Assessing breakthrough times for denuder samplers with emphasis on volatile organic compounds

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Abstract

This paper presents a theoretical background useful for the prediction of cylindrical denuder sampler performance, applied to volatile organic compounds (VOC). Two methods are presented that can be used together with any type of adsorption isotherm. One computer method is based on a simple recursive modelling of the Gormley–Kennedy equation with a time-dependent denuder length. The other model uses an equation derived directly from the Gormley–Kennedy expression. In practice, the latter, simpler model can readily be used. The most crucial part in the breakthrough assessment is associated with modelling the adsorption isotherm. Two types of models have been considered: the Langmuir and the Freundlich adsorption isotherms. In order to facilitate the comparison between samplers with different adsorption capacities and different physical dimensions, a reduced length versus time plot is introduced.

Keywords: Breakthrough times; Denuder samplers; Sampling devices; Volatile organic compounds

1. Introduction

The separation of gas and particulate phases in air sampling has become necessary because it has been shown that the physical state of organic hazards may have an impact on health effects. This emphasizes the need for a method to sample gas and particles without interferences to the mass ratio, for both ambient and occupational air. For example, in Sweden, the occupational threshold limit value (TLV) for oil mist is 1 mg/m^3 [1], and the TLVs for the components in the oil, such as aliphatics, present in the gaseous phase is 350 mg/m^3 or more [1].

Sampling of organic compounds in the work environment is often performed with adsorbent tubes when gaseous hazards are considered. For particles or both vapours and particles, the sampling could be performed with impingers or filters. When the compounds of interest are known to exist in both gas and particulate phases simultaneously, a common sampling approach is to use a filter together with an adsorbent, thus removing the particulate phase from the gas phase before entering the adsorbent sampler. A drawback with this method could be the blow-off of compounds situated on the particles. These will consequently be analysed as gaseous [2,3]. Often, the gaseous phase is considered semi-volatile, i.e., pure gaseous compounds cannot be

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distinguished from the semi-volatile phase. A way to solve this problem is the use of denuder samplers, where the collection of the hazardous materials is performed in the opposite way, i.e., the gas phase is stripped off the total sample in the denuder tube owing to its higher diffusion coefficient. The particulate phase will, owing to its lower difusivity, pass the sampler and finally be collected on, e.g., a filter at the end of the denuder sampler. The time for strip-off of compounds from the particles will in this case be limited to the time when the particles pass through the denuder tube. Later strip-off can easily be discerned and measured, e.g., by using a back-up sampler.

For denuder sampling of inorganic and reactive organic compounds, a reagent is coated on the tube wall and the compounds diffusing towards the denuder tube walls will, through a reaction, be chemisorbed on the surface [3–12].

The collection of non-reactive organic compounds in a denuder can be considered as more difficult owing to a limitation in the sampling capacity of most adsorbents. For sampling of compounds having comparatively low vapour pressure, e.g., polycyclic aromatic hydrocarbons, a silicone polymer can be used for the collection of gaseous material [13–15]. However, for more volatile molecules, a stronger adsorbent is needed to retain the trapped solutes.

Parallel plate [2], cylindrical [3,4,10,12,13,15, 16], annular [2,5–9,11,14,17] and wet effluent denuders with both cylindrical [18] annular and parallel-plate configurations [19] are the constructions presented in the literature. Only a few of the reported denuder samplers are suitable for personal sampling [7,11,16,17].

A crucial part in the use of denuders as samplers of volatile organic compounds is associated with the determination of breakthrough volumes. Even small gaseous breakthrough volumes can deteriorate the determination of particle associated compounds. A number of methods for the determination of breakthrough times or volumes have been described. The modified Wheeler equation, also termed the reaction kinetic equation [20,21], is often used for the assessment of breakthrough in adsorbent car-

tridges. However, apart from the need to assess the adsorption isotherm parameters, the rate coefficient must also be determined. This rate coefficient has been observed by, e.g., Wood and Moyer [22], to be non-constant. This was observed also in this work.

