

Determination of 1-Octanol-Air Partition Coefficient Using Gaseous Diffusion in the Air Boundary Layer

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Exact determination of the partition coefficient between 1-octanol and air (K_{OA}) is very important because it is a key descriptor for describing the thermodynamic partitioning between the air and organic phases. In spite of its importance, the number and quality of experimental K_{OA} values for hydrophobic organic chemicals are limited because of experimental difficulties. Thus, to measure K_{OA} values, a high-throughput method was developed that used liquid-phase extraction with 1-octanol drop at the tip of a microsyringe needle. The concentration in the headspace surrounding the 1 μ L octanol drop was equilibrated with liquid octanol containing polycyclic aromatic hydrocarbons (PAHs). The change in concentrations of PAHs in the octanol drop was measured to obtain mass transfer rate constants, and these rate constants were then converted into K_{OA} values using a film diffusion model. Thirteen polycyclic aromatic hydrocarbons with log K_{OA} between 5 and 12 were chosen for the proof of the principle. Experimental determination of log K_{OA} was accomplished in 30 h for PAHs with their log K_{OA} less than 11. The measured log K_{OA} values were very close to those obtained by various experimental and estimation methods in the literature, suggesting that this new method can provide a fast and easy determination of log K_{OA} values for many chemicals of environmental interests. In addition, the applicability of the method can be extended to determine Henry's law constant for compounds with low vapor pressure and to estimate gaseous transfer rate of semivolatile compounds for environmental fate modeling.

Introduction

The fate and transport of hydrophobic organic chemicals are often characterized by thermodynamic partitioning processes. Among various partition coefficients used for describing the processes, the partition coefficient between 1-octanol and air (K_{OA}) is thought to be crucial for chemical transport through the atmosphere, either by gaseous form or sorbed to particulates (1, 2). It has been widely used for the evaluation of long-range transport and deposition of persistent organic pollutants (3–5), screening persistence of new and existing chemicals (6), bioaccumulation in terrestrial organisms (7), and multimedia fate models for the terrestrial environment (8, 9). The significance of K_{OA} has been

highlighted by the fact that organic compounds with low K_{OW} but high K_{OA} can biomagnify to a high degree in terrestrial food webs emphasizing that K_{OA} is a better predictor of biomagnifications in air-breathing organisms than K_{OW} , conventional descriptor for hydrophobicity (7).

Although precise K_{OA} values are required in many related areas, there are high uncertainties in estimated or indirectly derived K_{OA} values, and experimental K_{OA} values are not easy to obtain. A generator column method is the conventional method for measuring K_{OA} values for various semivolatile organic compounds such as polycyclic aromatic hydrocarbons (PAHs) (10, 11), chlorinated benzenes (12), polychlorinated biphenyls (12, 13), polychlorinated naphthalenes (11), dibenzo-*p*-dioxins and dibenzofurans (14), polybrominated diphenyl ethers (15), organochlorine pesticides (2), and perfluorinated compounds (16, 17). However, the generator column method is time-consuming, especially at low temperatures and for compounds with low volatility, and it needs many analytical steps which may result in experimental artifacts during the measurement of K_{OA} (18, 19).

In order to simplify the measurement of K_{OA} , many researchers developed gas chromatographic methods using chromatographic retention time or gas chromatographic capacity factor in comparison with that of a standard chemical (18, 20, 21). Although these methods have been successfully applied to various types of semivolatile organic compounds, their success depends on the availability of reliable data that served as standard reference, and derived relations may not be applicable for different classes of chemicals. Therefore, there are still needs for high-throughput methods by which reliable K_{OA} can be measured.

Recent progress in solid-phase and liquid-phase microextraction showed that the extraction-time profile can be explained by a two-film model (22, 23). Thus, the rate of extraction is related with diffusivities in both phases and the distribution coefficient between the extracting phase and the medium (23, 24). For example, Jeannot and Cantwell (22) showed that solvent microextraction using a 1 μ L octanol drop from the tip of a microsyringe needle in the aqueous solution is useful for the determination of mass transfer coefficient using a film theory of convective-diffusive mass transfer. Similarly, a dynamic permeation method was developed to determine high partition coefficients between poly(dimethylsiloxane) and water in a reasonably short experimental time using two parallel polymer disks separated by agitated deionized water (25). Thus, it would be possible to measure high K_{OA} in a reasonably short time with a simple experimental apparatus using mass transfer in the air boundary layer surrounding a liquid octanol drop if the phenomenon is well characterized by a film diffusion model.

