

INTRODUCTION:-

The branch of chemistry which deals with chemical characterization of a substance is called ANALYTICAL CHEMISTRY. A complete chemical characterization includes two types of Analysis.

- (i) Qualitative Analysis
- (ii) Quantitative Analysis

QUALITATIVE ANALYSIS:- It is concerned with determination of nature of substance. In this type of analysis we are concerned with determination of which elements are present in a compound.

QUANTITATIVE ANALYSIS:- In this type of analysis we are concerned with determination of amounts of different elements present in a chemical compound.

STEPS IN QUANTITATIVE ANALYSIS It involves four major steps

- 1) Obtaining a sample for analysis
- 2) Separation of desired constituent
- 3) Measurement and calculation of result
- 4) Drawing conclusion from analysis

Q:- WRITE A NOTE ON FILTRATION PROCESS:

It is a process by which insoluble particles are separated from liquid. It can be performed by different types of filter media for nature of precipitate, nature of solvent and nature of solvent. In which type of filter media should be used. The most commonly used filter media are

- 1) Filter paper
- 2) Filter crucibles.

FILTER PAPERS

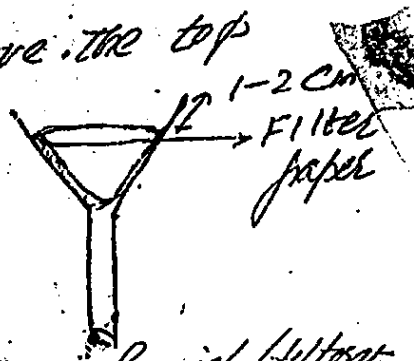
Filtration by glass funnel and filter paper is a slow process. When mixture of liquid and solid particles is poured on to the filter paper, the solvent passes through filter paper and suspended particles are left behind as residue. The liquid which passes through filter paper is called FILTRATE.

CHARACTERISTICS OF FILTER PAPER

The filter papers have different pore sizes. The choice of filter paper depends upon size of particles in the precipitate.

SIZE OF FILTER PAPER - The size of filter paper should be such that it should be one fourth to one half full of precipitate at the end of filtration.

SIZE OF FUNNEL - The size of funnel should be such that its upper rim is 1-2 cm above the top circumference of filter paper.



STEM OF FUNNEL - The stem of funnel should be several inches long so that it can extend a few centimeters down into the receiver beaker. The tip of stem should touch with walls of beaker so that liquid filtrate runs down along the side of beaker without splashing.

If process of filtration is to be smooth the stem of funnel should remain continuously full of liquid, as long as there is liquid in conical portion.

HOW TO FOLD FILTER PAPER - The paper should be folded twice. The first fold is along diameter of paper. The second fold is such that edges do not quite match. The paper should be opened on slightly larger section. There is three fold thickness on one side and one thickness on other side. The apex angle is slightly greater than 60°.

The paper is moistened with water and pressed down in to 60° funnel.

TIME OF FILTRATION - Filtration process is quite time consuming. However, it is aided by gentle suction produced when liquid passes down the stem of funnel. For this suction the upper circumference of paper

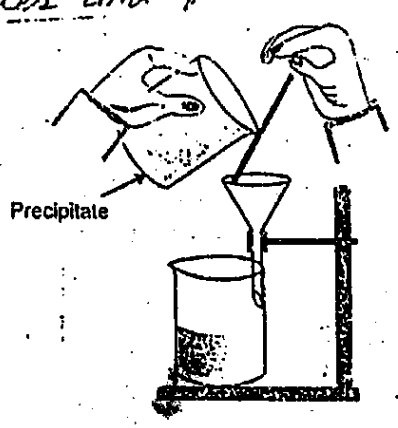
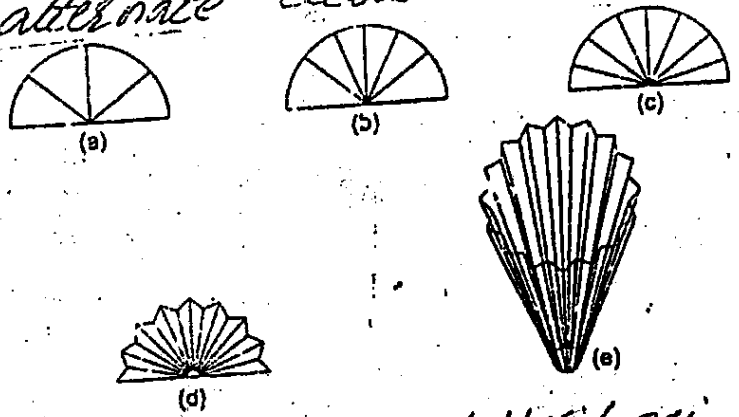


Fig. (2.1) Filtration assembly

should be closely attached with walls of funnel.

