One-Sided Single-Pellet Technique for Adsorption and Intraparticle Diffusion

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The one-sided single-pellet dynamic technique introduced in this article is shown to be a very effective and simple method for the analysis of adsorption and diffusion in porous solids. Moment expressions are presented for reversible and irreversible adsorption processes. Since the adsorption equilibrium constant is the only unknown parameter in the first moment expression, this parameter can be evaluated from a single set of pulse-response experiments. This technique to evaluate the adsorption equilibrium constant is illustrated using ethylbromide as tracer. It is also shown that for a very strongly adsorbing tracer, such as 1,2-dichloroethane in soil, modified moment expressions derived with a semiinfinite boundary condition are necessary unless a criterion developed in this work is satisfied.

Introduction

Gas chromatographic techniques were frequently used for the investigation of adsorption and diffusion in packed columns. In one of the earlier studies, Schneider and Smith (1968) improved gas chromatography theory and showed that the effective diffusivities and adsorption equilibrium constants could be obtained from the pulse-response experiments conducted in packed-bed systems. The method is based on the fact that the moments of the response peaks at the exit of the system are functions of the transport, adsorption rate, and adsorption equilibrium parameters. For packed-bed systems the moment expressions include the intraparticle rate parameter as well as film mass transfer and axial dispersion coefficients.

Doğu and Smith (1975, 1976) developed a single-pellet chromatographic technique for the study of intrapellet rate processes. In this dynamic method, the Wicke–Kallenbach-type diffusion cell was used. The major advantage of the single-pellet technique over bed chromatography is the elimination of interpellet effects and the related parameters (Moffatt, 1978; Burghardt and Smith, 1979; Baiker et al., 1982; Doğu et al., 1987, 1991). This technique was later modified to investigate diffusion in porous solids having a bidispersed pore size distribution (Doğu and Ercan, 1983) to determine the rate parameters for noncatalytic fluid–solid reactions (Doğu et al., 1986) and to analyze viscous flow and diffusion in porous solids (Doğu et al., 1989; Lu et al., 1992).

In more recent studies, the technique was extended to sorption and migration of volatile organic pollutants in soil (Doğu et al., 1993; Cabbar et al., 1994). In this technique, the first moment expression contains both effective diffusivity and the adsorption equilibrium constant for adsorbing tracers. The measurement of the adsorption equilibrium constant from the first moment data requires an independent evaluation of effective diffusivity, either by conducting inert pulse-response experiments from which the tortuosity factor was evaluated or by calibrating the zeroth moment values (Cabbar et al., 1994).

In the present work, a new one-sided single-pellet system was proposed for easier evaluation of adsorption characteristics. This new system was originally designed to investigate adsorption and migration of volatile organic pollutants in soil, although the application is not limited to such studies. As

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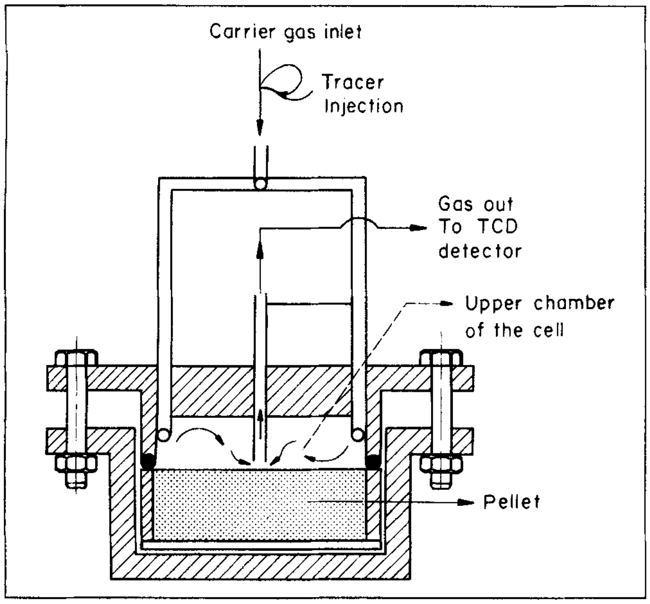

Figure 1. One-sided single-pellet sorption cell.

discussed in this article, this new procedure can be applied to any case where adsorption and diffusion in a porous solid is to be evaluated.

Method and Theory

The one-sided single-pellet adsorption cell is shown in Figure 1. In this system, the upper end face of the pellet is exposed to the flow of an inert gas. The cell is designed so that the chamber above the pellet can be assumed as perfectly mixed. A pulse of a tracer is injected into this chamber and the response peak was detected by using a suitable detector (TCD) placed in the exit stream.

