Analysis of Static Headspace Technique for Partially Volatile Matrices

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Abstract

A theoretical analysis of static headspace gas chromatography for partially volatile matrices has been developed. The existing headspace theory in the literature can be applied to the sample matrices that are nonvolatile in nature. This theoretical analysis has been modified here so that it can be applied to volatile matrices as well. A factor (ϕ) is introduced to account for partial evaporation of the matrix. This matrix evaporation factor can be calculated from the vapor pressure, density, and molecular weight of the matrix. Though the effect of matrix evaporation is insignificant for most aqueous samples, it could be appreciable for various organic matrices having relatively higher molecular weight or vapor pressure than water.

Introduction

Headspace techniques are employed in conjunction with gas chromatographic (GC) analysis for certain types of samples. The GC can handle any gaseous sample and any liquid sample that can be vaporized completely and instantaneously before it goes to a proper column for separation. Unfortunately there are many liquid samples (especially environmental samples) that cannot be directly injected into the GC. For such samples, the analyte is first allowed to equilibrate with air inside a closed sample vial. After the end of the equilibration, the vapor space above the liquid sample matrix inside the vial is injected into the GC for analysis. This technique is known as headspace GC and has enormous practical applications (1). Headspace technique has made GC analysis applicable to any type of sample matrix, including solid-sample matrices. Two important pieces of information can be obtained from the headspace analysis of a sample: the concentration of the analyte in the matrix and the distribution coefficient of the analyte between the sample matrix and air.

There are two types of headspace techniques: dynamic headspace (or purge and trap) and static headspace. Compared with the dynamic headspace, static headspace is a simple tech-

nique in principle. The theory for headspace analysis available in the literature is developed with an assumption that the matrix is completely nonvolatile. The negligible effect of matrix volatility is taken for granted irrespective of the type of sample analyzed. However, the error in applying this analysis for a partially volatile matrix could be significant. Matrix-independent full evaporation technique (2) is an ingenious technique for determining an unknown concentration of an analyte in any matrix including volatile matrices. However, it does not provide any information about the determination of a distribution coefficient. In this article, the existing theoretical analysis of static headspace technique has been modified to accommodate matrix vaporization. The importance of this generalized analysis to partially volatile matrices is also discussed.

Experimental

Existing and modified analyses

The basic principle involved in headspace theory is the establishment of equilibrium between the sample phase and the headspace above the sample. In a vial, at the end of the equilibration process, the material balance of the distributing species can be written as:

$$V_l C_o = V_l C_l + V_g C_g \qquad \text{Eq 1}$$

where C_o is the initial concentration of the analyte (mol/mL); V_l and V_g are the liquid sample volume and headspace volume, respectively (cm^3); and C_l and C_g are the equilibrium concentrations of the analyte in the liquid phase (mol/mL) and headspace (mol/cm^3), respectively. They are related as follows:

$$H = C_l / C_g \qquad \text{Eq 2}$$

where H is the distribution coefficient or the dimensionless Henry's law constant. Combining Equations 1 and 2 and rearranging them results in the following:

$$\frac{1}{C_g} = \frac{H}{C_0} + \frac{1}{C_0}\frac{V_g}{V_l} \qquad\qquad \text{Eq 3}$$

In most cases at a low concentration range, the GC area count is directly proportional to the gas phase concentration (C_g). Hence Equation 3 can be rewritten as:

$$\frac{1}{A} = \frac{HR_f}{C_0} + \frac{R_f}{C_0}\frac{V_g}{V_l} \qquad\qquad \text{Eq 4}$$

where A is the GC area count and R_f is the GC response factor. In this technique, a number of sample vials of fixed volumetric capacity are partially filled with different volumes of a liquid sample and sealed. Equilibrium is attained between the liquid phase and the headspace at a specified temperature. The headspace sample is then injected into the GC for analysis. This process is repeated for each vial. A plot of the inverse of the GC area count ($1/A$) versus V_g/V_l results in a straight line, as predicted by Equation 4. The original concentration, C_0, can be obtained from the slope of the straight line, whereas the dimensionless Henry's law constant (H) can readily be calculated as the ratio of intercept to slope (3–4). This experimental technique is known as the variable volume headspace technique.