FLUTED FILTER PAPER

The rate of filtration could be increased by using fluted filter papers. For this purpose ordinary filter paper is folded in such a way that there is fan like arrangement with alternate elevations and depressions.



FILTER CRUCIBLES

It is method to filter precipitate through suction. Two types of crucibles are used. GOOCH CRUCIBLE It is made of porcelain. It has a perforated bottom. The bottom is covered with paper pulp or filter paper. The Gooch crucible is placed in suction filtering apparatus.

ADVANTAGES It is useful for filtering precipitates which are to be ignited at high temp. If perforations are covered with asbestos mat then it may be used to filter solution which reacts with paper. For example solution containing Conc HCl, $K_2Cr_2O_7$ etc.

SINTERED GLASS CRUCIBLES Sintered glass crucible is a glass crucible with porous glass disc sealed into bottom. It is quite easy to use because no preparation is required for using it.

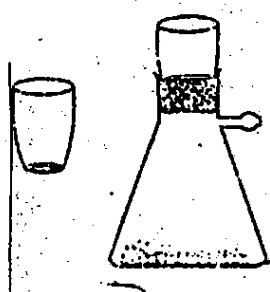


Fig. (2.3a) Gooch Crucible with filtering apparatus

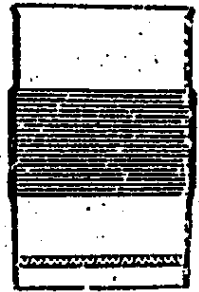


Fig. (2.3b) Sintered glass Crucible

CRYSTALLIZATION:-

NEED OF CRYSTALLIZATION:- In most of the synthetic reactions, chemical compound is obtained in an impure form. It is purified by crystallization from suitable solvent. Thus crystallization is used to purify crude products.

BASIC PRINCIPLE:- The solute should be more soluble in a suitable solvent and when solution is cooled the solute should be separated as crystals.

(The process of filtration involves

following steps.

CHOICE OF SOLVENT:- The solvent is chosen on H.T. and

TRIAL BASIS. ^{and many} A number of solvents are tried before reaching a conclusion.

CHARACTERISTICS OF SOLVENT:- An ideal solvent should possess following characteristics

- 1:- It should dissolve a large amount of solute at its boiling point and only a small amount at room temperature.
- 2:- It should not react chemically with solute.
- 3:- It should not dissolve impurities. If impurities are soluble then they should not crystallize out along with desired substance when solution is cooled.
- 4:- On cooling solution, well-formed crystals of pure compound must be obtained.
- 5:- It should be inexpensive.
- 6:- It should be safe to use and should be easily removable.

COMMONLY USED SOLVENTS:- The solvents which are mostly used for crystallization are

WATER, ABSOLUTE ETHANOL, DIETHYL ETHER,
RECTIFIED SPIRIT (95% ETHANOL), ACETONE, CHLORFORM,
CARBON TETRACHLORIDE, ACETIC ACID, PA
PETROLEUM ETHER

COMBINATION OF SOLVENTS

If none of the solvents is found suitable for crystallization, a combination of two or more MISCIBLE solvents may be used.

If solvent is inflammable, water bath is used for heating purposes.

P-5

2. PREPARATION OF SATURATED SOLUTION: - The solute and substance is heated on water bath or burner with minimum amount of solvent to prepare saturated solution. Add more solvent to boiling solution, if required, until all solute has dissolved.

3. FILTRATION: - The hot saturated solution is filtered through a normal or fluted filter paper. The insoluble impurities are removed as residue. The premature crystallization during filtration is avoided by using hot filtered saturated solution or by using hot water funnel.

4. COOLING: - The hot filtrate is cooled at a moderate rate so that medium size crystals are formed. V. Slow cooling produce large size crystals which carries larger amount of solvent containing impurities in it. Finer larger size crystals are difficult to dry.

