CHAPTER 1
INTRODUCTION

1.1. Background

Chemical Engineers are required to have skills in terms of analyzing metal content (Ca, Ba, Sr, Cu, Zn, Cd, Bi, Al, Sc, Hg, Ni, Co, Mg), hardness (expressed as $CaCO_3$, HCO_3) and/or CaO content in the sample, either a liquid or a solid sample. Ultimate analysis of metals in the sample, or the water hardness conditions, are generally required to know the specifications of the materials to be processed in the unit production. One of the ways to analyze the parameters mentioned above is by using complexometric analysis methods. There are many laboratories in various types of industries that use complexometric analysis methods to measure the parameters mentioned above such as the cement industry, steel industry and industry which uses steam, bottled water industry, and so on. For example, analysis standards for water hardness can refer to Standar Nasional Indonesia (SNI) Number 3554: 2015.

Complexometric analysis is a volumetric titration analysis which involves the formation of complexes or complex ions which are soluble but barely dissociated. Standard solutions that can be used include EDTA (Ethylene Diamine Tetra Acetate), DCYTA (Diamino Cyclohexane Tetraacetic Acid), EGTA (Ethylene Glycol Tetraacetic Acid), NTA (Nitrilo Triacetate), and Trien. Complexometric analysis which will be done in this practicum use the standard solution of EDTA (Ethylene Diamine Tetra Acetate). To find out the end point of the titration in the complexometry analysis using EDTA, indicator is required. One of them is EBT (Eriochrom Black T). The end point of the titration is indicated by the change in color of the sample from burgundy to blue. As a titrant using salt Na_2EDTA. If the sample contains Ca, Mg, or Fe metal, there will be a substitution between heavy metals with sodium ions in the Na_2EDTA titrant. From the results of the substitution or the needs of EDTA, the metal content in the sample can be determined. In this practicum, students use complexometric analysis to analyze the hardness of various water samples and analyze the CaO content of samples such as limestone or other materials.

1.2. Experiment Objectives

1. Analyzing temporary hardness, fixed hardness, and total hardness in a liquid sample.
2. Analyzing the CaO content in solid samples such as limestone rocks or other rocks.

1.3. Experiment Benefits

1. Praticant understand and have the skills to analyze temporary hardness, fixed hardness, and total hardness in a liquid sample.
2. Praticant understand and have the skills to analyze the CaO content in rocks.

CHAPTER II
LITERATURE REVIEW

2.1. Definition of Complexometry

Complexometry is a type of quantitative chemical analysis which involves the formation of complex compounds or complex ions that are soluble but barely dissociated (Maulizar dkk., 2022). The standard solution used includes EDTA (Ethylene Diamine Tetra Acetate), DCYTA (Diamino Cyclohexane Tetraacetic Acid), EGTA (Ethylene Glycol Tetraacetic Acid), NTA (Nitrilo Triacetate), Trien and indicators used is a methallochromic indicator, in the form of an organic compound that can produce intense color when forming complex metal compounds. These indicators include EBT, Murexide, Metalphthalein, Pyridylazo Naphthol, Pyrocatechol Violet, Xylenol Orange, Calcon and Calgamite. Complex compound is formed from a metal ion reaction with a cation, an anion, or neutral molecule. The metal ion in a complex molecule is called the central atom while the ion or the group attached to the central atom is called a ligand. The number of bonds formed by the central metal atom is called the metal coordination number. Reactions that form this complex may be referred to as a Lewis acid-base reaction, with the ligand acting as a base that donates a pair of electrons to the cation which act as the acid (Day & Underwood, 1992). The indicator can also react with H_3O^+ forming a colored compounds, similar to metal-indicator complexes. Therefore in this case, it is very important to control the pH to prevent competition between metal ions with H_3O^+.

2.2. EDTA (Ethylene Diamine Tetra Acetate) Standard Solution

EDTA is a ligand that can potentially coordinate with metal ion with the support of both nitrogen and four free acetate groups often abbreviated as H_2Y^{2-} (Migisya, 2020). EDTA is a chelate-forming penetration solution that can be used for chemical analysis of various metals. Metal ion titration with chelating formation is called chelometric titration. Na_2EDTA is used as titrant in this complexometric titration.

