Republic of Iraq
Ministry of Higher Education & Scientific research
Diyala University
Science College
Chemistry Department

Analytical chemistry

For

Second Year Student

By Assist. Prof.

Dr. Ahmed M. Saeed. Alanbakey

2016 – 2017

Analytical samples and methods:

Many factors are involved in the choice of a specific analytical method. Among the most important factors are the amount of sample and the concentration of the analyte.

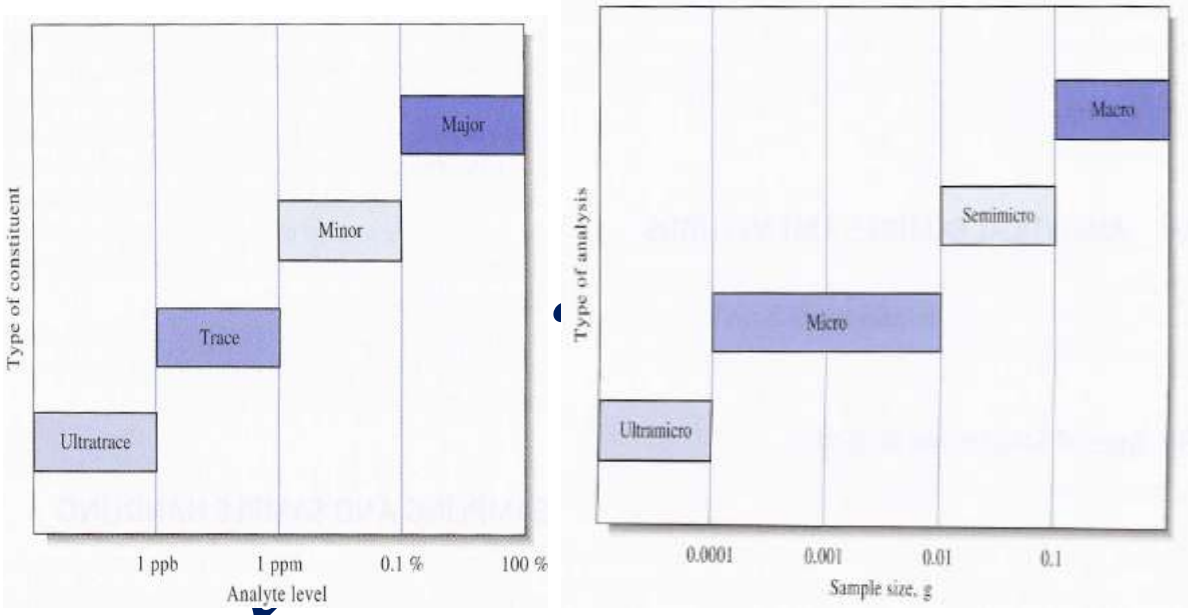
Types of Samples and Methods

Analytical methods can be classified **in** many different ways. Often we distinguish a method of identifying chemical species, a qualitative analysis, from one **that** determines the amount of a constituent, a quantitative analysis. Quantitative methods are traditionally classified as gravimetric, volumetric, or instrumental. Another way to distinguish methods is based on the size of the sample and the level of the constituents.

Sample Size:

The size of the sample is often used to classify the type of analysis performed. As shown in Figure.

A typical analytical laboratory handles samples ranging from the macro size to the micro and even ultramicro size. Techniques for handling very small samples are quite different from those for treating macro samples.



In some cases, analytical methods are used to determine **major constituents**. These constituents are present in the relative weight range of 0.1% to 100%. As shown in Figure, species present in the range of 0.01 % to 0.1% are usually termed minor constituents, whereas those present in amounts between 100 ppm (0.01 %) and 1 ppb are termed **trace constituents**. Components present in amounts less than 1 ppb are usually considered to be **ultra trace constituents.**

Real Samples:

The analysis of real samples is complicated by the presence of the sample matrix.

This matrix can contain species that have chemical properties similar to the analyte. Such species can react with the same reagents as the analyte or they can cause an instrument response that cannot be easily distinguished from the analyte.

If these interferences are caused by extraneous species in the matrix, they are often called **matrix effects**. Such effects can be induced not only by the sample itself but also by the reagents and solvents used to prepare the samples for the determination.

Sampling and sample handling:

A chemical analysis is most often performed on only a small fraction of the material whose composition is of interest. The process by which a representative fraction is acquired is termed **sampling**. Often, sampling is the most difficult step in the entire analytical process and the step that limits the accuracy of the procedure. This statement is particularly true when the material to be analyzed is a large and inhomogeneous liquid, such as a lake, or an inhomogeneous solid, such as an ore, a soil, or a piece of animal tissue. Sampling for a chemical analysis necessarily involves statistics because conclusions will be drawn about a much larger amount of material from the analysis of a small laboratory sample.

(Sampling is the process by which a sample population is reduced in size to an amount of homogeneous material that can be conveniently handled in the laboratory and whose composition is representative of the population).

Obtaining a Representative Sample:

The sampling process must ensure that the items chosen are representative of the bulk of material or population. To avoid confusion, chemists usually call the collection of sampling units or increments the gross sample. For analysis in the laboratory, the gross sample is usually reduced in size and made homogeneous to become the **laboratory sample.** Such materials may not be homogeneous because they may consist of microscopic particles of different compositions or, in the case of fluids, zones where concentrations differ. With these materials, we can assure a representative sample by taking our sample increments from different regions of the bulk material. Statistically, the goals of the sampling process are:

1. To obtain a mean value. This goal can be realized only if all members of the population have an equal probability of being included in the sample.

2. To obtain a variance, so that valid confidence limits can be found for the mean and various hypothesis tests can be applied. This goal can be reached only if every possible sample is equally likely to be drawn.

The Gross Sample:

The gross sample is the collection of individual sampling units. It must be representative of the whole in composition and in particle size distribution. Basically, gross sample weight is determined by (1) the uncertainty that can be tolerated between the composition of the gross sample and that of the whole, (2) the degree of heterogeneity of the whole, and (3) the level of particle size at which heterogeneity begins.

Sampling Homogeneous Solutions of Liquids and Cases:

For solutions of liquids or gases, the gross sample can be relatively small, since ordinarily nonhomogeneity first occurs at the molecular level, and even small volumes of sample will contain many more particles than the number computed from.

Sampling Particulate Solids:

It is often difficult to obtain a random sample from a bulky particulate material.

Random sampling can best be accomplished while the material is being transferred. Mechanical devices have been developed for handling many types of particulate matter.

Sampling Metals and Allays:

Samples of metals and alloys are obtained by sawing, milling, or drilling. In general, it is not safe to assume that chips of the metal removed from the surface are representative of the entire bulk, so solid material from the interior must be sampled as well.

Preparing a Laboratory Sample:

For nonhomogeneous solids, the gross sample may weigh from hundreds of grams to kilograms or more; therefore, reduction of the gross sample to a finely ground and homogeneous laboratory sample, weighing at the most a few hundred grams, is necessary. This process involves a cycle of operations that includes crushing and grinding, sieving, mixing, and dividing the sample (often into halves) to reduce its weight.

Automated Sample Handling:

Once sampling has been accomplished and the number of samples and replicates chosen, sample processing begins. Because of their reliability and cost-effectiveness, many laboratories are using automated sample handling methods. In some cases, automated sample handlings is used for only a few specific operarrons, such as dissolving the sample and removing interferences; in other cases all the remaining steps in the analytical procedure are automated. Two different methods of automated sample handling are described here' the **batch or discrete approach,** and the **continuous flow approach.**

Gravimetric Methods of Analysis:

Types of Gravimetric Methods:

The four examples are illustrating different ways in which the measurement of mass may serve as an analytical signal. When the signal is the mass of a precipitate, we call the method **precipitation gravimetry**. In **electrogravimetry**, we deposit the analyte as a solid film an electrode in an electrochemical cell. When we use thermal or chemical energy to remove a volatile species, we call the method **volatilization gravimetry**.

Finally, in **particulate gravimetry** we determine the analyte by separating it from the sample's matrix using a filtration or an extraction.

Why Gravimetry is Important:

The answer is that gravimetry is one of only a small number of **definitive techniques** whose measurements require only base SI units, such as mass or the mole, and defined constants. Although most analysts never use gravimetry to validate their results, they often verifying an analytical method by analyzing a standard reference material whose composition are traceable to a definitive technique. All precipitation gravimetric analysis is share two important attributes. First, the precipitate must be of low solubility, of high purity, and of known composition if its mass is to accurately reflect the analyte's mass. Second, the precipitate must be easy to separate from the reaction mixture.

Precipitation gravimetry:

In precipitation gravimetry, the analyte is converted to a sparingly soluble precipitate. This precipitate is then filtered, washed free of impurities, converted to a product of known composition by suitable heat treatment, and weighed. For example, determination of calcium in natural waters, an excess of oxalic acid, $H_2C_2O_4$, is added to an aqueous solution of the sample. Ammonia is then added, which neutralizes the acid and causes essentially all of the calcium in the sample to precipitate as calcium oxalate. The reactions are:

$$2NH_3 + H_2C_2O_4 \rightarrow 2NH_4^+ + C_2O_4^{2-}$$

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightarrow CaC_2O_4(s)$$

The precipitate is filtered using a weighed filtering crucible, then dried and ignited.

This process converts the precipitate entirely to calcium oxide. The reaction is:

$$CaC_2O_4(s) \xrightarrow{\Delta} CaO(s) + CO(g) + CO_2(g)$$

After cooling, the crucible and precipitate are weighed, and the mass of calcium oxide is determined by subtracting the known mass of the crucible. The calcium content of the sample is then computed.

Properties of Precipitates and Precipitating Reagents:

Ideally, a gravimetric precipitating agent should react specifically or at least selectively with the analyte. Specific reagents, which are rare, react only with a single chemical species. Selective reagents, which are more common, react with a limited number of species. In addition to specificity and selectivity, the ideal precipitating reagent would react with the analyte to give a product that is:

1. Easily filtered and washed free of contaminants.
2. Of sufficiently low solubility that no significant loss of the analyte occurs during filtration and washing.
3. Unreactive with constituents of the atmosphere.
4. Of known chemical composition after it is dried or, if necessary, ignited.

Mechanism of Precipitate Formation:

The effect of relative supersaturation on particle size can be explained if we assume that precipitates form in two ways; by nucleation and by particle growth. The particle size of a freshly formed precipitate is determined by the mechanism that predominates.

In nucleation, a few ions, atoms, or molecules (perhaps as few as four or five) come together to form a stable solid (1 – 100 nm diameter). Often, these nuclei form on the surface of suspended solid contaminants, such as dust particles. Further precipitation then involves a competition between additional nucleation and growth on existing nuclei (particle growth). If nucleation predominates, a precipitate containing a large number of small particles results; if growth predominates, a smaller number of larger particles are produced.

The rate of nucleation is believed to increase enormously with increasing relative supersaturation. In contrast, the rate of particle growth is only moderately enhanced by high relative supersaturations. Thus, when a precipitate is formed at high relative supersaturation, nucleation is the major precipitation mechanism, and a large number of small particles are formed. At low relative supersaturations, the rate of particle growth tends to predominate, and deposition of solid on existing particles occurs to the exclusion of further nucleation; a crystalline suspension results.

How to Perform a Successful Gravimetric Analysis:

The following factors determine a successful analysis by precipitation:

1 – The precipitate must be so insoluble that on appreciable loss occurs when it is collected by filtration.

2 – The physical nature of the precipitate must be such that it can be readily separated from the solution by filtration, and can be washed free soluble impurities.

3 – The particles are of such size that they not pass through the filtering medium, and that the particles size is unaffected (or at least, not diminished) by the washing process.

4 – The precipitate must be convertible into pure substance of definite chemical composition; this may be affected either by ignition or by a simple chemical operation, such as evaporation, with suitable liquid.

What steps are needed?

The steps required in a gravimetric analysis, after the sample has been dissolved, can be summarized as follows:

1 – Preparation of the solution.
2 – Precipitation.
3 – Digestion.
4 – Filtration.
5 – Washing.
6 – Drying or igniting.
7 – Weighing.
8 – Calculation.

Prepare the solution:

The first step in performing gravimetric analysis is to prepare the solution. Some form of preliminary separation may be necessary to eliminate interfering materials. Also, we must adjust the solution conditions to maintain low solubility of the precipitate and to obtain it in a form suitable for filtration. Proper adjustment of the solution conditions prior to precipitation may also mask potential interferences. Factors that must be considered include the volume of the solution during precipitation, the concentration range of the test substance, the presence and concentrations of other constituents, the temperature, and the pH.

The pH is important because it often influences both the solubility of the analytical precipitate and the possibility of interferences from other sub – stances.

Then do the precipitation but under the right conditions:

After preparing the solution, the next step is to do the precipitation. The precipitate should first be sufficiently insoluble that the amount lost due to solubility will be negligible. It should consist of large crystals that can be easily filtered. All precipitates tend to carry some of the other constituents of the solution with them. This contamination should be negligible. Keeping the crystals large can minimize this contamination.

We can achieve an appreciation of the proper conditions for precipitation by first looking at the precipitation process: The precipitation process involves heterogeneous equilibria and, as such, is not instantaneous. The equilibrium condition is described by the solubility product.

First, supersaturation occurs, that is, the solution phase contains more of the dissolved salt than occurs at equilibrium. This is a meta stable condition, and the driving force will be for the system to approach equilibrium (saturation). This is started by nucleation. The formation of a greater number of nuclei per unit time will ultimately produce more total crystals of smaller size. The total crystal surface area will be larger, and there will be more danger that impurities will be adsorbed.

Following nucleation, the initial nucleus will grow by depositing other precipitate particles to form a crystal's of a certain geometric shape. An increased growth rate increases the chances of imperfections in the crystal and trapping of impurities.

Von Weimarn discovered that the particle size of precipitates is inversely proportional to the relative supersaturation of the solution during the precipitation process:

$$\text{Relative supersaturation} = \frac{Q - S}{S}$$

Where *Q* is the concentration of the mixed reagents before precipitation occurs and is the degree of supersaturation, and ***S*** is the solubdity of the precipitate at equilibrium. This ratio is also called the **Von Weimarn ratio.** That is:

High relative supersaturation ⟶ many, small crystals (high surface area).

Low relative supersaturation ⟶ fewer, larger crystals (low surface area).

Obviously, then, we want to keep ***Q*** low and ***S*** high during precipitation.

Several steps are commonly taken to maintain favorable conditions for precipitation.

Here is how to minimize supersaturation and obtain large crystals:

1 – Precipitate from dilute solution. This keeps ***Q*** low.

2 – Add dilute precipitating agents slowly, with effective string. This also keeps ***Q*** low. Stirring prevents local excesses of reagent.

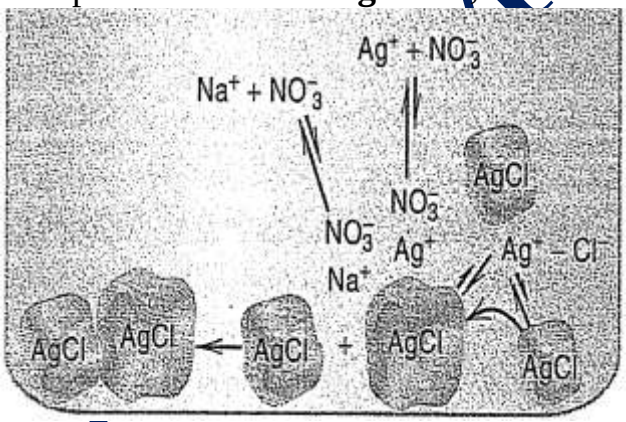
3 – Precipitate from hot solution. This increase ***S*** .The solubility should not be too great or the precipitation will not be quantitative (with less than 1 part per thousand remaining). The bulk of the precipitation may be performed in the hot solution, and then the solution may be cooled to make the precipitation quantitative.

4 – Precipitation at low pH as is possible to maintain quantitative precipitation.

Most of these operations can also decrease the degree of contamination. The concentration of impurities is kept lower and their solubility is increased, and the slower rate of precipitation decreases their chance of being trapped.

Digest the precipitation to make larger and more pure crystals:

When a precipitate is allowed to stand in the presence of the mother liquor (the solution from which it was precipitated), the large crystals grow at the expense of the small ones. This process is called **digestion**, or **Ostwald ripening**, and is illustrated in Figure.



Ostwald ripening improves the purity and crystallinity of the precipitate.

The small particles tend to dissolve and reprecipitated on the surfaces of the larger crystals. Digestion is usually done at elevated temperatures to speed the process, although in some cases it is done at room temperature. It improves both the filterability of the precipitate and its purity.

Many precipitates do not give a favorable **'Von Weimarn ratio**, especially very insoluble ones. Hence, it is impossible to yield a crystalline precipitate (small number of large particles), and the precipitate is first colloidal (large number of small particles).

Colloidal particles are very small (1 to 100 μm) and have a very large surface to mass ratio, which promotes surface adsorption. They are formed by virtue of the precipitation mechanism. As a precipitate forms, the ions are arranged in a fixed pattern.

When coagulated particles are filtered, they retain the adsorbed primary-and secondary ion layers along with solvent. **Washing** the particles with water increases the extent of solvent (water) molecules between the layers, causing the secondary layer to be loosely

bound, and the particles revert to the colloidal state, this process is called **peptization**. **Adding** an electrolyte will result in a closer secondary layer and will promote coagulation. Heating tends to decrease adsorption and the effective charge in the adsorbed layers, thereby aiding coagulation. Stirring will also help.

There are two types of colloids, hydrophilic and hydrophobic. Hydrophilic means (water loving), and these colloids have a strong affinity for water. A solution of a hydrophilic colloid is therefore viscous. A hydrophobic colloid has little attraction for water. A solution of this type of colloid is called a **sol**.

Coagulation of a hydrophobic colloid is fairly easy and results in a curdy precipitate. An example is silver chloride. Coagulation of a hydrophilic colloid, such as hydrous ferric oxide, is more difficult, and it produces a gelatinous precipitate that is difficult to filter because it tends to clog the pores of the filter. In addition, gelatinous precipitates adsorb impurities readily because of their very large surface area. Sometimes a reprecipitation of the filtered precipitate is required. During the reprecipitation, the concentration of impurities in solution (from the original sample matrix) has been reduced to a low level, and adsorption will be very small.

Impurities in precipitates:

Precipitates tend to carry down from the solution other constituents that are normally soluble, causing the precipitate to become contaminated.

Co – precipitation:

The phenomenon in which soluble compounds are removed from solution during the precipitate formation. There are four types of coprecipitation: **surface adsorption, mixed-crystal formation, occlusion,** and **mechanical entrapment**," Surface adsorption and mixed – crystal formation are equilibrium processes, whereas occlusion and mechanical entrapment arise from the kinetics of crystal growth.

Surface adsorption: is a common source of coprecipitation and is likely to cause significant contamination of precipitates with large specific surface areas-that is, coagulated colloids. Although adsorption does occur in crystalline solids, its effects on purity are usually undetectable because of the relatively small specific surface area of these solids.

Minimizing Adsorbed Impurities on Colloids:

1 – Digestion: During this process, water is expelled from the solid to give a denser mass that has a smaller specific surface area for adsorption. Washing a coagulated colloid with a solution containing a volatile electrolyte may also be helpful because any nonvolatile electrolyte added earlier to cause coagulation is displaced by the volatile species.

2 – Reprecipitation: A drastic but effective way to minimize the effects of adsorption is reprecipitation**.** In this process, the filtered solid is redissolved and reprecipitated.

The first precipitate ordinarily carries down only a fraction of the contaminant present in the original solvent. Thus, the solution containing the redissolved precipitate has a significantly lower contaminant concentration than the original, and even less adsorption occurs during the second precipitation. Reprecipitation adds substantially to the time required for an analysis but is often necessary for such precipitates.

Mixed-Crystal Formation:

In mixed-crystal formation, one of the ions in the crystal lattice of a solid is replaced by anion of another element. For this exchange to occur, it is necessary that the two ions

have the same charge and that their sizes differ by no more than about 5%. Furthermore, the two salts must belong to the same crystal class. For example, barium sulfate formed by adding barium chloride to a solution containing sulfate, lead, and acetate ions is found to be severely contaminated by lead sulfate even though acetate ions normally prevent precipitation of lead sulfate by complexing the lead. The extent of mixed-crystal contamination is governed by the law of mass action and increases as the ratio of contaminant to analyte concentration increases.

When mixed-crystal formation occurs, the interfering ion may have to be separated before the final precipitation step. Alternatively, a different precipitating reagent that does not give mixed crystals with the ions in question may be used.

Occlusion and Mechanical Entrapment:

In the process of occlusion, material that is not part of the crystal structure is trapped within a crystal. When a crystal is growing rapidly during precipitate formation, foreign ions in the counter-ion layer may become trapped, or occluded, within the growing crystal. Because supersaturation and thus growth rate decrease as precipitation progresses, the amount of occluded material is greatest in that part of a crystal that forms first. Inclusion occurs when ions, generally of similar size and charge, are trapped within the crystal lattice. For example, water may be trapped in pockets when $AgNO_3$ crystals are formed, and this can be driven off by melting.

Mechanical entrapment occurs when crystals lie close together during growth.

Several crystals grow together and in so doing trap a portion of the solution in a tiny pocket. If such mechanical trapping occurs during a precipitation process, the water will contain dissolved impurities.

Both occlusion and mechanical entrapment are at a minimum when the rate of precipitate formation is low that is, under conditions of low supersaturation. In addition, digestion is often remarkably helpful in reducing these types of coprecipitation. Digestion may help some but is not completely effective. The impurities cannot be removed by washing. Purification by dissolving and reprecipitation may be helpful.

Post – precipitation.

Sometimes, when the precipitate is allowed to stand in contact with the mother liquor, a second substance will slowly form a precipitate with the precipitating reagent. This is called **post precipitation**. Post precipitation is a slow equilibrium process.

The difference between post – precipitate and co – precipitate:

1 – The contamination increase with the time that the precipitate is left in contact with the mother liquor in post – precipitation, but usually decreases in co – precipitation.

2 – With post – precipitation, contamination increases the faster the solution is agitated by either mechanical or thermal means. The reverse is usually true with co – precipitation.

3 – The magnitude of contamination by post – precipitation may be much greater than in co – precipitation.

4 – The post – precipitation was occurs either the pollutants are found through the precipitation operation or addition after the operation.

5 – The quantity of post – precipitate may be some time equal 50% of the true precipitate.

6 – The post – precipitation increase with temperature increasing.

Particle Size and Filterability of Precipitates:

Precipitates consisting of large particles are generally desirable for gravimetric work because these particles are easy to filter and wash free of impurities. In addition, precipitates of this type are usually purer than are precipitates made up of fine particles.

Factors That Determine the Particle Size of Precipitates:

The particle size of solids formed by precipitation varies enormously. At one extreme are colloidal suspensions, whose tiny particles are invisible to the naked eye (10^{-7} to 10^{-4} cm in diameter). Colloidal particles show no tendency to settle from solution and are not easily filtered. At the other extreme are particles with dimensions on the order of tenths of a millimeter or greater. The temporary dispersion of such particles in the liquid phase is called a crystalline suspension. The particles of a crystalline suspension tend to settle spontaneously and are easily filtered. It is certain, however, that the particle size of a precipitate is influenced by such experimental variables as precipitate solubility, temperature, reactant concentrations, and rate at which reactants are mixed. The net effect of these variables can be accounted for, at least qualitatively, by assuming that the particle size is related to a single property of the system called the **relative supersaturation**, where:

$$\text{relative supersaturation} = \frac{Q - S}{S}$$

In this equation, ***Q*** is the concentration of the solute at any instant and ***S*** is its equilibrium solubility.

Generally, precipitation reactions are slow, so that even when a precipitating reagent is added drop by drop to a solution of an analyte, some supersaturation is likely. Thus, when ***(Q -S)/S*** is large, the precipitate tends to be colloidal; when ***(Q - S)/S*** is small, a crystalline solid is more likely.

Experimental Control of Particle Size:

Experimental variables that minimize supersaturation and thus produce crystalline precipitates include elevated **temperatures** to increase the solubility of the precipitate (***S***), **dilute** solutions (to minimize ***Q***), and **slow addition** of the precipitating agent with good stirring. The last two measures also minimize the concentration of the solute ***(Q)*** at any given instant. Larger particles can also be obtained by controlling **pH**, provided the solubility of the precipitate depends on pH.

A colloidal solid is generally encountered when a precipitate has such a low solubility that ***S*** in equation always remains negligible relative to ***Q***.

Colloidal Precipitates:

Individual colloidal particles are so small that they are not retained by ordinary filters. Fortunately, however, we can coagulate, or agglomerate, the individual particles of most colloids to give a filterable, amorphous mass that will settle out of solution.

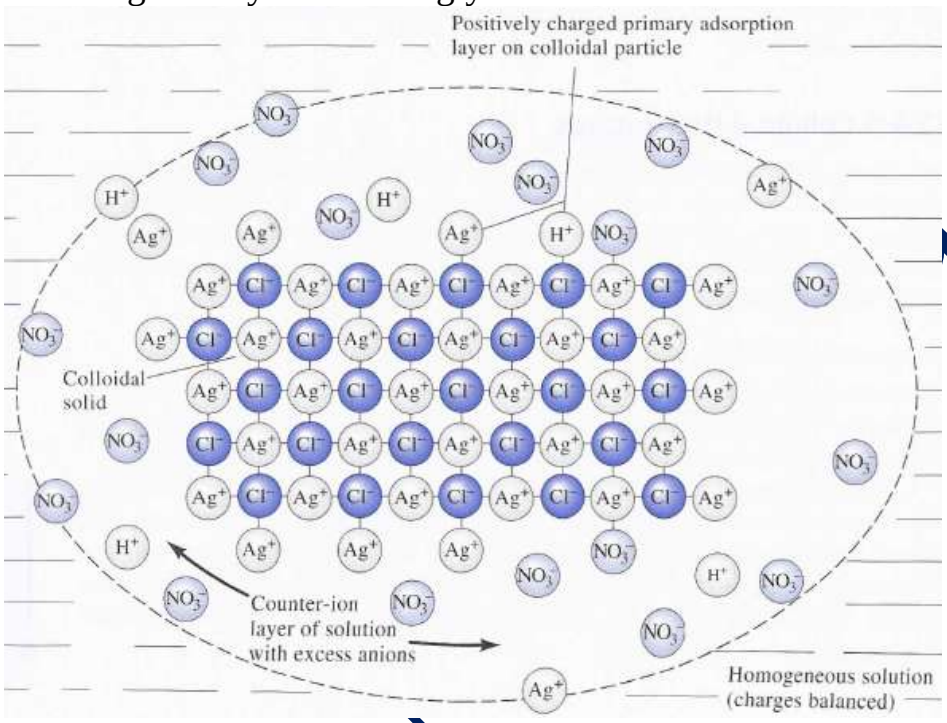
(Precipitates that have very low solubilities, such as many sulfides and hydrous oxides, generally form as colloids).

Coagulation of Colloids:

Coagulation can be hastened by heating, by stirring, and by adding an electrolyte to the medium. Colloidal suspensions are stable and do not coagulate spontaneously, because all of the particles of the colloid are either positively or negatively charged. This charge results from cations or anions that are bound to the surface of the particles. The process by which ions are retained on the surface of a solid is known as **adsorption.**

(Adsorption is a process in which a substance (gas, liquid, or solid) is held on the surface of a solid. In contrast, absorption involves retention of a substance within the pores of a solid).

The adsorption of ions on an ionic solid originates from the normal bonding forces that are responsible for crystal growth. The kind of ions retained on the surface of a colloidal particle and their number depend, in a complex way, on several variables. For a suspension produced in the course of a gravimetric analysis, however, the species adsorbed, and hence the charge on the particles, can be easily predicted because lattice ions are generally more strongly held than others.



The surface charge is at a minimum when the supernatant liquid contains an excess of neither ion. The extent of adsorption and thus the charge on a given particle increase rapidly as the concentration of a common ion becomes greater. Eventually, however, the surface of the particles becomes covered with the adsorbed ions, and the charge becomes constant and independent of concentration. Figure shows a colloidal silver chloride particle in a solution that contains an excess of silver nitrate. Attached directly to the solid surface is the **primary adsorption layer,** which consists mainly of adsorbed silver ions. Surrounding the charged particle is a layer of solution, called the **counter-ion layer,** which contains sufficient excess of negative ions (principally nitrate) to just balance the charge on the surface of the particle. The primarily adsorbed silver ions and the negative counter-ion layer constitute an **electric double layer** that imparts stability to the colloidal suspension. As colloidal particles approach one another, this double layer exerts an electrostatic repulsive force that prevents particles from colliding and adhering.

Peptization of Colloids:

Peptization is the process by which a coagulated colloid reverts to its original dispersed state. When a coagulated colloid is washed, some of the electrolyte responsible for its coagulation is leached from the internal liquid in contact with the solid particles. Removal of this electrolyte has the effect of increasing the volume of the counter-ion layer. The repulsive forces responsible for the original colloidal state are then reestablished, and particles detach themselves from the coagulated mass. The washings become cloudy as the freshly dispersed particles pass through the filter. The chemist is

thus faced with a dilemma in working with coagulated colloids. On the one hand, washing is needed to minimize contamination; on the other, there is a risk of losses resulting from peptization if pure water is used. The problem is commonly solved by washing the precipitate with a solution containing an electrolyte that volatilizes when the precipitate is dried or ignited. For example, silver chloride is ordinarily washed with a dilute solution of nitric acid. While the precipitate undoubtedly becomes contaminated with the acid, no harm results, since the nitric acid is volatilized during the ensuing drying step.

Practical Treatment of Colloidal Precipitates:

Colloids are best precipitated from hot, stirred solutions containing sufficient electrolyte to ensure coagulation. The filterability of a coagulated colloid frequently improves if it is allowed to stand for an hour or more in contact with the hot solution from which it was formed. During this process, which is known as **digestion,** weakly bound water appears to be lost from the precipitate; the result is a denser mass that is easier to filter.

Crystalline Precipitates:

Crystalline precipitates are generally more easily filtered and purified than are coagulated colloids. In addition, the size of individual crystalline particles, and thus their filterability, can be controlled to a degree.

Methods of Improving Particle Size and Filterability:

The particle size of crystalline solids can often be improved significantly by minimizing ***Q*** or maximizing ***S***, or both, in Equation. Minimization of Q is generally accomplished by using dilute solutions and adding the precipitating reagent slowly and with good mixing. Often, S is increased by precipitating from hot solution or by adjusting the pH of the precipitation medium.

Digestion of crystal1ine precipitates (without stirring) for some time after formation frequently yields a purer, more filterable product. The improvement in filterability undoubtedly results from the dissolution and recrystallization that occur continuously and at an enhanced rate at elevated temperatures. Recrystallization apparently results in bridging between adjacent particles, a process that yields larger and more easily filtered crystalline aggregates. This view is supported by the observation that little improvement in filtering characteristics occurs if the mixture is stirred during digestion.

Precipitation from Homogeneous Solution:

Precipitation from homogeneous solution is a technique in which a precipitating agent is generated in a solution of the analyte by a slow chemical reaction. Local reagent excesses do not occur because the precipitating agent appears gradually and homogeneously throughout the solution and reacts immediately with the analyte. As a result, the relative supersaturation is kept low during the entire precipitation. In general, homogeneously formed precipitates, both colloidal and crystalline, are better suited for analysis than a solid formed by direct addition of a precipitating reagent. The precipitate is dense and readily filterable; co – precipitate is reduced to minimum. The slower the reaction, the larger (in general) are the crystal formed. Many different anions can be generated at slow rate.

