

## CHAPTER II

### THEORY



#### 2.1 Basic Theory of Headspace Analysis ( 6,11,33,40,41 )

Headspace analysis technique ( HSA ) is an indirect method for determination of volatile components in liquid or solid by gas chromatographic analysis of the vapor phase which is in thermodynamic equilibrium with the sample to be analysed in a closed system. This technique is based on the distribution of a substance in two immiscible phases, i.e. gas - liquid or gas - solid. A component when added to a two phases system, will distribute itself in the two phases in a definite manner. Once an equilibrium state is established in the different phase system, the phenomenon of component i can be expressed mathematically by distribution law.(40)

$$\frac{C_{i,1}}{C_{i,2}} = K = \text{distribution coefficient} \quad ( 2.1 )$$

where  $C_{i,1}$  and  $C_{i,2}$  are the equilibrium concentrations of the component i in the phases 1 and 2, respectively and K is a constant.

In liquid sample system of HSA, the phase 1 is the liquid phase and the phase 2 is the gas phase. Therefore the gas-liquid distribution coefficient can be expressed as the following (11).

$$K = \frac{C_{i,l}}{C_{i,g}} \quad (2.2)$$

where  $C_{i,l}$  and  $C_{i,g}$  are the equilibrium concentrations of the component  $i$  in liquid phase and gas phase, respectively.

Such an expression of the distribution law is valid only for ideal system as can be seen from thermodynamic derivation of the law. The change in free energy in a system, is expressed by the differential (41)

$$\begin{aligned} dG = & \left( \frac{\partial G}{\partial T} \right)_{P, n_1, n_2, \dots} dT + \left( \frac{\partial G}{\partial P} \right)_{T, n_1, n_2, \dots} dP \\ & + \left( \frac{\partial G}{\partial n_1} \right)_{T, P, n_2, \dots} dn_1 + \left( \frac{\partial G}{\partial n_2} \right)_{T, P, n_1, \dots} dn_2 \\ & + \dots \end{aligned} \quad (2.3)$$

Since, by definition

$$\begin{aligned} \left( \frac{\partial G}{\partial n_1} \right)_{T, P, n_2, \dots} &= \text{Partial molar free energy} \\ &= \text{Chemical potential} = \mu_1 \end{aligned} \quad (2.4)$$

$$\begin{aligned} dG = & \left( \frac{\partial G}{\partial T} \right)_{P, n_1, n_2, \dots} dT + \left( \frac{\partial G}{\partial P} \right)_{T, n_1, n_2, \dots} dP \\ & + \mu_1 dn_1 + \mu_2 dn_2 + \dots \end{aligned} \quad (2.5)$$

At constant temperature and pressure,

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \dots \quad (2.6)$$

Since there is no change in the total amount of material involved in the system and the system is thermodynamically closed. Thus  $dG$  is equal to 0 for equilibrium at constant temperature and pressure, Therefore,

$$\mu_1 dn_1 + \mu_2 dn_2 + \dots = 0$$

or 
$$\sum \mu dn = 0 \quad (2.7)$$

This condition applies to the entire closed system. If a small quantity of the component  $i$  is moved within the system from phase 1 to phase 2 at equilibrium. (40)

$$-\mu_{i,1} dn_i + \mu_{i,2} dn_i = 0$$

and 
$$\mu_{i,1} = \mu_{i,2} \quad (2.8)$$

That is, the chemical potential of a component distributed between two phases at equilibrium is the same in both phases.

The chemical potential of any solute in solution can be written as (47)

$$\mu = \mu^{\circ} + RT \ln a \quad (2.9)$$

where  $a$  is the activity of solute in solution.

$\mu^\circ$  is the chemical potential of solute in a specific reference state and is a constant independent of the composition but is dependent of the temperature and pressure of system.

T is the absolute temperature.

R is the gas constant.

