Chapter 4

Reactions Kinetics and Pathways

4.1 Dynamic Headspace Gas Chromatography Analysis[1]

4.1.1 Introduction

Gas chromatography (GC) is a very commonly used chromatography in analytic chemistry for separating and analyzing compounds that are gaseous or can be vaporized without decomposition. Because of its simplicity, sensitivity, and effectiveness in separating components of mixtures, gas chromatography is an important tools in chemistry. It is widely used for quantitative and qualitative analysis of mixtures, for the purification of compounds, and for the determination of such thermochemical constants as heats of solution and vaporization, vapor pressure, and activity coefficients. Compounds are separated due to differences in their partitioning coefficient between the stationary phase and the mobile gas phase in the column.

4.1.2 Physical components of a GC system

A gas chromatograph (Figure 4.1) consists of a carrier gas system, a sampling system, a separation system, a detection system, and a data recording system.

[1] This content is available online at <http://cnx.org/content/m34622/1.2/>.

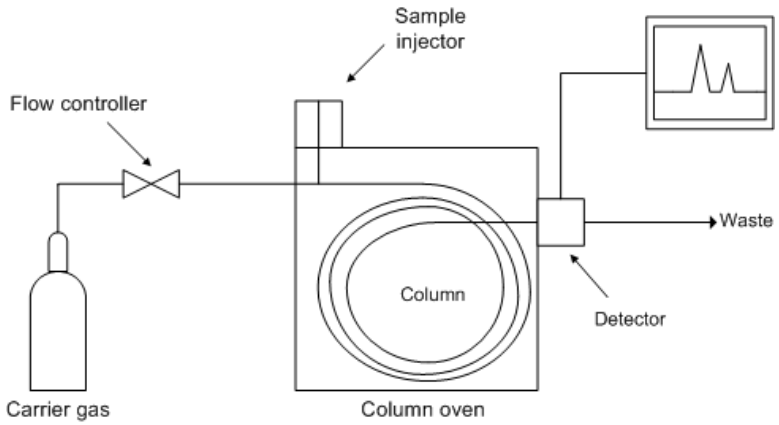

Figure 4.1: Physical components of a typical GC system. Adapted from http://en.wikipedia.org/wiki/Gas_chromatography

4.1.2.1 Carrier gas system

The carrier gas system consists of carrier gas sources, purification, and gas flow control. The carrier gas must be chemically inert. Commonly used gases include nitrogen, helium, argon, and carbon dioxide. The choice of carrier gas often depends upon the type of detector used. A molecular sieve is often contained in the carrier gas system to remove water and other impurities.

4.1.2.2 Auto sampling system

An auto sampling system consists of auto sampler, and vaporization chamber. The sample to be analyzed is loaded at the injection port via a hypodermic syringe and it will be volatilized as the injection port is heated up. Typically samples of one micro liter or less are injected on the column. These volumes can be further reduced by using what is called a split injection system in which a controlled fraction of the injected sample is carried away by a gas stream before entering the column.

4.1.2.3 Separation system

The separation system consists of columns and temperature controlling oven. The column is where the components of the sample are separated, and is the crucial part of a GC system. The column is essentially a tube that contains different stationary phases have different partition coefficients with analytes,and determine the quality of separation. There are two general types of column: packed (Figure 4.2) and capillary also known as open tubular (Figure 4.3).

- Packed columns contain a finely divided, inert, solid support material coated with liquid stationary phase. Most packed columns are $1.5 - 10$ m in length and have an internal diameter of $2 - 4$ mm.
- Capillary columns have an internal diameter of a few tenths of a millimeter. They can be one of two types; wall-coated open tubular (WCOT) or support-coated open tubular (SCOT). Wall-coated columns consist of a capillary tube whose walls are coated with liquid stationary phase. In support-coated columns, the inner wall of the capillary is lined with a thin layer of support material such as diatomaceous earth, onto which the stationary phase has been adsorbed. SCOT columns are generally

less efficient than WCOT columns. Both types of capillary column are more efficient than packed columns.

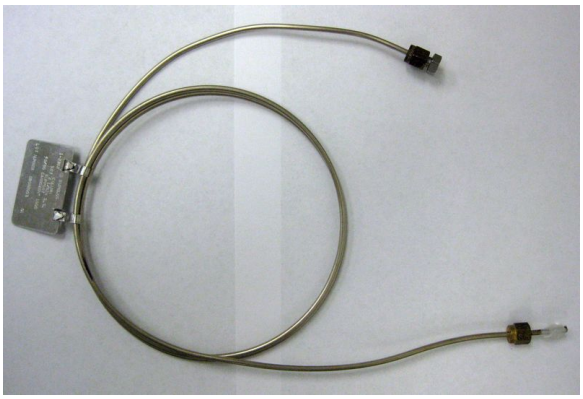

Figure 4.2: An example of a packed GC column.

Figure 4.3: An example of a capillary column.

4.1.2.4 Detectors

The purpose of a detector is to monitor the carrier gas as it emerges from the column and to generate a signal in response to variation in its composition due to eluted components. As it transmits physical signal into recordable electrical signal, it is another crucial part of GC. The requirements of a detector for GC are listed below.

Detectors for GC must respond rapidly to minute concentration of solutes as they exit the column, i.e., they are required to have a fast response and a high sensitivity. Other desirable properties of a detector are: linear response, good stability, ease of operation, and uniform response to a wide variety of chemical species or, alternatively predictable and selective response to one or more classes of solutes.

4.1.2.5 Recording devices

GC system originally used paper chart readers, but modern system typically uses an online computer, which can track and record the electrical signals of the separated peaks. The data can be later analyzed by software to provide the information of the gas mixture.

4.1.3 How does GC work?

4.1.3.1 Separation terminology

An ideal separation is judged by resolution, efficiency, and symmetry of the desired peaks, as illustrated by Figure 4.4.

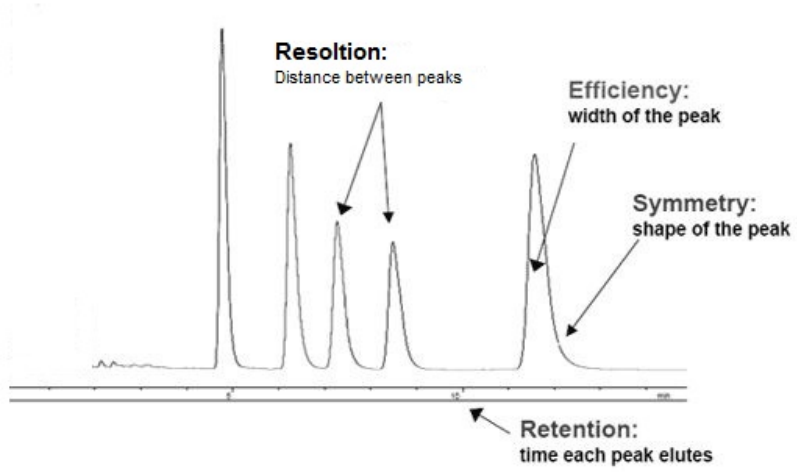

Figure 4.4: Separation terminology. Adapted from http://www.gchelp.tk

4.1.3.1.1 Resolution (R)

Resolution can be simply expressed as the distance on the output trace between two peaks. The highest possible resolution is the goal when developing a separation method. Resolution is defined by the R value, (4.1), which can be expressed mathamatically, (4.2), where k is capacity, α is selectivity, and N is the number

of theoretical plates. An R value of 1.5 is defined as being the minimum required for baseline separation, i.e., the two adjacent peaks are separated by the baseline. Separation for different R values is illustrated in Figure 4.5.

$$R = \text{capacity} \times \text{selectivity} \times \text{efficiency} \tag{4.1}$$

$$R = [k/(1+k)](\alpha - 1/\alpha)(N^{0.5}/4) \tag{4.2}$$

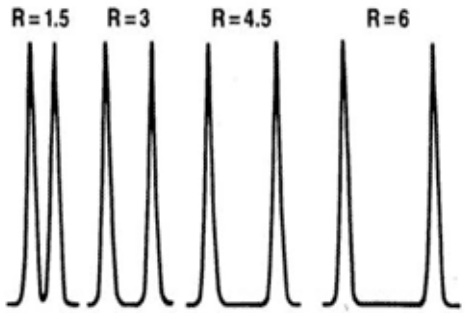

Figure 4.5: Different separation resolutions. Adapted from http://www.gchelp.tk

4.1.3.1.2 Capacity (k´)

Capacity (k´) is known as the retention factor. It is a measure of retention by the stationary phase. It is calculated from (4.3), where t_r = retention time of analyte (substance to be analyzed), and t_m = retention time of an unretained compound.

$$k' = (t_r - t_m)/t_m \tag{4.3}$$

4.1.3.1.3 Selectivity

Selectivity is related to α, the separation factor (Figure 4.6). The value of α should be large enough to give baseline resolution, but minimized to prevent waste.

