

12 PURIFICATION OF MATERIALS

There are many cases in which we cannot utilize materials without purification whether these are obtained from nature (for example, crude oil) or prepared in the laboratory. Separation-purification by some method is necessary.

In this text we first learn about synthesis of materials and then learn purification. In practice, synthesis and purification cannot be separated from each other. We shall now learn that whenever some new separation-purification method was developed, chemistry always made great progress.

12.1 Pure materials and mixtures

Materials can be classified into two categories, pure materials and mixtures, which are composed of two or more than two materials. This statement will be found on the 1st page of any high school chemistry textbook, and appears to be quite obvious. However, it is not so simple in practice. Firstly, most materials around us are mixtures, and most of them are multicomponent mixtures. The air is a good example. The main components of the air are nitrogen and oxygen. Hence the air is a mixture, and not a pure material. Furthermore, it will be shown by a detailed analysis that the air contains a small amount of water vapor, carbon dioxide and several rare gases in small amounts.

It may be argued that in the world there is no strictly pure material. You may believe that distilled water is completely pure water. This is too optimistic! A certain amount of carbon dioxide is dissolved in water. In addition a very small amount of sodium ion Na^+ might be found, which came from the wall of the distillation apparatus made of glass. Special care is necessary to remove these completely.

Artificially synthesizing materials or extracting natural products from nature serve various technological goals. In most cases a pure material is required. Hence the art of synthesis and that of purification are two sides of one coin.

12.2 Elemental analysis

The episode given in the coffee break might suggest to you that it is difficult to define “completely pure materials.” A more practical way is to define the allowable disparity from complete purity. It must be added that, without an appropriate method to estimate purity, one cannot judge the effectiveness of any purifying method. In short, how chemists can decide whether this compound is pure and that one is not.

Let us consider organic compounds for example. Until the middle of the 20th century, the criterion of the purity of organic compounds was based on several experiments: the **elemental analysis** and measurements of physical constants such as melting and boiling points. The results of elemental analysis should coincide with the calculated values, and the physical constants should be equal to the values reported in the literature (these criteria could be applied only for known compounds).

The elemental analysis of organic compounds was carried out as follows. A weighed amount of the sample was combusted and the carbon dioxide and water generated were trapped by appropriate absorbents, and the increased weights of the absorbents were measured. The increase corresponded to the amount of carbon dioxide and water generated by combustion, and from these values the amount of carbon and hydrogen could be determined. This combustion method has a long history. It was used by Lavoisier and greatly improved by Liebig. The modern method is to determine the amount of carbon dioxide and water by gas chromatography rather than by direct weighing. However, the principle itself has not changed at all.

It must be pointed out, however, that the possibility that some experimental error was involved was inevitable. The manipulation involved in weighing could not be made free of several types of errors (including inaccuracy of balances).

Coffee break

Absolutely pure water

Chemistry textbooks indicate that the ionic product of pure water is 10^{-14} (mol dm⁻³)² at 25°C. If you try to determine the ionic product of distilled water that you obtained by standard distillation by measuring its electrical conductivity, you will find that the value is much larger than the theoretical value, as explained above.

The German physicist Friedrich Wilhelm Georg Kohlrausch (1840-1910) directed all his energies to obtain accurate physical data. He realized that he had to be very careful in determining the electrical conductivity of water to obtain a very accurate value.

He made all the apparatus from quartz (not glass!) to avoid contamination from glassware. With bubbling purified nitrogen, he repeatedly distilled water. The electrical resistance of water thus obtained was very small; from one hundredth to one thousandth of that of conventional distilled water. From the electrical resistance thus obtained, the ionic product of water was calculated to be equal to the theoretical value.



Trapping of carbon dioxide and water was another difficult procedure. Contamination by carbon dioxide and water vapor from the air might be another possible source of error. Taking all these possibilities in consideration, it has been a general custom that disagreement between the experimental and calculated (theoretical) values is allowable if it would be less than 0.3 %. This is a good example of a practical definition of purity.