5. COLLECTING THE CRYSTALS: - The mixture of liquid and crystals is filtered through Gooch crucibles using a vacuum pump. Full suction is applied to remove mother liquor from crystals. When filter cake is rigid, it is pressed with a cork to remove remaining liquid.

WASHING OF CRYSTALS: - The crystals are then washed with a small amount of cold solvent. The process of washing is repeated several times.

The filtrate (mother liquor) is concentrated by evaporation, and second crop of crystals is obtained by cooling. The success of process depends upon % of crystallized product.

6 DRYING or CRYSTALLIZATION There are three methods of drying crystals.

By PRESSING the crystals between several folds of filter paper. The process is repeated several times.

DISADVANTAGE:- 1) The crystals are crushed to a fine powder.
2) Fibres of filter paper contaminate product.

By USING OVEN The crystals are dried in an oven provided the substance does not melt or decompose on heating at 100°C.

VACUUM DESICCATOR - It's a safe and reliable method. The crystals are spread over a watch glass. These will be placed in a vacuum desiccator for several hours. The drying agent used in a desiccator are CaCl_2 , Silicagel or Phosphorous pentoxide (P_2O_5).

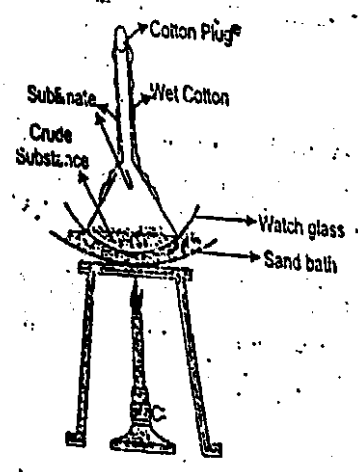
7 DECOLOURIZATION OF UNDESIRABLE COLOURS. Some times

undesirable coloured due to some impurities in the crystals are boiled with sufficient quantity of animal charcoal. The coloured impurities are adsorbed by animal charcoal. The pure decolourized substance is crystallized out from cooling filtrate.

WRITE A NOTE ON SUBLIMATION: REFINATION: The process in which a solid is directly converted into vapours without passing through liquid phase is called sublimation. When vapours are cooled they are directly changed into solid.

EXAMPLE AND USES: - It is used to purify a solid. For example Ammonium chloride, Benzoic acid, naphthalene, iodine can be purified by sublimation.

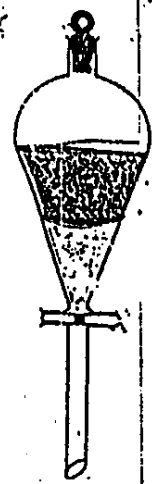
PROCESS: The substance is taken in a watch glass. It is covered with an inverted funnel. The funnel is covered with wet



cotton to keep it cool. The substance is heated slowly over a sand bath. The solid vaporizes and the vapours condense as solid on inner walls of funnel.

In a better method, the process is carried out in a cold finger.

SOLVENT EXTRACTION:-



BASIC PRINCIPLE According to this technique a solute can be separated from a solution by shaking solution with an immiscible solvent. The solute should be more soluble in solvent in that solvent.

PROCEDURE:- Usually it is done by placing the solution and second solvent in a separating funnel. The funnel is stoppered and two liquids are shaken together.

EXAMPLE The most common laboratory example of solvent extraction is ether extraction. The product of organic synthesis from water. The aqueous solution of organic compound containing some inorganic impurities is taken in separating funnel. Then some ether is added to it. The mixture is shaken and layers are allowed to separate. The organic compounds mostly go into ether layer and impurities remain in aqueous layer. The ether layer is separated. Same process is repeated with aqueous layer once again. It is more suitable to use small portions of ether several times rather than using all of the volume just once. The ether layer is easily evaporated and organic compound is obtained. This technique is particularly useful when product is volatile or thermally unstable.

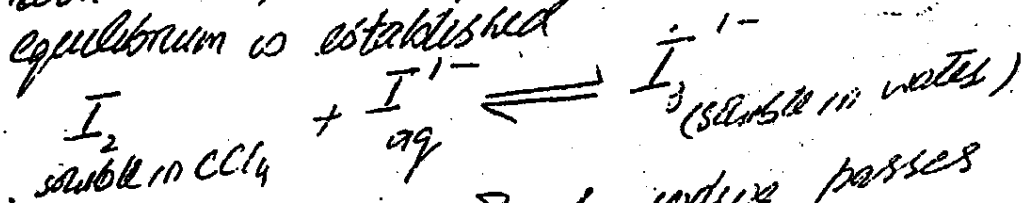
DISTRIBUTION LAW Solvent extraction is an equilibrium process and it is controlled by distribution law or partition law which states that,

A mathematically constant ratio exists between concentration of a given compound in two immiscible solvents. This ratio is independent of amount of solute added. Mathematically it could be written as $\frac{C_1}{C_2} = "K"$

This law is based on experimental evidence.

