Extraction

Extraction is a method to separate compounds based on their relative solubilities in two different immiscible liquids.

Distribution coefficient is often quoted as a measure of how well-extracted a species is. The distribution coefficient is equal to the concentration of a solute in the organic phase divided by its concentration in the aqueous phase. A density difference is required between the two phases.

$$K = \frac{The\ concentration\ of\ the\ solute\ in\ the\ organic\ phase}{The\ concentration\ of\ the\ solute\ in\ the\ aqueous\ phase}$$

When choosing a solvent system for extraction, it is important to pick two immiscible solvents. Most extractions involve water because it is highly polar and immiscible with most organic solvents. The desired properties of solvents are good selectivity towards solute and little or no miscibility with feed solution. Other factors affecting solvent selection are boiling point, density, interfacial tension, viscosity, corrosiveness, flammability, toxicity, stability, availability and cost.

(1): The selection of a suitable solvent

The purpose

Choosing the suitable solvent for extraction by comparing between distribution coefficient of the solvents, the higher distribution coefficient is the better.

Tools and materials used

Separatory funnel 100ml, pipette 10ml, Burette, funnel, conical flask, benzoic acid C_6H_5COOH, sodium hydroxide, diethyl ether, benzene, ph.ph. indicator.

Procedure

1- Pipette 10 ml of benzoic acid into conical flask and add two drops from ph.ph.
2- Titrate with NaOH (repeat this step twice) and calculate the acid concentration.
3- Pipette 10 ml of acid into separatory funnel then add 10 ml benzene.
4- Shake gently and wait until the separation of layers.
5- Down precisely the aqueous layer in conical flask, then titrate with sodium hydroxide (add two drops from ph.ph) until the pink color appears.
6- Calculate acid concentration in the aqueous layer and organic layer.
7- Calculate the distribution coefficient.
8- Repeat all the steps with another solvent (diethyl ether).

(2): Extraction efficiency

Purpose of the experiment

Identification of a number of times necessary to obtain a quantitative extraction (99.9%) and answer these questions:

- Is extraction once is enough using a large amount of the organic solvent?
- Is extraction once is enough using a small amount of the organic solvent?
- Is extraction many times using small amounts of solvent at a time is enough?

Tools and materials used

Separatory funnel 100ml, pipette 10ml, Burette, funnel, conical flask, benzoic acid, sodium hydroxide, Diethyl ether, Phenolphthalein indicator.

Procedure

First:

1. Transfer 10ml of benzoic acid into separatory funnel, then add 30ml from Diethyl ether using cylinder.
2. Shake gently and wait until the separation of layers.
3. Down precisely the aqueous layer in conical flask, then titrate with sodium hydroxide (add two drops from ph.ph) until the pink color appears.
4. Calculate the remaining concentration from acid in aqueous layer.

Second:

1. Transfer 10ml of benzoic acid into separatory funnel, then add 10ml from Diethyl ether using cylinder.
2. Shake gently and wait until the separation of layers.
3. Down precisely the aqueous layer in conical flask, then titrate with sodium hydroxide (add two drops from ph.ph) until the pink color appears.
4. Calculate the remaining concentration from acid in aqueous layer.

Third:

1. Transfer 10ml of benzoic acid into separatory funnel, then add 10ml from Diethyl ether using cylinder.
2. Shake gently and wait until the separation of layers.
3. Take aqueous layer, add 10ml from Diethyl ether, shake gently and wait until the separation of layers.
4. Again, take aqueous layer, add 10ml from diethyl ether, shake gently and wait until the separation of layers.

5. Down precisely the aqueous layer in conical flask, then titrate with sodium hydroxide (add two drops from ph.ph) until the pink color appears.
6. Calculate the remaining concentration from acid in aqueous layer.

(3): Spectrophotometric determination of Iron (III) using Thiocyanate

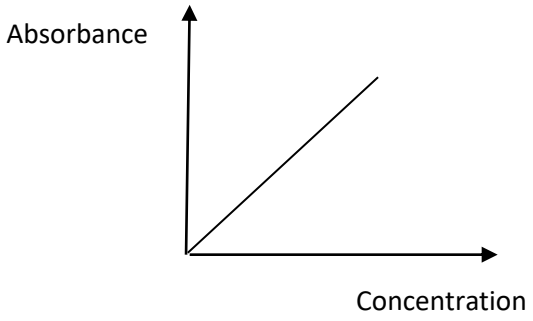
Purpose:

The Iron (III) (Fe^{3+}) is determined qualitatively by using thiocyanate (SCN) as an indicator.

If (SCN) is added to a solution containing (Fe^{3+}), a blood red solution is formed due to the formation of $Fe(SCN)_3$.

$$FeCl_3 + 3SCN^- \longrightarrow Fe(SCN)_3 + 3Cl^-$$

The Iron (III) is determined quantitatively by using Spectrophotometer at 500 nm with tungsten filament and quartz cuvette.



