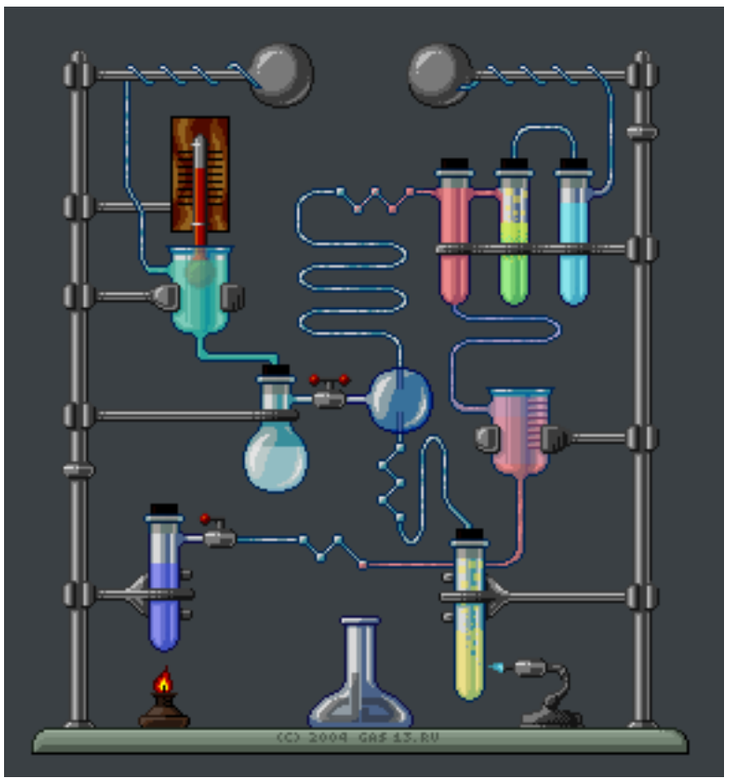
CHAPTER

2 EXPERIMENTAL TECHNIQUES IN CHEMISTRY



Animation 2.1 :Basic Concepts
Source & Credit: chem.ucsb

Analytical chemistry is the science of chemical characterization. A complete chemical characterization of a compound must include both qualitative and quantitative analyses.In qualitative analysis, the chemist is concerned with the detection or identification of the elements present in a compound. Whereas in quantitative analysis, the relative amounts of the elements are determined. A complete quantitative determination generally consists of four major steps (i) Obtaining a sample for analysis (ii) Separation of the desired constituent (iii) Measurement, and calculation of results (iv) Drawing conclusion from the analysis. In this chapter, we will restrict ourselves to only important techniques of separation. The students will practice these techniques during their laboratory work whereas their theoretical treatment is given here.