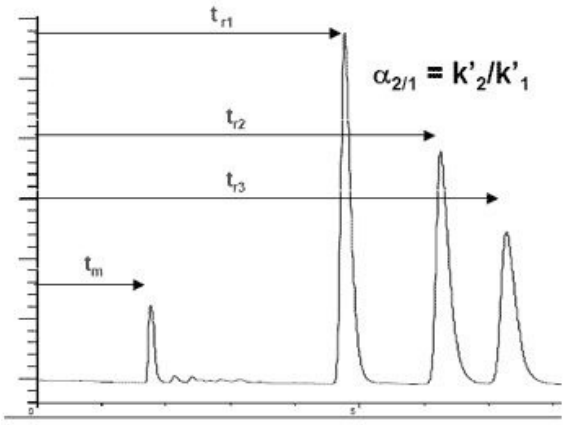

Figure 4.6: Scheme for the calculation of selectivity. Adapted from http://www.gchelp.tk

4.1.3.1.4 Efficiency

Narrow peaks have high efficiency (Figure 4.7), and are desired. Units of efficiency are "theoretical plates" (N) and are often used to describe column performance. "Plates" is the current common term for N, is defined as a function of the retention time (t_r) and the full peak width at half maximum ($W_{b1/2}$), EQ.

$$N = 5.545 (t_r/W_{b1/2})^2 \tag{4.4}$$

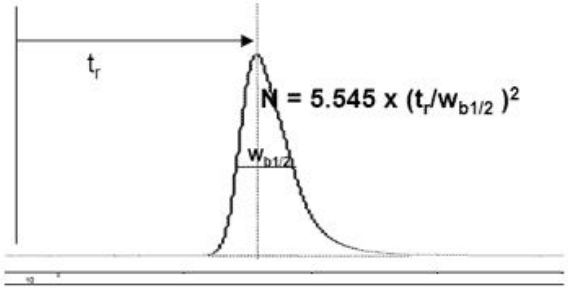

Figure 4.7: Scheme for calculating efficiency. Adapted from http://www.gchelp.tk

4.1.3.1.5 Peak symmetry

The symmetry of a peak is judged by the values of two half peak widths, *a* and *b* (Figure 4.8). When *a* = *b*, a peak is called symmetric, which is desired. Unsymmetrical peaks are often described as "tailing" or

"fronting".

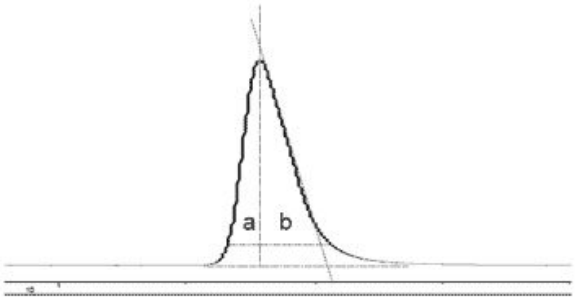

Figure 4.8: Scheme for the symmetry of a peak. Adapted from http://www.gchelp.tk

4.1.3.1.6 An ideal separation

The attributions of an ideal separation are as follows:

- Should meet baseline resolution of the compounds of interest.
- Each desired peak is narrow and symmetrical.
- Has no wasted dead time between peaks.
- Takes a minimal amount of time to run.
- The result is reproducible.

4.1.3.2 How does GC work?

In its simplest form gas chromatography is a process whereby a sample is vaporized and injected onto the chromatographic column, where it is separated into its many components. The elution is brought about by the flow of carrier gas (Figure 4.9). The carrier gas serves as the mobile phase that elutes the components of a mixture from a column containing an immobilized stationary phase. In contrast to most other types of chromatography, the mobile phase does not interact with molecules of the analytes. Carrier gases, the mobile phase of GC, include helium, hydrogen and nitrogen which are chemically inert. The stationary phase in gas-solid chromatography is a solid that has a large surface area at which adsorption of the analyte species (solutes) take place. In gas-liquid chromatography, a stationary phase is liquid that is immobilized on the surface of a solid support by adsorption or by chemical bonding.

Gas chromatographic separation occurs because of differences in the positions of adsorption equilibrium between the gaseous components of the sample and the stationary phases (Figure 4.9). In GC the distribution ratio (ratio of the concentration of analytes in stationary and mobile phase) is dependent on the component vapor pressure, the thermodynamic properties of the bulk component band and affinity for the stationary phase. The equilibrium is temperature dependent. Hence the importance of the selection the stationary phase of the column and column temperature programming in optimizing a separation.

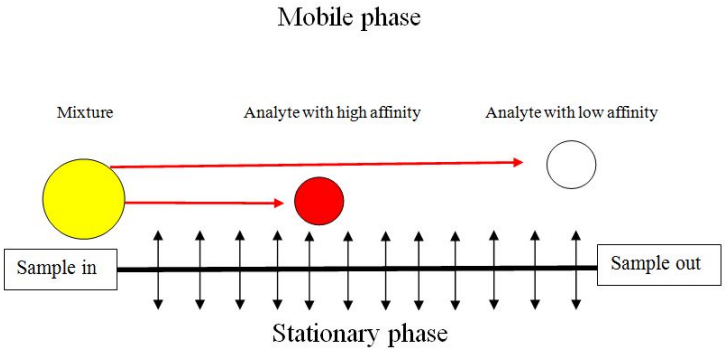

Figure 4.9: Scheme for partition in mobile and stationary phases.

4.1.3.3 Choice of method

4.1.3.3.1 Carrier gas and flow rate

Helium, nitrogen, argon, hydrogen and air are typically used carrier gases. Which one is used is usually determined by the detector being used, for example, a discharge ionization detection (DID) requires helium as the carrier gas. When analyzing gas samples, however, the carrier is sometimes selected based on the sample's matrix, for example, when analyzing a mixture in argon, an argon carrier is preferred, because the argon in the sample does not show up on the chromatogram. Safety and availability are other factors, for example, hydrogen is flammable, and high-purity helium can be difficult to obtain in some areas of the world.

The carrier gas flow rate affects the analysis in the same way that temperature does. The higher the flow rate the faster the analysis, but the lower the separation between analytes. Furthermore, the shape of peak will be also effected by the flow rate. The slower the rate is, the more axial and radical diffusion are, the broader and the more asymmetric the peak is. Selecting the flow rate is therefore the same compromise between the level of separation and length of analysis as selecting the column temperature.

4.1.3.3.2 Column Selection

Table 4.1 shows commonly used stationary phase in various applications.

Stationary phase	Common trade name	Maximum temperature (°C)	Common applications

continued on next page

Polydimethyl siloxane	OV-1, SE-30	350	General-purpose non-polar phase, hydrocarbons, polynuclear aromatics, drugs, steroids, PCBs
Poly(phenylmethyl-dimethyl) siloxane (10% phenyl)	OV-3, SE-52	350	Fatty acid methyl esters, alkaloids, drugs, halogenated compounds
Poly(phenylmethyl) siloxane (50% phenyl)	OV-17	250	Drugs, steroids, pesticides, glycols
Poly(trifluoropropyl-dimethyl) siloxane	OV-210	200	Chlorinated aromatics, nitroaromatics, alkyl-substituted benzenes
Polyethylene glycol	Carbowax 20M	250	Free acids, alcohols, ethers, essential oils, glycols
Poly(dicyanoallyldimethyl) siloxane	OV-275	240	Polyunsaturated fatty acid, rosin acids, free acids, alcohols

Table 4.1: Some common stationary phases for gas-liquid chromatography. Adapted from http://www.cem.msu.edu/∼cem333/Week15.pdf

4.1.3.3.3 Column temperature and temperature program

For precise work, the column temperature must be controlled to within tenths of a degree. The optimum column temperature is dependent upon the boiling point of the sample. As a rule of thumb, a temperature slightly above the average boiling point of the sample results in an elution time of 2 - 30 minutes. Minimal temperatures give good resolution, but increase elution times. If a sample has a wide boiling range, then temperature programming can be useful. The column temperature is increased (either continuously or in steps) as separation proceeds. Another effect that temperature may have is on the shape of peak as flow rate does. The higher the temperature is, the more intensive the diffusion is, the worse the shape is. Thus, a compromise has to be made between goodness of separation and retention time as well as peak shape.

4.1.3.3.4 Detector selection

A number of detectors are used in gas chromatography. The most common are the flame ionization detector (FID) and the thermal conductivity detector (TCD). Both are sensitive to a wide range of components, and both work over a wide range of concentrations. While TCDs are essentially universal and can be used to detect any component other than the carrier gas (as long as their thermal conductivities are different from that of the carrier gas, at detector temperature), FIDs are sensitive primarily to hydrocarbons, and are more sensitive to them than TCD. However, an FID cannot detect water. Both detectors are also quite robust. Since TCD is non-destructive, it can be operated in-series before an FID (destructive), thus providing complementary detection of the same analytes.For halides, nitrates, nitriles, peroxides, anhydrides and organometallics, ECD is a very sensitive detection, which can detect up to 50 fg of those analytes. Different types of detectors are listed below in Table 4.2, along with their properties.

Detector	**Type**	**Support gases**	**Selectivity**	**Detectability**	**Dynamic range**
Flame ionization (FID)	Mass flow	Mass flow	Most organic compounds	100 pg	10^7
Thermal conductivity (TCD)	Concentration	Reference	Universal	1 ng	10^7
Electron capture (ECD)	Concentration	Make-up	Halides, nitrates, nitriles, peroxides, anhydrides, organometallics	50 fg	10^5
Nitrogen-phosphorus	Mass flow	Hydrogen and air	Nitrogen, phosphorus	10 pg	10^6
Flame photometric (FPD)	Mass flow	Hydrogen and air possibly oxygen	Sulphur, phosphorus, tin, boron, arsenic, germanium, selenium, chromium	100 pg	10^3
Photoionization (PID)	Concentration	Make-up	Aliphatics, aromatics, ketones, esters, aldehydes, amines, heterocyclics, organosulphurs, some organometallics	2 pg	10^7

continued on next page

Hall electrolytic conductivity	Mass flow	Hydrogen, oxygen	Halide, nitrogen, nitrosamine, sulphur	-	-

Table 4.2: Different types of detectors and their properties. Adapted from http://teaching.shu.ac.uk/hwb/chemistry/tutorials/chrom/gaschrm.htm

4.1.4 Headspace analysis using GC

Most consumer products and biological samples are composed of a wide variety of compounds that differ in molecular weight, polarity, and volatility. For complex samples like these, headspace sampling is the fastest and cleanest method for analyzing volatile organic compounds. A headspace sample is normally prepared in a vial containing the sample, the dilution solvent, a matrix modifier, and the headspace (Figure 4.10). Volatile components from complex sample mixtures can be extracted from non-volatile sample components and isolated in the headspace or vapor portion of a sample vial. An aliquot of the vapor in the headspace is delivered to a GC system for separation of all of the volatile components.

