EDTA Titration for Determination of Calcium and Magnesium

Before attempting this experiment, you may need to consult the section in the textbook dealing with complexometric titrations. In this procedure a stock solution of EDTA will be standardized against primary standard $CaCO_3$. This standardized EDTA solution is then used to determine water "hardness" – the total calcium and magnesium content, typically expressed as equivalent calcium carbonate mass concentration. 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” – clogging pipes and decreasing the effectiveness of the cleanser. Therefore, very hard water is undesirable for use as tap water. Guidelines for classification of water as provided by the U.S. Geologic Survey are listed in the table below. The USGS website has more information about water hardness and alkalinity if you are interested. We're fortunate in that most of the water in the Portland area is soft.

Table 1 U.S. Geological Survey Classification of Water Hardness

(Source: http://water.usgs.gov/owq/hardness-alkalinity.html)

$CaCO_3$ (mg/L)	**Hardness**
0-60	soft
61-120	moderately hard
121-180	hard
>180	very hard

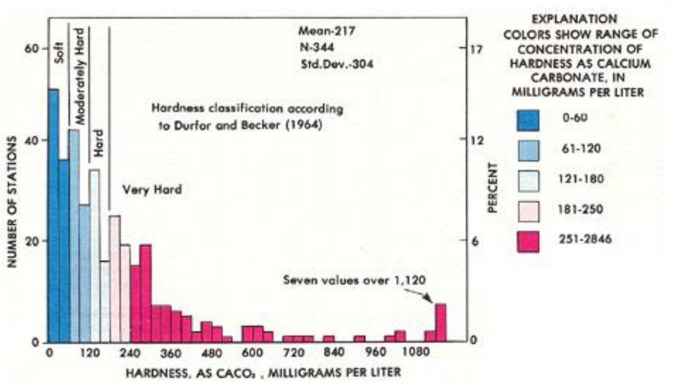


Figure 1 Hardness classification from Briggs et al. 1977

Briggs, J.C., and Ficke, J.F., 1977, Quality of Rivers of the United States, 1975 Water Year -- Based on the National Stream Quality Accounting Network (NASQAN): U.S. Geological Survey Open-File Report 78-200, 436 p.

A complex is a molecule or ion formed from the reaction of two or more individually stable ions or molecules, but the reaction is driven by the electron deficiency of metal ions. The most important complexation reactions from an analytical point of view are those between a metal ion in solution and a complexing agent known as a ligand or chelate. The metal ions are Lewis acids and readily share electron pairs with the electron-donating ligands (Lewis bases). As an example, cyanide (CN^-) binds to a metal ion through a lone pair on one atom and is thus a monodentate (one tooth) ligand. Many transition metal ions will share up to six electron pairs with ligands. A ligand that bonds to a metal ion using more than one ligand atom is called a multidentate (many toothed) ligand or a chelate (or sometimes a chelating agent).

In a complexometric titration, a solution containing the free metal ion of interest is titrated with a solution of a chelating agent until all of the metal ions are bound. The endpoint is usually signaled by an indicator ligand that forms a colored complex with the free metal ion.

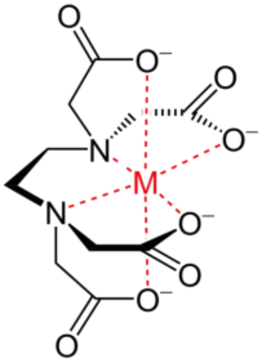
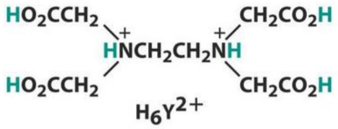


Figure 2 EDTA – a chelate used by industry and analytical chemists

The most important chelating agent in analytical chemistry is ethylenediaminetetraacetic acid (EDTA). EDTA is a hexadentate ligand (Figure 2) and can exist as a hexaprotic acid H_6Y^{2+} although the neutral form is tetraprotic (all of the pKa values are listed in Figure 3).