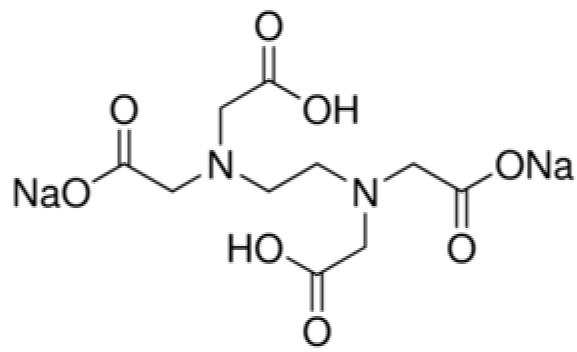


Figure 2.1 Structure of Na_2EDTA

2.3. EBT (Eriochrom Black T)

EBT (Eriochrom Black T) is an indicator of the metal ion used in complexometric analysis with molecular structures as shown in Figure 2.2 and is often represented by the acronym H_2In.

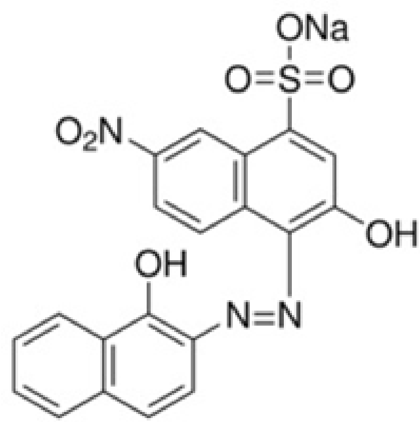


Figure 2.2 Structure of Eriochrom Black T

Changes in EBT at various pH:

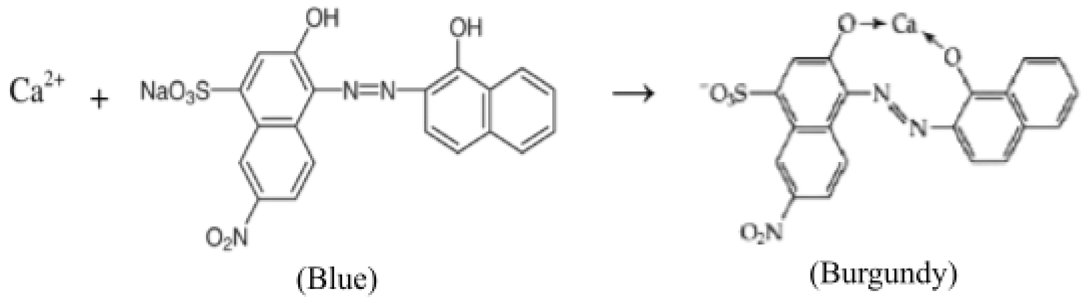
H_2In^-	HIn^{2+}	In^{3-}
red	blue	orange
pH	pH	pH >
5,3-7,3	10,5-12,5	12,5

2.4. Reactions

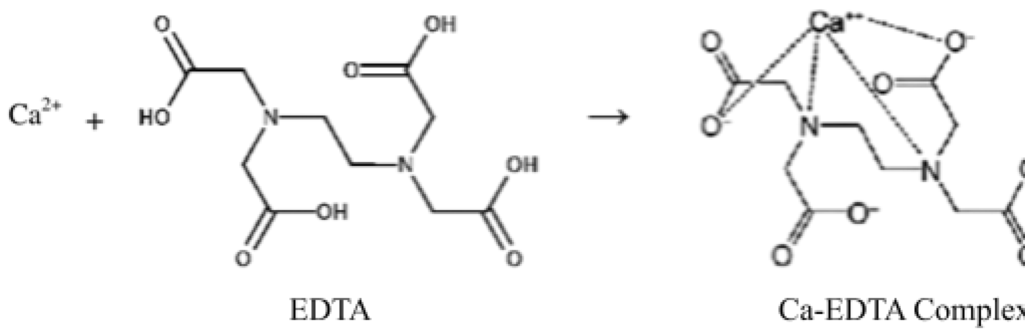
$Ca^{2+} + H_2In \longrightarrow CaIn\ (red) + 2H^+$

