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Computer program for simulating the performance of thick-bed diffusive samplers: predicted and experimental sample loss due to reversible adsorption

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Abstract

Using experimentally determined adsorption isotherm constants, a computer model of the performance characteristics of thick-bed diffusive samplers was developed. The model has previously been used to calculate effective uptake rates, and it is now shown that it will predict the loss of sample due to reversible adsorption. The predicted losses of pentane, hexane, heptane and toluene from Tenax[®] TA and Chromosorb[®] 106 compare well with experimental data. The samplers were exposed for 2–16 h, followed by desorption for 2–21 h. The largest deviation between predicted and experimental values was found for pentane on Tenax TA, where the average experimental loss was 30% and the average predicted loss was 41%. Pentane on Chromosorb 106 showed an average experimental loss of 20% while the predicted loss was 19%. Possible applications are the measurements of strongly bound compounds in air, determined with high accuracy, while doing screening measurements of weaker bound compounds, with a less but estimated accuracy, on the same adsorbent.

1. Introduction

Diffusive sampling, where air pollutants are collected on a sorbent by diffusion rather than by active pumping, is a continuously growing technique. The applications include sampling of both organic and inorganic compounds in air [1–5]. The growing interest in the technique is due to its relatively low price and simplicity; no pumps are needed and the sampler can be made small and low-weight. Diffusive samplers are, therefore, well suited for long-time personal exposure measurements and for other long-time measurements requiring a large number of sampling points.

The practical use of diffusive samplers, containing an adsorbent, is usually limited to compounds that are strongly retained by the sorbent. The uptake rate for strongly retained compounds will essentially be constant, irrespective of concentration levels and exposure time. Weakly retained compounds will not show constant uptake rates, as the sorption is balanced by desorption. The problems are generally greater for samplers designed for thermal desorption than for samplers intended for liquid desorption, as the adsorbents used for thermal desorption usually are weaker than those used for liquid desorption.

In the present work a thick-bed tubular diffu-

sive sampler containing adsorbents designed for thermal desorption has been studied in view of this problem.

It is now possible to predict the effective (reduced) uptake rates for thick-bed diffusive samplers by a computer model based on experimentally determined adsorption isotherms [6–8]. Prediction can also be based on retention volumes [9,10]. However, the applicability of retention volumes is limited to the linear region of the adsorption isotherm, whereas an accurate determination of the adsorption isotherm constants gives the possibility to describe the adsorption/desorption behavior of the sampler over the entire range of the measured adsorption isotherms.

Severe problems arise when adsorbents having a weak interaction with a specific analyte are used for monitoring of that compound if the air concentration decreases. In such cases, a net loss of the analyte will occur due to desorption. Such desorptive losses can be large, and the suitability of an adsorbent for specific analytes and sampling conditions should be evaluated bearing this in mind [11,12]. If the concentration of an analyte varies greatly during the sampling period, the average concentration could be greatly underestimated if the analyte is lost by reversible adsorption; high concentrations in the beginning or in the end of a sampling period would thus give different time weighted average (TWA) concentrations. In terms of the error bounds in diffusive sampling, the effects of such sample losses on sampling precision have been discussed by Underhill [11] and Bartley et al. [12,13].

The loss of weakly sorbed analytes from different types of diffusive samplers has been described by assuming a linear sorption isotherm [14,15]. This approximation is valid for liquid sorbents, but for solid sorbents it is applicable only over a limited concentration range. Some adsorbent/adsorbate interactions, e.g. the adsorption of benzene and chloroform on Tenax® TA, are adequately described by linear adsorption isotherms at low concentrations [11]. At higher concentrations the adsorption isotherms for solid adsorbents are, in most cases, non-

linear [11,14], and thus the desorptive losses are not accurately described by models based on linear adsorption isotherms.

Van den Hoed and Van Asselen [7] presented a computer program for predicting effective uptake rates by thick-bed diffusive samplers, based on experimentally determined adsorption isotherms. Nordstrand and Kristensson [6] expanded this program to include, among other things, a model for net desorption effects due to reversible adsorption. A test of the capability of this computer model to estimate desorptive losses is presented here. The method was to load the sampling tube with the investigated compound by diffusion and then study the loss of the compound from the adsorbent in clean air. This loss is not very dependent upon a stable exposure concentration, as long as it is continuous and at about the same level of concentration over the whole exposure period. Chromosorb® 106 and Tenax TA were used as adsorbents, and *n*-pentane, *n*-hexane, *n*-heptane and toluene as adsorbates.

2. Experimental

2.1. Generation of test atmospheres

An exposure chamber consisting of a brass tube (50 × 3 cm I.D.) with fittings to attach 12 diffusive samplers was fed with compressed air via PTFE tubing. A short section of PTFE tubing was replaced by silicon tubing which led the vapour, via a fused-silica capillary, from the vapour generator (*vide infra*) into the air stream. The linear airflow, calculated from the airflow and the cross-sectional area, was 12 cm/s.

The standard gas atmosphere was generated either by diffusion cells or static pressure pumps. The diffusion cell was a stainless steel container, coupled to a piece of stainless steel tubing, simplified after Schoene and Steinhanses [16] (no electronic flow control valve or differential manometer). A static pressure pump was obtained by putting one end of a fused-silica capillary under the surface of the liquid under investigation and applying pressure with compressed air (Fig. 1).