DISTRIBUTION OF IODINE BETWEEN AQUEOUS SOLUTION OF KI AND CARBON TETRACHLORIDE

In aqueous solution of KI, iodine reacts with I^{-} ion to form triiodide ion, in a reversible reaction. The following equilibrium is established



At this point the rate at which iodine passes from CCl_4 to aq. layer, becomes equal to rate at which it passes from water to CCl_4 .

Thus when CCl_4 is added to brown coloured solution of I_3^{-} ion in water, the brown colour of aq. solution fades and a purple colour appears in CCl_4 layer due to I_2 .

For good separation, the two liquids are gently shaken to increase area of contact of two layers. The ratio of concentration of iodine in two layers remains constant. It is independent of amount of iodine added. This constant is called distribution coefficient denoted by K.

$$K = \frac{[I_2 \text{ (in } CCl_4)]}{[I_2 \text{ as } I_3^{-} \text{ (in aq.)}]}$$

CHROMATOGRAPHY:-

The word chromatography originates from *Chromatos* meaning coloured writing. It is an important application of distribution phenomenon. It is used for separation of sample mixtures.

PRINCIPLE:- The solute distributes itself between a stationary phase and mobile phase. On the basis of stationary phase chromatography may be divided into two types

1. ADSORPTION CHROMATOGRAPHY - Chromatography in which stationary phase is a solid is called adsorption chromatography. The solid may be supported as a thin film on the surface of an inert solid. The substance leaves the mobile phase and get adsorbed on the surface of solid phase.

2. PARTITION CHROMATOGRAPHY - Chromatography in which stationary phase is a liquid is called partition chromatography. The substance being separated distribute throughout between stationary phase and mobile phases.

MOBILE PHASE - The mobile phase flowing over the surface of stationary phase may be liquid or gas.

In chromatography substances are separated due to their relative affinities for stationary and mobile phases. The separation of the components of mixture is based upon their distribution co-efficient "K" which is different for each component.

$$K_i = \frac{\text{Conc. of component in mobile phase}}{\text{Conc. of component in stationary phase}}$$

SMALL K VALUE:- The component with small "K" value mostly remains in stationary phase as mobile phase passes over it.

LARGE K VALUE:- The components with large "K" value remains dissolved in mobile phase and passes over the stationary phase quickly.

2. There are different techniques of chromatography. Most commonly used is paper chromatography.

PAPER CHROMATOGRAPHY

CHROMATOGRAPHY. Both mobile phase and stationary phases are liquids. It is a type of PARTITION¹⁰

STATIONARY PHASE Stationary phase is water adsorbed on paper. The adsorbed water is immiscible liquid to mobile phase which paper passes over it.

MOBILE PHASE The mobile phase is usually an organic liquid. The nature of solvent depends upon sample mixture being separated.

The paper chromatography may be (1) ASCENDING (2) DESCENDING (3) RADIAL/CIRCULAR

In ascending chromatography solvent is taken in a pool at the bottom of chromatographic tank. The lower end of paper dips in solvent & the solvent travels upwards by capillary action.

PROCEDURE The solvent mixture is taken in chromatographic tank. Cover the tank to homogenise its inner atmosphere.

Take about 20 cm strip of Whatmann's chromatographic paper no. 1. Draw a thin pencil line about 2.5 cm from one end.

The sample mixture is applied in the form a spot on pencil line, with a capillary tube.

The spots of pure components may also be applied along sides of sample spot on same line.

The spots are dried.

The paper is suspended with clips such that the impregnated end dips into the solvent mixture but base line remains outside the liquid.

Cover the tank to homogenise inner atmosphere.

The solvent rises due to capillary action. When the solvent passes the spots, the solute begins to move upward. The rate at which spots move upward is, depend upon their distribution co-efficient.

When the solvent front has moved $\frac{3}{4}$ th length of the paper, the strip is removed. The solvent front is marked with pencil. The strip is allowed to dry.