Nelson and Harder [23] presented another approach in assessing breakthrough times. Their method is excellent in predicting breakthrough data provided that the breakthrough time at a particular concentration is known with the specific set-up. This demands that a particular denuder must experimentally be run once under the same conditions as will be used during sampling with the exception of concentration. This makes the method rather impractical and it cannot be used in a general case where varying flow-rates and denuder dimensions are to be used.

This paper focuses on cylindrical denuder tubes as sampling devices for non-reactive, volatile organic compounds. The aim is to provide an understanding of the collection process within the tube and thereby the possibility of modelling the breakthrough curve. The basis of the model should be to use the adsorption isotherm parameters for the adsorbent and adsorbate as a general method to predict the capacity of the denuder sampler. This is advantageous owing to the independence of the isotherm parameters on sampling rate, denuder dimensions and amount of adsorbent.

2. Theory

2.1. The Gormley–Kennedy equation

The Gormley–Kennedy equation [24] describes the separation between gas and particles in a cylindrical tube based on diffusion. The higher the diffusion coefficient, the shorter is the tube length necessary for a high percentage strip-off in the denuder. Owing to the lower diffusion coefficient of particles compared with molecules in the gas phase, particles will be transported through the denuder in good yield.

The Gormley–Kennedy equation can be simplified to

$$\frac{C}{C_0} = 0.819 \exp(-3.6568 \pi DL/F) \tag{1}$$

where C and C_0 are the concentrations of adsorbate at the tube outlet and inlet, respectively, D is the gaseous diffusion coefficient for the solute, L is the tube length and F the sampling flow rate.

The original equation contains additional exponential functions of $\pi DL/F$, but in practice, when $\pi DL/F \geqslant 0.10$, Eq. 1 is valid with the following assumptions: (1) laminar flow must be obtained in the tube; (2) all the molecules reaching the wall must be completely trapped; and (3) the capacity of the trapping medium should be infinite.

In practice, the collecting medium (chemisorbent or adsorbent) has a finite sample capacity. The reagent will be consumed during sampling. This yields a decrease in the effective length of the tube, L in Eq. 1. Tube depletion depends upon sample concentration and the concentration of adsorption sites per unit area. The useful length of the denuder will thus be dependent on the elapsed sampling time and indirectly on a large number of physical properties of the denuder sampler.

Braman et al. [12] used a model for the denuder tube length decrease which was based on an assumption that the reduction in L followed an exponential function. However, this assumption is too simple and can theoretically be shown to yield an erroneous mass balance of the denuder if the equation of Gormley and Kennedy is considered to be correct.

A time constant, t_0, which is equal to the equilibrium adsorption capacity [25] is introduced; t_0 corresponds to the time to feed into the tube the amount of adsorbate equivalent to the adsorption capacity:

$$t_0 = m_{cap}/FC_0 \tag{2}$$

where m_{cap} is the adsorption capacity of a sampler at a particular air concentration of the adsorbate. The time constant t_0 is also a measure

of the breakthrough time of a sampler with 100% trapping efficiency until complete saturation is achieved, i.e., the adsorbent is filled up as in a closed box. The effective denuder length at any time t from the start of sampling will thus become

$$L = L_0(1 - t/t_0) \tag{3}$$

When adsorbents are used as the collecting medium, neither chemisorption nor infinite capacity is obtained. In these cases, it is necessary to assess the adsorption isotherm of the compound to be sampled. The amount of a particular compound taken up by an adsorbent is proportional to the amount of the adsorbent, but also depends on temperature, the partial pressure of the gas and the nature of both the compound and the adsorbent [26]. Depending on the type of isotherm that is used, m_{cap} will take different values. Two simple types of isotherms will further be considered, the Langmuir and the Freundlich adsorption isotherms.

2.2. The Langmuir adsorption isotherm

One of the simplest ways to describe the equilibrium between a particular compound in the gas phase and a specific solid at constant temperature is the Langmuir isotherm [21] (type I isotherm). It applies to monolayer adsorption on completely homogeneous surfaces, with negligible interaction between adsorbed molecules.