By substituting the chemical potential expressed in equation ( 2.9 ) into equation ( 2.8 ), it gives

$$\mu^\circ_{i,1} + RT \ln ( a_{i,1} ) = \mu^\circ_{i,2} + RT \ln ( a_{i,2} ) \quad ( 2.10 )$$

$$\text{or} \quad \ln \left( \frac{a_{i,1}}{a_{i,2}} \right) = \frac{\mu^\circ_{i,2} - \mu^\circ_{i,1}}{RT} \quad ( 2.11 )$$

The right-hand side of this expression is a constant, hence the ratio of the activity of solute i in immiscible phases also must be constant.

$$\frac{a_{i,1}}{a_{i,2}} = P = \text{Partition coefficient} \quad ( 2.12 )$$

The activity of any solute in solution can be written as (42)

$$a = \gamma C \quad ( 2.13 )$$

where  $\gamma$  is the respective activity coefficient.

C is the concentration of solute in solution.

However, an approximation holds true for dilute solution and ideal behaviour,  $\gamma$  is equal to 1 and equation ( 2.12 ) can be change to the original form as equation (2.1).

$$\frac{C_{i,1}}{C_{i,2}} = K = \text{distribution coefficient}$$

Since headspace analysis depends on an equilibrium existing between the liquid and gas phase that is injected into the gas chromatograph ( GC ). The resultant peak area ( A ) from GC detector is a measure of the amount of component i in gas phase and is thus proportional to its partial vapor pressure,  $p_i$  : ( 44 )

$$A = fp_i \quad ( 2.14 )$$

where f is the detector response factor and constant.

The partial pressure of the volatile solute i above the solution depends on the concentration of component i in the vapor phase (  $C_{i,g}$  ), peak area can be shown to the concentration form, is directly proportional to the concentration of component i in the vapor phase.

$$A = rC_{i,g} \quad ( 2.15 )$$

where  $C_{i,g}$  is the concentration of the component i in vapor phase which introduces into gas chromatograph. and r is the proportional constant .

In addition, according to Raoult's and Dalton's laws the partial vapor pressure ( $p_i$ ) is generally expressed as (45)

$$p_i = \gamma_i P_i^0 x_{i,l} = P x_{i,g} \quad (2.16)$$

where  $x_{i,g}$ ,  $x_{i,l}$  are the mole fraction of component  $i$  in gas and liquid phases, respectively,  $P_i^0$  is the vapor pressure of pure liquid component  $i$ ,  $P$  is total vapor pressure and  $\gamma_i$  is the activity coefficient.

Generally, the activity coefficient can be assumed to be a constant in dilute solution (the concentrations less than or equal to 1% or 10,000 ppm (28)). With constant activity coefficient, Raoult's law ( $\gamma_i P_i^0$ ) can be simplified to Henry's law, which stated that vapor pressure of the pure component  $i$  is given by

$$p_i = H x_{i,l} = P x_{i,g} \quad (2.17)$$

where  $H$  is the Henry's constant and is the product of  $\gamma_i$  and  $P_i^0$

In such a relationship with the distribution coefficient,  $K$  (43).

$$K = \frac{x_{i,l}}{x_{i,g}} = \frac{P}{H} \quad (2.18)$$

This expression shows that the Henry's constant,  $H$  is



inversely proportional to the distribution coefficient,  $K$  and is used frequently in practical thermodynamic computations while the distribution coefficients are more convenient for analytical applications.

The aim of the analysis is to determine the initial concentration of analyzed sample in solution. Under such conditions the formula acquired a special value satisfying this requirement, which is derived in the following manner.

In the equilibrium condition for any component between liquid sample and headspace gas, the relationship is given by Vitenberg(33) can be identified from a mass balance.

$$C^0_1 V_1 = C_1 V_1 + C_g V_g \quad ( 2.19 )$$

where  $C^0_1$  is the initial concentration of solute in liquid sample before equilibration.

$C_1$  and  $C_g$  are the concentrations of solute in liquid phase and gas phase, respectively after equilibration.