Consequently, we developed a simple experimental device using liquid-phase microextraction by a microsyringe for measuring K_{OA} values of selected PAHs with log K_{OA} values ranging between 5 and 12 to provide proof of concept. The concentration in the headspace surrounding a 1 μ L octanol drop at the tip of a microsyringe needle was equilibrated with liquid octanol containing PAHs. The change in concentration in the octanol drop was measured to obtain mass transfer rate constants, and these rate constants were then converted into K_{OA} values using a film diffusion model. The measured log K_{OA} values were compared with literature values determined by various experimental and estimation methods. Potential applications of this device are also suggested.

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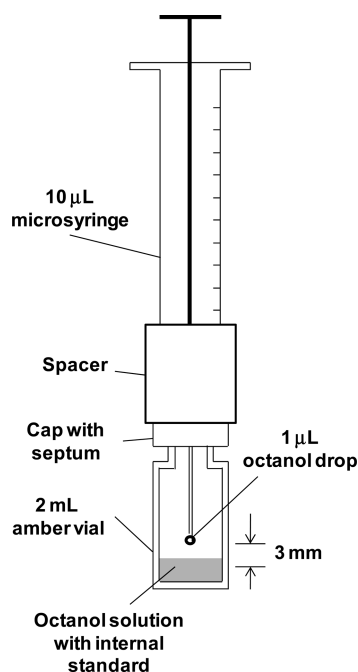


FIGURE 1. Schematic diagram of the apparatus used in this study.

Theory

The migration of chemical vapor from a 1-octanol solution to octanol drop can be modeled by a film diffusion model (Figure 1). As shown, the volume of octanol solution (200 µL) is sufficiently high compared with the volume of headspace (approximately 1.8 mL) and octanol drop (1 µL) that it is reasonable to assume that the concentration of chemical species in the head space remains unchanged during the course of the experiment. In a simple two compartment model, the increase in the concentration of chemical species in octanol drop with respect to time is given by

$$\frac{dC_{drop}}{dt} = k_a C_a - k_d C_{drop} \quad (1)$$

where C_{drop} and C_a are the concentration of a chemical in the octanol drop and air (mol L⁻¹), respectively, k_a is the absorption rate constant ($L_{air} \cdot L_{drop}^{-1} h^{-1}$), and k_d is the desorption rate constant (h^{-1}). Although effects of surface adsorption onto the small-sized octanol drop may influence mass transfer of compounds having low partition coefficients (26), it is reasonable to neglect adsorption when partition coefficient is sufficiently large (22, 27). Assuming that the headspace concentration (C_a) is in equilibrium with the concentration in the octanol dosing solution (C_{oct}), one finds that the kinetic equilibrium constant, K_{OA} , is given by

$$K_{OA} = \frac{C_{oct}}{C_a} = \frac{k_a}{k_d} \quad (2)$$

Therefore, a simplified differential equation (eq 3) is obtained, and the desorption rate constant (k_d) can be obtained by time course measurement of chemical concentration in the octanol drop (eq 4).

$$\frac{dC_{drop}}{dt} = k_d (C_{oct} - C_{drop}) \quad (3)$$

$$\ln\left(1 - \frac{C_{drop}(t)}{C_{oct}}\right) = -k_d t \quad (4)$$

Using a film-diffusion model, the two rate constants, k_a and k_d , are described by (25, 28)

$$k_a = \frac{1}{\frac{\delta_a}{D_a} + \frac{\delta_{drop}}{D_{drop} K_{OA}}} \frac{A}{V_{drop}} \quad (5)$$

$$k_d = \frac{1}{\frac{\delta_a}{D_a} K_{OA} + \frac{\delta_{drop}}{D_{drop}}} \frac{A}{V_{drop}} \quad (6)$$

where δ represents the thickness of diffusive boundary layer (m), D represents molecular diffusion coefficient (m² s⁻¹), A is the interface area (m²), V is the volume of octanol drop (m³), and subscripts a and $drop$ denote air and octanol drop, respectively.