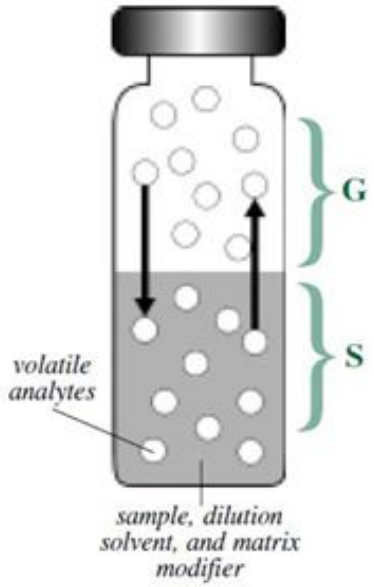

Figure 4.10: Schematic representation of the phases of the headspace in the vial. Adapted from *A Technical Guide for Static Headspace Analysis Using GC*, Restek Corp. (2000).

The gas phase (G in Figure 4.10) is commonly referred to as the headspace and lies above the condensed sample phase. The sample phase (S in Figure 4.10) contains the compound(s) of interest and is usually in the form of a liquid or solid in combination with a dilution solvent or a matrix modifier. Once the sample phase is introduced into the vial and the vial is sealed, volatile components diffuse into the gas phase until the headspace has reached a state of equilibrium as depicted by the arrows. The sample is then taken from the headspace.

4.1.4.1 Basic principles of headspace analysis

4.1.4.1.1 Partition coefficient

Samples must be prepared to maximize the concentration of the volatile components in the headspace, and minimize unwanted contamination from other compounds in the sample matrix. To help determine the concentration of an analyte in the headspace, you will need to calculate the partition coefficient (K), which is defined by (4.5), where C_s is the concentration of analyte in sample phase and C_g is the concentration of analyte in gas phase. Compounds that have low K values will tend to partition more readily into the gas phase, and have relatively high responses and low limits of detection. K can be lowered by changing the temperature at which the vial is equilibrated or by changing the composition of the sample matrix.

$$K = C_s/C_g \tag{4.5}$$

4.1.4.1.2 Phase ratio

The phase ratio (β) is defined as the relative volume of the headspace compared to volume of the sample in the sample vial, (4.6), where V_s=volume of sample phase and V_g=volume of gas phase. Lower values for β (i.e., larger sample size) will yield higher responses for volatile compounds. However, decreasing the β value will not always yield the increase in response needed to improve sensitivity. When β is decreased by increasing the sample size, compounds with high K values partition less into the headspace compared to compounds with low K values, and yield correspondingly smaller changes in C_g. Samples that contain compounds with high K values need to be optimized to provide the lowest K value before changes are made in the phase ratio.

$$\beta = V_g/V_s \tag{4.6}$$

4.1.5 Bibliography

- D. L, Pavia, G. M. Lampman, G. S. Kritz, and R. G. Engel, *Introduction to Organic Laboratory Techniques*, 4th ed. Thomson Brooks/Cole (2006).
- D. C. Harris, *Quantitative Chemical Analysis*, 5th ed., Freeman and Company (1999).
- M. O. Nutt, J. B. Hughes, and M. S. Wong, *Environ. Sci. Technol.*, 2005, **39**, 1346.

4.2 Gas Chromatography Analysis of the Hydrodechlorination Reaction of Trichloroethene[2]

4.2.1 Introduction

Trichloroethene (TCE) is a widely spread environmental contaminant and a member of the class of compounds known as dense non-aqueous phase liquids (DNAPLs). Pd/Al_2O_3 catalyst has shown activity for the hydrodechlorination (HDC) of chlorinated compounds.

To quantify the reaction rate, a 250 mL screw-cap bottle with 77 mL of headspace gas was used as the batch reactor for the studies. TCE (3 μL) is added in 173 mL DI water purged with hydrogen gas for 15 mins, together with 0.2 μL pentane as internal standard. Dynamic headspace analysis using GC has been applied. The experimental condition is concluded in the table below (Table 4.3).

[2]This content is available online at <http://cnx.org/content/m34634/1.2/>.

TCE	3 μL
H_2	1.5 ppm
pentane	0.2 μL
DI water	173 mL
1 wt% Pd/Al_2O_3	50 mg
Temperature	25 °C
Pressure	1 atm
Reaction time	1 h

Table 4.3: The experimental condition in HDC of TCE.

4.2.2 Reaction kinetics

First order reaction is assumed in the HDC of TCE, (4.7), where K_{means} is defined by (4.8), and C_{cat} is equal to the concentration of Pd metal within the reactor and k_{cat} is the reaction rate with units of $L/g_{Pd}/min$.

$$-dC_{TCE}/dt = k_{meas} \times C_{TCE} \tag{4.7}$$

$$k_{meas} = k_{cat} \times C_{cat} \tag{4.8}$$

4.2.3 The GC method

The GC methods used are listed in Table 4.4.

GC type	Agilent 6890N GC
Column	Supelco 1-2382 40/60 Carboxen-1000 packed column
Detector	FID
Oven temperature	210 °C
Flow rate	35 mL/min
Injection amount	200 μL
Carrier gas	Helium
Detection time	5 min

Table 4.4: GC method for detection of TCE and other related chlorinated compounds.

4.2.4 Quantitative method

Since pentane is introduced as the inert internal standard, the relative concentration of TCE in the system can be expressed as the ratio of area of TCE to pentane in the GC plot, (4.9).

$$C_{TCE} = (\text{peak area of TCE})/(\text{peak area of pentane}) \tag{4.9}$$

4.2.5 Results and Analysis

The major analytes (referenced as TCE, pentane, and ethane) are very well separated from each other, allowing for quantitative analysis. The peak areas of the peaks associated with these compounds are integrated by the computer automatically, and are listed in (Table 4.5) with respect to time.

Time/min	Peak area of pentane	Peak area of TCE
0	5992.93	13464
5.92	6118.5	11591
11.25	5941.2	8891
16.92	5873.5	7055.6
24.13	5808.6	5247.4
32.65	5805.3	3726.3
43.65	5949.8	2432.8
53.53	5567.5	1492.3
64.72	5725.6	990.2
77.38	5624.3	550
94.13	5432.5	225.7
105	5274.4	176.8

Table 4.5: Peak area of pentane, TCE as a function of reaction time.

Normalize TCE concentration with respect to peak area of pentane and then to the initial TCE concentration, and then calculate the nature logarithm of this normalized concentration, as shown in Table 4.6.

Time (min)	TCE/pentane	$TCE/pentane/TCE_{initial}$	$ln(TCE/Pentane/TCE_{initial})$
0	2.2466	1.0000	0.0000
5.92	1.8944	0.8432	-0.1705
11.25	1.4965	0.6661	-0.4063
16.92	1.2013	0.5347	-0.6261
24.13	0.9034	0.4021	-0.9110
32.65	0.6419	0.2857	-1.2528
43.65	0.4089	0.1820	-1.7038
53.53	0.2680	0.1193	-2.1261
64.72	0.1729	0.0770	-2.5642
77.38	0.0978	0.0435	-3.1344
94.13	0.0415	0.0185	-3.9904
105	0.0335	0.0149	-4.2050

Table 4.6: Normalized TCE concentration as a function of reaction time.

From a plot normalized TCE concentration against time shows the concentration profile of TCE during reaction (Figure 4.11), while the slope of the logarithmic plot provides the reaction rate constant ().

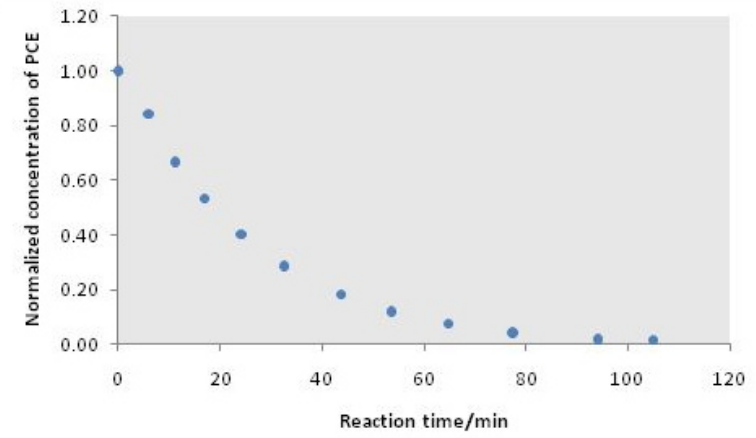

Figure 4.11: A plot of the normalized concentration profile of TCE.