Another empirical criterion of purity is the **mixed-melting-point test**. This method is based on the following fact. When the melting point of a mixture of two solids with the same melting point is determined, it will decrease if the two compounds are not identical. This test was one of the logical foundations of organic chemistry when it was developing by adding new members to its family. If one of two compounds is not pure enough, a depression of melting point should also be observed.

The problem was how chemists could obtain samples which were correctly analyzed and which did not show a depression of melting points.

12.3 Standard method of separation

There is no royal way to separate a mixture into its components. The only possible method is to use differences in chemical and physical properties of each component. The critical point is how you can take advantage of very small differences.

(a) Filtration

Filtration, the process to remove solids from liquids, is the most fundamental method for purification of liquids and solutions. Filtration is used not only on a small scale in laboratories but also on a large scale in water purification plants. Filter paper and sieves are used to remove solid materials from liquids or solutions. By adjusting the size of mesh, the size of particles to be removed can be selected.

Usually natural filtration is employed. For instance, the sample to be filtered will be poured into a funnel at the bottom of which a filter paper is placed. The liquid fraction passes through the filter paper and the solid particles remain on the filter paper. When the liquid sample is too viscous, **suction filtration** is used. An special device to accelerate filtration by evacuating the receiver of the filtrate is used.

The suction filtration is not appropriate when the liquid is a volatile organic solvent. In such cases pressure should be applied to the surface of the liquid or solution (**pressure filtration**).

(b) Adsorption

It is not easy to remove very minute particles by filtration because such particles tend to clog the mesh. In such cases use of a filter aid that can selectively adsorb minute impurities is recommended. Any filter aid will do if it is porous, hydrophilic or solvophilic and has a rigid lattice. Celite, diatom earth and activated clay are frequently used. Activated charcoal has a wide surface area and can adsorb many organic compounds and is frequently used to remove smelly substances (in most cases organic compounds) from the air or water. Silica gel can adsorb water and is widely used as a desiccant.

Filtrating layers in water purification plants are composed of layers of these materials. Similar filtrating layers for domestic use are now commercially available.

(c) Recrystallization

As a method of purification of solids, **recrystallization** has a long history akin to that of distillation. Though several more sophisticated methods have been introduced, recrystallization is one of the most important methods of purification because of its simplicity (no special device is required) and its effectiveness. In the future recrystallization will remain as the standard method to purify solids.

The method is simple; the solid material is dissolved in an appropriate solvent at high temperature (at or near the boiling point of the solvent) to obtain a saturated or nearly saturated solution. When the hot solution is gradually cooled, crystals will deposit since the solubility of solids usually decreases as the temperature is lowered. It is expected that impurities will not crystallize since their concentration in the solution is not so high as to reach saturation.

Though recrystallization seems to be a very simple method, in practice, it is by no means easy. Helpful suggestions will be given below.

Advices to facilitate recrystallization

1. The solubility of the material to be purified should have a large temperature dependence. For instance, the temperature dependence of the solubility of sodium chloride is negligible. Hence purification of NaCl by recrystallization is impossible.
2. Crystals do not necessarily deposit from a saturated solution upon cooling because of super saturation. In such a case addition of a piece of crystal, a so-called "seed", may be effective. If no seed is available, scratching the wall of the container may be helpful.
3. In order to avoid any chemical reaction between the solute and the solvent, use of non-polar solvents is advisable. However, non-polar solvents tend to be poor solvents for polar compounds. Care should be taken when you have to use polar solvents. Even if no reaction takes place between the solute and the solvent, formation of solute-solvent complexes may take place.
4. Generally speaking, solvents with low boiling points are desirable. Again, however, solvents with low boiling points are generally non-polar. Thus, choice of solvents is not a simple matter.