Because the values of K_{OA} for the selected PAHs are very high ($10^5 \sim 10^{12}$), mass transfer resistance in the octanol drop (δ_{drop}/D_{drop}) should be negligibly small compared to that in air boundary layer ($\delta_a K_{OA}/D_a$). Thus, eq 6 is reduced to

$$k_d = \frac{D_a}{K_{OA} \delta_a} \frac{A}{V_{drop}} \quad (7)$$

Equation 7 suggests that k_d and K_{OA} are inversely related. The thickness of air boundary layer in the stagnant experimental system does not depend highly on chemicals (29), and the molecular diffusion coefficient in the air (m² s⁻¹) can be estimated from the molecular weight of chemical (M , g mol⁻¹) by (30)

$$D_a = \frac{0.000155}{M^{0.65}} \quad (8)$$

Given the thickness of air boundary layer and estimated molecular diffusion coefficient in air, K_{OA} can be calculated by measuring the experimental desorption rate constant k_d . In other words, an empirical constant can be used to relate K_{OA} and k_d if a reference compound with known K_{OA} is used.

Materials and Methods

Materials. Thirteen polycyclic aromatic hydrocarbons (PAHs) with two to six aromatic rings were chosen for this study for the proof of principle. Their log K_{OA} values reported in the literature ranged from 5 to 12. Each mixture contained 4 PAHs. All PAHs and 1-octanol were of high purity (over at least 98%) and were purchased from Sigma-Aldrich (St. Louis, MO, USA), Supelco (Bellefonte, PA, USA), or Fluka (Buchs, Switzerland).

Chemical Analyses. All PAHs were analyzed using an HPLC system equipped with a quaternary gradient pump (Waters 600E, Milford, MA, USA), an autosampler (Waters 717+), and a fluorescence detector (Waters 2475). Deionized water and methanol were used as eluent solvents in a gradient mode with the flow rate of 1 mL min⁻¹. PAHs were separated on a Waters PAH C18 column (4.6 × 150 mm, 5 µm particle size) at 40 °C and detected using the fluorescence detector with the excitation wavelength (λ_{ex}) of 275 nm and the emission wavelength (λ_{em}) of 350 nm for mixture 1 (naphthalene, acenaphthene, fluorene, phenanthrene), λ_{ex} = 260 nm and λ_{em} = 420 nm for mixture 2 (anthracene, fluoranthene, pyrene, and benz[*a*]anthracene), and λ_{ex} = 290 nm and λ_{em} = 430 nm for mixture 3 (chrysene, perylene, benzo[*a*]pyrene, and dibenzo[*a,h*]anthracene).

Determination of Desorption Constants and K_{OA} Values.

Partition coefficients between octanol and air were determined by diffusion of PAHs in the air boundary layer into a single drop at the tip of a microsyringe needle placed in a chamber maintained at $25 \pm 2^\circ\text{C}$ (Figure 1). The volume of octanol solution containing PAHs mixture and the internal standard in a 2.0 mL amber vial was 200 μL . Benzo[ghi]perylene was chosen as the internal standard due to its extremely low vapor pressure, 10^{-8} Pa, at 25°C (31). The initial concentration of PAHs in the octanol solution ranged from 0.00035 mol L^{-1} (benzo[a]pyrene) to 0.060 mol L^{-1} (fluorene), depending on their solubility in octanol. The corresponding mole fractions were less than 0.01 (acenaphthene), assuring that the PAHs were considered to be dissolved, not mixed with octanol. The sampling volume by a single drop was 1 μL . Thus, this sampling did not affect significantly the overall mass balance of PAHs in the experimental system and the gaseous concentration in the headspace. Measurement of the concentration of analyte mixtures in the dosing solution confirmed that the concentration in octanol solution was unchanged during the experiment. Both the octanol solution and octanol drop contained a fixed concentration of the internal standard (79.6 $\mu\text{mol L}^{-1}$ for mixture 1 and mixture 2, 3.79 $\mu\text{mol L}^{-1}$ for mixture 3). Because the deviation of drop size affects the amount of analytes in a drop and A/V_{drop} in eq 7, both quantities were corrected by the measured quantity of the internal standard in a drop.