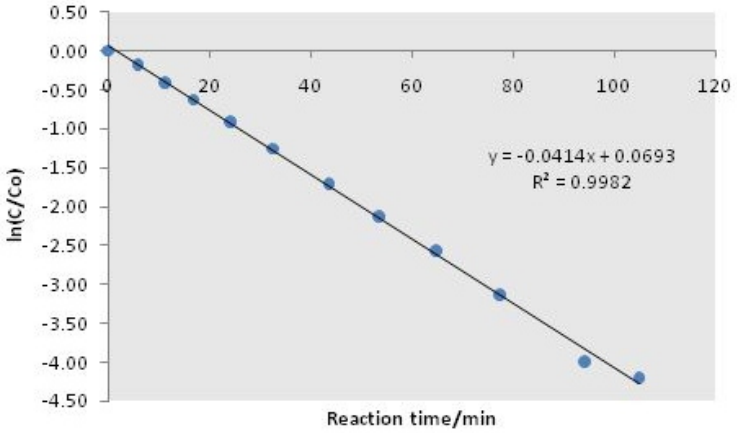

Figure 4.12: A plot of $\ln(C_{TCE}/C_0)$ versus time.

From Figure 4.11, we can see that the linearity, i.e., the goodness of the assumption of first order reaction, is very much satisfied throughout the reaction. Thus, the reaction kinetic model is validated. Furthermore, the reaction rate constant can be calculated from the slope of the fitted line, i.e., $k_{meas} = 0.0414\ min^{-1}$. From this the k_{cat} can be obtained, (4.10).

$$k_{cat} = k_{meas}/C_{Pd} = \frac{0.0414\ min^{-1}}{(5 \times 10^{-4}\ g/0.173\ L)} = 14.32 L/g_{Pd}\ min \quad (4.10)$$

4.2.6 Bibliography

- M, O. Nutt, J, B. Hughes, and M, S. Wong, *Environ. Sci. Technol.*, 2005, **39**, 1346.
- *A Technical Guide for Static Headspace Analysis Using GC*, Restek Corp. (2000).

4.3 Temperature-Programmed Desorption Mass Spectroscopy Applied in Surface Chemistry[3]

4.3.1 Introduction

The temperature-programmed desorption (TPD) technique is often used to monitor surface interactions between adsorbed molecules and substrate surface. Utilizing the dependence on temperature is able to discriminate between processes with different activation parameters, such as activation energy, rate constant, reaction order and Arrhenius pre-exponential factorIn order to provide an example of the set-up and results from a TPD experiment we are going to use an ultra-high vacuum (UHV) chamber equipped with a quadrupole mass spectrometer to exemplify a typical surface gas-solid interaction and estimate several important kinetic parameters.

4.3.2 Experimental system

4.3.2.1 Ultra-high vacuum (UHV) chamber

When we start to set up an apparatus for a typical surface TPD experiment, we should first think about how we can generate an extremely clean environment for the solid substrate and gas adsorbents. Ultra-high vacuum (UHV) is the most basic requirement for surface chemistry experiments. UHV is defined as a vacuum regime lower than 10^{-9} Torr. At such a low pressure the *mean free path* of a gas molecule is approximately 40 Km, which means gas molecules will collide and react with sample substrate in the UHV chamber many times before colliding with each other, ensuring all interactions take place on the substrate surface.

Most of time UHV chambers require the use of unusual materials in construction and by heating the entire system to ∼180 °C for several hours baking to remove moisture and other trace adsorbed gases around the wall of the chamber in order to reach the ultra-high vacuum environment. Also, outgas from the substrate surface and other bulk materials should be minimized by careful selection of materials with low vapor pressures, such as stainless steel, for everything inside the UHV chamber. Thus bulk metal crystals are chosen as substrates to study interactions between gas adsorbates and crystal surface itself. Figure 4.13 shows a schematic of a TPD system, while Figure 4.14 shows a typical TPD instrument equipped with a quadrupole MS spectrometer and a reflection absorption infrared spectrometer (RAIRS).

[3] This content is available online at <http://cnx.org/content/m38319/1.1/>.

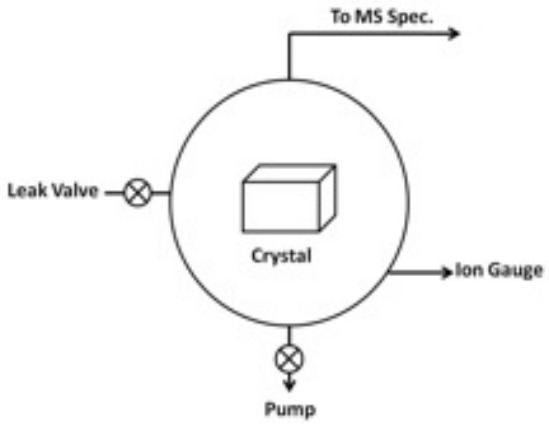

Figure 4.13: Schematic diagram of a TPD apparatus.

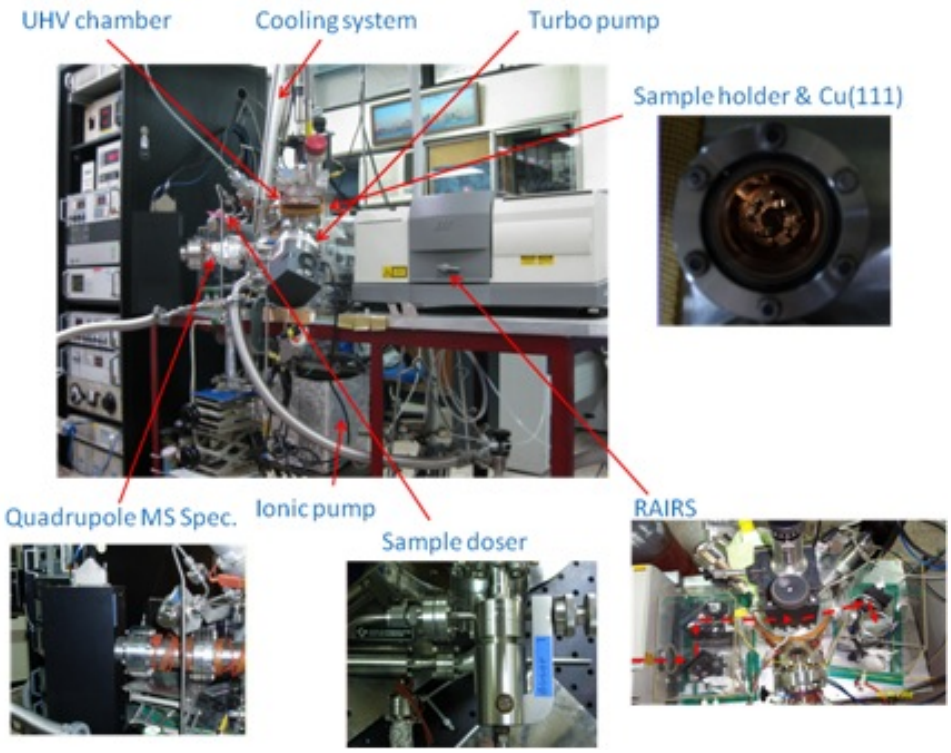

Figure 4.14: A typical TPD apparatus composed of a UHV chamber equipped with a serious of pumping systems, cooling system, sample dosing system as well as surface detection instruments including a quadrupole MS Spectrometer and a reflection absorption infra red spectrometer (RAIRS).

4.3.2.2 Pumping system

There is no single pump that can operate all the way from atmospheric pressure to UHV. Instead, a series of different pumps are used, according to the appropriate pressure range for each pump. Pumps are commonly used to achieve UHV include:

- Turbomolecular pumps (turbo pumps).
- Ionic pumps.
- Titanium sublimation pumps.
- Non-evaporate mechanical pumps.

UHV pressures are measured with an ion-gauge, either a hot filament or an inverted magnetron type. Finally, special seals and gaskets must be used between components in a UHV system to prevent even trace leakage. Nearly all such seals are all metal, with knife edges on both sides cutting into a soft (e.g., copper) gasket. This all-metal seal can maintain system pressures down to $\sim 10^{-12}$ Torr.

4.3.2.3 Manipulator and bulk metal crystal

A UHV manipulator (or sample holder, see Figure 4.14) allows an object that is inside a vacuum chamber and under vacuum to be mechanically positioned. It may provide rotary motion, linear motion, or a combination

of both. The manipulator may include features allowing additional control and testing of a sample, such as the ability to apply heat, cooling, voltage, or a magnetic field. Sample heating can be accomplished by thermal radiation. A filament is mounted close to the sample and resistively heated to high temperature. In order to simplify complexity from the interaction between substrate and adsorbates, surface chemistry labs often carry out TPD experiments by choosing a substrate with single crystal surface instead of polycrystalline or amorphous substrates (see Figure 4.13).

4.3.2.4 Pretreatment

Before selected gas molecules are dosed to the chamber for adsorption, substrates (metal crystals) need to be cleaned through argon plasma sputtering, followed by annealing at high temperature for surface reconstruction. After these pretreatments, the system is again cooled down to very low temperature (liquid N_2 temp), which facilitating gas molecules adsorbed on the substrate surface. Adsorption is a process in which a molecule becomes adsorbed onto a surface of another phase. It is distinguished from absorption, which is used when describing uptake into the bulk of a solid or liquid phase.

4.3.2.5 Temperature-programmed desorption processes

After gas molecules adsorption, now we are going to release theses adsorbates back into gas phase by programmed-heating the sample holder. A mass spectrometer is set up for collecting these desorbed gas molecules, and then correlation between desorption temperature and fragmentation of desorbed gas molecules will show us certain important information. Figure 4.15 shows a typical TPD experiment carried out by adsorbing CO onto Pd(111) surface, followed by programmed-heating to desorb the CO adsorbates.