Theoretical expressions are derived for the moments of the response peak for reversibly and irreversibly adsorbed and for inert tracers. For an adsorbing tracer, the conservation equation applied to the pellet is

$$\epsilon_p \frac{\partial C_i}{\partial t} = D_e \frac{\partial^2 C_i}{\partial z^2} - \rho_p N_i. \qquad (1)$$

Here, N_i corresponds to the adsorption rate, N_i expressions are given in Table 1 for equilibrium, reversible, and irreversible adsorption. In all these cases linear adsorption processes are considered. This assumption is generally justified for dilute mixtures (Doğu and Smith, 1976; Cabbar et al., 1994; Doğu et al., 1993).

The mass conservation equation for the tracer in the upper chamber of the single-pellet cell is written as

$$-FC_A + D_e\left(\frac{\partial C_i}{\partial z}\right)_{z=0} A = V_t \frac{dC_A}{dt}. \qquad (2)$$

For a finite pellet length, boundary and initial conditions for Eqs. 1 and 2 are expressed as

$$C_i = C_A \quad \text{at} \quad z = 0 \quad \text{(for all } t) \qquad (3)$$

$$\frac{\partial C_i}{\partial z} = 0 \quad \text{at} \quad z = L \quad \text{(for all } t) \qquad (4)$$

$$C_A = C_o \quad \text{at} \quad t = 0 \qquad (5)$$

$$C_i = 0 \quad \text{at} \quad t = 0 \quad \text{(for all } z). \qquad (6)$$

Further discussion of these boundary conditions and the solution of the problem with a semiinfinite boundary condition are discussed later.

Moment expressions for a finite pellet

Solution of Eqs. 1 and 2 with the boundary conditions expressed in Eqs. 3–6 yields the following expression for the Laplacian of C_A.

$$\overline{C_A} = \frac{C_o \tau}{(D_e A/FL)(\mathrm{mL})\tanh(\mathrm{mL}) + s\tau + 1}, \qquad (7)$$

where m is defined in Table 1 for the different models, and τ corresponds to space time in the upper chamber ($\tau = V_t/F$).

The moment expressions corresponding to the response peak measured at the outlet of the top chamber of the one-sided single-pellet cell were derived from the following definition of nth moment:

$$m_n = \int_o^\infty t^n C_A \quad dt = (-1)^n \lim \frac{d^n \overline{C_A}}{ds^n}. \qquad (8)$$

Equilibrium Adsorption. If the adsorption of a tracer on the porous solid is very fast, instantaneous equilibrium may be assumed between the adsorbed and the gas phase concentration in the pores. For such a tracer, zeroth (m_0), first absolute (μ_1), and second central moment (μ_2') expressions are

$$m_0 = C_o \tau \qquad (9)$$

$$\mu_1 = \frac{m_1}{m_0} = \tau + \frac{AL}{F}(\epsilon_p + \rho_p K_i) \qquad (10)$$

Table 1. Adsorption Relations for Different Mechanisms

Adsorption Mechanism	N_i	m
Equilibrium adsorption	$K_i \frac{\partial C_i}{\partial t}$	$\left[\frac{(\epsilon_p + \rho_p K_i)}{D_e} s\right]^{1/2}$
Reversible adsorption	$\frac{\partial n_i}{\partial t} = k_a\left(C_i - \frac{n_i}{K_i}\right)$	$\left\{\frac{(\epsilon_p + \rho_p K_i)s + \epsilon_p (K_i/k_a)s^2}{D_e[(K_i/k_a)s + 1]}\right\}^{1/2}$
Irreversible adsorption	$k_a C_i$	$\left(\frac{\rho_p k_a + \epsilon_p s}{D_e}\right)^{1/2}$
Inert	—	$\left(\frac{\epsilon_p s}{D_e}\right)^{1/2}$

$$\mu'_2 = \frac{m_2}{m_0} - \mu_1^2 = \left[\tau + \left(\frac{AL}{F}\right)(\epsilon_p + \rho_p K_i)\right]^2 + \frac{2}{3}\left(\frac{AL^3}{FD_e}\right)(\epsilon_p + \rho_p K_i)^2. \tag{11}$$

The first moment expression derived here for equilibrium adsorption (Eq. 10) was shown to be in agreement with the limiting form of the expression derived by Burghardt and Smith (1979) for the two-sided single-pellet system, corresponding to the zero downstream carrier gas flow rate and zero lower chamber volume.