$pK_1 = 0.0\ (CO_2H)$ $pK_4 = 2.69\ (CO_2H)$
$pK_2 = 1.5\ (CO_2H)$ $pK_5 = 6.13\ (NH^+)$
$pK_3 = 2.00\ (CO_2H)$ $pK_6 = 10.37\ (NH^+)$

Figure 3. Top: structure o EDTA acidic form; bottom: pK_a values

(source: D. C. Harris Quantitative Chemical Analysis 8th Ed)

The most basic form of EDTA (Y^{4-}) forms complexes with virtually all metal ions, except the alkali metals. EDTA always complexes metals with 1:1 stoichiometry.

Unfortunately EDTA cannot be easily used as a primary standard. The H_4Y form can be dried at 140°C for 2 hrs and used as a primary standard, but is only sparingly soluble in water. The reagent-grade $Na_2H_2Y_2 \cdot 2H_2O$ contains 0.3% excess water and must be dried at 80°C for several days to remove the excess water and obtain the dihydrate. Standardization of EDTA against a primary standard metal ion (in this case, the one to be determined) is easier and more reliable.

The electron pairs of the carboxylic acid groups of EDTA are only available to the metal ion when the acid is dissociated, implying that the effectiveness of the complexing agent is maximized at high pH. Unfortunately many metal ions form complexes or insoluble precipitates with hydroxide ions, so for a given chelating agent and metal ion, there may be an optimum pH for the titration. In the case of EDTA titrations of calcium and magnesium there is little chance of reaction with hydroxide and the effectiveness of the EDTA must be maximized, so the pH is buffered at a high value, near 10.

Calmagite (3-hydroxy-4-(2-hydroxy-5-methylphenylazo) naphthalene-1-sulfonic acid) earns its name by serving as the indicator of choice for this titration, but it is necessary to add a small amount of Mg^{2+} to obtain a sharp end point. This necessitates a blank titration to separate the contribution from the added magnesium.

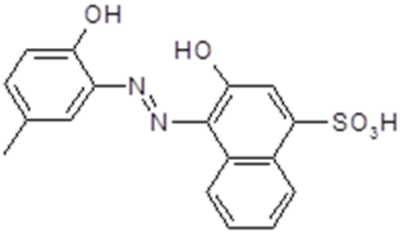


Figure 4. Calmagite structure

In the titration EDTA forms a weaker complex with Mg^{2+} than Ca^{2+}, so Y^{4-} reacts with Ca^{2+} first, leaving the red $MgIn^-$ solution

$$Ca^{2+} + MgIn^- \text{ (red)} + Y^{4-} \leftrightarrows CaY^{2-} + MgIn^- \text{ (red)}$$

When all the Ca^{2+} is bound by Y^{4-}, MgIn- reacts with Y^{4-} to release the indicator

$$MgIn^- \text{ (red)} + Y^{4-} \leftrightarrows MgY^{2-} + In^{3-} \text{ (colorless)}$$

In^{3-} which then hydrolyzes to produce the color change that signals the endpoint of the titration.

$$In^{3-} \text{ (colorless)} + H_2O \leftrightarrows HIn^{2-} \text{ (blue)} + OH^-$$

Standardization of EDTA

Prepare 0.01 M EDTA solution in 0.16 M Sodium Glycine Buffer: Add approximately 0.88 g of dry disodium EDTA salt and 25 mL glycine buffer solution to about 100 mL of DI water in a 250 mL beaker and swirl periodically. (*Water used in the preparation of standard EDTA solutions must be totally free of polyvalent cations. The volume of the beaker doesn't really matter, it is a container to dissolve the solid.*) Dissolution may take 15 min. or longer, so start this part as soon as possible. If complete dissolution does not occur in 15 min. the solution can be decanted and used, since it will be standardized in the next step, but the remaining solid must be removed to prevent additional dissolution.

Test the pH of the solution using universal pH paper. Ideally, pH should be ≥ 10.3 (if not, consult your TA). Transfer to a 250 mL volumetric flask, dilute to the mark with DI water, and mix well.

Prelab calculation: Calculate the expected molarity of the EDTA solution, correcting the mass of the Na_2H_2Y salt for the 0.3% moisture it ordinarily retains after drying.