Once the paper is dried, the pattern is called Chromatogram. If components of mixture are colored they can be easily identified. If components are colourless, the chromatogram has to be developed by chemical method or physical method and spots are identified.

Each component has a specific retardation factor called " R_f " value.

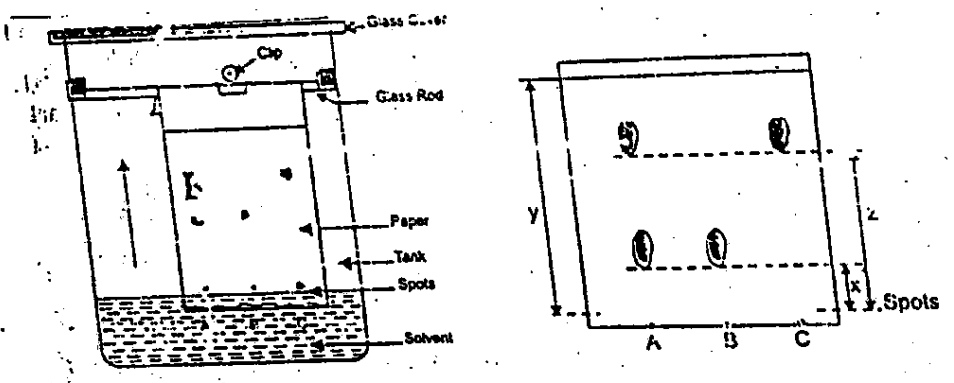
The " R_f " value is related to its distribution co-efficient.

$$R_f = \frac{\text{Distance covered by component from original spot}}{\text{Distance covered by solvent}}$$

Consider following diagram. It shows that mixture contains components A and B. Their R_f values are

$$R_{f(A)} = \frac{x}{y}$$

$$R_{f(B)} = \frac{z}{y}$$



- Uses:
- 1) It is quite useful for identification, separation, isolation and purification of products of organic synthesis.
 - 2) It is used to identify purity of a substance.
 - 3) It is equally important for qualitative and quantitative analysis.

EXERCISE

Q.1 Fill in the blanks.

- (a) A complete chemical characterization of a compound must include qualitative and quantitative analysis.
- (b) During filtration the tip of the stem of the funnel should touch the side of the beaker to avoid splashing.
- (c) A fluted filter paper is used to speed up the process of filtration.
- (d) A solvent used for crystallization is required to dissolve large amount of the substance at its boiling point and small amount at the room temperature.
- (e) Repeated solvent extractions using small portions of solvent are more efficient than using a single extraction with larger volume of the solvent.

Q.2 Multiple choice questions.

- (a) Solvent extraction is an equilibrium process and it is controlled by:
- law of mass action.
 - the amount of solvent used.
 - distribution law.
 - the amount of solute.
- (b) The comparative rates at which the solutes move in paper chromatography depend on:
- the size of paper used.
 - R_f values of solutes.
 - temperature of the experiment.
 - size of the chromatographic tank used.
- (c) A filtration process could be very time consuming if it were not aided by gentle suction which is developed:
- if the paper covers the funnel upto its circumference.
 - if the paper has got small sized pores in it.
 - if the stem of the funnel is large so that it dips into the filtrate.
 - if the paper fits tightly.
- (d) Solvent extraction method is a particularly useful technique for separation when the product to be separated is:
- non-volatile or thermally unstable.
 - volatile or thermally stable.
 - non-volatile or thermally stable.
 - volatile or thermally unstable.
- (e) During the process of crystallization, the hot saturated solution:
- is cooled very slowly to get large sized crystals.

- is cooled at a moderate rate to get medium sized crystals.
- is evaporated to get the crystals of the product.
- is mixed with an immiscible liquid to get the pure crystals of the product.

Q.3 Tick the correct sentences. If the sentence is incorrect, write the correct statements.

- A qualitative analysis involves the identification of elements present in a compound. **TRUE**
- If the process of filtration is to run smoothly, the stem of the funnel should remain empty. **FALSE (SHOULD REMAIN FILLED WITH FILTRATE)**
- If none of the solvents is found suitable for crystallization a combination of two or more immiscible solvents may be used. **(FALSE) miscible**
- Paper chromatography is a technique of partition chromatography. **TRUE**
- A solute distributes itself between two immiscible liquids in a constant ratio of concentrations depending upon the amount of solvent added. **(TRUE)**