(d) Distillation

Distillation is an art of the separating and purifying liquids by using a difference in the boiling points. It has a long history, and the origins of distillation can be found in ancient effects to obtain plant extracts thought to be the source of life. The technique of distillation was improved when condensers (coolers) were introduced. Gin and whisky, with their high concentrations of alcohol, were obtained by this improved technique.

Separation of liquid mixtures into components is accomplished by **fractional distillation**. The principle of fractional distillation can be explicable by use of the **boiling point-composition diagram** (Fig. 12. 1). In this Figure, the upper curve represents the composition of vapor at various boiling points given in the ordinate, and the lower curve corresponding the composition of the liquid. When the liquid with the composition l_2 is heated, it boils at b_1 . The composition of the vapor which is in equilibrium with the liquid at the temperature b_1 is v_1 . This vapor will condense when it is cooled at the cooler (upper) part of the distilling column (Fig 12.2), and flows down to the lower (hotter) part of the column. This portion will boil again at the temperature b_2 to give the vapor with composition v_2 . This vapor condenses to give the liquid with the composition l_3 .

Thus, by repeating the process of vaporization-condensation, the composition of the vapor changes from v_1 to v_2 and finally to v_3 to obtain a higher concentration of the more volatile component A.

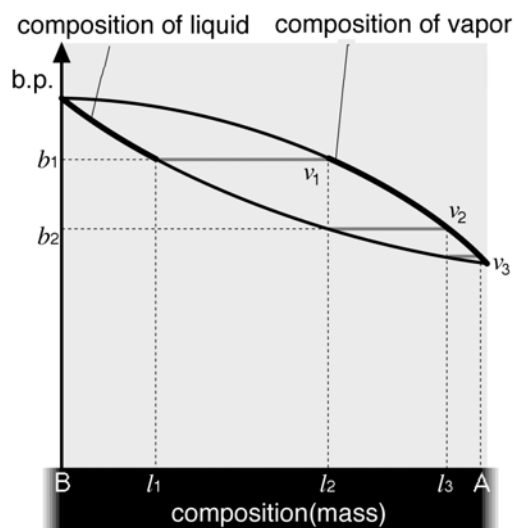


Figure 12.1 The boiling point-composition diagram of an ideal solution a mixture of two liquids A and B.

The composition of liquid phase changes from l_1 to l_2 and finally l_3 . At each stage the concentration of less volatile component B in the liquid phase is higher than that in the vapor phase.

Sample exercise 12.1 Fractional distillation

The vapor pressures of benzene and toluene are $10.0 \times 10^4 \text{ N m}^{-2}$ and $4.0 \times 10^4 \text{ N m}^{-2}$, respectively, at 80°C . Calculate the molar fraction of toluene in the vapor that is in equilibrium with a liquid composed of 0.6 molar fraction of toluene and 0.4 molar fraction of benzene. Calculate the molar fraction of toluene x in the vapor phase.

Answer

With the aid of Raoult's law (Ch. 7.4(b)), the composition of vapor in question can be calculated as follows.

$$\text{molar fraction of toluene in vapor} / \text{molar fraction of benzene in vapor} = \\ [0.60 \times (4.0 \times 10^4)] / [0.40 \times (10.0 \times 10^4)] = 0.60$$

The molar fraction of toluene x is:

$$x/(1-x) = 0.60, x = 0.60 / (1.0 + 0.60) = 0.375$$

As compared with the initial state, the concentration of toluene in the vapor phase substantially decreased to indicate the effect of fractional distillation.

The long distillation column of the distillation apparatus used in laboratories (Fig. 12.2) provides a wide cross-section area for ascending vapor and descending liquid to contact each other. At the top of the column, a thermometer is set to measure the temperature of the first fraction that is rich in the more volatile component A. As the distillation proceeds, the reading of the thermometer rises to indicate that the less volatile component B is distilling out. The receiver should be changed at appropriate intervals.

