INTRODUCTION

Titrmetric methods based upon complex formation, sometimes called complexometric methods have been used for at least a century. A complexation reaction involves a reaction between a metal ion M and another molecular or ionic entity (a ligand) D containing at least one atom with an unshared pair of electrons that can be represented as:

\[ M \cdot D \rightleftharpoons MD \]

where charges on ions are omitted for the sake of generality. It is important to recognize that all the coordination positions on the metal ion M are occupied either by solvent or by other electron pair donors. So the above equation simply involves replacement of a molecule of solvent (water) by the ligand D. Again for generality, solvent molecules are omitted in writing the reactions.

Ligands are called unidentate when they can donate one pair of electrons (ammonia, for example) and multidentate when two or more pairs can be donated to form coordinate bonds with the metal ion. When a multidentate ligand forms two or more coordinate bonds with the same acceptor metal ion, a ring structure results, and the compound is said to be a chelate. The coordination number, or number of electron pairs that a metal ion shares with donor atoms, usually is 4 or 6 and less frequently may be 2 or 8.

Thus a chelating agent that has two donor groups available for coordination bonding is called bidentate, whereas one with three groups is called tridentate; tetradentate, pentadentate and hexadentate chelating agents are also known. Chelation process is essentially a single-step process. Equilibrium constants in complexation reactions are usually expressed as formation or stability constants.

Formation constants associated with polydentate ligands tend to be larger (indicating more stable complexes) than those involving unidentate ligands.

Some of the common unidentate ligands in analysis are halides for analysis of mercury (II) and cyanide (CN⁻) for analysis of Ag⁺.

One of the most important polydentate ligands in complexometric analysis is ethylene diamine tetraacetic acid (EDTA). It has the structure given below:

\[
\begin{align*}
&\text{HOOC} - \text{CH}_2 \\
&\vdots \text{N} - \text{CH}_2 - \text{CH}_2 - \text{N} : \\
&\text{HOOC} - \text{CH}_2 \\
&\text{CH}_2 - \text{COOH} \\
&\text{CH}_2 - \text{COOH}
\end{align*}
\]

It is a weak tetraprotic acid. In addition to four acidic hydrogens, each nitrogen atom has an unshared pair of electrons thus the molecule may be considered to be a hexadentate ligand. The abbreviations H₄Y, H₃Y⁺, H₂Y²⁻, HY³⁻ and Y⁴⁻ are used in referring to EDTA and its ions. The disodium salt, Na₂H₂Y, is the most useful EDTA salt for analytical purposes.
One of the valuable properties of EDTA as a titrant is that it combines with metal ions (except alkali metals) in a 1:1 ratio regardless of the charge on the cation. Formation of EDTA complex can be shown by the following general equation with the expression of formation constant, $K_{MY}$

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{(n-4)+}$$

$$K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}][Y^{4-}]}$$

Formation of metal ion-EDTA complex is dependent upon the pH of the solution. An alkaline medium is needed for the titrations involving cations such as Ca$^{2+}$ and Mg$^{2+}$ which form weak complexes with EDTA. On the other hand, titrations can be done in moderately acidic solutions with the cations that form more stable complexes, such as Zn$^{2+}$ and Ni$^{2+}$. Because of this pH dependence EDTA titrations are generally carried out in solutions that are buffered to a constant and predetermined pH.

End points for EDTA titrations can be established by using metal-ion indicators. These indicators are organic dyes that form intensely colored chelates with metal ions. **Eriochrome Black T** (or **Erio T**) is one of the most common metal-ion indicators. It contains three ionizable protons, so it may be represented by $H_3In$.

In acidic and moderately basic solutions, the predominant acid/base equilibrium exhibited by the indicator is as follows:

$$H_2In^- \rightleftharpoons Hln^{2+} + H^+$$

The metal complexes of Eriochrome Black T are generally red. To observe a color change with this indicator, then, it is necessary to adjust the pH to 7 or above so that the blue form of the indicator $Hln^{2+}$ predominates in solution. The end point of reaction is then

$$Mln^+ , HY^{3+} \rightleftharpoons Hln^{2+} \cdot MY^{2-}$$

**Titration Methods Employing EDTA**

Several procedures are employed in the application of EDTA to volumetric analysis. The most common of these are given below.