According to the Langmuir adsorption isotherm, m_{cap} in Eq. 2 can be expressed as

$$m_{cap} = \Theta m_{max} m_{ads} \tag{4}$$

where m_{max} and m_{ads} are the maximum adsorbent capacity and the amount of adsorbent, respectively, and Θ is the fraction of occupied sites at equilibrium according to

$$\Theta = KC_0/(1 + KC_0) \tag{5}$$

where K is the equilibrium distribution constant. When Langmuir adsorption isotherm parameters are employed, t_0 becomes

$$t_0 = \frac{Km_{max}m_{ads}}{F(1 + KC_0)} \qquad (6)$$

A high incoming concentration of adsorbate means that the capacity will approach the maximum capacity value, m_{max}, and the velocity of the adsorbate front will be dependent on concentration. At low concentrations, the behaviour will be similar as in linear chromatography, i.e., the breakthrough time, or retention time, becomes independent of concentration.

2.3. The Freundlich adsorption isotherm

If the active sites are non-equivalent there will be a deviation from the Langmuir expression. According to Freundlich [21], m_{cap} in Eq. 2 can be expressed as

$$m_{cap} = m_{ads}AC_0 1/b \qquad (7)$$

where b is expected to be larger than unity in type I adsorption isotherms. In terms of t_0, this will yield

$$t_0 = \frac{AC_0^{1/b-1}}{F} \cdot m_{ads} \qquad (8)$$

This isotherm differs from the former mainly in two ways. The expression of Eq. 7 will not approach an asymptote at elevated concentrations. Consequently, if $b > 1$, the slope at low concentrations will be unlimited, reaching infinity for $C = 0$. Linear chromatography will not be obtained at any concentration. In column chromatography, this would correspond to the retention time being dependent on solute concentration. Very low compound concentrations would yield very long retention times.

2.4. Combinations of the Gormley–Kennedy equation with adsorption isotherm parameters

When the time dependence of L is known, this can be introduced in the Gormley–Kennedy equation (Eq. 1). For the closed-box model of Eq. 3, this will become

$$\frac{C}{C_0} = 0.819 \exp\left[\frac{-3.6568\pi DL_0}{F}\left(1 - \frac{t}{t_0}\right)\right] \qquad (9)$$

t_0 can be derived from any type of isotherm but in particular Eqs. 6 and 8 will give the values for the Langmuir and the Freundlich adsorption isotherms, respectively. Eq. 9 represents a model which is somewhat contradictory. The denuder is not assumed to let any gas molecules pass through until the time of observation. However, this model will prove to be very useful and will further be referred to as Model 1. For example, at 5% breakthrough, Eq. 9 will permit the calculation of the breakthrough time (BT) according to

$$t_{5\%\,BT} = t_0\left(1 - \frac{0.243F}{DL_0}\right) \qquad (10)$$

In order to simulate the adsorption process more correctly, a recursive equation is introduced. Time intervals of Δt are regarded in a recursive process based on the fact that a mass of $FC\,\Delta t$ is introduced into the denuder at each time interval and the assumption that compounds either are passed through the denuder or adsorbed at the first available site according to the Gormley–Kennedy distribution of Eq. 1. The number of available sites can be expressed by means of t_0 yielding a recursive equation according to

$$L_n = L_{n-1} - \frac{L_0\,\Delta t}{t_0}$$

$$\times\,[1 - 0.819\exp(-3.6568\pi DL_{n-1}/F)] \qquad (11)$$

$$t_n = t_{n-1} + \Delta t \qquad (12)$$

The process starts with $t_n = 0$ and $L_n = L_0$. Thus, in every time interval that is a multiple of Δt, C/C_0 can be determined according to the original equation of Gormley and Kennedy (Eq. 1), yielding the breakthrough concentration at any time, t_n.