When the difference of boiling points of A and B is small, fractional distillation should be repeated to obtain better separation. The production of petrol is nothing other than fractional distillation on an extremely large scale.

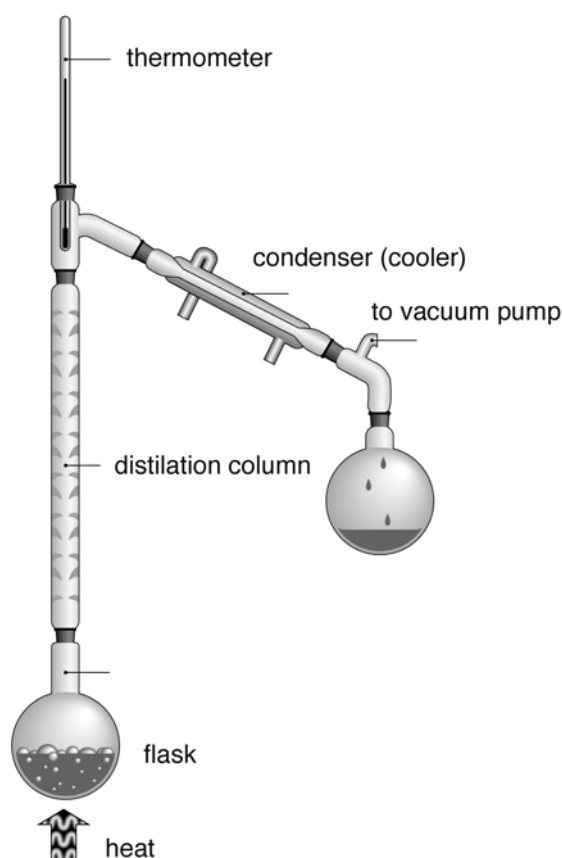


Fig. 12.2 An apparatus for fractional distillation

(e) Extraction

Extraction is a frequently used technique when organic compounds (mostly hydrophobic) are dissolved or dispersed in water. An appropriate solvent (sufficient to dissolve the organic compound; it should not be hydrophilic) is added to the aqueous phase, and the mixture is shaken well so that the organic compound is sure to be extracted by the organic solvent. The organic and aqueous layers are separated by means of a separatory funnel, and the organic compound is recovered from the organic layer by removing the solvent. The most frequently used solvent is diethyl ether $C_2H_5OC_2H_5$, which has a low boiling point (making it easy to remove) and can dissolve a variety of organic compounds.

Extraction is useful for the separation of a mixture of compounds with different chemical properties. A good example is a mixture of phenol C_6H_5OH , aniline $C_6H_5NH_2$ and toluene $C_6H_5CH_3$, all of which are soluble in diethyl ether. First aniline is extracted with a dilute acid. Then phenol is

extracted with dilute alkali. Toluene is recovered by evaporating the solvent. The acid used to extract aniline is made alkaline to recover the aniline, and the alkali used to extract the phenol is made acidic to recover the phenol.

If the organic compounds are completely insoluble in water, the separation should be complete. In fact, however, many organic compounds, especially organic acids and bases, are soluble in water to some extent. This is an inevitable problem for extraction. To lessen the loss caused by this problem, repeated extractions are recommended. Suppose you are allowed to use a given amount of the solvent. Instead of extracting once with all of your solvent, you had better extract several times with small portions of the solvent. Then combine the portions of solvent; you will find that you have extracted the compound more effectively. The reason can be explained by the **partition law**.

Suppose an organic compound which is soluble in both diethyl ether and water is added to a mixture of these two immiscible solvents. The ratio of the organic compound dissolved in each solvent is constant. Thus,

$$c_{\text{ether}} / c_{\text{water}} = k \text{ (constant)} \quad (12.1)$$

where c_{ether} and c_{water} are the concentration of the solute in diethyl ether and water, respectively. k is a kind of equilibrium constant and called the **partition coefficient**. It varies with the temperature.