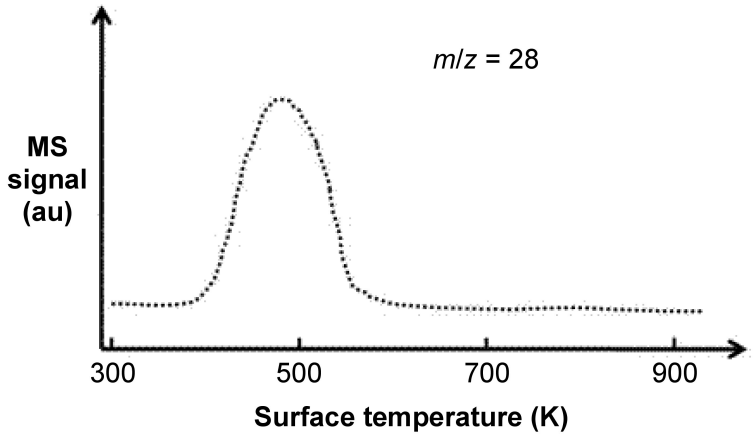

Figure 4.15: MS spectrum taken from a TPD experiment that CO ($m/z = 28$) was first adsorbed on Pd(111) surface, followed by desorbing at a fixed heating rate. The desorption rate which is proportional to the MS signal reaches its maximum around 500 K.

4.3.3 Theory of the TPD experiment

4.3.3.1 Langmuir isotherm

The Langmuir isotherm describes the dependence of the surface coverage of an adsorbed gas on the pressure of the gas above the surface at a fixed temperature. Langmuir isotherm is the simplest assumption, but it provides a useful insight into the pressure dependence of the extent of surface adsorption. It was Irving Langmuir who first studied the adsorption process quantitatively. In his proposed model, he supposed that molecules can adsorb only at specific sites on the surface, and that once a site is occupied by one molecule, it cannot adsorb a second molecule. The adsorption process can be represented as (4.11), where A is the adsorbing molecule, S is the surface site, and A[U+2500]S stands for an A molecule bound to the surface site.

$$A + S \longrightarrow A - S \tag{4.11}$$

In a similar way, it reverse desorption process can be represented as (4.12).

$$A - S \longrightarrow A + S \tag{4.12}$$

According to the Langmuir model, we know that the adsorption rate should be proportional to k_a[A](1-θ), where θ is the fraction of the surface sites covered by adsorbate A. The desorption rate is then proportional to $k_d\theta$. k_a and k_d are the rate constants for the adsorption and desorption. At equilibrium, the rates of these two processes are equal, (4.13) - (4.16). We can replace [A] by P, where P means the gas partial pressure, (4.17).

$$k_a[A](1-\theta) = k_d\theta \tag{4.13}$$

$$\frac{\theta}{1-\theta} = \frac{k_a}{k_d}[A] \tag{4.14}$$

$$K = \frac{k_a}{k_d} \tag{4.15}$$

$$\theta = \frac{K[A]}{1 + K[A]} \tag{4.16}$$

$$\theta = \frac{KP}{1 + KP} \tag{4.17}$$

We can observe the equation above and know that if [A] or P is low enough so that K[A] or KP $\ll$ 1, then θ $\sim$ K[A] or KP, which means that the surface coverage should increase linearly with [A] or P. On the contrary, if [A] or P is large enough so that K[A] or KP $\gg$ 1, then θ $\sim$ 1. This behavior is shown in the plot of θ versus [A] or P in Figure 4.16.

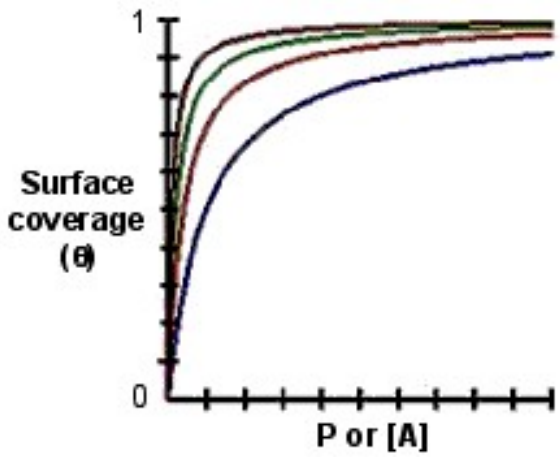

Figure 4.16: Simulated Langmuir isotherms. Value of constant K (k_a/k_d) increases from blue, red, green and brown.

4.3.3.2 Derivation of kinetic parameters based on TPD results

Here we are going to show how to use the TPD technique to estimate desorption energy, reaction energy, as well as Arrhenius pre-exponential factor. Let us assume that molecules are irreversibly adsorbed on the surface at some low temperature T_0. The leak valve is closed, the valve to the pump is opened, and the "density" of product molecules is monitored with a mass spectrometer as the crystal is heated under programmed temperature (4.18), where β is the heating rate ($\sim$10 °C/s). We know the desorption rate depends strongly on temperature, so when the temperature of the crystal reaches a high enough value so that the desorption rate is appreciable, the mass spectrometer will begin to record a rise in density. At higher temperatures, the surface will finally become depleted of desorbing molecules; therefore, the mass spectrometer signal will decrease. According to the shape and position of the peak in the mass signal, we can learn about the activation energy for desorption and the Arrhenius pre-exponential factor.

$$T = T_0 + \beta T \tag{4.18}$$

4.3.3.2.1 First-order process

Consider a first-order desorption process (4.19), with a rate constant k_d, (4.20), where A is Arrhenius pre-exponential factor. If θ is assumed to be the number of surface adsorbates per unit area, the desorption rate will be given by (4.21).

$$A - S \longrightarrow A + S \tag{4.19}$$

$$k_d = A\exp(^{-\Delta E_a}/_{RT}) \tag{4.20}$$

$$\frac{-d\theta}{dt} = k_d\theta = \theta A \exp(\frac{-\Delta E_a}{RT}) \tag{4.21}$$

Since we know the relationship between heat rate β and temperature on the crystal surface T, (4.22) and (4.23).

$$T = T_0 + \beta t \tag{4.22}$$

$$\frac{1}{dt} = \frac{\beta}{dT} \tag{4.23}$$

Multiplying by $-d\theta$ gives (4.24), since (4.25) and (4.26). A plot of the form of $-d\theta/dT$ versus T is shown in Figure 4.17.

$$\frac{-d\theta}{dt} = -\beta\frac{d\theta}{dT} \tag{4.24}$$

$$\frac{-d\theta}{dt} = k_d\theta = \theta A \exp(\frac{-\Delta E_a}{RT}) \tag{4.25}$$

$$\frac{-d\theta}{dT} = \frac{\theta A}{\beta}\exp(\frac{-\Delta E_a}{RT}) \tag{4.26}$$

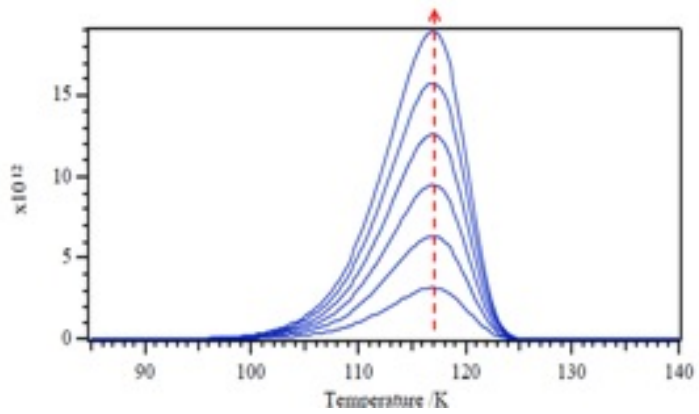

Figure 4.17: A simulated TPD experiment: Consider a first order reaction between adsorbates and surface. Values of T_m keep constant as the initial coverage θ from 1.0 x 10^{13} to 6.0 x 10^{13} cm^{-2}. E_a = 30 KJ/mol; β = 1.5 °C/s; A = 1 x 10^{13}.

We notice that the T_m (peak maximum) in Figure 4.17 keeps constant with increasing θ, which means the value of T_m does not depend on the initial coverage θ in the first-order desorption. If we want to use different desorption activation energy E_a and see what happens in the corresponding desorption temperature T. We are able to see the T_m values will increase with increasing E_a.

At the peak of the mass signal, the increase in the desorption rate is matched by the decrease in surface concentration per unit area so that the change in $d\theta/dT$ with T is zero: (4.27) - (4.29). Since (4.30), then (4.31) and (4.32).

$$\frac{-d\theta}{dT} = \frac{\theta A}{\beta}\exp(\frac{-\Delta E_a}{RT}) \tag{4.27}$$

$$\frac{d}{dT}[\frac{\theta A}{\beta}\exp(\frac{-\Delta E_a}{RT})] = 0 \tag{4.28}$$

$$\frac{\Delta E_a}{RT_M^2} = -\frac{1}{\theta}(\frac{d\theta}{dT}) \tag{4.29}$$

$$-\frac{d\theta}{dT} = \frac{\theta A}{\beta}\exp(-\frac{\Delta E_a}{RT}) \tag{4.30}$$

$$\frac{\Delta E_a}{RT_M^2} = \frac{A}{\beta}\exp(\frac{-\Delta E_a}{RT_M}) \tag{4.31}$$

$$2\ln T_M - \ln\beta = \frac{\Delta E_a}{RT_M} + \ln\frac{\Delta E_a}{RA} \tag{4.32}$$

This tells us if different heating rates β are used and the left-hand side of the above equation is plotted as a function of $1/T_M$, we can see that a straight line should be obtained whose slope is $\Delta E_a/R$ and intercept is $\ln(\Delta E_a/RA)$. So we are able to obtain the activation energy to desorption ΔE_a and Arrhenius pre-exponential factor A.

