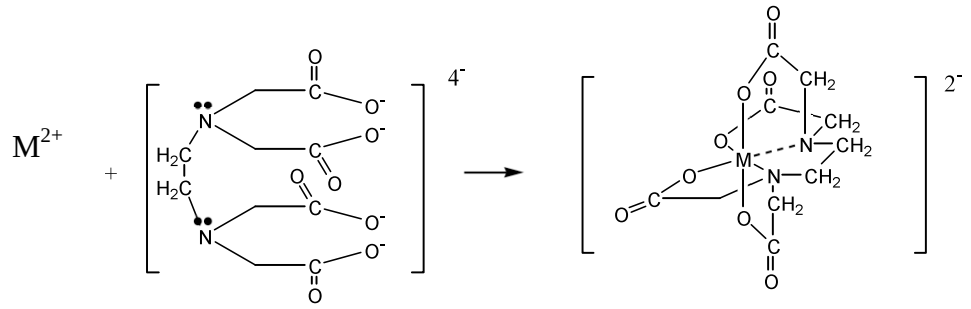
# EXPERIMENT 1: HARDNESS OF WATER BY EDTA TITRATION

## INTRODUCTION

Water 'hardness' is a measure of the amount of hard water cations in water. These hard water cations include calcium, magnesium, iron, zinc and the other polyvalent metal ions. In most water samples, calcium and magnesium are the chief contributors to water hardness.

Calcium and magnesium are easily measured by titration with the complexing agent ethylene-diaminetetraacetate (EDTA). The EDTA complexes the $Ca^{2+}$ or $Mg^{2+}$ metal ion as shown in the equation below.



Metal ion EDTA EDTA-Metal Complex

$$M^{2+} + Y^{4-} \longrightarrow MY^{2-}$$

The $Y^{4-}$ ion that forms a 1:1 complex with the metal ion is the completely deprotonated anion of ethylenediaminetetraacetic acid ("$H_4Y$"). At pH=10, the EDTA is present in solution primarily as its monoprotonated form, $HY^{3-}$. The endpoint of an EDTA titration is determined with a *metallochromic* indicator. These indicators are themselves complexing agents that change color as they combine with a metal ion. Two popular indicators for titrating $Ca^{2+}$ or $Mg^{2+}$ are *eriochrome black* T and *calmagite*. These indicators (shown as $In^{3-}$ in the equations below) change from blue to red color when they combine with a metal ion to form a complex ion:

$$M^{2+} + HIn^{2-} + H_2O \text{ <--> } MIn^{-} + H_3O^{+}$$

blue red

In a titration, EDTA, a stronger complexing agent than the indicator, displaces the indicator form the metal ion allowing the indicator to return (through shades of violet) to a pure blue color, indicating the end of the reaction.

$$MIn^{-} + HY^{3-} \text{ <--> } MY^{2-} + HIn^{2-}$$

red blue

Since $Ca^{2+}$ does not form a stable red complex with the indicator, some $Mg^{2+}$ (and an equivalent amount of EDTA) is added to the titration solution to assure a good color change in samples that do not have $Mg^{2+}$ in them naturally.

***Comments***

The sharpness of the titration endpoint increases with increasing pH, since more of the EDTA is in the free $Y^{4-}$ form at higher pH. However, the pH cannot be increased indefinitely because $CaCO_3$ or $Mg(OH)_2$ will precipitate at very high pH. The pH can also change the color of the indicator, since only the $HIn^{2-}$ form is blue ($H_2In^{-}$ is red and

$In^{3-}$ is orange).Some metal ions (commonly $Fe^{3+}$ and $Cu^{2+}$) interfere with the endpoint by causing fading or indistinct endpoints. This interference can be eliminated by adding appropriate inhibitors, one of which is the hydroxylamine hydrochloride added to the indicator solution in this procedure. The titrations are best done at room temperature. The chemical reactions causing the color changes become slow at low temperatures and the indicators may decompose at high temperature.

**EXPERIMENTAL PROCEDURE**

In this experiment, an EDTA solution is prepared and standardized with standard calcium solution. The standardized EDTA is then used to analyze an unknown sample.

