

CHAPTER I

INTRODUCTION

1.1. Background

Titrimetric analysis is widely used in chemical reactions that involving oxidation reduction. The ions of various elements can be present under different oxidation states, resulting in the possibility of many redox reactions. Iodo-iodimetric are one of them. Iodo-iodimetric are redox titrations whose determination are based on the amount of I_2 that reacts with sample. Iodo-iodimetric analysis have a stoichiometric ratio that is simple to use, practical, and not much of a problem (Iskandar, 2017). Many of these reactions qualify for use in titrimetric analysis and have many applications (Underwood, 1986, 248).

1.2. Experiment Objectives

Determine the Cu^{2++} content in the sample.

1.3. Experiment Benefits

- a. As a tool in applicative determination of Cu^{2++} levels in various samples containing Cu^{2+} ions.
- b. Knowing and observing the processes and changes that occur in iodo iodimetric analysis.

CHAPTER II

LITERATURE REVIEW

2.1. Definition of Oxidation Reduction

The process of reduction - oxidation (redox) is a process which involves the transfer of electrons from one reagent to another. Reduction is the capture of one or more electrons by an atom, ion or molecule. Whereas oxidation is the removal of one or more electrons from an atom, ion or molecule.

No electrons are free in the system chemistry, and the release of electrons by a chemical substance always accompanied by the capture of electrons by parts of the other, with other words the oxidation reaction is always followed by a reduction reaction. In oxidation-reduction (redox) reactions there is a change in the valence of the substances that carry out the reaction. Here there is a transfer of electrons from the reducing pair to the oxidizing pair (Underwood, 1986, 248).

The two parts of a redox reaction can generally be written as:

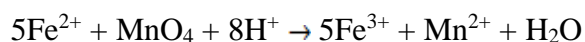


Where red denotes oxidized substance (also known as reducing agent), oks is the reduced form (oxidant or oxidizing agent), n is the number of electrons transferred and e^{-} is the electron.

2.2. Redox Reaction

Redox reactions are widely used in titrimetric analysis for inorganic and organic substances. Determination of the end point in a redox titration can be done potentiometrically or with the aid of an indicator.

Examples of redox reactions:



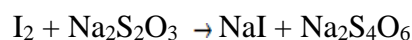
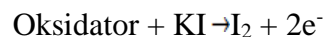
In which:



2.3. Iodometry

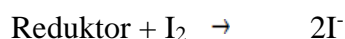
Iodometry is a titrimetric analysis that is indirectly for oxidizing substances such as iron III, copper II, where these substances will oxidize iodide which is added to form

iodine. The iodine formed will be determined using a standard solution of thiosulfate (Vogel, 1989, 384).



2.4. Iodimetry

Iodimetry is a direct titrimetric analysis used to analyze reducing agents or sodium thiosulfate using iodine solution or by adding excess standard solutions. The excess iodine is retitrated with thiosulfate solution (Vogel, 1989, 384-385).

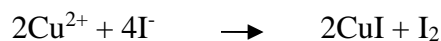


2.5. Amylum Indicator Theory

Starch is a specific indicator that is used as an indication that the equivalence point has occurred in iodometric titrations (Pursitasari, 2014). Indicators specific is a substance that reacts with the way that is specific to one of the reagents are in a titration to produce colors. Starch indicator can be used in redox titrations, which will produce a dark blue color when reacted with iodine (Underwood, 1986, 279). This reaction between iodine and starch forms a dark blue iodine-starch complex and acts as a sensitive test for iodine. The mechanism of formation of this colored complex is unknown, but it is thought that iodine molecules are retained on the surface of β -amylose, a constituent of starch (Underwood, 1986, 297).

2.6. Reaction Mechanism

Reaction mechanisms are reaction steps that describe the entire series of a chemical reaction. Iodo-iodimetric reaction mechanism:



2.7. Things that Need to be Considered

- Titration should be conducted in a state of cold, in the flask without a catalyst in order to reduce the oxidation of I^- by O_2 from the air into I_2 .
- $Na_2S_2O_3$ is a secondary standard solution which must be standardized firstly.
- Add an indicator at the end of the titration (just before TAT).
- Titration cannot be done in a strong acid medium because the amylum hydrolysis will occur.
- Titration cannot be carried out in a strong alkaline medium because I_2 will oxidize the thiosulfate to sulfate.
- The $Na_2S_2O_3$ solution must be protected from light because light helps the activity of the annoying thiophorus bacteria.