Experimental values of the moments are determined from the observed response peaks by the numerical integration of Eq. 8. These moment values include contributions due to all dead volumes in the injection and detection lines. Especially for nonadsorbing and weakly adsorbing tracers, relative significance of retention times in the dead volumes might not be negligible as compared to the retention time in the sorption cell. In order to make corrections for these contributions, it is proposed to repeat pulse-response experiments with an impermeable Teflon plate placed over the pellet. For such a system, the moment expressions become

$$m_{0t} = C_o \tau \tag{12}$$

$$\mu_{1t} = \tau \tag{13}$$

$$\mu'_{2t} = \tau^2. \tag{14}$$

The corrected, first absolute, and second central moments for the tracer were then evaluated taking the difference of the moments obtained without and with the Teflon plate placed over the pellet. With this procedure all the contributions of dead volumes to the moments were eliminated. The corrected and rearranged moment expressions for equilibrium adsorption are

$$\mu_{1c} = \mu_1 - \mu_{1t} = \frac{AL}{F}(\epsilon_p + \rho_p K_i) \tag{15}$$

$$Y = \mu'_{2c} - \mu_{1c}^2 - 2\tau\mu_{1c} = \frac{2}{3}\frac{AL^3(\epsilon_p + \rho_p K_i)^2}{D_e}\left(\frac{1}{F}\right). \tag{16}$$

In Eq. 15 the only unknown in the corrected first-moment expression is the adsorption equilibrium constant. In principle, $\rho_p K_i$ may be evaluated from the slope of μ_{1c} vs. $(1/F)$ data.

With the value of $\rho_p K_i$ from the first-moment analysis, effective diffusivity can be evaluated from the second-moment data using Eq. 16.

Reversible Adsorption. If the adsorption process is reversible but not fast enough to achieve instantaneous equilibration, the second central moment expression becomes,

$$\mu'_{2c} = \left[\frac{2}{3}\left(\frac{AL^3}{D_e}\right)(\epsilon_p + \rho_p K_i)^2 + 2L\rho_p K_i \frac{K_i}{k_a} A\right](1/F) + \left[(AL)^2(\epsilon_p + \rho_p K_i)^2 + 2V_t(AL)(\epsilon_p + \rho_p K_i)\right](1/F)^2. \tag{17}$$

The zeroth and first absolute moment expressions found for reversible adsorption are the same as the corresponding expressions obtained in equilibrium adsorption. The adsorption equilibrium constant, K_i, may again be determined from the first moment data. The effective diffusion coefficient, D_e, and adsorption rate constant, k_a, appear in the second-moment expression as unknown parameters so that, the slope of Y vs. $1/F$ relation contains both D_e and k_a as unknowns:

$$Y = \mu'_{2c} - \mu_{1c}^2 - 2\tau\mu_{1c} = \left[\frac{2}{3}\left(\frac{AL^3}{D_e}\right)(\epsilon_p + \rho_p K_i)^2 + 2AL\rho_p K_i \frac{K_i}{k_a}\right](1/F), \tag{18}$$

In principle, it may be possible to evaluate D_e and k_a independently from the slope values of Eq. 18 by conducting experiments with pellets having different lengths.

Inert Tracer. Moment expressions corresponding to an inert tracer may be obtained by taking K_i as zero in Eqs. 10, 11 and 16. In this case, effective diffusivity appears as the only unknown in the rearranged second-moment expression (Eq. 16).

Irreversible Adsorption. In the case of irreversible adsorption, the zeroth-moment data becomes very useful. The ratio of zeroth moments obtained with and without the impermeable plate placed over the pellet was expressed as

$$\frac{m_{0t}}{m_0} = \left(\frac{D_e A}{FL}\right)(ZL)\tanh(ZL) + 1, \tag{19}$$

where

$$Z = \left(\frac{\rho_p k_a}{D_e}\right)^{1/2}. \tag{20}$$

In the case of reversible adsorption the m_{0t}/m_0 ratio becomes unity. The slope of m_{0t}/m_0 vs. $1/F$ relation contains the Thiele modulus for irreversible adsorption (ZL).

For irreversible adsorption, the corrected and rearranged first moment expression becomes

$$\frac{1}{\mu_{1c}} = \left(\frac{1}{T}\right)\left[F + \left(\frac{D_e A}{L}\right)(ZL)\tanh(ZL)\right], \tag{21}$$

where

$$T = \left(\frac{LA\epsilon_p}{2}\right)\left[1 - \tanh^2(ZL) + (ZL)^{-1}\tanh(ZL)\right] - \left(\frac{D_e A}{L}\right)\tau(ZL)\tanh(ZL). \tag{22}$$

Equation 21 shows a linear relation between $1/\mu_{1c}$ and F. In principle, effective diffusivity and adsorption rate constants can be evaluated by the simultaneous analysis of zeroth- and first-moment data.