After a predetermined extraction time, the 1 μL octanol drop was carefully retracted and diluted with 700 μL of methanol for mixture 1 or 100 μL for mixture 2 and mixture 3, and 50 μL was injected for HPLC analysis. Desorption rate constants (k_d) were calculated using eq 4. After estimating the thickness of air boundary layer using anthracene as a standard, corresponding K_{OA} values were obtained using eq 7. Area-to-volume ratio (A/V_{drop}) was calculated assuming that the drop is spherical.

Results and Discussion

Determination of $\log K_{OA}$. Figure 2 shows the increase in the concentration of PAHs in octanol drop with determination of k_d by linearization for acenaphthene, anthracene, and chrysene as examples. Linear lines represent predicted kinetics using eq 4. Determination of k_d for all other PAHs was presented in Figure S1 (Supporting Information). The desorption rate constant values were listed for 10 PAHs (Table 1) with 95% confidence intervals. The desorption rate constant cannot be determined for perylene and dibenzo[a,h]anthracene due to their slow diffusion into octanol drop. The concentration of perylene in octanol drop was not sufficiently high to obtain reliable k_d , and dibenzo[a,h]anthracene was not detected for all samples using the HPLC method described above. The measured desorption rate constants ranged from 0.674 h^{-1} (naphthalene) to $3.37 \times 10^{-6} \text{ h}^{-1}$ (benzo[a]pyrene). Typical 95% confidence interval of k_d was less than 10% of the fitted values, confirming that the method can give narrow range of k_d . In order to translate k_d into K_{OA} (eq 7), anthracene was chosen as a standard PAH to calibrate the thickness of the air boundary layer (δ_a) because its literature K_{OA} values were in the middle of the anticipated range of all selected PAHs in this study and the deviation of literature values were less than 0.4 log unit. In addition, anthracene showed the best linearity in the determination of k_d in this study (Figure 2(b)). The thickness of the air boundary layer (δ_a) was estimated to be 0.725 mm assuming that the experimental K_{OA} for anthracene is equal to $10^{7.71}$ as obtained by Odabasi et al. (19). Using this value, calculated $\log K_{OA}$ values for 10 PAHs are listed in Table 1. Because the uncertainty of the method may be dominated by the estimated thickness of the air boundary layer,