**a- Direct Titration**: About 25 metal ions can be determined by direct titration with EDTA using metal-ion indicators for the end-point detection. It is limited to those reactions for which a method for end point detection exists and to those metal ions that react rapidly with EDTA.

**b- Back Titration**: This method is useful for the analysis of cations that form very stable EDTA complexes and for which a satisfactory indicator is not available. In this process, a measured excess of standard EDTA solution is added and the excess EDTA is determined by a back-titration with a standard Mg$^{2+}$ or Zn$^{2+}$ solution using Eriochrome Black T indicator. In order to apply this method, the metal-EDTA complex should be more stable than the Mg-EDTA or Zn-EDTA complex.

**c- Displacement Titration**: In this process, an unmeasured excess of a solution containing EDTA in the form of Mg (or Zn) complex is introduced. If the metal ion forms a more stable complex than that of magnesium (or Zinc) the following displacement reaction occurs.

$$MgY^{2-} + M^{2+} \rightleftharpoons MY^{2-} + Mg^{2+}$$
where $M^{2+}$ shows the analyte cation.

The liberated $Mg^{2+}$ or $Zn^{2+}$ is then titrated with a standard EDTA solution. This procedure is useful where no satisfactory indicator is available for the metal ion being determined.

**d- Alkalimetric Titration:** In this procedure an excess of $Na_2H_2Y$ is added to a neutral solution of the metal ion

\[
M^{2+} + H_2Y^{2-} \rightleftharpoons MY^{2-} + 2H^+
\]

The liberated $H^+$ ions are titrated with a standard solution of a base.

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### REAGENTS AND APPARATUS

- Mg(NO$_3$)$_2$.6H$_2$O, Ca(NO$_3$)$_2$.4H$_2$O (unknown solutions, already prepared)
- Standard EDTA solution (already prepared, do not forget to ask for exact concentration of EDTA from your assistant)
- Standard MgSO$_4$ solution (already prepared, do not forget to ask for exact concentration of MgSO$_4$ from your assistant).
- Mg/EDTA solution (already prepared).
- Eriochrome black T (Erio T) indicator, methyl red (in droppers).
- pH 10 buffer (already prepared).
- 25 mL of 6.0 M HCl (for 3 students).
- 25 mL of 6.0 M NaOH (for 3 students).
- buret
- 250mL conical flasks X2
- 100 mL graduated cylinder

### PROCEDURE

**A. Determination of Magnesium by Direct Titration**

1) Take your unknown sample into a 250 mL conical flasks, add 50 mL distilled water and then, add 2 mL of pH 10 buffer solution and 4 drops of Erio T indicator solution.
2) Titrate with 0.10 M EDTA to a color change from red to blue.
   - *The color change of indicator is slow in the vicinity of the end point. Care must be taken to avoid over titration.*
3) Express the result of analysis in terms of mg Mg$^{2+}$.

**B. Determination of Calcium by Displacement Titration**

1) Take your unknown sample into a 250 mL conical flask and add 50 mL distilled water.
2) Add 2.0 mL of pH 10 buffer, 10 mL of 0.10 M Mg/EDTA solution and 4 to 5 drops of Erio T indicator.
3) Titrate with standard 0.10 M EDTA until a color change from red to blue occurs.
4) Report the results as mg Ca$^{2+}$ in the unknown sample.

**C. Determination of Water Hardness by Titration with EDTA**

1) Acidify 100 mL tap water with a few drops of 6.0 M HCl (use Pasteur pipette) and boil gently for a few minutes to remove CO$_2$. 

• \( \text{CO}_3^{2-} \) and \( \text{HCO}_3^- \) present in water sample is removed by adding HCl.

\[
\begin{align*}
2\text{H}^+ + \text{CO}_3^{2-} &\rightarrow \text{H}_2\text{O} + \text{CO}_2 \\
\text{H}^+ + \text{HCO}_3^- &\rightarrow \text{H}_2\text{O} + \text{CO}_2
\end{align*}
\]

2) Cool and then, add a few drops methyl red (pH:4.2-6.3) and change the color of solution from red to yellow using 6.0 M NaOH (use pasteur pipette).

3) Introduce 2.0 mL of pH 10 buffer and 4 drops of Erio T indicator.

4) Titrate the mixture with standard 0.10 M EDTA until the color changes from red to blue or green.