Tools and materials used

Separatory funnel 100ml, funnel, Iron (III) solution, Thiocyanate ammonium 30%, Diethyl ether.

Procedure

1. Pipette (1, 2, and 2.5) ml of iron (III) solution into three separatory funnels.
2. Add 6 ml of thiocyanate ammonium 30% to each separatory funnel.
3. Extract using diethyl ether three times (7 ml each time), then collect all extracts in volumetric flask 25 ml. Dilute to volume with diethyl ether.
4. Record the absorbance at 500 nm using1 cm quartz cuvette.
5. Repeat all steps with the unknown solution (1.5 ml).
6. Calculate the concentration of the unknown solution

Chromatography

Chromatography is the collective term for a set of laboratory techniques for the separation of mixtures. The mixture is dissolved in a fluid called the "mobile phase", which carries it through a structure holding another material called the "stationary phase". The various constituents of the mixture travel at different speeds, causing them to separate. The separation is based on differential partitioning between the mobile and stationary phases.

Chromatography techniques:

1. Column chromatography
2. Liquid chromatography (LC)
3. Gas chromatography (GC)
4. Paper chromatography
5. Thin layer chromatography (TLC)
6. Ion exchange chromatography

The applications of these techniques are wide reaching and cross many disciplines including biology, biochemistry, microbiology and medicine.

Column chromatography

Column chromatography is a method used to separate and purify individual chemical compounds from mixtures of compounds. Chromatography involves a sample being dissolved in a mobile phase. The mobile phase is then forced through an immobile, immiscible stationary phase. The phases are chosen such that components of the sample have differing solubilities in each phase. A component which is quite soluble in the stationary phase will take longer to travel through it than a component which is not very soluble in the stationary phase but very soluble in the mobile phase. As a result of these differences in mobilities, sample components will become separated from each other as they travel through the stationary phase.

The distribution of analytes between phases can often be described quite simply. An analyte is in equilibrium between the two phases;

$$A_{mobile} \rightleftharpoons A_{stationary}$$

The equilibrium constant, *K*, is termed *the partition coefficient*; defined as the molar concentration of analyte in the stationary phase divided by the molar concentration of the analyte in the mobile phase.

The mobile phase is either a pure solvent or a mixture of different solvents. By changing the solvent, or perhaps using a mixture, the separation of components can be adjusted. Usually begins by using less polar mobile phase and then the polarity is increased by mixing more than one solvent or replacing the solvent by another one.

Table 1: Polarity index

Solvents	**Polarity**
Heptane	0.0
Hexane	0.0
Toluene	2.4
Benzene	2.7
Diethyl Ether	2.8
Dichloromethane	3.1
Tetrahydrofuran	4
Chloroform	4.1
Acetone	5.1
Methanol	5.1
Ethanol	5.2
Acetic Acid	6.2
Water	9

