

## CHAPTER 2

### THEORY

#### 2.1 Basic Theory of Headspace Analysis ( 22, 54 )

Headspace analysis ( HSA ) is an indirect method for the determination of volatile constituents in liquid or solid by gas chromatographic analysis of the vapor phase which is in thermodynamic equilibrium with the sample to be analyzed in a closed system. It is a gas extraction technique which is based on the distribution of a substance in two immiscible phases, i.e., gas-liquid or gas-solid. When a substance is added to a two phases system, it will distribute itself in the two phases in a definite manner. The equilibrium distribution of substance  $i$  between two immiscible phases can be expressed by the distribution law

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

where  $C_{i,1}$  is the concentration of solute  $i$  in the phase 1.

$C_{i,2}$  is the concentration of solute  $i$  in the phase 2.

$K$  is the distribution coefficient or distribution constant

In gas-liquid system, it is conventional in the HSA method to consider the liquid phase as phase 1 and gas phase as phase 2, hence the gas-liquid distribution coefficient in headspace technique can be expressed as the following

$$K = \frac{C_l}{C_g} \quad (2.2)$$

where  $C_l$ ,  $C_g$  are the equilibrium concentration of the solute in liquid phase and gas phase, respectively.

$K$  is the gas-liquid distribution coefficient.

The expression of the distribution law is valid only for ideal system as can be seen from a thermodynamic derivation of the law. From the studied system, it is the thermodynamic closed system. Thus, when it reaches the equilibrium, the chemical potential,  $\mu$ , of solute between two phases are equal. Therefore

$$\mu_{i,l} = \mu_{i,g} \quad (2.3)$$

where  $\mu_{i,l}$  is the chemical potential of solute  $i$  in liquid phase.

$\mu_{i,g}$  is the chemical potential of solute  $i$  in gas phase.

Since the chemical potential of any solute in the solution can be expressed as

$$\mu_i = \mu_i^0 + RT \ln (\gamma_i x_i) \quad (2.4)$$

where  $\gamma_i$  is the activity coefficient of the solute  $i$  in solution.

$x_i$  is the mole fraction of the solute  $i$  in solution.

$\mu_i^0$  is the chemical potential of the solute  $i$  in a specific reference state and is a constant independent of composition but is dependent on the temperature and pressure of the system.

By substituting the chemical potential expressed in Equation (2.4) into Equation (2.3), it gives

$$\mu_{i,l}^{\circ} + RT \ln ( \gamma_{i,l} x_{i,l} ) = \mu_{i,g}^{\circ} + RT \ln ( \gamma_{i,g} x_{i,g} ) \quad (2.5)$$

or

$$\ln \frac{\gamma_{i,l} x_{i,l}}{\gamma_{i,g} x_{i,g}} = \frac{\mu_{i,g}^{\circ} - \mu_{i,l}^{\circ}}{RT} \quad (2.6)$$

The right-hand side of this expression, which contains the difference of the standard values of chemical potentials of the solute in liquid and gas phases, is a constant. Therefore, the ratio of activities,  $\gamma_i x_i$ , in different phase also must be constant.

$$\frac{\gamma_{i,l} x_{i,l}}{\gamma_{i,g} x_{i,g}} = K' = \text{partition coefficient} \quad (2.7)$$

The ratio of the mole fractions  $x_{i,l}/x_{i,g}$  would retain its integrity only if the activity coefficients remain uniform as in diluted and ideal solutions. In the latter case,  $\gamma_i = 1$  over the entire interval of mole fraction 0 to 1. Thus, the distribution law takes the form

$$\frac{x_{i,l}}{x_{i,g}} = K \quad (2.8)$$

It would be used without concentration limitations only in heterogeneous systems in which the phases can be considered as ideal solution. In real solution the consistency of the ratio of mole fraction  $x_{i,l}/x_{i,g}$  is maintained as  $x_i$  approached to zero. When the concentration of such solutions is calculated, the mole fractions is

not only a concentration unit which can be used, but also any concentration unit can be expressed.

Since headspace analysis depends on an equilibrium existing between the liquid or solid phase and the vapor phase that is injected into the gas chromatograph. The parameter measured in headspace analysis i.e., the peak height (h), or the peak area (A) is proportional to the partial vapor pressure,  $P_i$ , of the volatile component i, in the headspace. Thus, it can be expressed as the following equation

$$A \text{ or } h = f P_i \quad (2.9)$$

where  $f$  = the detector response factor.

$P_i$  = the partial vapor pressure of component i.

