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# **ANALYTICAL CHEMISTRY II Lab-Work**

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# ANALYTICAL CHEMISTRY II

## LAB WORK



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## PREFACE

Analytical chemistry in its broadest sense encompasses the theory and practice of all means of acquiring information about the composition of matter. Quantitative analysis constitutes the largest part of analytical chemistry and is devoted to the techniques, methods, and instrumentation involved in determining the amount or concentration of constituents in sample. The instruments and techniques used in modern analytical chemistry laboratories change constantly but many principles and much underlying theory remain fundamentally important to the practice of analytical chemistry.

We began this book with three major goals in mind: (1) to develop and explain the theories upon which the principles of various analytical procedures are based, (2) to give instruction for lab work in analytical separation, (3) to give skill experience lab work in laboratories. This book includes the matter of separation by precipitation, distillation extraction, and chromatography.

A great many colleagues aided in the development of this book by constructing and reviewing the manuscript. We owe special thanks to my rector that was budgeting the project and to my colleague that was contribute to the constructing and reviewing the book. We hope the book give some value for my student and for all reader.

**Yogyakarta, December 2014**

**Team**

## **CHAPTER I**

### **SEPARATION BY PRECIPITATION**

Precipitation is the creation of a solid in a solution or inside another solid during a chemical reaction or by diffusion in a solid. When the reaction occurs in a liquid solution, the solid formed is called the 'precipitate'. The chemical that causes the solid to form is called the 'precipitant'. Without sufficient force of gravity (settling) to bring the solid particles together, the precipitate remains in suspension. After sedimentation, especially when using a centrifuge to press it into a compact mass, the precipitate may be referred to as a 'pellet'. The precipitate-free liquid remaining above the solid is called the 'supernate' or 'supernatant'.

Sometimes the formation of a precipitate indicates the occurrence of a chemical reaction. If silver nitrate solution is poured into a solution of sodium chloride, a chemical reaction occurs forming a white precipitate of silver chloride. When potassium iodide solution reacts with lead nitrate solution, a yellow precipitate of lead iodide is formed.

Precipitation may occur if the concentration of a compound exceeds its solubility (such as when mixing solvents or changing their temperature). Precipitation may occur rapidly from a supersaturated solution.

In solids, precipitation occurs if the concentration of one solid is above the solubility limit in the host solid, due to e.g. rapid quenching or ion implantation, and the temperature is high enough that diffusion can lead to segregation into precipitates. Precipitation in solids is routinely used to synthesize nanoclusters.

In this section, it will explain some of separation by precipitation technique i.e. electrogravimetry and fractional precipitation.

#### **I.1 FRACTIONAL PRECIPITATION**

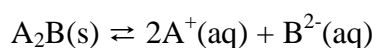
##### **A. Objective**

Students are expected to separate a mixture of substances based on their different solubilities

## B. Theory

There is no definite dividing lines between insoluble salts, sparingly soluble, and soluble salts, but concentrations of their saturated solutions are small, medium, and large. The solubility process reaches a dynamic equilibrium described by an equilibrium constant. This equilibrium constant is called the solubility product constant, and is given the symbol  $K_{sp}$ .

The *solubility product constant*  $K_{sp}$  is just one more version of the standard equilibrium constant expression. Here, it's applied to the equilibrium between a solid and the corresponding ions in solution. For example, if there is an equilibrium:



the corresponding solubility product constant expression will be:

$$K_{sp} = [A^+]^2[B^{2-}]$$

The solubility product can be calculated given a compound's solubility. The solubility constant can be used to calculate whether a precipitate will form given the concentrations of ionic species. Compounds having a common ion but different solubility constants can be separated by fractional precipitation. The  $K_{sp}$  values for various salts are valuable information, and some data are given in the table 1.

Table 1.  $K_{sp}$  measured in 25<sup>0</sup>C

Compound	$K_{sp}$
Al(OH) <sub>3</sub>	$1,3 \times 10^{-23}$
AgCl	$1,8 \times 10^{-10}$
CaCO <sub>3</sub>	$4,8 \times 10^{-9}$
Cu(OH) <sub>2</sub>	$2,2 \times 10^{-20}$
Fe(OH) <sub>3</sub>	$6,3 \times 10^{-38}$
Fe(OH) <sub>2</sub>	$1,6 \times 10^{-16}$
Mg(OH) <sub>2</sub>	$1,8 \times 10^{-11}$
Mn(OH) <sub>2</sub>	$1,9 \times 10^{-13}$
PbCl <sub>2</sub>	$1,7 \times 10^{-5}$

The reaction quotient,  $Q$ , can be used to determine whether a precipitate will form with a given concentration of ions. (The reaction quotient is also called the **ion product** when it is calculated using concentrations of species involved in solubility equilibria). One first calculates  $Q$ , then compares it with  $K_{sp}$ .