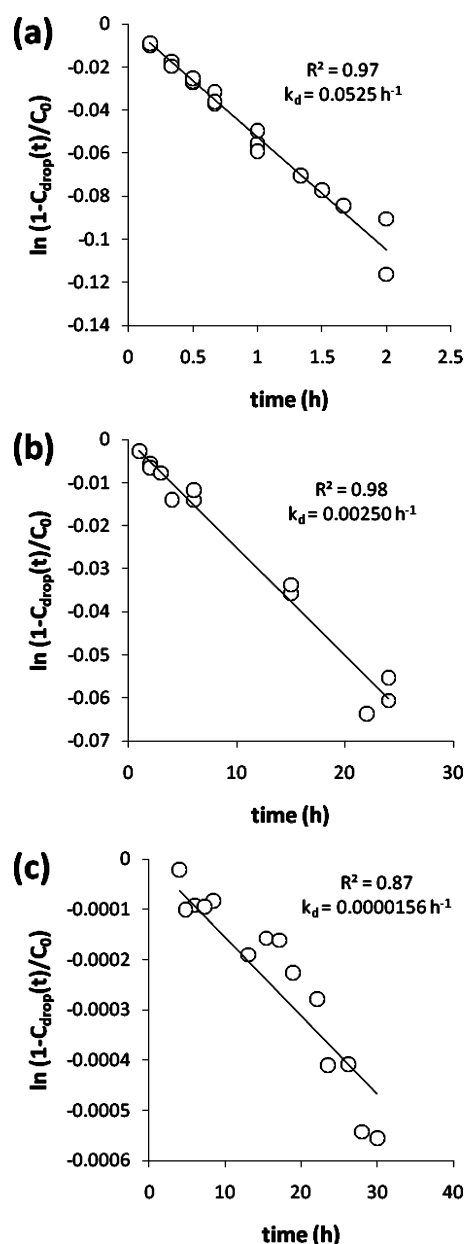


FIGURE 2. Determination of the desorption rate constant (k_d), using eq 4 for (a) acenaphthene (mixture 1), (b) anthracene (mixture 2), and (c) chrysene (mixture 3). Linear lines are fitted using eq 4.

confidence interval of $\log K_{OA}$ was calculated by an error propagation analysis using 95% confidence interval of k_d and assumed range of air boundary layer, 0.58–0.87 mm, which corresponds to 80–120% of the estimated value. Resulting deviation of $\log K_{OA}$ values was about 0.1 log unit, as shown in Table 1. The experimental $\log K_{OA}$ values in this study were close within 0.5 log unit to experimental and estimated values in the literature except for benz[a]anthracene (Table 1).

Although the method showed that the liquid-phase microextraction is feasible for the determination of K_{OA} , experimental data were limited to PAHs having similar physicochemical properties. Further validation of this method can be made with different types of chemicals such as phthalate esters.

Robustness of the Method. Because the method relies on the stability of the spherical octanol drop, the concentration of the internal standard was measured. Figure 3 shows the variation of the recovered concentration of the internal

TABLE 1. Summary of k_d and K_{OA} Values of the Selected PAHs Determined in This Study with Values Reported in the Literature

chemicals	CAS reg. no.	D_a ($\times 10^{-6} \text{ m}^2 \text{ s}^{-1}$)	k_d (h^{-1}) ^a	log K_{OA} ^b	literature K_{OA}	
					experimental	estimated
naphthalene	91-20-3	6.61	$6.74 (6.29, 7.18) \times 10^{-1}$	5.37 (5.27, 5.46)	5.13 ^c	5.01 ^d , 4.99 ^e
acenaphthene	83-32-9	5.86	$5.25 (5.04, 5.46) \times 10^{-2}$	6.43 (6.33, 6.51)	6.52 ^f	6.09 ^e , 6.28 ^f
fluorene	86-73-7	5.58	$1.92 (1.84, 1.99) \times 10^{-2}$	6.84 (6.75, 6.92)	6.79 ^g , 6.90 ^f	6.58 ^f , 6.59 ^g , 6.68 ^h , 6.76 ^e , 6.83 ⁱ
mix 1	phenanthrene	85-01-8	$3.05 (2.84, 3.26) \times 10^{-3}$	7.62 (7.52, 7.71)	7.45 ^c , 7.57 ^g , 7.68 ^f	7.33 ^f , 7.41 ^g , 7.45 ^h , 7.51 ⁱ , 7.58 ^e , 7.66 ^d , 7.09 ^f , 7.34 ^h , 7.45 ^d , 7.70 ^e
	anthracene	120-12-7	$2.50 (2.33, 2.67) \times 10^{-3}$	7.71 (7.61, 7.79)	7.34 ^c , 7.71 ^f	8.32 ^f , 8.49 ^g , 8.60 ^h , 8.63 ^e , 8.86 ⁱ
	fluoranthene	206-44-0	$3.94 (3.58, 4.31) \times 10^{-4}$	8.48 (8.37, 8.56)	8.76 ^f , 8.88 ^g	8.30 ^d , 8.60 ^g , 8.61 ^h , 8.70 ^e , 8.84 ⁱ
mix 2	pyrene	129-00-0	$2.65 (2.36, 2.94) \times 10^{-4}$	8.65 (8.54, 8.74)	8.43 ^c , 8.80 ^g	9.10 ^f , 9.54 ^h , 9.85 ^e , 10.18 ^d
	benzo[a]anthracene	56-55-3	$2.22 (1.93, 2.51) \times 10^{-4}$	8.69 (8.57, 8.78)	10.28 ^f , 10.80 ^c	9.40 ^f , 10.21 ^e , 10.44 ^h , 10.59 ^d
	chrysene	218-01-9	$1.56 (1.36, 1.76) \times 10^{-5}$	9.85 (9.73, 9.94)	10.30 ^f , 10.44	11.55 ^d , 11.15 ^e
mix 3	perylene	198-55-0	n.d.	—	11.70 ^c	11.40 ^d
	benzo[a]pyrene	50-32-8	$3.37 (2.56, 4.17) \times 10^{-6}$	10.48 (10.32, 10.60)	10.71 ^c , 11.56 ^f	10.77 ^h , 10.86 ^f
	dibenzo[a,h]anthracene	53-70-3	n.d.	—	12.59 ^f , 13.91 ^c	13.67 ^f , 13.84 ^d