4.3.3.2.2 Second-order process

Now let consider a second-order desorption process (4.33), with a rate constant k_d. We can deduce the desorption kinetics as (4.34). The result is different from the first-order reaction whose T_m value does not depend upon the initial coverage, the temperature of the peak T_m will decrease with increasing initial surface coverage.

$$2A - S \rightarrow A_2 + 2S \tag{4.33}$$

$$-\frac{d\theta}{dT} = A\theta^2\exp(-\frac{\Delta E_a}{RT}) \tag{4.34}$$

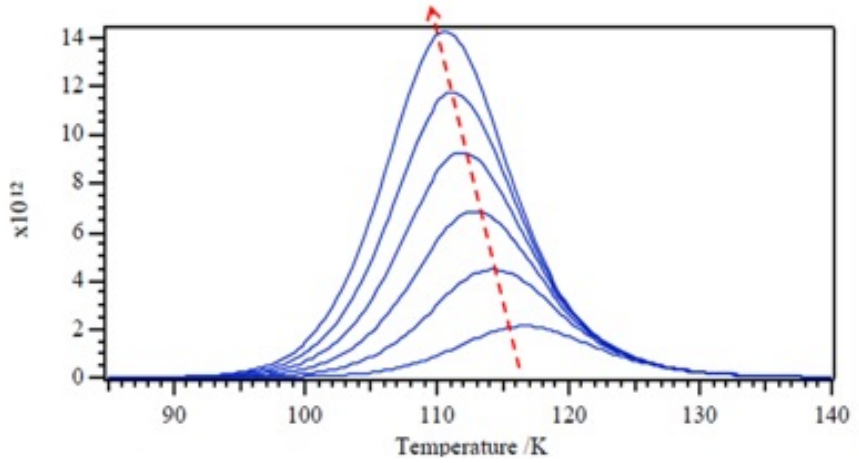

Figure 4.18: A simulated second-order TPD experiment: A second-order reaction between adsorbates and surface. Values of T_m decrease as the initial coverage θ increases from 1.0 x 10^{13} to 6.0 x 10^{13} cm^{-2}; E_a = 30 KJ/mol; β = 1.5 °C/s; A = 1 x 10^{-1}.

4.3.3.2.3 Zero-order process

The zero-order desorption kinetics relationship as (4.35). Looking at desorption rate for the zero-order reaction (Figure 4.19), we can observe that the desorption rate does not depend on coverage and also implies that desorption rate increases exponentially with T. Also according to the plot of desorption rate versus T, we figure out the desorption rate rapid drop when all molecules have desorbed. Plus temperature of peak, T_m, moves to higher T with increasing coverage θ.

$$-\frac{d\theta}{dT} = A\exp(-\frac{\Delta E_{\alpha}}{RT}) \tag{4.35}$$

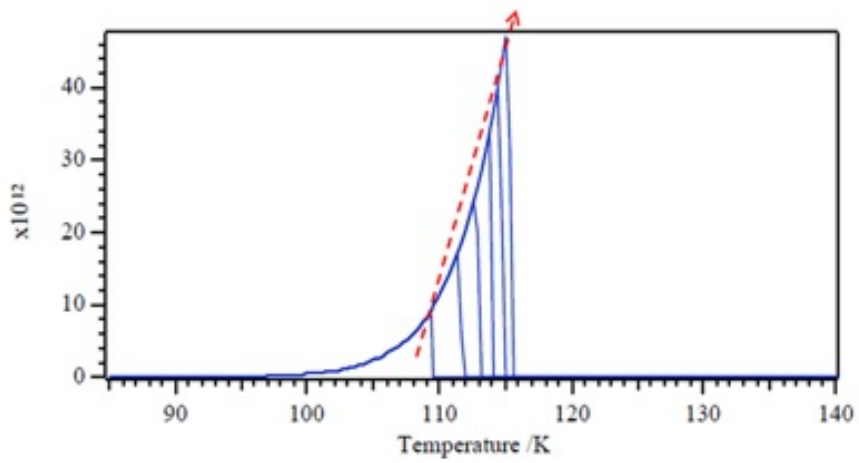

Figure 4.19: A simulated zero-order TPD experiment: A zero-order reaction between adsorbates and surface. Values of T_m increase apparently as the initial coverage θ increases from 1.0 x 10^{13} to 6.0 x 10^{13} cm^{-2}; E_a = 30 KJ/mol; β = 1.5 °C/s; A = 1 x 10^{28}.

4.3.4 A typical example

A typical TPD spectra of D_2 from Rh(100) for different exposures in Langmuirs (L = 10^{-6} Torr-sec) shows in Figure 4.20. First we figure out the desorption peaks from g to n show two different desorbing regions. The higher one can undoubtedly be ascribed to chemisorbed D_2 on Rh(100) surface, which means chemisorbed molecules need higher energy used to overcome their activation energy for desorption. The lower desorption region is then due to physisorbed D_2 with much lower desorption activation energy than chemisorbed D_2. According to the TPD theory we learnt, we notice that the peak maximum shifts to lower temperature with increasing initial coverage, which means it should belong to a second-order reaction. If we have other information about heating rate β and each T_m under corresponding initial surface coverage θ then we are able to calculate the desorption activation energy E_a and Arrhenius pre-exponential factor A.

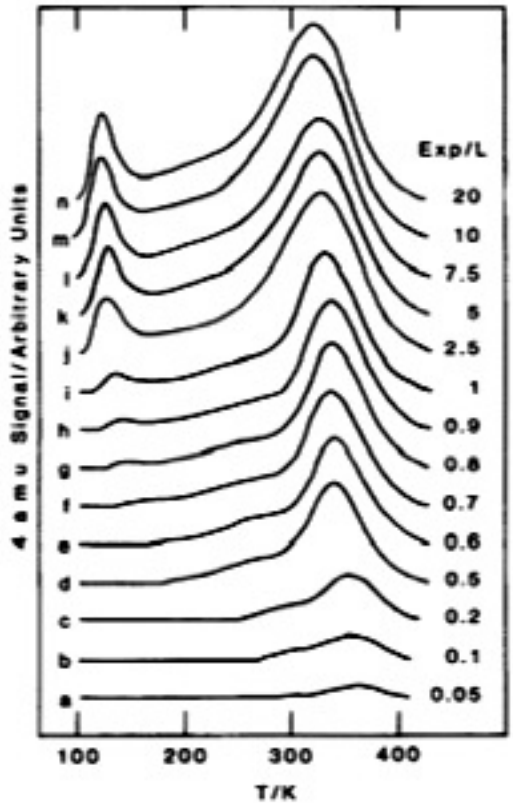

Figure 4.20: TPD spectra of D_2 from Rh(100) for different exposures in L (1 Langmuir = 10^{-6} Torr-s)[6].

4.3.5 Conclusion

Temperature-programmed desorption is an easy and straightforward technique especially useful to investigate gas-solid interaction. By changing one of parameters, such as coverage or heating rate, followed by running a serious of typical TPD experiments, it is possible to to obtain several important kinetic parameters (activation energy to desorption, reaction order, pre-exponential factor, etc). Based on the information, further mechanism of gas-solid interaction can be deduced.

4.3.6 Bibliography

- M. N. Roger, An Introduction to Surface Chemistry, http://www.chem.qmul.ac.uk/surfaces/scc/[4]
- P. L. Houston, *Chemical Kinetics and Reaction Dynamics*, McGraw Hill, New York (2001).
- I. Langmuir, *J. Am. Chem. Soc.*, 1916, **38**, 221.
- P. A. Redhead, *Vacuum*, 1962, **12**, 203.
- Y. Kim, H. C. Peebles, and J. M. White, *Surface Sci.*, 1982, **114**, 363.

[4] http://www.chem.qmul.ac.uk/surfaces/scc/

4.4 Basic Principles of Supercritical Fluid Chromatography and Supercrtical Fluid Extraction[5]

4.4.1 Introduction

The discovery of supercritical fluids led to novel analytical applications in the fields of chromatography and extraction known as supercritical fluid chromatography (SFC) and supercritical fluid extraction (SFE). Supercritical fluid chromatography is accepted as a column chromatography methods along with gas chromatography (GC) and high-performance liquid chromatography (HPLC). Due to to the properties of supercritical fluids, SFC combines each of the advantages of both GC and HPLC in one method. In addition, supercritical fluid extraction is an advanced analytical technique.

4.4.2 Definition and formation of supercritical fluids

A supercritical fluid is the phase of a material at critical temperature and critical pressure of the material. Critical temperature is the temperature at which a gas cannot become liquid as long as there is no extra pressure; and, critical pressure is the minimum amount of pressure to liquefy a gas at its critical temperature. Supercritical fluids combine useful properties of gas and liquid phases, as it can behave like both a gas and a liquid in terms of different aspects. A supercritical fluid provides a gas-like characteristic when it fills a container and it takes the shape of the container. The motion of the molecules are quite similar to gas molecules. On the other hand, a supercritical fluid behaves like a liquid because its density property is near liquid and, thus, a supercritical fluid shows a similarity to the dissolving effect of a liquid.

The characteristic properties of a supercritical fluid are density, diffusivity and viscosity. Supercritical values for these features take place between liquids and gases. Table 4.7 demonstrates numerical values of properties for gas, supercritical fluid and liquid.