Two general methods are used for homogeneous precipitation. If the precipitate's solubility is pH-dependent, then we can mix the analyte and the precipitant under conditions where precipitation does not occur, and then increase or decrease the pH by

chemically generating OH^- or H_3O^+. For example, the hydrolysis of urea is a source of OH^-.

$$CO(NH_2)_2(aq) + H_2O(l) \rightleftharpoons 2NH_3(aq) + CO_2(g)$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$$

Because the hydrolysis of urea is temperature-dependent, it is negligible at room temperature, we can use temperature to control the rate of hydrolysis and the rate of precipitate formation. Precipitates of CaC_2O_4, for example, have been produced by this method. After dissolving the sample containing Ca^{2+}, the solution is made acidic with HCl before adding a solution of 5% w/v $(NH4)_2C_2O_4$. Because the solution is acidic, a precipitate of CaC_2O_4does not forms. The solution is heated to approximately 50 ^oC and urea is added. After several minutes, a precipitate of CaC_2O_4begins to form, with precipitation reaching completion in about 30 min.

The urea hydrolysis method may be applied also to:

1 – Precipitation of barium as barium chromate in presence of ammonium acetate.

2 – Precipitation of nickel as Dimethylglyoxime.

3 – Precipitation of aluminium as Oxime.

Sulphates: sulphate ion may be generated by the hydrolysis of aminosulphonic acid (sulphamic acid).

$$NH_2SO_3H + H_2O = NH_4^+ + H^+ + SO_4^{2-}$$

The reaction has been used to produce barium sulphate. The hydrolysis of dimethyl sulphate also provides a source of sulphate ion and used for precipitation of Ba, Sr, Ca and Pb.

$$(CH_3)_2SO_4 + 2H_2O = 2CH_3OH + 2H^+ + SO_4^{2-}$$

Phosphates: insoluble orthophosphates may be precipitated with phosphate ion derived from trimethyl or triethyl phosphate by hydrolysis. Thus 1.8 M sulphuric acid containing zirconyl ions and trimethyl phosphate yield ZrP_2O_7. Metaphosphoric acid used for bismuth precipitate.

In the second method of homogeneous precipitation, the precipitant is generated by a chemical reaction. For example, Pb^{2+} is precipitated homogeneously as $PbCrO_4$ by using bromate, BrO^{3-}, to oxidize Cr^{3+} to CrO_4^{2-}.

$$6BrO_3^-(aq) + 10Cr^{3+}(aq) + 22H_2O(l) \rightleftharpoons$$

$$3Br_2(aq) + 10CrO_4^{2-}(aq) + 44H^+(aq)$$

Figure shows the result of preparing $PbCrO_4$ by the direct addition of $KCrO_4$ (Beaker A) and by homogenous precipitation (Beaker B). Both beakers contain the same amount of $PbCrO_4$. Because the direct addition of $KCrO_4$ leads to rapid precipitation and the formation of smaller particles, the precipitate remains less settled than the precipitate prepared homogeneously. Note, the difference in the color of the two precipitates.

A homogeneous precipitation produces large particles of precipitate that are relatively free from impurities. These advantages, however, are offset by requiring more time to produce the precipitate and a tendency for the precipitate to deposit as a thin film on the container's walls. The latter problem is particularly severe for hydroxide precipitates generated using urea.

Representative methods based on precipitation by homogeneously generated reagents are given in Table.

Precipitant	Reaction
OH^-	$(NH_2)_2CO(aq) + 3H_2O(l) \rightleftharpoons 2NH_4^+(aq) + CO_2(g) + 2OH^-(aq)$
SO_4^{2-}	$NH_2HSO_3(aq) + 2H_2O(l) \rightleftharpoons NH_4^+(aq) + H_3O^+(aq) + SO_4^{2-}(aq)$
S^{2-}	$CH_3CSNH_2(aq) + H_2O(l) \rightleftharpoons CH_3CONH_2(aq) + H_2S(aq)$
IO_3^-	$HOCH_2CH_2OH(aq) + IO_4^-(aq) \rightleftharpoons 2HCHO(aq) + H_2O(l) + IO_3^-(aq)$
PO_4^{3-}	$(CH_3O)_3PO(aq) + 3H_2O(l) \rightleftharpoons 3CH_3OH(aq) + H_3PO_4(aq)$
$C_2O_4^{2-}$	$(C_2H_5)_2C_2O_4(aq) + 2H_2O(l) \rightleftharpoons 2C_2H_5OH(aq) + H_2C_2O_4(aq)$
CO_3^{2-}	$Cl_3CCOOH(aq) + 2OH^-(aq) \rightleftharpoons CHCl_3(aq) + CO_3^{2-}(aq) + H_2O(l)$

Urea is often used for the homogeneous generation of hydroxide ion. The reaction can be expressed by the equation:

$$(H_2N)_2CO + 3H_2O \rightarrow CO_2 + 2NH_4^+ + 2OH^-$$

This hydrolysis proceeds slowly at temperatures just below 100°C, and 1 to 2 hours is needed to complete a typical precipitation. Urea is particularly valuable for the precipitation of hydrous oxides or basic salts. For example, hydrous oxides of Iron (III) and aluminum, formed by direct addition of base, are bulky and gelatinous masses that are heavily contaminated and difficult to filter. In contrast, when these same products are produced by homogeneous generation of hydroxide ion, they are dense and easily filtered and have considerably higher purity. Homogeneous precipitation of crystalline precipitates also results in marked increases in crystal size as well as improvements in purity.

Washing and filtering the precipitates:

Coprecipitated impurities, especially those on the surface, can be removed by washing the precipitate after filtering. The precipitate will be wet with the mother liquor, which is also removed by washing. Many precipitates cannot be washed with pure water, because peptization occurs. This is the reverse of coagulation, as previously mentioned.

As we have seen, coagulated particles have a neutral layer of adsorbed primary and counterions. This can be prevented by adding an electrolyte to the wash liquid, for example, HNO_3 or NH_4NO_3 for AgCl precipitate (but not KNO_3 since it is nonvolatile).

The electrolyte must be one that is volatile at the temperature to be used for drying or ignition, and it must not dissolve the precipitate. For example, dilute nitric acid is used as the wash solution for silver chloride. Ammonium nitrate is used as the wash electrolyte for hydrous fettle oxide.

When you wash a precipitate, you should conduct a test to determine when the washing is complete. This is usually done by testing the filtrate for the presence of an ion of the precipitating reagent.

Drying or igniting the precipitate:

After filtration, a gravimetric precipitate is heated until its mass becomes constant.

Heating removes the solvent and any volatile species carried down with the precipitate. Some precipitates are also ignited to decompose the solid and form a compound of known composition. This new compound is often called the weighing form. The temperature required to produce a suitable weighing form varies from precipitate to precipitate. If the collected precipitate is a form suitable for weighing, it must be heated to remove water and to remove the adsorbed electrolyte from the wash liquid. This drying can usually be done by heating at 110 to 120.C for 1 to 2 h. Ignition at a much higher temperature is usually required if a precipitate must be converted to a more suitable form for weighing. For example, magnesium ammonium phosphate, $MgNH_4PO_4$, is decomposed to the pyrophosphate, $Mg_2P_2O_7$, by heating at 900°C. Hydrous ferric oxide, $Fe_2O_3.xH_2O$, is ignited to the anhydrous ferric oxide. Many metals that are precipitated by organic reagents (e.g., 8-hydroxyquinoline) or by sulfide can be ignited to their oxides.

Gravimetric Calculation:

The precipitate we weigh is usually in a different form than the analyte whose weight we wish to report. We introduced the gravimetric factor (GF), which represents the weight of analyte per unit weight of precipitate. It is obtained from the ratio of the formula weight of the analyte to that of the precipitate, multiplied by the moles of analyte per mole of precipitate obtained from each mole of analyte, that is:

$$GF = \frac{\text{f wt analyte (g/mol)}}{\text{f wt precipitate (g/mol)}} \times \frac{a}{b} \text{ (mol analyte/mol precipitate)}$$
$$= \text{g analyte/g precipitate}$$

So, if Cl_2 in a sample is converted to chloride and precipitated as AgCl, the weight of Cl_2 that gives 1 g of AgCl is:

$$\text{g } Cl_2 = \text{g AgCl} \times \frac{\text{f wt } Cl_2 \text{ (g } Cl_2\text{/mol } Cl_2)}{\text{f wt AgCl (g AgCl/mol AgCl)}} \times \frac{1}{2} \text{ (mol } Cl_2\text{/mol AgCl)}$$
$$= \text{g AgCl} \times GF \text{ (g } Cl_2\text{/g AgCl)}$$
$$= \text{g AgCl} \times 0.2473_7 \text{ (g } Cl_2\text{/g AgCl)}$$

Calculate the grams of analyte per gram of precipitate for the following conversions:

Analyte	*Precipitate*
P	Ag_3PO_4
K_2HPO_4	Ag_3PO_4
Bi_2S_3	$BaSO_4$

Solution

$$\text{g P/g } Ag_3PO_4 = \frac{\text{at wt P (g/mol)}}{\text{g wt } Ag_3PO_4 \text{ (g/mol)}} = \frac{1}{1} \text{ (mol P/mol } Ag_3PO_4)$$

$$= \frac{30.97 \text{ (g P/mol)}}{418.58 \text{ (g } Ag_3PO_4\text{/mol)}} \times \frac{1}{1} = 0.07399 \text{ g P/g } Ag_3PO_4 = GF$$

$$\text{g } K_2HPO_4\text{/g } Ag_3PO_4 = \frac{\text{f wt } K_2HPO_4 \text{ (g/mol)}}{\text{f wt } Ag_3PO_4 \text{ (g/mol)}} \times \frac{1}{1} \text{ (mol } K_2HPO_4\text{/mol } Ag_3PO_4)$$

$$= \frac{174.18 \text{ (g } K_2HPO_4\text{/mol)}}{418.58 \text{ (g } Ag_3PO_4\text{/mol)}} \times \frac{1}{1} = 0.41612 \text{ g } K_2HPO_4\text{/g } Ag_3PO_4$$

$$= GF$$

$$\text{g } Bi_2S_3\text{/g } BaSO_4 = \frac{\text{f wt } Bi_2S_3 \text{ (g/mol)}}{\text{f wt } BaSO_4 \text{ (g/mol)}} \times \frac{1}{3} \text{ (mol } Bi_2S_3\text{/mol } BaSO_4)$$

$$= \frac{514.15 \text{ (g } Bi_2S_3\text{/mol)}}{233.40 \text{ (g } BaSO_4\text{/mol)}} \times \frac{1}{3} = 0.73429 \text{ g } Bi_2S_3\text{/g } BaSO_4$$

$$= GF$$

In gravimetric analysis, we are generally interested in the percent composition by weight of the analyte in the sample, that is:

$$\% \text{ substance sought} = \frac{\text{weight of substance sought (g)}}{\text{weight of sample (g)}} \times 100\%$$

We obtain the weight of substance sought from the weight of the precipitate and the corresponding weight/mole relationship.

$$\text{Weight of substance sought (g)} = \text{weight of precipitate (g)} \times \frac{\text{f wt substance sought (g/mol)}}{\text{f wt precipitate (g/mol)}} \times \frac{a}{b} \text{ (mol substance sought/mol precipitate)}$$

$$= \text{weight of precipitate (g)} \times \text{GF (g sought/g precipitate)}$$

Calculations are usually made on a percentage basis:

$$\% \text{ A} = \frac{g_A}{g_{sample}} \times 100\%$$

Where g_A represents the grams of analyte (the desired test substance) and g sample represents the grams of sample taken for analysis. We can write a general formula for calculating the percentage composition of the substance sought:

$$\% \text{ sought} = \frac{\text{weight of precipitate (g)} \times \text{GF (g sought/g precipitate)}}{\text{weight of sample (g)}} \times 100\%$$

Wien we compare this approach with the gravimetric factor calculation, we see that the setups are really identical. However, this approach better shows which units cancel and which remain.

Orthophosphate (PO_4^{3-}) is determined by weighing as ammonium phosphomolybdate, $(NH_4)PO_4 \cdot 12MoO_3$. Calculate the percent P in the sample and the percent P_2O_5 if 1.1682 g precipitate (ppt) were obtained from a 0.2711-g sample. Perform the % P calculation using the gravimetric factor and just using dimensional analysis.

Solution

$$\%\ P = \frac{1.1682\ g\ ppt \times \frac{P}{(NH_4)_3PO_4 \cdot 12MoO_3}\ (g\ P/g\ ppt)}{0.2711\ g\ sample} \times 100\%$$

$$= \frac{1.1682\ g \times (30.97/1876.5)}{0.2711\ g} \times 100\% = 7.111\%$$

$$\%\ P_2O_5 = \frac{1.1682\ g\ ppt \times \frac{P_2O_5}{2(NH_4)_3PO_4 \cdot 12MoO_3}\ (g\ P_2O_5/g\ ppt)}{0.2711\ g\ sample} \times 100\%$$

$$= \frac{1.1682\ g \times [141.95/(2 \times 1876.5)]}{0.2711\ g} \times 100\%$$

$$= 16.30\%$$

Let's do the same calculation using dimensional analysis for the % P setup.

$$\%\ P = \frac{1.982\ g\ \cancel{(NH_4)_2PO_4 \cdot MoO_4} \times (30.97/1867.5)g\ P/g\ \cancel{(NH_4)_2PO_4 \cdot 12MoO_4}}{0.2771\ g\ sample} \times 100\%$$

$$= (7.111\ g\ P/g\ sample) \times 100\% = 7.111\%\ P$$

Note that the $(NH_4)_2PO_4 \cdot MoO_4$ species cancel one another (dimensional analysis), leaving only g ·P in the numerator.

An ore is analyzed for the manganese content by converting the manganese to Mn_3O_4 and weighing it. If a 1.52-g sample yields Mn_3O_4 weighing 0.126 g, what would be the percent Mn_2O_3 in the sample? The percent Mn?

Solution

$$\%\ Mn_2O_3 = \frac{0.126\ g\ Mn_3O_4 \times \frac{3Mn_2O_3}{2Mn_3O_4}\ (g\ Mn_2O_3/g\ Mn_3O_4)}{1.52\ g\ sample} \times 100\%$$

$$= \frac{0.126\ g \times [3(157.9)/2(228.8)]}{1.52\ g} \times 100\% = 8.58\%$$

$$\%\ Mn = \frac{0.126\ g\ Mn_3O_4 \times \frac{3Mn}{Mn_3O_4}(g\ Mn/g\ Mn_3O_4)}{1.52\ g\ sample} \times 100\%$$

$$= \frac{0.126\ g \times [3(54.94)/228.8]}{1.52\ g} \times 100\% = 5.97\%$$

What weight of pyrite ore (impure FeS_2) must be taken for analysis so that the $BaSO_4$ precipitate weight obtained will be equal to one-half that of the percent S in the sample?

Solution

If we have A% of S, then we will obtain $\frac{1}{2}$A g of $BaSO_4$. Therefore,

$$A\%\ S = \frac{\frac{1}{2}A(\text{g } BaSO_4) \times \frac{S}{BaSO_4}(\text{g S/g } BaSO_4)}{\text{g sample}} \times 100\%$$

or

$$1\%\ S = \frac{\frac{1}{2} \times \frac{32.064}{233.40}}{\text{g sample}} \times 100\%$$

$$\text{g sample} = 6.869\ \text{g}$$

The calcium in a 200.0-mL sample of a natural water was determined by precipitating the cation as CaC_2O_4. The precipitate was filtered, washed, and ignited in a crucible with an empty mass of 26.6002 g. The mass of the crucible plus CaO (56.077 g/mol) was 26.7134 g. Calculate the concentration of Ca (40.078 g/mol) in water in units of grams per 100 mL of the water.

The mass of CaO is

$$26.7134\ \text{g} - 26.6002\ \text{g} = 0.1132\ \text{g}$$

The number of moles Ca in the sample is equal to the number of moles CaO or

$$\text{amount of Ca} = 0.1132\ \text{g CaO} \times \frac{1\ \text{mol CaO}}{56.077\ \text{g CaO}} \times \frac{1\ \text{mol Ca}}{\text{mol CaO}}$$
$$= 2.0186 \times 10^{-3}\ \text{mol Ca}$$

$$\text{conc. Ca} = \frac{2.0186 \times 10^{-3}\ \text{mol Ca} \times 40.078\ \text{g Ca/mol Ca}}{200\ \text{mL sample}} \times 100\ \text{mL}$$
$$= 0.04045\ \text{g}/100\ \text{mL}$$

An iron ore was analyzed by dissolving a 1.1324-g sample in concentrated HCl. The resulting solution was diluted with water, and the iron(III) was precipitated as the hydrous oxide $Fe_2O_3 \cdot xH_2O$ by the addition of NH_3. After filtration and washing, the residue was ignited at a high temperature to give 0.5394 g of pure Fe_2O_3 (159.69 g/mol). Calculate (a) the % Fe (55.847 g/mol) and (b) the % Fe_3O_4 (231.54 g/mol) in the sample.

For both parts of this problem, we need to calculate the number of moles of Fe_2O_3. Thus,

$$\text{amount } Fe_2O_3 = 0.5394\ \text{g } Fe_2O_3 \times \frac{1\ \text{mol } Fe_2O_3}{159.69\ \text{g } Fe_2O_3}$$
$$= 3.3778 \times 10^{-3}\ \text{mol } Fe_2O_3$$

(a) The number of moles of Fe is twice the number of moles of Fe_2O_3, and

$$\text{mass Fe} = 3.3778 \times 10^{-3}\ \text{mol } Fe_2O_3 \times \frac{2\ \text{mol Fe}}{\text{mol } Fe_2O_3} \times 55.847\ \frac{\text{g Fe}}{\text{mol Fe}}$$

$$= 0.37728\ \text{g Fe}$$

$$\%\ \text{Fe} = \frac{0.37728\ \text{g Fe}}{1.1324\ \text{g sample}} \times 100\% = 33.32\%$$

(b) As shown by the following balanced equation, 3 mol of Fe_2O_3 are chemically equivalent to 2 mol of Fe_3O_4. That is,

$$3Fe_2O_3 \rightarrow 2Fe_3O_4 + \frac{1}{2}O_2$$

$$\text{mass } Fe_3O_4 = 3.3778 \times 10^{-3}\ \text{mol } Fe_2O_3 \times \frac{2\ \text{mol } Fe_3O_4}{3\ \text{mol } Fe_2O_3} \times \frac{231.54\ \text{g } Fe_3O_4}{\text{mol } Fe_3O_4}$$

$$= 0.52140\ \text{g } Fe_3O_4$$

$$\%\ Fe_3O_4 = \frac{0.5140\ \text{g } Fe_3O_4}{1.1324\ \text{g sample}} \times 100\% = 46.04\%$$

Applications of gravimetric methods:

Gravimetric methods have been developed for most inorganic anions and cations, as well as for such neutral species as water, sulfur dioxide, carbon dioxide, and iodine. A variety of organic substances can also be easily determined gravimetrically. Examples include lactose in milk products, salicylates in drug preparations, phenolphthalein in laxatives, nicotine in pesticides, cholesterol in cereals, and benzaldehyde in almond extracts. Indeed, gravimetric methods are among the most widely applicable of all analytical procedures.

Quantitative Applications

Although no longer a commonly used technique, precipitation gravimetry still provides a reliable means for assessing the accuracy of other methods of analysis, or for verifying the composition of standard reference materials. In this section we review the general application of precipitation gravimetry to the analysis of inorganic and organic compounds.

Inorganic analysis:

The majority of inorganic precipitants show poor selectivity for the analyte. Many organic precipitants, however, are selective for one or two inorganic ions.

Inorganic Precipitating Agents:

Table lists common inorganic precipitating agents.

Analyte	Precipitant	Precipitate Formed	Precipitate Weighed
Ba^{2+}	$(NH_4)_2CrO_4$	$BaCrO_4$	$BaCrO_4$
Pb^{2+}	K_2CrO_4	$PbCrO_4$	$PbCrO_4$
Ag^+	HCl	AgCl	AgCl
Hg_2^{2+}	HCl	Hg_2Cl_2	Hg_2Cl_2
Al^{3+}	NH_3	$Al(OH)_3$	Al_2O_3
Be^{2+}	NH_3	$Be(OH)_2$	BeO
Fe^{3+}	NH_3	$Fe(OH)_3$	Fe_2O_3
Ca^{2+}	$(NH_4)_2C_2O_4$	CaC_2O_4	$CaCO_3$ or CaO
Sb^{3+}	H_2S	Sb_2S_3	Sb_2S_3
As^{3+}	H_2S	As_2S_3	As_2S_3
Hg^{2+}	H_2S	HgS	HgS
Ba^{2+}	H_2SO_4	$BaSO_4$	$BaSO_4$
Pb^{2+}	H_2SO_4	$PbSO_4$	$PbSO_4$
Sr^{2+}	H_2SO_4	$SrSO_4$	$SrSO_4$
Be^{3+}	$(NH_4)_2HPO_4$	NH_4BePO_4	$Be_2P_2O_7$
Mg^{2+}	$(NH_4)_2HPO_4$	NH_4MgPO_4	$Mg_2P_2O_7$
Zn^{2+}	$(NH_4)_2HPO_4$	NH_4ZnPO_4	$Zn_2P_2O_7$
Sr^{2+}	KH_2PO_4	$SrHPO_4$	$Sr_2P_2O_7$
CN^-	$AgNO_3$	AgCN	AgCN
I^-	$AgNO_3$	AgI	AgI
Br^-	$AgNO_3$	AgBr	AgBr
Cl^-	$AgNO_3$	AgCl	AgCl
ClO_3^-	$FeSO_4/AgNO_3$	AgCl	AgCl
SCN^-	$SO_2/CuSO_4$	CuSCN	CuSCN
SO_4^{2-}	$BaCl_2$	$BaSO_4$	$BaSO_4$

Precipitating Agent	Element Precipitated*
$NH_3(aq)$	**Be** (BeO), **Al** (Al_2O_3), **Sc** (Sc_2O_3), Cr (Cr_2O_3)†, **Fe** (Fe_2O_3), Ga (Ga_2O_3), Zr (ZrO_2), **In** (In_2O_3), Sn (SnO_2), U (U_3O_8)
H_2S	Cu (CuO)†, **Zn** (ZnO, or $ZnSO_4$), **Ge** (GeO_2), As (As_2O_3, or As_2O_5), Mo (MoO_3), Sn (SnO_2)†, Sb (Sb_2O_3), or Sb_2O_5), Bi (Bi_2S_3)
$(NH_4)_2S$	Hg (HgS), Co (Co_3O_4)
$(NH_4)_2HPO_4$	**Mg** ($Mg_2P_2O_7$), Al ($AlPO_4$), Mn ($Mn_2P_2O_7$), Zn ($Zn_2P_2O_7$), Zr ($Zr_2P_2O_7$), Cd ($Cd_2P_2O_7$), Bi ($BiPO_4$)
H_2SO_4	Li, Mn, **Sr, Cd, Pb, Ba** (all as sulfates)
H_2PtCl_6	K (K_2PtCl_6, or Pt), Rb (Rb_2PtCl_6), Cs (Cs_2PtCl_6)
$H_2C_2O_4$	Ca (CaO), Sr (SrO), **Th** (ThO_2)
$(NH_4)_2MoO_4$	Cd ($CdMoO_4$)†, Pb ($PbMoO_4$)
HCl	**Ag** (AgCl), Hg (Hg_2Cl_2), Na (as NaCl from butyl alcohol), **Si** (SiO_2)
$AgNO_3$	**Cl** (AgCl), Br (AgBr), I(AgI)
$(NH_4)_2CO_3$	**Bi** (Bi_2O_3)
NH_4SCN	Cu [$Cu_2(SCN)_2$]
$NaHCO_3$	Ru, Os, Ir (precipitated as hydrous oxides; reduced with H_2 to metallic state)
HNO_3	Sn (SnO_2)
H_5IO_6	Hg [$Hg_5(IO_6)_2$]
NaCl, $Pb(NO_3)_2$	F (PbClF)
$BaCl_2$	SO_4^{2-} ($BaSO_4$)
$MgCl_2$, NH_4Cl	PO_4^{3-} ($Mg_2P_2O_7$)

Reducing Agents:

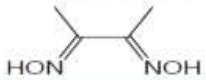
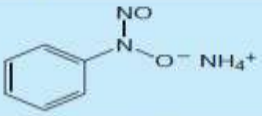
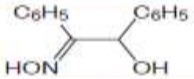
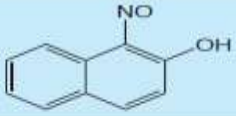
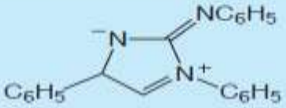
Table lists several reagents that convert an analyte to its elemental form for weighing.

Some Reducing Agents Employed in Gravimetric Methods

Reducing Agent	Analyte
SO_2	Se, Au
$SO_2 + H_2NOH$	Te
H_2NOH	Se
$H_2C_2O_4$	Au
H_2	Re, Ir
HCOOH	Pt
$NaNO_2$	Au
$SnCl_2$	Hg
Electrolytic reduction	Co, Ni, Cu, Zn Ag, In, Sn, Sb, Cd, Re, Bi

Organic Precipitating Agents:

Numerous organic reagents have been developed for the gravimetric determination of inorganic species. Separation of one or more metal ions from mixture may be made with the aid of organic reagents, with which they yield sparingly soluble and often coloured compounds. Some of these reagents are significantly more selective in their reactions than are most of the inorganic reagents. We encounter two types of organic reagents. One forms slightly soluble nonionic products called **coordination compounds;** the other forms products in which the bonding between the inorganic species and the reagent is **largely ionic**. Organic reagents that yield sparingly soluble coordination compounds typically contain at least two functional groups. Each of these groups is capable of bonding with a cation by donating a pair of electrons. The functional groups are located in the molecule such that a five- or six-membered ring results from the reaction. Reagents that form compounds of this type are called **chelating agents** and their products are called chelates.

Analyte	Precipitant	Structure	Precipitate Formed	Precipitate Weighed
Ni^{2+}	dimethylglyoxime		$Ni(C_4H_7O_2N_2)_2$	$Ni(C_4H_7O_2N_2)_2$
Fe^{3+}	cupferron		$Fe(C_6H_5N_2O_2)_3$	Fe_2O_3
Cu^{2+}	cupron		$CuC_{14}H_{11}O_2N$	$CuC_{14}H_{11}O_2N$
Co^{2+}	1-nitrso-2-napthol		$Co(C_{10}H_6O_2N)_3$	Co or $CoSO_4$
K^+	sodium tetraphenylborate	$Na[B(C_6H_5)_4]$	$K[B(C_6H_5)_4$	$K[B(C_6H_5)_4$
NO_3^-	nitron		$C_{20}H_{16}N_4HNO_3$	$C_{20}H_{16}N_4H$-NO_3

The most advantages of these compounds are:

1 – These compounds usually have high relative molecular masses, so the small amount of ions will yield a relatively large amount of the precipitate.

2 – The organic precipitants are specific, should give precipitate with only one ion, or can make it specific by masking or solution conditioning (pH, concentration of reagent).

3 – The precipitate can be drying easily, and bellow 100°C.

4 – The precipitate can be weighed after drying at suitable temperature.

5 – These compounds are nonionic, and do not adsorb impurities (minimized co – precipitation).

6 – The precipitate is easily soluble in organic solvents.

Disadvantages:

1 – These compounds are volatile; therefore the drying of precipitate should be drying below 130°C.

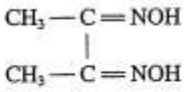
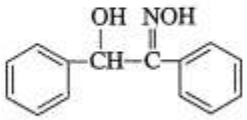
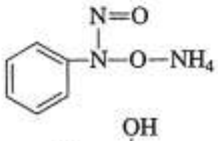
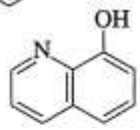
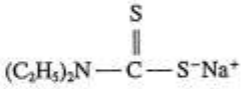
2 – Impurities in reagents, it is difficult to prepare organic reagent of the same degree of purity of inorganic compounds.

3 – Low solubility of the reagents in water.

4 – The precipitate will be viscous, so; it adhesive on equipment wall.

5 – The very high molecular weight of chelate complexes formed with metal ions reduce, proportionately, small errors in precipitation and weighing.

Some Organic Precipitating Agents

Reagent	Structure	Metals Precipitated
Dimethylglyoxime		Ni(II) in NH_3 or buffered HOAc; Pd(II) in HCl ($M^{2+} + 2HR \rightarrow \underline{MR_2} + 2H^+$)
α-Benzoinozime (cupron)		Cu(II) in NH_3 and tartrate; Mo(VI) and W(VI) in H^+ ($M^{2+} + H_2R \rightarrow \underline{MR} + 2H^+$; $M^{2+} = Cu^{2+}$, MoO_2^{+}, WO_2^{2+}) Metal oxide weighed
Ammonium nitrosophenylhydroxylamine (cupferron)		Fe(III), V(V), Ti(IV), Zr(IV), Sn(IV), U(IV) ($M^{n+} + nNH_4R \rightarrow \underline{MR_n} + nNH_4^+$) Metal oxide weighed
8-Hydroxyquinoline (oxine)		Many metals. Useful for Al(III) and Mg(II) ($M^{n+} + nHR \rightarrow \underline{MR_n} + nH^+$)
Sodium diethyldithiocarbamate		Many metals from acid solution ($M^{n+} + n\text{NaR} \rightarrow \underline{MRn} + n\text{Na}^+$)
Sodium tetraphenylboron	$NaB(C_6H_5)_4$	K^+, Rb^+, Cs^+, Tl^+, Ag^+, Hg(I), Cu(I), NH_4^+, RNH_3^+, $R_2NH_2^+$, R_3NH^+, R_4N^+. Acidic solution ($M^+ + \text{NaR} \rightarrow \underline{MR} + \text{Na}^+$)
Tetraphenylarsonium chloride	$(C_6H_5)_4AsCl$	$Cr_2O_7^{2-}$, MnO_4^-, ReO_4^-, MoO_4^{2-}, WO_4^{2-}, ClO_4^-, I_3^-. Acidic solution ($A^{n-} + n\text{RCl} \rightarrow R_nA + n\text{Cl}^-$)

Organic Functional Group Analysis:

Several reagents react selectively with certain organic functional groups and thus can be used for the determination of most compounds containing these groups. A list of gravimetric functional group reagents is given in Table. Many of the reactions shown can also be used for volumetric and Spectrophotometric determinations.