The factor $[1 - 0.819\exp(-3.6568\pi DL_{n-1}/F)]$ in Eq. 11 is the mass fraction adsorbed in the denuder. The time of calculation is thus dependent on the time interval Δt, and all parameters that affect the time of breakthrough. The time interval Δt in Eqs. 11 and 12 can preferably be set to $t_0/1000$, yielding a time of calculation for the entire experiment to only a few seconds using

an ordinary personal computer [27]. This model will subsequently be referred to as Model 2.

2.5. Introduction of reduced time versus length plot

If the useful denuder length and the sampling time are given in reduced parameters:

$$L' = L/L_0 \tag{13}$$

$$t' = t/t_0 \tag{14}$$

a reduced time versus denuder length plot can be constructed (see, e.g., Fig. 1b). This plot becomes independent on the physical dimensions of the denuder, thus permitting the comparison of breakthrough times of different denuders in the same plot. The closed-box assumption, Model 1, will always be represented by a straight line from $L' = 1$ to $t' = 1$. All other models must be present above this line, if they are based on correct data from the isotherm. The experimental curve in Fig. 1b is an example of a slight underestimation of the capacity of the denuder. This will further be discussed in the Application section. Model 1 represents the case where all compounds are adsorbed in the denuder. This is the case where the useful length of a denuder is decreasing at maximum speed (no loss of compounds).

3. Experimental

3.1. Denuder tubes

The denuder tubes consisted of 15 cm × 0.4 cm I.D. clear borosilicate glass and the inner walls were coated with solid sorbent, fixed to the walls by a liquid polymer. The adsorbents used in this work were either a divinylbenzene polymer, HayeSep D, 100–120 mesh (Supelco, Bellefonte, PA, USA) or a synthetic active carbon, Anasorb 747, 20–40 mesh (SKC, Eighty Four, PA, USA). These adsorbents were chosen owing to their comparatively high adsorption capacities for the model substance, hexane.

After the solid sorbent had been fixed to the

polymer-coated tube walls, the denuder tubes were conditioned at 300°C for 11 h with a gentle flow of helium through the tubes.

Excessive adsorbent, not fixed to the walls, was forced out by tapping on the denuder tube with a glass rod. The amount of adsorbent was measured by weighing the denuder before the deposition step and after the final conditioning and forcing out of excess adsorbent.

The denuder configuration applied here must be used at low sampling flow-rates, i.e., less than 100 ml/min, to be able to collect 99.9% of hexane (diffusion constant $D_g = 7.44 \cdot 10^{-6}$ m^2/s) in the gaseous phase. The flow-rate was maintained between 70 and 20 ml/min.

3.2. Apparatus

Breakthrough curves were obtained by connecting a wall-coated tube to tedlar bags filled with different air concentrations of hexane (HPLC grade) (Rathburn Chemicals, Walkerburn, UK). The other end of the tube was connected to an HNU photoionization detector (PID), 10.2 eV lamp (HNU Systems, Newton, MA, USA). A low-flow pump (Airchek Sampler Model 224-PCXR7; SKC) was connected to the outlet of the detector. The detector was connected to a laboratory data system (ELDS-Pro; Kungshög, Stenhamra, Sweden). All recordings and signal calculations were performed with this system.

3.3. Evaluations of isotherms

Frontal chromatograms for hexane were obtained by use of denuder tubes coated with solid sorbents as described above to a length of 7 cm. The tubes were connected to tedlar bags containing known concentrations of hexane and to the PID. The detector response was measured continuously up to 100% breakthrough and, by graphical integration of the frontal chromatogram, the amount of adsorbate within the tube at equilibrium could be calculated.

Owing to different properties of the two adsorbents, different concentration ranges were

employed. The hexane concentration range for the isotherm on HayeSep D was 100–1000 mg/ m³ (at four levels with three measurements at each level) and 1000–3500 mg/m³ (at five levels with two or three measurements at each level) on Anasorb 747.

From these data, adsorption isotherms were constructed. By adjusting a graph to experimental values of m_{cap} and C_0, either the maximum adsorbate capacity and distribution coefficient could be determined according to the Langmuir equation (Eqs. 4 and 5), or the constants in the Freundlich equation (Eq. 7, A and b). This was made by adjustment of the non-linear curves according to the sum of least squares by computer optimization. For the optimization of data, a laboratory-written computer program for an IBM-PC was used [28].