Table 2. Chemical Composition of the Clay (Montmorillonite)

	wt. %		wt. %
SiO_2	70.82	MgO	3.22
TiO_2	0.41	CaO	0.32
Al_2O_3	15.86	Na_2O	1.31
Fe_2O_3	2.56	Ignition loss	5.50

Carbon content: 0.05%.

Experimental Work

One of the most important factors in the design of this new single-pellet sorption cell is to have perfect mixing in the chamber above the porous pellet. To achieve this, the inlet gas stream is introduced tangentially into the cylindrical chamber from four different points and the outlet is taken from the center (Figure 1). Circulation of carrier gas improves mixing in the chamber. To check the mixing characteristics a set of initial pulse-response experiments was carried out by covering the upper surface of the pellet with an impermeable Teflon plate. Perfect mixing was closely approached.

Pulse-response experiments were then carried out in the one-sided single-pellet unit with a natural clay pellet. Ethylbromide was used as tracer and helium as the carrier gas. Chlorinated and brominated volatile hydrocarbons are frequently detected in the soil gas and migration of such hydrocarbons in soil has significant environmental implications (Smith and Jaffe, 1991; Aochi et al., 1992; Cabbar et al., 1994; Miller and Pedit, 1992). Ethylbromide is a typical brominated volatile hydrocarbon that has attracted attention in soil pollution studies.

The chemical composition of the natural clay used in the preparation of the pellet is given in Table 2. The X-ray diffraction analysis of dried and ethylene glycolated samples indicated that the crystalline fraction of this clay is montmorillonite. Cylindrical pellets of 3 cm in diameter and 0.41 cm in length are prepared by pressing this clay into a ring-shaped stainless steel mold. The pore and surface area distributions of the soil pellets were determined using a Quantachrome 60 mercury intrusion porosimeter, a Micrometrics ASAP 2000 sorptometer, and a Micrometrics helium pycnometer. Physical properties of the pellet and the important dimensions of the cell are summarized in Table 3.

The single-pellet cell was placed in a constant temperature oven. Pulses of the adsorbing tracer (1 μL ethylbromide) were then injected into the carrier gas stream flowing past the upper face of the pellet. Experiments were conducted at 40°C.

Table 3. Physical Properties of the Natural Clay Pellet

Surface area (BJH nitrogen desorption)	58.7 m^2/g
Apparent density	1.21 g/cm^3
Porosity*	0.48
Total porosity	0.54
Pellet length	0.41 cm
Exposed area of pellet (A)	7.07 cm^2
Vol. of upper chamber (V_t)	7.43 cm^3

*This value from mercury intrusion porosimeter corresponds to pores having radii larger than 1.75 nm.

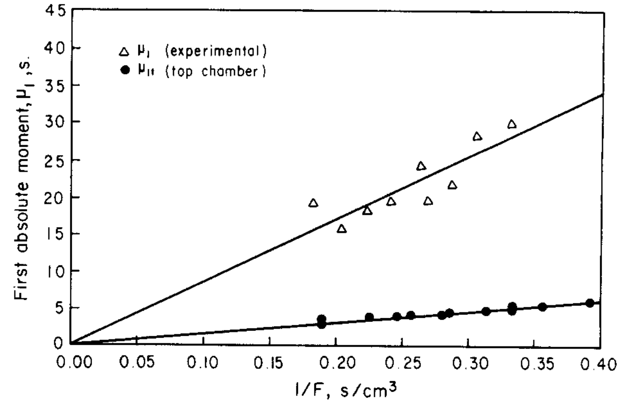

Figure 2. First absolute moment data for ethylbromide at 40°C (L = 0.41 cm).

μ_{1t} values correspond to first absolute moments obtained with an impermeable Teflon plate covering the upper surface of the pellet.