Gravimetric Methods for Organic Functional Groups

Functional Group	Basis for Method	Reaction and Product Weighed*
Carbonyl	Mass of precipitate with 2,4-dinitrophenylhydrazine	$RCHO + H_2NNHC_6H_3(NO_2)_2 \rightarrow$ $R{-}CH = NNHC_6H_3(NO_2)_2(s) + H_2O$ (RCOR' reacts similarly)
Aromatic carbonyl	Mass of CO_2 formed at 230°C in quinoline; CO_2 distilled, absorbed, and weighed	$ArCHO \xrightarrow[CuCO_3]{230^\circ C} Ar + CO_2(g)$
Methoxyl and ethoxyl	Mass of AgI formed after distillation and decomposition of CH_3I or C_2H_5I	$ROCH_3 + HI \rightarrow ROH + CH_3I$; $RCOOCH_3 + HI \rightarrow RCOOH + CH_3I$; $ROC_2H_5 + HI \rightarrow ROH + C_2H_5I$ } $CH_3I + Ag^+ + H_2O \rightarrow AgI(s) + CH_3OH$
Aromatic nitro	Mass loss of Sn	$RNO_2 + \frac{3}{2}Sn(s) + 6H^+ \rightarrow RNH_2 + \frac{3}{2}Sn^{4+} + 2H_2O$
Azo	Mass loss of Cu	$RN = NR' + 2Cu(s) + 4H^+ \rightarrow RNH_2 + R'NH_2 + 2Cu^{2+}$
Phosphate	Mass of Ba salt	$ROP(OH)_2 + Ba^{2+} \rightarrow ROPO_2Ba(s) + 2H^+$
Sulfamic acid	Mass of $BaSO_4$ after oxidation with HNO_2	$RNHSO_3H + HNO_2 + Ba^{2+} \rightarrow ROH + BaSO_4(s) + N_2 + 2H^+$
Sulfinic acid	Mass of Fe_2O_3 after ignition of Fe(III) sulfinate	$3ROSOH + Fe^{3+} \rightarrow (ROSO)_3Fe(s) + 3H^+$; $(ROSO)_3Fe \xrightarrow{O_2} CO_2 + H_2O + SO_2 + Fe_2O_3(s)$

Analyte	Treatment	Precipitant	Precipitate
Organic halides R–X X = Cl, Br, I	Oxidation with HNO_3 in the presence of Ag^+	$AgNO_3$	AgX
Organic halides R–X X = Cl, Br, I	Combustion in O_2 (with a Pt catalyst) in the presence of Ag^+	$AgNO_3$	AgX
Organic sulfur	Oxidation with HNO_3 in the presence of Ba^{2+}	$BaCl_2$	$BaSO_4$
Organic sulfur	Combustion in O_2 (with Pt catalyst) with SO_2 and SO_3 collected in dilute H_2O_2	$BaCl_2$	$BaSO_4$
Alkoxy groups –O–R or –COO–R R = CH_3 or C_2H_5	Reaction with HI to produce RI	$AgNO_3$	AgI

The conditioning of precipitation:

1 – Precipitation should be carried out in dilute solution, due regard being paid to the solubility of the precipitate, the time required for filtration, and the subsequent operations to be carried out with the filtrate. This will minimize the errors due to co – precipitation.

2 – The reagent should be mixed slowly and with constant stirring. This will keep the degree of supersaturation small and will assist the growth of large crystals, a slight excess of the reagent is generally required.

3 – Precipitation may be affected under conditions which increase the solubility of the precipitate, thus reducing the degree of supersaturation.

4 – Precipitation is affected in hot solutions, provided the solubility and the stability of precipitate permit. At the high temperature:

- The solubility is increased with a consequent reduction in the degree of the supersaturation.
- Coagulation is assisted and sol formation decreased.
- The velocity of crystallization is increased, thus leading to better – formed crystals.

5 – Crystalline precipitate should be digested for as long as practical, preferably overnight, except in those cases where post – precipitation may occur. Digestion decreases the effect of co – precipitation and gives more readily filterable precipitate.
6 – The precipitate should be washed with appropriate dilute solution of an electrolyte.
7 – If the precipitate is still appreciably contaminated, the error may be often reduced by dissolving in a suitable solvent and then re – precipitating it.

Volatilization Gravimetry:

The two most common gravimetric methods based on volatilization are those for determining water and carbon dioxide.

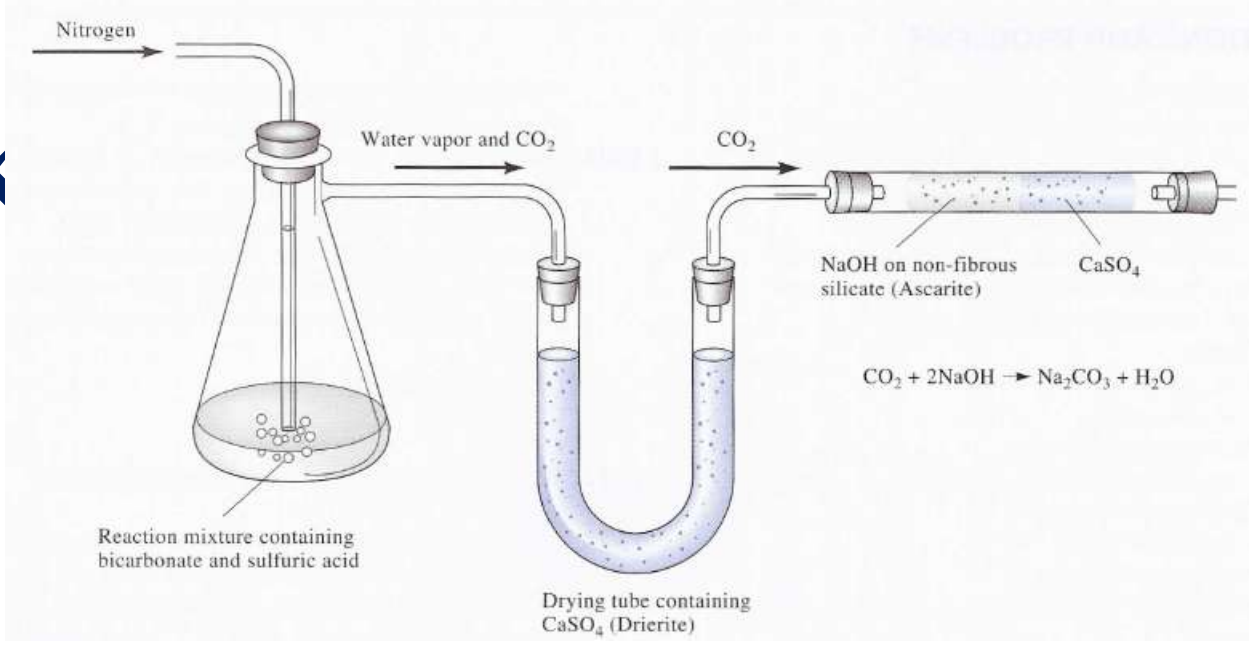
Water is quantitatively distilled from many materials by heating. In direct determination, water vapor is collected on any of several solid desiccants, and its mass is determined from the mass gain of the desiccant. The indirect method, in which the amount of water is determined by the loss of mass of the sample during heating, is less satisfactory because it must be assumed that water is the only component volatilized. An example of a gravimetric procedure involving volatilization of carbon dioxide is the determination of the sodium hydrogen carbonate content of antacid tablets. Here, a weighed sample of the finely ground tablets are treated with dilute sulfuric acid to convert the sodium hydrogen carbonate to carbon dioxide:

$$NaHCO_3(aq) + H_2SO_4(aq) \rightarrow CO_2(g) + H_2O(l) + NaHSO_4(aq)$$

Sodium hydroxide absorb carbon dioxide by the reaction:

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

The absorption tube must also contain a desiccant to prevent loss of the water produced by the reaction. Sulfides and sulfites can also be determined by volatilization. Hydrogen sulfide or sulfur dioxide evolved from the sample after treatment with acid is collected in a suitable absorbent. Finally, the classical method for the determination of carbon and hydrogen in organic compounds is a gravimetric volatilization procedure in which the combustion products (H_2O and CO_2) are collected selectively on weighed absorbents.



INORGANIC ANALYSIS

Determining the inorganic ash content of an organic material, such as a polymer, is an example of a direct volatilization gravimetric analysis. After weighing the sample, it is placed in an appropriate crucible and the organic material carefully removed by combustion, leaving behind the inorganic ash. The crucible containing the residue is heated to a constant weight using either a burner or an oven before determining the mass of the inorganic ash.

Another example of volatilization gravimetry is the determination of dissolved solids in natural waters and wastewaters. In this method, a sample of water is transferred to a weighing dish and dried to a constant weight at either 103–105 ^{o}C or at 180 ^{o}C. Samples dried at the lower temperature retain some occluded water and lose some carbonate as CO_2. The loss of organic material, however, is minimal. At the higher temperature, the residue is free from occluded water, but the loss of carbonate is greater. In addition, some chloride, nitrate, and organic material is lost through thermal decomposition. In either case, the residue that remains after drying to a constant weight at 500 ^{o}C is the amount of fixed solids in the sample, and the loss in mass provides an indirect measure of the sample's volatile solids. Indirect analyses based on the weight of residue remaining after volatilization are commonly used in determining moisture in a variety of products, and in determining silica in waters, wastewaters, and rocks. Moisture is determined by drying a preweighed sample with an infrared lamp or a low temperature oven. The difference between the original weight and the weight after drying equals the mass of water lost.

ORGANIC ANALYSIS

The most important application of volatilization gravimetry is for the elemental analysis of organic materials. During combustion with pure O_2, many elements, such as carbon and hydrogen, are released as gaseous combustion products, such as CO_2 *(g)* and H_2O*(g)*. Passing the combustion products through preweighed tubes containing selective absorbents and measuring the increases in mass provides a direct analysis for the mass of carbon and hydrogen in the organic material.

Alkaline metals and earths in organic materials can be determined by adding H_2SO_4 to the sample before combustion. After combustion is complete, the metal remains behind as a solid residue of metal sulfate. Silver, gold, and platinum can be determined by burning the organic sample, leaving a metallic residue of Ag, Au, or Pt. Other metals are determined by adding HNO_3 before combustion, leaving a residue of the metal oxide.

Examples of gravimetric analysis:

Some of the most precise and also accurate analyses are gravimetric analyses. There are many examples, and you should be familiar with some of the more common ones. These are summarized in Table, which lists the substance sought, the precipitate formed, the form in which it is weighed, and the common elements that will interfere and must be absent. You should consult more advanced texts and comprehensive analytical reference books for details on these and other determinations.

Some Commonly Employed Gravimetric Analyses

Substance Analyzed	Precipitate Formed	Precipitate Weighed	Interferences
Fe	$Fe(OH)_3$	Fe_2O_3	Many. Al, Ti, Cr, etc.
	Fe cupferrate	Fe_2O_3	Tetravalent metals
Al	$Al(OH)_3$	Al_2O_3	Many. Fe, Ti, Cr, etc.
	$Al(ox)_3$[a]	$Al(ox)_3$	Many. Mg does not interfere in acidic solution
Ca	CaC_2O_4	$CaCO_3$ or CaO	All metals except alkalis and Mg
Mg	$MgNH_4PO_4$	$Mg_2P_2O_7$	All metals except alkalis
Zn	$ZnNH_4PO_4$	$Zn_2P_2O_7$	All metals except Mg
Ba	$BaCrO_4$	$BaCrO_4$	Pb
SO_4^{2-}	$BaSO_4$	$BaSO_4$	NO_3^-, PO_4^{3-}, ClO_3^-
Cl^-	AgCl	AgCl	Br^-, I^-, SCN^-, CN^-, S^{2-}, $S_2O_3^{2-}$
Ag	AgCl	AgCl	Hg(I)
PO_4^{3-}	$MgNH_4PO_4$	$Mg_2P_2O_7$	MoO_4^{2-}, $C_2O_4^{2-}$, K^+
Ni	$Ni(dmg)_2$[b]	$Ni(dmg)_2$	Pd

[a]ox = Oxine (8-hydroxyquinoline) with 1 H^+ removed.
[b]dmg = Dimethylglyoxime with 1 H^+ removed.

Precipitation Equilibria:

Solubility:

The analytical composition of a saturated solution, expressed in terms of the proportion of a designated solute in a designated solvent, is the solubility of that solute. The solubility may be expressed as a concentration, molality, mole fraction, mass fraction, mole ratio, etc.

Solubility Product:

When substances have limited solubility and their solubility is exceeded, the ions of the dissolved portion exist in equilibrium with the solid material. So called insoluble compounds generally exhibit this property.

When a compound is referred to as insoluble, it is actually not completely insoluble but is **slightly soluble**. For example, if solid AgCl is added to water, a small portion of it will dissolve:

$$AgCl \rightleftharpoons (AgCl)_{aq} \rightleftharpoons Ag^+ + Cl^-$$

The precipitate will have a definite solubility (i.e., a definite amount that will dissolve) in g/L, or mol/ L, at a given temperature (a saturated solution). A small amount of undissociated compound usually exists in equilibrium in the aqueous phase (eg., on the order of 0.1%), and its concentration is constant. It is difficult to measure the undissociated molecule, and we are interested in the ionized form as a measure of a compound's solubility and chemical availability. Hence, we can generally neglect the presence of any undissociated species.

We can write an overall equilibrium constant for the above stepwise equilibrium, called the **solubility product** K_{SP} $(AgCl)_{aq}$ cancels when the two stepwise equilibrium constants are multiplied together. $\boldsymbol{K_{SP} = [Ag^+][Cl^-]}$.

The "concentration" of any solid such as AgCl is constant and is combined in the equilibrium constant to give K_{SP}. The above relationship holds regardless of the presence of any undissociated intermediate; that is, the concentrations of free ions, and we will take these as a measure of a compound's solubility. From a knowledge of the

value of the solubility product at a specified temperature, we can calculate the equilibrium solubility of the com- pounds. (The solubility product is determined in the reverse order, by measuring the solubility.) The amount of a slightly soluble salt that dissolves does not depend on the amount of the solid in equilibrium with the solution, so long as there is enough to saturate the solution. Instead, the amount that dissolves depends on the volume of the solvent. A non symmetric salt such as Ag_2CrO_4 would have a K_{sp} as follows:

$$Ag_2CrO_4 \rightleftharpoons 2\ Ag^+ + CrO_4^{2-}$$

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

Such electrolytes do not dissolve or dissociate in steps because they are really strong electrolytes. That portion that dissolves ionizes completely. Therefore, we do not have stepwise K_{sp} values. As with any equilibrium constant, the K_{sp} product holds under all equilibrium conditions at the specified temperature. Since we are dealing with heterogeneous equilibria, the equilibrium state will be achieved more slowly than with homogeneous solution equdibria.

The K_{sp} of AgCl at 25°C is 1.0×10^{-10}. Calculate the concentrations of Ag^+ and Cl^- in a saturated solution of AgCl, and the molar solubility of AgCl.

Solution

When AgCl ionizes, equal amounts of Ag^+ and Cl^- are formed; $AgCl \rightleftharpoons Ag^+ + Cl^-$ and $K_{sp} = [Ag^+][Cl^-]$. Let s represent the molar solubility of AgCl. Since each mole of AgCl that dissolves gives one mole of either Ag^+ or Cl^-, then

$$[Ag^+] = [Cl^-] = s$$
$$s^2 = 1.0 \times 10^{-10}$$
$$s = 1.0 \times 10^{-5}\ M$$

The solubility of AgCl is $1.0 \times 10^{-5}\ M$.

Factors that affect solubility and rate of solution:

The **solubility** of a solute is: the maximum amount of solute that can dissolve in a certain amount of solvent or solution at a certain temperature.

Nature of the solute and solvent:

The amount of solute that dissolves depends on what type of solute it is. While only 1 gram of lead (II) chloride can be dissolved in 100 grams of water at room temperature, 200 grams of zinc chloride can be dissolved. This means that a greater amount of zinc chloride can be dissolved in the same amount of water than lead (II) chloride.

Temperature:

Generally, an increase in the temperature of the solution increases the solubility of a solid solute. For example, a greater amount of sugar will dissolve in warm water than in cold water. A few solid solutes, however, are less soluble in warmer solutions. For all gases, solubility decreases as the temperature of the solution rises. An example of this is Soda. The solubility of the carbon dioxide gas decreases when a soda is warm, making the soda flat.

Pressure:

For solid and liquid solutes, changes in pressure have practically no effect on solubility. For gaseous solutes, an increase in pressure increases solubility and a decrease in pressure decreases solubility. Example: When the cap on a bottle of soda pop is removed, pressure is released, and the gaseous solute bubbles out of solution.

The rate of solution is: a measure of how fast a substance dissolves.

Size of the particles:

When a solute dissolves, the action takes place only at the surface of each particle. When the total surface area of the solute particles is increased, the solute dissolves more rapidly. Breaking a solute into smaller pieces increases its surface area and increases its rate of solution.

Stirring:

With liquid and solid solutes, stirring brings fresh portions of the solvent in contact with the solute. Stirring, therefore, allows the solute to dissolve faster.

Amount of solute already dissolved:

When you have very little solute in the solution, dissolving takes place quickly.When you have a lot of solute in the solution, dissolving takes place more slowly.

Temperature:

For liquids and solid solutes, increasing the temperature not only increases the amount of solute that will dissolve but also increases the rate at which the solute will dissolve. For gases, the reverse is true. An increase in temperature decreases both solubility and rate of solution.

Le Châtelier's Principle;

(When stressed, a system that was at equilibrium returns to its equilibrium state by reacting in a manner that relieves the stress).

The equilibrium position for any reaction is defined by a fixed equilibrium constant, not by a fixed combination of concentrations for the reactants and products. This is easily appreciated by examining the equilibrium constant expression for the dissociation of acetic acid.

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.75 \times 10^{-5}$$

At constant temperature, different solutions of acetic acid may have different values for $[H_3O^+]$, $[CH_3COO^-]$ and $[CH_3COOH]$, but will always have the same value of K_a. If a solution of acetic acid at equilibrium is disturbed by adding sodium acetate, the $[CH_3COO^-]$ increases, suggesting an apparent increase in the value of K_a. Since K_a must remain constant, however, the concentration of all three species in equation must change in a fashion that restores K_a to its original value. In this case, equilibrium is reestablished by the partial reaction of $CH_3COO–$ and H_3O^+ to produce additional CH_3COOH.

The observation that a system at equilibrium responds to a stress by reequilibrating in a manner that diminishes the stress, is formalized as **Le Châtelier's principle.**

One of the most common stresses that we can apply to a reaction at equilibrium is to change the concentration of a reactant or product. We already have seen, in the case of sodium acetate and acetic acid, that adding a product to a reaction mixture at equilibrium converts a portion of the products to reactants. In this instance, we disturb the equilibrium by adding a product, and the stress is diminished by partially reacting the excess product. Adding acetic acid has the opposite effect, partially converting the excess acetic acid to acetate. In our first example, the stress to the equilibrium was applied directly. It is also possible to apply a concentration stress indirectly. Consider, for example, the following solubility equilibrium involving AgCl.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

The effect on the solubility of AgCl of adding $AgNO_3$ is obvious, but what is the effect of adding a ligand that forms a stable, soluble complex with Ag^+? Ammonia, for example, reacts with Ag^+ as follows

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$$

Adding ammonia decreases the concentration of Ag^+ as the $Ag(NH_3)^{2+}$ complex forms. In turn, decreasing the concentration of Ag^+ increases the solubility of AgCl as reaction reestablishes its equilibrium position. Adding together reactions clarifies the effect of ammonia on the solubility of AgCl, by showing that ammonia is a reactant.

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq)$$

A Simple Problem: Solubility of Pb $(IO_3)_2$ in Water:

When an insoluble compound such as Pb $(IO_3)_2$ is added to a solution a small portion of the solid dissolves. Equilibrium is achieved when the concentrations of Pb^{2+} and IO^{3-} are sufficient to satisfy the solubility product for Pb $(IO_3)_2$. At equilibrium the solution is saturated with Pb $(IO_3)_2$. How can we determine the concentrations of Pb2+ and IO3–, and the solubility of Pb $(IO_3)_2$ in a saturated solution prepared by adding Pb $(IO_3)_2$ to distilled water?

We begin by writing the equilibrium reaction

$$Pb(IO_3)_2(s) \rightleftharpoons Pb^{2+}(aq) + 2IO_3^-(aq)$$

and its equilibrium constant

$$K_{sp} = [Pb^{2+}][IO_3^-]^2 = 2.5 \times 10^{-13}$$

As equilibrium is established, two IO^{3-} ions are produced for each ion of Pb^{2+}. If we assume that the molar concentration of Pb^{2+} at equilibrium is x then the molar concentration of IO^{3-} is $2x$.

Substituting the equilibrium concentrations into equation

$$(x)(2x)^2 = 2.5 \times 10^{-13}$$

$$4x^3 = 2.5 \times 10^{-13}$$

$$x = 3.97 \times 10^{-5}$$

and solving gives

The equilibrium concentrations of Pb^{2+} and IO^{3-}, therefore, are:

$[Pb^{2+}] = x = 4.0 \times 10^{-5}$ M

$[I^-] = 2x = 7.9 \times 10^{-5}$ M

Since one mole of Pb $(IO_3)_2$ contains one mole of Pb^{2+}, the solubility of Pb $(IO_3)_2$ is the same as the concentration of Pb^{2+}; the solubility of Pb $(IO_3)_2$ is 4.0 x10^{-5} M.

A More Complex Problem: The Common Ion Effect:

The **common-ion** effect is a mass-action effect predicted from the **Le Châtelier's principle** and is demonstrated by the following examples:

.

Calculate the molar solubility of $Ba(IO_3)_2$ in a solution that is 0.0200 M in $Ba(NO_3)_2$.

The solubility is no longer equal to $[Ba^{2+}]$ because $Ba(NO_3)_2$ is also a source of barium ions. We know, however, that the solubility is related to $[IO_3^-]$:

$$\text{molar solubility of } Ba(IO_3)_2 = \frac{1}{2}[IO_3^-]$$

There are two sources of barium ions: $Ba(NO_3)_2$ and $Ba(IO_3)_2$. The contribution from the former is 0.0200 M, and that from the latter is equal to the molar solubility, or $\frac{1}{2}[IO_3^-]$. Thus,

$$[Ba^{2+}] = 0.0200 + \frac{1}{2}[IO_3^-]$$

Substitution of these quantities into the solubility-product expression yields

$$\left(0.0200 + \frac{1}{2}[IO_3^-]\right)[IO_3^-]^2 = 1.57 \times 10^{-9}$$

Since the exact solution for $[IO_3^-]$ requires solving a cubic equation, we seek an approximation that simplifies the algebra. The small numerical value of K_{sp} suggests that the solubility of $Ba(IO_3)_2$ is not large, and this is confirmed by the result obtained in Example 9-3. Moreover, barium ion from $Ba(NO_3)_2$ will further repress the limited solubility of $Ba(IO_3)_2$. Thus, it is reasonable to seek a provisional answer to the problem by assuming that 0.0200 is large with respect to $\frac{1}{2}[IO_3^-]$. That is, $\frac{1}{2}[IO_3^-] \ll 0.0200$, and

$$[Ba^{2+}] = 0.0200 + \frac{1}{2}[IO_3^-] \approx 0.0200 \text{ M}$$

The original equation then simplifies to

$$0.0200\,[IO_3^-]^2 = 1.57 \times 10^{-9}$$

$$[IO_3^-] = \sqrt{1.57 \times 10^{-9}/0.0200} = \sqrt{7.85 \times 10^{-8}} = 2.80 \times 10^{-4}\text{ M}$$

The assumption that $(0.0200 + \frac{1}{2} \times 2.80 \times 10^{-4}) \approx 0.0200$ does not appear to cause serious error because the second term, representing the amount of Ba^{2+} arising from the dissociation of $Ba(IO_3)_2$, is only about 0.7% of 0.0200. Ordinarily, we consider an assumption of this type to be satisfactory if the discrepancy is less than 10%.[1] Finally, then,

$$\text{solubility of } Ba(IO_3)_2 = \frac{1}{2}[IO_3^-] = \frac{1}{2} \times 2.80 \times 10^{-4} = 1.40 \times 10^{-4}\text{ M}$$

If we compare this result with the solubility of barium iodate in pure water (Example 9-3), we see that the presence of a small concentration of the common ion has lowered the molar solubility of $Ba(IO_3)_2$ by a factor of about 5.

Calculate the solubility of $Ba(IO_3)_2$ in a solution prepared by mixing 200 mL of 0.0100 M $Ba(NO_3)_2$ with 100 mL of 0.100 M $NaIO_3$.

First establish whether either reactant is present in excess at equilibrium. The amounts taken are

$$\text{no. mmol } Ba^{2+} = 200 \text{ mL} \times 0.0100 \text{ mmol/mL} = 2.00$$

$$\text{no. mmol } IO_3^- = 100 \text{ mL} \times 0.100 \text{ mmol/mL} = 10.0$$

If the formation of $Ba(IO_3)_2$ is complete,

$$\text{no. mmol excess } NaIO_3 = 10.0 - 2 \times 2.00 = 6.00$$

Thus,

$$[IO_3^-] = \frac{6.00 \text{ mmol}}{200 \text{ mL} + 100 \text{ mL}} = \frac{6.00 \text{ mmol}}{300 \text{ mL}} = 0.0200 \text{ M}$$

As in Example 9-3,

$$\text{molar solubility of } Ba(IO_3)_2 = [Ba^{2+}]$$

Here, however,

$$[IO_3^-] = 0.0200 + 2[Ba^{2+}]$$

where $2[Ba^{2+}]$ represents the iodate contributed by the sparingly soluble $Ba(IO_3)_2$. We can obtain a provisional answer after making the assumption that $[IO_3^-] \approx 0.0200$; thus

$$\text{solubility of } Ba(IO_3)_2 = [Ba^{2+}] = \frac{K_{sp}}{[IO_3^-]^2} = \frac{1.57 \times 10^{-9}}{(0.0200)^2}$$

$$= 3.93 \times 10^{-6} \text{ mol/L}$$

Since the provisional answer is nearly four orders of magnitude less than 0.02 M, our approximation is justified, and the solution does not need further refinement.

Solubility depends on the stoichiometry:

Table lists some solubility products along with the corresponding calculated molar solubilities for some slightly soluble salts.

Solubility Product Constants of Selected Slightly Soluble Salts

Salt	K_{sp}	Solubility, s (mol/L)
$PbSO_4$	1.6×10^{-8}	1.3×10^{-4}
AgCl	1.0×10^{-6}	1.0×10^{-5}
AgBr	4×10^{-13}	6×10^{-7}
AgI	1×10^{-16}	1×10^{-8}
$Al(OH)_3$	2×10^{-32}	5×10^{-9}
$Fe(OH)_3$	4×10^{-38}	2×10^{-10}
Ag_2S	2×10^{-49}	4×10^{-17}
HgS	4×10^{-53}	6×10^{-27}

The molar solubility is not necessary directly proportional to the K_{sp} value since it depends on the stoichiometry of the salt. The K_{sp} of AgI is 5 X 10^{15} larger than that of $Al(OH)_3$, but its molar solubility is only twice that of $Al(OH)_3$.

What must be the concentration of added Ag^+ to just start precipitation of AgCl in a 1.0×10^{-3} *M* solution of NaCl?

Solution

$$[Ag^+](1.0 \times 10^{-3}) = 1.0 \times 10^{-10}$$
$$[Ag^+] = 1.0 \times 10^{-7}\ M$$

The concentration of Ag^+ must, therefore, just exceed 10^{-7} *M* to begin precipitation.

What is the solubility of PbI_2, in g/L, if the solubility product is 7.1×10^{-9}?

Solution

The equilibrium is $PbI_2 \rightleftharpoons Pb^{2+} + 2I^-$, and $K_{sp} = [Pb^{2+}][I^-]^2 = 7.1 \times 10^{-9}$. Let *s* represent the molar solubility of PbI_2. Then

$$[Pb^{2+}] = s \quad \text{and} \quad [I^-] = 2s$$
$$(s)(2s)^2 = 7.1 \times 10^{-9}$$
$$s = \sqrt[3]{\frac{7.1 \times 10^{-9}}{4}} = 1.2 \times 10^{-3}\ M$$

Therefore, the solubility, in g/L, is

$$1.2 \times 10^{-3}\ \text{mol/L} \times 461.0\ \text{g/mol} = 0.55\ \text{g/L}$$

Note that the concentration of I^- was *not* doubled before squaring; $2s$ represented its actual equilibrium concentration, not twice its concentration. We could have let *s* represent the concentration of I^-, instead of the molar solubility of PbI_2, in which case $[Pb^{2+}]$ and the solubility of PbI_2 would have been $\frac{1}{2}s$. The calculated *s* would have been twice as great, but the concentrations of each species would have been the same. You try this calculation!

Calculate the molar solubility of $PbSO_4$ and compare it with that of PbI_2.

Solution

$$PbSO_4 \rightleftharpoons Pb^{2+} + SO_4^{2-}$$
$$[Pb^{2+}][SO_4^{2-}] = 1.6 \times 10^{-8}$$
$$(s)(s) = 1.6 \times 10^{-8}$$
$$s = 1.3 \times 10^{-4}\ M$$

Although the K_{sp} of PbI_2 is smaller than that of $PbSO_4$, the solubility of PbI_2 is greater (see Example 10.9), due to the nonsymmetrical nature of the precipitate.

Effect of electrolyte:

For electrolytes of the same valence type, the order of solubility will be the same as the order of the corresponding solubdity products. But when we compare salts of difference valence type, the order may be different. Compound AB will have a smaller molar solubility than compound AC_2 when both have identical K_{sp} values. We take advantage of the common ion effect to decrease the solubility of a precipitate in gravimetric analysis.

Ion effect on solubility; K^o_{sp} and Activity Coefficients:

The presence of diverse salts will generally increase the solubility of precipitates due to the shielding of the dissociated ion species. (Their activity is decreased.) Consider the solubility of AgCl. The thermodynamic solubility product K^o_{sp} is:

$$K^o_{sp} = a_{Ag^+} \cdot a_{Cl^-} = [Ag^+] f_{Ag^+} [Cl^-] f_{Cl^-}$$

$$K^o_{sp} = K_{sp} f_{Ag^+} f_{Cl^-}$$

$$K_{sp} = \frac{K^{\circ}_{sp}}{f_{Ag^+} f_{Cl^-}}$$

The numerical value of K^{o}_{sp} holds at all activities. K_{sp} equals K^{o}_{sp} at zero ionic strength, but at appreciable ionic strengths, a value must be calculated for each ionic strength using Equation. Note that this equation predicts, as we predicted qualitatively, that decreased activity of the ions will result in an increased K_{sp} and, therefore, increased molar solubility.

Calculate the solubility of silver chloride in 0.10 *M* $NaNO_3$.

Solution

The equilibrium constants listed in the Appendix C are for zero ionic strength; that is, they are really thermodynamic equilibrium constants.[1] Therefore, from Table C.3, $K^{\circ}_{sp} = 1.0 \times 10^{-10}$.

We need the activity coefficients of Ag^+ and Cl^-. The ionic strength is 0.10. From Ref. 9 in Chapter 6, we find that $f_{Ag^+} = 0.75$ and $f_{Cl^-} = 0.76$. (You could also have used the values of α_{Ag^+} and α_{Cl^-} in the reference to calculate the activity coefficients using Equation 6.19.) From Equation 10.12

$$K_{sp} = \frac{1.0 \times 10^{-10}}{(0.75)(0.76)} = 1.8 \times 10^{-10} = [Ag^+][Cl^-] = s^2$$

$$s = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5}\ M$$

This is 30% greater than at zero ionic strength ($s = 1.0 \times 10^{-5}\ M$).

The increase in solubility is greater with precipitates containing multiply charged ion. At very high ionic strengths, where activity coefficients may become greater than unity, the solubility is decreased. In gravimetric analysis, a sufficiently large excess of precipitating agent is added so that the solubility is reduced to such small value that we do not need to worry about this effect. Similarly, a complexing agent that reacts with the metal ion of the precipitate will increase the solubility.

Effect of acidity on solubility of precipitate:

Acids frequently affect the solubility of a precipitate. As the H^+ concentration increases, it competes more effectively with the metal ion of interest for the precipitating agent.