^a Values in parentheses represent 95% confidence interval of regression. ^b Values in parentheses are the corresponding ranges obtained by error propagation. ^c Reference 33. ^d Reference 34. ^e Reference 35. ^f Reference 19. ^g Reference 11. ^h Reference 1. ⁱ Reference 36.

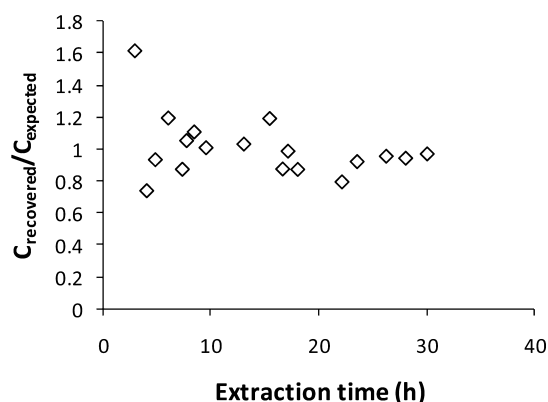


FIGURE 3. The ratio of the amount of the internal standard (benzo[ghi]perylene) recovered after the extraction to that expected in 1 μL octanol drop containing 3.79 $\mu\text{mol/L}^{-1}$ internal standard with respect to extraction time.

standard with respect to extraction time obtained during the experiment with mixture 3 as an example. The variation of the recovered concentration was probably due to the subtle difference in drop size and potential loss during the retraction of the drop. However, the loss of internal standard was not significant indicating that drop size did not change significantly during the course of the experiment. The vapor pressure of octanol is 10.6 Pa at 25 °C (32). In the closed system used in this study, it is not expected that the octanol drop evaporate in 30 h. Because it is useful to measure K_{OA} as a function of temperature, the developed method may be applied at different temperature unless the evaporation of octanol becomes significant.

Another critical factor affecting the robustness of the method should be the calibration of δ_a . Table 2 shows the potential variation of estimated δ_a values when other chemicals were chosen as the reference chemical. The choice of the standard chemical may result in different values of δ_a . However, δ_a did not change significantly when any PAHs with log K_{OA} less than 9.0 was chosen. Further investigation is needed to define the robustness of the method for compounds having log K_{OA} greater than 9.0. However, the method can provide a tool for fast and reliable determination of log K_{OA} for many chemicals with log K_{OA} between 5 and 9.

TABLE 2. Estimated Thickness of Air Boundary Layer (δ_a) Using Eq 7 When Various Experimental log K_{OA} Values in the Literature Were Chosen As the Reference Value

chemical	δ_a ($\times 10^{-3} \text{ m}$)
naphthalene	1.67
acenaphthene	0.587
fluorene	0.822
	0.638
phenanthrene	1.08
	0.820
anthracene	0.637
	1.70
fluoranthene	0.725
	0.378
pyrene	0.286
	1.20
benzo[a]anthracene	0.512
	0.0187
chrysene	0.00565
	0.254
benzo[a]pyrene	0.184
	0.429
	0.0606