4. Applications

When the described theories of denuder breakthrough times are to be applied experimentally, the selection of the isotherm is of crucial importance. The depletion rate of a denuder can generally be expressed by the models of Eqs. 9 and 11, but the included t_0 term is directly proportional to the denuder capacity which is ruled by the adsorption isotherm. The success in the application of the denuder breakthrough equations, given in this paper, is thus strongly associated with the task of selecting an isotherm model that depicts, as correctly as possible, the adsorbent–adsorbate behaviour. In this section, two isotherms are considered, the Langmuir and

the Freundlich isotherms, but the equations are valid for any other type. Gaseous hexane is further chosen as an example of non-polar organic vapour to be trapped on two different adsorbents, Anasorb 747 and HayeSep D.

In Table 1, the isotherm parameters are listed for the two adsorbents when applied to hexane. The overall fits of the two isotherms to the experimental values are approximately the same based on RMS values.

In Fig. 1a, two theoretical and one experimental breakthrough curves are shown for the trapping of hexane on HayeSep D. Both models show steeper curve shapes than the experimental curve. Thus, the predicted breakthrough times are shorter than in reality, and shortest for Model 1. The corresponding reduced depletion plot is shown in Fig. 1b. The scaling factor on the t-axis, t_0, is calculated from data based on a Langmuir isotherm. The intercept of the different curves with the horizontal, dotted breakthrough percentages will indicate the time of that particular breakthrough for each model. Several interesting observations can be made from this simple dot. First, the experimental curve can be observed to pass under the straight-line model for very low breakthrough values. This indicates an error in the determination of the constants in the Langmuir isotherm or that the Langmuir isotherm is not sufficiently correct at low breakthrough concentrations. The capacity of the denuder has been slightly over-estimated at that particular gas-phase concentration. Second, the straight-line model and the recursive model will depict the experimental values fairly well at low breakthrough values.

Table 1
Langmuir and Freundlich adsorption isotherm parameters for hexane on HayeSep D and Anasorb 747

Adsorbent[a]	Langmuir			Freundlich		
	m_{max} (mg/g ads.)	K (×1000) (m³/mg)	RMS	A	$1/b$	RMS
HayeSep D	27.75	2.74	1.031	0.743	0.479	1.230
Anasorb 747	276.85	3.66	18.417	85.8	0.136	18.075

[a] Concentration ranges during experiments: HayeSep D, 100–1000 mg/m³; Anasorb 747, 1000–3500 mg/m³.
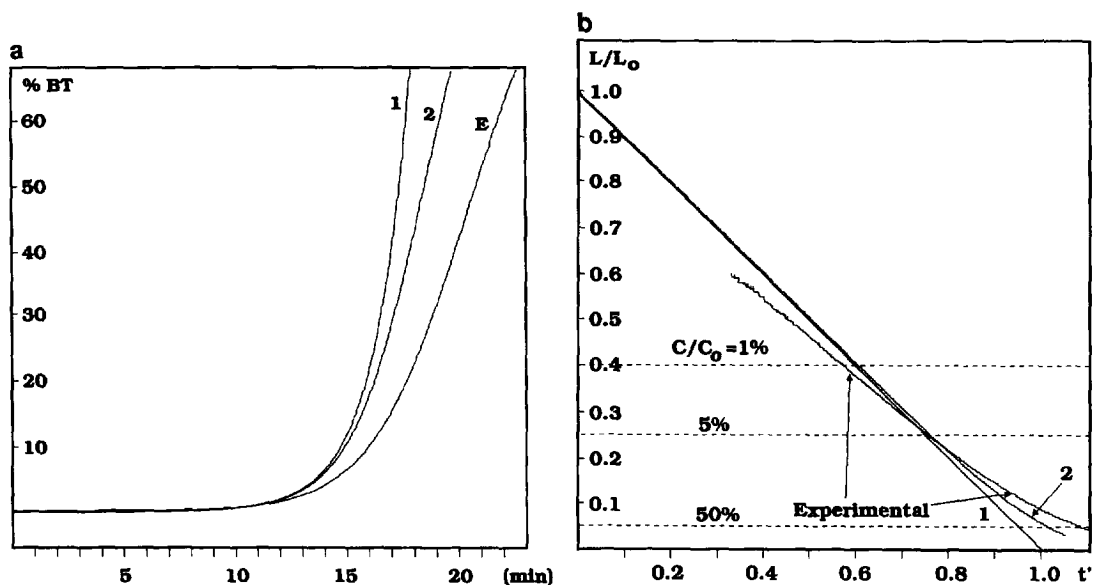
Fig. 1. (a) Experimental (E) and calculated (1, Model 1; 2, Model 2) breakthrough curves for hexane, based on the Langmuir adsorption isotherm, on a denuder ($L_0 = 140$ mm, I.D. $= 4$ mm) coated with 51 mg of HayeSep D; (b) the corresponding reduced parameter plot ($t' = t/t_0$, $L' = L/L_0$). Hexane concentration, 790 mg/m³; flow-rate, 65 ml/min.