Volatile matrices

In developing the above analysis, it is assumed that the matrix volume remains constant during the equilibration process (i.e., the matrix sample is assumed to be completely nonvolatile). This is essentially true for any aqueous or relatively nonvolatile organic matrix. However, this may not be true for various organic matrices, especially when the analyte has a high affinity toward the matrix (i.e., high distribution coefficient). For such matrices, V_l and V_g in Equations 1, 2, and 4 will change during the experiment. When the matrix sample is partially volatile, the sample dispensed into the vial will partially vaporize depending on the temperature and available headspace volume in the vial.

Therefore, at the end of the equilibration process, both V_g and V_l will be different from their respective original values. The material balance equation (Equation 1) can no longer be used. The new material balance equation for the present case would be

$$V_l C_{0,vm} = V_r C_l + V_{g'} C_g \qquad\qquad \text{Eq 5}$$

Here V_r is the residual volume of the sample matrix (mL), $V_{g'}$ is the expanded headspace volume after the matrix evaporation (cm³), and $C_{0,vm}$ is the original concentration of the solute in the matrix (mol/mL) when matrix evaporation is taken into consideration. Because the total volume of the sample vial remains constant, the following is true:

$$V_g + V_l = V_{g'} + V_r \qquad\qquad \text{Eq 6}$$

By substituting Equation 2 into Equation 5 and rearranging, an expression similar to Equation 4 can be obtained.

$$\frac{1}{A} = \frac{V_r}{V_l}\frac{R_f H_{vm}}{C_{0,vm}} + \frac{V_{g'}}{V_l}\frac{R_f}{C_{0,vm}} \qquad \text{Eq 7}$$

Here H_{vm} is considered to be the distribution coefficient when matrix evaporation is taken into account. Though V_l is known in the above equation, V_r and $V_{g'}$ are unknown variables. If one is known, the other can be calculated from Equation 6. However, the realistic measurement of either V_r or $V_{g'}$ will be very difficult. It is also difficult to calculate the exact volume of matrix that vaporizes in the equilibration process. An approximate method for finding the expressions of V_r/V_l and $V_{g'}/V_l$ in terms of the known variable V_g/V_l is shown here.

Assuming the ideal gas law, the maximum amount of sample matrix that would be vaporized in the equilibration process at a constant temperature can be written as:

$$V_e = \frac{P^0_m M_m V_{g'}}{dRT} \qquad\qquad \text{Eq 8}$$

where P^0_m is the vapor pressure (atm) of the matrix material at the equilibrium temperature T (K), R is the universal gas constant (cm³ atm/mol K), and M_m and d are the molecular weight (g/mol) and density (g/mL) of the matrix, respectively. Because V_e is the volume of the matrix sample that is vaporized, the following can be obtained from Equation 6:

$$V_e = V_l - V_r = V_{g'} - V_g \qquad\qquad \text{Eq 9}$$

Hence Equation 8 can be rearranged as:

$$\frac{V_e}{V_{g'}} = \frac{V_l - V_r}{V_{g'}} = \frac{V_{g'} - V_g}{V_{g'}} = \frac{P^0_m M_m}{dRT} \qquad \text{Eq 10}$$

From Equation 10, the following two expressions can be derived.

$$\frac{V_{g'}}{V_l} = \frac{1}{1-\phi}\frac{V_g}{V_l} \qquad\qquad \text{Eq 11}$$

$$\frac{V_r}{V_l} = 1 - \frac{\phi}{1-\phi}\frac{V_g}{V_l} \qquad\qquad \text{Eq 12}$$

where $\phi = P^0_m M_m/dRT$ and can be considered the matrix evaporation factor. Substitution of Equations 11 and 12 into Equation 7 results in the following:

$$\frac{1}{A} = \frac{R_f H_{vm}}{C_{0,vm}} + (1-\phi H_{vm})\frac{V_g}{V_l}\frac{R_f}{C_{0,vm}(1-\phi)} \qquad \text{Eq 13}$$

The above expression is an equation of a straight line. Taking the ratio of intercept to slope and rearranging, the expression for H_{vm} is obtained as:

$$H_{vm} = \frac{I/S}{1 + \phi(I/S - 1)} \qquad\qquad \text{Eq 14}$$

Here, I and S are the intercept and slope of the straight line, respectively. Once the H_{vm} value is known, the original concentration ($C_{0,vm}$) can be obtained either from the slope or from the intercept of the straight line Equation 13 as:

$$C_{0,vm} = \frac{R_f/S}{1 + \phi(I/S - 1)} \qquad\qquad \text{Eq 15}$$

Results and Discussion

When matrix evaporation is not considered ($\phi = 0$), $H_{vm} = I/S$ = H, and $C_{0,vm} = R_f/S = C_0$. The effect of matrix evaporation on the determination of two unknown parameters (namely the original analyte concentration and the distribution coefficient) by the static headspace variable volume technique is shown in Figure 1. Here theoretical errors associated with the distribution coefficient and original concentration estimation without considering matrix evaporation are plotted against the evaporation factor ϕ (in logarithmic scale). The errors were calculated based on H_{vm} and $C_{0,vm}$. The effect of matrix evaporation becomes more pronounced for higher ϕ and I/S values. From Figure 1, it is also clear that as long as ϕ is below 0.001, the errors between H_{vm} and H or $C_{0,vm}$ and C_0 will be well within 10% unless the I/S value is very high. As ϕ increases above 0.001, errors become more significant, especially for higher I/S values. The value of the matrix evaporation factor essentially depends on two important properties of the matrix: molecular weight and vapor pressure at the operating headspace temperature. When the concentration of the analyte in the matrix is too low (parts per billion level) and it is distributed more toward the matrix, it is necessary to increase the headspace temperature up to a possible limit (reasonably below the boiling point of the matrix) to get an appreciable GC response. For an aqueous matrix at 100°C, the value of ϕ will be $1 \times 18 / (82.06 \times 373 \times 0.96) = 6.1 \times 10^{-4}$. Because the distribution coefficient of an organic analyte in an aqueous matrix is generally low (well within 100), the error is insignificant (less than 1% [Figure 1]). For lower alcohol and organic acids in water, the

I/S value will be high; for an I/S value of 100, the error will be about 6%. Hence even for an aqueous sample, the effect of matrix evaporation could be appreciable, based on the system. As an arbitrary example, ethyl acrylate as a matrix has a boiling point of 373 K and a molecular weight of 100.12; the value of ϕ at 100°C is calculated as 3.5×10^{-3}. If the I/S value obtained from an experiment is assumed to be about 200 for an organic analyte present as an impurity in ethyl acrylate, the error becomes close to 65%, which is quite significant. Similar error figures can be calculated for any other matrix. Depending on the system and extraction condition, the effect of matrix volatility could be either negligible or appreciable. One may easily find the effect of matrix vaporization through calculation of ϕ and accordingly may use the above analysis for variable volume headspace technique.

Conclusion

A generalized theoretical analysis for variable volume static headspace technique considering matrix evaporation has been presented. In most applications of headspace method, the effect of matrix evaporation may be negligible. However, this could be appreciable for many organic matrices, depending on their molecular weight and vapor pressure at the working headspace temperature. While working with a new system, one may calculate the ϕ factor to estimate the importance of the matrix evaporation on determination of the distribution coefficient and analyte concentration instead of ignoring this effect completely.
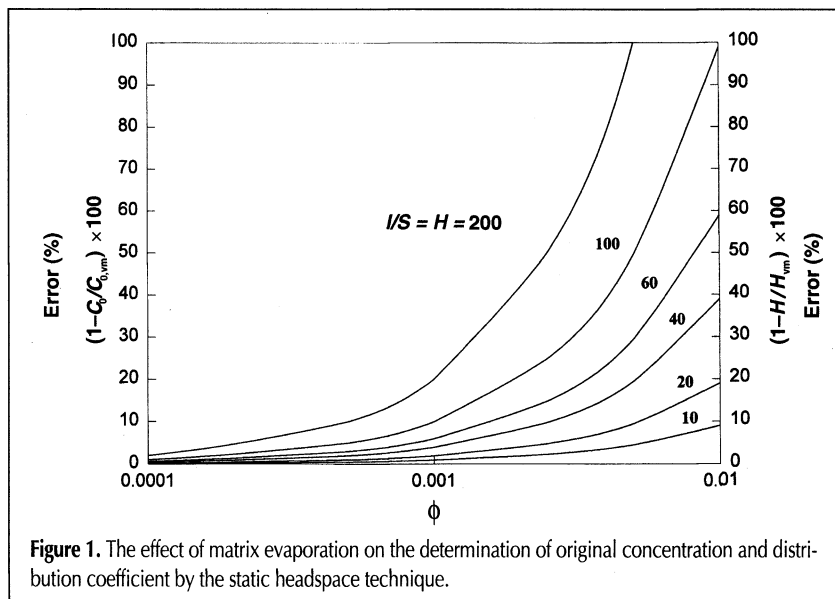
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Figure 1. The effect of matrix evaporation on the determination of original concentration and distribution coefficient by the static headspace technique.