Results and Discussion

Results of ethylbromide experiments

Moments of the experimental response peaks were determined by the numerical integration of Eq. 8. The first absolute moment (μ_1) data obtained (with ethylbromide) at different flowrates are illustrated in Figure 2. On the same figure, first absolute moment data corresponding to the top chamber of the cell (data obtained with an impermeable Teflon plate placed over the pellet), μ_{1t}, are also shown. The results show a linear relation between μ_1 and $1/F$ as indicated by Eqs. 10 and 13. These moment values also include the contributions due to dead volumes at the injection and detection lines. By taking the difference of μ_1 and μ_{1t} such contributions cancel out. By the evaluation of the slope of μ_{1c} vs. $1/F$ curve from the least square fit, the adsorption equilibrium constant of ethylbromide was determined using Eq. 15 as $\rho_p K_i = 23.1$ at 40°C. This result indicated that ethylbromide is mildly adsorbed.

Second moments obtained for the same tracer are illustrated in Figure 3. Results indicate that the second moments of the system with an impermeable plate covering the pellet are negligible compared to the second-moment values ob-

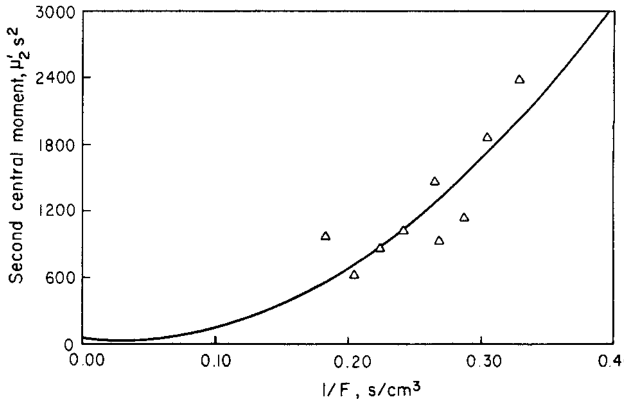

Figure 3. Second central moment data for ethylbromide at 40°C (L = 0.41 cm).

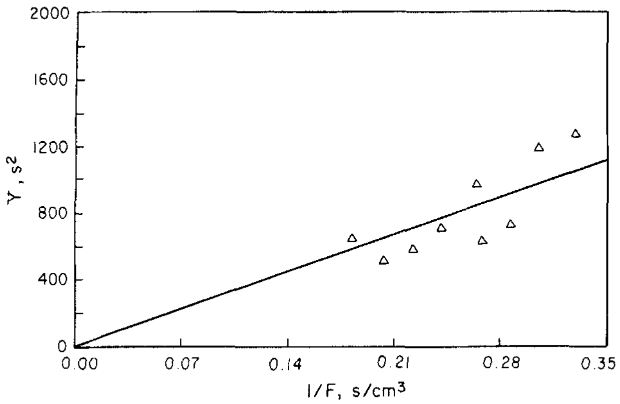

Figure 4. Second moment analysis: Y vs. $1/F$, for ethylbromide at 40°C ($L = 0.41$ cm).

tained in adsorption runs. The second-moment data are rearranged and the values of the parameter Y ($Y = \mu'_{2c} - \mu_{1c}^2 - 2\tau\mu_{1c}$) are evaluated. A lot of Y as a function of $1/F$ gave the expected linear relation (Figure 4). Considering an equilibrium adsorption process, effective diffusivity of ethylbromide was determined to be 0.057 cm²/s from the slope of Y vs. $1/F$ relation (Figure 4) using Eq. 16. This value is close to the effective diffusivities of some other halogenated volatile hydrocarbons reported in soil (Cabbar et al., 1994). For instance, the effective diffusivity value reported for monochloroethane is 0.028 cm²/s for a soil pellet having a macro porosity of 0.36 (total porosity 0.49).

This technique allows the evaluation of adsorption equilibrium constant from the first moment data. Since $\rho_p K_i$ is the only unknown in the first moment expression, data analysis becomes very simple. This is an advantage of this new one-sided single-pellet technique over the conventional single-pellet technique (Doğu and Smith, 1976). In that procedure the first-moment expression contained both the adsorption equilibrium constant and the effective diffusivity for an adsorbing tracer.

Discussion of the finite pellet boundary condition

If the adsorption equilibrium constant of a tracer is large, then a long tail of the response peak is expected. Precise detection of this tail is limited by the measuring sensitivity of the detector. For such a case, the adsorbing tracer may not penetrate all through the pellet (until $z = L$) within the duration, t_1, of a pulse-response experiment. This would be the case especially if the pellet is long. For a pellet of infinite length the first moment should also approach infinity as indicated by Eq. 15.