4.1. Influence of gas-phase concentration

Neither of the two isotherms is very useful over the total gas-phase concentration intervals considered. In Fig. 2, breakthrough times for hexane on HayeSep D are shown as a function of the concentration. The calculated lines are based on Eq. 9 with t_0 from the Langmuir and the Freundlich isotherms. The graphs in Fig. 2 indi-

cate that the Langmuir isotherm is highly inaccurate at low concentrations for this set-up. Deviations from the experimentally assessed breakthrough values increase with decreasing concentration. The Freundlich adsorption isotherm seems to model the experimental values more accurately.

Large differences between the two isotherm concepts were further demonstrated by applying
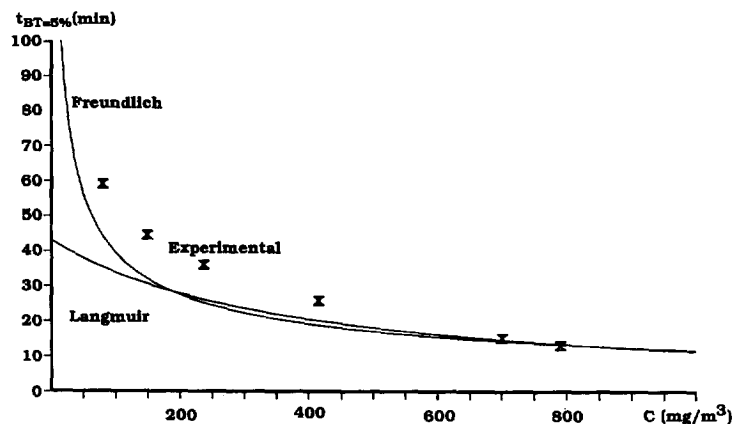

Fig. 2. Experimental and calculated (with Langmuir and Freundlich adsorption isotherm parameters in Model 1) 5% breakthrough times versus hexane concentration. Adsorbent, HayeSep D; sampling flow-rate, 65 ml/min.
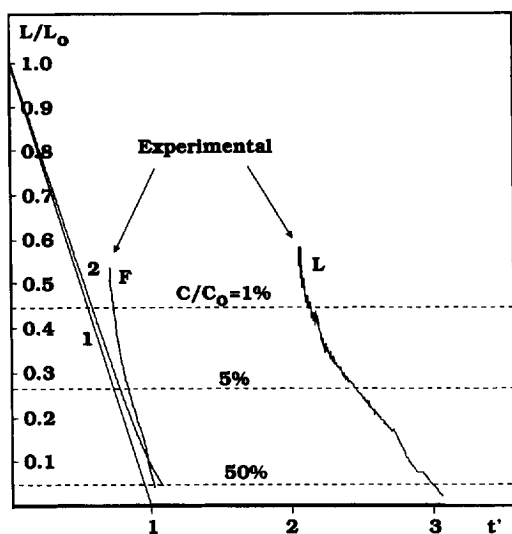
Fig. 3. Reduced parameter depletion plot ($t' = t/t_0$, $L' = L/L_0$) based on the Langmuir isotherm (L) and the Freundlich isotherm (F) for hexane on a denuder ($L_0 = 140$ mm, I.D. = 4 mm) coated with 385 mg of Anasorb. Hexane concentration, 62 mg/m^3; flow-rate, 70 ml/min. Curve 1, Model 1; curve 2, Model 2.