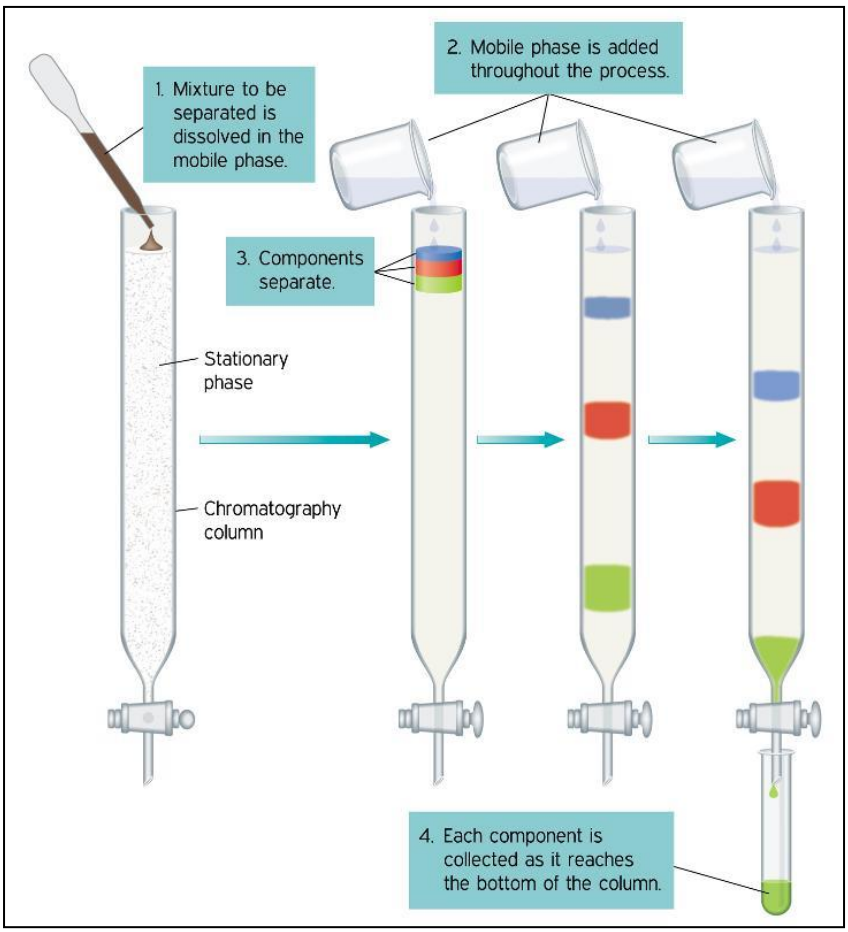


Figure1: Column chromatography

(4): Separation of colored compounds by column chromatography

Purpose:

Separation of mixture of potassium permanganate and potassium dichromate by column chromatography.

Tools and materials used:

Separation column, conical flask, pipettes 1ml, burette, graduated pipette.
Silica gel, mixture of potassium permanganate and potassium dichromate, Distilled water, sulfuric acid, oxalic acid.

Procedure:

1- Wash the column with distilled water.
2- Place a cotton plug or glass wool at the end of the column.
3- Mount the column on the stand.
4- Put about 40 gm of silica gel in flask 250 ml and add some of distilled water (the solvent).
5- Prepare the separation column from silica gel the length of column 30-40 cm until the water level slightly above the surface of the silica and then close the tap separation column.
6- Pipette 0.5 ml from the mixture of potassium permanganate and potassium dichromate into the solvent layer above the silica gel in the packed column.
7- Open the tap and continue filling the column with distilled water and elute it until the permanganate layer runs down the column.
8- Pipette 5 ml from potassium permanganate into a conical flask and add 2 ml from sulfuric acid (2 M) and heat it in a water bath before reaching its boiling point.
9- Titrate with hot oxalic acid until the color of potassium permanganate disappears.
10- Calculate the concentration.

Ion Exchange

Ion-exchange chromatography retains analyte molecules on the column based on coulombic (ionic) interactions. The stationary phase surface displays ionic functional groups (R-X) that interact with analyte ions of opposite charge.

An **ion-exchange resin** or **ion-exchange polymer** is an insoluble matrix normally in the form of small (1–2 mm diameter) beads fabricated from an organic polymer substrate. The material has highly developed structure of pores on the surface of which are sites with easily trapped and released ions. The trapping of ions takes place only with simultaneous releasing of other ions; thus the process is called ion-exchange. Ion exchangers are either **cation exchangers** that exchange positively charged ions (cations) or **anion exchangers** that exchange negatively charged ions (anions).

Cation exchanger:

- strongly acidic (typically, sulfonic acid groups, e.g. sodium polystyrene sulfonate or polyAMPS)

$$nR_2SO_3^- H^+ + M^{n+} \rightleftharpoons (R_2SO_3)_n M + nH^+$$

- weakly acidic (mostly, carboxylic acid groups)

$$nR_2CO_2^- H^+ + M^{n+} \rightleftharpoons (R_2CO_2)_n M + nH^+$$

Anion exchnahger:

- strongly basic, (quaternary amino groups, for example, trimethylammonium groups, e.g. polyAPTAC)

$$nR_2N^+R_3OH^- + A^{n-} \rightleftharpoons (R_2NR_3)_n A + nOH^-$$

- weakly basic (primary, secondary, and/or ternary amino groups, e.g. polyethylene amine)

$$nR_2N^+H_3OH^- + A^{n-} \rightleftharpoons (R_2NH_3)_n A + nOH^-$$

(5): Determination of total ion concentration using ion exchange chromatography

Purpose:

Positive ions concentration is determined using cation exchanger. Cation exchange resin is the stationary phase and the solvent containing the analyte ion is the mobile phase. The cation is separated from the sample at par with the displacement of hydrogen protons from the column. The liberated H^+ are equal to the concentration of cation. The liberated H^+ are titrated with a strong base, NaOH to determine the concentration of cation.

Tools and materials used:

Column packed with cation exchanger Amberlite resin IR-120, burette, pipette 25 ml, conical flask, mixture of HCl/KCl, mixture of HCl/$MgSO_4$, distilled water, ph.ph, NaOH.

Procedure:

1. Pipette 25 ml from the mixture in a conical flask.
2. Titrate with NaOH + two drops from ph.ph.
3. Calculate the concentration of HCl.
4. Pipette 25 ml from the mixture in the column and open the tap.
5. Wash the column with distilled water three times (25 ml each time) and collect distilled water in the same flask.
6. Titrate with NaOH + two drops from ph.ph.
7. Calculate the concentration of HCl.