$CaIn^- + H_2Y^{2-} \longrightarrow CaY^{2-} + HIn^{2-}\ (blue) + H^+$

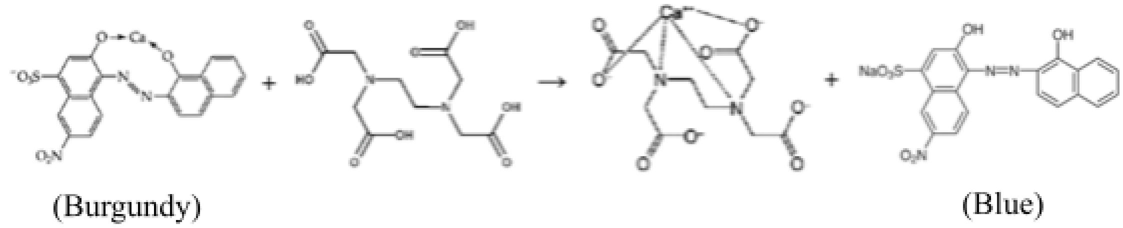
1. Sample + indicator



2. Sample + titrant



3. Sample + indicator + titrant



2.5. Buffer Solution and pH

A buffer solution is a mixture of a weak acid or base of the salt (Vogel, 1979). Buffer solutions can be divided into three types, namely acid buffer solutions, alkaline buffer solutions, and neutral buffer solutions. These three types of buffer solutions can be produced using different ingredients. A mixture of a solution of CH_3COOH and CH_3COONa forms an acid buffer solution, a mixture of NH_4OH and NH_4Cl forms an alkaline buffer solution, as well as a mixture of a solution of NaH_2PO_4 and Na_2HPO_4 forms a neutral buffer solution. Buffer solutions have the following properties :

1. pH is considered unchanged even though the solution is diluted.
2. pH is considered unchanged even if a little acid or base is added.

The degree of acidity, the minimum pH for metal titration with EDTA are as follows : Fe^{3+} (1,5); Hg^{2+} (2,2); Cu^{2+} dan Ni^{2+} (3,2); Pb^{2+} (3,3); Cd^{2+} (4,0); Co^{2+} and Zn^{2+} (4,1); Fe^{2+} (5,1); Ca^{2+} (7,3); Mg^{2+} (10).

2.6. Hardness

Hard water is water that contains Ca^{2+} and/or Mg^{2+}. Hardness can be expressed in ppm $CaCO_3$, ppm HCO_3, German degrees (°D), as well as French degrees (°F).

Convertion formula ppm $CaCO_3$ to German degrees (ºD):

1 ppm $CaCO_3$ = 1/17,8 ºD

Convertion formula ppm $CaCO_3$ to French degrees (ºF):

1 ppm $CaCO_3$ = 1/10 ºF

According to Achmad & Evana. (2018) hardness is classified into two types, namely:

1. Temporary hardness

   Contains Ca and Mg bicarbonate salts. Can be removed by heating.

2. Fixed hardness

   Contains Ca^{2+} and/or Mg^{2+} in the form of SO_4^{2-} and Cl^- salts. Can be removed by adding soda or zeolite.

How to soften hard water:

a. Temporary hardness is removed by heating process.

   $Ca(HCO_3)_2 \rightarrow CaCO_3 \downarrow \text{(white)} + H_2O + CO_2$

b. Fixed hardness is removed by adding sodium salt.

   $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$

   $MgSO_4 + Na_2CO_3 \rightarrow MgCO_3 + Na_2SO_4$

c. Hard water that contains sulfate salts can also be removed by filtration process using zeolite stone filter so that the anion SO_4^{2-} in water will be absorbed in the zeolite and eventually become soft.