	Gas	**Supercritical fluid**	**Liquid**
Density (g/cm^3)	0.6 x 10^{-3} – 2.0 x 10^{-3}	0.2 - 0.5	0.6 - 2.0
Diffusivity (cm^2/s)	0.1 - 0.4	10^{-3} - 10^{-4}	0.2 x 10^{-5} - 2.0 x 10^{-5}
Viscosity (cm/s)	1 x 10^{-4} - 3 x 10^{-4}	1 x 10^{-4} - 3 x 10^{-4}	0.2 x 10^{-2} - 3.0 x 10^{-2}

Table 4.7: Supercritical fluid properties compared to liquids and gases

The formation of a supercritical fluid is the result of a dynamic equilibrium. When a material is heated to its specific critical temperature in a closed system, at constant pressure, a dynamic equilibrium is generated. This equilibrium includes the same number of molecules coming out of liquid phase to gas phase by gaining energy and going in to liquid phase from gas phase by losing energy. At this particular point, the phase curve between liquid and gas phases disappears and supercritical material appears.

In order to understand the definition of SF better, a simple phase diagram can be used. Figure 4.21 displays an ideal phase diagram. For a pure material, a phase diagram shows the fields where the material is in the form of solid, liquid, and gas in terms of different temperature and pressure values. Curves, where two phases (solid-gas, solid-liquid and liquid-gas) exist together, defines the boundaries of the phase regions. These curves, for example, include sublimation for solid-gas boundary, melting for solid-liquid boundary, and vaporization for liquid-gas boundary. Other than these binary existence curves, there is a point where all three phases are present together in equilibrium; the triple point (TP).

[5]This content is available online at <http://cnx.org/content/m46150/1.2/>.

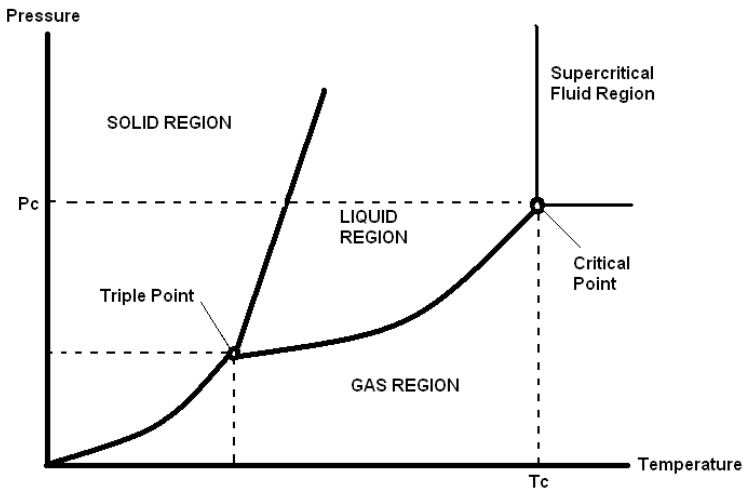

Figure 4.21: Schematic representation of an idealized phase diagram.

There is another characteristic point in the phase diagram, the critical point (CP). This point is obtained at critical temperature (T_c) and critical pressure (P_c). After the CP, no matter how much pressure or temperature is increased, the material cannot transform from gas to liquid or from liquid to gas phase. This form is the supercritical fluid form. Increasing temperature cannot result in turning to gas, and increasing pressure cannot result in turning to liquid at this point. In the phase diagram, the field above T_c and P_c values is defined as the supercritical region.

In theory, the supercritical region can be reached in two ways:

- Increasing the pressure above the P_c value of the material while keeping the temperature stable and then increasing the temperature above T_c value at a stable pressure value.
- Increasing the temperature first above T_c value and then increasing the pressure above P_c value.

The critical point is characteristic for each material, resulting from the characteristic T_c and P_c values for each substance.

4.4.3 Physical properties of supercritical fluids

As mentioned above, SF shares some common features with both gases and liquids. This enables us to take advantage of a correct combination of the properties.

4.4.3.1 Density

Density characteristic of a supercritical fluid is between that of a gas and a liquid, but closer to that of a liquid. In the supercritical region, density of a supercritical fluid increases with increased pressure (at constant temperature). When pressure is constant, density of the material decreases with increasing temperature. The dissolving effect of a supercritical fluid is dependent on its density value. Supercritical fluids are also better carriers than gases thanks to their higher density. Therefore, density is an essential parameter for analytical techniques using supercritical fluids as solvents.

4.4.3.2 Diffusivity

Diffusivity of a supercritical fluid can be 100 x that of a liquid and $^{1}/_{1,000}$ to $^{1}/_{10,000}$ x less than a gas. Because supercritical fluids have more diffusivity than a liquid, it stands to reason a solute can show better diffusivity in a supercritical fluid than in a liquid. Diffusivity is parallel with temperature and contrary with pressure. Increasing pressure affects supercritical fluid molecules to become closer to each other and decreases diffusivity in the material. The greater diffusivity gives supercritical fluids the chance to be faster carriers for analytical applications. Hence, supercritical fluids play an important role for chromatography and extraction methods.

4.4.3.3 Viscosity

Viscosity for a supercritical fluid is almost the same as a gas, being approximately $^{1}/_{10}$ of that of a liquid. Thus, supercritical fluids are less resistant than liquids towards components flowing through. The viscosity of supercritical fluids is also distinguished from that of liquids in that temperature has a little effect on liquid viscosity, where it can dramatically influence supercritical fluid viscosity.

These properties of viscosity, diffusivity, and density are related to each other. The change in temperature and pressure can affect all of them in different combinations. For instance, increasing pressure causes a rise for viscosity and rising viscosity results in declining diffusivity.

4.4.4 Supercritical fluid chromatography (SFC)

Just like supercritical fluids combine the benefits of liquids and gases, SFC bring the advantages and strong aspects of HPLC and GC together. SFC can be more advantageous than HPLC and GC when compounds which decompose at high temperatures with GC and do not have functional groups to be detected by HPLC detection systems are analyzed.

There are three major qualities for column chromatographies:

- Selectivity.
- Efficiency.
- Sensitivity.

Generally, HPLC has better selectivity that SFC owing to changeable mobile phases (especially during a particular experimental run) and a wide range of stationary phases. Although SFC does not have the selectivity of HPLC, it has good quality in terms of sensitivity and efficiency. SFC enables change of some properties during the chromatographic process. This tuning ability allows the optimization of the analysis. Also, SFC has a broader range of detectors than HPLC. SFC surpasses GC for the analysis of easily decomposable substances; these materials can be used with SFC due to its ability to work with lower temperatures than GC.

4.4.4.1 Instrumentation for SFC

As it can be seen in Figure 4.22, SFC has a similar setup to an HPLC instrument. They use similar stationary phases with similar column types. However, there are some differences. Temperature is critical for supercritical fluids, so there should be a heat control tool in the system similar to that of GC. Also, there should be a pressure control mechanism, a restrictor, because pressure is another essential parameter in order for supercritical fluid materials to be kept at the required level. A microprocessor mechanism is placed in the instrument for SFC. This unit collects data for pressure, oven temperature, and detector performance to control the related pieces of the instrument.

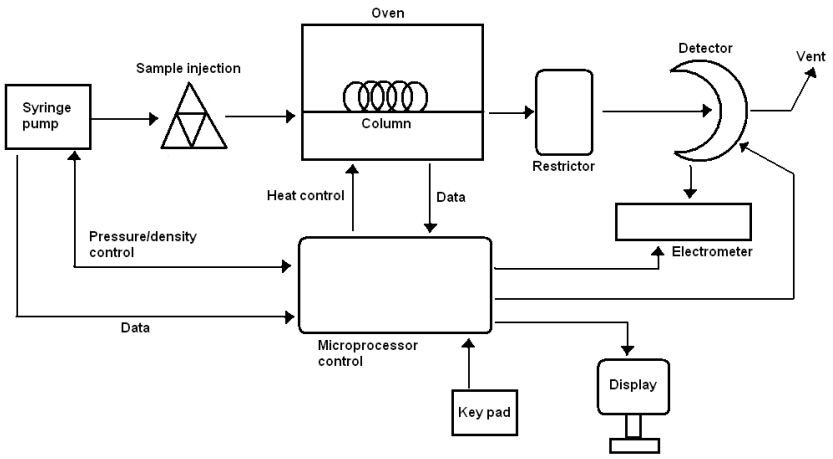

Figure 4.22: Scheme of a supercritical fluid chromatography instrument. Adapted from D. A. Skoog and J. J. Leary, *Principles of Instrumental Analysis*, Saunders College Publishing, Philadelphia (1992).

4.4.4.2 Stationary phases

SFC columns are similar to HPLC columns in terms of coating materials. Open-tubular columns and packed columns are the two most common types used in SFC. Open-tubular ones are preferred and they have similarities to HPLC fused-silica columns. This type of column contains an internal coating of a cross-linked siloxane material as a stationary phase. The thickness of the coating can be 0.05-1.0 μm. The length of the column can range from of 10 to 20 m.

4.4.4.3 Mobile phases

There is a wide variety of materials used as mobile phase in SFC. The mobile phase can be selected from the solvent groups of inorganic solvents, hydrocarbons, alcohols, ethers, halides; or can be acetone, acetonitrile, pyridine, etc. The most common supercritical fluid which is used in SFC is carbon dioxide because its critical temperature and pressure are easy to reach. Additionally, carbon dioxide is low-cost, easy to obtain, inert towards UV, non-poisonous and a good solvent for non-polar molecules. Other than carbon dioxide, ethane, n-butane, N_2O, dichlorodifluoromethane, diethyl ether, ammonia, tetrahydrofuran can be used. Table 4.8 shows select solvents and their T_c and P_c values.