According to Raoult's law, the partial pressure ( $P_i$ ) of the solute above the solution depends on the mole fraction,  $x_i$ , of the solute i, and the vapor pressure,  $P_i^0$ , of the pure compound i at a given temperature corrected for any deviation from ideality by the activity coefficient,  $\gamma_i$  (22,48,55-56)

$$P_i = x_i \gamma_i P_i^0 \quad (2.10)$$

Generally, for diluted solutions (ppm range) the activity coefficient can be assumed to be a constant (57). Therefore, Raoult's law can be simplified to Henry's law, which states that the partial pressure of a volatile component i is directly proportional to its mole fraction in the liquid phase

$$P_i = H_i x_{i,l} \quad (2.11)$$

where  $H_i$ , Henry's constant, is the product of the activity coefficient,  $\gamma_i$ , and the vapor pressure of the pure component,  $P_i^0$ . At the pressures approach ideal gas behavior, the mole fraction of component  $i$  in the vapor phase is numerically equal to the relationship between the partial pressure  $P_i$  and the total pressure  $P$ . Therefore

$$P_i = P x_{i,g} = H_i x_{i,l} \quad (2.12)$$

Compared Equation (2.12) with Equation (2.8) this gives

$$H_i = \frac{P}{K} \quad \text{or} \quad K = \frac{P}{H_i} \quad (2.13)$$

where  $P$  is the total pressure.

$H_i$  is the Henry's constant.

$K$  is the distribution coefficient.

This expression shows that the Henry's constant  $H_i$  is inversely proportional to the distribution coefficient  $K$  and is used frequently in practical thermodynamic computations while the distribution coefficients are more convenient for any analytical applications.

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

While an equilibrium is being established between a liquid sample of volume  $V_l$  and a gas that occupies volume  $V_g$ , a certain

portion of the volatile substance, contained in the liquid, would distribute itself into the gas phase. The equilibrium concentration of the volatile substance ( $C_1$ ) then would be less than its initial concentration ( $C_1^0$ ). Their relationship can be derived from a mass balance

$$C_1^0 V_1 = C_1 V_1 + C_g V_g \quad (2.14)$$

and according to distribution law in Equation (2.2),  $C_1 = K C_g$ , thus

$$C_1^0 V_1 = K C_g V_1 + C_g V_g \quad (2.15)$$

or

$$C_1^0 = C_g \left( K + \frac{V_g}{V_1} \right) \quad (2.16)$$

This formula is the foundation of headspace analysis and it also forms the basis of the more useful methods of measuring distribution coefficients. Therefore, if the initial concentration  $C_1^0$ , the volume  $V_1$  of the liquid phase, the volume  $V_g$  of the gas phase and the concentration  $C_g$ , which can be determined from gas phase by gas chromatograph, are known, then the distribution coefficient of the solute can be easily determined with this formula.

## 2.2 Sensitivity of Headspace Analysis Technique ( 22, 58-59)

The basic parameters determining the sensitivity of an analysis are the values of the distribution coefficient and the relationship of the phase volumes in the container in which the equilibrium has been established. In reality, the sensitivity (S) is

defined as the ratio of signal to sample size (58). Thus, the sensitivity of the HSA method can be expressed as the following

$$S = \frac{A_g}{C_1^0} \quad (2.17)$$

Since the area of the peak on a chromatogram is proportional to the mass,  $m$ , of the component (59). Therefore, it can be written as follow

$$A_g = f m_g = f C_g v_g \quad (2.18)$$

where  $f$  is the detector response factor

$m_g$  is the mass of the substance introduced into the chromatographic column per sample of equilibrium gas.

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

If the values of  $A_g$  from Equation (2.18) and  $C_1^0$  from Equation (2.16) is substituted into Equation (2.17), then it would result as

$$S = f \frac{v_g}{K + \frac{V_g}{V_1}} \quad (2.19)$$

This equation shows the relationship of the sensitivity of headspace analysis with the nature of the analyzed substance, the liquid phase, and the conditions under which the experiment is conducted.

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

#### 2.3.1 Temperature (22,54,56,60)

The distribution coefficient is related to the temperature and vapor pressure by the following Equation (22)

$$K = \frac{R T d_L}{f_i P_i^{\circ} M_L} \quad (2.20)$$

where  $d_L$  = the density of the liquid phase.

$M_L$  = the molar mass of the liquid phase.

$P_i^{\circ}$  = the vapor pressure of pure component i.