Primary standard calcium carbonate should have been oven dried for at least two hours at 110 ºC (Note 1). Weigh (to 0.1 mg) about 0.3 grams of calcium carbonate and transfer to a beaker. Add 25 mL of calcium free DI water, and then slowly add one full Pasteur pipet loading of 6 M HCl with a dropper until all of the calcium carbonate dissolves (Note 2a). Be careful to avoid loss of solution due to rapid foaming or splattering as CO_2 is evolved. Make certain dissolution is complete - undissolved solid may stick to the upper wall of the flask and very small particles are difficult to see. Warm the solution gently (Note 2b). Then cool and transfer quantitatively to your calibrated 250 mL volumetric flask. Fill to the mark with DI water and mix well. Calculate the molar concentration of calcium.

Pipet 25.00 mL aliquots of the standard calcium solution into three 250-mL Erlenmeyer flasks. **Right before titrating**, add 1.00 mL of 0.001 M magnesium solution ($MgCl_2$) and 4.0 mL Calmagite indicator solution. (Note 3) Titrate with EDTA until the color changes to a clear blue. There should be no reddish or purple tint at the end point.

In the above titrations, magnesium was added in order to obtain a sharper color change at the end point. However, EDTA reacts with magnesium in exactly the same way as it does with calcium. It is therefore necessary to subtract the volume of EDTA required to titrate the added magnesium. This is called an **indicator blank**. Repeat the titration with EDTA exactly as above; but substitute 25 mL of DI water for the standard calcium solution. This titration will require very little titrant. Repeat the blank determination three times or more until you are confident of the volume. You will subtract the mean of **the blank volume measurements** from all titrations in which calcium was present. With the results above, you can now calculate the concentration of your standardized EDTA solution.

Determination of Water Hardness

Measure out 100 mL aliquots of the hard water sample using a volumetric pipet into three 250-mL Erlenmeyer flasks. To each sample, add the magnesium solution and the Calmagite indicator as above. (Note 3) Titrate with the standardized EDTA solution. Correct the volume of titrant by subtracting the indicator blank. Calculate the molar concentration of "calcium" in the hard water sample.

It is common practice to report water hardness in terms of the number of milligrams of $CaCO_3$ *per liter. That is, regardless of the form of the calcium (or whether it even was calcium, since magnesium would be indistinguishable) we calculate the result as if all of the material that reacted with EDTA was calcium carbonate. This is a common analytical practice. For example, you will see the phosphates in fertilizer reported as phosphoric acid.*

REQUIRED MEASUREMENTS

At the end of the period, you must present the results for the standardization of the EDTA and for the calcium content (hardness as mg $CaCO_3$ per liter) of the hard water to your lab TA before leaving. The results include the mean, standard deviation, and relative standard deviation (in ppth) of your replicate determinations.

Sample Results Table

	Concentration	Stdev	RSD (‰)
EDTA (M)			
Hardness (mg/L)			

NOTES

1) Standard operating procedure is to dry for one hour at 110 ºC. However, in a lab with many students opening and closing the oven, the temperature will drop. Please replace the solid and close the oven when you are done dispensing and do not use the solid if it has been out of the oven for more than a minute or two.

2a) Ideally you should add the minimum amount of HCl needed to dissolve the $CaCO_3$. If you add too much HCl, then the glycine buffer in the EDTA titrant will not work properly – i.e. we have to keep the pH near the endpoint of the titration at or slightly above 10. This is important

because reactions between metal ions and EDTA are pH dependent - for divalent ions solutions must be kept basic for the reaction to go to completion.
Buffer range of the glycine/NaOH: 8.6-10.6
Calmagite indicating pH: 8.5-11 for Ba, Ca, Mg, Zn

2b) "Warm" means just that. Not hot, and certainly not boiling! The acidification and heating step is to remove carbonates; which if present, will precipitate $CaCO_3$ when the solution is made basic. The precipitate obscures the end point.

3) Always use the same bottle of magnesium solution and Calmagite indicator!

Last update: Oct. 2015