a very long time of sampling. In Fig. 3, the reduced depletion plot of hexane on Anasorb 747 is illustrated for a sampling time exceeding 220 h (>9 days). The adsorption capacity of Anasorb 747 is much higher than that of HayeSep D when applied to hexane (Table 1). The t_0 values were similar when applying the two isotherms at a hexane concentration of 700 mg/

m^3, i.e., 23 and 24 h, respectively. However, at the lower concentration, 62 mg/m^3, the t_0 value was 74 h, based on the Langmuir isotherm estimation, whereas the corresponding t_0 value from the Freundlich isotherm was 214 h. The breakthrough data from the experiment are presented in Table 2. They indicate that the calculated breakthrough times from the two isotherms are fairly close when applied to a hexane concentration of 700 mg/m^3, but at 62 mg/m^3 the Freundlich values are still useful whereas the Langmuir values are erroneous. Over a large range of concentration, e.g., very low and high values, the Freundlich isotherm is preferably used, yielding a fairly good fit over the entire interval.

4.2. Influence of sampling flow-rate

In Table 3, hexane breakthrough data on HayeSep D are shown for a concentration of 400 mg/m^3 at different flow-rates. Both isotherm models predict the 5% breakthrough time highly accurately in the flow-rate range considered and only a slight difference could be observed between the linear and the recursive models.

However, at higher breakthrough percentages the discrepancies between the experimental and calculated values increase for Model 1. This can be observed in Fig. 1, where the benefit of Model 2 is more obvious at higher breakthrough. In

Table 2
Comparison of calculated and experimental breakthrough times at 1 and 5% BT for hexane on Anasorb 747 at 700 and 62 mg/m^3.

Concentration (mg/m^3)	BT (%)	m_{ads} (mg)	Breakthrough time (h)				
			Experimental	1L[a]	1F[a]	2L[a]	2F[a]
700	5	311	14.1[b]	15.3	16.1	15.6	16.4
62	5	385	175	53.1	154	56	165
700	1	311	12.5	13.6	14.3	12.2	12.8
62	1	385	153	43.2	127	43.9	129

$F = 70$ ml/min; $D_g = 7.44 \cdot 10^{-6}$ m^2/s. Adsorption isotherm parameters from Table 1.
[a] 1L and 1F from Eq. 9 with t_0 from the Langmuir and Freundlich adsorption isotherms, respectively; 2L and 2F from Eq. 11 with t_0 from the Langmuir and Freundlich adsorption isotherms, respectively.
[b] The result is extrapolated from the breakthrough curve.

Table 3
Comparison of calculated and experimental 5% breakthrough times for hexane at various flow-rates on HayeSep D

Flow-rate (ml/min)	Breakthrough time (min)				
	Experimental	1L[a]	1F[a]	2L[a]	2F[a]
70	18.2	18.5	17.2	18.7	17.5
60.5	21.8	22.3	20.9	22.5	21.1
47.5	29.9	30.8	28.8	31.3	28.6
36	41.3	42.3	39.6	42.8	40.1
24	67.0	66.8	62.6	67.8	63.6

$C = 400$ mg/m^3; $m_{ads} = 0.051$ g; $D_g = 7.44 \cdot 10^{-6}$ m^2/s. Adsorption isotherm parameters from Table 1.
[a] 1L and 1F from Eq. 9 with t_0 from the Langmuir and Freundlich adsorption isotherms, respectively; 2L and 2F from Eq. 11 with t_0 from the Langmuir and Freundlich adsorption isotherms, respectively.

terms of curve shape, this means that the breakthrough curve according to Model 1 is steeper than both the experimental curve and Model 2.

