant figures.

pH 10 Buffer Dissolve 6.8 g of ammonium chloride, NH_4Cl, in 25 mL of deionized water contained in an 8 ounce, screw-cap bottle,. To this add 57 mL of concentrated aqueous ammonia and dilute to approximately 100 mL.

6 M NaOH Dissolve 2 g of NaOH pellets in 10 mL of deionized water in a 4 ounce, screw-cap bottle.

EXPERIMENTAL PROCEDURE:

Standardization of EDTA Solution

The standardization will be done in triplicate. *Each sample must be prepared and titrated immediately before preparing the next sample for analysis*. Pipet 50.0 mL of the $CaCO_3$ standard into a 500 mL Erlenmeyer flask, and add 1 *small* drop of methyl red indicator. Add 6 M NaOH drop-wise, with stirring, until the solution becomes yellow. N Add 10 mL of pH 10 buffer and 20 drops of Calmagite indicator. Titrate with the EDTA solution to the *red to blue* color change. The end point is that point at which the last trace of red has *just* disappeared. A purple solution will be observed just prior to the end point; however, neither red nor purple should be visible at the end point. Calculate the molarity of the EDTA solution in each trial to the *fifth* place after the decimal.

Titration of Magnesium in an Unknown Sample

> Since the end point in this titration is easier to see than that in the EDTA standardization, you may want to perform this analysis first.

Weigh out accurately to four decimal places about 1.7 g of magnesium unknown (dried from 1 to 2 hours at 110°C) and quantitatively transfer it to a *calibrated* 250.0 mL volumetric flask using a powder funnel. Add 100 mL of deionized water to the flask, rinsing the funnel into the flask, and shake the mixture until the solid is completely dissolved. Dilute this solution to the mark with deionized water and ensure homogeneity by thoroughly shaking and inverting the stoppered flask. Pipet 50.0 mL of this solution into a 500 mL Erlenmeyer flask and proceed as above starting at the N with the addition of the buffer. (Since acid is not used to dissolve the unknown, neither the methyl red nor base is needed here.) Report the percentage of MgO in the sample.

CALCULATIONS: The titration equation given below can be used to calculate the exact molarity of the EDTA solution.

$$V_{CaCO_3} \times M_{CaCO_3} = V_{EDTA} \times M_{EDTA}$$

The percentage of MgO is the mass of MgO in the sample divided by the mass of the sample itself, times 100%. The mass of MgO equals the number of mol of MgO (which is identical to the number of mol of EDTA) times its formula weight, 40.30. The following equation illustrates this calculation

$$\%\ MgO = \frac{V_{EDTA\ (in\ mL)} \times M_{EDTA} \times \left(\frac{(FW\ MgO)}{1000}\right)}{(mass\ of\ entire\ sample \div 5)} \times 100\%$$

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here the mass of the sample is that in one aliquot (one-fifth) of the solution of the unknown. Report 3 or 4 significant figures so you have two decimal places. The expected tolerance is ±0.3%.

REPORT SHEET: COMPLEXIMETRIC DETERMINATION OF MAGNESIUM OXIDE USING EDTA

Name ____ Date: ___________________
Please print; last name first
Sample Number ___________________

Preparation of the 0.02 M $CaCO_3$ Standard	
mass of weighing paper + sample:	
mass of weighing paper:	
mass of $CaCO_3$ sample:	
final solution volume, mL:	
Molarity of $CaCO_3$ Standard:	

Standardization of the EDTA Solution

	Trial 1	Trial 2	Trial 3
final buret reading (EDTA):			
initial buret reading (EDTA):			
volume of EDTA :			
volume of $CaCO_3$:			
Molarity of EDTA:			

Average Molarity of EDTA ± s.d.: ____

(continues on the following page.)

Analysis of the Magnesium Unknown

mass of weighing paper + sample:			
mass of weighing paper:			
mass of MgO unknown sample:			
	Sample 1	Sample 2	Sample 3
final buret reading (EDTA):			
initial buret reading (EDTA):			
volume of EDTA:			
volume of sample aliquot, mL:			
% MgO:			

Average % MgO ± s.d. : ______________________________________

Sample Calculations: Show the calculation of one trial for the standardization of the EDTA solution and for one sample in the analysis of the magnesium oxide unknown.

DETERMINATION OF THE HARDNESS OF WATER

DISCUSSION:

Water from most regions of the United States is regarded as "hard water" as it comes from the ground because of the presence of metal ions, such as Ca^{2+}, Mg^{2+}, Fe^{3+}, or Mn^{2+}. Hardness due to calcium or magnesium, present as bicarbonates, is produced when water containing carbon dioxide trickles through limestone or dolomite, both very common in cave regions. Well water from cave regions tends to be harder than well water from sandy regions.

