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Determination of solid–liquid partition coefficient of volatile compounds by solid phase ratio variation based headspace analysis

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ABSTRACT

A novel method has been developed for the determination of the solid–liquid partition coefficient of volatile analytes using headspace gas chromatography (HS–GC). The method is based on the headspace measurement for the three-phase equilibrium in sample vials containing different amounts of solid sample. Theory is presented that allows calculation of partition coefficient of the analyte from the HS–GC data obtained at the condition of solid phase ratio variation (SPRV). Analysis of errors demonstrates that this solid phase ratio variation method generates results with reasonable precision for all volatile compounds, much better than the liquid-focused (i.e., liquid phase ratio variation) method reported early.

The solid phase ratio variation method was used to determine the solid–liquid partition coefficient of toluene in a water–polystyrene system, using polymer particles with average size ranging from 0.4 to 2.1 μm. The results show that the partition coefficient of toluene in the given system is proportional to the specific surface area of the polymer particles, as expected.

In summary, the method is a simple and practical tool for determining the solid–liquid partition coefficient of volatile analytes.

1. Introduction

Solid–liquid partition (or distribution) coefficient of an analyte is defined as the equilibrium ratio of its concentration in and/or on the solid phase to its concentration in the liquid phase. It is an important parameter in a number of applications; e.g., estimation of the migration and ultimate fate of organic contaminations present in effluents, soil, sludge and sediments [1,2]; evaluation of the capacity of packaging materials minimizing the loss of aroma compounds in food [3–5]; and probing the thermodynamic activity and micellar equilibria of lipophilic drugs in model lipid digestion products [6]. Therefore, development of accurate and reliable methods for the determination of solid–liquid coefficients of target compounds is important in many fields.

Most methods reported in the literature are based on the determination for the concentration of target compound in the solid phase and in the liquid phase, separately [7]. Typically, the quantitative analyses for the compounds in these phases are performed by gas chromatography (GC) [8] or high performance liquid chromatography (HPLC) [9–11]. These analytical methods involve many procedures, typically filtration and solvent extraction, in order to minimize matrix effects on the measurement, resulting in complicated operations that are subject to significant sources of error. For example, it is difficult to prepare an ideal equilibrated solid phase sample because some of the residual liquid containing the analyte remained on the solid surface is hardly removed. As a result, the concentration of the analyte in the equilibrated solid phase would be overestimated. Therefore, an in-situ measurement technique; that is, one that does not require separation of the solid and liquid phases, is highly desirable.

For volatile analytes, several methods are well-established for the determination of their vapor–liquid and vapor–solid partition coefficients [12–18]. Among these methods, headspace gas chromatography (HS–GC) plays an important role [15–18], especially for the techniques based on in-situ measurement [18]. These techniques include the vapor–liquid phase ratio variation (LPRV) for Henry's law constant or partition coefficient measurement [17]. Recently, we developed a HS–GC technique for in-situ determination of the adsorption constant of ethane in a shale sample through solid phase ratio variation (SPRV) in a two-phase system [19]. Tehrany et al. [20] developed a technique similar to the LPRV method for measuring the solid–liquid partition coefficients

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of volatile migrants in solid (polymer) and liquid phases, simulating the circumstances that exist in food packaging. Their work was based on three-phase equilibrium, from which the partition coefficients of a volatile analyte moving between the solid and liquid phases can be determined by measuring the analyte in the vapor phase using HS–GC. Unlike the LPRV or SPRV methods used in two-phase system that the ratio change is directly related to the phases studied [17,19], the vapor phase volume also varied in their method. According to our previous study on the vapor–liquid phase equilibrium (VLE) using LPRV technique [17] and the recent work on vapor–solid phase equilibrium (VSE) using SPRV technique [19], we realized that the selection of phase ratio is very important to the error level in these methods. Selecting an improper ratio of phases; i.e., without considering the error propagation, could lead to an unacceptably large error; e.g., up to 100% [17,19]. Therefore, it is necessary to conduct an analysis of errors in the method development.

Like the LPRV approach [20], the SPRV approach could also be an alternative to determine solid–liquid partition coefficient of volatile compounds for the three-phase system. Therefore, it is also necessary to examine whether the SPRV approach is more appropriate way to be used in such applications, from error analysis point of view, in the method development.

In the present work, we developed a new headspace analytical technique based on SPRV (where the volume ratio of liquid-to-vapor is fixed) for the three-phase system. A major aim of the work was to derive the mathematical expressions for calculating the partition coefficient of a volatile analyte between solid–liquid phases and examine the propagation of errors in the method. As a comparison, an error analysis for LPRV method was also conducted. As a specific application, we use the method to determine the partition coefficient of toluene between water and polystyrene phases.