4.3. Denuder efficiency

The denuder efficiency is defined here as the square of the retention time for 5% breakthrough divided by the square of the difference in retention times between the 1 and 5% breakthrough levels:

$$N_{den} = (t_{5\%}/\Delta t)^2 \qquad (15)$$

The absolute values may then be compared; the higher the number, the better is the efficiency.

In Fig. 4, the experimental denuder efficiency is plotted together with the calculated efficiency from Models 1 and 2, versus the flow-rate for the adsorbate–adsorbent pair hexane on HayeSep D. It can be observed that the denuder efficiency increases with decreasing flow-rate. Further, it is seen that the models predict a better efficiency than reality and the discrepancy increases as the flow-rate decreases.

The models assume, for both adsorbents, that the efficiency is independent on the solute concentration. Comparing the absolute efficiencies
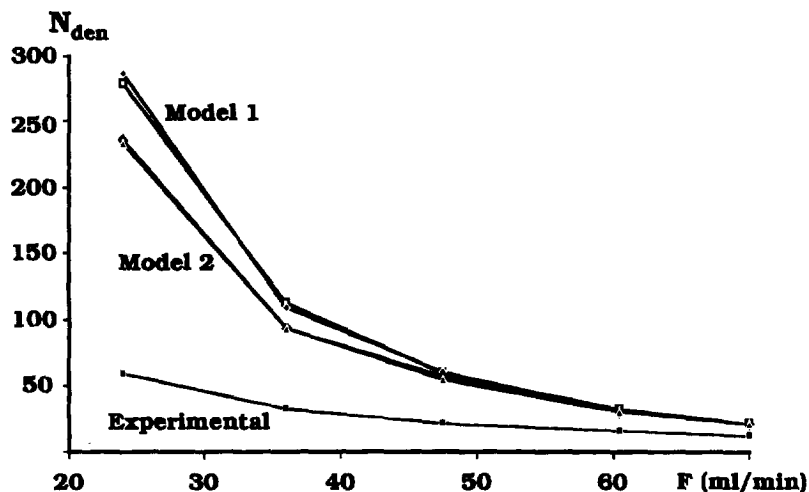

Fig. 4. Denuder efficiency (N) versus flow-rate. Adsorbent, HayeSep D; hexane concentration, 400 mg/m^3.

at constant flow-rate, the models show almost no differences in calculated efficiency, i.e., N is approximately 20–25 on both adsorbents, but the experimental data on Anasorb 747 gave a plate number of 70–80 and the experimental data on HayeSep D gave 15–20.

5. Conclusions

Eqs. 9 and 11 are simplifications that do not take into account that compounds are distributed over the adsorbent according to a particular distribution function and will further move upwards in the flow direction based on chromatographic movement. In spite of this, the rectangular distribution function, represented by Eqs. 9 and 11, seems to yield a good simulation of experimental results.

Two equations are suggested to be used for the determination of breakthrough times for denuder tubes used in the adsorption mode. The models differ from a number of commonly used methods for assessing breakthrough values. Eqs. 9 and 11 present a more general approach than, for example, the Nelson and Harder [22] model, or the modified Wheeler equation [19], the latter requiring the calculation of a rate coefficient.

The linear model is surprisingly correct considering its simplicity and shows, at least in the experiments carried out by us, only slightly less accurate determinations for breakthrough concentrations of up to 5% compared with the recursive model of Eq. 11. Both methods require compound–adsorbent specific constants from the isotherm selected. These methods seem to be useful, practical approaches, but are still a simplification of a rather complex distribution process of compounds in a denuder sampling system. Another approach is possibly a simulation of the entire adsorption and diffusion process in the denuder. Such calculations would be straightforward, but would require a substantial increase in the number of operations performed by the computer compared with the recursive model described here.

Acknowledgements

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