   $SiO_2AlO_2Na_2O + Ca(HCO_3)_2 \rightarrow 2SiO_2Al_2O_3CaO + 2NaHCO_3$

d. With synthetic resin

$R - SO_3H + Ca^{2+} \rightarrow R(SO_3)_2Ca + 2H^+$

There are two kinds of resin:

- Cationic resin for cation exchange
  Resin containing COOH / SO_3H groups
  Formula: RCOOH / $R(SO_3H)$
- Amine resin for anion exchange
  Resin contains the NH_2 group
  Formula: $R(NH_2)_2$

e. Ion exchanger

The overall principle is the same as synthetic resins, cation resins from anions are needed to bind Ca, Mg, and chloride, carbonate, or sulfate ions. The resulting water will be free from the ions mentioned above. Water that will be softened (demineralization) is passed through the ion-exchange resin until the resin becomes saturated. The resin that has been saturated is regenerated to reactivate resin.

2.7. Water Quality Standards

Water quality standards are limits or levels of living things, substances, energies, or components existing or must exist or pollutant elements whose existence is tolerable inside water. Quality standards are used to determine whether a product is appropriate or not. Parameter of hardness in water can refer to Peraturan Menteri Kesehatan Republik Indonesia Nomor 32 Tahun 2017 tentang Standar Baku Mutu Kesehatan Lingkungan dan Persyaratan Kesehatan Air untuk Keperluan Higiene Sanitasi, Kolam Renang, *Solus per Aqua*, dan Pemandian Umum, which establishes environmental health quality standards for water media Sanitation Hygiene requirements for hardness ($CaCO_3$) is a maximum of 500 mg/L. Meanwhile, the limit of drinking water hardness parameter refers to the Peraturan Menteri Kesehatan Republik Indonesia Nomor : 492/MENKES/PER/IV/2010 tentang Persyaratan Kualitas Air Minum which state that the maximum hardness ($CaCO_3$) of drinking water is 500 mg/L.

2.8. Use of Complexometry in Industries

Complexometric analysis can be used in industries.

1. To determine the CaO content in limestone, gypsum, and cement.
2. To determine the levels of Co, Cu, Fe, Pb, Zn in steel.
3. To determine the metal content of Al, Ca, Mg, Zn, Pb, Cu, Co, Fe, Ni, Pb.
4. To determine the water hardness of the feed water boiler ($CaCO_3$, HCO_3,°D, °F)
5. Used in the drinking water industry to determine whether the water meets the requirements (heavy metal content) or not.

2.9. Reagent Function

1. HCl = dissolve dirt or impurities in the sample
2. KOH = make an alkaline solution (pH = 10) so that the indicator can works properly
3. KCN = make complexes with interfering substances because cations can react with EDTA
4. EDTA = standard titration solution
5. Buffer = maintain pH
6. EBT = indicator to show the end point of titration
7. MgEDTA = prevent the end point of titration appear earlier in the mixture of Ca and Mg, thereby increasing the selectivity of CaEDTA complex formation

2.10. Physical and Chemical Properties of Materials

1. HCl

Physical Properties :

- Molecular Weight = 36,47 gram/mol
- Boiling Point = -85,5ºC
- Melting Point = -111ºC
- Density = 1,268 gram/ml
- Colorless
- Solubility in 100 parts of water (hot water = 82.3 parts, cold water = 56.1 part)

Chemical Properties :

- In a concentrated and heated state can reduce the chromate and produce chrome ion through reaction :

  $2K_2CrO_4 + 10HCl \rightarrow 2Cr^{3+} + 8Cl_2 + 2K^+ + 8H_2O$
- In diluted state can precipitate mercury as Kalomel

2. KOH

Physical Properties :

- Molecular Weight = 50,1 gram/mol
- Boiling Point = 1520ºC
- Melting Point = 380ºC
- White
- Solubility in 100 parts of water (hot water = 126 parts, cold water = 97 parts)

Chemical Properties :

- A strong base that ionized in water through reaction :

  $KOH \rightarrow K^+ + OH^-$
- Turn red lacmus into blue
- Absorb CO_2 though reaction :

