CHAPTER II

THEORY

Metal cans have dominated sectors of the food and beverage markets because of their cost effectiveness, durability and the overall protection they provide for their contents. It is possible to make food cans from variety forms of steel and several aluminum alloys. This chapter reviews the epoxy resins, the can making methods and metals used in the can manufacturing.

1. Epoxy resins

Epoxy resins have been commercially available for more than forty years and are used in one of the most diverse range of applications in the modern world. The use of epoxy resins is not restricted to the surface coating industry. They are used in most thermal and ambient cure applications industries such as aerospace, civil engineering, automotive, chemical, electrical marine, and many others. Epoxy resins are extremely adaptable, finding applications in major industry. It is obvious that there are two main uses of epoxy resins, namely surface coatings and engineering (structural). The consumption of epoxy resins between these two areas is approximately equal [29].

Epoxy resins can be considered to have been commercially available since 1948 with the world-wide consumption of epoxy resins being 1.5 million tons in 1999 [31]. The types of surface coatings utilizing epoxy resins can be divided into [29]:

- paints
- can coatings
- automotive paints powder coatings
- radiation cure inks and coatings

In general, epoxy resins are available as solid or liquid. Grade of liquid resins vary in viscosity. It is possible to obtain epoxy resins dissolve in organic solvents to reduce the viscosity. Water based emulsions of some epoxy resins are also

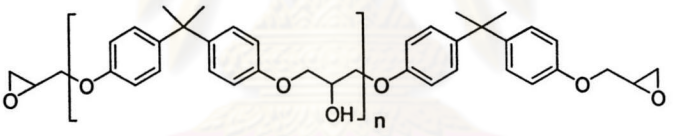
commercially available. Epoxy resins molecules contain at least one and normally two glycidyl groups. Normally the higher molecular weight epoxy resins contain the same basic repeating units. The bulk of the epoxy resins in commercial use are based upon the di-epoxide of bisphenol A. They are produce by the condensation of epichlorohydrin with bisphenol A [1-3, 30, 31].

2. Type of epoxy resins

The majority of epoxy resins used commercially for liquid surface coatings are based upon the higher molecular weight homologues of the bisphenol-A-glycidyl ether (BADGE) [30, 31].

2.1. Epoxy resins based on bisphenol A

The major constituent of BADGE resins is as follows:



Where n ranges from 0 (pure BADGE) to an average value >40 for high molecular mass phenoxy resins.

Bisphenol A based epoxy resins are produced by the condensation of epichlorohydrin (ECH) with bisphenol A (BPA) in the presence of a catalyst as shows in Figure 2-1. Bases that may be used to catalyze this step include sodium hydroxide, lithium salts and quaternary ammonium salts. Dehydrohalogenation of the chlorohydrin intermediate with a stoichiometric amount of base affords the glycidyl ether.