Hardness in water is objectionable because: a) it causes precipitates (scale) to form in hot water systems, b) it causes soaps to form insoluble curds commonly called soap scum (which is not formed with many synthetic detergents), and c) metal ions, most notably Fe^{3+}, can impart a disagreeable taste to drinking water. Since ethylenediaminetetraacetic acid (EDTA) forms very stable complexes with these ions, it can be used to assay these ion using compleximetric titration. In doing so, a quantitative measure of the hardness of water can be determined.

Hardness can be expressed quantitatively in terms of the milligrams of metal ion per liter of water, or, grouping all the cations together, it can be stated in milligrams of $CaCO_3$ per liter. The unit milligrams per liter, mg/L, is numerically the same as parts per million, ppm.[1] Water low in divalent and trivalent metal ions is considered "soft water." Stated in terms of $CaCO_3$, natural water can be classified as follows:

Soft water:	< 65 ppm $CaCO_3$
Slightly hard:	65 - 228 ppm $CaCO_3$
Moderately hard:	228 - 455 ppm $CaCO_3$
Hard:	455 - 682 ppm $CaCO_3$
Very hard:	> 682 ppm $CaCO_3$

In homes, hard water is softened by removing the 2+ and 3+ metal ions by ion exchange replacing them with Na^{+}. In laboratories, a double ion exchange technique is employed in which *both* cations

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A concentration of 1 part per million means 1 g in 1,000,000 g of sample, a weight-weight term. Milligrams per liter is a weight-volume term, but since the density of tap water is essentially 1.00 g/mL, equating the weight-volume and weight-weight terms does not cause a significant error.

and anions are replaced with $H^+_{(aq)}$ and $OH^-_{(aq)}$ which rapidly combine to form water. Such water is termed "deionized."

REAGENTS:

The reagents required for the analysis of hard water are the same as those used in the previous procedure. Refer to the reagents section in the "Compleximetric Determination of Magnesium Oxide Using EDTA" analysis. You will need:

standard 0.025 M EDTA
methyl red indicator
concentrated $HCl_{(aq)}$
6 M NaOH
pH 10 buffer
Calmagite indicator.

EXPERIMENTAL PROCEDURE:

This procedure will determine the total Ca^{2+} and Mg^{2+} content of water by compleximetric titration with standard EDTA.

Obtain about 500 mL of tap water or water from a natural source. In three clean and dry 250 Erlenmeyer flasks, pipet 100 mL aliquots and acidify each with three drops of concentrated HCl. Boil each gently for a few minutes to expel CO_2.

Cool each sample and add one drop of methyl red, and neutralize the excess $HCl_{(aq)}$ with 6 M NaOH, delivered one drop at a time, to the orange-yellow color of the indicator. Add 2 mL of pH 10 buffer to each sample, and 20 drops of Calmagite indicator. Titrate each sample with standard EDTA to a color change from red to pure blue. The volume of EDTA required to do this will be small.

CALCULATIONS:

Report the results of the water analysis in parts per million of $CaCO_3$. Remember, 1 ppm $CaCO_3$ equals 1 mg of $CaCO_3$ per liter.

$$\text{ppm } CaCO_3 = \left(V_{EDTA} \times M_{EDTA} \times FW_{CaCO_3}\right) \times \text{Sampling Factor}$$

To determine the value of the Sampling Factor, you need to do a unit analysis of the terms within the parentheses of this equation.

$$\left(V_{EDTA\ (in\ mL)} \times M_{EDTA} \times FW_{CaCO_3}\right) = \text{mg } CaCO_3$$

The product of V_{EDTA} (in mL) times M_{EDTA} equals the number of millimole of $CaCO_3$ in the analyzed sample. The number of mmol of $CaCO_3$ times its formula weight expressed as mg/mmol equals the number of mmol of $CaCO_3$ in the analyzed 100 mL volume of water. Since there is a one-to-one stoichiometric relationship between EDTA and Ca^{2+} (1 mmol EDTA Ô 1 meq $CaCO_3$), the unit analysis is:

$$mL_{EDTA} \times \frac{mmol_{EDTA}}{mL_{EDTA}} \times \frac{mmol_{CaCO_3}}{mmol_{EDTA}} \times \frac{mg_{CaCO_3}}{mmol_{CaCO_3}} = mg\ CaCO_3$$

The sampling factor, which is to convert mg $CaCO_3$/100 mL to mg $CaCO_3$/1000 mL, should now be obvious.

REPORT: Submit your results on the Report Sheet for the water analysis at the same time you submit the results of the MgO determination. Be certain to indicate where you obtained the water sample you analyzed, such as, a particular well in Barren County or Owensboro city water.

REPORT SHEET: DETERMINATION OF THE HARDNESS OF WATER

Name ____ Date: _____________
Please print; last name first

Source of water sample: ____

Analysis of the Water Sample			
	Sample 1	Sample 2	Sample 3
volume of water sample, mL:			
final buret reading (EDTA):			
initial buret reading (EDTA):			
volume of EDTA, mL:			
N_{EDTA}:			
ppm $CaCO_3$ in water:			
Average ppm $CaCO_3$ ± std. dev.			

Sample Calculations: Show the complete calculation of one sample in the analysis.