  $CO_2 + 2K^+ + 2OH^- \rightarrow K_2CO_3 + H_2O$

3. KCN

Physical Properties :

- Molecular Weight = -65,11gram/mol
- Density = 1,529 gram/ml
- Melting Point = 6,345ºC
- Clear

- Solubility in 100 parts of hot water = 122,2 parts
- In the form of crystalline calcite

Chemical Properties :

- Salt
- Can form complex compound with metals from transition groups

  $6\ CN^- + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$

  $6\ CN^- + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$

CHAPTER III
PRACTICUM METHODOLOGY

3.1. Materials and Tools

3.1.1. Materials

1. HCl
2. KOH
3. EDTA
4. EBT Indicator
5. Buffer Solution
6. Na_2EDTA 0,01 N
7. MgEDTA 0,01 N

3.1.2. Tools

1.	Stative	7.	Dropper pipette
2.	Clamps	8.	Funnel
3.	Burette	9.	Volume pipette
4.	Beaker glass	10.	Stirrer
5.	Erlenmeyer	11.	Porcelain cup

6.	Measuring glass	12.	Measuring flask

3.2. Experimental Methods

3.2.1. Total Hardness Determination

1. Take 10 ml of liquid sample, adjust the pH to 10 with KOH (if pH reached 12, Mg will precipitate so EDTA only form complex with Ca).
2. Add 1 ml buffer, 1 ml KCN, and a little EBT indicator.
3. Titrate with Na_2EDTA until the burgundy color turns into light blue.
4. Take a note of the required titrant volume.

$$\text{Total Hardness} = \frac{(V.N)EDTA\ .\ EW\ CaCO_3\ .\ 1000}{\text{Titrated } V}\ \text{,ppm } CaCO_3$$

Notes :

V = Volume (ml)

N = Normality (N)

MW = Molecular weight (g/mol)

ppm = Part per million (mg/L)

3.2.2. Fixed Hardness Determination

1. Take 100 ml of liquid sample, put it in a beaker glass, boil it for 20-30 minutes.
2. Cool down the sample, then filter it using Whatmann filter paper with pore diameter < 0.5 μm.
3. Dilute the filtrate to 100 ml in the measuring flask.
4. Take 10 ml of the diluted filtrate, adjust the pH to 10 with KOH.
5. Add 1 ml buffer, 1 ml KCN, and a little EBT indicator.
6. Titrate with Na_2EDTA until the burgundy color turns into light blue.
7. Take a note of the required titrant volume

$$\text{Fixed Hardness} = \frac{(V.N)EDTA\ .\ EW\ CaCO_3\ .\ 1000}{\text{Titrated } V}\text{,ppm } CaCO_3$$

Temporary Hardness = Total Hardness – Fixed Hardness

Notes:

V = Volume (ml)

N	= Normality (N)
MW	= Molecular weight (g/mol)
ppm	= Part per million (mg/L)

3.2.3. Determination of CaO Content in Solid Sample

1. Put solid sample (oven dry base) in a pyrex glass beaker 250 ml, dissolve it with 10 ml HCl.
2. Steam it until dry using an electric stove.
3. Dissolve the residue with sufficient concentrated HCl, max. 25 ml.
4. Dilute with 100 ml water, heat it for 15 minutes, dilute again with water until the volume is 100 ml.
5. Transfer 5 ml of the solution to a 250 ml measuring flask. Dilute with water up to the mark.
6. Take 5 ml and put in a 100 ml measuring flask. Dilute with water up to the mark.
7. Take 10 ml of the solution that was diluted earlier, adjust the pH to 10 with KOH solution.
8. Add 1 ml buffer, 1 ml KCN, 2-3 drops MgEDTA, and a little indicator EBT.
9. Titrate with Na_2EDTA until the burgundy color turns light blue.
10. Take a note of the required titrant volume.

$$\text{CaO Content} = \frac{(V.N)\ \text{EDTA} \cdot \text{EW CaO} \cdot 100}{\text{Sample (mg)}} \times fp\%$$

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