Sample exercise 12.2 The efficiency of extraction

The partition coefficient k (for diethyl ether and water; $c_{\text{ether}} / c_{\text{water}}$) of an organic compound S is 40.0 at room temperature. You are supposed to extract S with 50 cm³ of diethyl ether from a solution of 5.0 g of S in 1 dm³ of water. Calculate the amount of extracted S when you try to extract (1) in one portion and (2) in two portions (each 25 cm³)

Answer

(1) The amount of S extracted, x_1 , is calculated as below.

$$k = c_{\text{ether}} / c_{\text{water}} = (x_1 / 50.0) / (5.0 - x_1) / 1000 = 40.0 \quad x_1 = 3.33 \text{ (g)}$$

(2) The amounts of S extracted, y_1 and y_2 , by each extraction, are calculated as below

$$k = c_{\text{ether}} / c_{\text{water}} = (y_1 / 25.0) / (5.0 - y_1) / 1000 = 40.0 \quad y_1 = 2.50 \text{ (g)}$$

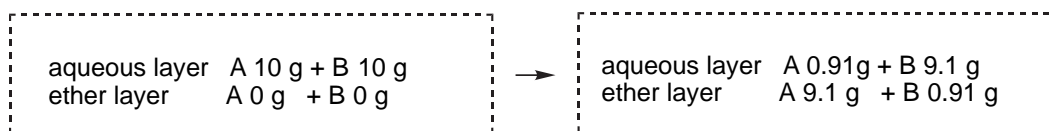
$$k = c_{\text{ether}} / c_{\text{water}} = (y_2 / 25.0) / (2.5 - y_2) / 1000 = 40.0 \quad y_2 = 1.25 \text{ (g)}$$

$$\therefore y_1 + y_2 = 2.50 + 1.25 = 3.75 \text{ (g)}$$

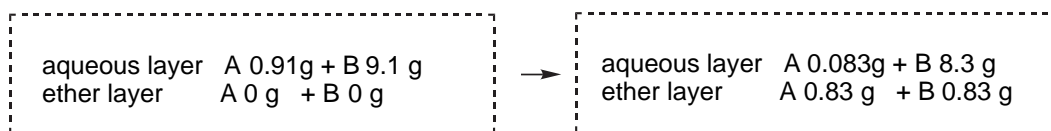
It is clear that the extraction is more advantageous when carried out by portions.

How the partition law works when there are two compounds to be extracted in the solution? Suppose two compounds, 10.0 g of A and 10.0 g of B, are dissolved in a sufficient amount of water. The partition coefficient $k = c_{\text{ether}} / c_{\text{water}}$ is 10.0 for A and 0.10 for B.

The 1st extraction is done with the same volume (as the solution) of diethyl ether. The result is as follows.



The ether layer is separated and the aqueous layer is extracted again with the same volume of diethyl ether. The result is as follows.



It is clear that the concentration of A in the aqueous layer will decrease as the extraction is repeated.

Sample exercise 12.3 The partition law

Confirm the above discussion with the aid of the partition law.

Answer

The amounts of A and B extracted by the 1st and the 2nd extractions are a_1 , b_1 and a_2 , b_2 , respectively. The result of the 1st extraction is as follows.

$$\text{For A; } k = c_{\text{ether}} / c_{\text{water}} = a_1 / (10.0 - a_1) = 10.0 \quad \therefore a_1 = 9.09 \text{ (g)}$$

$$\text{For B; } k = c_{\text{ether}} / c_{\text{water}} = b_1 / (10.0 - b_1) = 0.10 \quad \therefore b_1 = 0.909 \text{ (g)}$$

The result of the 2nd extraction is as follows.

$$\text{For A; } k = c_{\text{ether}} / c_{\text{water}} = a_2 / (0.91 - a_2) = 10.0 \quad \therefore a_2 = 0.83 \text{ (g)}$$

$$\text{For B; } k = c_{\text{ether}} / c_{\text{water}} = b_2 / (10.0 - b_2) = 0.10 \quad \therefore b_2 = 0.83 \text{ (g)}$$

12.4 Chromatography

Though a little inconspicuous, the contribution of **chromatography** to the development of modern chemistry should never be overestimated. Without the technique of chromatography, the preparation of (almost completely) pure substances would be much more difficult, and in many instances, utterly impossible.