This equation shows that the distribution coefficient,  $K$ , is directly proportional to the temperature, and

$$\frac{d P^{\circ}}{d T} = \frac{P^{\circ} \Delta H_{\text{vap}}}{R T^2} \quad (2.21)$$

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

This equation is known as Clausius-Clapeyron equation which is shown the relationship between vapor pressure and temperature (54, 60). Since  $P^{\circ}$ ,  $\Delta H_{\text{vap}}$  and  $RT^2$  are positive, hence, the right-hand side of Equation (2.21) is positive, and, therefore, the vapor pressure,  $P^{\circ}$ , would be increased with the increasing of the temperature. When the vapor pressure,  $P^{\circ}$ , of component i is



increased, the solubility of the component  $i$  in aqueous solution would be reduced. Thus, this results in the enhancement of the extraction of the solute into the gas phase.

Moreover, the enhancement of the sensitivity in headspace technique can be achieved by lowering the distribution coefficient,  $K$ , as can be seen from Equation (2.19). However, increasing the temperature of system would result in increasing of the vapor pressure of component  $i$  as can be seen from the Clausius-Clapeyron equation and also the distribution coefficient is inversely proportional to the vapor pressure of pure component as shown in Equation (2.20). Thus, increasing in temperature would lower the distribution coefficient, and, therefore, it would be enhancing the sensitivity of the headspace analysis.

However, enhancing the sensitivity of headspace analysis technique 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 (54).

### 2.3.2 Phase Ratio (22)

Equation (2.19) 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 ( 22 ) as can be seen from Equation (2.22) which is the differential form of Equation (2.16)

$$\frac{\Delta C_1^0}{C_1^0} = \frac{\Delta C_g}{C_g} + \frac{\Delta K}{K} \left( \frac{K}{K + \frac{V_g}{V_1}} \right) \quad (2.22)$$

This equation shows that the increase of the ratio  $V_g/V_1$  lowers the contribution of the error in the determination of  $K$  to the total error of an analysis (especially in the most favorable cases with low  $K$ ). Therefore, if the conditions of gas-chromatographic analysis ensure sufficient sensitivity for the determination of  $C_g$ , the ratio of  $V_g/V_1$  should be increased to the limits allowed by the system used to establish the distribution coefficient ( $K$ ).

### 2.3.3 Injection Volume (61-62)

The sensitivity of the headspace analysis technique can be increased by increasing the injection volume. Since the flame ionization detector is classified as a mass-sensitive detector. It gives a response,  $R$ , proportional to the mass of solute reaching the detector in unit time,  $dm/dt$  ( 61-62 ). Therefore, the response,  $R$ , can be expressed as

$$R = f \frac{dm}{dt} \quad (2.23)$$

where  $R$  is the response of the mass-sensitive detector.

$f$  is the detector response factor.

$\frac{dm}{dt}$  is the mass flow rate of the sample.

By definition, the peak area, A, on a chromatogram is an integration of the detector signal with time ( 61 ). Therefore,

$$A = \int R dt \tag{2.24}$$

Substitution of R from Equation (2.23) into Equation (2.24) yields

$$A = \int f \frac{dm}{dt} dt \tag{2.25}$$

$$= f m \tag{2.26}$$

- where A is the peak area on a chromatogram.
- m is the total mass of sample introduced into the chromatographic column.
- f is the detector response factor.

Equation (2.26) can be rewritten in the form of the concentration and the injection volume of the gas phase as follow

$$A = f C_g v_g \tag{2.27}$$

- where C<sub>g</sub> is the equilibrium concentration of the solute in gas phase.
- v<sub>g</sub> is the injection volume.

It is evident from Equation (2.27) that the peak area can be increased by increasing the injection volume. Therefore, the sensitivity, S, which is proportional to the area of the peak on a chromatogram as shown in Equation 2.17 would be increased as the increase of injection volume.

### 2.3.4 Salting Out Effect (63-64)

Another way of increasing the sensitivity of the headspace analysis technique is the increase of the activity coefficient,  $\gamma_i$ . It can be achieved by the addition of an electrolyte such as sodium chloride, sodium sulfate, ammonium chloride, etc, into the aqueous solution. This technique is known as "salting out". 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

$$\log S = \log S_0 - k_s M \quad (2.25)$$

where  $S_0$  is the solubility of organic compound in pure water.

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

$M$  is the molarity of the salt

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

The physicochemical basis of salting out is rather complex; one factor is that the high concentration of salt may remove water of hydration from the organic species, thus their solubilities in water are reduced and their partial vapor pressures are increased. The result of this is the enhancement of extraction of the solute into the gas phase (64).