Experimental Time Required for the Method. As shown in Figure 2, short experimental times are required for the determination of desorption rate constants. Measurable concentrations of relatively volatile compounds were reached after a few minutes (mixture 1), within an hour (mixture 2), and after a few hours (chrysene and benzo[a]pyrene). However, the chosen experimental time was not sufficient for perylene and dibenzo[a,h]anthracene. Figure 4 shows a model calculation of $C_{drop}(t)/C_0$ with respect to experimental time for hypothetical chemicals with various log K_{OA} values assuming that the molecular diffusion coefficient is equal to $5.0 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$, where the calculated molecular diffusion coefficients for the selected PAHs were between 4.0 and $6.6 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ (Table 1). Although the result depended on the initial concentration in the octanol solution, a measurable concentration was reached if $C_{drop}(t)/C_0$ becomes greater than 10^{-5} . Thus, a log K_{OA} value of up to approximately 11.0 can be measured within a few days using the method developed. This experimental limit may change with the instrumental

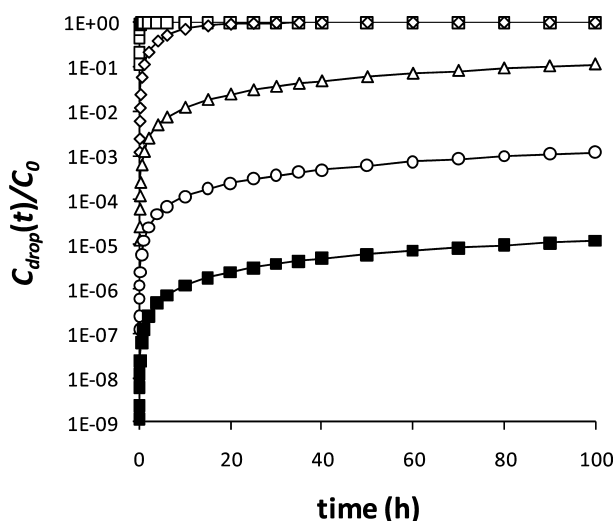


FIGURE 4. Expected $C_{drop}(t)/C_0$ with increasing extraction time in the experimental conditions used in this study for a hypothetical compounds with $\log K_{OA} = 4$ (open squares), 6 (open diamonds), 8 (open triangles), 10 (open circles), and 12 (closed square). The thickness of the air boundary layer and the molecular weight of the hypothetical compound were assumed 0.000725 m and 250 g/mol, respectively.

detection limit and the chemical solubility in octanol. Measurable range of $\log K_{OA}$ may be extended if the method is coupled with a highly sensitive gas chromatographic detection method by injecting the whole drop into the instrument. Currently, this kinetic determination method may not be applicable for chemicals with $\log K_{OA}$ greater than 12 as shown in Figure 4. However, most chemical species of environmental concern in terms of their environmental toxicity have $\log K_{OA}$ values less than 12 (6, 7). Although there are many chemicals with $\log K_{OA}$ larger than 12 in the atmosphere, measuring reliable K_{OA} values may not be needed because their gas/particle partitioning is not likely to be important for the evaluation of atmospheric transport. Thus, this method will provide a promising tool to generate experimental $\log K_{OA}$ for many chemicals in a reasonably short time.

Potential Applications of the Method in Environmental Sciences. Although the experimental work was limited to the determination of $\log K_{OA}$ values for selected PAHs, uses of this experimental device may be extended to related areas of environmental science. The main idea that the experiment supports is that a liquid phase microextraction technique can be used for the determination of partition coefficient between the liquid and the surrounding medium. This method may be extended to the aqueous solution surrounding the octanol drop to obtain K_{OW} . Then, Henry's law constant for compounds with low solubility in water and low vapor pressure can also be calculated from kinetic K_{OA} and K_{OW} . Similar data using other organic solvents which can dissolve these compounds better may also be used. This experimental system may also provide a good estimate of gaseous transfer rate of semivolatile compounds. The contribution of gaseous diffusion processes can be isolated from the overall distribution of semivolatile chemicals obtained in the field observation in the terrestrial environment by knowing the laboratory rate of gaseous diffusion.

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Supporting Information Available

Determination of the desorption rate constant (k_d) was shown for all PAHs in Figure S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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