Planar chromatography

Planar chromatography is a separation technique in which the stationary phase is present as or on a plane. The solvent moves up the plate by capillary action. There are two types of planar chromatography: thin layer chromatography (TLC) and paper chromatography.

Thin layer chromatography (TLC) is a chromatography technique used to separate mixtures. Thin layer chromatography is performed on a sheet of glass, plastic, or aluminum foil, which is coated with a thin layer of adsorbent material (stationary phase), usually silica gel, or aluminium oxide.

In paper chromatography, Separations in paper chromatography involve the same principles as those in thin layer chromatography. However, the paper is made of cellulose (stationary phase).

The retention factor (R_f) may be defined as the ratio of the distance traveled by the substance to the distance traveled by the solvent. If R_f value of a solution is zero, the solute remains in the stationary phase and thus it is immobile. If R_f value = 1 then the solute travels with the solvent front. To calculate the R_f value, take the distance traveled by the substance divided by the distance traveled by the solvent (mobile phase).

R_f = Distance from origin to center of spot/Distance from origin to solvent front

The factors affect R_f value:

1- The nature of the mobile phase.
2- The nature of the stationary phase.
3- Temperature.

(6): Choose the appropriate mobile phase

The idea of the experiment:

Such series are useful for determining necessary solvents needed for chromatography of chemical compounds. Normally such a series progresses from non-polar solvents, such as n-hexane, to polar solvents such as methanol or water. Characteristics of the appropriate mobile phase:

1- Good separation between substances.
2- $R_f \neq 1$
3- Achieve the desired resolution in an acceptable time.

Materials and tools used:

Thin layer (a sheet of glass coated with silica gel). Substances: Sudan yellow, Bromocresol purple, Bromophenol blue. Mobile phases: (Methanol 2:8 Ethyl acetate), (Methanol 8:2 Ethyl acetate), Benzene 8:2 Ethyl acetate).

Procedure:

1- Draw a line (in pencil not pen) across the bottom edge of the plate 1 cm up from the bottom.
2- Spot three spots along the line drawn on the plate.
3- Pour 10 ml of mobile phase in the jar and leave it few minutes to help to saturate the atmosphere with solvent vapor.
4- Put the plate inside the jar.
5- Remove the plate and mark the solvent front with a pencil.
6- Allow the plate to dry for a few minutes.
7- Calculate R_f for each substance.
8- Repeat the same steps for the other two phases.
9- Compare between the mobile phases, which one is the best?why?

(7): Separation of a mixture of dyes by thin layer chromatography (TLC)

The idea of the experiment:

Separation of a mixture of dyes by thin layer chromatography. TLC can be used to support the identity of a compound in a mixture when the R_f of a compound is compared with the R_f of a known compound.

Materials and tools used:

Thin layer (a sheet of glass coated with silica gel). Dyes: Bromothymol blue, Bromophenol blue, Phenol red. Unknown dye mixture, Mobile phase: (Ammonia: Ethanol: Butanol) (1: 1: 3)

Procedure:

1- Draw a line (in pencil not pen) across the bottom edge of the plate 1 cm up from the bottom.
2- Spot three spots along the line drawn on the plate.
3- Pour 10 ml of mobile phase in the jar and leave it few minutes to help to saturate the atmosphere with solvent vapor.
4- Put the plate inside the jar.
5- Remove the plate and mark the solvent front with a pencil.
6- Allow the plate to dry for a few minutes.
7- Calculate R_f for each substance.
8- Compare between R_f values of an unknown dye and the known dyes.
9- Determine the components of an unknown dye mixture.

(8): Separation of a mixture of phenols by thin layer chromatography (TLC)

The idea of the experiment:

Separation of a mixture of phenols (colorless compounds) by thin layer chromatography.

Observing the separated spots can be performed using:

1- UV light.
2- An iodine (I2) chamber. Iodine sublimes and will absorb to organic molecules in the vapor phase.

Materials and tools used:

Thin layer (a sheet of glass coated with silica gel). Phenols : phenol, catechol, pyrogallol.
Unknown mixture, two mobile phases: 1- (hexane 5: 2ethylacetate),
2- (ethyl acetate 2: 5 dichloromethane), iodine.

Procedure:

1- Draw a line (in pencil not pen) across the bottom edge of the plate 1 cm up from the bottom.
2- Spot three spots along the line drawn on the plate.
3- Pour 10 ml of mobile phase in the jar and leave it few minutes to help to saturate the atmosphere with solvent vapor.
4- Put the plate inside the jar.
5- Remove the plate and mark the solvent front with a pencil.
6- Allow the plate to dry for a few minutes.
7- Calculate R_f for each substance.
8- Compare between R_f values of an unknown mixture and the known phenols.
9- Determine the components of an unknown mixture of phenols.
10- Repeat the same steps with another mobile phase and compare between R_f values of two mobile phases.