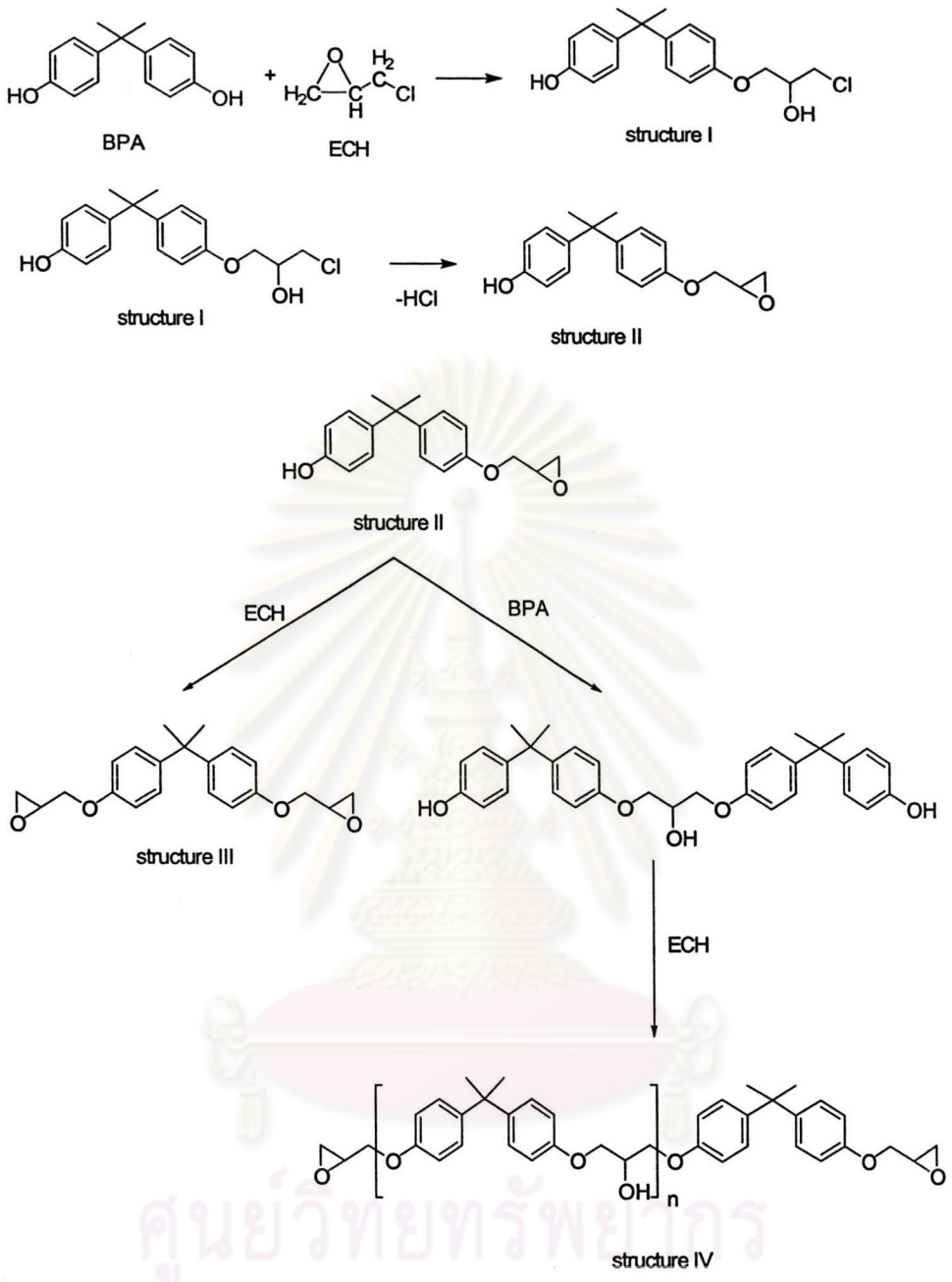


Figure 2-1. The production of epoxy resin (BADGE).

Properties of bisphenol A based resins

A wide variety of epoxy resins based on bisphenol A are sold commercially, both neat and in solution. These resins are characterized according to their epoxide equivalent mass (EEM), chemical and physical properties, purity determined by well-defined analytical procedures. More recently, gel-permeation chromatography and

high performance liquid chromatography have been used to understand the molecular composition of epoxy resins more completely.

Table 2-1 lists a few physical properties of several common BADGE resins. This table compares only four of the many commercially available epoxy resins. In general, few differences exist between liquid BADGE resins from various manufacturers. However, the differences that do exist can affect the performance of a resin in a particular application [31].

Table 2.1. Typical properties and handling characteristic of epoxy resin based on the diglycidyl ether of bisphenol A.

Property	Resin			
	Low M_r	Medium M_r	High M_r	Medium M_r solution
EEM, g/equivalent	182-192	500-560	1600-2000	500-560[a]
Epoxide content, wt%	20.8-23.6	7.7-8.6	2.1-2.7	7.7-8.6[a]
Repeating unit (n)[b]	0.06-0.14	2.3-2.7	10-13	2.3-2.7[a]
Melt viscosity, Pa.s	11.0-14.5	0.4-0.8	30-100	3.5-8.5
	at 25 °C	at 150 °C	at 150 °C	at 25 °C
Mettler softening point, °C	<25	75-85	120-135	<25
Volatiles, wt%	0	3-5	3-5	19-21 (acetone)
Relative density d_4^{25}	1.16	1.19	1.19	1.10
Specific heat at 25 °C	0.5	0.5	0.5	0.4
Color (Gardner)	1	1	1	2
Flash point (PMCC), °C	135			<65

[a] based on resin solution.

[b] theoretical, assumption two epoxide per chain.

[c] Pensky-Martens closed cup.

2.2. Epoxy resins not based on bisphenol A.

There are many epoxy resins not based upon bisphenol A. It must be remembered that their usage is normally limited. This is frequently due to a much higher cost than their BADGE countertype.

1. Bisphenol F based epoxy resins

Bisphenol F based liquid epoxy resins have much lower viscosity for the same value of 'n' than their corresponding bisphenol A resins. Currently the cost of bishenol F epoxy resins are higher than those for bisphenol A, thus severely restricting their usage. The preparation and structure for bisphenol F is given in figure 2-2. The reaction is from formaldehyde and phenol and that three isomers are possible because substitution can occur at the ortho, meta and para positions.