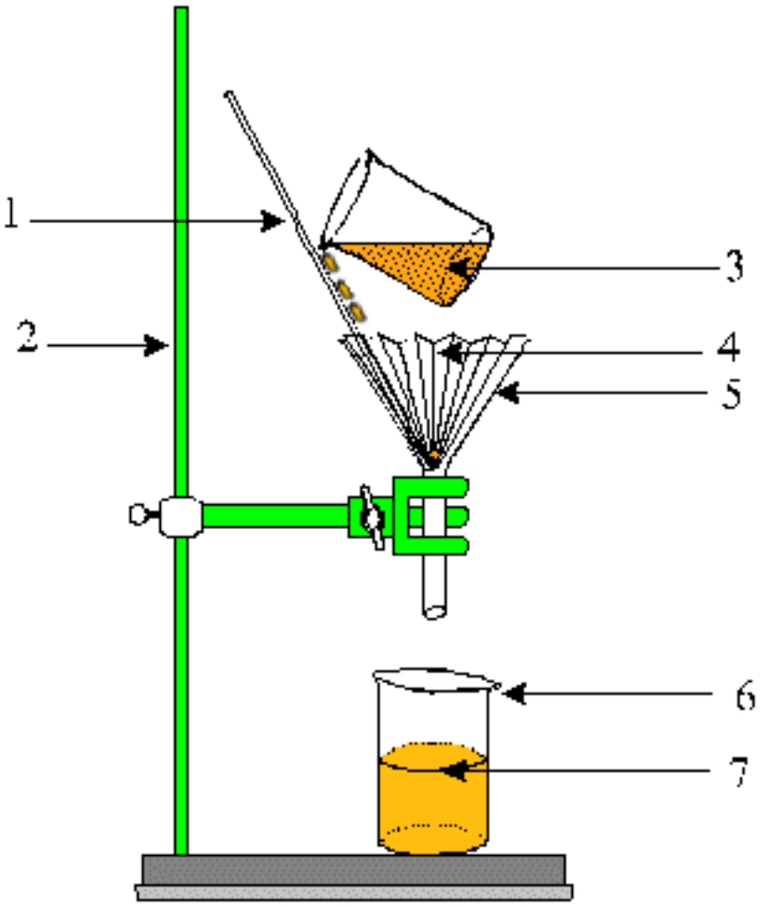
2.1 FILTRATION

Theprocessoffiltrationisusedtoseparateinsolubleparticlesfromliquids.Itcanbeperformedwithseveral typesoffiltermedia.Natureoftheprecipitateandotherfactorsdictatewhichfiltermediummustbeused.The most convenient ways of filtration are either through a filter paper or through a filter crucible.

Animation 2.2: Filtration Assembly
Source & Credit:eLearn.punajb

2.1.1 Filtration Through Filter Paper

Filtration by a glass funnel and filter paper is usually a slow process. As the mixture is poured onto the filter paper, the solvent (water) passes through leaving behind the suspended particles on the filter paper. Filter papers are available in a variety of porosites (pore sizes) . Which pore size is to be used, depends upon the size of particles in the precipitate. The filter paper should be large enough so that it is one-fourth to one-half full of precipitate at the end of filtration. The funnel should, in turn, be large enough for its rim to extend 1 to 2 cm above the top circumference of the paper. If the process of filtration is to run smoothly, the stem of the funnel should remain continuously full of liquid as long as there is liquid in the conical portion.



Animation 2.3: filtration
Source & Credit:shermanqmatrangas

The stem of the funnel should be several inches long so that it can extend a few centimeters down into the receiving beaker, and the tip should touch the side of the beaker. In this way, the filtrate runs down the side of beaker without splashing. A complete filter paper assembly is shown in Fig(2.1).

Folding of Filter Paper

The folding of filter paper is important and the following points should be kept in mind. The paper should be folded twice. The first fold should be along the diameter of the paper.The second fold should be such that edges do not quite match.

The paper should be opened on the slightly larger section. This provides a cone with three fold thickness halfway around and one thickness the other halfway around, and an apex angle very slightly greater than 60 degrees.

The paper may then be inserted into 60 degree funnel, moistened with water and firmly pressed down. The filtering operation could be very time consuming if it were not aided by a gentle suction as liquid passes through the stem. This suction cannot develop unless the paper fits tightly all around its upper circumference.

Fig. (2.1)Filtration assembly

Fluted Filter Paper

The rate of filtration through conical funnel can be considerably increased using a **Fluted Filter Paper.** For preparation of such a paper ordinary filter paper is folded in such a way that a fan like arrangement with alternate elevations and depressions at various folds is obtained Fig (2.2).

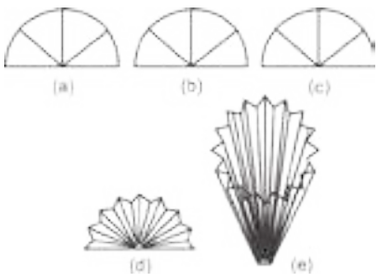


Fig. (2.2) Fluted filter paper

2.1.2 Filtration Through Filter Crucibles

Another convenient way to filter a precipitate is by suction through a crucible. Two types of crucibles are generally used.

Gooch Crucible

It is made of porcelain having a perforated bottom which is covered with paper pulp or a filter paper cut to its size Fig (2.3 a). Quick filtration can be done by placing the Gooch crucible in a suction filtering apparatus. It is useful for the filtration of precipitates, which need to be ignited at high temperature. If its perforations are covered with asbestos mat then it may be used to filter solutions that react with paper e.g. concentrated HCl and $KMnO_4$ solutions.