2.8. Physical and Chemical Properties of Reagents

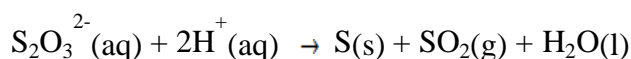
1. $Na_2S_2O_3 \cdot 5H_2O$ (Sodium Thiosulfate)

Physic

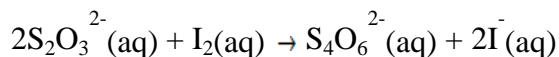
- Molecular Weight: 158,09774 gr/mol
- Specific Gravity: 1,667 g/cm³, solid
- Melting Point: 48,3°C
- Boiling Point: decomposed

Chemist

- Thiosulfate anions react typically with acid (H^+) to give sulfur, sulfur dioxide, and water.



- Thiosulfate anions react stoichiometry with iodine and a redox reaction occurs.



2. HCl (Hydrochloric Acid)

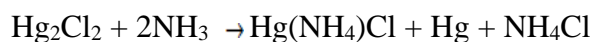
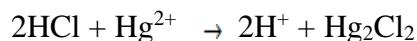
Physic

- Molecular Weight: 36.47 gr/mol
- Specific Gravity: 1.268 gr/cm³
- Melting Point: -110°C
- Boiling Point: 85°C
- Solubility in 100 parts of water 0°C: 82.3

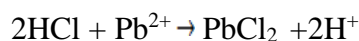
- Solubility in 100 parts of water 100°C: 56.3

Chemist

- It reacts with Hg^{2+} to form a white precipitate of Hg_2Cl_2 which is insoluble in hot water and dilute acid but dissolves in dilute ammonia, KCN solution, and thiosulfate.



- React with Pb^{2+} to form white precipitate of PbCl_2 .



- It evaporates easily, especially when heated.
- Concentration does not change easily due to air/light.
- It is a strong acid because of its high degree of dissociation.

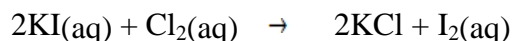
3. KI (Potassium Iodide)

Physic

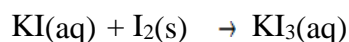
- Molecular Weight: 166.0 g/mol
- Specific Gravity: 3,13 g/cm³, solid
- Melting Point: 681°C
- Boiling Point: 1330°C
- Solubility in water at 6°C: 128 g/100 ml

Chemist

- Iodide ion is a reducing agent, so it is easily oxidized to I_2 by a strong oxidising agent such as Cl_2 .



- KI forms I_3^- when reacted with iodine.



(Perry, 1973)

4. $\text{K}_2\text{Cr}_2\text{O}_7$ (Potassium Dichromate)

Physic

- Molecular Weight: 294,185 g/mol
- Specific Gravity: 2.676 g/cm³, solid
- Melting Point: 398°C
- Boiling Point: 500°C
- Solubility in 100 parts of water 0°C: 4,9

- Solubility in 100 parts of water 100°C: 102

Chemist

- $\text{K}_2\text{Cr}_2\text{O}_7$ is a strong oxidizer because it has the ability to oxidize other substances.
- Corrosive.
- When heated strongly, it decomposes with the formation of oxygen.



CHAPTER III

RESEARCH METHODOLOGY

3.1. Instruments and Materials

3.1.1. Materials

1. Samples 1 and 2 in the amount of 10 mL
2. $\text{Na}_2\text{S}_2\text{O}_3$
3. $\text{K}_2\text{Cr}_2\text{O}_7$ 0.01 N 10 mL
4. 2.4 ml concentrated HCl
5. KI 0.1 N 12 mL
6. Amylum
7. Aquadest 130 mL
8. Starch 6 gr

3.1.2. Instruments

1. Burette, statif, clamp
2. Erlenmeyer
3. Measuring Cup
4. Beaker Glass
5. Pipette drops
6. pH indicator
7. Volume pipette
8. Aspirator
9. Mixer
10. Electric Stove
11. Thermometer

3.2 Experimental Methods

3.2.1 Making Starch Indicator

1. 6 grams of starch are put into a 250 mL beaker glass, add 100 mL of aquadest, stir the mixture until a solution is formed.
2. Turn on the electric stove, heat the solution on the electric stove. Stir slowly the solution while observing the increase in temperature with a thermometer.
3. When you've reached a temperature of 40°C, stop stirring. Leave the solution until a temperature of 60°C.

4. After reaching a temperature of 60°C, remove the beaker glass and let it sit for 5-10 minutes in a closed state.
5. The finished starch will form 2 layers, take carefully the white top layer using a dropper.
6. The initial starch test is carried out by dropping starch to a little of sample containing iodine.