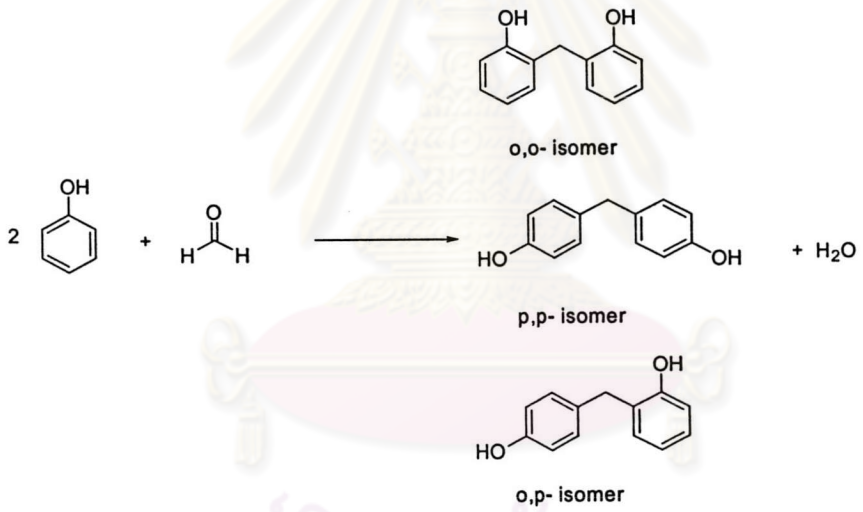


Figure 2-2. Bisphenol F production and structure of isomers.

2. Epoxy novolac resins.

Epoxy novolac resins are multifunctional epoxies that exhibit better high temperature performance and chemical resistance after curing than BADGE. Novolac are prepared by the acid catalyzed condensation of formaldehyde with phenol (Bisphenol F can be considered as the first member of novolac). The epoxidation of the novolac with epichlorohydrin furnishes the epoxy novolac (Figure 2-3.). The bisphenol-F-diglycidyl ether is the simplest member of the epoxy novolac family.

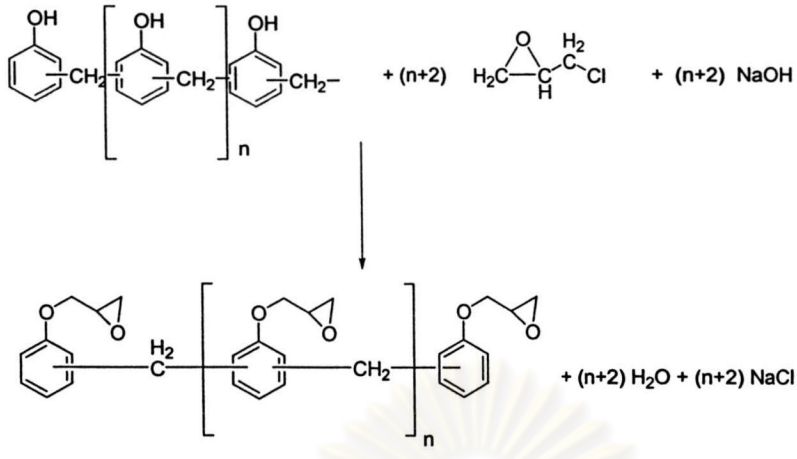


Figure 2-3. Typical reaction for preparation of epoxy novolac resin.

3. Hydrogenated bisphenol A epoxy resins.

It is possible to obtain hydrogenated bisphenol A based epoxy resins. It has improve weathering characteristics and obviously are more expensive than the standard bisphenol A based epoxy resins. This polymer frequently use in paint more than surface coating.

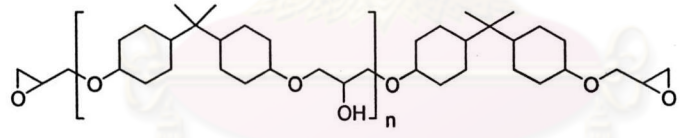


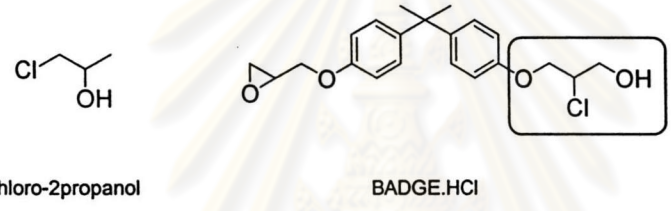
Figure 2-4. Structure of a hydrogenated bisphenol A based epoxy resins.