At the beginning of the 20th century, the Russian chemist Mikhail Semënovich Tsvet (1872-1919) prepared a column packed with powder of calcium carbonate, and poured into it a mixture of plant pigments dissolved in petroleum ether. Surprisingly, the pigments separated out and formed colorful layers as descended down the column. He gave the name **chromatography** to this novel technique of separation (1906). Later the Swiss chemist Richard Martin Willstätter (1872-1942) applied this technique for his research on chlorophyll to demonstrate its usefulness, and since then much attention has been focused on chromatography.

Chromatography is a technique for separating a mixture into its components with the aid of the differences in the physical properties of each component. The device consists in a column in which an appropriate **stationary phase** (solid or liquid) is packed. The mixture is added to the column from one end and the mixture is moved with the help of appropriate **developer (mobile phase)**. Separation is achieved by the difference of each component in its rate of moving down the column, which is determined by the strength of adsorption or the partition coefficient between the stationary and mobile phases.

The main constituents of chromatography are the stationary and mobile phases and chromatography is divided into several groups depending on the type of mobile phase or the mechanism of separation as shown in Table 12.1

Table 12.1 Classification of chromatography

critierion	name
mobile phase	liquid chromatography, gas chromatography
mechanism	adsorption chromatography, partition chromatography, ion exchange chromatography, gel chromatography
stationary phase	column chromatography, thin layer chromatography, paper chromatography

Some examples of chromatography frequently used in the laboratories will be given below.

(a) Partition chromatography

The principle of partition chromatography is explicable in terms of the partition law applied to a multicomponent system described in the past section. In partition chromatography, extraction is repeated during one process. During the experiment, the solutes are distributed between the

stationary and mobile phases. The stationary phase is in most cases the solvent adsorbed to the adsorbent and the mobile phase is solvent molecules which fill the gaps among adsorbent particles.

A typical example of partition chromatography is **column chromatography** which is most widely used since this is a very efficient method for the separation of organic compounds (Fig. 12.3).

The column (a glass tube) is packed with such adsorbents as alumina, silica gel or starch which are mixed with the adsorbent, and the slurry is packed into the column. The solution of the sample is charged to the column from the top so that the sample is adsorbed by the adsorbent. Then the solvent (mobile phase; developer) is dropwise added from the top of the column.

Partition of the solutes takes place between the descending solvent (mobile phase) and the solvent adsorbed by the adsorbent (stationary phase). During the descending of the solutes, adsorption and partition are repeated. The rate of descending is different for each solute and depends on the partition coefficient of each solute. In the end, the solutes are separated to form several layers.

Finally each layer is separately eluted by appropriate solvents to give the purified specimens. The R value is defined for each solute by the following equation.

$$R = (\text{distance that the solute moves}) / (\text{distance the mobile phase (solvent) moves}) \quad (12.2)$$