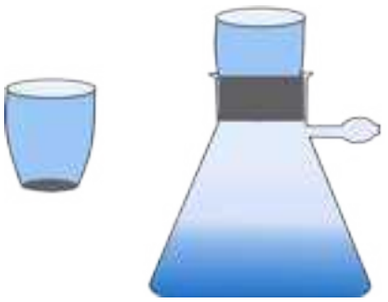


Fig. (2.3a) Gooch Crucible with filtering apparatus

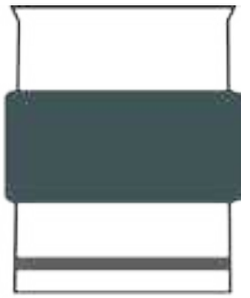


Fig. (2.3b) Sintered glass Crucible

Sintered glass crucible

Sintered glass crucible is a glass crucible with a porous glass disc sealed into the bottom. It is very convenient to use because no preparation is needed as with the Gooch crucible Fig (2.3b)

2.2 CRYSTALLIZATION

Crystallization is the removal of a solid from solution by increasing its concentration above the saturation point in such a manner that the excess solid separates out in the form of crystals.

The preparation of a chemical compound usually affords a crude product and there is a need to purify it by crystallization from a suitable solvent. The basic principle of crystallization is the fact that the solute should be soluble in a suitable solvent at high temperature and the excess amount of the solute is thrown out as crystals when it is cooled. The process of crystallization involves the following steps.

Animation 2.4: crystilization
Source & Credit: evilforalltime

2.2.1 Choice of a Solvent

The solvent is chosen on hit and trial basis and it is necessary to try a number of solvents before arriving at a conclusion. An ideal solvent should have the following features.

i. It should dissolve a large amount of the substance at its boiling point and only a small amount at the room temperature.
ii. It should not react chemically with the solute.
iii. It should either not dissolve the impurities or the impurities should not crystallize from it along with the solute.
iv. On cooling it should deposit well-formed crystals of the pure compound.
v. It should be inexpensive.
vi. It should be safe to use and should be easily removable.

The solvents which are mostly used for crystallization are, water, rectified spirit (95% ethanol), absolute ethanol, diethyl ether, acetone, chloroform, carbon tetrachloride, acetic acid and petroleum ether. If none of the solvents is found suitable for crystallization, a combination of two or more miscible solvents may be employed. If the solvent is inflammable then precaution should be taken while heating the solution so that it does not catch fire. In such cases, water bath is used for heating purpose.

2.2.2 Preparation of the Saturated Solution

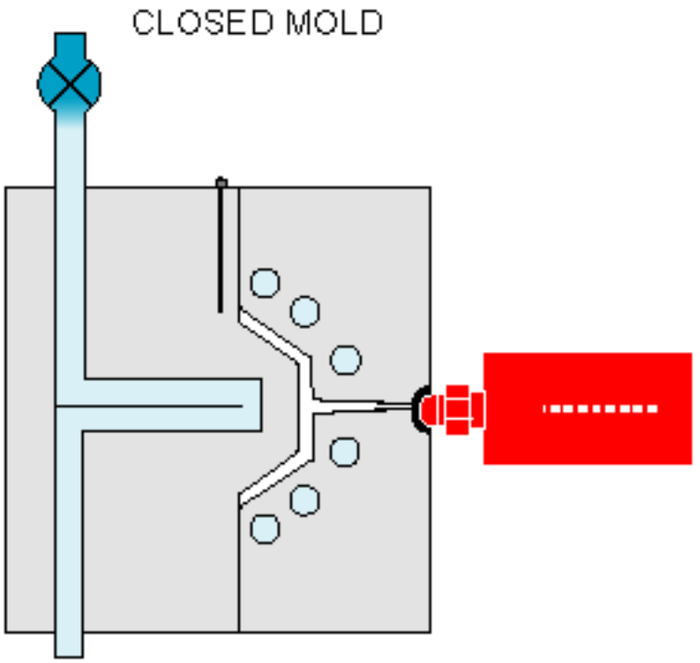
After selecting a suitable solvent, the substance is then dissolved in a minimum amount of solvent and is heated directly or on a water bath with constant stirring. Add more solvent to the boiling solution if necessary until all the solute has dissolved.

2.2.3 Filtration

The insoluble impurities in the saturated solution are then removed by filtering the hot saturated s olution, through a normal or a fluted filter paper. This avoids the premature crystallization of the solute on the filter paper or in the funnel stem. If necessary hot water funnel should be used for this purpose.

2.2.4 Cooling

The hot filtered solution is then cooled at a moderate rate so that medium sized crystals are formed. Slow cooling yields bigger crystals which are likely to include considerable amount of solvent carrying impurities with it and complicating the drying process.