3. Toxicology

From the research of Gardiner et al. [33], the epoxy resin is estrogen mimic. Estrogen hormone is female sex hormone. Both male and female have this hormone and it controls the secondary sex characteristic in male. The effect of the estrogen mimic reduces the amount of sperm cell and abnormal sex characteristic in male. In addition, BADGE and BFDGE are carcinogenic agents from the in-vitro tests and are mutagenic agents in mice. Since, the structures of chlorohydroxy derivatives are

similar to 1-chloro-2-propanol that is carcinogenic. Then, it is highly possible that the chlorohydroxy derivatives could be carcinogenic as well [34].

In the present day, no TDI (Tolerable Daily Intake) has been set so far but the Scientific Committee on Food has recommended an upper limit of 1 mg/kg food as a temporary guidance level. Taking into account a daily consumption of 2-3 kg of food per day, a daily maximally tolerated exposure of 3 mg/person can be assessed. Given both its use as a food additive and the concerns arising from its migration from can coating, contaminated food represents the major source of human exposure. In this context, BADGE is regulated by numerous Directives such as 90/128/EEC and 2001/61/CE by the European Commission.



1-chloro-2propanol BADGE.HCl

Figure 2-5. The structure of 1-chloro-2-propanol compare to the BADGE.HCl

4. Metal used in can manufacturing

Containers for heat processing foods are made form variety forms of steels and several aluminum [1, 3, 32].

4.1. Steel

Steel, usually in the form of tinplate, is the most common metal used in the manufacture of the heat processing food cans. Over 50 billions such cans are made each year. The gauge and the level of tin coatings vary with container size and the product to be packed. Typical ranges are:

- Nominal gauge, 0.15-0.30 mm
- Tin coating weight, 0.5 – 15 g

The generic name for steel-based materials is tin-mill products (a name derived form the equipment used in their production). In fact tinplate and various tin free steel are produced on the same equipment.

4.2. Tin-free steels (TFS) and blackplate

Blackplate, defined as uncoated mild steel, has been considered for the manufacture of food cans but only suitable for a very limited range of products even when fully lacquered because of its tendency to rust and poor chemical resistance.

Tin-free steel (ECCS) had found fairly wide usage, typical examples being draw-redraw containers and fixed (non-easy-open) ends for processed food cans. It is necessary to lacquer the surface of TFS material prior to fabrication of containers. Steel-based products are available in a wide range of strengths and ductility and with difference in chemical composition for different applications [18].

4.3. Aluminium

The dominant position of tinplate as the packaging material of choice for canned seafood products has been with the development of aluminium alloys. Alloys frequently lack the chemical resistance of pure aluminium. However, they have greater hardness than the pure metal, alloys are well suited for the construction of can. Aluminium alloys are widely used for the manufacture of straight sided round cans. The advantages of the aluminium for the construction of can are:

1. Easy for fabrication.
2. Attractive appearance.
3. Good corrosion resistance.
4. Ease of opening tear-off ("easy open") ends.
5. Recyclability.
6. Elimination of side seam with drawn cans.

5. Type of cans

There are varieties of metal cans available all depend on types of metal use, type of food and its processing, and shape of can. Nowadays there 2 major can types.

5.1. The three-piece cans

A three-piece can composes of a body and two ends [20, 21]. While usually cylindrical, the body can have other shapes e.g., rectangular, truncated, pyramid, etc. It is formed from plain or enameled tinplate in accordance with the intended use. The ends are manufactured from tinplate or TFS. The one end is applied by the can manufacturer, called the *manufacture's end.* The other end is prepared by the canner and is called the *canner's end.* The essential steps in manufacture are as followed: cut up coil into rectangular sheets; apply protective lacquer and external decorate as appropriate; form a cylinder and a side-seam; hook and solder the side-seams together to form the body; reduce the seam thickness by milling wheels; fitting of manufacture's end.

1. Normal resistance welding of seam

Normal resistance welding is hooked the edge of metal sheet together with solder. Typical solder is lead-tin alloy (98:2), 100% tin, copper wire. Pure tin solder are used in baby canned food and soft drink welding. Normally, resistance welding the steel edge overlaps approximate 0.5 mm. Only TFS can be welded and need to have clean surface before welding which is the major disadvantage.