If  $Q < K_{sp}$ , no precipitate will form.

If  $Q = K_{sp}$ , a precipitate will form.

If  $Q > K_{sp}$ , a precipitate will form.

Note that precipitation may not happen immediately if  $Q$  is equal to or greater than  $K_{sp}$ . A solution could be supersaturated for some time until precipitation occurs. It can be used as a rule when separate mixture by using fractional precipitation.

Fractional precipitation is a method for separating elements or compounds with similar solubilities by means of their gradual precipitation from the solution. It is a series of analytical precipitations, each one improving the purity of the desired element. The possibility of quantitative separation of a mixture depends on the ratio of the original concentrations of compounds being precipitated and on the values of their solubility product (McGraw-Hill Dictionary of Scientific & Technical Terms, 6E, 2003). Fractional precipitation can be done in many ways, like ordering acidity, precipitating by sulfide reagent or other anorganic reagent like phosphate, carbonate, chloride, and sulphate. Such organic reagent like dimethylglyoxime (DMG), and oxyn can also be used as precipitant. Besides that, by using electrical current, the substances in a solution can be separated each others, known as electrodeposition.

### C. Materials and Apparatus

Materials : 1. NaCl

2.  $K_2CrO_4$

3.  $AgNO_3$

4. Fe(III)

5. Zn(II)

6. buffer acetate

7.  $NH_3$

Apparatus : 1. Beaker glass

2. Volumetric glass

3. Filter paper

4. Centrifuge

5. pHmeter

6. Heater

#### D. Experimental Procedures

##### 1. Experiment 1

- a. A 100 ml solution containing 0.001 mole NaCl and  $K_2CrO_4$  add in a beaker glass
- b. Dropwise adding  $AgNO_3$  into the glass slowly
- c. When precipitation begin, observe your volume of  $AgNO_3$  adding
- d. Separate precipitate by filter paper
- e. Dropwise adding  $AgNO_3$  again into the glass
- f. Separate the second precipitate form from solution

##### 2. Experiment 2

- a. A 100 ml solution containing 0.1 mole Fe (III) and 0,1 mole Zn(II) ions add in a beaker glass
- b. Measure pH at 1 with an acid reagent
- c. Dropwise buffer acetate until pH 6, while observe your solution. Let your precipitate .
- d. Add water and let it be slightly warm by a heater, then filtered
- e. Add  $NH_3$  solution until pH 9.
- f. Filter the occurred precipitate

#### E. Data

Write down your observation on the table below:

No	Treatment	Quantitative factor of treatment	Observation
1			
Etc			

#### F. Task

1. The experiment is a kind of fractional precipitation. What the way is done?
2. In the first experiment, what compounds made in the first and second precipitate? Why?
3. When the first precipitate has separated, what percentage of ion that precipitated remain?

## I.2. ELECTROGRAVIMETRY

### A. Objective

After performing the experiment, the experimentalist skillfully in electrogravimetric separation method.

### B. Theory

#### 1. Definition

Electrogravimetry is classified a quantitative analysis method. The principle of electro gravimetric, analyzed components deposited on an electrode that has been known weight and after perfect precipitation occurs, electrode and precipitate is weighed again. Metals which will be determined in the solution should be in the form of a cation, where these cations will move to the cathode during electrolysis and attached as a free metal.