$V_1$  and  $V_g$  are the volume of the liquid phase and gas phase, respectively.

According to the distribution law in equation ( 2.2 ),

$C_1 = K C_g$  , thus

$$C^0_1 V_1 = K C_g V_1 + C_g V_g \quad ( 2.20 )$$

and simplifying yield ( 46 ).

$$C^0_1 = C_g \left( K + \frac{V_g}{V_l} \right) \quad ( 2.21 )$$

This formula is the principle of headspace analysis which indicates that the initial concentration of any component in solution is directly proportional to their concentration after equilibration in gas phase that relate with the peak area from gas chromatograph in equation ( 2.15 ) and it also forms the basic of more useful methods of measuring distribution coefficients. Therefore, if the initial concentration  $C^0_1$ , the volume  $V_l$  of liquid phase, the volume  $V_g$  of gas phase and the concentration  $C_g$  after equilibration, which can be determined from headspace gas by gas chromatograph, are known, the distribution coefficient  $K$  of the solute can be easily calculate or measured with this equation.

## 2.2 Sensitivity of Headspace Analysis Technique.

The basic parameters determining the sensitivity of headspace analysis are the values of the distribution coefficient,  $K$  and the relationship of the two phases volumes in equilibrium closed container. In reality, the sensitivity,  $S$  is supposed to mean the ratio of signal to sample size(46). In this method, the sensitivity can be expressed as a following

$$S = \frac{A}{C^0_1} \quad ( 2.22 )$$

where  $A$  is the peak area of gas chromatographic analysis.  
 $C^0_1$  is the initial concentration of component.



Since the peak area depends on the mass of the component,  $m$  which is introduced into the chromatographic column and the detector response factor,  $f$ . Therefore, it can be written as (48)

$$A = fm = fC_g v_g \quad ( 2.23 )$$

where  $C_g$  is the concentration of solute in gas phase after equilibration.

and  $v_g$  is the volume of sample of equilibrium headspace gas introduced into the column or injection volume.

If the values of  $A$  from equation ( 2.23 ) and  $C^0_1$  from equation ( 2.21 ) are substituted and simplified into equation ( 2.22 ), then it would yield as

$$S = \frac{f v_g}{( K + V_g/V_1 )} \quad ( 2.24 )$$

This equation shows the relationship of the sensitivity of headspace analysis with the nature of analyte ( or detector response factor ), the injection volume, the ratio of two phases and the distribution coefficient.

### 2.3 Method of Increasing the Analytical Sensitivity of Headspace Analysis Technique.

#### 2.3.1 Temperature.

The distribution coefficient is related to the temperature and vapor pressure by the following equation (6,11)

$$\left( \frac{\partial \ln K}{\partial P} \right)_{T,n} = \frac{-V_L}{RT} \quad ( 2.25 )$$

where  $V_L$  is the partial molar volume of analyte in liquid phase.

and the Clausius-Clapeyron equation (41,45) is shown the relationship between vapor pressure and temperature.

$$\frac{d P}{d T} = \frac{P \Delta H_{VAP}}{RT^2} \quad ( 2.26 )$$

where  $\Delta H_{VAP}$  is the molar heat of vaporization, which is the change in enthalpy accompanying the transfer of 1 mol of component from a solution into the gas phase.

Since  $P$ ,  $\Delta H_{VAP}$  and  $RT^2$  are positive, hence the right hand side of equation ( 2.26 ) is positive. Therefore, The left hand side of this equation must be positive as well, it means that the vapor pressure,  $P$  will be increased if the temperature,  $T$  is increased. By comparison with equation ( 2.25 ), if increasing temperature causes the increasing vapor pressure and all parameters on the right hand side of this equation are positive, the distribution coefficient,  $K$  would be decreased owing to the negative value of the right hand side of the equation. So the enhancement of sensitivity of headspace technique can be achieved by lowering the

distribution coefficient,  $K$  as can be seen from equation ( 2.24 ). Hence the increasing temperature would be enhancing the sensitivity of the headspace analysis.