What pH is required to just precipitate iron(III) hydroxide form from a 0.10 *M* $FeCl_3$ solution?

$$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$$

$$[Fe^{3+}][OH^-]^3 = 4 \times 10^{-38}$$

$$(0.1)[OH^-]^3 = 4 \times 10^{-38}$$

$$[OH^-] = \sqrt[3]{\frac{4 \times 10^{-38}}{0.1}} = 7 \times 10^{-13}\ M$$

$$pOH = -\log 7 \times 10^{-13} = 12.2$$

$$pH = 14.0 - 12.2 = 1.8$$

The solubility of a precipitate whose anion is derived from a weak acid will increase in the presence of added acid because the acid will tend to combine with the anion and thus remove the anion from solution. For example, the precipitate MA that partially dissolves to give M^+ and A^- ions w ill exhibit the following equilibria:

$$MA \rightleftharpoons M^+ + A^- \left.\begin{array}{l} \\ + \\ H^+ \\ \Updownarrow \\ HA \end{array}\right\} C_{HA}$$

The anion A^- can combine with protons to increase the solubility of the precipitates. Consider, for example, the solubility of $Ca_2C_2O_4$ in the presence o f a strong acid. The equilibria are:

$$CaC_2O_4 \rightleftharpoons Ca^{2+} + C_2O_4^{2-} \quad K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = 2.6 \times 10^{-9}$$

$$C_2O_4^{2-} + H^+ \rightleftharpoons HC_2O_4^- \quad K_{a2} = \frac{[H^+][C_2O_4^{2-}]}{[HC_2O_4^-]} = 6.1 \times 10^{-5}$$

$$HC_2O_4^- + H^+ \rightleftharpoons H_2C_2O_4 \quad K_{a1} = \frac{[H^+][HC_2O_4^-]}{[H_2C_2O_4]} = 6.5 \times 10^{-2}$$

The solubility ***S*** of $Ca_2C_2O_4$ is equal to $[Ca^{2+}] = C_{H2C2O4}$, where it represents the concentrations of all the oxalate species in equilibrium (= $[H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}]$). We can substitute $C_{H2C2O4}\alpha_2$ for $[C_2O_4^{2-}]$ in the K_{sp} expression:

$$K_{sp} = [Ca^{2+}]C_{H_2C_2O_4}\alpha_2$$

Where α_2 is the fraction of the oxalate species present as ($\alpha_2 = (C_2O_4^{2-})/ HC_2O_4^-$):

$$\alpha_2 = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$ We can write: $\frac{K_{sp}}{\alpha_2} = K'_{sp} = [Ca^{2+}]\, C_{H_2C_2O_4} = s^2$

Where K'_{sp} is the conditional solubdity product.

Calculate the solubility of CaC_2O_4 in a solution containing 0.0010 *M* hydrochloric acid.

Solution

$$\alpha_2 = \frac{(6.5 \times 10^{-2})(6.1 \times 10^{-5})}{(1.0 \times 10^{-3})^2 + (6.5 \times 10^{-2})(1.0 \times 10^{-3}) + (6.5 \times 10^{-2})(6.1 \times 10^{-5})}$$

$$= 5.7 \times 10^{-2}$$

$$s = \sqrt{K_{sp}/\alpha_2} = \sqrt{2.6 \times 10^{-9}/5.7 \times 10^{-2}} = 2.1 \times 10^{-4}\ M$$

Calculating solubilities by the systematic methods:

The use of the systematic method is illustrated in the sections that follow with examples involving the solubility of precipitates under various conditions.

The Solubility of Metal Hydroxides:

Examples involve calculating the solubilities of two metal hydroxides. These examples illustrate how to make approximations and check their validity.

Calculate the molar solubility of $Mg(OH)_2$ in water.

Step 1. **Write Equations for the Pertinent Equilibria** Two equilibria that need to be considered are

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+} + 2OH^-$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Step 2. **Define the Unknown** Since 1 mol of Mg^{2+} is formed for each mole of $Mg(OH)_2$ dissolved,

$$\text{solubility } Mg(OH)_2 = [Mg^{2+}]$$

Step 3. Write All Equilibrium-Constant Expressions

$$[Mg^{2+}][OH^-]^2 = 7.1 \times 10^{-12} \quad (11\text{-}5)$$

$$[H_3O^+][OH^-] = 1.00 \times 10^{-14} \quad (11\text{-}6)$$

Step 4. Write Mass-Balance Expressions As shown by the two equilibrium equations, there are two sources of hydroxide ions: $Mg(OH)_2$ and H_2O. The hydroxide ion concentration resulting from dissociation of $Mg(OH)_2$ is twice the magnesium ion concentration, and the hydroxide ion concentration from the dissociation of water is equal to the hydronium ion concentration. Thus,

$$[OH^-] = 2[Mg^{2+}] + [H_3O^+] \quad (11\text{-}7)$$

Step 5. Write the Charge-Balance Expression

$$[OH^-] = 2[Mg^{2+}] + [H_3O^+]$$

Note that this equation is identical to Equation 11-7. Often, a mass-balance and a charge-balance equation are the same.

Step 6. Count the Number of Independent Equations and Unknowns We have developed three independent algebraic equations (Equations 11-5, 11-6, and 11-7) and have three unknowns ($[Mg^{2+}]$, $[OH^-]$, and $[H_3O^+]$). Therefore, the problem can be solved rigorously.

Step 7a. Make Approximations We can make approximations only in Equation 11-7. Since the solubility-product constant for $Mg(OH)_2$ is relatively large, the solution will be somewhat basic. Therefore, it is reasonable to assume that $[H_3O^+] << [OH^-]$. Equation 11-7 then simplifies to

$$2[Mg^{2+}] \approx [OH^-] \quad (11\text{-}8)$$

Step 8. Solve the Equations Substitution of Equation 11-8 into Equation 11-5 gives

$$[Mg^{2+}](2[Mg^{2+}])^2 = 7.1 \times 10^{-12}$$

$$[Mg^{2+}]^3 = \frac{7.1 \times 10^{-12}}{4} = 1.78 \times 10^{-12}$$

$$[Mg^{2+}] = \text{solubility} = (1.78 \times 10^{-12})^{1/3} = 1.21 \times 10^{-4} \text{ or } 1.2 \times 10^{-4}\ M$$

Step 9. Check the Assumptions Substitution into Equation 11-8 yields

$$[OH^-] = 2 \times 1.21 \times 10^{-4} = 2.42 \times 10^{-4}\ M$$

and from Equation 11-6,

$$[H_3O^+] = \frac{1.00 \times 10^{-14}}{2.42 \times 10^{-4}} = 4.1 \times 10^{-11}\ M$$

Thus, our assumption that $[H_3O^+] << [OH^-]$ is certainly valid.

The Effect of pH on Solubility

The solubility of precipitates containing an anion with basic properties, a cation with acidic properties, or both will depend on pH.

Solubility Calculations when the pH is Constant:

Analytical precipitations are usually performed in buffered solutions in which the pH is fixed at some predetermined and known value. The calculation of solubility under this circumstance is illustrated by the following example.

Calculate the molar solubility of calcium oxalate in a solution that has been buffered so that its pH is constant and equal to 4.00.

Step 1. Write Pertinent Equilibria

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+} + C_2O_4^{2-} \quad (11\text{-}9)$$

Oxalate ions react with water to form $HC_2O_4^-$ and $H_2C_2O_4$. Thus, there are three other equilibria present in this solution:

$$H_2C_2O_4 + H_2O \rightleftharpoons H_3O^+ + HC_2O_4^- \quad (11\text{-}10)$$

$$HC_2O_4^- + H_2O \rightleftharpoons H_3O^+ + C_2O_4^{2-} \quad (11\text{-}11)$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Step 2. Define the Unknown Calcium oxalate is a strong electrolyte, so that its molar analytical concentration is equal to the equilibrium calcium ion concentration. That is,

$$\text{solubility} = [Ca^{2+}] \quad (11\text{-}12)$$

Step 3. Write All the Equilibrium-Constant Expressions

$$[Ca^{2+}][C_2O_4^{2-}] = K_{sp} = 1.7 \times 10^{-9} \quad (11\text{-}13)$$

$$\frac{[H_3O^+][HC_2O_4^-]}{[H_2C_2O_4]} = K_1 = 5.60 \times 10^{-2} \quad (11\text{-}14)$$

$$\frac{[H_3O^+][C_2O_4^{2-}]}{[HC_2O_4^-]} = K_2 = 5.42 \times 10^{-5} \quad (11\text{-}15)$$

$$[H_3O^+][OH^-] = K_w = 1.0 \times 10^{-14}$$

Step 4. Mass-Balance Expressions Because CaC_2O_4 is the only source of Ca^{2+} and the three oxalate species.

$$[Ca^{2+}] = [C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4] = \text{solubility} \quad (11\text{-}16)$$

Moreover, the problem states that the pH is 4.00. Thus,

$$[H_3O^+] = 1.00 \times 10^{-4} \text{ and } [OH^-] = K_w/[H_3O^+] = 1.00 \times 10^{-10}$$

Step 5. Write Charge-Balance Expression A buffer is required to maintain the pH at 4.00. The buffer most likely consists of some weak acid HA and its conjugate base, A^-. The nature of the three species and their concentrations have not been specified, however, so we do not have enough information to write a charge-balance equation.

Step 6. Count the Number of Independent Equations and Unknowns We have four unknowns ($[Ca^{2+}]$, $[C_2O_4^{2-}]$, $[HC_2O_4^-]$, and $[H_2C_2O_4]$) as well as four independent algebraic relationships (Equations 11-13, 11-14, 11-15, and 11-16). Therefore, an exact solution can be obtained, and the problem becomes one of algebra.

Step 7a. Make Approximations An exact solution is so readily obtained in this case that we will not bother with approximations.

Step 8. Solve the Equations A convenient way to solve the problem is to substitute Equations 11-14 and 11-15 into 11-16 in such a way as to develop a relationship between $[Ca^{2+}]$, $[C_2O_4^{2-}]$, and $[H_3O^+]$. Thus, we rearrange Equation 11-15 to give

$$[HC_2O_4^-] = \frac{[H_3O^+][C_2O_4^{2-}]}{K_2}$$

Substituting numerical values for $[H_3O^+]$ and K_2 gives

$$[HC_2O_4^-] = \frac{1.00 \times 10^{-4}[C_2O_4^{2-}]}{5.42 \times 10^{-5}} = 1.85\,[C_2O_4^{2-}]$$

Substituting this relationship into Equation 11-14 and rearranging gives

$$[H_2C_2O_4] = \frac{[H_3O^+][C_2O_4^{2-}] \times 1.85}{K_1}$$

Substituting numerical values for $[H_3O^+]$ and K_1 yields

$$[H_2C_2O_4] = \frac{1.85 \times 10^{-4}[C_2O_4^{2-}]}{5.60 \times 10^{-2}} = 3.30 \times 10^{-3}\,[C_2O_4^{2-}]$$

Substituting these expressions for $[HC_2O_4^-]$ and $[H_2C_2O_4]$ into Equation 11-16 gives

$$[Ca^{2+}] = [C_2O_4^{2-} + 1.85\,[C_2O_4^{2-}] + 3.30 \times 10^{-3}\,[C_2O_4^{2-}]$$
$$= 2.85\,[C_2O_4^{2-}]$$

or $$[C_2O_4^{2-}] = [Ca^{2+}]/2.85$$

Substituting into Equation 11-13 gives

$$\frac{[Ca^{2+}][Ca^{2+}]}{2.85} = 1.7 \times 10^{-9}$$

$$[Ca^{2+}] = \text{solubility} = \sqrt{2.85 \times 1.7 \times 10^{-9}} = 7.0 \times 10^{-5}\,M$$

Solubility calculations when the pH is variable:

Computing the solubility of a precipitate such as calcium oxalate in a solution in which the pH is not fixed and known is considerably more complicated than in the example that we just explored. Thus, to determine the solubility of CaC_2O_4 in pure water, we must take into account the change in OH^- and H_30^+ that accompanies the solution process. In this example, there are four equilibria to consider.

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+} + C_2O_4^{2-}$$
$$C_2O_4^{2-} + H_2O \rightleftharpoons HC_2O_4^- + OH^-$$
$$HC_2O_4^- + H_2O \rightleftharpoons H_2C_2O_4 + OH^-$$
$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Here, as in Example 11-7, the solubility is equal to the cation concentration, $[Ca^{2+}]$.

$$\text{solubility} = [Ca^{2+}] = [C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4]$$

In this case, however, we must take into account one additional equilibrium—the dissociation of water. The equilibrium-constant expressions for the four equilibria are then

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = 1.7 \times 10^{-9} \quad (11\text{-}17)$$
$$K_2 = \frac{[H_3O^+][C_2O_4^{2-}]}{[HC_2O_4^-]} = 5.42 \times 10^{-5} \quad (11\text{-}18)$$
$$K_1 = \frac{[H_3O^+][HC_2O_4^-]}{[H_2C_2O_4]} = 5.60 \times 10^{-2} \quad (11\text{-}19)$$
$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \quad (11\text{-}20)$$

The mass-balance equation is

$$[Ca^{2+}] = [C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4] \quad (11\text{-}21)$$

The charge-balance equation is

$$2[Ca^{2+}] + [H_3O^+] = 2[C_2O_4^{2-}] + [HC_2O_4^-] + [OH^-] \quad (11\text{-}22)$$

We now have six unknowns ($[Ca^{2+}]$, $[C_2O_4^{2-}]$, $[HC_2O_4^-]$, $[H_2C_2O_4]$, $[H_3O^+]$, and $[OH^-]$) and six equations (11-17 through 11-22). Thus, in principle, the problem can be solved exactly.

Effect of Complexation on Solubility: Conditional Solubility Product:

Complexing agents can compete for the metal ion in- a precipitate, just as acids compete for the anion. A precipitate MA that dissociates to give M^+ and A^- and whose metal complexes with the ligand L to form ML^+ would have the following equilibria:

$$MA \rightleftharpoons M^+ + A^- \quad (C_M)$$
$$M^+ + L \rightleftharpoons ML^+ \quad (C_M)$$

The sum o f $[M^+]$ and $[ML^+]$ is the analytical concentration C_m in equilibrium, which is equal to $[A^-]$.

Consider the solubility of AgBr in the presence of NH_3. The equilibria are:

$$AgBr \rightleftharpoons Ag^+ + Br^-$$
$$Ag^+ + NH_3 \rightleftharpoons Ag(NH_3)^+$$
$$Ag(NH_3)^+ + NH_3 \rightleftharpoons Ag(NH_3)_2^+$$

The solubility ***S*** of AgBr is equal to $[Br^-] = C_{Ag}$, where C_{Ag} represents the concentrations of all the silver species in equilibrium [] = $[Ag^+] + [Ag(NH_3)^+] + [Ag(NH_3)_2^+]$. As before, we can substitute $C_{Ag}\,\beta^o$ for $[Ag^+]$ in the Ksp expression, where β^o is the fraction of silver species present as Ag^+

$$K_{sp} = [Ag^+][Br^-] = C_{Ag}\beta_0[Br^-] = 4 \times 10^{-13}$$ Then $$\frac{K_{sp}}{\beta_0} = K'_{sp} = C_{Ag}[Br^-] = s^2$$

where K'_{sp} is the conditional solubdity product.

Calculate the molar solubility of silver bromide in a 0.10 M ammonia solution.

Solution

From Example 9.5, β_0 for 0.10 M $NH_3 = 4.0 \times 10^{-6}$.

$$s = \sqrt{\frac{K_{sp}}{\beta_0}} = \sqrt{4 \times 10^{-13}/4.0 \times 10^{-6}} = 3.2 \times 10^{-4}\ M$$

Particulate Gravimetry

Precipitation and volatilization gravimetric methods require that the analyte, or some other species in the sample, participate in a chemical reaction. In a direct precipitation gravimetric analysis, for example, we convert a soluble analyte into an insoluble form that precipitates from solution. In some situations, however, the analyte is already present as in a particulate form that is easy to separate from its liquid, gas, or solid matrix. When such a separation is possible, we can determine the analyte's mass without relying on a chemical reaction.

Theory and Practice

There are two methods for separating a particulate analyte from its matrix.

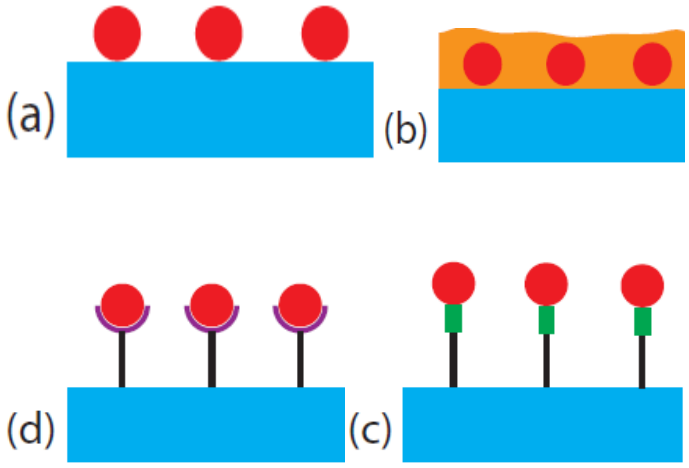
The most common method is filtration, in which we separate solid particulates from their gas, liquid, or solid matrix. A second method, which is useful for gas particles, solutes, and solids, is an extraction.

FILTRATION

To separate solid particulates from their matrix we use gravity or apply suction from a vacuum pump or aspirator to pull the sample through a filter. The type of filter we use depends upon the size of the solid particles and the sample's matrix. Filters for liquid samples are constructed from a variety of materials, including cellulose fibers, glass fibers, cellulose nitrate, and polytetrafluoroethylene (PTFE). Particle retention depends on the size of the filter's pores. When collecting samples from a gas line, we place the filter directly in the line. Atmospheric gases are sampled with a high volume sampler that uses a vacuum pump to pull air through the filter at a rate of approximately 75 m^3/h. In either case, the filtering media for liquid samples also can be used to collect aerosol particulates. The particulates in a solid matrix are separated by size using one or more sieves (Figure). Sieves are available in a variety of mesh sizes ranging from approximately 25 mm to 40 μm.

EXTRACTION

We can extend particulate gravimetry to the analysis of gas phase analytes, solutes, and poorly filterable solids by extracting them with a suitable solvent. After the extraction, we evaporate the solvent before determining the analyte's mass. Alternatively, we can determine the analyte indirectly by measuring the change in the sample's mass after extracting the analyte. Solid-phase extractions, such as those described in another method for extracting an analyte from its matrix is by adsorption onto a solid substrate, by absorption into a thin polymer or chemical film coated on a solid substrate, or by chemically binding to a suitable receptor that is covalently bound to a solid substrate (Figure).



Sieves

Four possible mechanisms for the solid-state extraction of an analyte: (a) adsorption onto a solid substrate; (b) absorption into a thin polymer film or chemical film coated on a solid substrate; (c) metal–ligand complexation in which the ligand is covalently bound to the solid substrate using an organic tether; and (d) antibody–antigen binding in which the receptor is covalently bound to the solid substrate using an organic tether.

Adsorption, absorption, and binding occur at the interface between the solution containing the analyte and the substrate's surface, the thin film, or the receptor. Although the amount of extracted analyte is too small to measure using a conventional balance, it can be measured using a quartz crystal microbalance.

The application of an alternating electrical field across quartz crystal induces an oscillatory vibrational motion in the crystal. Every quartz crystal vibrates at a characteristic resonant frequency that depends on the crystal's properties, including the mass per unit area of any material coated on the crystal's surface. The change in mass following adsorption, absorption, or binding of the analyte, therefore, can be determined by monitoring the change in the quartz crystals characteristic resonant frequency. The exact relationship between the change in frequency and mass is determined by a calibration curve.

Quantitative Applications:

Particulate gravimetry is important in the environmental analysis of water, air, and soil samples. The analysis for suspended solids in water samples, for example, is accomplished by filtering an appropriate volume of a well-mixed sample through a glass fiber filter and drying the filter to constant weight at 103–105 ^{o}C.

The microbiological testing of water also uses particulate gravimetry. Several standard quantitative analytical methods for agricultural products are based on measuring the sample's mass following a selective solvent extraction. Particulate gravimetric sensors also have been developed. For example, a piezoelectric immunosensor has been developed that shows a high selectivity for human serum albumin, and is capable of detecting microgram quantities.

Separations:

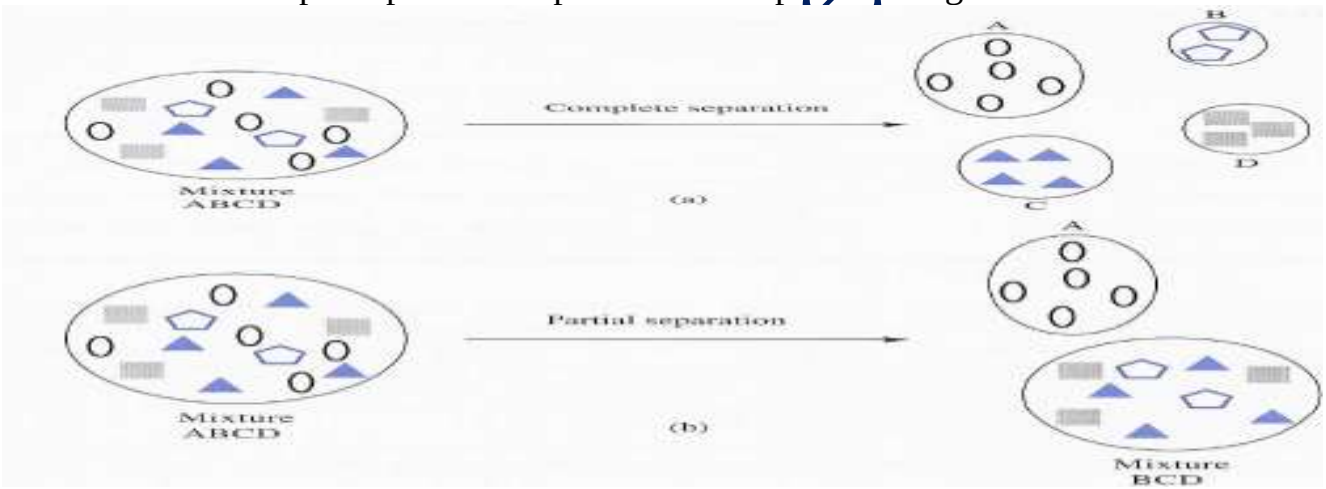
Isolate the analyte from potentially interfering constituents. In addition, techniques such as matrix modification, masking, dilution, and saturation are often used to offset the effects of interferant. The internal standard and standard addition methods can sometimes be employed to compensate for or reduce interference effects.

Anderson, 1987: Physical transfer of a particular chemical substance from one phase or medium to another or the actual physical separation of the components of a mixture into separate fractions.

Meloan, 1999: Is a process whereby compounds of interest are removed from the other compounds in the sample that may react similarly and interfere with a quantitative determination.

Seader and Henley, 1998: The separation of chemical mixtures into their constituents.

A separation is including enrichment, concentration, purification, refining, and isolation. The basic principles of a separation are depicted in Figure.



As shown; separations can be complete or partial. The separation process involves transport of material and spatial redistribution of the components. We should note that a separation always requires energy, because the reverse process, mixing at constant volume, is spontaneous, being accompanied by an increase in entropy. Separations can be preparative or analytical. The goals of an analytical separation are usually to eliminate or reduce interferences so that quantitative analytical information can be obtained about complex mixtures. Separations can also allow identification of the separated constituents if appropriate correlations are made or a structurally sensitive measurement technique, such as mass spectrometry, is used. With techniques such as chromatography, quantitative information is obtained nearly simultaneously with the separation. Table lists a variety of separation methods that are in common use, including (1) Chemical or electrolytic precipitation, (2) distillation, (3) solvent extraction, (4) Ion exchange, (5) chromatography, (6) electrophoresis, and (7) field-flow fractionation.

Separation Methods

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

Classifying Analytical Separations

Analytical separations may be classified in three ways:

Physical state of the mobile phase and stationary phase. **Method of contact** between the mobile phase and stationary phase. **The chemical or physical** mechanism responsible for separating the sample constituents.

Solvent extraction and its application:

Introduction:

Solvent extraction is a method of separation of elements from liquids. This method has some properties in common with fractional distillation. It involves the partition or distribution of a solute between two immiscible liquids in contact with each other. This process gains much importance in the analysis of metals because it furnishes clean separation. The time required is less, and also the technique is simple.

Principles of solvent Extraction:

When a liquid or solid distributes itself between two liquids and remains in the same form, i.e. no compound formation takes place in any of the phases, where no dissociation or even association takes place, and then the ratio of its concentrations in the two liquid phases is constant at constant temperature.

$$A(aq) \rightleftharpoons A(org)$$

Distribution law:

When K_a is the distribution constant, C_o is the solute concentration in the organic species and C_w is the solute concentration in the water layer.

$$Ka = \frac{Co}{Cw} \qquad K = \frac{(a_A)_{org}}{(a_A)_{aq}} \approx \frac{[A]_{org}}{[A]_{aq}} \qquad [A]_i = \left(\frac{V_{aq}}{V_{org}K + V_{aq}}\right)^i [A]_0$$

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 $[A]_o$ with I portions of the organic solvent, each with a volume of $V_{org.}$.

The distribution constant is also known as the partition coefficient. On this basis, distribution law was formulated. It is stated as follows (**When a solute distribute itself between two immiscible phases in contact and is in equilibrium with each other, ratio of the concentrations of the substances in the two phases is constant at constant temperature, provided the molecular state of the distributed solute is the same in both the phases).**

Efficiency of Extraction:

It is very important that the efficiency of extraction under given set of conditions must be higher. This will prevent the loss of substance during the extraction process. The percent of extraction can be explained as:

$$\%E = \frac{100DV_0}{DV_0 + Vw} \qquad D = \frac{K_D}{1 + K_a/[H^+]_a} \qquad \% E = \frac{100D}{D + (V_a/V_o)}$$

D =Distribution ratio – It refers to the concentration of the metal ion each of the two solvents V_o = Volume of organic solvent V_w = Volume of water.

The efficiency of extraction has been proved to be higher when several extractions using small volumes of extractants were made than one extraction with a large volume.

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.

Substitution into Equation 30-3 gives

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

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

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

Note the increased extraction efficiencies that result from dividing the original 50 mL of solvent into two 25-mL or five 10-mL portions.

Twenty milliliters of an aqueous solution of 0.10 *M* butyric acid is shaken with 10 mL ether. After the layers are separated, it is determined by titration that 0.5 mol butyric acid remains in the aqueous layer. What is the distribution ratio, and what is the percent extracted?

Solution

We started with 2.0 mmol butyric acid, and so 1.5 mmol was extracted. The concentration in the ether layer is 1.5 mmol/10 mL = 0.15 *M*. The concentration in the aqueous layer is 0.5 mmol/20 mL = 0.025 *M*. Therefore,

$$D = \frac{0.15}{0.025} = 6.0$$

Since 1.5 mmol was extracted, the percent extracted is (1.5/2.0) × 100% = 75%. Or

$$\% E = \frac{100 \times 6.0}{6.0 + (20/10)} = 75\%$$

Extraction Techniques:

The extraction process involves the three basic steps such as formation of distributable species, distribution of distributable species and interactions in the organic phase. Based on these steps, the extraction occurs.

Batch Extraction:

Here the organic liquid such as acetone, alcohol is added to the solution to be extracted in a separating funnel. Following the addition, the funnel is agitated for enough time and the layers are allowed to settle.

The lower heavier layer is allowed to drain through the stopcock. Further the organic liquid with the solute is collected separately. The process is repeated until satisfactory separation is obtained. The organic liquid with the solute is agitated with an aqueous solution having a complexing agent which reacts with metals to form metal complexes, soluble in water than in the organic liquid used in the extraction.

Continuous Extraction:

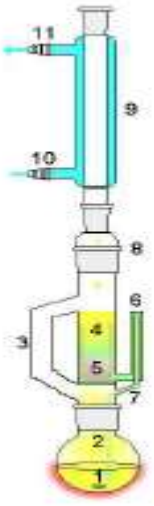
This method is applicable when the distribution ratio is less. Here the solvent is made to flow continuously through the solute containing solution. Solute gets removed with the solvent.

Extraction of solids:

The separation of a desired constituent from a solid sample can be achieved by extraction with an organic solvent in which the solubility of any other substance is too small or even negligible. Its applications include (1) the separation of lithium chloride from sodium and potassium chloride may be done using n-butanol or higher alcohols, because of the solubility of $LiCl_2$ in these solvents. (2) The Potassium per chlorate could be separated from lithium sodium and magnesium per chlorates using n-butanol and ethyl acetate. It is possible because of the solubility of potassium per chlorate alone in the solvent mixture.

Soxhlet apparatus:

It was originally designed for the extraction of a lipid from a solid material. However, a Soxhlet extractor is not limited to the extraction of lipids.



1: Stirrer bar 2: Still pot 3: Distillation path 4: Thimble 5: Solid 6: Siphon top 7: Siphon exit 8: Expansion adapter 9: Condensor 10: Cooling water in 11: Cooling water out

Typically, a Soxhlet extraction is only required where the desired compound has only a limited solubility in a solvent, and the impurity is insoluble in that solvent.

Applications of solvent extraction:

Determination of radioactive elements:

The radioactive element namely uranium could be estimated using solvent extraction. The extraction involves the presence of EDTA, which masks the interfering atoms like Fe, Al, etc.

Determination of heavy metals:

The heavy metals such as Ferric ion, nickel, lead, copper, cadmium, molybdenum can be determined. Ferric ion can be extracted with a 1% solution of 8-hydroxy quinoline in chloroform. Similarly Nickel could be extracted with dimethyl glyoxime solution, lead with dithizone, etc.

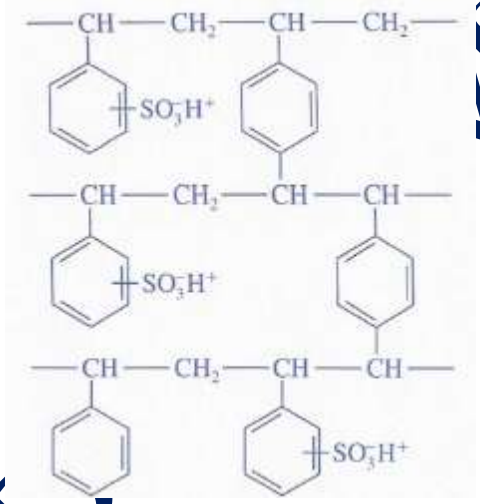
Ion exchange:

Introduction:

Ion exchange is a reversible process in which ions of the same sign are exchanged between a liquid and a solid, the solid is called as an ion exchanger. This method helps for quantitative separations, it has some properties common to that of chromatography. But the principle of separation is that it deals with the separation of ionized substances in particular.

Ion exchange resins:

Normally polymers of higher molecular weight are used to make an ion exchange resin. Some of the polymeric substance present in nature includes the cellulose, starch, rubber, proteins and resins.



Similar resins are used in which the $-SO_3^-H^+$ group is replaced by $-COO^-H^+$, $-NH_3^+OH^-$, and $-N(CH_3)_3^+OH^-$ groups.

Cation exchange resins:

A cation exchange resin may be defined as a high molecular weight, cross linked polymeric anions and active cations. Resins having sulphanoic groups as the exchange sites are known as strongly acidic cation exchange resins. For a strongly acidic cation exchange resin, the exchange affinity for cations depends on the charge of the cation. Thus tripositive cations are held firmly than dipositive cations. These dipositive cations are held well when compared with unipositive ones. It is denoted as R.

$$n\mathrm{RzSO_3^-H^+} + \mathrm{M}^{n+} \rightleftharpoons (\mathrm{RzSO_3})_n\mathrm{M} + n\mathrm{H^+}$$

$$n\mathrm{RzCO_2^-H^+} + \mathrm{M}^{n+} \rightleftharpoons (\mathrm{RzCO_2})_n\mathrm{M} + n\mathrm{H^+}$$

Anion exchange resins:

An anion exchange resins is a polymer containing amine or quaternary ammonium groups as integral parts of the resin and also equivalent amount of anions such as Cl^-, SO_4^{-2}, OH^-, ions. It is denoted as R – NH2.

$$n\mathrm{RzNR_3^+OH^-} + \mathrm{A}^{n-} \rightleftharpoons (\mathrm{RzNR_3})_n\mathrm{A} + n\mathrm{OH^-}$$

$$n\mathrm{RzNH_3^+OH^-} + \mathrm{A}^{n-} \rightleftharpoons (\mathrm{RzNH_3})_n\mathrm{A} + n\mathrm{OH^-}$$

Properties of Ion exchange resins:

The important properties of ion exchange resins are colour, density, mechanical strength, particle size, selectivity, amount of cross linking, swelling, porosity, surface area and chemical resistance. And a useful resin must be chemically stable, must have cross linkage. So as to have only a negligible solubility, swollen resin must be denser than water, and must contain sufficient number of accessible ionic exchange groups.