Animation 2.5: Cooling
Source & Credit: Pulsecooling

2.2.5 Collecting the Crystals

When the crystallization is complete, the mixture of crystals and the mother liquor is filtered through a Gooch crucible using a vacuum pump. Full suction is applied in order to drain the mother-liquor from the crystals as effectively as possible. When the filter cake is rigid enough it is pressed firmly with a cork to drain the left-over liquid. The crystals are then washed with a small portion of cold solvent and the process is repeated several times. The mother liquor is quite often concentrated by evaporation and cooled to obtain a fresh crop of crystals. The process of crystallization appears to be very simple yet the success of operation lies in the amount or the percentage of crystallized product obtained from the crude substance.

2.2.6 Drying of the Crystallized Substance

Pressing it between several folds of filter papers and repeating the process several times dries the crystallized substance. This process has the disadvantage that the crystals are crushed to a fine powder and sometimes the fibres of filter paper contaminate the product. Alternatively,the crystals are dried in an oven provided the substance does not melt or decompose on heating at 100° C.
A safe and reliable method of drying crystals is through a vacuum desiccator. In this process the crystals are spread over a watch glass and kept in a vacuum desiccator for several hours. The drying agents used in a desiccator are $CaCl_2$, silica gel or phosphorus pentaoxide.

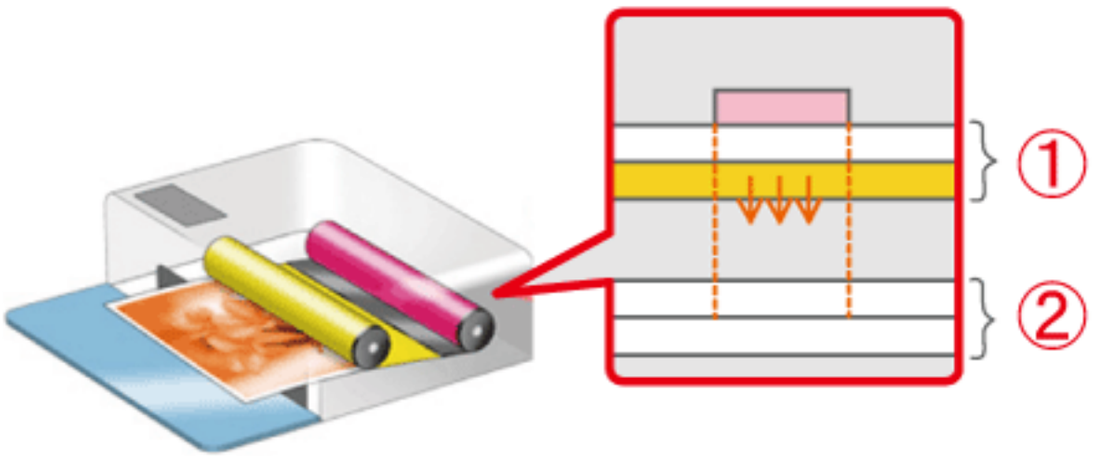
2.2.7 Decolourization of Undesirable Colours

Sometimes during the preparation of a crude substance, the colouring matter or resinous products affect the appearance of product and it may appear coloured. Such impurities are conveniently removed by boiling the substance in the solvent with the sufficient quantity of finely powdered animal charcoal and then filtering the hot solution.
The coloured impurities are adsorbed by animal charcoal and the pure decolourized substance crystallizes out from the filtrate on cooling.

2.3 SUBLIMATION

It is a process in which a solid, when heated, vapourizes directly without passing through the liquid phase and these vapours can be condensed to form the solid again. It is frequently used to purify a solid. Examples of such solids are ammonium chloride, iodine, naphthalene, benzoic acid, etc. To carry out the process, the substance is taken in a watch-glass covered with an inverted funnel. The substance is then heated slowly over a sand-bath and the funnel is cooled with wet cotton. The pure solid deposits on the inner side of the funnel Fig (2.4).

Fig (2.4) SUBLIMATION

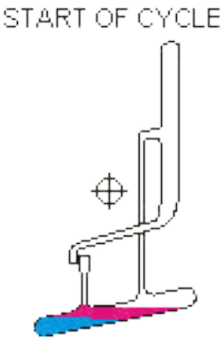


Animation 2.6: SUBLIMATION
Source & Credit: support-th

2.4 SOLVENT EXTRACTION

Solvent extraction is an important technique in chemical analysis. According to this technique a solute can be separated from a solution by shaking the solution with a solvent in which the solute is more soluble and the added solvent does not mix with the solution. Usually it is done by placing the solution and the second liquid into a separating funnel Fig (2.5). The funnel is stoppered and the two liquids are shaken together.

The most common laboratory example of solvent extraction is ether extraction. This is used to separate the products of organic synthesis from water. In a typical organic synthesis, the aqueous solution containing the organic product is shaken up with ether in a separating funnel and allowed to separate.



Animation 2.7: Solvent extraction
Source & Credit: chem

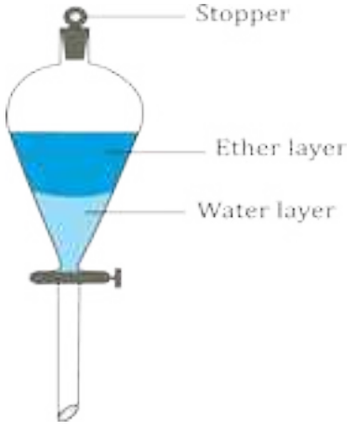


Fig.(2.5) Separating funnel

The inorganic impurities remain in aqueous phase whereas the organic compound goes to the ether layer. The ether layer is separated and the organic product is obtained by evaporating the ether. Repeated extractions using small portions of solvent (ether) are more efficient than using a single but larger volume of solvent. The technique is particularly useful when the product is volatile or thermally unstable.

Solvent extraction is an equilibrium process and follows the distribution law or partition law. This law states that a solute distributes itself between two immiscible liquids in a constant ratio of concentrations irrespective of the amount of solute added.

The law is based on experimental evidence. Consider, for example, the distribution of iodine between two immiscible solvents, water in the presence of KI and carbon tetrachloride. Iodine reacts with iodide ion to produce tri-iodide ion in a reversible reaction.

The following dynamic equilibrium is established.

$$I_2 + I^-(aq) \rightleftharpoons I_3^-(aq)$$

soluble in CCl_4 soluble in water

At this point the rate at which iodine passes from CCl_4 to water equals the rate at which it passes from water to CCl_4.

So, if we add CCl_4 to an aqueous solution of I_3^- ions, the iodine will transfer from the aqueous layer into the organic layer. As a result, the brown colour of the tri-iodide ions fades and the purple colour of free iodine molecules appears in organic phase. To achieve a good separation, the two liquids are gently shaken to increase their area of contact and improve the chances of transferring iodine molecules. No matter how much iodine is used, the ratio of the final concentrations at equilibrium is constant. The constant is called distribution coefficient, K and is given by

$$K=[I_2(CCl_4)]/[I_{3(aq)}^-]$$

2.5 CHROMATOGRAPHY

Another important application of the distribution phenomenon is chromatography. The word chromatography originates from the Greek word “Khromatos” meaning colour writing.

Chromatography is a method used primarily for the separation of a sample of mixture. It involves the distribution of a solute between a stationary phase and a mobile phase. The stationary phase may be a solid or a liquid supported as a thin film on the surface of an inert solid. The mobile phase flowing over the surface of the stationary phase may be a gas or a liquid.

In chromatography, substances are separated due to their relative affinities for the stationary and mobile phases. The distribution of the components of a mixture between the two phases is governed by distribution coefficient K.

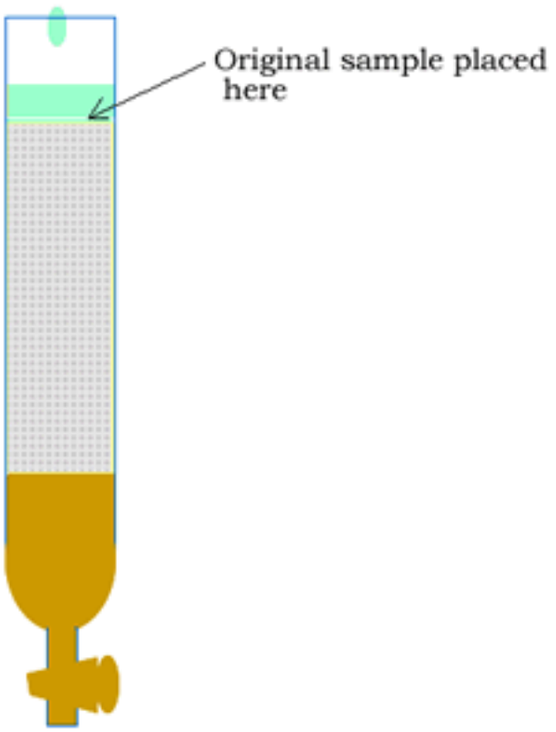
$$K = \frac{\text{Concentration of a component in the moving phase}}{\text{Concentration of that component in the Stationary phase}}$$

The component of a mixture with a small value of K mostly remains in the stationary phase as the moving phase flows over it. The component with a greater value of K remains largely dissolved in the mobile phase and passes over the stationary phase quickly.

Chromatography in which the stationary phase is a solid, is classified as adsorption chromatography. In this type, a substance leaves the mobile phase to become adsorbed on the surface of the solid phase.

Chromatography in which the stationary phase is a liquid, is called partition chromatography. In this type, the substances being separated are distributed throughout both the stationary and mobile phases.

There are various techniques of chromatography. One such technique namely paper chromatography is discussed below.



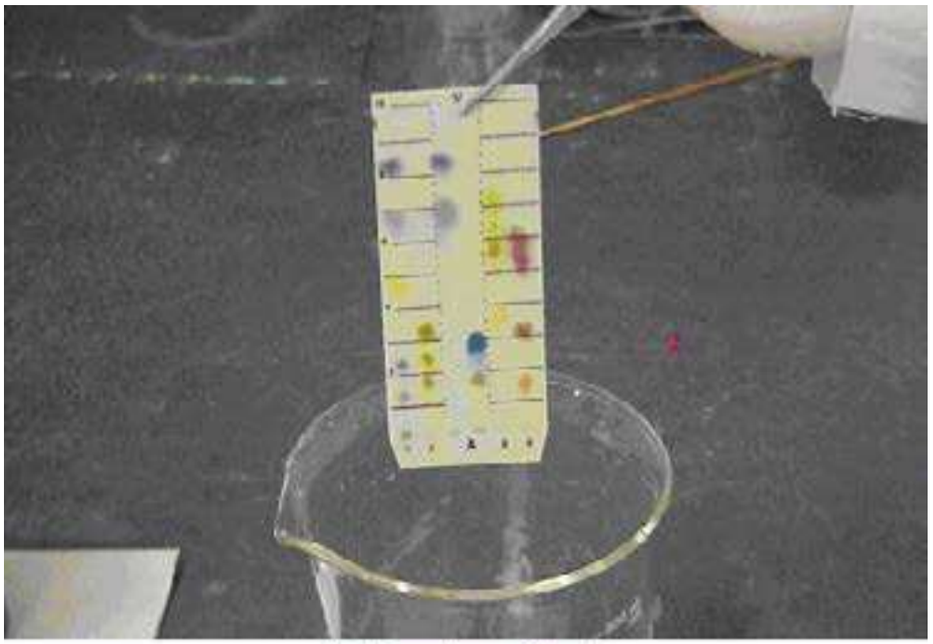
Animation 2.8:Chromatography
Source & Credit: Support-th

2.5.1 PAPER CHROMATOGRAPHY

It is a technique of partition chromatography. Here the stationary phase is a liquid (say H_2O) adsorbed on paper. The adsorbed water behaves as an immiscible liquid towards the mobile phase, which passes over the paper. The mobile phase is usually an organic liquid.

There are three common ways of carrying out paper chromatography namely (i) ascending (ii) descending (iii) radial/circular. Only the ascending type will be discussed here. In this technique the solvent is in a pool at the bottom of a vessel in which the paper is supported and the solvent travels upwards by capillary action.

A solvent mixture, specially composed in accordance with the sample to be separated, is poured into the chromatographic tank Fig (2.6). Cover the tank to homogenise its inner atmosphere. Take about 20 cm strip of Whatmann's chromatographic paper No.1 and draw on it a thin pencil line about 2.5 cm from one end. Spot a point, on the pencil line, with the sample mixture solution. To facilitate identification of the components of the mixture, spots of the known compounds may also be placed alongside.



Animation 2.9: PAPER CHROMATOGRAPHY
Source & Credit: chem

When the spots have dried, suspend the paper with clips so that the impregnated end dips into solvent mixture to a depth of 5-6 mm. Cover the tank. As the solvent front passes the spots, the solutes begin to move upward. The rate at which they move depends on their distribution coefficients. When the solvent front has risen to about 3/4 th of the length of the paper, remove the strip, mark the solvent front with a pencil and allow the strip to dry.

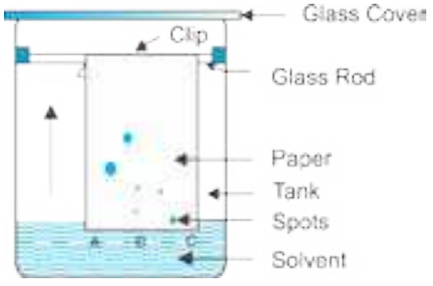


Fig. (2.6) Paper chromatography

Once the paper is dried, the pattern on the paper is called a chromatogram. The different components of the mixture, if coloured, can visually be identified. If colourless, the chromatogram has to be developed by chemical methods or physical techniques used to identify the spots. Each component has a specific retardation factor called R_f value. The R_f value is related to its distribution coefficient and is given by:

$$R_f = \frac{\text{Distance travelled by a component from the original spot}}{\text{Distance travelled by solvent from the original spot}}$$

With reference to Fig 2.7 the chromatogram shows that the sample A contains both components B and C. The R_f values for B and C are given by:

$$\mathbf{R_f(B) = x/y}$$

$$\mathbf{R_f(C) = z/y}$$

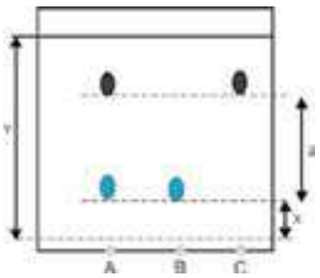
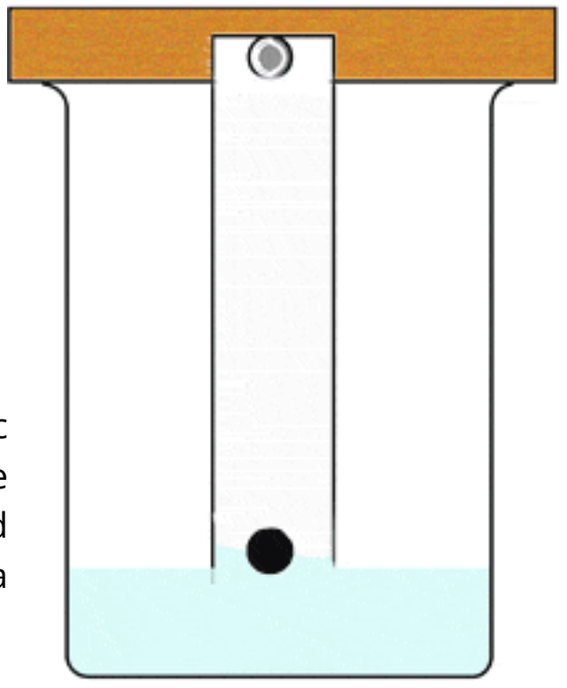


Fig. (2.7) Chromatogram

Uses of Chromatography

The techniques of chromatography are very useful in organic synthesis for separation, isolation and purification of the products. They are equally important in qualitative and quantitative analyses and for determination of the purity of a substance.



Animation 2.10: Uses of Chromatography
Source & Credit: Dynamicscience

KEY POINTS

1. A complete characterization of a compound must include both qualitative and quantitative analyses.
2. A complete quantitative analysis of a compound generally involves four major steps.
3. The process of filtration is used to separate insoluble particles from liquids and it can be performed with several types of filter media.
4. If the process of filtration with the filter paper is to run smoothly, the stem of the funnel should remain continuously full of liquid as long as there is liquid in the conical portion.
5. The filtering operation with the filter paper could be very time consuming if it were not aided by a gentle suction as liquid passes through the stem. This suction cannot develop unless the paper fits tightly all around the upper circumference of the funnel.
6. The rate of filtration can be considerably increased using a fluted filter paper.
7. A solid compound is purified by crystallization from a suitable solvent. A solvent for crystallization should be able to dissolve the solute at high temperature and the maximum amount of the solute should be thrown out by the solvent when the solution is cooled. The process of crystallization involves many steps.
8. The process of sublimation involves converting a solid directly into vapours and these vapours are then condensed to form solid again. It is frequently used to purify a solid.
9. Solvent extraction technique involves the separation of a solute from a solution by shaking it with an immiscible solvent in which the solute is more soluble. The technique is mostly applied to separate organic compounds from water.
10. Repeated extractions using small portions of solvent are more efficient than using a single extraction but large volume of solvent.
11. Solvent extraction is an equilibrium process and it is controlled by distribution law. The technique is particularly useful when the compound to be separated is volatile or thermally unstable.
12. Chromatography is a technique used for separating the components of a mixture. These components are distributed between a stationary and a mobile phase. The stationary phase may be a solid or a liquid supported on a solid. It adsorbs the mixture under separation. The mobile phase may be a liquid or a gas and while passing over the stationary phase, competes with it for the constituents of the mixture.
13. In paper chromatography, the stationary phase is water adsorbed on paper. The mobile phase is usually an organic liquid.
14. The techniques of chromatography are very useful in organic synthesis for separation, isolation and purification of the products.