**Standard Calcium Solution**

Accurately weigh 0.5 g of dried, pure $CaCO_3$ into a 250 mL beaker. Add approximately 25 mL of distilled $H_2O$, then add 1 mL of conc. HCl carefully (operate in hood!), cover with watchglass spaced with glass hooks until dissolved. **Note**: If $CaCO_3$ does not dissolve completely, add another 0.5 mL of conc. HCl (operate in hood!). Next, evaporate volume to about 2 mL maintaining watchglass on beaker to expel carbon dioxide. Rinse watchglass, transfer quantitatively into a 500 mL volumetric flask and make up volumetrically to 500 mL. Calculate the molarity of your standard calcium solution.

**EDTA Solution Preparation**

Weigh out approximately 2 g of reagent grade disodium EDTA into a 250 mL beaker. Add 0.05 g magnesium chloride hexahydrate, three pellets of NaOH and add about 200 mL of distilled water to dissolve. The EDTA will dissolve slowly over a period of a half an hour. Magnesium chloride is added to enhance the sharpness of the endpoint (It forms a more stable complex with the indicator). Filter the EDTA solution into a 0.5 or 1 L bottle, then add approximately 250 mL of distilled water.

**Titration Procedure**

*Standardization Titration for EDTA*

Fill your burette with the EDTA solution. Pipet three 25 mL aliquots of standard calcium solution into 250 mL Erlenmeyer flasks, add 3 mL ammonium chloride buffer (pH 10) (operate in hood!) and 2-3 drops of Eriochrome Black T indicator solution. Titrate with EDTA from violet through wine-red to blue. It is recommended to experiment with a 5 mL aliquot to get an idea of the color and titre. The indicator color changes slowly, thus, the titrant must be added slowly near the endpoint with thorough stirring. Calculate the molarity of the EDTA. Now you have your EDTA solution standardized and your standard EDTA solution should be ~0.01 M.

*Titration of Unknown Calcium Sample*

Prepare a clean beaker and ask your GA for 100 mL of unknown solution. Titrate with standard EDTA, 25 mL of unknown solution after addition of 3 mL ammonium chloride buffer (pH 10) (operate in hood!) and 2-3 drops of Eriochrome Black T indicator solution following the procedure above. Repeat this in triplicate. Express the concentration of calcium carbonate in the unknown sample in ppm.

**Additional notes**: It is recommended that you also do some preliminary steps for the nickel experiment (refer to nickel experiment for more details), especially if it is your next experiment. Ask for your nickel ore unknown and dry it to constant weight. As a second priority, clean the glass crucibles and dry them to constant weight.

**Informal report** Date submitted_____

Experiment: Hardness of Water by EDTA Titration Time submitted_____

Name_____ Values Obtained:

Locker #_____ (1)_____ppm $CaCO_3$

(2)_____ppm $CaCO_3$

(3)_____ppm $CaCO_3$

Average value_____

Std Deviation_____

Weight of calcium carbonate (by differences) _____(g)

Molarity of your standard calcium solution _____(M)

Standardization Titration for EDTA solution

| | I | II | III |
|---|---|---|---|
| Buret reading at start of titration (mL) | ___ | ___ | ___ |
| Buret reading at end of titration (mL) | ___ | ___ | ___ |
| Volume of EDTA solution used (mL) | ___ | ___ | ___ |
| Molarity of EDTA (M) | ___ | ___ | ___ |

Average molarity of EDTA _____(M)

Titration of Unknown Sample

| | | | |
|---|---|---|---|
| Buret reading at start of titration (mL) | ___ | ___ | ___ |
| Buret reading at end of titration (mL) | ___ | ___ | ___ |
| Volume of EDTA solution used (mL) | ___ | ___ | ___ |
| Concentration of calcium carbonate in unknown | ___ | ___ | ___ |

Sample calculations: FW of $CaCO_3$ = 100.09 g/mol = 100.09 mg/mmol; 1 ppm = 1 mg/L
Let's say you titrate 25 mL of unknown:

$$\text{ppm } CaCO_3 = \frac{(M_{EDTA})(V_e \text{ in } mL)(\frac{100.09 mg}{mmol})}{(25 mL \text{ of } ukn)(\frac{1L}{10^3 mL})}$$