Types of Ion Exchange Resins

Type of Exchanger	Functional Exchanger Group	Trade Name
Cation		
Strong acid	Sulfonic acid	Dowex[a] 50; Amberlite[b] IR120; Ionac[c] CGC-240; Rexyn[d] 101; Permutit[e] Q
Weak acid	Carboxylic acid	Amberlite IRC 50; Ionac CGC-270; Rexyn 102; Permutit H-70
Anion		
Strong base	Quaternary ammonium ion	Dowex 1; Amberlite IRA 400; Ionac AGA-542; Rexyn 201; Permutit S-1
Weak base	Amine group	Dowex 3; Amberlite IR 45; Ionac AGA-316; Rexyn 203; Permutit W

Applications of Ion exchange resins:

Demineralization of water:

The Ion-exchange resins have been used for the demineralization of water. When the water is allowed to pass through a anion exchanger, the anions get replaced by OH^- ions and when it passes through cation exchanger, the cations get replaced by H^+ ions. This process results in water which is pure in nature.

Softening of hard water:

Normally the hard water consists higher amount of Ca^{2+} & Mg^{2+} tons. When such water is passed through the resin, the Ca^{2+} will be replaced by Na^+ ions. The Na^+ ions pass into the solution. Thereby the water becomes harmless for washing. After a long time usage, the column needs to be regenerated.

Separation of Isotopes:

Isotopes of various elements such as Boron, Beryllium, Calcium, Cobalt and Uranium are separated on Ion exchange columns.

Removal of carbonate from sodium hydroxide solution:

The solution of sodium hydroxide containing carbonate is allowed to pass through an OH^- form of an anion exchange resin. The carbonate will be replaced by hydroxide.

Other applications of Ion Exchange Resins:

Ion exchange resins are used in the manufacture of fruit juices such as orange juice where they are used to remove bitter tasting components and so improve the flavor.

Sugar Manufacturing:

Ion exchange resins are used in the manufacturing of sugar from various sources.

Home Water Softeners:

Hard water is water that is rich in the salts of calcium, magnesium, and iron. The cations of hard water combine with fatty acid anions from soap to form insoluble salts known as **curd or soap curd.**

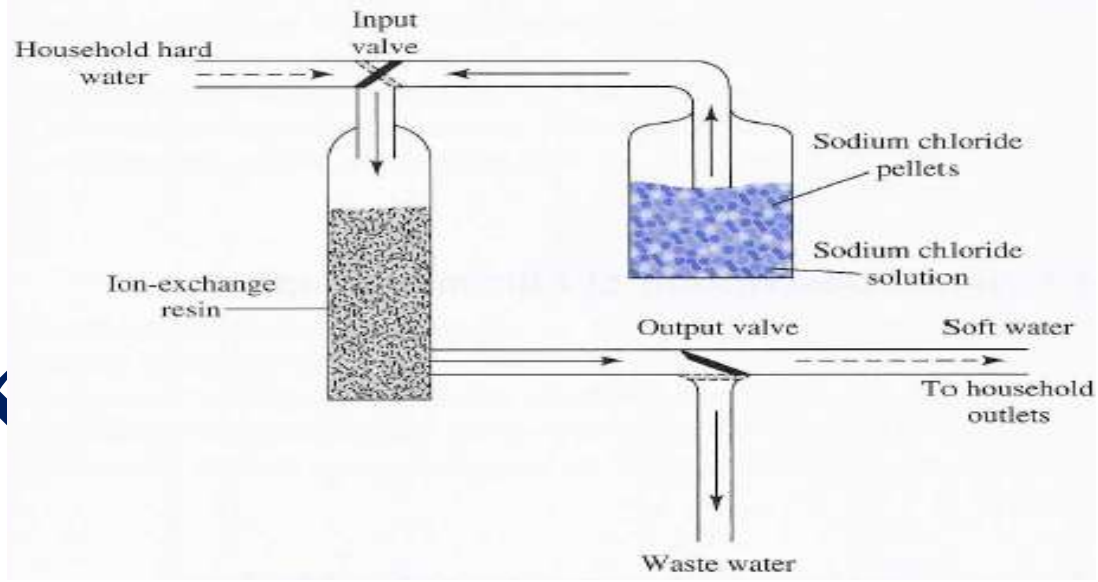
One method of solving the problem of hard water in homes is to exchange the calcium, magnesium, and iron cations for sodium ions, which form soluble fatty acid salts. During the charging or regeneration cycle, concentrated salt water from the reservoir is directed through the ion-exchange resin, where the resin sites are occupied by Na^+ ions.

$$\underset{\text{solid}}{(RSO_3^-)_xM^{x+}} + \underset{\text{water}}{xNa^+} \rightleftharpoons \underset{\text{solid}}{xRSO_3^-Na^+} + \underset{\text{water}}{M^{x+}} \quad \text{(regeneration)}$$

The M^{x+} cations (calcium, magnesium, or iron) released are sent to waste during this cycle. After the regeneration cycle, the valves controlling the inlet to the ion exchange resin and the outlet from the resin change so that water from the household supply passes through the resin and out to the household faucets. When the hard water passes through the resin, the cations M^{x+} are exchanged for Na^+ ions, and the water is softened.

$$\underset{\text{solid}}{xRSO_3^-Na^+} + \underset{\text{water}}{M^{x+}} \rightleftharpoons \underset{\text{solid}}{(RSO_3^-)_xM^{x+}} + \underset{\text{water}}{xNa^+} \quad \text{(household use)}$$

With use, the ion-exchange resin gradually accumulates the cations from the hard water.



Hence, the softener must be periodically recharged by passing salt water through it and venting the hard-water ions to waste. After softening, soaps are much more effective because they remain dispersed in the water and do not form soap curds. Potassium chloride is also used instead of sodium chloride and is particularly advantageous for people on a sodium-restricted diet. Potassium chloride for water softeners is, however, more expensive than sodium chloride.

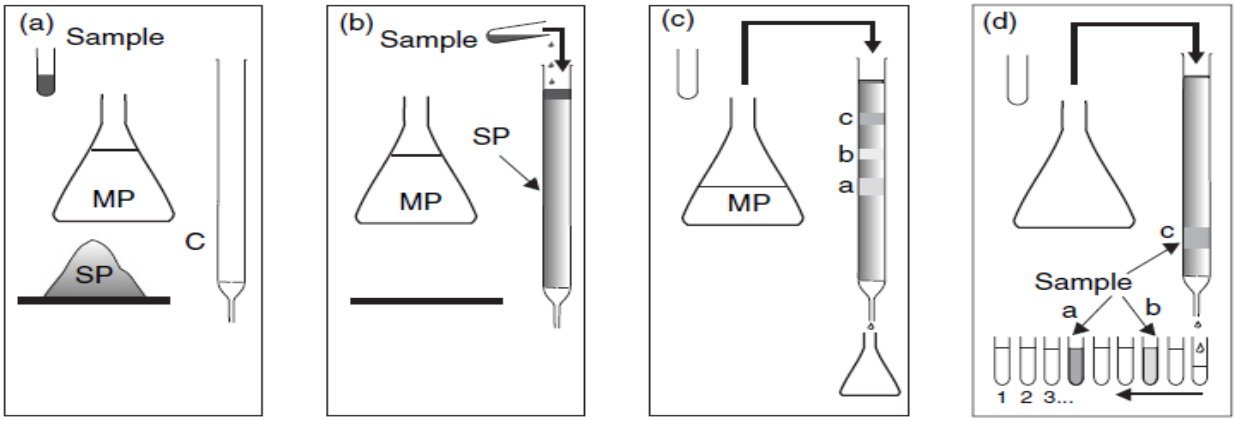
Chromatographic Separations:

In an extraction, the sample is initially present in one phase, and the component of interest is extracted into a second phase. Separations can also be accomplished by continuously passing one sample-free phase, called the mobile phase, over a second sample-free phase that remains fixed or stationary. The sample is injected or placed into the mobile phase. As the sample's components move with the mobile phase, they partition themselves between the mobile and stationary phases. Those components having the largest partition coefficients are more likely to move into the stationary phase, taking longer to pass through the system. This is the basis of all chromatographic separation techniques. Modern chromatography provides a means both of separating analytes and interferents and of performing a qualitative or quantitative analysis of the analyte.

General aspects of chromatography:

It is traditional to assign the invention of modern chromatography to Michael S. Tswett, shortly after 1900. Chromatography, the process by which the components of a mixture can be separated, has become one of the primary analytical methods for the identification and quantification of compounds in the gaseous or liquid state. The basic principle is based on the concentration equilibrium of the components of interest, between two immiscible phases. One is called the stationary phase, because it is immobilized within a column or fixed upon a support, while the second, called the mobile phase, is forced through the first. The phases are chosen such that components of the sample have differing solubilities in each phase. The differential migration of compounds leads to their separation.

Chromatography is a physico-chemical method of separation of components within mixtures, liquid or gaseous, in the same vein as distillation, crystallization, or the fractionated extraction. The applications of this procedure are therefore numerous since many of heterogeneous mixtures, or those in solid form, can be dissolved by a suitable solvent (which becomes, of course, a supplementary component of the mixture). A basic chromatographic process may be described as follows:



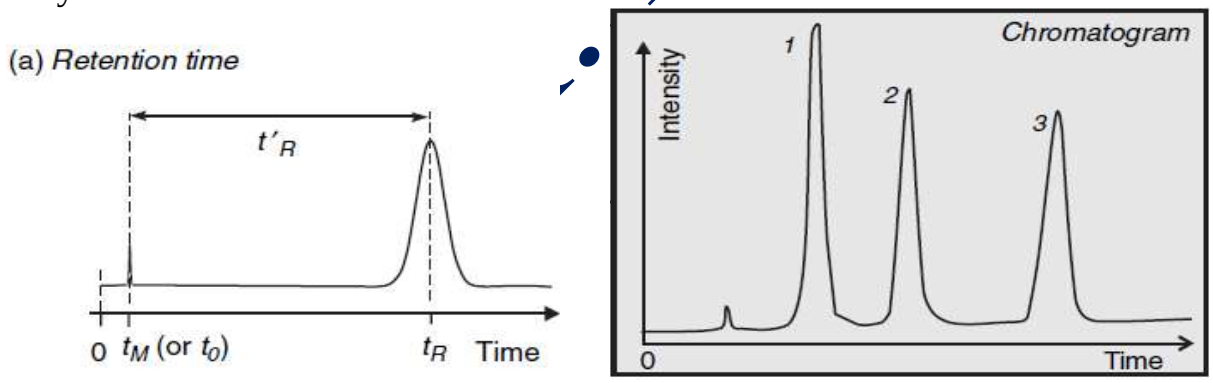
A basic experiment in chromatography. (a) The necessary ingredients (C, column; SP, stationary phase; MP, mobile phase; and S, sample); (b) introduction of the sample; (c) start of elution; (d) recovery of the products following separation.

1. A vertical hollow glass tube (the column) is filled with a suitable finely powdered solid, the stationary phase.
2. At the top of this column is placed a small volume of the sample mixture to be separated into individual components.
3. The sample is then taken up by continuous addition of the mobile phase, which goes through the column by gravity, carrying the various constituents of the mixture along with it. This process is called elution. If the components migrate at different velocities, they will become separated from each other and can be recovered, mixed with the mobile phase.

The identification of a compound by chromatography is achieved by comparison to identify a compound which may be A or B, a solution of this unknown is run on a column. Next, its retention time is compared with those for the two reference compounds A and B previously recorded using the same apparatus and the same experimental conditions. The choice between A and B for the unknown is done by comparison of the retention times. The essential recording that is obtained for each separation is called a chromatogram.

The chromatogram:

The chromatogram is the representation of the variation, with time (rarely volume), of the amount of the analyte in the mobile phase exiting the chromatographic column. It is obtained from variations, as a function of time, of an electrical signal emitted by the detector. It is a curve that has a baseline which corresponds to the trace obtained in the absence of a compound being eluted. The separation is complete when the chromatogram shows as many chromatographic peaks as there are components in the mixture to be analyzed.



Chromatographic peaks. (a) The concept of retention time. The hold-up time t_M is the retention time of an unretained compound in the column (the time it took to make the trip through the column); (b) An example of a real chromatogram showing that while travelling along the column, each analyte is assumed to present a Gaussian distribution of concentration.

A constituent is characterized by its retention time t_R, which represents the time elapsed from the sample introduction to the detection of the peak maximum on the chromatogram. In an ideal case, t_R is independent of the quantity injected. The **retention time** t_R, of the solute on the column can be sub-divided into two terms: t_M (hold-up time), or dead time (formerly designated t_o). It is the time required for the mobile phase to pass through the column, and t_S the cumulative times spent in the stationary phase, during

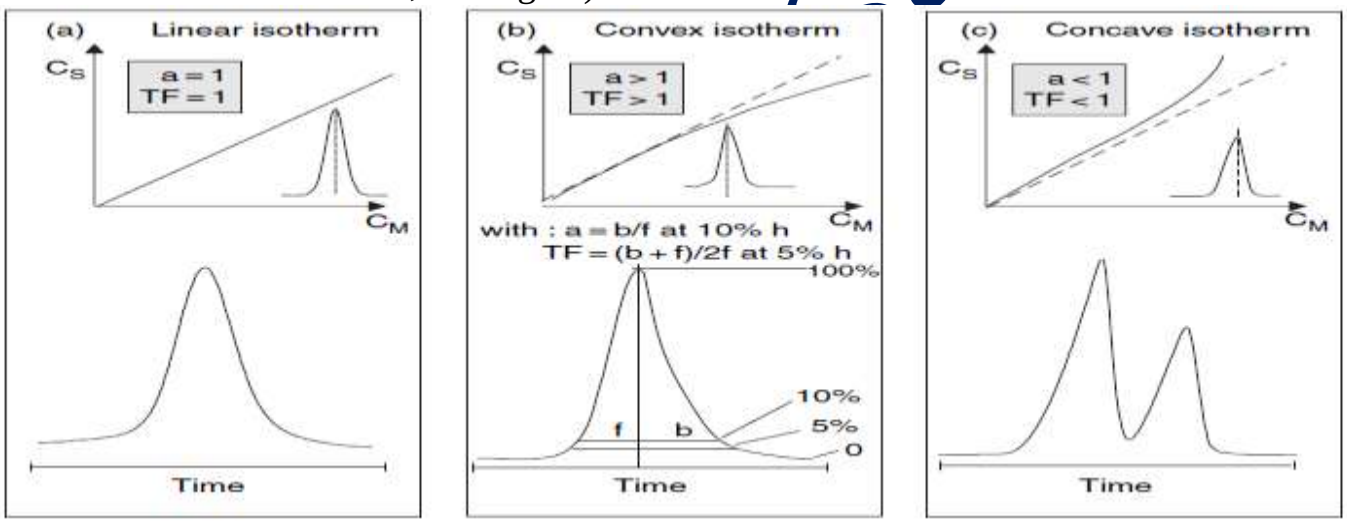
which it is immobile. The difference between the retention time and the hold-up time is designated by the adjusted retention time of the compound , $\overline{t}_R$. If the signal sent by the sensor varies linearly with the concentration of a compound, then the same variation will occur for the area under the corresponding peak on the chromatogram. This is a basic condition to perform quantitative analysis from a chromatogram.

Gaussian-shaped elution peaks:

On a chromatogram the perfect elution peak would have the same form as the graphical representation of the law of Normal distribution of random errors. In keeping with the classic notation, μ would correspond to the retention time of the eluting peak while σ to the standard deviation of the peak (σ^2 represents the variance), y represents the signal as a function of time x, from the detector located at the outlet of the column (Figure).

$$y = \frac{1}{\sigma\sqrt{2\pi}} \cdot \exp\left[-\frac{(x-\mu)^2}{2\sigma^2}\right] \qquad y = \frac{1}{\sqrt{2\pi}} \cdot \exp\left[-\frac{x^2}{2}\right]$$

The observed asymmetry of a peak is measured by two parameters, the skewing factor a measured at 10 per cent of its height and the tailing factor TF measured at 5 per cent (for the definition of these terms, see Figure):



Distribution isotherms. (a) The ideal situation corresponding to the invariance of the concentration isotherm. (b) Situation in which the stationary phase is saturated – as a result of which the ascent of the peak is faster than the descent (skewing factor greater than 1); (c) The inverse situation: the constituent is retained too long by the stationary phase, the retention time is therefore extended and the ascent of the peak is slower than the descent apparently normal.

The plate theory:

To explain the mechanism of migration and separation of compounds on the column, the oldest model, known as Craig's *theoretical plate model* is a static approach now judged to be obsolete, but which once offered a simple description of the separation of constituents. In liquid–solid chromatography this elementary process is represented by a cycle of adsorption/desorption. Each step corresponds to a new state of equilibrium for the *entire* column. These successive equilibria provide the basis of *plate theory* according to which a column of length *L* is sliced horizontally into *N* fictitious, small plate-like discs of same height *H* and numbered from 1 to N. For each of them, the concentration of

the solute in the mobile phase is in equilibrium with the concentration of this solute in the stationary phase. At each new equilibrium, the solute has progressed through the column by a distance of one disc (or plate), hence the name *theoretical plate theory*. The *height equivalent to a theoretical plate* (HETP or H) will be given by equation:

$$H = \frac{L}{N}$$

Nernst partition coefficient (K)

The fundamental physico-chemical parameter of chromatography is the equilibrium constant *K*, termed the *partition coefficient*, quantifying the ratio of the concentrations of each compound within the two phases.

$$K = \frac{C_S}{C_M} = \frac{\text{Molar concentration of the solute in the stationary phase}}{\text{Molar concentration of the solute in the mobile phase}}$$

Values of *K* are very variable since they can be large (e.g. 1000), when the mobile phase is a gas or small (e.g. 2) when the two phases are in the condensed state.

Each compound occupies only a limited space on the column, with a variable concentration in each place, therefore the true values of C_M and C_S vary in the column, but their ratio is constant.

Column efficiency:

Theoretical efficiency (number of theoretical plates):

As the analyte migrates through column, it occupies a continually expanding zone (Figure). Reminding the plate theory model this approach also leads to the value of the height equivalent to one theoretical plate H and to the number N, of theoretical plate:

H =L/N

$$N = 16\frac{t_R^2}{w^2} \qquad N = 5.54\frac{t_R^2}{w_{1/2^2}}$$

N is a relative parameter, since it depends upon both the solute chosen and the operational conditions adopted, w is peak width.

Effective plates number (real efficiency):

In order to compare the performances of columns of different design for a given compound – or to compare, in gas chromatography, the performances between a capillary column and a packed column – more realistic values are obtained by replacing the *total retention time* t_R, by the *adjusted retention time* $\overline{t}_R$ which does not take into account the *hold-up time* t_M spent by any compound in the mobile phase $\overline{t}_R = t_R - t_M$. The three preceding expressions become:

$$N_{eff} = 16\frac{t_R'^2}{w^2} \qquad N_{eff} = 5.54\frac{t_R'^2}{w_{1/2}{}^2}$$

Height equivalent to a theoretical plate (HETP):

The *equivalent height of a theoretical plate* H, as already defined, is calculated for reference compounds to permit a comparison of columns of different lengths. H does not behave as a constant; its value depends upon the compound chosen and upon the experimental conditions. For a long time in gas chromatography an adjustment value called the effective height of a theoretical plate H_{eff} was calculated using the true efficiency. This corresponds to the Equation;

$$H_{\text{eff}} = \frac{L}{N_{\text{eff}}}$$

Retention parameters:

Hold-up times or volumes are used in chromatography for various purposes, particularly to access to retention factor **k**. and thermodynamic parameters. Only basic expressions are given below.

Retention times:

The definition of retention times, *hold-up time*, t_M, *retention time*, t_R and *adjusted retention time*, $\bar{t}_R$

Retention volume (or elution volume) V_R:

The *retention volume* V_R of an analyte represents the volume of mobile phase necessary to enable its migration throughout the column from the moment of entrance to the moment in which it leaves. On a standard chromatogram with time in abscissa, V_R is calculated from expression bellow, if the flow rate *F* is constant,

$$V_{\text{R}} = t_{\text{R}} \cdot F \qquad V_{\text{peak}} = w \cdot F \qquad V_{\text{M}} = t_{\text{M}} \cdot F$$

The volume of a peak, V_{peak} corresponds to that volume of the mobile phase in which the compound is diluted when leaving the column.

Hold-up volume (or dead volume) V_M:

The volume of the mobile phase in the column (known as the dead volume), V_M, corresponds to the accessible interstitial volume. It is often calculated from a chromatogram, provided a solute not retained by the stationary phase is present.

Retention (or capacity) factor k:

When a compound of total mass $\mathbf{m_T}$ is introduced onto the column, it separates into two quantities: $\mathbf{m_M}$, the mass in the mobile phase and $\mathbf{m_S}$, the mass in the stationary phase. Their ratio, called the ***retention factor* k,** is constant and independent of $\mathbf{m_T}$:

$$k = \frac{m_{\text{S}}}{m_{\text{M}}} = \frac{C_{\text{S}}}{C_{\text{M}}} \cdot \frac{V_{\text{S}}}{V_{\text{M}}} = K\frac{V_{\text{S}}}{V_{\text{M}}}$$

The retention factor, also known as the ***capacity factor k***, is a very important parameter in chromatography for defining column performances. Though it does not vary with the flow rate or the column length, **k** is it not a constant as it depends upon the experimental conditions.

Ideally, **k** should be superior to one but less than five, otherwise the time of analysis is unduly elongated. An experimental approach of k can be as follows:

$$\frac{n_S}{n_M} = \frac{m_S}{m_M} = \frac{t_S}{t_M} = k$$

Knowing that the retention time of a compound t_R is such that $t_R = t_M + t_S$, the value of k is therefore accessible from the chromatogram ($t_S = t'_R$); see Figure 1.7:

$$k = \frac{t'_R}{t_M} = \frac{t_R - t_M}{t_M} \qquad (1.20)$$

This important relation can also be written:

$$t_R = t_M(1 + k) \qquad (1.21)$$

Bearing in mind the relations (1.16) and (1.18), the retention volume V_R of a solute can be written :

$$V_R = V_M(1 + k) \qquad (1.22)$$

or

$$V_R = V_M + KV_S \qquad (1.23)$$

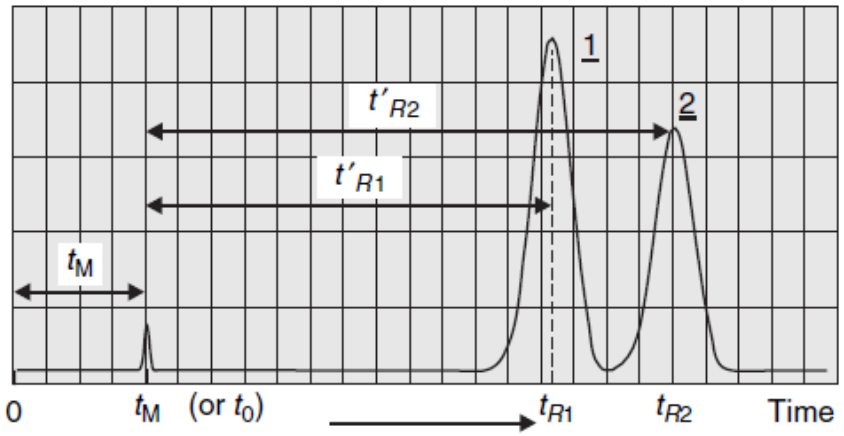
This final expression linking the experimental parameters to the thermodynamic coefficient of distribution ***K***, is valid for the ideal chromatography.

Separation (or selectivity) factor between two solutes:

The separation factor ***α***, enables the comparison of two adjacent peaks 1 and 2 present in the same chromatogram (Figure). It can be concluded that the separation factor can be expressed by Equation:

$$\alpha = \frac{t'_{R(2)}}{t'_{R(1)}} \qquad \alpha = \frac{k_2}{k_1} = \frac{K_2}{K_1}$$

By definition ***α*** is greater than unity (species 1 elutes faster than species 2).



here,

$k_1 = \frac{t'_{R1}}{t_M}$ $k_1 = 3.07$

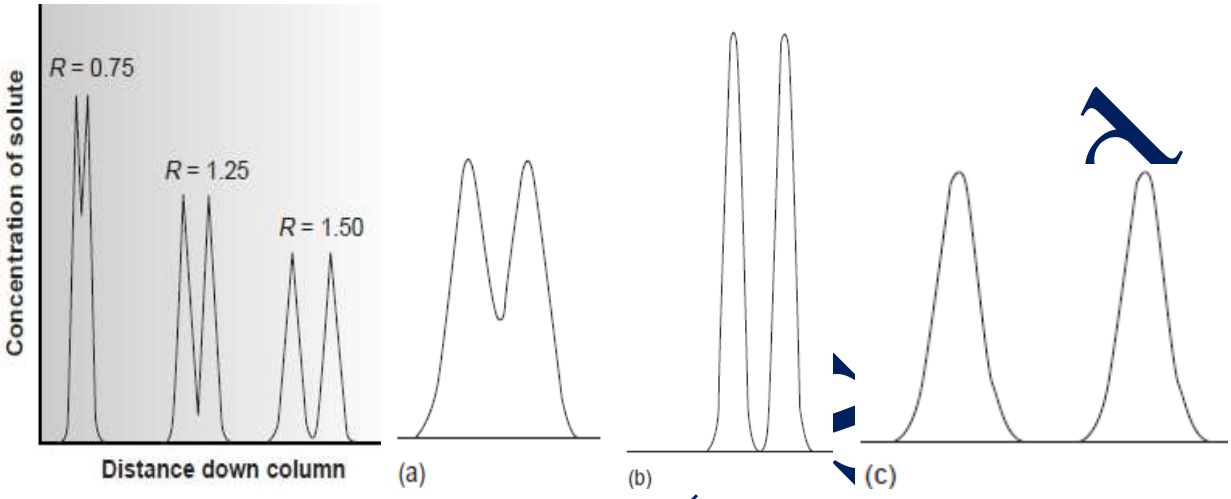
$k_2 = \frac{t'_{R2}}{t_M}$ $k_2 = 3.92$

$\alpha = \frac{t'_{R2}}{t'_{R1}}$ $\alpha = 1.27$

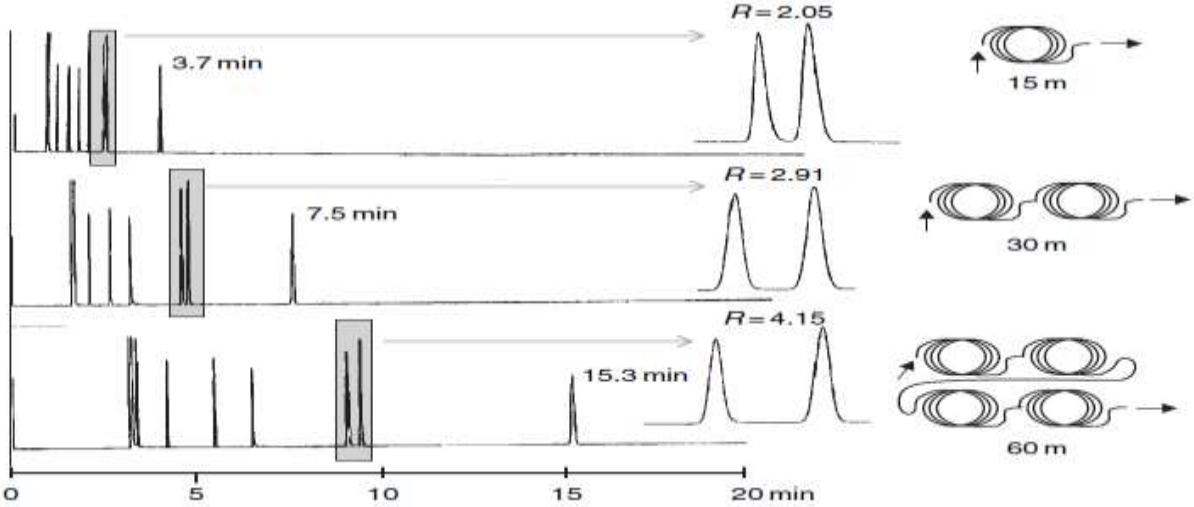
Resolution factor between two peaks:

To quantify the separation between two compounds, another measure is provided by the *resolution factor* ***R***. The following expression is used to calculate ***R*** between two compounds 1 and 2 (Figure):

$$R = 2\frac{t_{R(2)} - t_{R(1)}}{w_1 + w_2} \qquad R = \frac{t_{r,B} - t_{r,A}}{0.5(w_B + w_A)} = \frac{2\Delta t_r}{w_B + w_A}$$



The methods for improving chromatographic resolution: (a) Original separation showing a pair of poorly resolved solutes; (b) Improvement in resolution due to an increase in column efficiency; (c) Improvement in resolution due to a change in column selectivity.



In a chromatographic analysis of lemon oil a peak for limonene has a retention time of 8.36 min with a baseline width of 0.96 min. γ-Terpinene elutes at 9.54 min, with a baseline width of 0.64 min. What is the resolution between the two peaks?

SOLUTION

Using equation 12.1, we find that the resolution is

$$R = \frac{2\Delta t_r}{w_B + w_A} = \frac{2(9.54 - 8.36)}{0.64 + 0.96} = 1.48$$

The rate theory of chromatography:

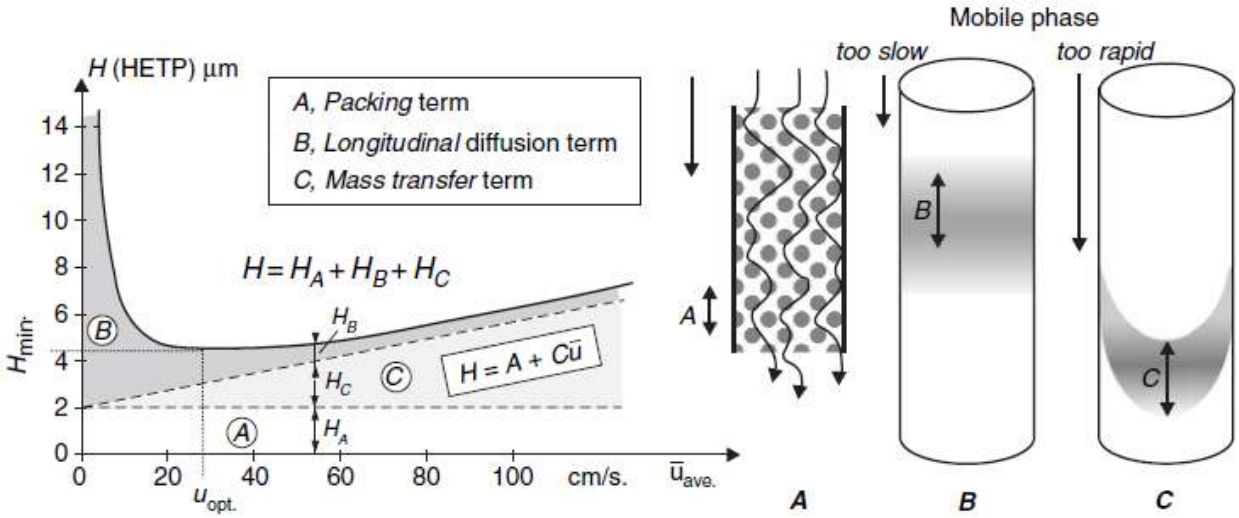
Rate theory is a more realistic description of the processes at work inside a column which takes account of the time taken for the solute to equilibrate between the two phases. It is the dynamics of the separation process which is concerned. The first kinetic equation *for packed columns in gas phase chromatography* was proposed by Van Deemter.