2. Laser welding of seam

Laser welding fused the edges together by laser beam and produced the side-seam without overlap of the metal sheet. Laser welding has a lot of advantages:

- All metal sheets (TFS, tin plate, steel, aluminium) can be welded.
- The cost is cheaper than the normal welding because it does not use the solder in the process.
- Laser welding is smooth and more easily protected.
- Variety can side can be welded.

However, both side seams need to be coated. If the metal sheet is polymer coated before forming the cylinder, side seams are coated after can production. If metal sheet is not polymer coated prior to the forming step, the can will be sprayed afterward.

5.2. The two-piece cans

Two-piece can compose of body and a lid. The container body is formed from one flat precut metal sheet by stamping or a combination of stamping and deep drawing. A combination of stamping and drawing is normally used to make round tall cans from uncoated aluminium alloy or steel sheets (stamping used to make round and nonround standard cans). In general, there are 2 method of making two-piece cans:

1. Drawn-redrawn (DRD)
2. Drawn and wall ironed (DWI)

The detail of each procedure are described below and in Table 2-2.

- Drawn: The process is one-cup formation from flat precut sheet via a punch through a circular die. In general term, the surface area of the cup is equal to the surface area of the blank form.

- Redrawn: In this process, diameter of the cup used in the first step is reduced and the height is increased by one or more operation. The redraw process is punched a cup through a smaller diameter circular die again. The thickness of all part is equal and equal to a flat precut.

- Ironing: Ironing reduces the thickness of the cup wall. This process forces the cup with a circular die of the same diameter and creates a cup of thinner wall. The wall thickness can be reduced up to 70%.

Table 2.2. Manufacturing steps for two-piece cans

Drawn and wall ironing (DWI)	Drawn and redrawn (DRD)
Unwind. Lubricate. Blank disk and form cup. Iron walls and form base. Trim body to correct height. Wash and treat (passivate). Decorate (optional). External protection. Internal protection.	Coil lacquer and cut to sheets and lacquer. Blank disk and form cup. Redraw (once or twice). Form base. Trim flange or from flange.

In Thailand, 2-piece cans are produced by both methods. For example, tuna in oil food and fried foods are packed in drawn and redrawn (DRD) 2-piece cans. Most beverage cans are made of aluminium and can be both Drawn and wall ironing (DWI) 2-piece cans.

6. Sample preparation

Because sample preparation is very important part of meaningful quantitative analysis that requires high skills and experience of the analyst. Sample preparations are wide range of complicate procedures, from simple dissolution to complex extraction, derivatization and further extraction. The key is to develop an operation procedure that achieves high accuracy and consistent quantitative results with minimum material losses. This part describes some useful extraction procedures performed in this work.

Extraction techniques [33]

The determination of trace materials in bulk solids and liquid samples such as pesticides in soil, drug metabolites in blood serum, etc, requires suitable extraction

and concentration methods. Good extraction method is necessary for pre-extraction procedures or sample clean-up and for separation of the analytes. Typical pre-extraction methods included centrifuge, precipitation, dialysis, and filtration. In general, extraction methods can be divided into:

1. Solvent extraction

Solvent extraction can be used for both solid and liquid samples. The continuous extraction at high temperature may cause sample degradation and molecular rearrangement. However, the technique is suitable for the removal of insoluble components in the sample. Solvent extraction often use for extracting the compounds in environment samples. Efficiency of the extraction depends on the solubility of the solute in selected solvent. The solvents used must be selective and can dissolve the solute more than the matrix and other immiscible. Solvent extraction can be separated into 2 categories depend on types of the sample phase.

1.1. Liquid-liquid extraction is an extraction of choice for liquid samples. Extraction disperses the analyte from liquid sample into the solvent.

1.2. Liquid-solid extraction is used for solid samples. It is applied to extract the analyte. Most solvent extract all compounds from sample at different ration, then the extractant is usually very complicated. After the first extraction, it is necessary to proceed further extraction by liquid-liquid extraction to remove some interference or analyte with suitable solvent.

2. Solid phase extraction (SPE)

Solid phase extraction (SPE) are very common in environmental and pollutant studies. It uses for preconcentration of trace analytes in sample. SPE is a short tube packed with appropriate adsorbent. Generally, the adsorbent in SPE tubes are silica or silica bonded with reverse phase and macro-porous polymers. A SPE tube is shown in figure 2-6. The choice of the adsorbent depends on the nature of the analyte and the matrix.