Solvent	Critical Temperature (°C)	Critical Pressure (bar)
Carbon dioxide (CO_2)	31.1	72
Nitrous oxide (N_2O)	36.5	70.6
Ammonia (NH_3)	132.5	109.8
Ethane (C_2H_6)	32.3	47.6
n-Butane (C_4H_{10})	152	70.6
Diethyl ether (Et_2O)	193.6	63.8
Tetrahydrofuran (THF, C_4H_8O)	267	50.5
Dichlorodifluoromethane (CCl_2F_2)	111.7	109.8

Table 4.8: Properties of some solvents as mobile phase at the critical point.

4.4.4.4 Detectors

One of the biggest advantage of SFC over HPLC is the range of detectors. Flame ionization detector (FID), which is normally present in GC setup, can also be applied to SFC. Such a detector can contribute to the quality of analyses of SFC since FID is a highly sensitive detector. SFC can also be coupled with a mass spectrometer, an UV-visible spectrometer, or an IR spectrometer more easily than can be done with an HPLC. Some other detectors which are used with HPLC can be attached to SFC such as fluorescence emission spectrometer or thermionic detectors.

4.4.4.5 Advantages of working with SFC

The physical properties of supercritical fluids between liquids and gases enables the SFC technique to combine with the best aspects of HPLC and GC, as lower viscosity of supercritical fluids makes SFC a faster method than HPLC. Lower viscosity leads to high flow speed for the mobile phase.

Thanks to the critical pressure of supercritical fluids, some fragile materials that are sensitive to high temperature can be analyzed through SFC. These materials can be compounds which decompose at high temperatures or materials which have low vapor pressure/volatility such as polymers and large biological molecules. High pressure conditions provide a chance to work with lower temperature than normally needed. Hence, the temperature-sensitive components can be analyzed via SFC. In addition, the diffusion of the components flowing through a supercritical fluid is higher than observed in HPLC due to the higher diffusivity of supercritical fluids over traditional liquids mobile phases. This results in better distribution into the mobile phase and better separation.

4.4.4.6 Applications of SFC

The applications of SFC range from food to environmental to pharmaceutical industries. In this manner, pesticides, herbicides, polymers, explosives and fossil fuels are all classes of compounds that can be analyzed. SFC can be used to analyze a wide variety of drug compounds such as antibiotics, prostaglandins, steroids, taxol, vitamins, barbiturates, non-steroidal anti-inflammatory agents, etc. Chiral separations can be performed for many pharmaceutical compounds. SFC is dominantly used for non-polar compounds because of the low efficiency of carbon dioxide, which is the most common supercritical fluid mobile phase, for dissolving polar solutes. SFC is used in the petroleum industry for the determination of total aromatic content analysis as well as other hydrocarbon separations.

4.4.5 Supercritical fluid extraction (SFE)

The unique physical properties of supercritical fluids, having values for density, diffusivity and viscosity values between liquids and gases, enables supercritical fluid extraction to be used for the extraction processes which cannot be done by liquids due to their high density and low diffusivity and by gases due to their inadequate density in order to extract and carry the components out.

Complicated mixtures containing many components should be subject to an extraction process before they are separated via chromatography. An ideal extraction procedure should be fast, simple, and inexpensive. In addition, sample loss or decomposition should not be experienced at the end of the extraction. Following extraction, there should be a quantitative collection of each component. Ideally, the amount of unwanted materials coming from the extraction should be kept to a minimum and be easily disposable; the waste should not be harmful for environment. Unfortunately, traditional extraction methods often do not meet these requirements. In this regard, SFE has several advantages in comparison with traditional techniques.

The extraction speed is dependent on the viscosity and diffusivity of the mobile phase. With a low viscosity and high diffusivity, the component which is to be extracted can pass through the mobile phase easily. The higher diffusivity and lower viscosity of supercritical fluids, as compared to regular extraction liquids, help the components to be extracted faster than other techniques. Thus, an extraction process can take just 10-60 minutes with SFE, while it would take hours or even days with classical methods.

The dissolving efficiency of a supercritical fluid can be altered by temperature and pressure. In contrast, liquids are not affected by temperature and pressure changes as much. Therefore, SFE has the potential to be optimized to provide a better dissolving capacity.

In classical methods, heating is required to get rid of the extraction liquid. However, this step causes the temperature-sensitive materials to decompose. For SFE, when the critical pressure is removed, a supercritical fluid transforms to gas phase. Because supercritical fluid solvents are chemically inert, harmless and inexpensive; they can be released to atmosphere without leaving any waste. Through this, extracted components can be obtained much more easily and sample loss is minimized.

4.4.5.1 Instrumentation for SFE

The necessary apparatus for a SFE setup is simple. Figure 4.23 depicts the basic elements of a SFE instrument, which is composed of a reservoir of supercritical fluid, a pressure tuning injection unit, two pumps (to take the components in the mobile phase in and to send them out of the extraction cell), and a collection chamber.

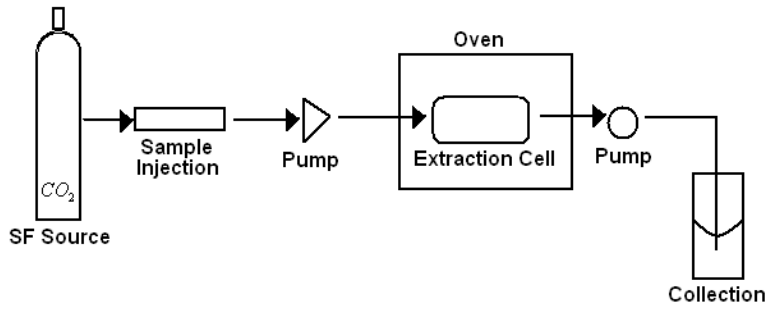

Figure 4.23: Scheme of an idealized supercritical fluid extraction instrument.

There are two principle modes to run the instrument:

- Static extraction.
- Dynamic extraction.

In dynamic extraction, the second pump sending the materials out to the collection chamber is always open during the extraction process. Thus, the mobile phase reaches the extraction cell and extracts components in order to take them out consistently.

In the static extraction experiment, there are two distinct steps in the process:

Step 1. The mobile phase fills the extraction cell and interacts with the sample.
Step 2. The second pump is opened and the extracted substances are taken out at once.

In order to choose the mobile phase for SFE, parameters taken into consideration include the polarity and solubility of the samples in the mobile phase. Carbon dioxide is the most common mobile phase for SFE. It has a capability to dissolve non-polar materials like alkanes. For semi-polar compounds (such as polycyclic aromatic hydrocarbons, aldehydes, esters, alcohols, etc.) carbon dioxide can be used as a single component mobile phase. However, for compounds which have polar characteristic, supercritical carbon dioxide must be modified by addition of polar solvents like methanol (CH^3OH). These extra solvents can be introduced into the system through a separate injection pump.

4.4.5.2 Extraction modes

There are two modes in terms of collecting and detecting the components:

- Off-line extraction.
- On-line extraction.

Off-line extraction is done by taking the mobile phase out with the extracted components and directing them towards the collection chamber. At this point, supercritical fluid phase is evaporated and released to atmosphere and the components are captured in a solution or a convenient adsorption surface. Then the extracted fragments are processed and prepared for a separation method. This extra manipulation step between extractor and chromatography instrument can cause errors. The on-line method is more sensitive because it directly transfers all extracted materials to a separation unit, mostly a chromatography instrument, without taking them out of the mobile phase. In this extraction/detection type, there is no extra sample preparation after extraction for separation process. This minimizes the errors coming from manipulation steps. Additionally, sample loss does not occur and sensitivity increases.

4.4.5.3 Applications of SFE

SFE can be applied to a broad range of materials such as polymers, oils and lipids, carbonhydrates, pesticides, organic pollutants, volatile toxins, polyaromatic hydrocarbons, biomolecules, foods, flavors, pharmaceutical metabolites, explosives, and organometallics, etc. Common industrial applications include the pharmaceutical and biochemical industry, the polymer industry, industrial synthesis and extraction, natural product chemistry, and the food industry.

Examples of materials analyzed in environmental applications: oils and fats, pesticides, alkanes, organic pollutants, volatile toxins, herbicides, nicotin, phenanthrene, fatty acids, aromatic surfactants in samples from clay to petroleum waste, from soil to river sediments. In food analyses: caffeine, peroxides, oils, acids, cholesterol, etc. are extracted from samples such as coffee, olive oil, lemon, cereals, wheat, potatoes and dog feed. Through industrial applications, the extracted materials vary from additives to different oligomers, and from petroleum fractions to stabilizers. Samples analyzed are plastics, PVC, paper, wood etc. Drug metabolites, enzymes, steroids are extracted from plasma, urine, serum or animal tissues in biochemical applications.

4.4.6 Summary

Supercritical fluid chromatography and supercritical fluid extraction are techniques that take advantage of the unique properties of supercritical fluids. As such, they provide advantages over other related methods in both chromatography and extraction. Sometimes they are used as alternative analytical techniques, while other times they are used as complementary partners for binary systems. Both SFC and SFE demonstrate their versatility through the wide array of applications in many distinct domains in an advantageous way.

4.4.7 Bibliography

- M. Caude and D. Thiebaut, *Practical Supercritical Fluid Chromatography and Extraction*, Harwood Academic Publishers, Switzerland (1999).
- M. D. Luque de Castro, M. Valcarcel, and M. T. Tena, *Analytical Supercritical Fluid Extraction*, Springer-Verlag, Berlin (1994).
- D. A. Skoog and J. J. Leary, *Principles of Instrumental Analysis*, Saunders College Publishing, Philadelphia (1992).
- L. T. Taylor, *Supercritical Fluid Extraction*, Wiley-Interscience Publication, New York, (1996).