Van Deemter's equation:

This equation is based on a Gaussian distribution, similar to that of plate theory. Its simplified form, proposed by Van Deemter in 1956, is well known. The expression links the plate high *H* to the average linear velocity of the mobile phase $\bar{u}$ in the column.

$$H = A + \frac{B}{\bar{u}} + C\bar{u}$$

The three experimental basic coefficients A, B and C are related to diverse physico-chemical parameters of the column and to the experimental conditions. If *H* is expressed in cm, A will also be in cm, B in cm^2/s and C in s (where velocity is measured in cm/s).



Van Deemter's curve in gas chromatography with the domains of parameters A, B and C indicated. There exists an equation similar to that of Van Deemter that considers temperature: H=A+B/T+CT

Packing related term $A=2\lambda d_p$:

Term A is related to the flow profile of the mobile phase passing through the stationary phase. The size of the particles (diameter d*p*), their dimensional distribution and the uniformity of the packing (factor characteristic of packing λ) can all be the origin of flow paths of different length which cause broadening of the solute band and improper exchanges between the two phases. This results in turbulent or Eddy diffusion, considered to have little importance in liquid chromatography and absent for WCOT capillary columns in GC. For a given column, nothing can be done to reduce the A term.

Gas (mobile phase) term $B=2\gamma D_G$:

Term B, which can be expressed from D_G, the diffusion coefficient of the analyte in the gas phase and λ, the above packing factor, is related to the longitudinal molecular diffusion in the column. It is especially important when the mobile phase is a gas.

Liquid (stationary phase) term C = C_G +C_L:

Term C, which is related to the resistance to mass transfer of the solute between the two phases, becomes dominant when the flow rate is too high for equilibrium to be attained. The diffusion of solute between the two phases is not instantaneous, so that it will be carried along out of equilibrium. The higher the velocity of mobile phase, the worse the broadening becomes. No simple formula exists which takes into account the different factors integrated in term C.

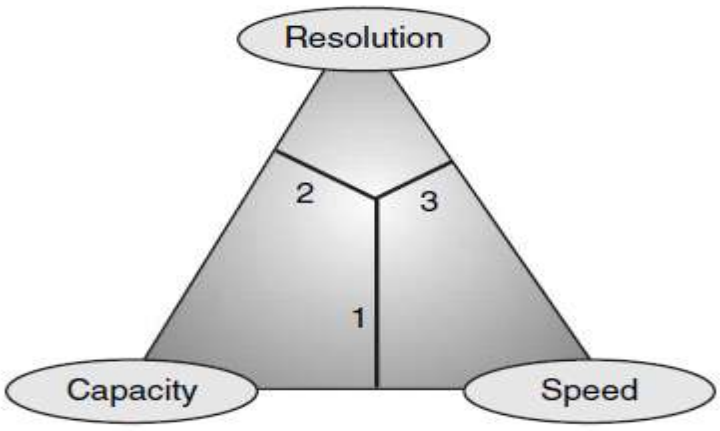
Optimization of a chromatographic analysis:

Analytical chromatography is used essentially in quantitative analysis. In order to achieve this effectively, the areas under the peaks must be determined with precision, which in turn necessitates well-separated analytes to be analyzed. A certain experience in chromatography is required when the analysis has to be optimized, employing all available resources in terms of apparatus and software that can simulate the results of temperature modifications, phases and other physical parameters.

(In gas phase chromatography, the separations can be so complex that it can be difficult to determine in advance whether the temperature should be increased or decreased. The choice of column, its length, its diameter, the stationary phase composition and the phase ratio (V_M/V_S) as well as the parameters of separation (temperature and flow rate), are amongst the factors which interact with each other).

The resolution and the elution time are the two most important dependent variables to consider. In all optimizations, the goal is to achieve a sufficiently complete separation of the compounds of interest in the minimum time, though it should not be forgotten that time will be required to readjust the column to the initial conditions to be ready for the next analysis. If the resolution is very good then optimization consists to save time in the analysis.

The chromatographer's triangle. The shaded areas indicate the domain corresponding to analytical chromatography based principally upon the five parameters K, N, k, α and R.



Ion chromatography:

Two types of ion chromatography are currently in use: **suppressor-based** and **single-column.** They differ in the method used to prevent the conductivity of the eluting electrolyte from interfering with the measurement of analyte conductivities.

Ion Chromatography Based on Suppressors:

The suppressor column is followed by suppressor column packed with a second ion-exchange resin or by a suppressor membrane that effectively converts the ions of the eluting solvent to a molecular species of limited ionization without affecting the conductivity due to analyte ions. For example, when cations are being separated and determined, hydrochloric acid is chosen as the eluting reagent, and the suppressor column is an anion-exchange resin in the hydroxide form. The product of the reaction in the suppressor is water. That is,

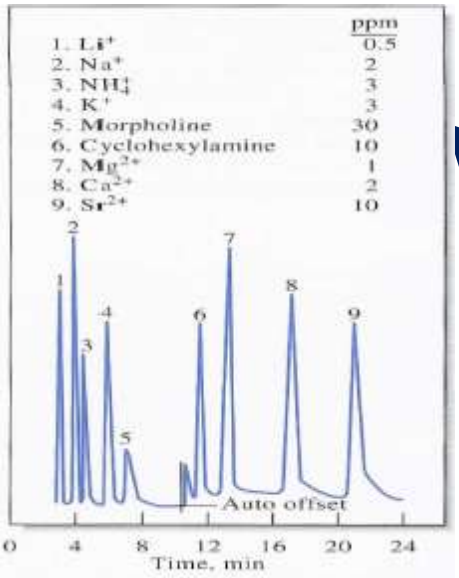
$$H^+(aq) + Cl^-(aq) + \text{resin}^+OH^-(s) \rightarrow \text{resin}^+Cl^-(s) + H_2O$$

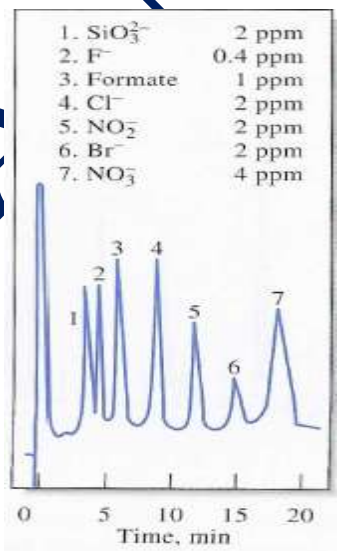
The analyte cations are not retained by this second column.

For anion separations, the suppressor packing is the acid form of a cation exchange resin, and sodium bicarbonate or carbonate is the eluting agent. The reaction in the suppressor is:

$$Na^+(aq) + HCO_3^-(aq) + \text{resin}^-H^+(s) \rightarrow \text{resin}^-Na^+(s) + H_2CO_3(aq)$$

The largely undissociated carbonic acid does not contribute significantly to the conductivity. Figures show applications of ion chromatography based on suppressor column and conductometric detection.





In each, the ions were present in the parts-per-million range; the sample size was 50 µL in one case and 20 µL in the other. The method is particularly important for anion analysis because there is no other rapid and convenient method of handling mixtures of this type.

Single-Column Ion Chromatography:

Single-column ion chromatography offers the advantage of not requiring special equipment for suppression. The analyte ions are separated on a low capacity ion exchanger by means of a low – ionic strength eluent that does not interfere with the conductometric detection of analyte ions. It is a somewhat less sensitive method of determining anions than being suppressor column methods, however.

Size exclusion chromatography:

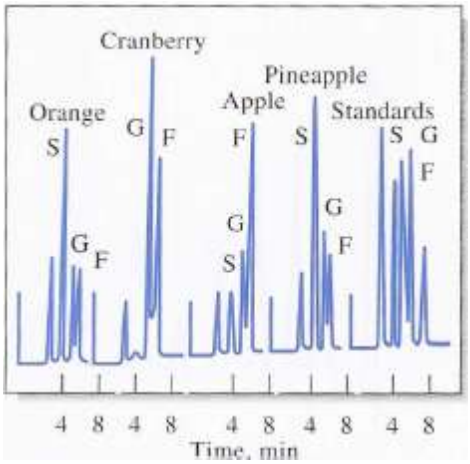
Size-exclusion, or gel, chromatography is the newest of the liquid chromatographic procedures. Is based on molecular size. It is a powerful technique that is particularly applicable to high molecular- weight species. Gel permeation is a type of size exclution chromatography in which packing is hydrophobic. It is used to separate nonpolar species. Gel filtration is a type of size exclution chromatography in which packing is hydrophilic. It is used to separate polar species.

Column Packing: Packing for size-exclusion chromatography consist of small (l0 µm) silica or polymer particles containing a network of uniform pores into which solute and solvent molecules can diffuse. While in the pores, molecules are effectively trapped and removed from the flow of the mobile phase. The average residence time of analyte molecules depends on their effective size. Molecules that are significantly larger than the average pore size of the packing are excluded and thus suffer no retention; that is, they travel through the column at the rate of the mobile phase. Molecules that are appreciably smaller than the pores can penetrate throughout the pore maze and are thus entrapped for the greatest time; they are last to elute. The fractionation that occurs within this group is directly related to molecular size and, to some extent, molecular shape. Note that size-exclusion separations differ from the other chromatographic procedures in the respect that no chemical or physical interactions between analytes and the stationary phase are involved. Some are hydrophilic for use with aqueous mobile phases; others are hydrophobic and are used with nonpolar organic solvents. Chromatography based on the hydrophilic packing is sometimes called gel filtration, while techniques based on hydrophobic packing are termed gel permeation. The average molecular weight suitable for a given packing may be as small as a few hundred or as large as several million.

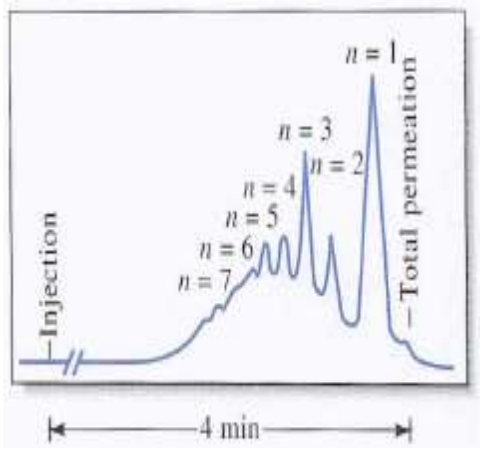
Applications:

Figures illustrate typical applications of size-exclusion chromatography. In the chromatograms shown in Figure one, a hydrophilic packing was used to exclude molecular weights greater than 1000. The chromatogram in Figure two was obtained with a hydrophobic packing in which the eluent was tetrahydrofuran.

Another important application of size-exclusion chromatography is the rapid determination of the molecular mass or the molecular mass distribution of large polymers or natural products. The key to such determinations is an accurate molecular mass calibration.



Gel – filtration



Gel – permeation

Planar chromatography:

Planar chromatographic methods include **thin-layer chromatography** (TLC), **paper chromatography** (PC), and **electro chromatography.** Each makes use of a flat, relatively thin layer of material that is either self-supporting or is coated on a glass, plastic, or metal surface. The mobile phase moves through the stationary phase by capillary action, sometimes assisted by gravity or an electrical potential.

Planar chromatography was once called two-dimensional chromatography, although the term has now come to signify the coupling of two chromatographic techniques with different separation mechanisms.

The Scope of Thin-Layer Chromatography:

Thin-layer chromatography has become the workhorse of the drug industry for the all-important determination of product purity. It has also found widespread use in clinical laboratories and is the backbone of many biochemical and biological studies. Finally, it finds extensive use in industrial laboratories." As a consequence of these many areas of application, TLC remains a very important technique.

Principles of Thin-Layer Chromatography:

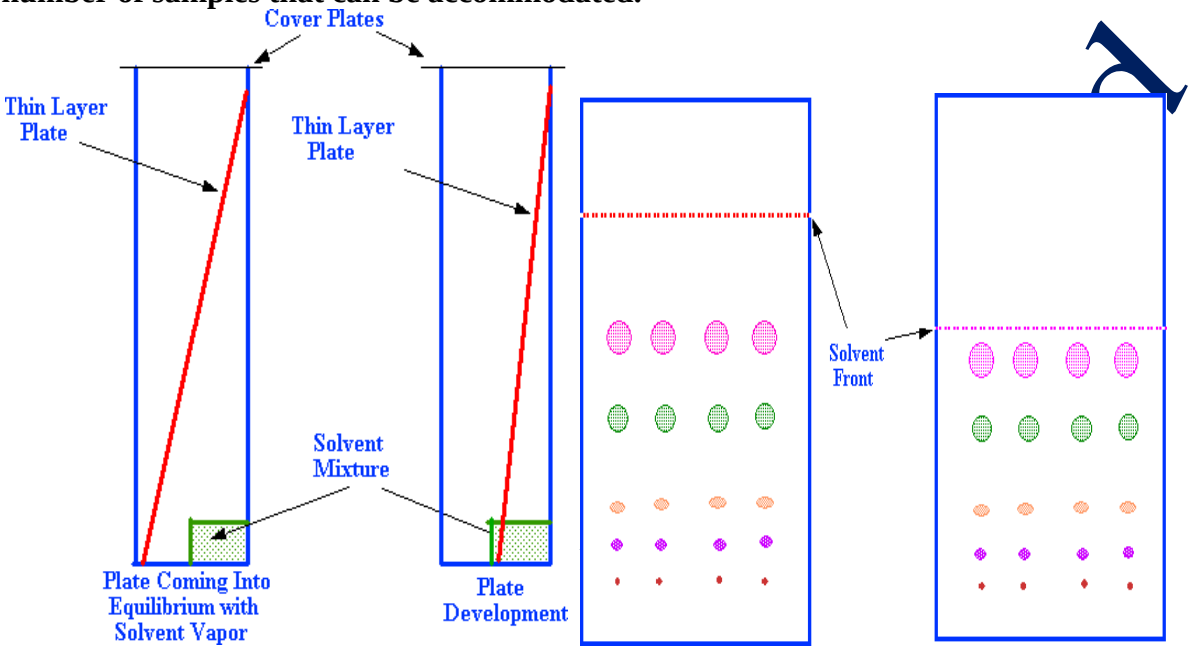
Typical thin-layer separations are performed on a glass plate that is coated with a thin and adherent layer of finely divided particles; this layer constitutes the stationary phase. The particles are similar to those described in the discussion of adsorption, normal- and reversed-phase partition, ion-exchange, and size-exclusion column chromatography. Mobile phases are also similar to those employed in high performance liquid chromatography.

Preparation of Thin-Layer Plates:

A thin-layer plate is prepared by spreading an aqueous slurry of the finely ground solid onto the clean surface of a glass or plastic plate or a microscope slide. Often, a binder is incorporated into the slurry to enhance adhesion of the solid particles to the glass and to one another. The plate is then allowed to stand until the layer has set and adheres tightly to the surface; for some purposes, it may be heated in an oven for several hours. Plate development is the process in which a sample is carried through the stationary phase by a mobile phase. The most common way of developing a plate is to place a drop of the

sample near one edge of the plate (most plates have dimensions of 5 x20 or 20 x20 cm) and mark its position with a pencil. After the sample solvent has evaporated, the plate is placed in a closed container saturated with the vapors of the developing solvent. One end of the plate is immersed in the developing solvent, with care being taken to avoid direct contact between the sample and the developer (Figure). After the developer has traversed one half or two thirds of the length of the plate, the plate is removed from the container and is dried. The positions of the components are then determined in any of several ways.

(a) Ascending-flow developing chamber. (b) Horizontal flow developing chamber, in which samples are placed on both ends of the plate and developed toward the middle, thus doubling the number of samples that can be accommodated.



Two-dimensional thin-layer chromatogram (silica gel) of some amino acids. Solvent A: toluene/2-chloroethanol/pyridine. Solvent B: chloroform/benzyl alcohol/acetic acid. Amino acids: (l) aspartic acid, (2) glutamic acid, (3) serine, (4) f3-alanine, (5) glycine, (6) alanine, (7) methionine, (8) valine, (9) isoleucine, (l0) cysteine.

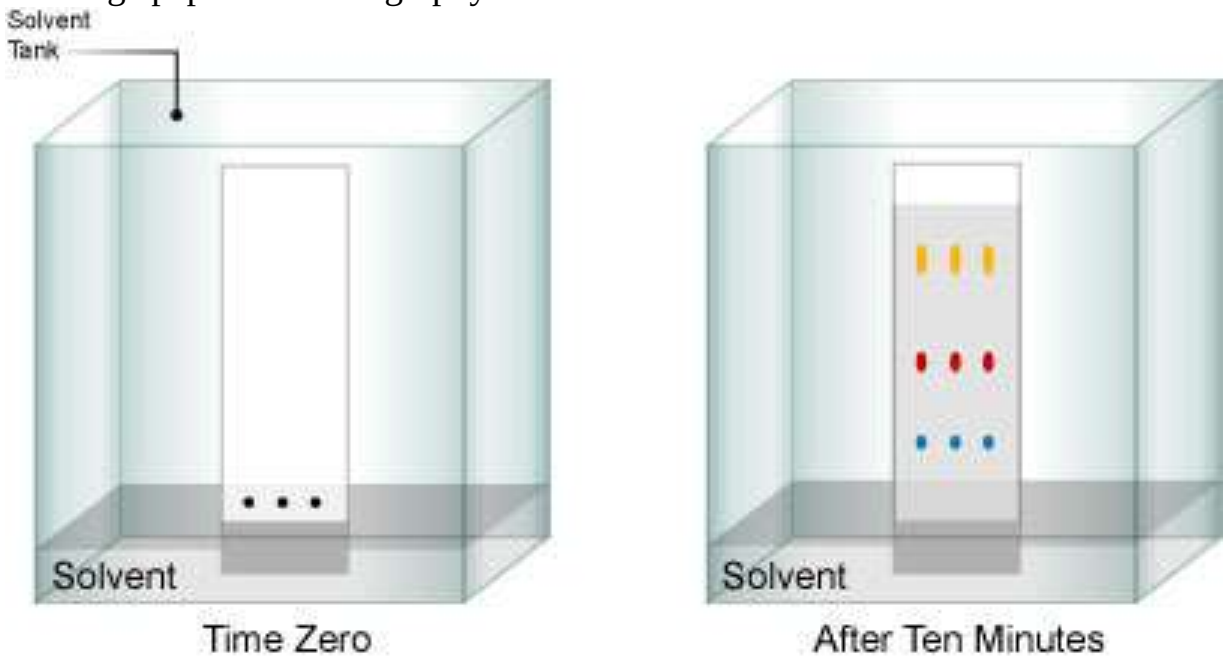
Locating Analytes on the Plate:

Several methods are employed to locate sample components after separation. Two common methods that can be applied to most organic mixtures involve spraying with a solution of iodine or sulfuric acid, both of which react with organic compounds to yield dark products. Several specific reagents (such as ninhydrin) are also useful for locating separated species. After development, the plate is examined under ultraviolet light. The sample components quench the fluorescence of the material so that all of the plate fluoresces except where the nonfluorescing sample components are located.

Paper Chromatography:

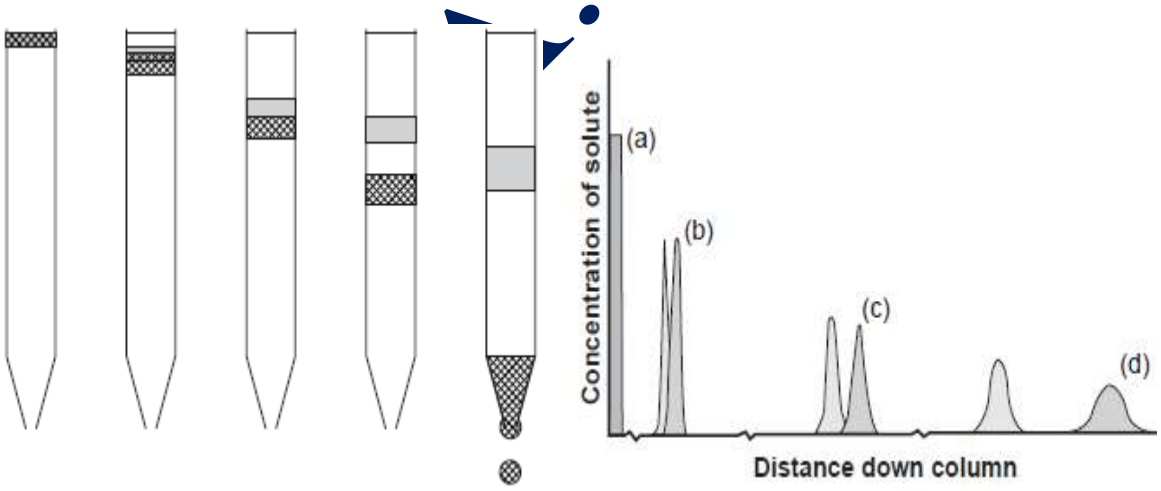
Separations by paper chromatography are performed in the same way as those on thin-layer plates. The papers are manufactured from highly purified cellulose, with close control over porosity and thickness. Such papers contain sufficient adsorbed water to make the stationary phase aqueous. Other liquids can be made to displace the water,

however, thus providing a different type of stationary phase. For example, paper treated with silicone or paraffin oil permits reversed-phase paper chromatography, in which the mobile phase is a polar solvent. Also available commercially are special papers that contain an adsorbent or an ion-exchange resin, thus permitting adsorption and ion-exchange paper chromatography.



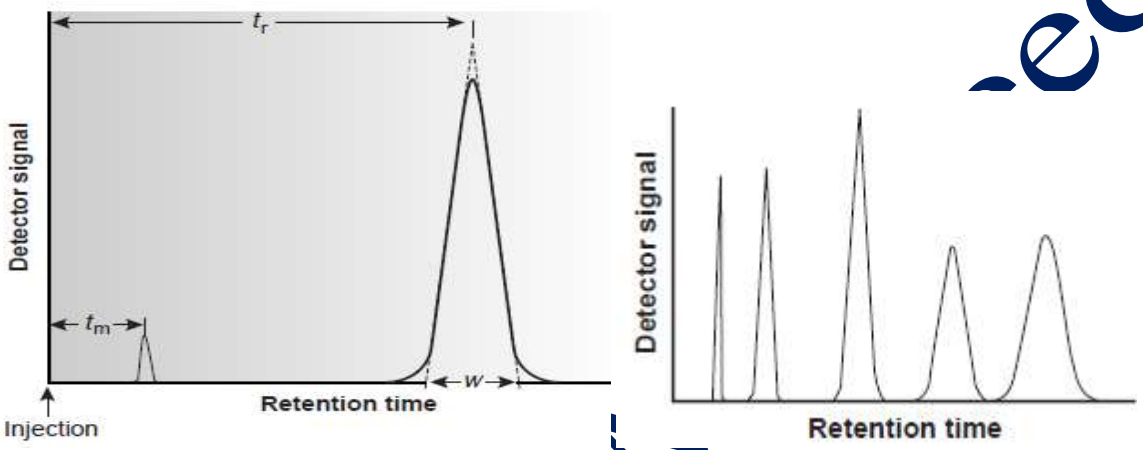
Column Chromatography:

Of the two methods for bringing the stationary and mobile phases into contact, the more important is column chromatography. A typical column chromatography experiment is outlined in Figure .



The progress of a chromatographic separation is monitored with a suitable detector situated at the end of the column. A plot of the detector signal as a function of time or volume of eluted mobile phase is known as a **chromatogram.** A chromatographic peak may be characterized in many ways. The **retention time,** t_r, is the elapsed time from the introduction of the solute to the peak maximum. The retention time also can be measured indirectly as the volume of mobile phase eluting between the solute introduction and the

appearance of the solute peak maximum. This is known as the **retention volume, V_r**. The second important parameter is the chromatographic peak width at the baseline, **w**. As shown in Figure, **baseline width** is determined by the intersection with the baseline of tangent lines drawn through the inflection points on either side of the chromatographic peak. Baseline width is measured in units of time or volume, depending on whether the retention time or retention volume is of interest. The figure also shows a small peak eluted soon after the sample is injected into the mobile phase. This peak results from solutes that move through the column at the same rate as the mobile phase. Since these solutes do not interact with the stationary phase, they are considered nonretained. The time or volume of mobile phase required to elute nonretained components is called the column's **void time, t_m**, or **void volume V_m.**



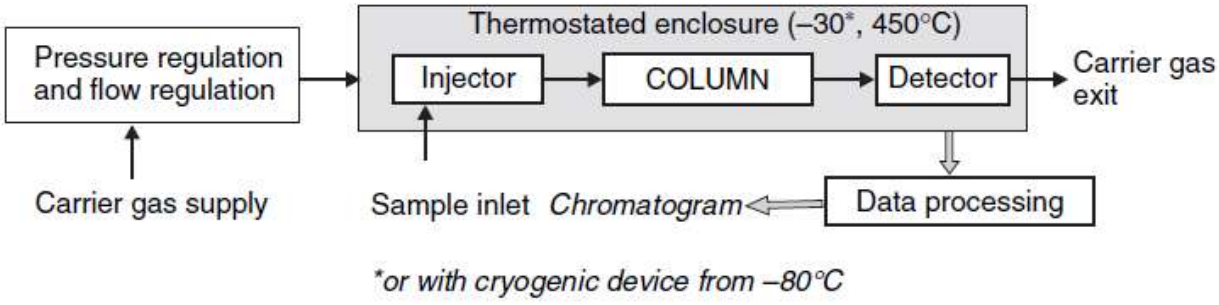
Gas chromatography:

In gas chromatography, the components of a vaporized sample are separated as a consequence of being partitioned between a mobile gaseous phase and a liquid or a solid stationary phase held in a column. In performing a gas chromatographic separation, the sample is vaporized and injected onto the head of a chromatographic column. Elution is brought about by the flow of an inert gaseous mobile phase. In contrast to most other types of chromatography, the mobile phase does not interact with the molecules of the analyte; its only function is to transport the analyte through the column. Two types of gas chromatography are encountered: **gas-liquid chromatography** (GLC) and **gas-solid chromatography** (GSC). Gas-liquid chromatography finds widespread use in all fields of science; its name is usually shortened to **gas chromatography** (GC). Gas-solid chromatography is based on a solid stationary phase in which retention of analytes occurs because of physical adsorption.

Components of a GC installation:

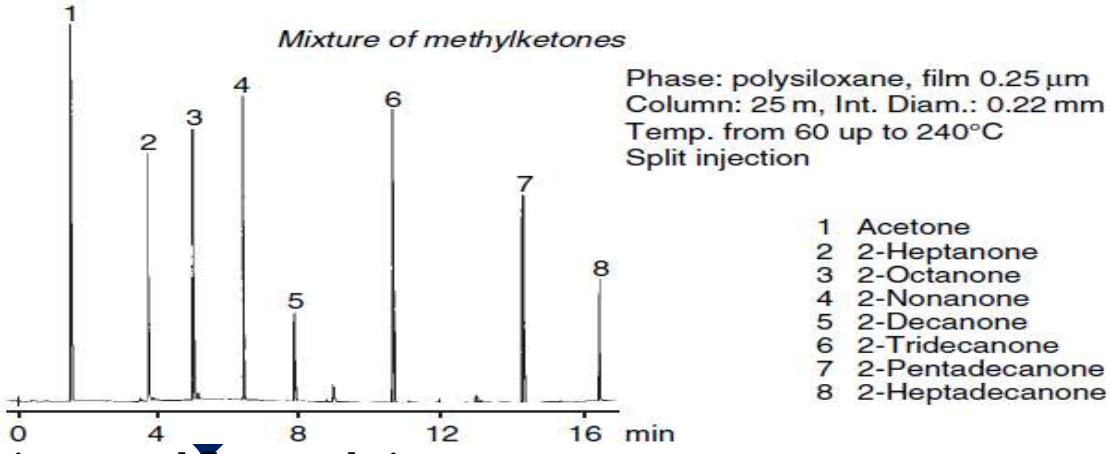
A gas chromatograph is composed of several components within a special frame.

These components include the injector, the column and the detector, associated with a thermostatically controlled oven that enables the column to attain high temperatures (Figure).



The mobile phase that transports the analytes through the column is a gas referred to as the **carrier gas**. The carrier gas flow, which is precisely controlled, enables reproducibility of the retention times. The analysis starts when a small quantity of sample is introduced as either liquid or gas into the injector, which has the dual function of vaporizing the sample and mixing it with the gas flow at the head of the column. The column is usually a narrow-bore tube which coils around itself with a length that can vary from 1 to over 100 m, depending upon the type and the contents of the stationary phase. The column, which can serve for thousands of successive injections, is housed in a thermostatically controlled oven. At the end of the column, the mobile phase (carrier gas), passes through a detector before it exits to the atmosphere.

In GC there are four operational parameters for a given stationary phase: L, length of the column, ū, velocity of the mobile phase (which affects the theoretical efficiency N), T, temperature of the column and, β phase ratio, which affects the retention factor k. The operating condition of the chromatograph allows modifications in terms of T and ū and therefore affects both the efficiency of the column and the retention factors.

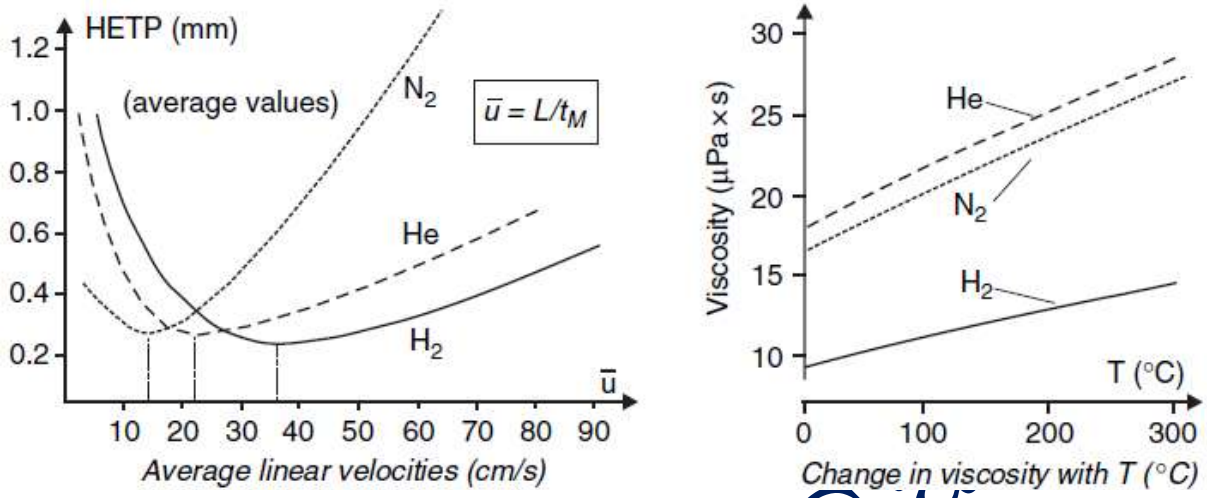


Carrier gas and flow regulation:

The mobile phase is a gas (helium, hydrogen or nitrogen), either drawn from a commercially available gas cylinder or obtained, in the case of hydrogen or nitrogen, from an on-site generator, which provides gas of very high purity. The carrier gas must be free of all traces of hydrocarbons, water vapor and oxygen, because all of these may deteriorate polar stationary phases or reduce the sensitivity of detectors. For these reasons the carrier gas system includes filters containing a molecular sieve to remove water and a reducing agent for other impurities. By contrast, the viscosity of the carrier gas and its flow rate have an effect on the analytes dispersion in the stationary phase and on their

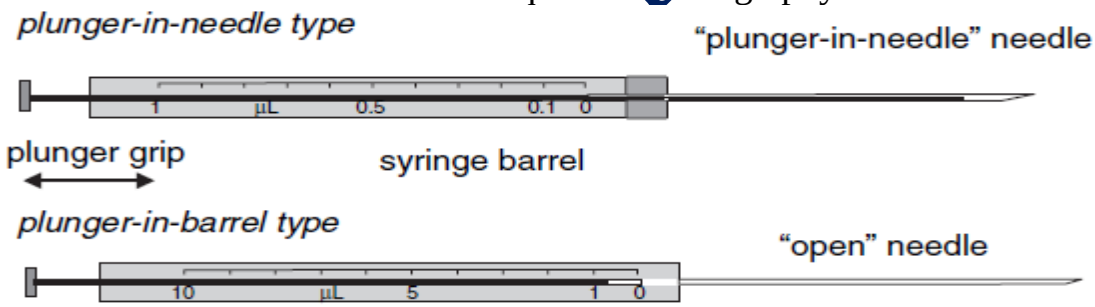
diffusion in the mobile phase (Van Deemter's equation), and by consequence upon the efficiency ***N*** and the sensitivity of detection (Figure).

The pressure at the head of the column (several tens to hundreds of kPa) is stabilized either mechanically or through an electronic pressure control (*EPC*) in order that the flow rate remains constant at its optimal value.



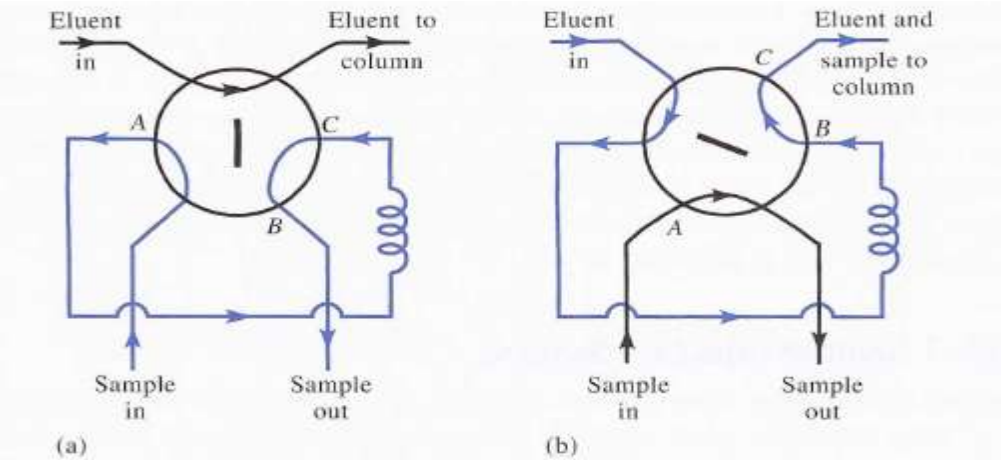
Sample introduction:

The most common injection method is where a microsyringe is used (Figure) to inject a very small quantity of sample in solution (e.g. 0.5 μL), through a rubber septum into a flash vaporizer port at the head of the column. For gaseous samples, loop injectors are used similar to those described in liquid chromatography.



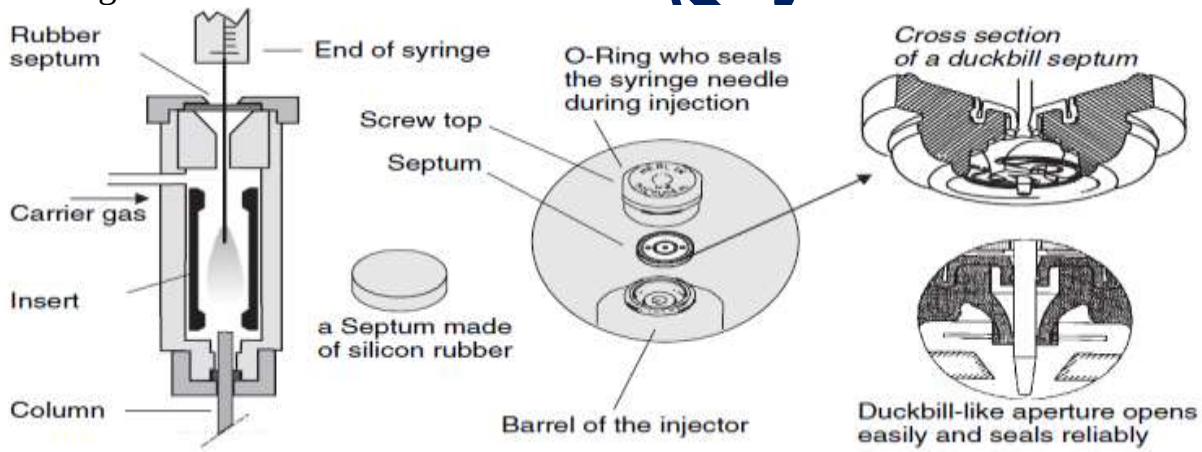
Injectors:

The injector, which is the sample entrance to the chromatograph, has different functions. Besides its role as an inlet for the sample, it must vaporize, mix with the carrier gas and bring about the sample at the head of the column. The characteristics of the injectors, as well as the modes of injection, differ according to the column type. The use of an automatic injection system can significantly enhance measurement precision.



Direct vaporization injector:

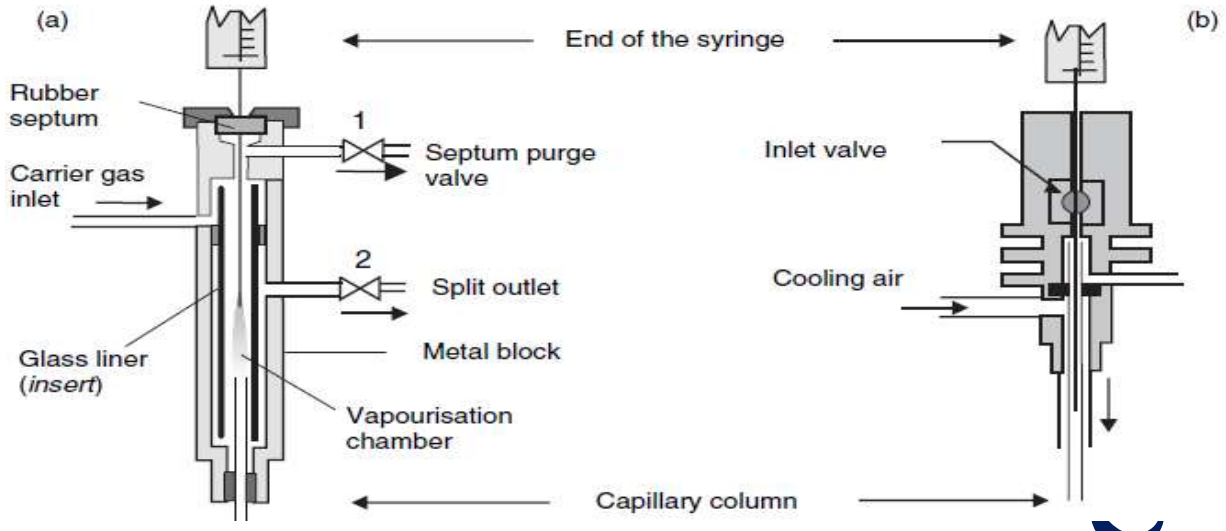
For packed and megabore columns, which typically use a flow rate of about 10 ml/min, direct vaporization is a simple way to introduce the sample. Any model of this type comprises a metal tube with a glass sleeve (called the insert). It is heated to the average boiling temperature of the compounds being alalysis. The needle of the micro-syringe containing the sample pierces the septum, made of silicone rubber, which closes the end of the injector. The other end, also heated, is connected directly to the column (Figure). Once all of the liquid plug has been introduced with a syringe it is immediately volatilized and enters the column entirely within a few seconds, swept along by the carrier gas.



Split/splitless injector:

For **capillary columns** able to handle only a small capacity of the sample, even the smallest volume that it is possible to inject with a micro-syringe 0.1µL, can saturate the column. Special injectors are used which can operate in two modes, with or without flow splitting (also called split or splitless). The split ratio typically varies between 1: 20 and 1: 500. Only the smallest fraction, containing an amount of sample equal to the ratio of division, will penetrate into the column.

$$\text{Split ratio} = \frac{(\text{split outlet flow rate} + \text{column outlet flow rate})}{\text{column outlet flow rate}}$$



Programmed temperature vaporization injector:

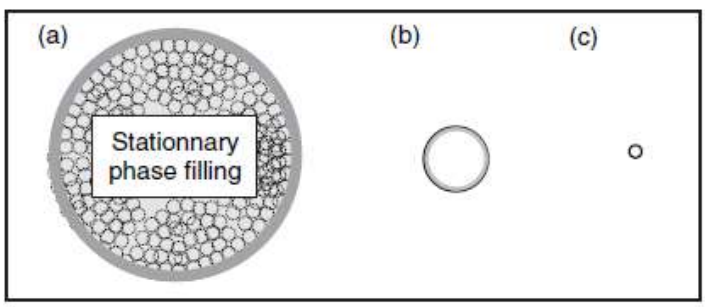
This injector, named PTV (programmed temperature vaporizer), is conceptually similar to the split/splitless model. The temperature of the injection chamber can be programmed to effect a gradient, e.g. from 20 up to 300 ^{o}C, in a few tens of seconds (Figure). So, the advantages of the split/splitless injection are combined with those of the cold injected onto the column. It becomes possible to inject greater volumes with standard syringes avoiding needle-induced discrimination. Furthermore, compounds having low boiling points (particularly solvents) can be eliminated. The three principal modes of operation are named split cold injection, splitless cold injection and injection with elimination of solvent.

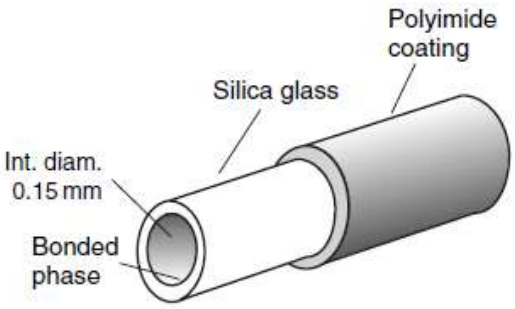
Thermostatically controlled oven:

The gas chromatograph comprises an oven with sufficient volume to hold one or two columns easily and which can heat up to more than 400^{o}C. A weak thermal inertia permits a rapid but controlled temperature climb (gradient able to attain 100 ^{o}C/ min). The temperature must be controlled to within 0.1 ^{o}C in order to get reproducible separations in isothermal or temperature programmed modes. By installation of a cryogenic valve fed with N_2 or CO_2 in the liquid state, the oven can be regulated at low temperature.

Columns:

There are two column types, which differ in their performance: **packed** columns and **capillary** columns (Figure).

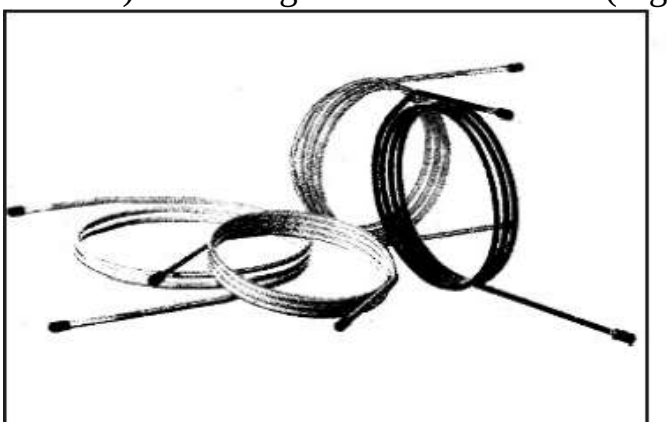


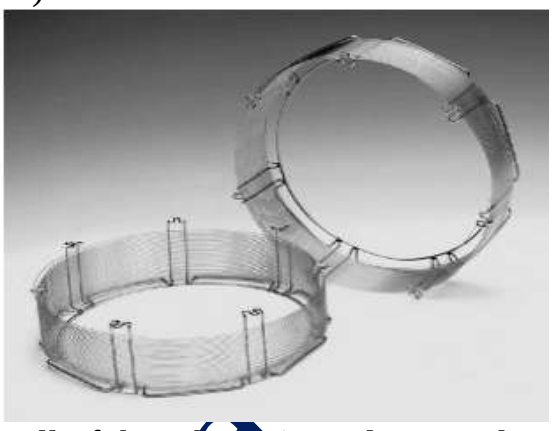


For packed columns the stationary phase is deposited or bonded by chemical reaction onto a porous support. For capillary columns a thin layer of stationary phase is deposited onto, or bound to the inner surface of the column.

Packed columns:

These columns, less commonly used today, have diameters of 1/8 or 1/4 inch (3.18 and 6.35mm) and a length of between 1–3m (Figures).





Manufactured from steel or glass, the internal wall of the tube is treated to avoid catalytic effects with the sample. They can withstand a carrier gas flow rate within the range 10 – 40 ml/min. They contain an inert and stable porous support on which the stationary phase can be impregnated or bounded (between 3 and 20 percent).

Capillary columns (open tubular):

They are usually made of the highest purity **fused silica** obtained by the combustion of tetrachlorosilane $SiCl_4$ in an oxygen-rich atmosphere. The internal diameter of the tube used for these columns varies from 100 to 530μm, its thickness is 50µm and the length is about 12 to 100 m. These columns are rendered flexible by the application of a polyimide outer coating, a thermally stable polymer T_{max} =370 ^{o}C or a thin aluminum film. They have the advantages of physical strength and can be wound into coils around a lightweight metallic circular support (Figure).

Properties and Characteristics of Typical GC Columns

	Type of Column			
	FSOT*	WCOT†	SCOT‡	Packed
Length, m	10–100	10–100	10–100	1–6
Inside diameter, mm	0.1–0.3	0.25–0.75	0.5	2–4
Efficiency, plates/m	2000–4000	1000–4000	600–1200	500–1000
Sample size, ng	10–75	10–1000	10–1000	10–10^6
Relative pressure	Low	Low	Low	High
Relative speed	Fast	Fast	Fast	Slow
Flexible?	Yes	No	No	No
Chemical inertness	Best	→	→	Poorest

*Fused-silica open tubular column.
†Wall-coated open tubular column.
‡Support-coated open tubular column (also called porous layer open tubular or PLOT).

Stationary phases:

For packed columns, for which impregnation techniques are very simple, over 100 stationary phases of various types have been proposed in the literature. On other hand, for bonded phase capillary columns the choice of stationary phase is limited because the generation of the film at the surface of the column requires a different principle than impregnation. The current phases correspond in principle to two families: the **polysiloxanes** and the **polyethylene glycols**. Each of these phases can be used between a minimum temperature beneath which concentration equilibria are too slow to occur, and a maximum temperature above which degradation of the polymer occurs. This high limit depends on the film thickness and the nature of the polymer.

Liquid Stationary Phases:

Desirable properties of the immobilized liquid phase in a gas-liquid chromatographic column include (1) low volatility (ideally, the boiling point of the liquid should be at least 100°C higher than the maximum operating temperature for the column); (2) thermal stability; (3) chemical inertness; and (4) solvent characteristics such that k and α values for the solutes to be resolved fall within a suitable range. To have a reasonable residence time in the column, an analyte must show some degree of compatibility (solubility) with the stationary phase. Here, the principle of "like dissolves like" applies, where "like" refers to the polarities of the analyte and the immobilized liquid. Polar stationary phases contain functional groups such as -CN, -CO, and -OH. Hydrocarbon-type stationary phases and dialkylsiloxanes are nonpolar, whereas polyester phases are highly polar. Polar analytes include alcohols, acids, and amines; solutes of medium polarity include ethers, ketones, and aldehydes. Saturated hydrocarbons are non polar. Generally, the polarity of the stationary phase should match that of the sample components. When the match is good, the order of elution is determined by the boiling point of the eluents.

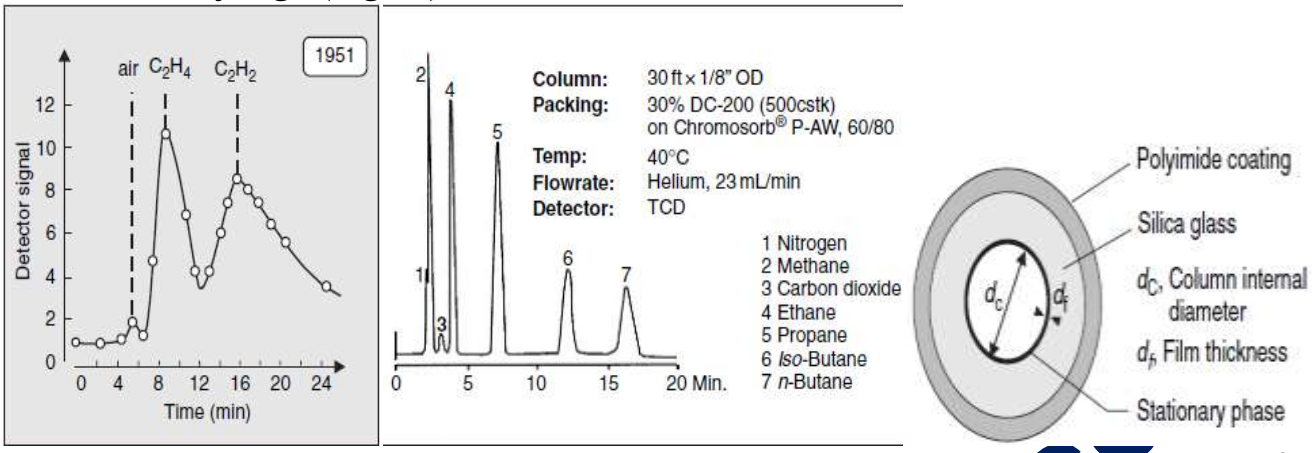
Some Common Liquid Stationary Phases for Gas-Liquid Chromatography

Stationary Phase	Common Trade Name	Maximum Temperature, °C	Common Applications
Polydimethyl siloxane	OV-1, SE-30	350	General-purpose nonpolar phase, hydrocarbons, polynuclear aromatics, steroids, PCBs
5% Phenyl-polydimethyl siloxane	OV-3, SE-52	350	Fatty acid methyl esters, alkaloids, drugs, halogenated compounds
50% Phenyl-polydimethyl siloxane	OV-17	250	Drugs, steroids, pesticides, glycols
50% Trifluoropropyl-polydimethyl siloxane	OV-210	200	Chlorinated aromatics nitroaromatics, alkyl substituted benzenes
Polyethylene glycol	Carbowax 20M	250	Free acids, alcohols, ethers, essential oils, glycols
50% Cyanopropyl-polydimethyl siloxane	OV-275	240	Polyunsaturated fatty acids, rosin acids, free acids, alcohols

Solid stationary phases:

These phases are constituted from a variety of adsorbent materials: silica or alumina deactivated by mineral salts, molecular sieves, porous glass, graphite (e.g. Chromosorb ® 100, Porapak®). Capillary columns made by deposition of these materials in the form of a fine porous layer are called PLOT. They are employed to separate gaseous or highly volatile samples. Columns containing graphitized carbon black have been developed for

the separation of N_2, CO, CO_2 and very light hydrocarbons. The efficiency of these columns is very high (Figure).



Historically, silica gel, a thermostable material and insensitive to oxygen, was one of the first compounds to serve as a solid stationary phase for GC columns (Figure).

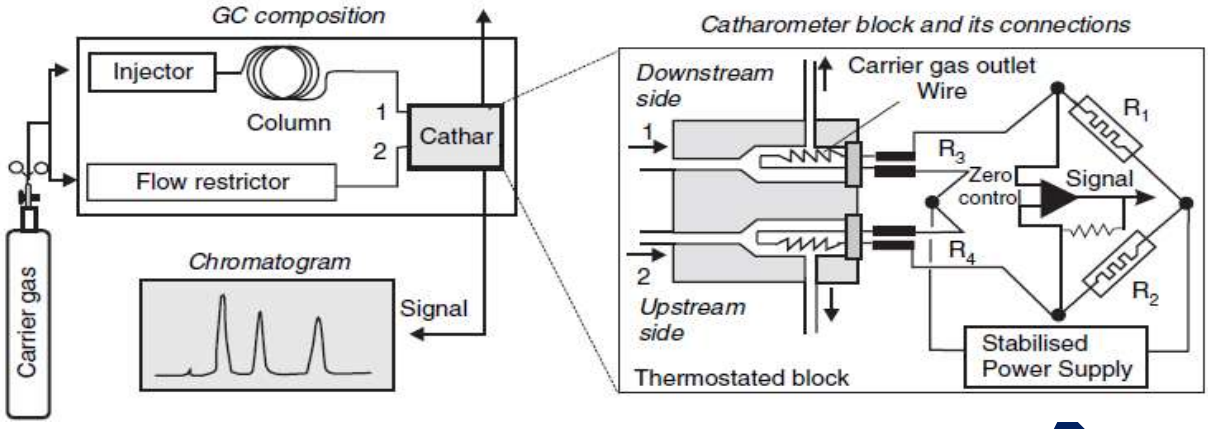
Principal gas chromatographic detectors:

Detectors are classified into two groups depending on whether they lead only to single information such as the retention time and those which yield, besides retention time, structural information of the analyte concerned. For this reason, some gas chromatographs are equipped with two or three detectors linked in series. Nonetheless, the response of all detectors is dependent on the molar concentration or on the mass of analyte in the carrier.The ideal situation to quantify an analyte would be to have a detector which sees only this analyte. They can be also categorized as *destructive* or *non-destructive* of the analytes. The ideal detector for gas chromatography has the following characteristics:

1. Adequate sensitivity. In general, the sensitivities of present-day detectors lie in the range of 10^{-8} to 10^{-15} g solute/s.
2. Good stability and reproducibility.
3. A linear response to solutes that extends over several orders of magnitude.
4. A temperature range from room temperature to at least 400°C.
5. A short response time that is independent of flow rate.
6. High reliability and ease of use. The detector should, to the greatest extent possible, be foolproof in the hands of inexperienced operators.
7. Similarity in response toward all solutes or, alternatively, a highly predictable and selective response toward one or more classes of solutes.
8. Nondestructive of sample.

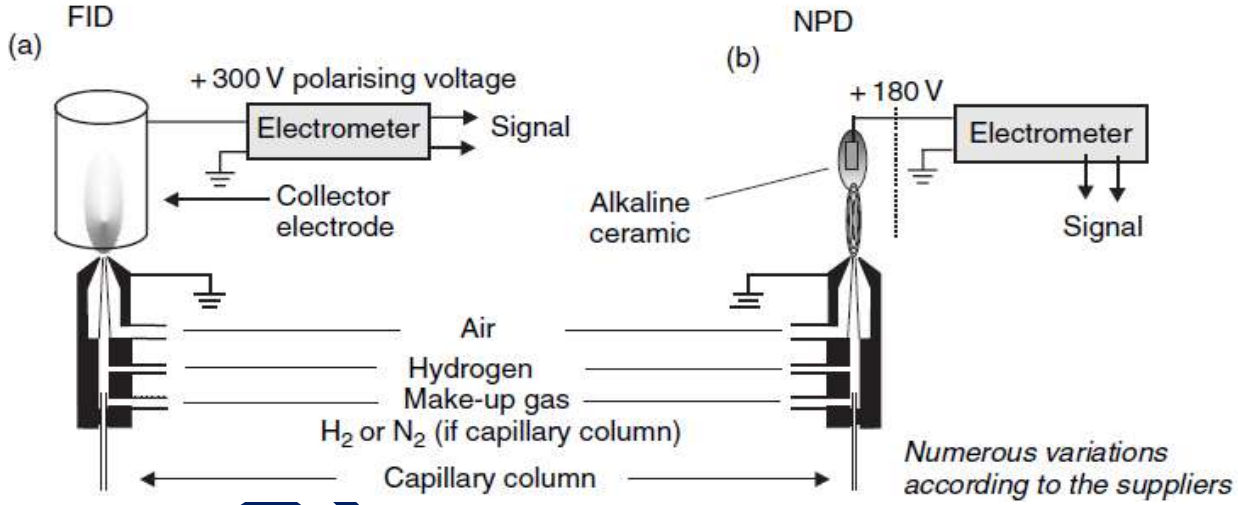
Thermal conductivity detector (TCD):

Its operating principle relies on the thermal conductivity of gas mixtures as a function of their composition.



Flame ionization detector (FID):

The gas flow issuing from the column passes through the flame of a small burner fed by a mixture of hydrogen and air. The detector destroys the organic compound present whose combustion results in the release of ions and charged particles responsible for the passage of a very weak current 10^{-12} A° between two electrodes (pd of 100 to 300 V). One end of the burner, held at ground potential, acts as a polarization electrode while the second electrode, called the collector, surrounds the flame rather like a collar. An electrometer amplifies the signal to a measurable voltage (Figure).



Nitrogen phosphorus detector (NPD):

Compared with the FID, this thermoionic detector has a smaller flame in which the catalytic decomposition of compounds containing nitrogen (N), or phosphorus (P) yields, fairly specifically, negative ions which are received by a collector electrode.

Electron capture detector (ECD):

This selective detector is considered to be excellent for trace analysis when analytes contain halogen atoms or nitro groups. A flow of nitrogen gas, which has been ionized by electrons generated from a low energy β^-radioactive source (a few mCi of $_{63}Ni$) passes between two electrodes maintained at a voltage differential of around 100V (Figure). At equilibrium, a base current I_o is generated, mainly due to free and very mobile electrons. If molecules (M), containing an electrophore such halogen (F, Cl, Br), cross the zone

between the two electrodes, they capture thermally excited electrons to form heavy negative ions, which by consequence are much less mobile, leading to a decrease in the signal.

$$N_2 \xrightarrow{\beta^-} N_2^+ + e^-$$

$$M + e^- \longrightarrow M^-$$

$$M^- + N_2^+ \longrightarrow M + N_2$$

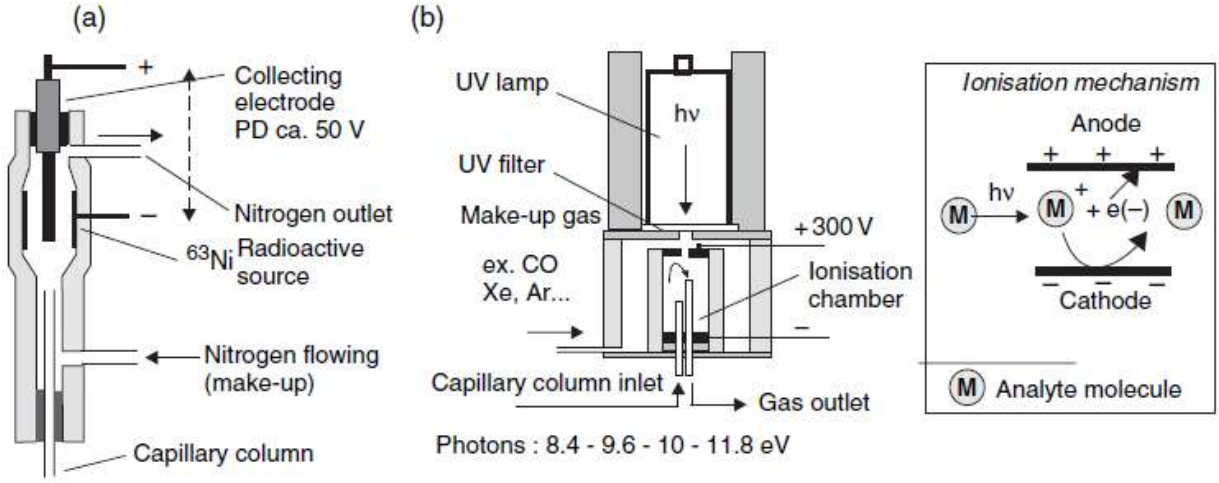


Photo-ionization detector (PID):

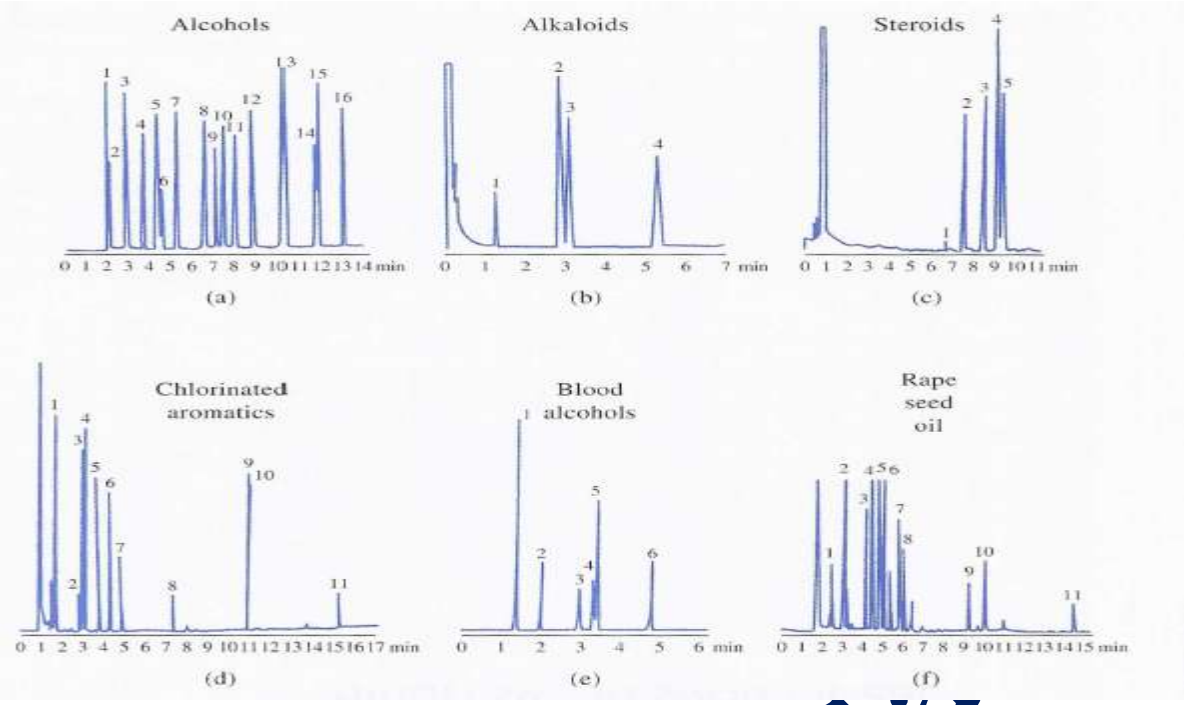
This detector is fairly selective, but it has only a narrow range of application, convenient for hydrocarbons as well as for S or P derivatives. This detector can function at more than 400 ^{o}C and is not destructive since the ionization is reversible and affects only a small fraction of the molecules of each compound passing through.

Gas Chromatographic Detectors

Type	Applicable Samples	Typical Detection Limit
Flame ionization	Hydrocarbons	0.2 pg/s
Thermal conductivity	Universal detector	500 pg/mL
Electron capture	Halogenated compounds	5 fg/s
Mass spectrometer	Tunable for any species	0.25–100 pg
Thermionic	Nitrogen and phosphorous compounds	0.1 pg/s (P) 1 pg/s (N)
Electrolytic conductivity (Hall)	Compounds containing halogens, sulfur, or nitrogen	0.5 pg Cl/s 2 pg S/s 4 pg N/s
Photoionization	Compounds ionized by UV radiation	2 pg C/s
Fourier transform IR	Organic compounds	0.2 to 40 ng

Applications of Gas – liquid Chromatography:

Gas-liquid chromatography is applicable to species that are appreciably volatile and thermally stable at temperatures up to a few hundred degrees Celsius. Consequently, gas chromatography has been widely applied to the separation and determination of the components in a variety of sample types. Figure shows chromatograms for a few such applications.



Qualitative Analysis

Gas chromatograms are widely used to establish the purity of organic compounds. Contaminants, if present, are revealed by the appearance of additional peaks; the areas under these peaks provide rough estimates of the extent of contamination. The technique is also useful for evaluating the effectiveness of purification procedures. In theory, GC retention times should be useful for identifying components in mixtures.