• If the color change of the indicator is very slow, the absence of magnesium is indicated. In this case add 2 mL of the 0.10 M Mg\(\text{Y}^2^- \) (magnesium-EDTA) solution before the titration.

5) Report the result of the analysis in terms of mg \( \text{CaCO}_3 \)/L of tap water.

D. Determination of Calcium by Back Titration

1) Take your unknown sample into a 250 mL conical flask and add 20.0 mL of 0.10 M EDTA and add 40 mL of distilled water.

2) Add 2.0 mL of pH 10 buffer and 4 drops Erio T indicator.

3) Titrate the excess chelating agent to a color change from blue to red with standard 0.10 M MgSO\(_4\) solution (Mg\(^{2+}\) solution).

Reactions:

\[
\begin{align*}
\text{Ca}^{2+} + \text{Y}^{4-}(\text{excess}) &\leftrightarrow \text{CaY}^{2-} + \text{Y}^{4-}(\text{excess}) \\
\text{Y}^{4-}(\text{excess}) + \text{Mg}^{2+} &\leftrightarrow \text{MgY}^{2-} (\text{Back - titration})
\end{align*}
\]

Calculation:

\[
\text{# of mmol of EDTA} = (\text{# of mmol Ca}^{2+}) + (\text{# of mmol Mg}^{2+})
\]

4) Report the results as mg Ca\(^{2+}\) in the unknown sample.

E. Treatment of Water-Hardness Data

In the treatment five students will combine their data. Each student will have 10 measurements of water hardness of water and will do his/her own calculation.

Do the following calculations:

1) Apply the Q test to the data in order to check any outlying result at 95% confidence level.

2) Calculate your own mean (average of two titration results) and mean of 10 results (pooled mean).

3) Find deviation of your sample mean from the pooled mean to see error in your data.

4) Calculate the standard deviation for the pooled data.

5) Calculate the coefficient of variation (CV) or (%RSD).
6) Find the confidence interval (limits) for the data at 95% confidence level.
7) Is the mean of 10 measurements and true value (given by the assistant) agree with each other at 95% confidence level?

PRE-LAB STUDIES

Read pages 401-437 from the textbook (9th Ed)

1) Define the followings and give examples to each one: Ligand, chelate, coordination number.
2) Draw the structure of EDTA and show the bonding sides.
3) Write the name of a typical metal-ion indicator used for metal ions in EDTA titrations. Write its dissociation equilibria.
4) Write the names of titration methods employing EDTA and explain them.
5) What do you understand from hard water?
6) What are the advantages of using EDTA as a complexing agent?
7) What are the advantages of multidentate ligands over their unidentate counterparts?

POSTLAB STUDIES

1) Explain the importance of pH control in complexometric titrations.
2) Can you determine Mg by displacement or back titration? (Hint: You are not restricted to use the reagents used in your experiment)
3) You need to know the amount of EDTA added to solution in back titration method but in displacement titration you do not need to know the amount of Mg/EDTA added. Why? Explain your answer by giving related reactions.
4) What are the effects of water hardness in our life?
5) What is the pH needed for satisfactory titrations of Ca²⁺ and Mg²⁺ cations with EDTA?
6) Why is a small amount of MgY²⁻ often added to a water specimen that is to be titrated for water hardness?
REPORT SHEET FOR TITRATIONS BASED ON COMPLEX FORMATION

A. Determination of Magnesium by Direct Titration

1<sup>st</sup> replicate: Volume of 0.10 M EDTA, mL=
1<sup>st</sup> replicate: Volume of 0.10 M EDTA, mL=

B. Determination of Calcium by Displacement Titration

1<sup>st</sup> replicate: Volume of 0.10 M EDTA, mL=
2<sup>nd</sup> replicate: Volume of 0.10 M EDTA, mL=

C. Determination of Water Hardness by Titration with EDTA

<table>
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<tr>
<th>Name of the Student</th>
<th>1&lt;sup&gt;st&lt;/sup&gt; replicate, mL EDTA</th>
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D. Determination of Calcium by Back Titration

1<sup>st</sup> replicate: Volume of Mg, mL=
2<sup>nd</sup> replicate: Volume of Mg, mL=

TRUE VALUES:

Concentration of EDTA, M=

Concentration of Mg, M=

TA’s Name and Signature: