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Analytical Separation Methods

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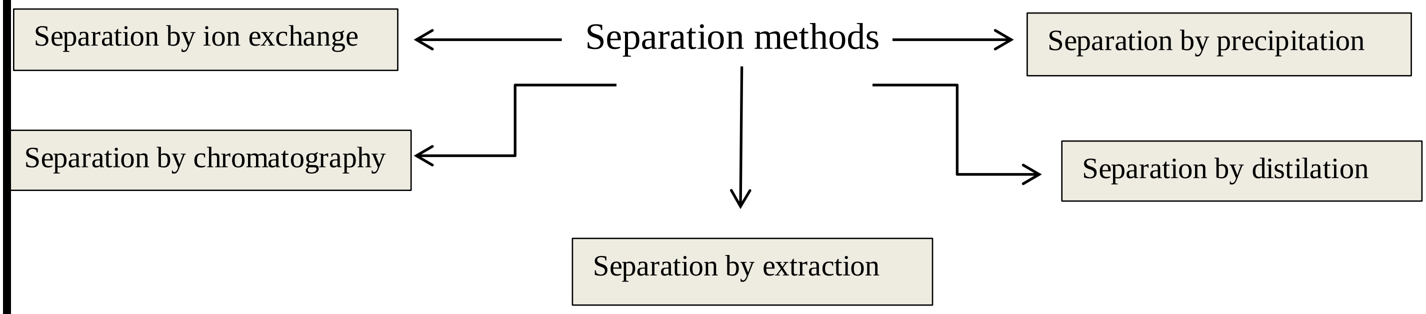
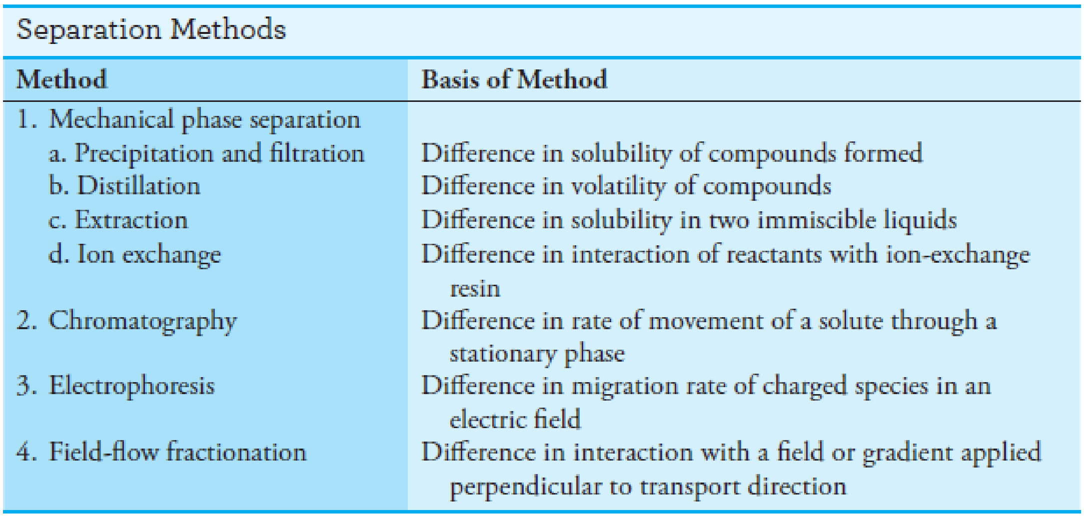
Analytical Separation Methods .

Separations are extremely important in synthesis, in industrial chemistry, in the biomedical sciences, and in chemical analysis. Many techniques for separating and concentrating the species of interest have thus been devised. Such techniques are aimed at exploiting differences in physico-chemical properties between the various components of a mixture. Volatility, solubility, charge, molecular size, shape and polarity are the most useful in this respect. A change of phase, as occurs during distillation, or the formation of a new phase, as in precipitation, can provide a simple means of isolating a desired component. Usually, however, more complex separation procedures are required for multi-component samples. Most depend on the selective transfer of materials between two immiscible phases. Most depend on the selective transfer of materials between two immiscible phases. The most widely used techniques and the phase systems associated with them are summarized in the following scheme .



All separation techniques involve one or more chemical equilibria, consequently the degree of separation achieved can vary greatly according to experimental conditions.



Separation Methods

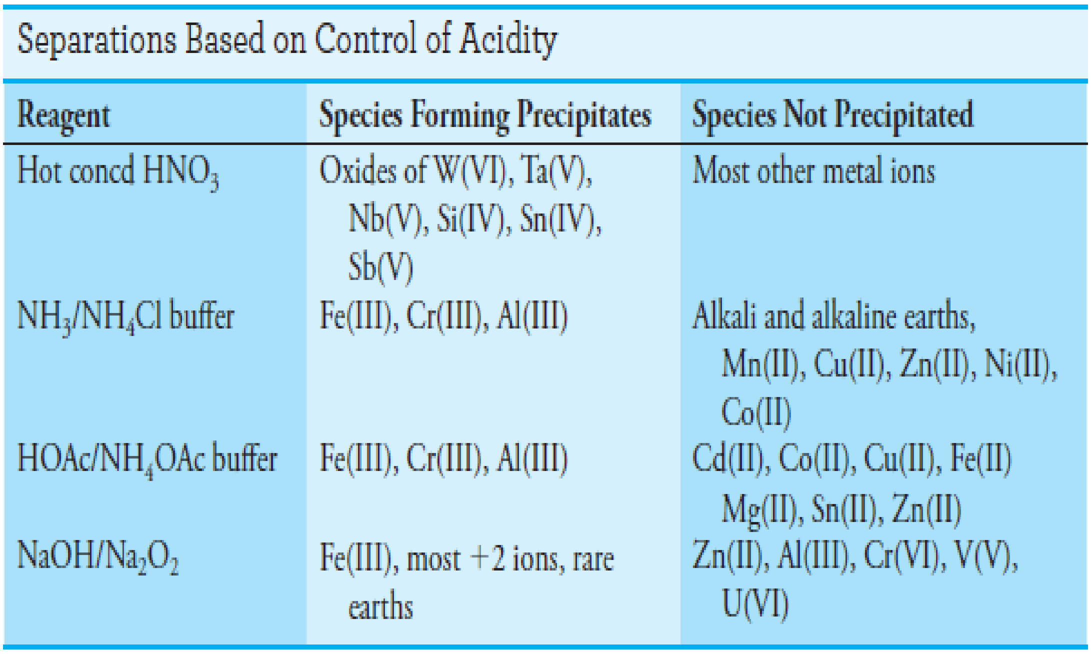
Method	Basis of Method
1. Mechanical phase separation	
a. Precipitation and filtration	Difference in solubility of compounds formed
b. Distillation	Difference in volatility of compounds
c. Extraction	Difference in solubility in two immiscible liquids
d. Ion exchange	Difference in interaction of reactants with ion-exchange resin
2. Chromatography	Difference in rate of movement of a solute through a stationary phase
3. Electrophoresis	Difference in migration rate of charged species in an electric field
4. Field-flow fractionation	Difference in interaction with a field or gradient applied perpendicular to transport direction

1. ***Separation by precipitation*****.**

Separations by precipitation require large solubility differences between the analyte and potential interferents. The theoretical feasibility of this type of separation can be determined by solubility calculations. When precipitates form as colloidal suspensions, coagulation may be difficult and slow, particularly when the isolation of a small quantity of a solid phase is attempted. Many precipitating agents have been used for quantitative inorganic separations.

1.1: **Separations Based on Control of Acidity.**

There are enormous differences among the solubilities of the hydroxides, hydrous oxides, and acids of various elements. Moreover, the concentration of hydrogen or hydroxide ions in a solution can be varied or can be easily controlled by the use of buffers. As a result, many separations based on pH control are in theory possible . In practice, these separations can be grouped in three categories: (1) those made in relatively concentrated solutions of strong acids,(2) those made in buffered solutions at intermediate pH values, and (3) those made in concentrated solutions of sodium or potassium hydroxide. lists common separations that can be achieved by control of acidity are show in the following table .

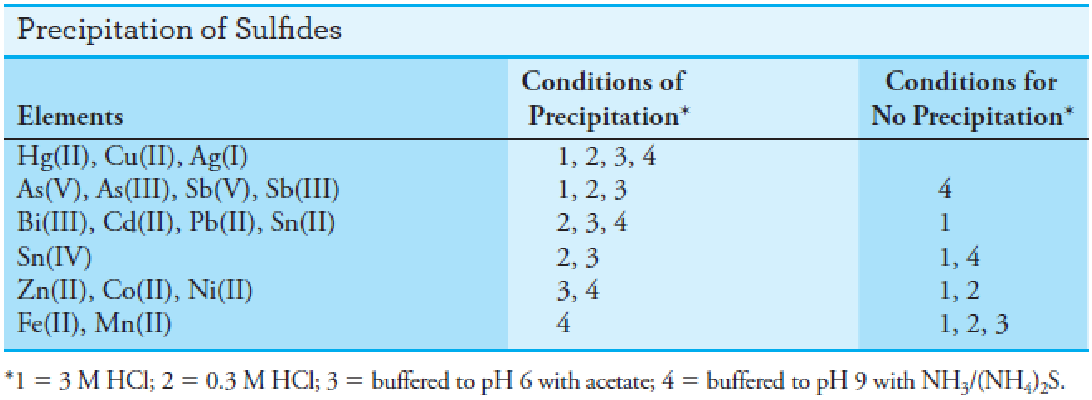


Separations Based on Control of Acidity

Reagent	Species Forming Precipitates	Species Not Precipitated
Hot concd HNO_3	Oxides of W(VI), Ta(V), Nb(V), Si(IV), Sn(IV), Sb(V)	Most other metal ions
NH_3/NH_4Cl buffer	Fe(III), Cr(III), Al(III)	Alkali and alkaline earths, Mn(II), Cu(II), Zn(II), Ni(II), Co(II)
$HOAc/NH_4OAc$ buffer	Fe(III), Cr(III), Al(III)	Cd(II), Co(II), Cu(II), Fe(II) Mg(II), Sn(II), Zn(II)
$NaOH/Na_2O_2$	Fe(III), most +2 ions, rare earths	Zn(II), Al(III), Cr(VI), V(V), U(VI)

1.2. **Sulfide Separations**.

With the exception of the alkali metals and alkaline-earth metals, most cations form sparingly soluble sulfides whose solubilities differ greatly from one another. Because it is relatively easy to control the sulfide ion concentration of an aqueous solution of H_2S by adjustment of pH, separations based on the formation of sulfides have found extensive use . The following table shows some common separations that can be accomplished with hydrogen sulfide through control of pH.



Precipitation of Sulfides

Elements	Conditions of Precipitation*	Conditions for No Precipitation*
Hg(II), Cu(II), Ag(I)	1, 2, 3, 4	
As(V), As(III), Sb(V), Sb(III)	1, 2, 3	4
Bi(III), Cd(II), Pb(II), Sn(II)	2, 3, 4	1
Sn(IV)	2, 3	1, 4
Zn(II), Co(II), Ni(II)	3, 4	1, 2
Fe(II), Mn(II)	4	1, 2, 3

*1 = 3 M HCl; 2 = 0.3 M HCl; 3 = buffered to pH 6 with acetate; 4 = buffered to pH 9 with $NH_3/(NH_4)_2S$.

1.3. **Separations by Other Inorganic Precipitants**.

No other inorganic ions are as generally useful for separations as hydroxide and sulfide ions. Phosphate, carbonate, and oxalate ions are often used as precipitants for cations, but they are not selective. Because of this drawback, separations are usually performed prior to precipitation. Chloride and sulfate are useful because of their highly selective behavior. Chloride can separate silver from most other metals, and sulfate can isolate a group of metals that includes lead, barium, and strontium.

1.4. **Separations by Organic Precipitants.**

The organic precipitants, such as dimethylglyoxime, are useful because of their remarkable selectivity in forming precipitates with only a few ions. Other reagents, such as 8-hydroxyquinoline, yield slightly soluble compounds with many different cations . The selectivity of this sort of reagent is due to the wide range of solubility among its reaction products and also to the fact that the precipitating reagent is usually an anion that is the conjugate base of a weak acid. Thus, separations based on pH control can be realized just as with hydrogen sulfide.

1.5. **Separation of Species Present in Trace Amounts by Precipitation**.

A problem often encountered in trace analysis is that of isolating from the major components of the sample the species of interest, which may be present in microgram quantities. Although such a separation is sometimes based on a precipitation, the techniques required differ from those used when the analyte is present in large amounts. Several problems can accompany the quantitative separation of a trace element by precipitation even when solubility losses are not important. Supersaturation often delays formation of the precipitate, and coagulation of small amounts of a colloidally dispersed substance is often difficult. In addition, it is common to lose an appreciable fraction of the solid during transfer and filtration. To minimize these difficulties, a quantity of some other ion that also forms a precipitate with the reagent is often added to the solution. The precipitate from the added ion is called a **collector** and carries the desired minor species out of solution. For example, in isolating manganese as the sparingly soluble manganese dioxide, a small amount of iron(III) is frequently added to the analyte solution before the introduction of ammonia as the precipitating reagent. The basic iron(III) oxide brings down even the smallest traces of the manganese dioxide. Other examples include basic aluminum oxide as a collector of trace amounts of titanium and copper sulfide for collection of traces of zinc and lead. Many other collectors are described by Sandell and Onishi. A collector may entrain a trace constituent as a result of similarities in their solubilities. Other collectors function by coprecipitation in which the minor component is adsorbed on or incorporated into the collector precipitate as the result of mixedcrystal formation. We must be sure that the collector does not interfere with the method selected for determining the trace component.

1.6. **Separation by Electrolytic Precipitation.**

Electrolytic precipitation is a highly useful method for accomplishing separations.In this process, the more easily reduced species, either the wanted or the unwanted component of the sample, is isolated as a separate phase. The method becomes particularly effective when the potential of the working electrode is controlled at a predetermined level . The mercury cathode has found wide application in the removal of many metal ions prior to the analysis of the residual solution. In general, metals more easily reduced than zinc are conveniently deposited in the mercury, leaving such ions as aluminum, beryllium, the alkaline earths, and the alkali metals in solution. The potential required to decrease the concentration of a metal ion to any desired level can be calculated from voltammetric data. Stripping methods use an electrode position step for separation followed by voltammetry for completion of the analysis.

1.7. **Salt-Induced Precipitation of Proteins**.

A common way to separate proteins is by adding a high concentration of salt. This procedure is termed **salting out** the protein. The solubility of protein molecules shows a complex dependence on pH, temperature, ionic strength, the nature of the protein, and the concentration of the salt used. At low salt concentrations, solubility is usually increased with increasing salt concentration. This **salting in effect** is explained by the Debye- Hückel theory. The counter ions of the salt surround the protein, and the screening results in decreasing the electrostatic attraction of protein molecules for each other. This decrease, in turn, leads to increasing solubility with increasing ionic strength. At high concentrations of salt, however, the repulsive effect of like charges is reduced as are the forces leading to solvation of the protein. When these forces are reduced enough, the protein precipitates and salting out is observed. Ammonium sulfate is an inexpensive salt and is widely used because of its effectiveness and high inherent solubility.

2. **Separation of Species by Distillation.**

The process of converting a liquid into its vapour and subsequently collecting it as liquid by condensation of the vapour is known as distillation. This operation is employed to separate a liquid from non-volatile impurities or to separate the various constituents of a mixture of liquids boiling at different temperatures. Amongst the numerous industrial applications of distillation, an interesting example is that of purification of metals like zinc, cadmium, mercury and bismuth which have comparatively low melting and boiling points and leave behind impurities in the retorts when subjected to distillation.

Detailed below are the various distillation techniques employed in the chemistry laboratory.

2.1. Simple Distillation.

The given liquid may be purified by simple distillation if it does not undergo decomposition before its boiling point is reached at atmospheric pressure. The non-volatile impurities as well as higher boiling impurities will be left behind in the distillation flask; impurities which are more volatile than the compound being purified will distil over earlier and can be removed before the desired compound begins to distil over. Distillation at atmospheric pressure is carried out using the set-up of apparatus shown in the fo;;owinf figure, which consists of distilla-tion flask (F), a water condenser (C) and a receiver (R). All distilla-tions should include the addition of a few chips of a broken porous plate to prevent bumping.

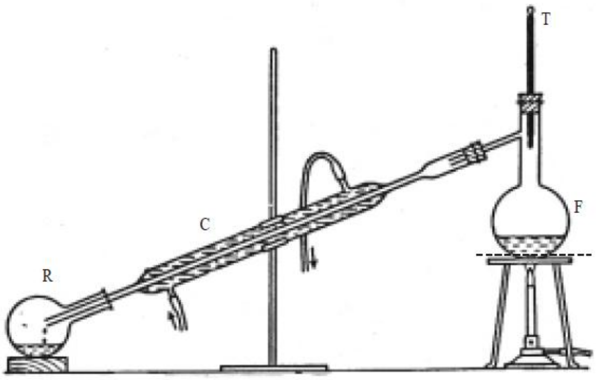


Figure 2.13 (a) Distillation assembly

2.2. Fractional Distillation (Rectification).

If a binary mixture of volatile substances contains a relatively large amount of each constituent, or if the two compounds have very similar vapour pressure characteristics, then a simple distillation is not a very efficient means of separating the two substances. It then becomes necessary to resort to the technique of fractional distillation, which is the process of collecting the distillate in several fractions and subjecting the fractions to systematic redistillation.

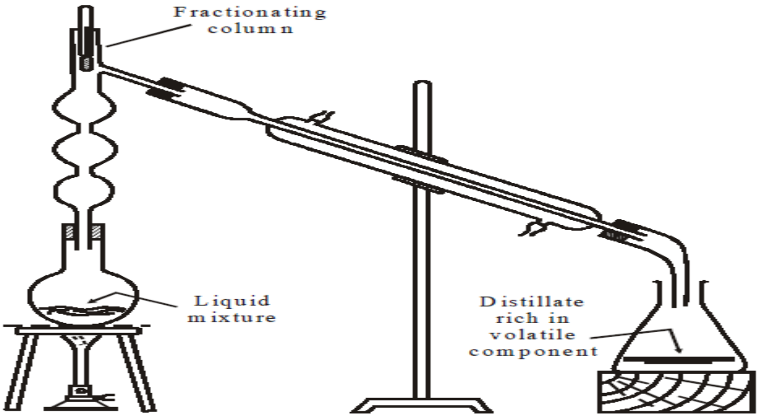


Figure 2.17 Fractional distillation

2.2.1. Fractionating Columns.

Separation of a mixture which contains two or more volatile liquids into its constituents can be effected in one step by using fractionating columns. A fractionating column is an apparatus that increases the degree of separation when a mixture of volatile components is distilled.

2.2.1a. *Column Efficiency* .

The heat exchange process within the fractionating column should, ideally, bring about complete separation of the substances in the mixture, but the degree of success that actually is achieved depends on a number of factors. The factors on which the efficiency of a fractionating column in achieving separations depends are:

(A) The amount of contact between vapour and liquid is determined by the length of the column, the diameter of the column, and the type of packing. In general the longer and narrower the tube, the more effective it will be. In order to achieve a more intimate and prolonged contact between vapour and liquid during their passage through the column, the available exposed surface area within the column of a given length is increased in one of several ways shown in following Figure .

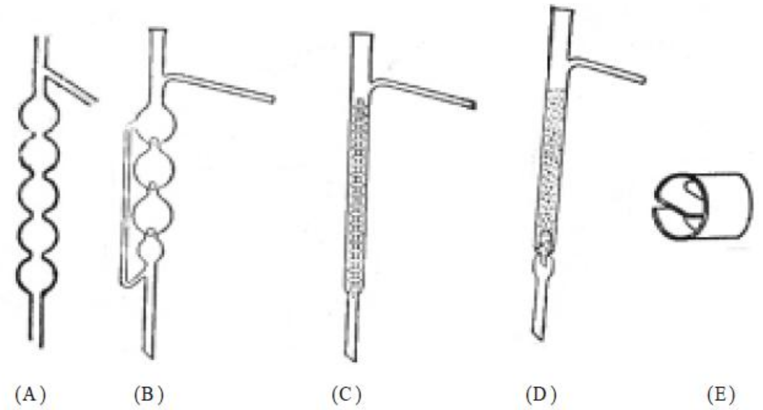


Figure: Types of column

(A) providing glass bulbs .

(B) glass balls .

(C) glass plates .

(D) more satisfactorily by various types of packing such as glass beads .

(E) Lessing's contact rings .

The 'fractional distillation curves' obtained by plotting percentage distilled against temperature summarise the results obtained by distilling a 1:1 mixture of benzene (b.p. 80º) and toluene (b.p. 111º) from: (I) An ordinary distilling flask with side tube, (II) a Hampel still-head (D) with glass beads, and (III) still-head packed with Lessing's contact rings (E). A particularly sharp separation into two fractions is noticeable in the last instance.

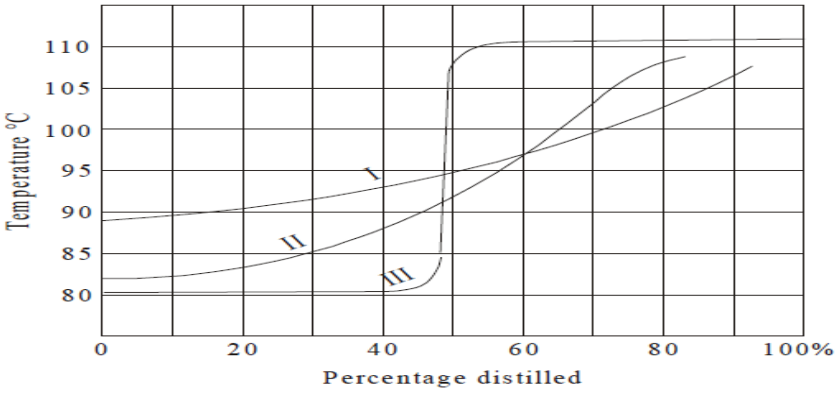


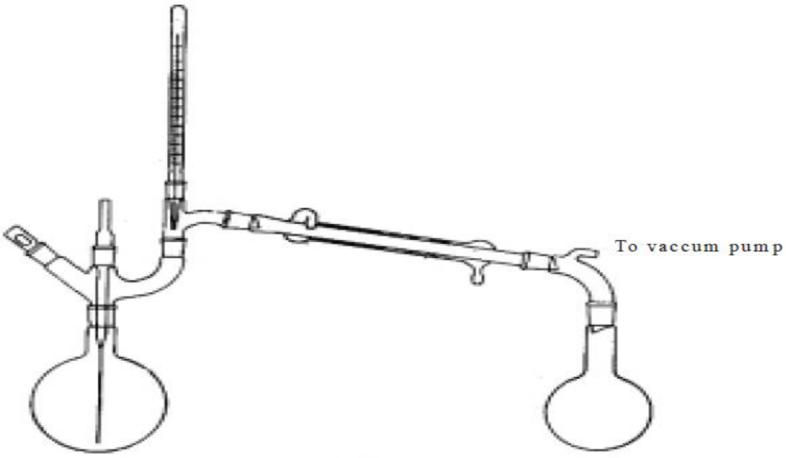
Figure 2.18 (b)
Fractional distillation curves

(2) Amount of reflux : The term ‘reflux ratio’ is used to designate the relative quantities of liquid returned and taken off. Appropriate reflux ratio is required to be maintained for conducting fractionation process efficiently. Usually, some means need to be provided for controlling the amount of liquid that is taken off and the amount returned to the column to attain the needed reflux ratio for the particular fractionation being conducted .

(3) The rate of distillation should be slow enough to allow sufficient time for equilibrium to be established between vapour and liquid. The rate of heating must be such that a temperature gradient (higher temperature at the bottom of the column, lower temperature at the top) is maintained.

2.3. Vacuum Distillation .

If a liquid boils at such a high temperature at atmospheric pressure that it undergoes partial decomposition, its distillation is done at a reduced pressure. Use is made of a water pump (which gives a residual pressure of 10-20 mm of mercury) or of an oil pump (which may give a residual pressure as low as tenths or hundredths of a fraction of a millimeter of a mercury column) to get the necessary reduced pressure in the system in which the distillation is carried out. Distillation in vacuum is applied to substances that boil above 200ºC at atmospheric pressure. At a residual pressure of 20 mm of mercury the boiling point decreases by about 100ºC. High-vacuum distillation is used to separate even higher-boiling compounds (300ºC and upwards). At a residual pressure of 0.02 – 0.05 mm of mercury the boiling temperature of such compounds is reduced by about 200ºC.



(b)
Figure 2.19 Distillation under reduced pressure

2.4. Molecular Distillation (Ideal Distillation) .

This type of distillation is employed to separate substances that decompose at the boiling temperature even in high vacuum. Under high vacuum (10^{-5} to 10^{-8} mm Hg) at temperatures ranging from 50ºC to 300ºC the molecules break away from the heated surface of the molten substance being subjected to distillation and pass, without occurrence of boiling, to the gas phase.

2.5. Steam Distillation .

If a mixture of two immiscible liquids is distilled, the composition of the vapour does not depend at all on the composition of the mixture. Each component exerts the same vapour pressure that it has when alone, and the boiling temperature is below that of the lower-boiling substance.

In the distillate the two components are obtained in the ratio :

$$\frac{\text{No. of moles of component A}}{\text{No. of moles of component B}} = \frac{\text{Vapour pressure of A at the distilling temp.}}{\text{Vapour pressure of B at the distilling temp.}}$$

Steam distillation is a particular case of this type of distillation in which one of the two components of the mixture of immiscible liquids is always water.

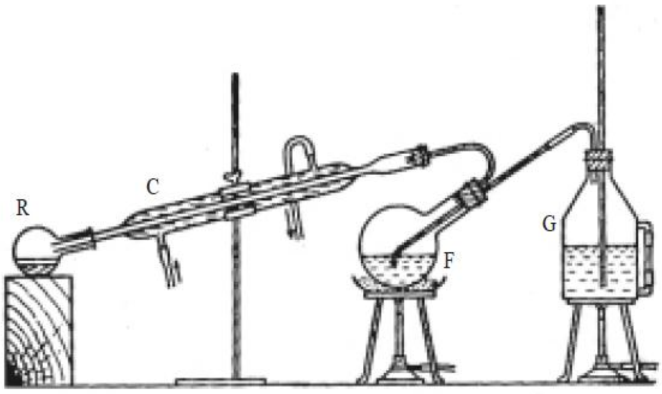


Figure 2.22 Steam distillation apparatus

3. **Separation by Extraction**.

Extraction is the removal of a substance from a solid or from a liquid by means of a solvent. The extracting solvent should preferably extract the required substance without extracting other materials. Extraction is frequently employed in the separation of substances from reaction mixtures or from natural sources and is also useful in the purification of substances. Extraction is carried out either as a *batch* process or as a continuous process .

3.1. **Principles.**

The partition of a solute between two immiscible phases is an equilibrium process that is governed by the distribution law. If the solute species A is allowed to distribute itself between water and an organic phase, the resulting equilibrium may be written as

$$A_{aq} \rightleftharpoons A_{org}$$

where the subscripts refer to the aqueous and the organic phases, respectively. Ideally, the ratio of activities for A in the two phases will be constant and independent of the total quantity of A so that, at any given temperature,

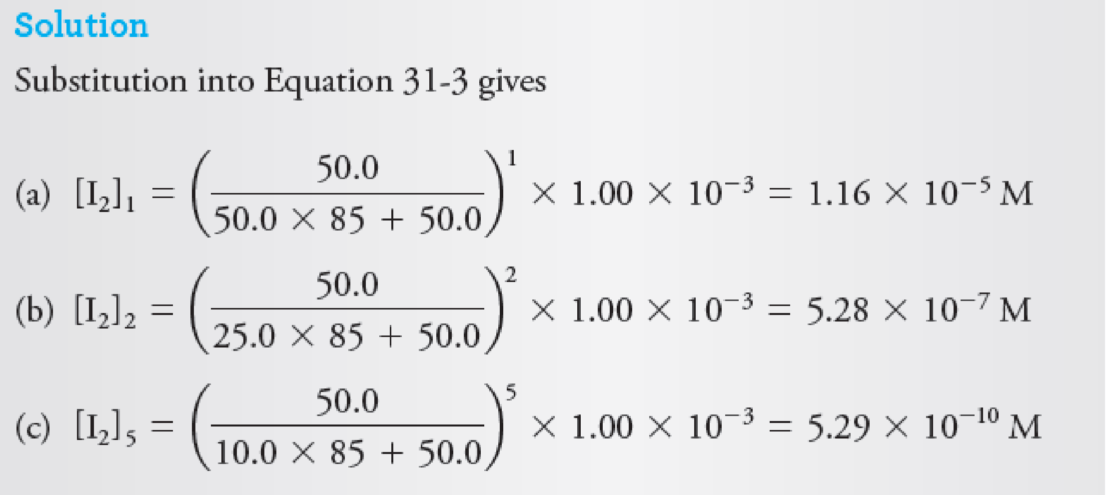
$$K = \frac{(a_A)_{org}}{(a_A)_{aq}} \approx \frac{[A]_{org}}{[A]_{aq}}$$

where $(aA)_{org}$ and $(aA)_{aq}$ are the activities of A in each of the phases and the bracketed terms are molar concentrations of A. The equilibrium constant K is known as the distribution constant. Generally, the numerical value for K approximates the ratio of the solubility of A in each solvent. Distribution constants are useful because they permit us to calculate the concentration of an analyte remaining in a solution after a certain number of extractions.The concentration of A remaining in an aqueous solution after i extractions with an organic solvent ($[A]_i$) is given by the equation

$$[A]_i = \left(\frac{V_{aq}}{V_{org}K + V_{aq}}\right)^i [A]_0$$

where $[A]_i$ is the concentration of A remaining in the aqueous solution after extracting V_{aq} mL of the solution with an original concentration of $[A]_0$ with i portions of the organic solvent, each with a volume of V_{org}.

EX1: The distribution constant for iodine between an organic solvent and H_2O is 85. Find the concentration of I_2 remaining in the aqueous layer after extraction of 50.0 mL of 1.00×10^{-3} M I_2 with the following quantities of the organic solvent: (a) 50.0 mL; (b) two 25.0-mL portions; (c) five 10.0-mL portions.



Solution

Substitution into Equation 31-3 gives

$$\text{(a)}\quad [I_2]_1 = \left(\frac{50.0}{50.0 \times 85 + 50.0}\right)^1 \times 1.00 \times 10^{-3} = 1.16 \times 10^{-5}\,\text{M}$$

$$\text{(b)}\quad [I_2]_2 = \left(\frac{50.0}{25.0 \times 85 + 50.0}\right)^2 \times 1.00 \times 10^{-3} = 5.28 \times 10^{-7}\,\text{M}$$

$$\text{(c)}\quad [I_2]_5 = \left(\frac{50.0}{10.0 \times 85 + 50.0}\right)^5 \times 1.00 \times 10^{-3} = 5.29 \times 10^{-10}\,\text{M}$$

3.2. **Extraction from solids** .

Fats and other naturally occurring organic non-volatile compounds may often be extracted from plant seeds, animal tissues etc. with a readily volatile solvent, such as ether, or ether mixed with alcohol. The Soxhlet apparatus is a very effective apparatus for this purpose. The macerated material is contained in a porous ‘thimble’ T, usually made of stout filter paper but also of porcelain or stoneware clay, and maintained in a glass cylinder provided with a syphon S. The volatile solvent, boiling gently in the flask F beneath, rises through the side-tube A and is condensed in the reflux condenser C forming the upper portion of the fit-up of the apparatus, so that a constant stream of pure solvent drops into the thimble, and a solution of the extracted matter returns periodically into the flask via the syphon S. The process is thus automatic and *continuous* and has the virtue of always being carried out with pure solvent. The extracted matter is then recovered from the solution collected in the flask by removal of the solvent by distillation.

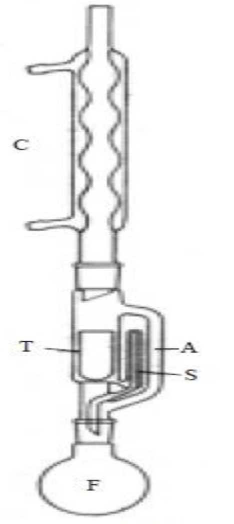


Figure 2.10
Soxhlet extraction apparatus

Application of solid-liquid extraction in the field of Inorganic Chemistry can be illustrated by taking the examples of separation of (1) lithium chloride from the chlorides of other members of the alkali metal group and (2) calcium nitrate from the nitrates of other members of the alkaline earth group. The solubilities of sodium chloride and potassium chloride are very small in *n*-hexanol and 2-ethylhexanol, whereas the solubility of lithium chloride is large enough so that it can be separated from a mixture of the three chlorides by extraction with these solvents. Similarly, using a 50-50 per cent mixture of absolute ethanol and ether calcium nitrate can be removed from a mixture of the anhydrous nitrates of calcium, barium and strontium.

3.3. **Extraction from liquids .**

3.3.1. Batch extraction .

Although no two liquids are absolutely immiscible, yet many examples of pairs of liquids, such as water and benzene are known which may be regarded as quite immiscible for all ordinary practical purposes. This property may sometimes be used to separate one component from a mixture of liquids. Thus in the *Batch* process, benzene is isolated from a solution of benzene and alcohol by shaking this mixture of the two liquids with an excess of water in a separating funnel.

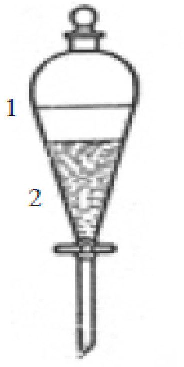


Figure: Separating funnel

3.3.2. Extraction by transfer to a more volatile solvent .

It is sometimes of advantage to transfer a dissolved solid from one solvent (usually water) to another which is more volatile (e.g. ether, benzene, chloroform, light petroleum etc.). Thus salicylic acid dissolved in water cannot easily be recovered by evaporating the solution to dryness, owing to its volatility in steam. When the aqueous solution is shaken with a relatively small amount of ether in a separating funnel and the mixture allowed to settle, a good deal of the salicylic acid is transferred to the ether; when the upper ether layer is separated and deprived of the ether by distillation, the extracted salicylic acid remains in the distillation flask.

3.3.3. Distribution coefficient (K_D).

In all the cases of extraction from liquids given above, the solute is distributed between the two solvents in such a manner that a definite ratio (the Distribution coefficient or the Partition coefficient) is maintained between the two concentrations i.e. in the instance under consideration.

$$\text{Distribution coefficient } (K_D) = \frac{\text{Concentration of solute in ether layer}}{\text{Concentration of solute in water layer}}$$

The ratio depends largely upon the respective solubility of the substance in each of the pure solvents, and for the process to be effective in the above example the solubility in ether must be considerably greater than the solubility in water. Urea, for instance, which is much more soluble in water than in ether, would not lend itself to extraction in this way. It follows from a consideration of the nature of the partition coefficient that a given amount of ether will afford a more efficient extraction when applied in successive quantities than when used all at once.

3.3.4. **Manipulations used for enhancing solubility .**

Solute solubility in the solvent chosen for extraction can be enhanced by various manipulations of which the more commonly employed are: Variation of the dielectric constant of the solvent, salting-in, hydrogen bonding and pH adjustment.

(i) ***Variation of the dielectric constant of the solvent:*** This is perhaps the most powerful method for increasing solubilities (and, also, for decreasing solubilities, as mentioned earlier under ‘Fractionation by Precipitation’), owing to the fundamental importance of the dielectric constant of the solvent in determining the solubility mechanism. In general, polar compounds are best extracted with polar solvents, and non-polar compounds with non-polar solvents, but selective extraction of polar compounds can often be carried out in media of reduced dielectric constant by making use of the enhanced salting-in effects under these conditions. Thus, although the total solubility may be markedly reduced by the reduction in the dielectric constant, the solubility of a particular component may be enhanced by the salting-in mechanism. Mixtures of methanol, ethanol, and dioxan with water are particularly useful for this purpose, although with labile solutes, it may be necessary to work at reduced temperatures.

(ii) Salting-in: The dilute aqueous salt solutions are among the most important extraction media for large dipolar ions such as proteins and peptides. In most cases salt solutions with concentrations in the range 0.05–0.2 M have been used, although higher salt concentrations up to 0.5–1M may be useful in certain instances, and considerably lower salt concentrations may be employed in solvents of lower dielectric constant. Sodium chloride solutions have been very widely used for extraction purposes, although the nature of the salting-in salt does not appear to be of primary importance. Salts such as potassium iodide and potassium thiocyanate have been employed with success in certain instances, although specific interactions may be involved in these cases.

(iii) Hydrogen bonding: Hydrogen bonding is one of the most important mechanisms of solute-solvent interactions and these interactions increase solute solubilities. Thus the presence of a proton donor or acceptor function in the solvent may be expected to increase the solubility of solutes having an appropriate hydrogen-bonding function.

(iv) pH Adjustment: The pH of the extraction medium is often of particular importance and the use of acidic or alkaline solvents to extract basic or acidic solutes . Dipolar ions such as proteins and peptides usually show their minimum solubilities at their isoelectric points where they have zero net charge, and they show greatly enhanced solubilities at even 0.5 pH unit on either side of the isoelectric point.

(v) Salt formation: The formation of certain salts by a particular component of a mixture of solutes may be used to enhance the solubility of that component. Some striking examples of the application of salt-formation include the enhanced solubilities of amine hydrochlorides compared with the free amines in non-polar solvents such as chloroform, and the highly specific solubilities of the trichloroacetates of serum albumin and insulin in organic solvents such as methanol, ethanol and acetone.

(vi) Temperature changes: Since the majority of solutes dissolve with the absorption of heat, their solubilities commonly increase with increasing temperature.

3.3.5. **Solvent extraction of metal ions** .

Many organic chelating agents are weak acids that react with metal ions to give uncharged complexes that are highly soluble in organic solvents such as ethers, hydrocarbons, ketones, and chlorinated species (including chloroform and carbon tetrachloride). Most uncharged metal chelates, on the other hand, are nearly insoluble in water. Similarly, the chelating agents themselves are often quite soluble in organic solvents but of limited solubility in water .The following figure shows the equilibria that develop when an aqueous solution of a divalent cation, such as zinc(II), is extracted with an organic solution containing a large excess of 8-hydroxyquinoline. Four equilibria are shown. In the first, 8-hydroxyquinoline, HQ, is distributed between the organic and aqueous layers. The second is the acid dissociation of the HQ to give H^+ and Q^-

ions in the aqueous layer. The third equilibrium is the complex-formation reaction giving MQ_2. Fourth is distribution of the chelate between the two solvents. If it were not for the fourth equilibrium, MQ_2would precipitate out of the aqueous solution.

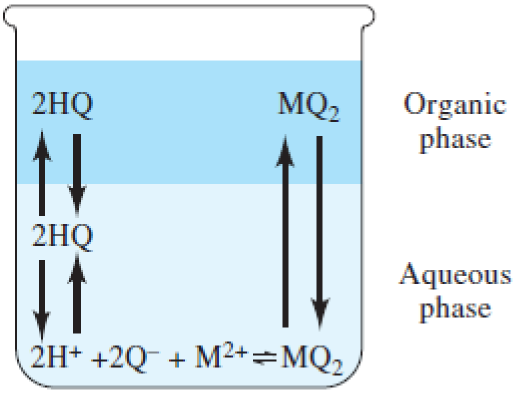


Fig: Equilibria in the extraction of an aqueous cation M^{+2} into an immiscible organic solvent containing 8-hydroxyquinoline.

The overall equilibrium is the sum of these four reactions or

$$2HQ(org) + M^{2+}(aq) \rightleftharpoons MQ_2(org) + 2H^+(aq)$$

The equilibrium constant for this reaction is

$$K' = \frac{[MQ_2]_{org}[H^+]^2_{aq}}{[HQ]^2_{org}[M^{2+}]_{aq}}$$

Usually, HQ is present in the organic layer in large excess with respect to M^{+2} in the aqueous phase so that [HQ]org remains essentially constant during the extraction. The equilibrium-constant expression can then be simplified to

$$K'[HQ]^2_{org} = K = \frac{[MQ_2]_{org}[H^+]^2_{aq}}{[M^{2+}]_{aq}}$$

or

$$\frac{[MQ_2]_{org}}{[M^{2+}]_{aq}} = \frac{K}{[H^+]^2_{aq}}$$

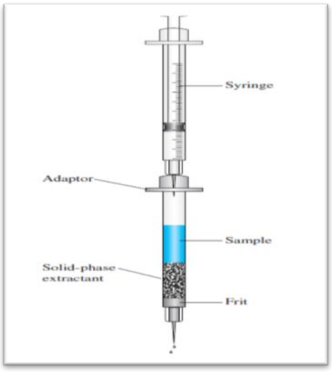
Thus, we see that the ratio of concentration of the metal species in the two layers is inversely proportional to the square of the hydrogen ion concentration of the aqueous layer . Equilibrium constants K vary widely from metal ion to metal ion, and these differences often make it possible to selectively extract one cation from another by buffering the aqueous solution at a level where one is extracted nearly completely and the second remains largely in the aqueous phase.

3.3.6.**Extracting Metal Chlorides and Nitrates .**

A number of inorganic species can be separated by extraction with suitable solvents. For example, a single ether extraction of a 6 M hydrochloric acid solution will cause better than 50% of several ions to be transferred to the organic phase, including iron(III), antimony(V), titanium(III), gold(III), molybdenum(VI), and tin(IV). Other ions, such as aluminum(III) and the divalent cations of cobalt, lead, manganese, and nickel, are not extracted.

3.3.7. **Solid-phase extraction**. techniques use membranes or small disposable syringe-barrel columns or cartridges . A hydrophobic organic compound is coated or chemically bonded to powdered silica to form the solid extracting phase. The compounds can be nonpolar, moderately polar, or polar. For example, an octadecyl (C18) bonded silica (ODS) is a common packing. The functional groups bonded to the packing attract hydrophobic compounds in the sample by van der Waals interactions and extract them from the aqueous solution. A typical cartridge system for solid-phase extractions is shown in the following figure. The sample is placed in the cartridge and pressure is applied by the syringe or from an air or nitrogen line. Alternatively, a vacuum can be used to pull the sample through the extractant. Organic molecules are then extracted from the sample and concentrated in the solid phase. They can later be displaced from the solid phase by a solvent such as methanol. By extracting the desired components from a large volume of water and then flushing them out with a small volume of solvent, the components can be concentrated. Preconcentration methods are often necessary for trace analytical methods. In some solid-phase extraction procedures, impurities are extracted into the solid phase while compounds of interest pass through unretained.

Solid-phase extraction performed in a small cartridge. The sample is placed in the cartridge and pressure is applied via a syringe plunger. Alternatively, a vacuum can be used to pull the sample through the extracting agent.



what are several limitations of liquid-liquid extractions?

1. The solvents that can be used must be immisicible with water and must not form emulsions.

2. Liquid-liquid extractions use relatively large volumes of solvent, which can cause a problem with waste disposal.

3. most extractions are performed manually, which makes them somewhat slow and tedious.

Questions:

1. What is a collector ion and how is it used?

2. What does the term salting out a protein mean? What is the salting in effect?

3. Name three methods based on mechanical phase separation ?

4. Define : a- distribution constant , b- Vacuum distillation , c- Molecular distillation

5. The distribution constant for X between *n*-hexane and water is 8.9. Calculate the concentration of X remaining in the aqueous phase after 50.0 mL of 0.200 M X is treated by extraction with the following quantities of *n*-hexane:

(a) one 40.0-mL portion. (b) two 20.0-mL portions. (c) four 10.0-mL portions. (d) eight 5.00-mL portions.

6. The distribution coefficient for Z between *n*-hexane and water is 5.85. Calculate the percent of Z remaining in 25.0 mL of water that was originally 0.0550 M in Z after extraction with the following volumes of *n*-hexane:

(a) one 25.0-mL portion. (b) two 12.5-mL portions. (c) five 5.00-mL portions. (d) ten 2.50-mL portions.

7. What volume of *n*-hexane is required to decrease the concentration of X in Problem 5 to 1×10^{-4} M if 25.0 mL of 0.0500 M X is extracted with

(a) 25.0-mL portions? (b) 10.0-mL portions? (c) 2.0-mL portions?

8. What volume of *n*-hexane is required to decrease the concentration of Z in Problem 6 to 1×10^{-5} M if 40.0 mL of 0.0200 M Z is extracted with

(a) 50.0-mL portions of *n*-hexane? (b) 25.0-mL portions? (c) 10.0-mL portions?

9. What is the minimum distribution coefficient that permits removal of 99% of a solute from 50.0 mL of water with

(a) two 25.0-mL extractions with toluene?

(b) five 10.0-mL extractions with toluene?

10. If 30.0 mL of water that is 0.0500 M in Q is to be extracted with four 10.0-mL portions of an immiscible organic solvent, what is the minimum distribution coefficient that allows transfer of all but the following percentages of the solute to the organic layer:

*(a) 1.00×10^{-4}

(b) 1.00×10^{-3}

(c) 1.00×10^{-2}