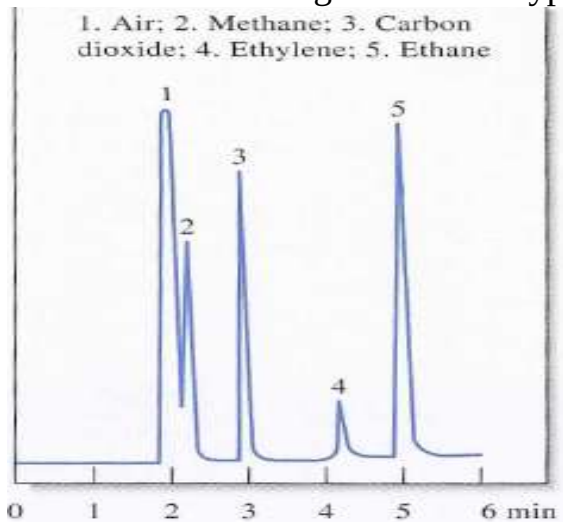
Quantitative Analysis

Gas chromatography owes its enormous growth in part to its speed, simplicity, relatively low cost, and wide applicability to separations. Quantitative GC is based on comparison of either the height or the area of an analyte peak with that of one or more standards. If conditions are properly controlled, both these parameters vary linearly with concentration. Peak area is independent of the broadening effects discussed earlier. From this standpoint, therefore, area is a more satisfactory analytical parameter than peak height. Peak heights are more easily measured, however, and, for narrow peaks, more accurately determined. Most modern chromatographic instruments are equipped with computers that provide measurements of relative peak areas. If such equipment is not available, a manual estimate must be made.

Gas – Solid Chromatography:

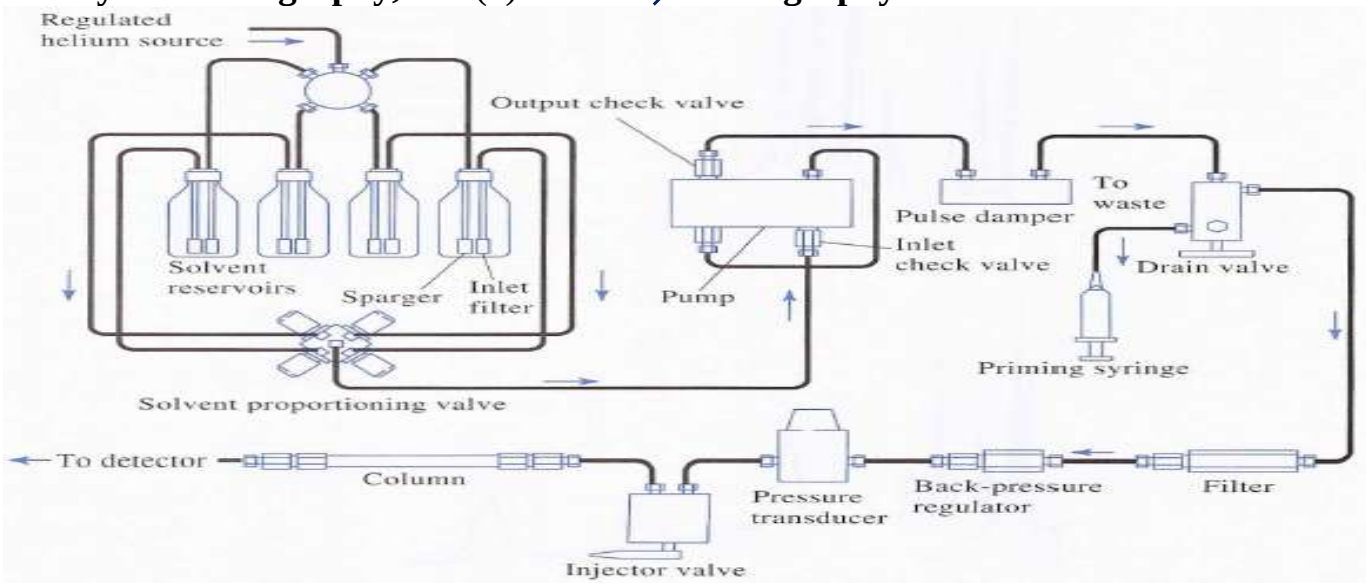
Gas-solid chromatography is based on adsorption of gaseous substances on solid surfaces. Distribution coefficients are generally much larger than those for gas liquid chromatography. Consequently, gas-solid chromatography is useful for the separation of species that are not retained by gas-liquid columns, such as the components of air, hydrogen sulfide, carbon disulfide, nitrogen oxides, carbon monoxide, carbon dioxide, and the rare gases. Gas-solid chromatography is performed with both packed and open tubular columns. For the latter, a thin layer of the adsorbent is affixed to the inner walls

of the capillary. Such columns are sometimes called porous-layer open tubular columns or PLOT columns. Figure shows a typical application of a PLOT column.



High-performance liquid chromatography:

High-performance liquid chromatography (HPLC) is the most versatile and widely used type of elution chromatography. The technique is used by chemists to separate and determine species in a variety of organic, inorganic, and biological materials. In liquid chromatography, the mobile phase is a liquid solvent containing the sample as a mixture of solutes. The types of high-performance liquid chromatography are often classified by separation mechanism or by the type of stationary phase. These include (1) **partition, or liquid-liquid, chromatography;** (2) **adsorption, or liquid-solid, chromatography;** (3) **ion-exchange, or ion chromatography;** (4) **size-exclusion chromatography;** (5) **affinity chromatography,** and (6) **chiral chromatography.**



General concept of an HPLC system:

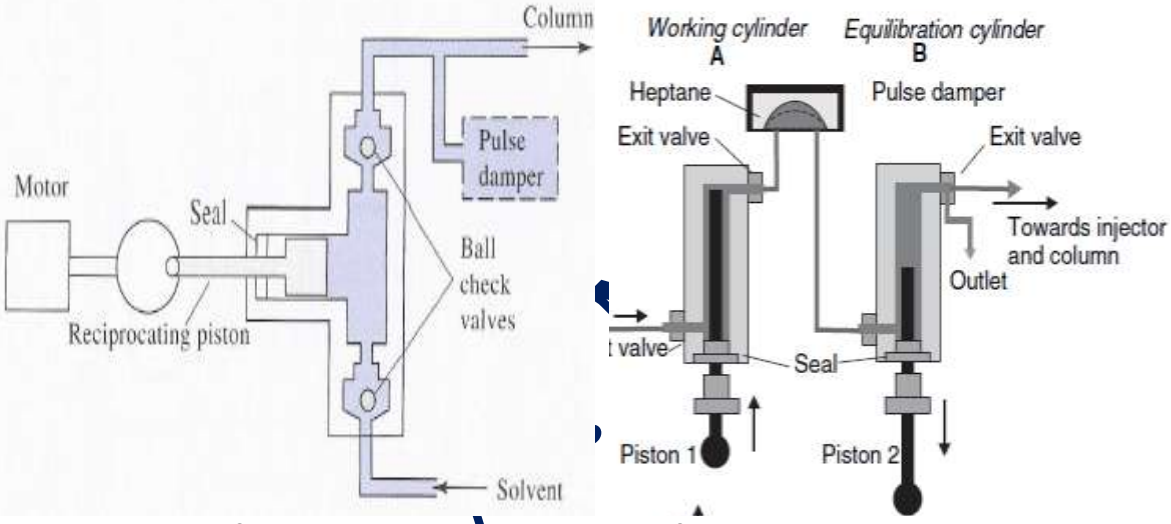
An HPLC installation is composed of several specialized units which can be found as separate entities or be integrated within a common framework, usually for reasons of hindrance (Figure). A tubing system of very small internal diameter (0.1mm) assures the circulation of the mobile phase between the modules. These transfer tubes are made of

stainless steel or of PEEK® (polyether-ether ketone), a colored and flexible polymer, able to resist the common solvents under high pressure (up to 350 bars).

Pumps and gradient elution:

Pumps:

All HPLC systems include at least one pump to force the mobile phase through the column whose packing is fairly compact. The result of this is a pressure increase at the injector which can attain 20000 kPa (200 bars) depending upon the flow rate imposed upon the mobile phase, its viscosity, and the size of the particles of the stationary phase. Pumps are designed in order to maintain a stable flow rate, avoiding pulsations even when the composition of the mobile phase varies. These flow rate metered pumps contain, in general, two pistons in series, working in opposition, to avoid interruptions to the flow rate (Figure). The pistons and valves of the pumps are made of sapphire, agate, Teflon or special alloys. It is obvious that these pumps deliver a series of 'pulses' of the mobile phase. The perfecting of flow rate regulation is achieved by the insertion of a pressure (or pulse) damper, between the pump(s) and the injector.



The presence of a non-negligible quantity of ambient gases (N_2, O_2, CO_2), dissolved in the solvents, can perturb the separations by modification of the compressibility of the mobile phases which leads to the eventual formation of bubbles. The solvents are therefore degassed either by ultrasound, rapid helium bubbling, or by diffusion for which they pass along a polymeric tube, of small diameter, permeable to gas, working like a membrane. These pumps are associated with a mixing chamber and are located either just before or immediately following. They are capable of delivering an eluent of fixed (**isocratic mode**), or of variable composition to create an **elution gradient**. For the second case the system must compensate for differences in solvent compressibility in order that the imposed composition be respected.

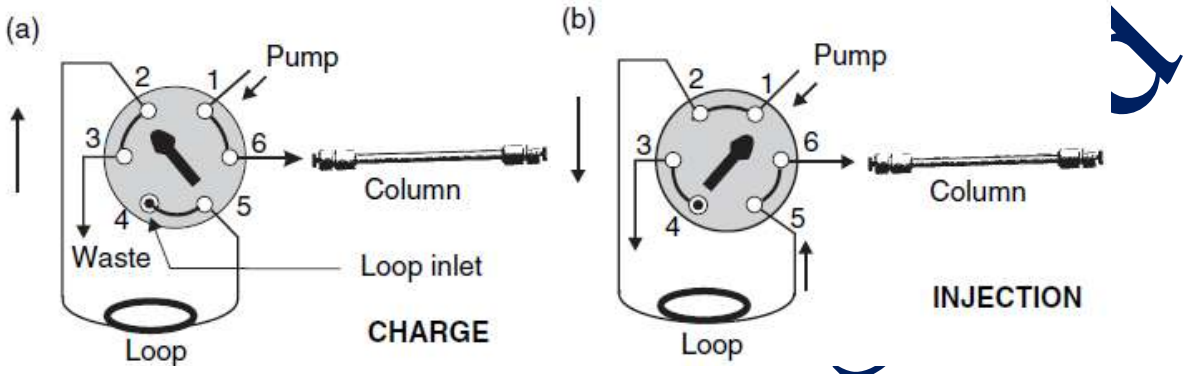
Injectors:

In HPLC, the injection of a precise volume of sample onto the head of the column must be made as fast as possible in order to cause the minimum disturbance to the dynamic regime of the mobile phase whose flow must be stable from column to detector. This is done by a special high pressure valve, either manual or motorized, possessing several

flow paths, which is situated just prior to the column (Figure). This must be a component of precision able to resist pressures greater than (30 000 kPa). The valve functions in two positions:

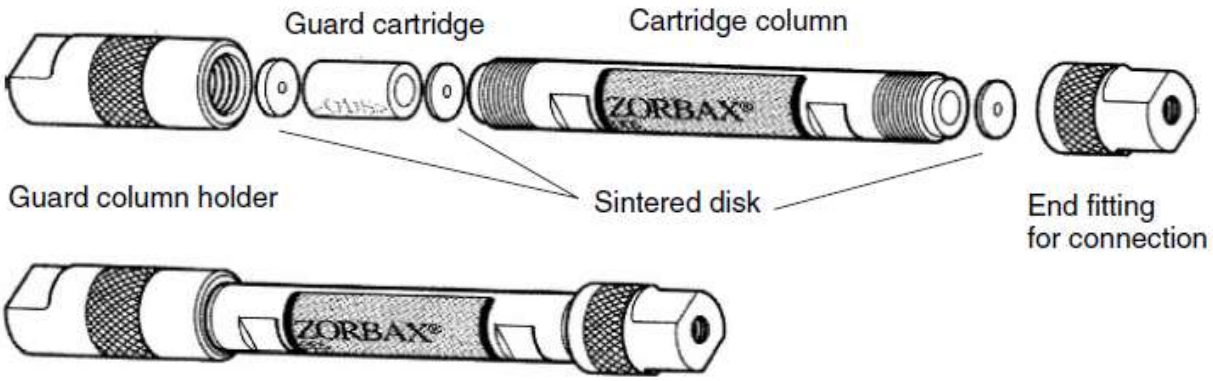
• In the **load** position only communication between the pump and the column is assured. The sample, contained in a solution, is introduced at atmospheric pressure with the aid of a syringe into a small tubular curved section named a loop.

• In the **inject** position, the sample (which is in the loop) is inserted into the flow of the mobile phase by the 60° rotation of a part of the valve, thus connecting the sample loop to the mobile phase circulation. Highly reproducible injections are attained only if the loop has been completely filled with the sample.



Columns:

The column is a straight stainless steel calibrated tube which measures between 3 and 15 cm in length and whose the inside wall is sometimes coated with an inert material such as glass or PEEK®. Stationary phase is held in the column between two porous discs situated at each of the extremities (Figure). The internal diameter of the column, for a long time standardized at 4.6mm (requiring a mobile phase flow rate of between 0.5 to 2 mL/min) is now often narrower. A wide choice of column now exists with names such as narrow-bore (2–4mm ID), microbore (1–2 mm), packed capillaries (< 1mm), for which the flow rate descends to a few µL/ min and therefore requires special pumps and detectors.



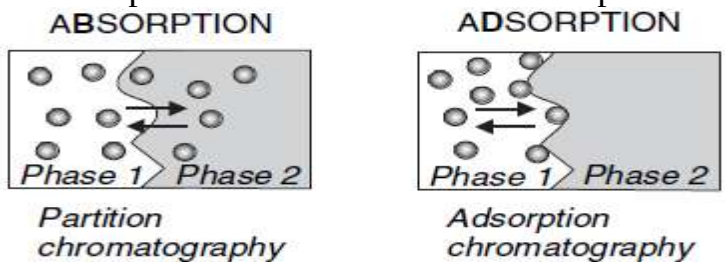
Stationary phases:

The stationary phase (SP) in contact with the mobile phase (MP) is the second medium with which the compounds initially dissolved in the mobile phase will interact. On the

column there will be as many particular associations of the three constituents [MP/compound/SP] as there are analytes in the sample. Many organic and inorganic materials have been tested for use as packing for columns.

Silica gel, the major material for current phases:

For the majority of applications **silica gel** still represents the basic material used to pack HPLC columns. It is a rigid, amorphous solid having a composition formula SiO_2 $(H_2O)_n$,quite different from natural crystalline silica (SiO_2). Silica gel is in the form of spherical particles, sometimes porous, with a diameter of between 2 to 5μm. This assures a compact and homogeneous packing of the column, which allows a regular circulation of the mobile phase without the formation of preferential routes in the column.

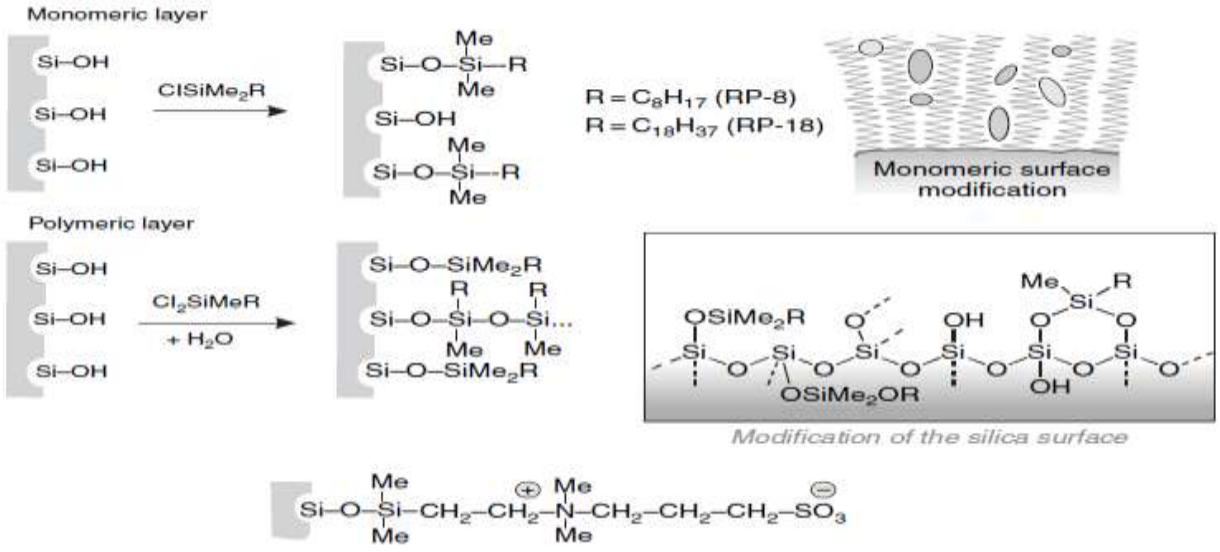


(The phenomena of adsorption and partition. Contrary to absorption, adsorption is a surface phenomenon. Separation is due to a series of adsorption/desorption steps. Absorption is due to solute partitioning between the two phases.)

Bonded silica:

Bonded silica gel, behave as a liquid in that the separation mechanism now depends on the **partition coefficient** instead of **adsorption coefficient**. These covalently bonded phases, whose polarity can be easily adjusted, constitute the bases of the reversed phase polarity partition chromatography or RP-HPLC, used in the majority of HPLC separations. Two types of syntheses lead to monomeric or polymeric bonded surfaces:

Monomeric phases (10–15µm thickness): They are obtained by reaction of an alkyl-monochlorosilane in the presence of an alkaline agent with surface silanol groups. The RP-8 (dimethyloctylsilane) or RP-18 (dimethyloctadecylsilane groups, ODS) are prepared in this way.



Polymeric phases: (25μm or greater thickness): Here a di- or trichlorosilane is used in the presence of water vapour which provokes a polymerization of the reactant in solution prior to deposit and bonding with the silica. A reticulated polymer layer is obtained.

Mobile phases:

The degree of interaction between the mobile phase and the stationary phase whether normal or reversed, affects the retention time of the analytes. In principle, the polarity of the stationary phase can lead to the following situations:

• If the stationary phase is polar, then the technique is said to be **normal phase chromatography** and a less polar mobile phase is used.

• If the stationary phase is non-polar, or only weakly polar then the technique is called **reversed phase chromatography** (RP-HPLC) – or chromatography on a hydrophobic phase. A polar mobile phase is selected (most commonly water with a modifying solvent such as methanol or acetonitrile).

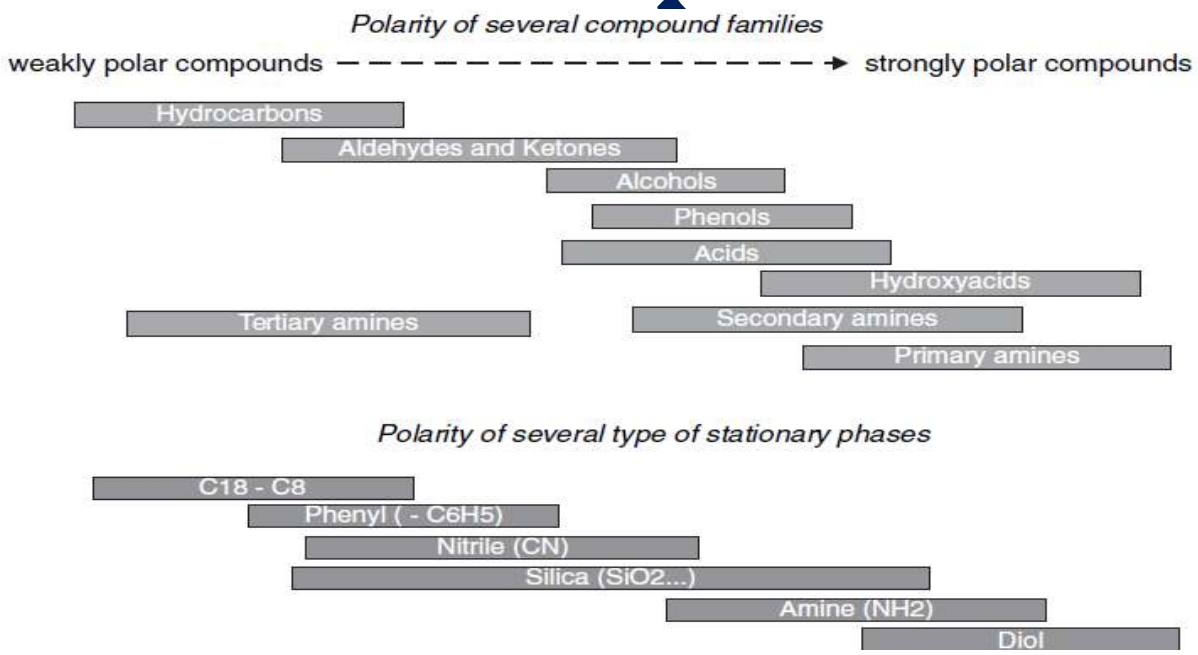
Factors affected the interaction between stationary phase and mobile phase:

Dipolar interactions when analyte and solvent both possess dipole moments.

Dispersion due to the attraction between molecules in proximity.

Dielectrics, which favour the solubility of ionic species in polar solvents.

Hydrogen bonding between solvent and analyte when one corresponds to that of a proton donor and the other a proton acceptor.



Principal detectors:

The object of chromatography is rarely to determine the global composition of a sample, but rather to measure the concentration of a compound that is present, for which a particularly well-adapted detector must be chosen. It should give, for each compound of interest, a response that is proportional to the instantaneous mass flow (indicated by its linear dynamic range), be sensitive, have a small inertia, filter most background noise and

be stable over time. The most widely used detection methods are based upon the optical properties of the analytes: absorption, fluorescence and refractive index.

Performance of HPLC Detectors*

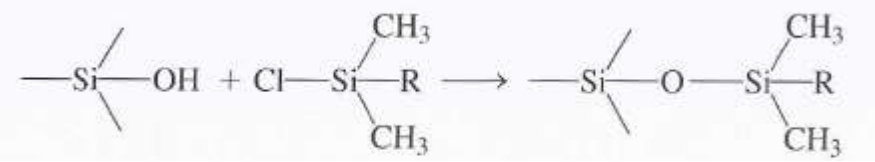
HPLC Detector	Commercially Available	Mass LOD† (typical)	Linear Range‡ (decades)
Absorbance	Yes	10 pg	3–4
Fluorescence	Yes	10 fg	5
Electrochemical	Yes	100 pg	4–5
Refractive index	Yes	1 ng	3
Conductivity	Yes	100 pg–1 ng	5
Mass spectrometry	Yes	<1 pg	5
FTIR	Yes	1 μg	3
Light scattering	Yes	1 μg	5
Optical activity	No	1 ng	4
Element selective	No	1 ng	4–5
Photoionization	No	<1 pg	4

High – performance partition chromatography:

The most widely used type of HPLC is partition chromatography, in which the stationary phase is a second liquid that is immiscible with the liquid mobile phase. Partition chromatography can be subdivided into liquid-liquid and liquid bonded- phase chromatography. The difference between the two lies in the way that the stationary phase is held on the support particles of the packing. The liquid is held in place by physical adsorption in liquid-liquid chromatography, while it is attached by chemical bonding in bonded-phase chromatography. Early partition chromatography was exclusively liquid-liquid; now, however, bonded-phase methods predominate because of their greater stability. Liquid-liquid packings are today relegated to certain special applications.

Bonded-Phase Packings:

Most bonded-phase packings are prepared by reaction of an organochlorosilane with the -OH groups formed on the surface of silica particles by hydrolysis in hot, dilute hydrochloric acid. The product is an organosiloxane. The reaction for one such SiOH site on the surface of a particle can be written as



Where R is often a straight-chain octyl or octyldecyl group. Other organic functional groups that have been bonded to silica surfaces include aliphatic amines, ethers, and nitriles, as well as aromatic hydrocarbons. Thus, many different polarities for the bonded stationary phase are available.

Bonded-phase packings have the advantage of markedly greater stability than physically held stationary phases. With the latter, periodic recoating of the solid surfaces is required because the stationary phase is gradually dissolved away in the mobile phase. Furthermore, gradient elution is not practical with liquid-liquid packings, again because

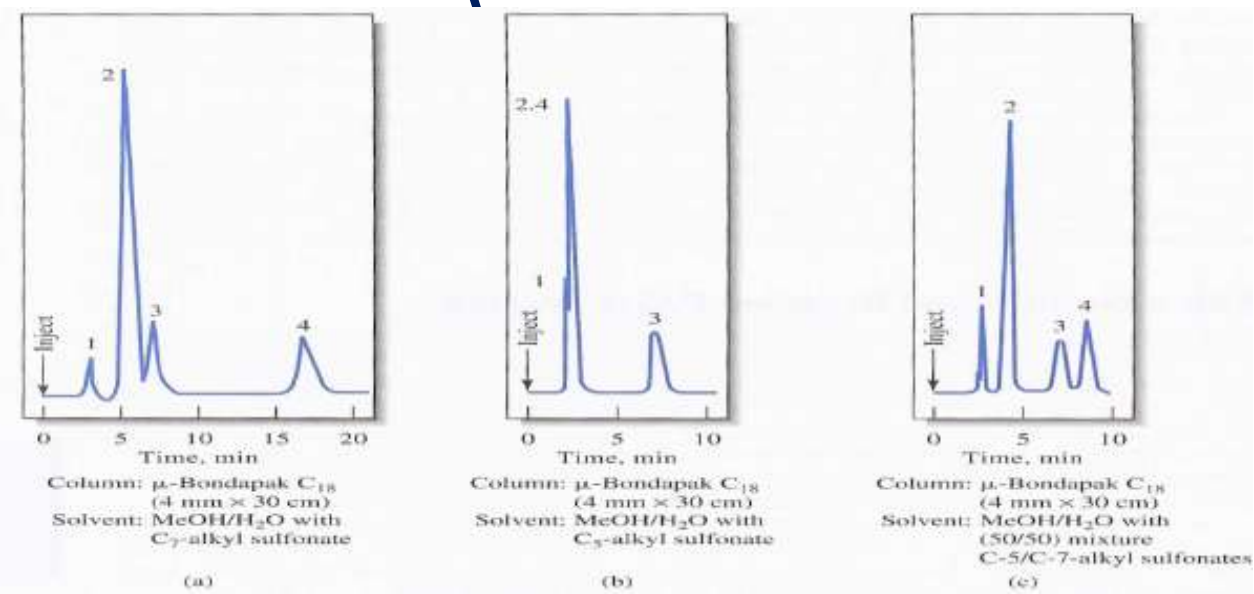
of losses by solubility in the mobile phase. The main disadvantage of bonded-phase packings is their somewhat limited sample capacity.

Normal- and Reversed-Phase Packings

Two types of partition chromatography are distinguishable based on the relative polarities of the mobile and stationary phases. Early work in liquid chromatography was based on highly polar stationary phases such as triethylene glycol or water; a relatively nonpolar solvent such as hexane or i-propyl ether then served as the mobile phase. For historic reasons, this type of chromatography is now called normal-phase chromatography. **In reversed-phase chromatography**, the stationary phase is nonpolar, often a hydrocarbon, and the mobile phase is a relatively polar solvent (such as water, methanol, acetonitrile, or tetrahydrofuran.

In normal-phase chromatography, the least polar component is eluted first; increasing the polarity of the mobile phase decreases the elution time. In contrast, with reversed-phase chromatography, the most polar component elutes first, and increasing the mobile-phase polarity increases the elution time. It has been estimated that more than three quarters of all HPLC separations are currently performed with reversed-phase, bonded, octyl- or octyldecyl-siloxane packings. With such preparations, the long-chain hydrocarbon groups are aligned parallel to one another and perpendicular to the surface of the particle, giving a brush-like, nonpolar, hydrocarbon surface. The mobile phase used with these packings is often an aqueous solution containing various concentrations of such solvents as methanol, acetonitrile, or tetrahydrofuran.

Ion-pair chromatography is a subset of reversed-phase chromatography in which easily ionizable species are separated on reversed-phase columns. In this type of chromatography, an organic salt containing a large organic counter-ion, such as a quarternary ammonium ion or alkyl sulfonate, is added to the mobile phase as an ion-pairing reagent.



Chrornatograms illustrating separations of mixtures of ionic and nonionic compounds by ion-pair chromatography. Compounds: (1) niacinamide, (2) pyridoxine, (3) riboflavin, (4) thiamine. At pH

3.5, niacinamide is strongly ionized, while riboflavin is nonionic. Pyridoxine and thiamine are weakly ionized. Column: u-Bondapak, C1S, 4 mm X 30 cm. Mobile phase: (a) MeOH/H20 with C_5-alkyl sulfonare; (b) MeOH/H20 with C_5-alkyl sulfonate; (c) MeOH/H20 with 1:1 mixture of C_5- and C_7 alkyl sulfonate.

Typical Applications of High-Performance Partition Chromatography

Field	Typical Mixtures Separated
Pharamaceuticals	Antibiotics, sedatives, steroids, analgesics
Biochemicals	Amino acids, proteins, carbohydrates, lipids
Food products	Artificial sweeteners, antioxidants, aflatoxins, additives
Industrial chemicals	Condensed aromatics, surfactants, propellants, dyes
Pollutants	Pesticides, herbicides, phenols, polychlorinated biphenyls (PCBs)
Forensic chemistry	Drugs, poisons, blood alcohol, narcotics
Clinical medicine	Bile acids, drug metabolites, urine extracts, estrogens

High – performance adsorption chromatography:

The pioneering work in chromatography was based on adsorption of analyte species on a solid surface. Here, the stationary phase is the surface of a finely divided polar solid. With such a packing, the analyte competes with the mobile phase for sites on the surface of the packing, and retention is the result of adsorption forces.

Stationary and Mobile Phases:

Finely divided silica and alumina are the only stationary phases that find extensive use in adsorption chromatography. Silica is preferred for most (but not all) applications because of its higher sample capacity and its wider range of useful forms. The adsorption characteristics of the two substances parallel one another. For both, retention times become longer as the polarity of the analyte increases.

In adsorption chromatography, the only variable that affects the distribution coefficient of analytes is the composition of the mobile phase (in contrast to partition chromatography, where the polarity of the stationary phase can also be varied). Fortunately, enormous variations in retention and thus resolution accompany variations in the solvent system, and only rarely is a suitable mobile phase not available. In adsorption chromatography, analyte species are adsorbed onto the surface of a polar packing. In adsorption chromatography, the mobile phase is usually an organic solvent or a mixture of organic solvents; the stationary phase is finely divided particles of silica or alumina.

Applications of Adsorption Chromatography:

Currently, liquid-solid **HPLC** is used extensively for the separations of relatively nonpolar, water-insoluble organic compounds with molecular masses that are less than about 5000. A particular strength of adsorption chromatography, which is not shared by other methods, is its ability to resolve isomeric mixtures such as meta and para substituted benzene derivatives.

Comparison of High-Performance Liquid Chromatography and Gas-Liquid Chromatography

Characteristics of both methods
Efficient, highly selective, widely applicable
Only small sample required
May be nondestructive of sample
Readily adapted to quantitative analysis
Advantages of HPLC
Can accommodate nonvolatile and thermally unstable compounds
Generally applicable to inorganic ions
Advantages of GC
Simple and inexpensive equipment
Rapid
Unparalleled resolution (with capillary columns)
Easily interfaced with mass spectrometry