Electrogravimetry process required amount of electrical current flowing through the electrode, causing chemical changes. Elemental analysis by electrolysis based on both Ohm's law and Faraday's law. The first Faraday's law states that the amount of substance deposited or removed in the electrodes in direct proportion to the amount of electricity flowing through the solution. The second Faraday's Law states that the number of substances that are deposited or removed from different substances by the same amount of electricity, is directly proportional to the weight equivalent. Two Faraday's law can be written in the following equation:

$$w = \frac{e \times i \times t}{F}$$

Description:

w = weight of a substance that is deposited (g)

e = equivalent weight of substances

i = electrical current (amperes)

t = time of electrolysis (seconds)

F = Faraday's number (96500 Coulomb)

Faraday's number is the amount of electricity needed to precipitate or dissolve one gram (gram equivalent) substances. Equivalent weight of a substance is the atomic mass of the substance divided by its valence

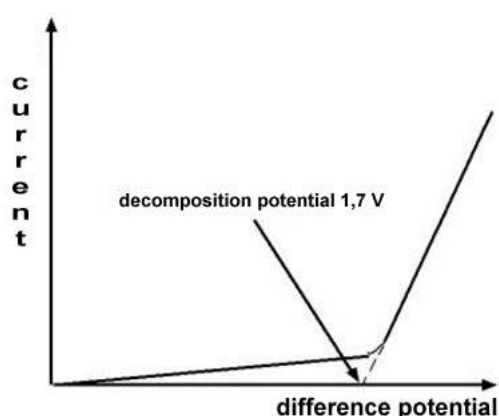


$$w = \frac{i \times t \times \text{the atomic mass of the element}}{96500 \times \text{valence}}$$

Atomic mass of the element divided by 96500 x valence called the electric chemistry, given symbol a, i.e. the number of substances that precipitate when one ampere electricity is passed electrolyte solution for one second. The above statement can be written as:

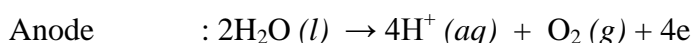
$$w = a \times i \times t$$

The relation between potential used in electrolysis and the electric current that flows can be seen in the following figure.



**Fig 1.** Relationship of current and difference potential to the electrolysis of sulfuric acid in the platinum electrode.

The graph shows that when a difference potential used greater, current flows only slightly increased and there is no electrolysis. However, at the decomposition potential the current flowing increased dramatically. At that moment electrolysis began to take place in the electron produces hydrogen and oxygen.



Performing of electrolysis needs a minimum potential, because:

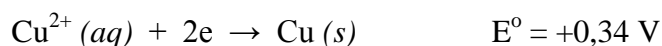
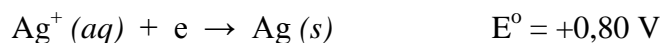
- a. The existence of the difference potential between the electrodes causes the ions in the system moves to the electrode. The difference potential must be at

least offset the DGL-back (back emf) which is caused by the absorption of electrolysis results on the electrode surface.

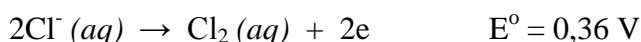
- b. Required additional potential to discharge ions in electrolysis is called over potential. Over potential is a measure of the activation energy for the electrode reaction. Reaction at the electrode that produces more gas requires a greater potential.

## 2. The Reaction on The Electrode

There is competition between the ions of the electrolyte and ions from water to react on the electrode surface. The reaction on the electrode can be explained by the value of the electrode potential. In the reduction reaction, the cation which has a more positive electrode potential will undergo reduction reaction first. For example, in a solution containing  $\text{Cu}^{2+}$  ions and  $\text{Ag}^+$  ions with the same concentration, first ions undergo reaction is  $\text{Ag}^+$  ions.



In contrast, at the formation of negative ions, oxidation reaction will be performed first by anion which have electrode potential more negative. For example, if there is  $\text{Cl}^-$  ions and  $\text{I}^-$  ions in solution, the ions  $\text{I}^-$  will perform oxidation first.

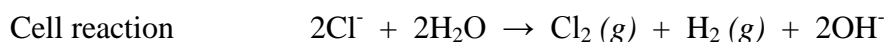
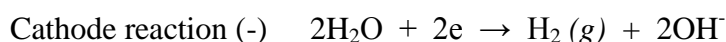
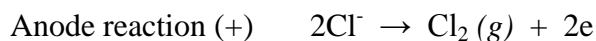


Here are the factors that determine the chemical electrolysis

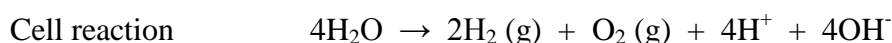
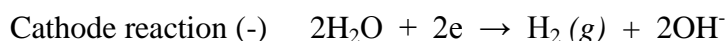
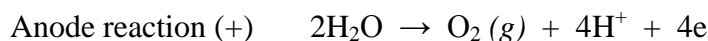
- a. Concentration of different electrolytes.