The penetration time through the pellet may be characterized by the first moment of the response peak that would be measured if a detector had been placed at $z = L$. For a reversible adsorption process, this first-moment expression (μ_{1p} at $z = L$) derived with the finite pellet boundary condition becomes

$$\mu_{1p} = \left(\frac{m_1}{m_0}\right)_{z=L} = \mu_1 + \frac{L^2}{2}\left(\frac{\epsilon_p + \rho_p K_i}{D_e}\right). \tag{23}$$

This expression was obtained by the solution of Eqs. 1–6 in the Laplace domain for $\bar{C}_i\,(L)$ and the moment definitions given in Eq. 8. In Eq. 23, μ_1 corresponds to the first moment of the response peak measured at the outlet of the sorption cell (Eq. 10). The duration of a pulse response experiment (t_1) should be significantly larger than the value of μ_{1p} in order to obtain meaningful results with the finite pellet boundary condition. The criterion to be used for the finite pellet boundary condition may be expressed as

$$(t_1 - \mu_1) \gg \frac{L^2}{2}\left(\frac{\epsilon_p + \rho_p K_i}{D_e}\right). \tag{24}$$

According to Eq. 24 it is advisable to use short pellets in pulse response experiments in the one-sided sorption apparatus. For the experimental results reported in the previous section with ethylbromide, the righthand side of Eq. 24 becomes 35 s. In all these experiments, the lefthand side of the inequality expressed in Eq. 24 was higher than 160 s, so that the criterion is justified.

The penetration length (L^*) of a tracer within the pellet may be defined as the distance from the top surface of the pellet where the first moment of the tracer within the pellet, μ_{1p}, is equal to the duration of a pulse-response experiment, (t_1). An expression for L^* may be written by taking $\mu_{1p} = t_1$ in Eq. 23:

$$L^* = \left[\frac{2(t_1 - \mu_1)D_e}{(\epsilon_p + \rho_p K_i)}\right]^{1/2}. \tag{25}$$

For long pellets it may be difficult to satisfy Eq. 24, unless the duration of each pulse-response experiment (t_1) is very large. This problem becomes more important for tracers having large adsorption equilibrium constants.

For a very strongly adsorbing tracer and in a system where pellet length is sufficiently long a semi-infinite pellet assumption becomes more realistic and the boundary condition written in Eq. 4 should be replaced by

$$C_i \rightarrow 0 \qquad \text{for} \qquad z \rightarrow \infty. \tag{26}$$

With this boundary condition, time-domain solution of Eqs. 1 and 2 gives the following expression for C_A:

$$\frac{C_A}{C_o} = \frac{U_1 \exp(U_1^2 t)\,\mathrm{erfc}(-U_1 t^{1/2}) - U_2 \exp(U_2^2 t)\,\mathrm{erfc}(-U_2 t^{1/2})}{(U_1 - U_2)}, \tag{27}$$

where

$$U_1 = -\frac{B}{2} + \left(\frac{B^2}{4} - \frac{1}{\tau}\right)^{1/2} \tag{28}$$

$$U_2 = -\frac{B}{2} + \left(\frac{B^2}{4} - \frac{1}{\tau}\right)^{1/2} \tag{29}$$

and

$$B = [D_e(\epsilon_p + \rho_p K_i)]^{1/2} A/V_t. \qquad (30)$$

Considering the difficulties in precise measurement of the tail of the response peaks for very strongly adsorbing tracers, modified moments are defined by taking the upper limit of the integral in the definition of moments (Eq. 8) at a finite time t_1 instead of infinity. Such modified moment expressions then become

$$\begin{aligned} m_0^* &= \int_0^{t_1} C_A \, dt \\ &= \left(\frac{1}{U_1 - U_2}\right)\left\{\frac{\exp(U_1^2 t_1)[\operatorname{erf}(U_1 t_1^{1/2}) + 1]}{U_1} \right. \\ &\qquad \left. - \frac{\exp(U_2^2 t_1)\left[\operatorname{erf}(U_2 t_1)^{1/2} + 1\right]}{U_2}\right\} + \frac{1}{U_1 U_2} \end{aligned} \qquad (31)$$

$$\begin{aligned} m_1^* &= \int_0^{t_1} C_A t \, dt = \frac{-2t_1^{1/2}}{\pi^{1/2}} \frac{(U_2 - U_1)}{(U_1 U_2)^2} + \frac{1}{U_1 - U_2} \\ &\times \left\{\frac{1}{U_1^3} - \frac{1}{U_2^3} + \frac{\exp(U_1^2 t_1)(U_1^2 t_1 - 1)[\operatorname{erf}(U_1 t_1^{1/2}) + 1]}{U_1^3} \right. \\ &\qquad \left. - \frac{\exp(U_2^2 t_1)(U_2^2 t_1 - 1)[\operatorname{erf}(U_2 t_1^{1/2}) + 1]}{U_2^3}\right\}. \end{aligned} \qquad (32)$$

The duration of a pulse-response experiment was denoted by t_1 and it can be arbitrarily selected. For instance, it may be selected as the time required to reduce the concentration to 1% of the maximum of the response curve. The modified moment expressions obtained for this case are much more complex than the moment expressions obtained with finite pellet boundary conditions. Analysis of the adsorption data using Eqs. 31 and 32 is illustrated with data obtained using a strongly adsorbing tracer (1,2-dichloroethane) in a longer pellet.