3.2.2 Standardization of Na₂S₂O₃ with K₂Cr₂O₇ 0.01 N

1. Take 10 ml of K₂Cr₂O₇, dilute with distilled water to 40 ml.
2. Add 2.4 ml of concentrated HCl.
3. Add 12 ml of 0.1 N KI.
4. Titrate the mixture with Na₂S₂O₃ until the yellow color is almost gone.
5. Then add 3 drops of amylum until it is blue.
6. Continue titrating until the blue color disappears.
7. Record the needs of Na₂S₂O₃ entirely.

$$N \text{ Na}_2\text{S}_2\text{O}_3 = \frac{(V.N) \text{ K}_2\text{Cr}_2\text{O}_7}{V \text{ Na}_2\text{S}_2\text{O}_3} \quad (3.1)$$

3.2.3 Determining Cu²⁺ content in the sample

1. Take 10 ml of the sample.
2. Test the pH of the sample. The pH of the sample is 3.
3. Enter 12 ml KI 0.1 N.
4. Titrate with Na₂S₂O₃ until the yellow color is almost gone.
5. Add 3 drops of amylum indicator until it is blue.
6. Continue titrating until the blue color disappears.
7. Record the needs of Na₂S₂O₃ entirely.

$$\text{Cu}^{2+} \text{ (ppm)} = (V.N) \text{ Na}_2\text{S}_2\text{O}_3. \text{ BM Cu. } \frac{1000}{V \text{ sampel yang dititrasi}} \quad (3.2)$$

or

$$\text{Cu}^{2+} \text{ (ppm)} = (V.N) \text{ Na}_2\text{S}_2\text{O}_3. \text{ BM Cu. } \frac{1000}{10} \text{ mgr/L} \quad (3.3)$$

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CHAPTER I

INTRODUCTION

1.1 Background

Titrimetric analysis is widely used in inorganic or organic substances reaction. To determine the end point of the redox titration, it can be done potentiometrically or with the help of an indicator.

One of the volumetric analyzes based on redox reactions is permanganometry. Permanganometry titration is based on redox reaction between potassium permanganate (KMnO_4) and sample. This reaction can occur in acid, neutral, or base condition. During the reaction usually need heating process to increase the speed of reaction (Apriyanti & Apriyani, 2018).

1.2 Experiment Objectives

Determine the levels of Fe^{2+} in the sample.

1.3 Experiment Benefits

- a. Knowing the level of Fe^{2+} in the sample and can apply permanganometry analysis in everyday life.
- b. Knowing and observing the processes and changes that occur in permanganometric analysis.

CHAPTER II

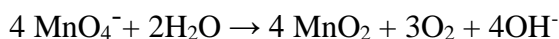
LITERATURE REVIEW

2.1 Definition of Permanganometry

Permanganometry is a volumetric quantitative analysis based on the permanganate ion oxidation reaction. The solution was a standard that is used is KMnO_4 . Before being used for titration, KMnO_4 solution must be standardized firstly because it is not a primary standard solution (Underwood, 1986, 290). In addition, KMnO_4 has some characteristics:

1. Cannot be obtained purely.
2. Contains MnO and Mn_2O_3 oxides.
3. The solution is unstable (if there are organic substances)

Reaction:



4. Should not be filtered with filter paper (organic substances) \rightarrow with glass wool.
5. Should be stored in a chocolate bottle.
6. Standardized with primary standard solutions.
7. Substances commonly used primary standards are: As_2O_3 , $\text{Na}_2\text{C}_2\text{O}_4$, $\text{H}_2\text{C}_2\text{O}_4$, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$, $\text{K}_4\text{Fe}(\text{CN})_6$, metal Fe, $\text{KHC}_2\text{O}_4\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

The oxidation of permanganate ions can take place in acidic, neutral and alkaline conditions.

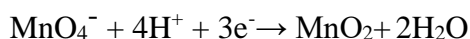
1. In an acidic medium, $\text{pH} \pm 1$



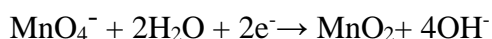
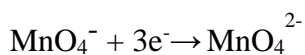
Potassium permanganate can act as an indicator, and titrations are generally carried out in an acidic medium because it is easier to observe the end point of the titration.