Example:

- 1) Concentrated NaCl solution



- 2) Very aqueous NaCl solution



b. The chemical composition of different electrode

1) Electrode inert (inactive)

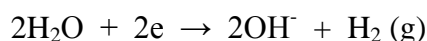
Example: electrolysis of  $\text{CuSO}_4$  solution with Cu as the anode.



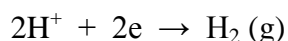
Electrolysis results can be summarized as follows.

a. Reaction at the cathode (cathode does not play a role)

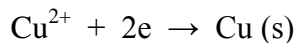
- 1) If a solution containing ions such as  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , the reaction takes place:



- 2) If electrolyte solution is acidic, the reaction takes place:



- 3) Solution containing other metal ions, the reaction takes place:



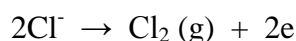
b. Reaction at the anode

1) inert anode (Pt, C)

- If the solution is alkaline, the reaction takes place:



- If the solution mengandung ion  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , the reaction takes place:



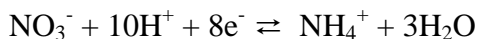
- If the residual acid solution containing another example  $\text{SO}_4^{2-}$ , the reaction takes place:



3. Deposition on Electrolysis

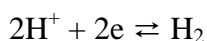
Ideally, the precipitate should be strongly attached to the electrode, gathering and fine so that the precipitate do not loss of weight when washed, dried and weighed. The precipitate that forms must be fine-grained, uniform and looks like metal. If form of sediment is sponge, powder, or clump which is not good attached to the electrode, it shows less pure precipitate. The main factors affecting the physical properties of the sediment is the current density, temperature, presence or absence of complexing agent. The magnitude of the density current in order to obtain a perfect sediment is  $<0.1 \text{ A} / \text{cm}^2$ .

Precipitation along with hydrogen gas may cause risk and unprofitable. The formation of hydrogen gas can be prevented by the addition of a cathode depolarization, e.g nitrate ions.

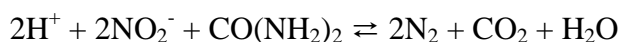


The electrodes used are platinum (Pt), the advantage is inert, can be burned to remove fat, organic matter or gas without damaging the Pt metal. For the metals Zn, Bi and Ga are not deposited directly on Pt electrode, but Pt electrode will be coated first with copper metal.

Copper can be deposited from a solution of  $\text{H}_2\text{SO}_4$  /  $\text{HNO}_3$  or a mixture of the two, in which the electric potential of 2-3 volts are used so that the reaction occurs:



Acid concentration in the solution should not be too high because the deposition of copper is not perfect and sediment is not attached perfectly. Nitric acid is used must be free of nitrite as nitrite ions can inhibit the deposition of copper perfectly. To overcome it, nitric acid is boiled before used and added with urea.



Nitric acid can be eliminated with the addition of a little sulfamic acid:



Reasons to safe the system from chloride ions, among others:

- a. Chlorine liberated at the anode will attack Pt. This can be overcome with an anodic depolarization substance like salt hydrazium or hydroxyl ammonium.
- b. Cu(I) is stabilized as a complex-chloro and remain in solution until oxidized back to the anode.

#### 4. Current Efficiency

In electrolysis, to precipitate metals from acid solution, 90% of the current is flowed to precipitate the metal and 10% of the current used to produce hydrogen. Thus, current efficiency of metal precipitate is 90% while current

efficiency of hydrogen forming is 10%. Current efficiency is very important in the electrochemical industry. However, 100% efficiency current is very rare.