2. Materials and methods

2.1. Chemicals and samples

All chemicals used in the study, including toluene and polystyrene latex beads (10%, w/w) with three different average particle sizes (0.402, 0.723, and 2.06 μm), were obtained from commercial sources and have been listed in Table 1. A toluene solution (85.4 mg/L) was prepared by adding a 100 μL of toluene to 1.0 L of distilled water. The polystyrene suspensions (10.0 g/L) were obtained by adding a 10.0 g of latex beads to volumetric flask and diluting with water to 100 mL.

2.2. Apparatus and operations

HS–GC measurements were carried out with an automatic headspace sampler (DANI HS 86.50, Italy) fitted to a GC system (Agilent GC 7890A, US). The flame ionization detector (FID) measurement system operating conditions were as follows: detector temperature = 250 °C; the flow rates of hydrogen and air = 40 and 400 mL/min, respectively; a DB-5 capillary column (30 m × 0.32 mm × 0.25 μm) operated with nitrogen carrier gas; and oven temperature = 30 °C. Headspace operating conditions were as follows: equilibration temperature = 32 °C; sampling needle and loop temperature = 40 °C; transfer line temperature = 50 °C; vial pressurization time = 0.2 min; sample loop fill time = 0.15 min; and sample loop volume = 0.5 mL.

Table 1
Suppliers and purities of the used chemicals.

Chemical	Supplier	Mass fraction purity (%)
Water	Distilled	
Toluene	Sigma-Aldrich	99.8%
Polystyrene latex beads	Duke Scientific	10% solid

Table 2
Symbols, definitions and units.

Symbol	Definition	Unit
m	Total mass of analytes in headspace vial	mg
m_L	Mass of analytes in liquid phase	mg
m_G	Mass of analytes in gaseous phase	mg
m_S	Mass of analytes on solid phase	mg
W_S	Mass of solid substrates added in vial	g
C_G	Concentration of analytes in gaseous phase	mg/mL
C_L	Concentration of analytes in liquid phase	mg/mL
C_S	Concentration of analytes on solid phase	mg/g
V_G	Volume of gaseous phase	mL
V_L	Volume of liquid phase	mL
V_S	Volume of solid phase	mL
V_T	Volume of headspace vial	mL
C_0	Content of analytes in solid sample	mg/g
H	Dimensionless Henry's law constant of analytes	–
K	Solid–liquid partition coefficient of analytes	mL/g
f	Response factor	mg/mL
a	Slope in Eqs. (6), (8) and (10)	mL, in Eq. (6) mL/mg^2, in Eq. (8) mL^2/mg, in Eq. (10)
b	Intercept in Eqs. (6), (8) and (10)	mL/mg
$f(i)$	Sensitivity coefficients to parameter 'i'	–
$\Delta i/i$	Relative error in quantity	–
d_i	Average particle size	μm
s	Specific surface area	m^2/g
ρ	Density of polystyrene	1.05 g/mL [24]

2.3. Sample preparation and measurement

A 10, 20, 30, 40, and 50 μL of the polystyrene suspensions were placed into three sets (one for each particle size) of headspace vials (21.6 mL), each of which contained 5 mL of toluene solution. After sealing the sample vials with PTFE/butyl rubber septum and aluminum cap, the vials were placed in the headspace sampler and allowed to equilibrate at 32 °C for 15 min. Finally, a portion of the vapor in headspace sample vial was withdrawn and analyzed by GC.

3. Results and discussion

3.1. Methodology

In a three-phase (solid, liquid, and vapor) system, a volatile species in the headspace vial containing original sample (solid) is distributed among these phases and the total mass of the species can be written as

$$m = m_G + m_L + m_S = C_G \times V_G + C_L \times V_L + C_S \times W_S \tag{1}$$

All symbols and their definitions are listed in Table 2.

When the phase equilibrium at given temperature is achieved, the partition coefficients between the vapor and liquid phases and between the soild and liquid phases can be expressed as

$$H = \frac{C_G}{C_L} \tag{2-1}$$

and

$$K = \frac{C_S}{C_L} \tag{2-2}$$

Merge Eqs. (1), (2-1) and (2-2), the concentration of the volatile species in the vapor phase (C_G) can be written as

$$C_G = \frac{m}{V_G + \left(V_L/H\right) + (W_S \times K)/H} \tag{3}$$