EXERCISE

Q.1 Multiple choice questions.

(i) A filtration process could be very time consuming if it were not aided by a gentle suction which is developed:
(a) if the paper covers the funnel upto its circumference.
(b) if the paper has got small sized pores in it.
(c) if the stem of the funnel is large so that it dips into the filtrate.
(d) if the paper fits tightly.

(ii) During the process of crystallization, the hot saturated solution:
(a) is cooled very slowly to get large sized crystals.
(b) is cooled at a moderate rate to get medium sized crystals.
(c) is evaporated to get the crystals of the product.
(d) is mixed with an immiscible liquid to get the pure crystals of the product.

(iii) Solvent extraction is an equilibrium process and it is controlled by.
(a) law of mass action. (b) the amount of solvent used.
(c) distribution law. (d) the amount of solute.

(iv) Solvent extraction method is a particularly useful technique for separation when the product to be separated is:
(a) non-volatile or thermally unstable. (b) volatile or thermally stable.
(c) non-volatile or thermally stable. (d) volatile or thermally unstable.

(v) The comparative rates at which the solutes move in paper chromatography, depend on:
(a) the size of paper (b) R values Of solutes.
(c) temperature of the experiment. (d) size of the chromatographic tank used.

Fill in the blanks.

1. A complete chemical characterization of a compound must include_____.
2. During filtration the tip of the stem of the funnel should touch the side of the beaker to avoid_____.
3. A fluted filter paper is used to_____ the process of filtration.
4. A solvent used for crystallization is required to dissolve of the substance at its boiling point and_____ at the room temperature.
5. Repeated solvent extractions using small portions of solvent are_____ than using a single extraction with larger volume of the solvent.

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

(i) A qualitative analysis involves the identification of elements present in a compound.

(ii) If the process of filtration is to run smoothly, the stem of the funnel should remain empty.

(iii) If none of the solvents is found suitable for crystallization a combination of two or more immiscible solvents may be used.

(iv) A solute distributes itself between two immiscible liquids in a constant ratio of concentrations depending upon the amount of solvent added.

(v) Paper chroma tography is a technique of partition chromatography.

Q.4 Why is there a need to crystallize the crude product?

Q.5 A water insoluble organic compound aspirin is prepared by the reaction of salicylic acid with a mixture of acetic acid and acetic anhydride. How will you separate the product from the reaction mixture?

Q.6 A solid organic compound is soluble in water as well as in chloroform. During its preparation, it remains in aqueous layer. Describe a method to obtain from this layer.

Q.7 The following figure shows a developed chromatogram on paper with five spots.

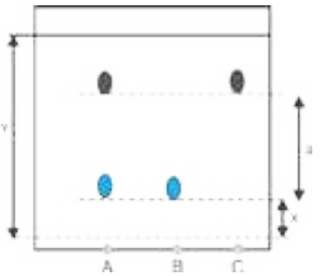
(i) Unknown mixture X

(ii) Sample A

(iii) Sample B

(iv) Sample C

(v) Sample D



Find out (i) the composition of unknown mixture X

(ii) which sample is impure and what is its composition.

Q.8 In solvent extraction technique, why repeated extraction using small portions of solvent are more efficient than using a single extraction but larger volume of solvent?

Q.9 Write down the main characteristics of a solvent selected for crystallization of a compound.

Q.10 You have been provided with a mixture containing three inks with different colours. Write down the procedure to separate the mixture with the help of paper chromatography.