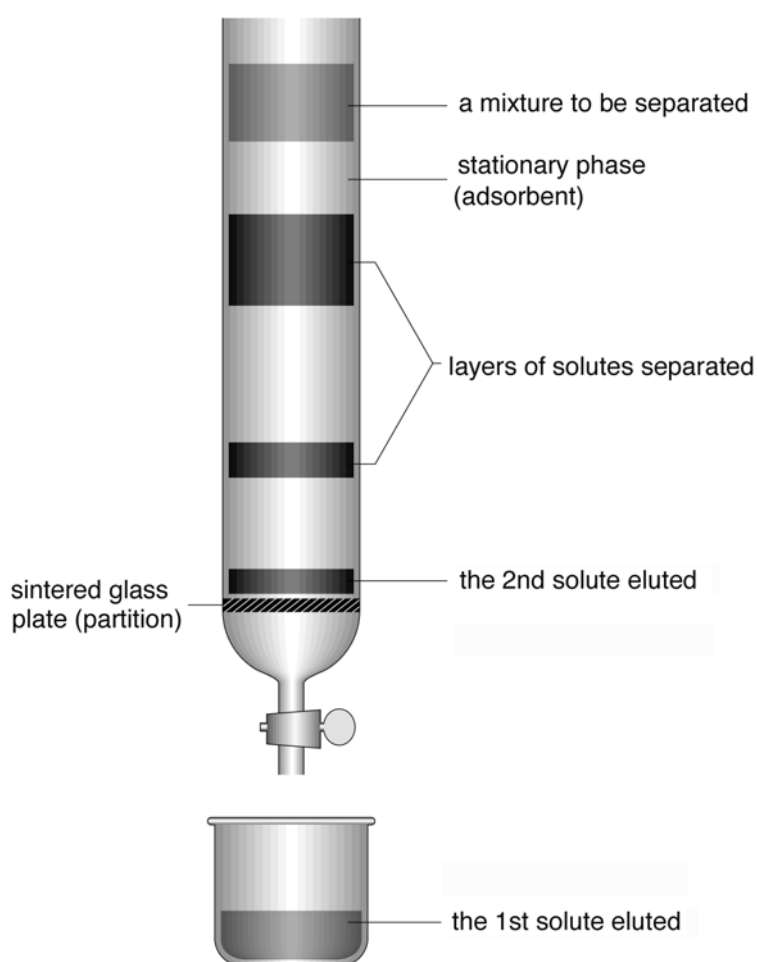


Fig 13.3 Schematic diagram of column chromatography

(b) Paper chromatography

The mechanism of separation by paper chromatography is essentially identical with that of column chromatography. The adsorbent for paper chromatography is filter paper, *i.e.*, cellulose. The sample to be analyzed is soaked into the end of a strip of filter paper which is hung in a vessel. Then

the bottom of the filter paper is dipped into the solvent in the bottom of the vessel. The mobile phase (solvent) may be various. Water, ethanol, acetic acid or a mixture of these may be used.

Paper chromatography was applied to analysis of mixtures of amino acids with splendid success. Since amino acids have very similar properties, and these are soluble in water and non-volatile (impossible to distil), the separation of amino acids was one of the most difficult problems for chemists in the late 19th and in the early 20th centuries. Hence the invention of paper chromatography was really good news to them.

It was the British chemist Richard Laurence Millington Synge (1914-1994) who established the method of analysis of amino acids by paper chromatography. While a mixture of amino acids dissolved in a solvent ascend the strip of filter paper vertically by the action of capillary phenomenon, partition of amino acids between the mobile phase and the stationary phase (water) adsorbed on cellulose takes place many times. When the solvent reaches to the top of the strip, the development is stopped. Each amino acid moves from the starting point a distance characteristic of each amino acid. From the *R* values, each amino acid is identified.

Two-dimensional (2D) paper chromatography uses a wide filter paper instead of a strip, and the sample is developed two-dimensionally by two different solvents.