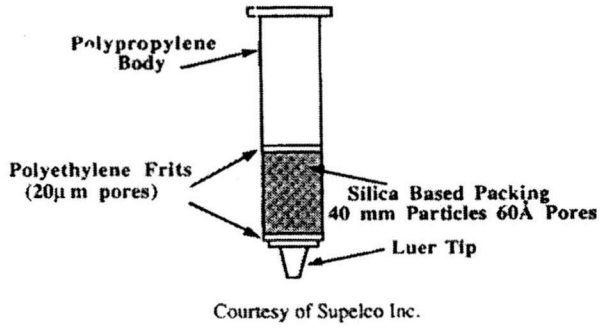


Figure 2-6. General SPE tube.

There are two types of mechanism in SPE procedure.

- Analytical trapping: The analytes are trapped in the SPE tube, after that they are removed by displacing with strong interaction solvent. This is a good way to increase the concentration of analyte.

- Interference trapping: The interferences are trapped in the SPE tube. This mechanism is in reversal to the first mechanism. The analytes pass through the SPE tube into a reservoir but interferences are trapped. The analyte concentration is not increased.

3. Super critical fluid (SCF) extraction

Super critical fluid (SCF) was recently developed for extraction. SCF extraction use gas at critical phase. The advantages of this method are: increase extraction efficiency, use less solvent, and easily to preconcentrate. General gas for extraction is carbon dioxide (CO_2) because its high abundance, inexpensive, safe, environmentally benign, and can become SCF very easy.

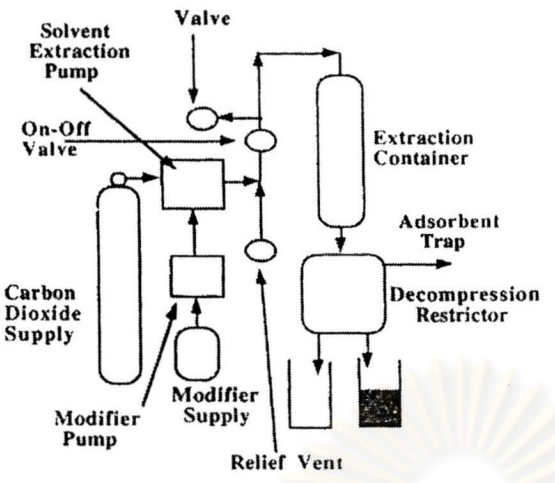
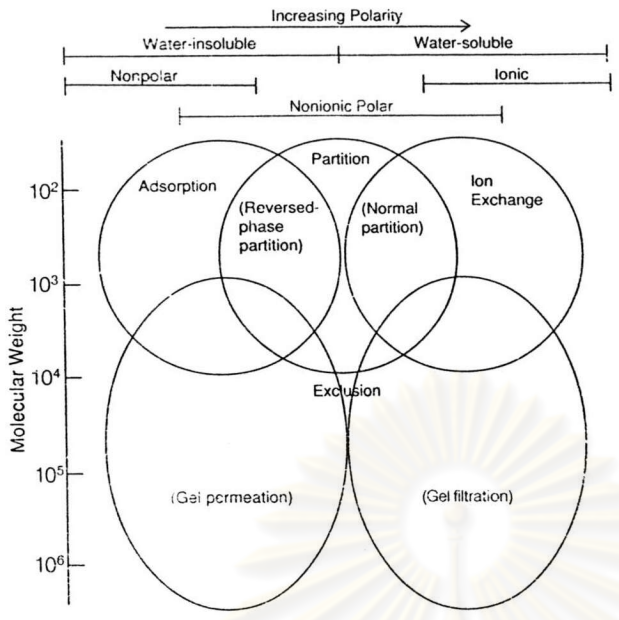


Figure 2-7. The diagram of SCF extraction apparatus.

7. High Performance Liquid Chromatography (HPLC) [36-39]

Liquid Chromatography (LC) is one type of the chromatography. It is an analytical technique that is used to separate a mixture in solution into individual components. The separation relies on the used of two different "phases" or "immiscible layers", one of which is held stationary while the other moves over it. Liquid chromatography is the generic name used to describe any chromatographic procedure in which the mobile phase is liquid. High performance liquid chromatography (HPLC) is the term use to describe liquid chromatography, which the liquid mobile phase is mechanically pumped through a column that contains the stationary phase.

Figure 2-8. show the five most widely used types of high performance liquid chromatography. The method include: *(1) partition* or *liquid-liquid chromatography; (2) adsorption* or *liquid solid chromatography; (3) ion-exchange chromatography,* and two types of *size-exclusion chromatography; (4) gel-permeation chromatography; and (5) gel-filtration chromatography.*



(From: D.L. Saunders, in Chromatography, 3rd ed, E. Heftmann, Ed., p. 81, Van Nostrand Reinhold: New York, 1975. With permission.)

Figure 2-8. Application of liquid chromatography

Partition chromatography is based on competition for neutral analytes, but in this case the stationary phase is considered to be a neutral liquid. Owing to the stability of liquid stationary phase. Partition chromatography is not commonly used in modern HPLC. Long chain (C18) "bonded phase" column have been developed which the long alkyl chain are considered to behave like a liquid.

Adsorption chromatography is based on competition for neutral analytes between the liquid mobile phase and a neutral solid stationary phase. The analytes interact with the stationary phase according to premise "like likes like": polar solute will be retained longest by polar stationary phases and nonpolar solutes will be retained by nonpolar stationary phases. In adsorption chromatography the solute are in contract with both the stationary and the mobile phase, simultaneously.

Ion-exchange chromatography (IEC) is based on the principle that opposites attract. IEC is used to separate charged analytes and therefore occurs as a result of interaction between a charge solute and oppositely charged, solid stationary phase. IEC can be applied to any solute that can acquire a charged in solution.

Size-exclusion chromatography (SEC) is based on the sieving principle. In SEC, the stationary phase particles are manufactured with a wide range of pore sizes. Then, the stationary phase behave like a molecular sieve. From sieving action, the solute are separated on the basis of size, with the larger one elute first.

HPLC instrument

There are many ways to discuss the components in HPLC system. The Figure 2-9 is a diagram showing the important components of a typical HPLC instrument.

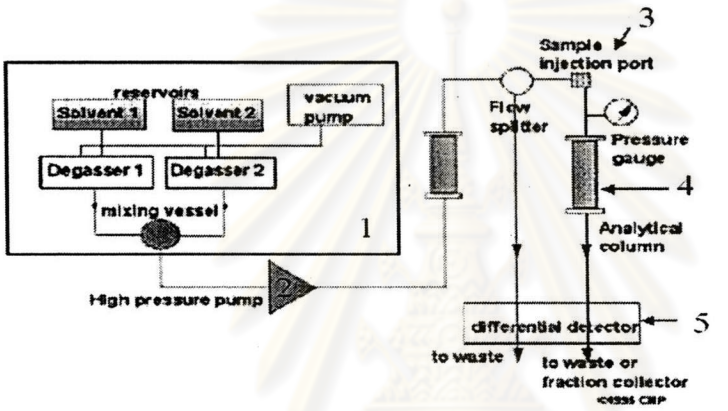


Figure 2-9. Schematic of HPLC instrument.

The typical HPLC instrument is consisted of:

1) Mobile phase reservoirs and solvent treating systems
2) Pumping system
3) Sampling injection system
4) Column
5) Detector

1). Mobile phase reservoirs and solvent treating systems

A modern HPLC apparatus is equipped with one or more glass or stainless steel reservoirs, each of which contains 500 mL or more of a solvent. The mobile phase preparations are often included steps to remove dissolved gases and dust from the liquids. Degassers may consist of a vacuum pumping system, a distillation system, a device for heating and stirring or a system for sparging.

2). Pumping system

The requirements for liquid chromatography pumps include (1) the generation of pressures up to 6000 psi, (2) pulse-free output, (3) flow rate ranging from 0.1 to 10 mL/min, (4) flow reproducibilities of 0.5% or better, and (5) resistance to corrosion by a variety of solvents.

There are 2 types of HPLC pumps:

1. Mechanical pumps

There are 2 types of mechanical pumps: a screw-driven syringe type and a reciprocating pump. These pumps produce a pulse delivery and flow rate is readily controlled. Reciprocating pumps are more widely used, usually consisted of small cylindrical chamber that is filled and then empty by the back and forth motion. The pumping motion produces a pulsed flow that must be subsequently damped. They are adaptable to gradient elution.

2. Pneumatic pumps

Some instruments use a pneumatic pump, which its simplest form consists of a solvent container housed in a vessel that can be pressurized by a compressed gas. This pump is simple, inexpensive and pulse-free. The limit of solvent capacity and pressure output are major disadvantages and the pumping rates depend on solvent viscosity. In addition, they are not adaptable to gradient elution.

3). **Sampling injection system**

The most widely used method of sample introduction in liquid chromatography is based on sampling loops. The devices are often an integral part of modern liquid chromatography equipment and have interchangeable loop. The loops provide a choice of sample sizes ranging from 5 to 500 μL.