Strong adsorption (semiinfinite pellet) experimental results obtained with 1,2-dichloroethane

In a previous study (Cabbar et al., 1994) it was shown that 1,2-dichloroethane was very strongly adsorbed on a different type of clay. In the present article, this volatile hydrocarbon was selected to illustrate sorption data analysis with the semiinfinite boundary condition. For this purpose a longer pellet with the same physical properties was prepared from the same soil. Pulse-response experiments were conducted at 40°C in the one-sided single-pellet apparatus. Experiments were also repeated with an impermeable Teflon plate placed over the pellet.

Sorption results showed long tails of the response peaks, which also indicated strong adsorption of this tracer. The experimental values of the first moments of the response peaks are illustrated in Figure 5. The duration of each pulse-response experiment, t_1 was selected arbitrarily. The tail of the response curve approaches to zero at t_1. Due to this arbitrary selection of t_1, first moment values showed some scatter. Experimental values of corrected first moments and t_1 values are listed in Table 4.

The first absolute moment values obtained for 1,2-dichloroethane were found to be about 7 times larger than the first absolute moment values determined with ethylbromide. Using the modified moment expressions (Eqs. 31 and 32) the value of the parameter B defined by Eq. 30 was evaluated for each data point. The average value of B was found as 2.17. With this average B value, calculated first absolute moments (from Eqs. 31 and 32) are plotted as a function of corresponding experimental, μ_{1c}, values in Figure 6. The scattering of the points is much less than the scattering of first-moment data shown in Figure 5. This is due to the use of t_1, in the evaluation of first absolute moments. Results reported in Figure 6 indicated that the experimental first-moment values and the calculated values with an average B value agreed reasonably well. Using $B = 2.17$ in Eq. 29 the product of adsorption equilibrium constant with the effective diffusivity was determined as

$$D_e \rho_p K_i \simeq 5.06 \text{ cm}^2/\text{S}.$$

Evaluation of $\rho_p K_i$ requires independent measurement of the effective diffusivity. With the semiinfinite boundary condition the second-moment expression becomes more complicated, so no further attempt was made for the analysis of second-moment data. The effective diffusivity of 1,2-dichloroethane in nitrogen was reported as 0.022 cm²/s in a different clay pellet of porosity 0.49 (Cabbar et al., 1994). Assuming that the value of D_e for our pellet is in the same order of magnitude, the adsorption equilibrium constant, $\rho_p K_i$, was

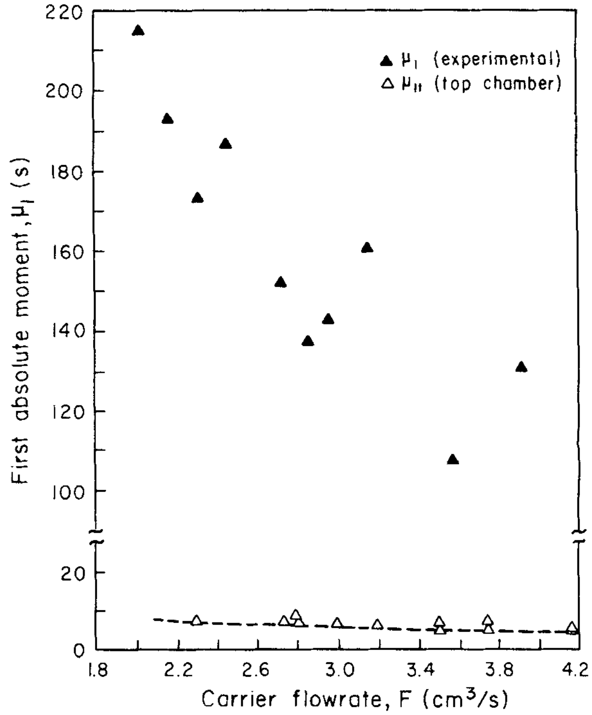

Figure 5. First moment data obtained with 1,2-dichloroethane ($T = 40°C$; $L = 1$ cm).