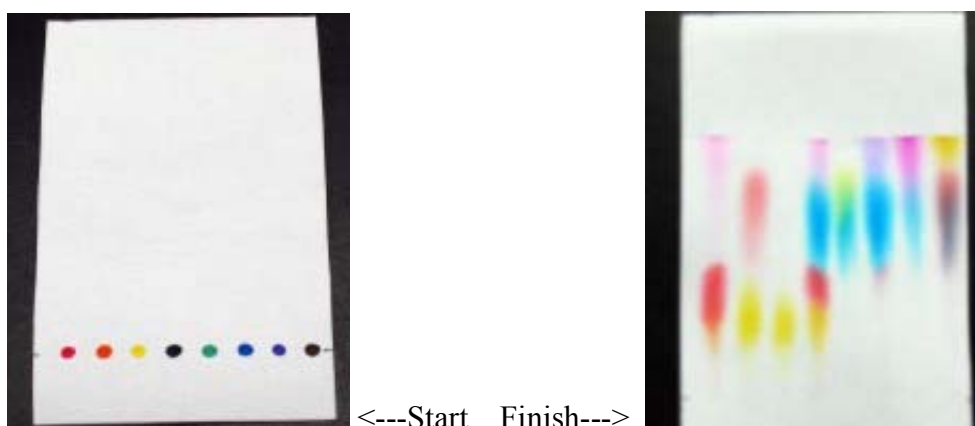


Fig. 12.4 An example of paper chromatography of pigments
from www.indigo.com/science-supplies/filter-paper.html

(c) Gas chromatography

A mixture of gases can be separated by **gas chromatography**. The stationary phase may be a solid (gas-solid chromatography) or a liquid (gas-liquid chromatography).

Typically, for gas-solid chromatography, minute powder of inert solid such as activated charcoal, activated alumina, silica gel or molecular sieve is packed in a long (2-10 m), thin (ID 2-10 mm) and coiled metal tube. The mobile phase is a gas such as hydrogen, nitrogen or argon and called a carrier gas. Separation of low boiling gas such as oxygen, carbon monoxide and carbon dioxide is possible.

In the case of gas-liquid chromatography, such an ester as phthalyl dodecylsulfate, adsorbed on the surface of activated alumina, silica gel or molecular sieve, is used as the stationary phase and packed in a similar column. A mixture of volatile compounds mixed with the carrier gas is introduced into the column, and each compound is partitioned between the gas (mobile) phase and the liquid (stationary) phase following the partition law. Compounds less soluble in the stationary phase will elute earlier.

This method is particularly useful for the analysis of volatile organic compounds such as hydrocarbons and esters. Analyses of crude oil and the scent components of fruit have been especially successful.

The efficiency of separation is determined by the extent of interaction between the samples and the liquid phase. It is advisable to try a standard liquid phase which is known to be effective to a wide range of compounds. Based on the results, a more specific liquid phase may be chosen. The

method of detection affects the sensitivity. The method of choice will be different whether the purpose is analytical or preparative.

(d) HPLC

Recently, for a large scale purification (*i.e.*, for synthetic purpose) of organic compounds, **HPLC** (high precision liquid chromatography or high performance liquid chromatography) is extensively used. If soluble in appropriate solvents, any type of compound can be analyzed. The feature of this technique is the use of high pressure to send the mobile phase to the column. By applying a high pressure, the rate and efficiency of separation is largely improved.

Silica gel or octadecylsilane bonded to silica gel are used for the stationary phase. Liquid stationary phases are not popular. The column used for HPLC is shorter than that used for gas chromatography. Most of columns are shorter than 1 m.

Ion-exchange chromatography uses ion-exchange materials for the stationary phase and is successfully employed for the analysis of cations, anions and organic ions.

Exercise

12.1 Fractional distillation

The vapor pressure of two pure liquids A and B are $1.50 \times 10^4 \text{ N m}^{-2}$ and $3.50 \times 10^4 \text{ N m}^{-2}$ at 20°C , respectively. Assuming that a mixture of A and B obeys Raoult's law, calculate the molar fraction of A when the total pressure of the mixture is $2.90 \times 10^4 \text{ N m}^{-2}$ at 20°C .

12.1 Answer

The molar fraction of A, n_A , is given below.

$$(n_A \times 1.50 \times 10^4) + (1 - n_A) \times 3.50 \times 10^4 = 2.90 \times 10^4 \quad \therefore n_A = 0.30$$