Example:

In the container, electrolysis copper(II) sulphate solution as much as 0.175 kg Cu will be deposited if electrified as  $5,5 \cdot 10^5$  C. Calculate the efficiency of the current in the metal deposition process.

$$\begin{aligned}M &= Q \times \frac{A}{Z} \times \frac{1}{96500} \\Q &= \frac{175 \times 2 \times 96500}{63,54} \\&= 531555 \text{ C}\end{aligned}$$

$$\text{Current efficiency} = \frac{531555}{550000} \times 100 = 96,65\%$$

Current efficiency can also be determined by comparing the weight of the cathode sediment of electrolysis result experimentally with the weight of the cathode sediment of electrolysis result theoretically. For this purpose, it should be noted duration of electrolysis and the amount of current (amperes) flowing during the electrolysis process.

$$\text{Current efficiency} = \frac{\text{the weight of electrolysis result experimentally}}{\text{the weight of electrolysis result theoretically}} \times 100\%$$

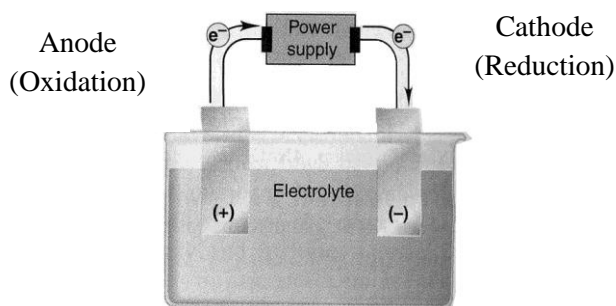
### C. Materials and Apparatus

1. Analytical balance
2. A set of tools electrolysis
3. Drying oven
4. Stopwatch
5. Pipette 25 mL
6. Mixer
7. Pasteur pipette
8. Test tube
9. Sample solution  $\text{CuSO}_4$
10. Nitrate-free concentrated nitric acid
11. Dilute nitric acid solution
12. Acetone or alcohol

13. Hexacyanoferrate(II) solution
14. Solution of concentrated sulfuric acid

#### D. Experimental Procedures

1. Clean the electrodes with dilute nitric acid and then rinse with acetone and dried in an oven.
2. Weigh electrode (cathode) with the analytical balance.
3. Taking a 25 mL sample solution of Cu(II) prepared using a pipette, pour solution into the 250 mL beaker, and add 2 mL of concentrated sulfuric acid and 1 mL of concentrated nitric acid, then dilute with distilled water to the appropriate volume of 100 mL.
4. Arrange electrolysis equipment like Figure below.



**Fig 2.** Electrolysis equipment arrangement.

5. Perform electrolysis at a potential of 3 volts and if possible do the stirring slowly in solution electrolysis. Note the start time of electrolysis.
6. After electrolysis runs a while (solution seems clear), test the solution by taking a few drops of copper. Drop a few of the copper solution into a test tube, then add reagents hexacyanoferrate(II) solution. If the result is negative, the electrolysis was stopped and the time noted. Once the electrode is rinsed with acetone, preheat the oven and weigh it carefully.
7. Clean the electrodes with dilute nitric acid solution and dried.
8. Observe the color of the precipitate and its physical structure as well as weigh heavy precipitation (cathode weight difference).

#### E. Task

1. Calculate levels of copper(II) in percent of the initial sample solution!
2. Calculate the efficiency of the current!

## TABLE OF CONTENT

	Page
Book Cover .....	i
Preface .....	ii
Table of Content .....	iii
CHAPTER I. SEPARATION BY PRECIPITATION .....	1
I.1. FRACTIONAL PRECIPITATION .....	1
I.2. ELECTROGRAVIMETRY .....	5
CHAPTER II. DISTILLATION .....	12
II.1. SIMPLE DISTILLATION AND FRACTIONAL DISTILLATION .....	13
II.2. STEAM DISTILLATION .....	18
II.3. VACUUM DISTILLATION .....	22
CHAPTER III. EXTRACTION .....	25
III.1. SOLVENTS EXTRACTION .....	27
III.2. METAL EXTRACTION .....	30
III.3. SOXHLET EXTRACTION .....	32
CHAPTER IV. CHROMATOGRAPHY .....	36
IV.1. PAPER CHROMATOGRAPHY .....	38
IV.2. IDENTIFICATION OF ANALGESICS USING TLC SEPARATION .....	48
IV.3. COLUMN CHROMATOGRAPHY .....	57
IV.4. GEL PERMEATION CHROMATOGRAPHY .....	62
IV.5. ION EXCHANGE CHROMATOGRAPHY .....	72
IV.6. THE DETERMINATION OF AMINO ACIDS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC) .....	74
IV.1. ANALYSIS OF FATTY ACIDS CONTEN IN CORN OIL BY GAS CHROMATOGRAPHY .....	81
REFERENCES .....	87