Table 4. First Moment Data Obtained with 1,2-dichloroethane*

Flow Rate F, cm^3/s	t_i s	μ_1 s
2.03	801	207.0
2.17	841	185.4
2.31	866	166.3
2.46	826	180.4
2.72	801	145.7
2.87	815	131.5
2.96	831	137.4
3.15	851	156.6
3.58	671	103.2
3.92	811	127.2

*$T = 40°C$; $L = 1$ cm.

estimated to be around 250. With these values of $\rho_p K_i$ and D_e, the penetration length L' is estimated from Eq. 25 to be less than 0.4 cm in all the pulse-response experiments conducted with 1,2-dichloroethane. Since pellet length was 1 cm in these experiments, it was clear that finite pellet boundary condition would not be appropriate for this set of experimental results.

Conclusion

The one-sided single-pellet technique introduced in this article was shown to be an efficient and simple method for the evaluation of the adsorption equilibrium constants as well as the effective diffusivity with a finite pellet. For equilibrium adsorption, adsorption equilibrium constant is the only unknown in the first-moment expression (Eq. 15), and effective diffusivity is evaluated from the second central moment (Eq. 16). However, effective use of this technique requires that the criteria stated in Eq. 24 should be satisfied. It is recommended that the pellet length should be as short as possible. For a pellet length of 1 mm adsorption equilibrium constants of even very strongly adsorbing species could be satisfactorily determined. In such experiments the tail region of the response peaks should be carefully measured.

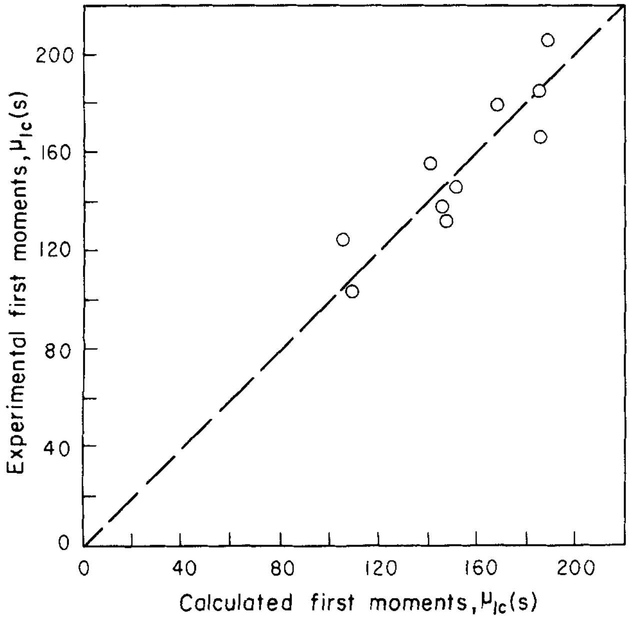

Figure 6. Calculated and experimental (corrected) first absolute moments for 1,2-dichloroethane at 40°C.

Calculated with $B = 2.17$ using Eqs. 31 and 32.

For very long pellets, the semiinfinite boundary condition should be used in the derivation of moment expressions (especially for very strongly adsorbing species). For this case, the first-moment expression includes both adsorption equilibrium constant and effective diffusivity so that an independent evaluation of D_e is required.

For strongly adsorbing tracers, the modified moment definitions reduce the errors due to the tailing of the response peaks. This idea could also be applied to packed bed chromatography. For very strongly adsorbing tracers the dimension of the porous adsorbent becomes very important. For such tracers, penetration of the tracer to all points of the adsorbent may not be possible within the timescale of a single pulse-response experiment.

It is concluded that by selecting a sufficiently short pellet, adsorption and diffusion of volatile tracers on any type of porous sorbent can be effectively investigated using this new one-sided single-pellet technique.

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Notation

C_A = concentration of tracer in the upper chamber
C_i = concentration of tracer in the pores of the pellet
C_o = initial concentration of tracer in the upper chamber
F = flow rate of the carrier gas, cm^3/s
L = pellet length, cm
m_n = nth moment defined by Eq. 8
m'_0 = modified zeroth moment defined by Eq. 31
m'_1 = modified first moment defined by Eq. 32
n_i = adsorbed concentration of tracer, mol/g
s = Laplace variable, s^{-1}
t = time, s
z = axial direction in the pellet
ϵ_p = pellet porosity
μ'_{2t} = second central moment for the upper chamber, s^2
ρ_p = pellet density, g/cm^3

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