4). Column

Liquid chromatography columns are usually constructed from stainless steel tubing. Most columns range in length from 10 to 30 cm and have inside diameters of 4 to 10 mm. Column packings typically have particle sizes of 5 or 10 μm. Column often contain 40,000 to 60,000 plates/m. The most common packing for liquid

chromatography is from silica with highly uniform diameters. The particles are coated with thin organic films that chemically or physically bonded to the surface. Other packing materials include alumina particles, porous polymer particles and ion-exchange resins.

5). Detector

The final component of the HPLC is the detector. There are wide range of detector available. In this part, we'll describe only UV-visible detector and fluorescence detector.

1. UV-visible detector

The basic UV-visible detector works by measuring the difference in intensity between an incoming beam of light and the same signal attenuated according to the concentration and absorbing power of the analyte. The two basic configurations of UV-visible detector are the fixed-wavelength and the photodiode array (PDA). The diagram of both types of UV-visible detector is shown in Figure 2-10.

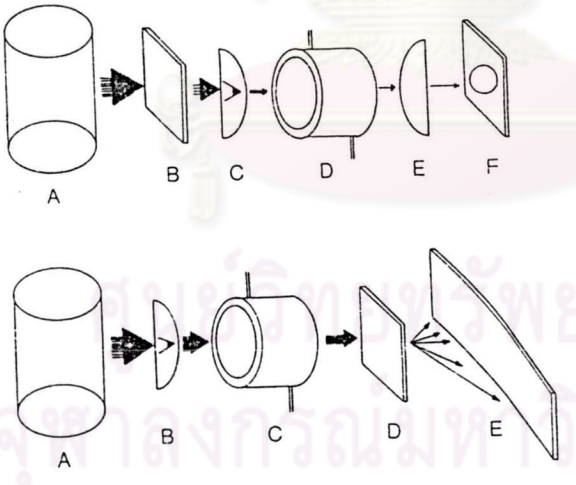


Figure 2-10. Top: Schematic for single-wavelength UV-visible detector: (A) source; (B) monochromator; (C) focusing lens; (D) flow cell; (E) photodiode. Bottom: Schematic photodiode-array detector: (A) source; (B) focusing element; (C) flow cell; (D) dispersing element (typically grating); (E) photodiode array.

The fixed-wavelength detector has a series of lenses and slits to focus the source beam on the flow cell and then focus the transmitted beam onto the diode. The basis resolution is achieved through the properties of monochromators and filters. A source monochromator is used to select the wavelength of the source output. A monochromator placed after the sample help exclude scattered light source.

The same principles apply for the PDA detector except there is no monochromator. The entire source light is focused on the detector cell. The transmitted light passes through a dispersive object (e.g., prism) that spreads the light into different wavelength regions. Photodiodes of specific width are placed along the spreading light curve. Each diode corresponds to a specific band of radiation determined by its width. PDA detectors are powerful tool for the analyst. They not only are excellent quantitation of the analyte but also can generate an absorbance-vs-wavelength curve for each analyte. It is used to confirm an analyte's identity.

2. Fluorescence detector

Fluorescence detectors utilize a dual nomochromator system, like a fixed-wavelength UV-visible detector but the incident beam and exit beam are at 90° to one another (see Figure 2-11.). Most commonly, the fluorescence process includes the adsorption of a short-wavelength incident radiation by the molecule, a molecular internal conversion-relaxation process to the first excited state of the molecule, and emission of radiation at a specific and longer wavelength. It is this emitted light that is detected.

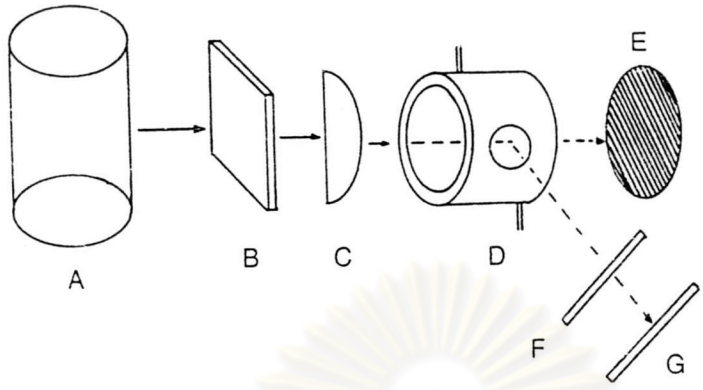


Figure 2-11. Schematic for fluorescence detector: (A) source; (B) monochromator or cutoff filter; (C) focusing lens; (D) flow cell; (E) light trap; (F) monochromator or bandpass filter; (G) photodiode. Note the excitation wavelength is lower wavelength from the emission wavelength.