2. In a neutral medium

Some compounds that are easier to be oxidized in a neutral or base medium include hydrazine, sulfites, sulfides, and thiosulfates. Reaction in a neutral medium:



3. In an alkaline medium:



2.2. Advantages and Deficiency of Permanganometric Analysis

Advantages

- The standard solution, KMnO_4 , is easy to obtain and cheap.
- Does not require indicators for TAT. This is because KMnO_4 can act as an indicator.
- The reaction is fast with many reagents.

Deficiency

- There should be standardization of the start up firstly.
- Can work better if done in acidic conditions.
- The time required for analysis is quite long.

(Underwood, 1986, 290)

2.3 Physical and Chemical Properties of Reagents

1. KMnO_4 (Potassium Permanganate)

Physic

- Molecular weight: 158.034 g/mol
- Color, crystalline form and andrefractive index: purple, rhb.
- Specific gravity: 2.703 g/cm³
- Melting point (°C): d. < 240
- Solubility in 100 parts cold water: 2.83 °
- Hot water: 32,3575 °

Chemist

- Strong oxidator.
- Very reactive with organic material, metal, and acid
- Decomposes when heated until 230 °C through reaction:
$$2 \text{KMnO}_4 \rightarrow \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$$
- React with $\text{H}_2\text{C}_2\text{O}_4$ with transparent solution as final product:



2. H_2SO_4 (Sulfuric Acid)

Physic

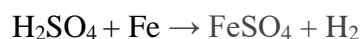
- Molecular weight: 98.08 g/mol
- Color, crystalline form and refractive index: col, viscouslq
- Specific gravity: 1.84 g/cm³

- Melting point (°C): 10.49
- Boiling point (°C): d. 340
- Solubility in 100 parts: Cold water: ∞
- Hot water: ∞

(Perry, 1973)

Chemist

- Corrosive.
- Strongly react with BrF_5 .
- Explode when mix with para-nitrotoluene at 80 °C.
- React with metal through reaction:



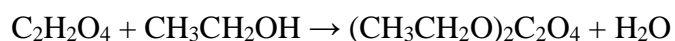
3. $\text{H}_2\text{C}_2\text{O}_4$ (Oxalic Acid)

Physics

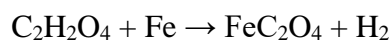
- Molecular weight: 90,03 g/mol
- Color, crystalline form and refractive index: white and col, viscouslq
- Specific gravity: 1.90 g/cm³
- Melting point (°C): 365
- Solubility in 100 parts water (25°C): 7,7

Chemist

- Corrosive.
- Reacts explosively with strong oxidizers and some silver compounds.
- Reacts with alcohol:



- Reacts with metals:



CHAPTER III

RESEARCH METHODOLOGY

3.1 Instruments and Materials

3.1.1 Materials

1. Sample 1, 2, 3
2. KMnO_4 0,1N
3. H_2SO_4 6 N
4. $\text{H}_2\text{C}_2\text{O}_4$ 0,1 N

3.1.2 Instruments

1. Erlenmeyer
2. Electric Stove
3. Funnel
4. Beaker Glass
5. Burette, statif, clamp
6. Pipette drops
7. Measuring Cup
8. Measuring pipette
9. Aspirator
10. Mixer
11. Thermometer

3.2. Experimental Methods

3.2.1. Standardization of KMnO_4 with $\text{Na}_2\text{C}_2\text{O}_4$

1. Take 10 ml of $\text{H}_2\text{C}_2\text{O}_4$ 0.1 N solution then put it in the erlenmeyer.
2. Add 6 ml of H_2SO_4 6 N solution.
3. Heat up to 83°C .
4. Titration in hot condition using KMnO_4 .
5. Stop the titration if a pink color appears that doesn't disappear by shaking.
6. Look for the needs KMnO_4 .

$$N \text{ KMnO}_4 = \frac{(V.N) \text{ H}_2\text{C}_2\text{O}_4}{V \text{ KMnO}_4} \quad (3.1)$$

3.2.2. Determining Fe^{2+} Levels in the Sample

1. Prepare samples, tools, and materials.

2. Take a sample and add 20 ml of 6 N sulfuric acid.
3. Heat up to 83°C.
4. Titrate in a hot state with potassium permanganate 0.1 N until a pink color appears which doesn't disappear by shaking.
5. Record the needs of KMnO_4 .
6. Calculation:

$$\text{mg material} = \text{ml titrant} \times \text{N titrant} \times \text{BE material} \quad (3.2)$$

$$\text{BE mat} = \frac{\text{BM Fe}}{\text{equivalent}} \quad (3.3)$$

$$\text{Kadar} = \frac{\text{mg material}}{\text{mg sample}} \times 100\% \quad (3.4)$$

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