However , enhancing the sensitivity by increasing the temperature is of limited experimental application owing to the risk of bursting the container or of losing the components as a result of chemical interaction with the material used as a septum (45).

### 2.3.2 Phase Ratio

Equation ( 2.24 ) indicates that the sensitivity of the analysis,  $S$  increases with the decreasing of the phase ratio,  $V_g/V_l$ . However, reducing the ratio  $V_g/V_l$  to a minimum value somewhat increases the error in the determination of the initial concentration of the substance in the solution due to the high concentration of the substance in gas phase. If there is a little error of the experimental performance such as a little error of liquid volume or injection volume, the precision of the analysis would decrease due to the different value of peak area in the same experiment. Therefore the ratio of  $V_g/V_l$  should be selected to the limits allowed by the system if the condition of headspace gas chromatographic analysis ensure sufficient precision for determination of substances.

### 2.3.3 Injection Volume

The sensitivity of headspace technique can be increased by increasing the injection volume as shown in equation ( 2.24 ) and Halasz (48) indicated the same result by deriving equation which was shown the relationship between the peak area , A and the concentration integral with time, (  $\int C dt$  ).

$$A = \gamma \int C dt = \gamma \int \frac{F_1}{F_1 + F_2} dt \quad ( 2.27 )$$

where  $\gamma$  is a factor of proportionality and C is the concentration of the sample in the carrier gas of gas chromatograph which depends on the flow rates of the sample,  $F_1$  and that of carrier gas,  $F_2$  .

In quantitative evaluation of analysis, this holds true for constant flow rate of gas mixture , (  $F_1 + F_2$  ) as can be seen from equation ( 2.28 )

$$A = \frac{\gamma}{F_1 + F_2} \int F_1 dt \quad ( 2.28 )$$

The integral,  $\int F_1 dt$  , is the quantity of the sample injected, m expressed in the number of moles or recalculated, in mass units and the constant values of (  $\gamma / ( F_1 + F_2 )$  ) maybe combined as follows

$$A = f m \quad ( 2.29 )$$

where f is the detector response.

Equation ( 2.29 ) can be rewritten in the form of the concentration and injection volume of the gas phase as

$$A = f C_g v_g \quad ( 2.30 )$$

where  $C_g$  is the equilibrium concentration of solute in gas phase.

and  $v_g$  is the injection volume.

It is evident from equation ( 2.31 ) that the peak area can be increased by increasing the injection volume. However, the sensitivity,  $S$  which is directly proportional to the peak area on a chromatogram as discussed in equation ( 2.22 ) would be increased as the increasing of injection volume.

#### 2.3.4 Salting Out Effect

Another way of increasing the sensitivity of the headspace analysis technique is addition of an electrolyte such as sodium chloride, sodium sulfate, ammonium chloride, etc. into the aqueous solution. This technique is known as " salting out effect ". In general, the addition of a soluble salt to an aqueous solution of an organic compound decreases the solubility of that compound according to Setschenow's equation,(49)

$$\log D = \log D_0 - kM \quad ( 2.31 )$$

where  $D_0$  denotes the solubility of the organic compound in pure water.

$D$  is the solubility of the organic compound in the salt solution.

$M$  is the molarity of the salt.

$k$  is the salting out constant whose value depends on the organic compound and on the nature of the salt.

The physicochemical basic of salting out is rather complex, one factor is that the high concentration of salt may remove water hydration from the organic species, thus their solubilities in water are reduced and their partial vapor pressure are increased (50). In addition, Curry (25) noticed that the salt also serve to decrease the vapor pressure of water. The result of this is the enhancement of extraction of solute into the gas phase and the decreasing of the distribution coefficient,  $K$ . It means that the sensitivity can be increased by addition of a soluble salt into the solution.