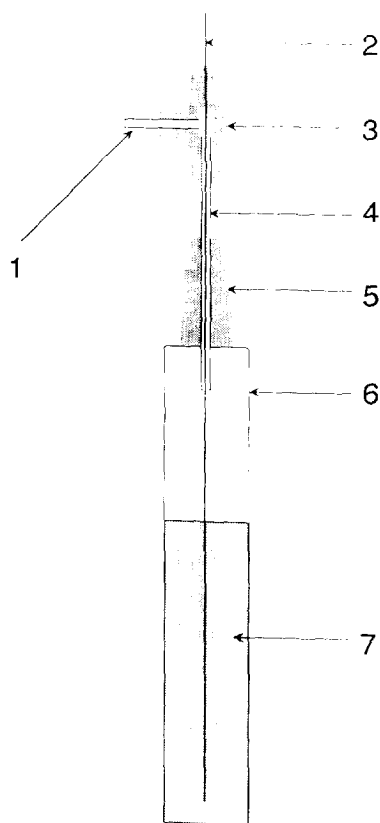


Fig. 1. Constant pressure pump for the exposure system. (1) Inlet for compressed nitrogen, pressure controlled; (2) fused-silica capillary; (3) Swagelock T-piece (1/16"); (4) steel tubing (1/16"); (5) Swagelock reducer (1/16" to 1/4"); (6) stainless steel canister; (7) liquid to be introduced into the exposure system.

The free end of the capillary was placed in the airstream by piercing the silicon tubing. The liquid was pressed at a constant speed into the air stream, vaporized, and further transported to the exposure chamber. The dimensions of the stainless steel tubing and fused-silica capillary (length and internal diameter) as well as the air pressure were adjusted to give the desired air concentrations in the exposure chamber.

Due to the high heat of vaporization of some analytes, such as pentane, water will condensate from the air and freeze on the tip of the capillary. To avoid this, a section of stainless steel tubing was inserted into the air stream, after the silicon tubing. The free end of the capillary was

put into contact with the wall of the stainless steel tube, which would then conduct a sufficient amount of heat to the tip of the capillary to keep the capillary tip free from frost.

The concentrations generated were determined at the beginning and the end of each exposure period by pumping air from the exposure chamber (50–250 ml) through two or three adsorbent tubes containing Tenax TA. The concentrations determined in this way differed in most cases by less than 2%, but at the most by 20%. The largest differences occurred when long exposure periods and low concentrations were used. The diffusion cell was preferable when low concentrations were desired, whereas the constant pressure pump was used to generate the higher concentrations.

The sample loss due to reversible adsorption was studied in a separate chamber under a flow of clean air. No special measures were taken to filter the air, since no detectable amounts of the investigated or other similar compounds were found when sampling actively one litre of the air onto an adsorbent tube.

2.2. Exposure of the diffusive samplers

Diffusive samplers, ATD (automatic thermal desorption) diffusive tube (mean cross-sectional area of 0.193 cm^2 , a mean air gap length of 1.51 cm [9]; Perkin-Elmer, Beaconsfield, Buckinghamshire, UK [17]), containing either Tenax TA (60/80, Alltech Associates, Deerfield, IL, USA) or Chromosorb 106 (60/80, Alltech), were exposed at 22°C unless otherwise specified. Twelve samplers could be exposed in each experiment. There was no detectable difference in analyte uptake among the twelve sampling positions. After exposure, four samplers were used to determine how much of the analyte had been taken up, the other tubes were sealed and removed to the clean air chamber for study of the loss due to reversible adsorption. In each experiment, four tubes were subject to the short desorption time (time 1) and four to the long desorption time (time 2), except where otherwise stated. The tubes were removed from the clean air chamber and sealed at the end of the

desorption periods. Exposure times were between 2 and 16 h, followed by desorption in the clean air chamber for 2 to 21 h.

2.3. Instrumentation

The samplers were analyzed on a Perkin-Elmer automatic thermal desorption unit, ATD 50, coupled to a Perkin-Elmer GC-8500 equipped with a flame ionization detector (FID). The desorption temperature varied between 220°C and 250°C depending on the adsorbent/analyte combination. Helium was used as desorption gas. The cold-trap was packed with Tenax TA, and the split flow was varied depending on the exposure concentration and sampling time, so as to give good peaks on the GC. The column was a CPWAX 52 CB (25 m × 0.32 mm I.D., 1.2 μm film thickness, Chrompak International, Middelburg, Netherlands) with helium at 1.6 ml/min as carrier gas. The temperature programme was adjusted to suit the individual analytes.

2.4. Determination of the adsorption isotherm constants

The adsorption isotherms used in this study have been measured for equilibrium concentrations on Tenax TA up to 30 ppm for pentane and up to 80 ppm for toluene [7]. The highest concentrations used for Chromosorb 106 were between 40 ppm (hexane) and 70 ppm (pentane and toluene) [7]. Adsorption isotherm constants for many compounds can be found in the literature. Adsorption isotherm constants for many compounds on Tenax TA, Chromosorb 106, Carbopack B can be found in Refs. [7,8,18,19].

3. Results and discussion

3.1. Experimental and predicted retention of compounds by the adsorbent

Experimentally determined and calculated exposure concentrations are presented in Tables 1 and 2. The calculated exposure concentrations

are based on the amount of the analyte adsorbed by the adsorbent tube after exposure, the exposure time, and the adsorption isotherm constants [6,7]. These are used by the programme to estimate sample loss due to reversible adsorption. The ratio between effective and ideal uptake rates, ($U_{\text{eff}}/U_{\text{id}}$), shows the error that results from using the ideal instead of the effective uptake rate for calculating the exposure concentration. The analyte loss ratio (W_x/W_{exp} , where $x = 1$ or 2) after each desorption period is calculated from the amount initially adsorbed in each exposure experiment.

The deviations between calculated and experimental results are summarized in Table 3. The average sum of the difference between the calculated and experimental desorption losses is a measure of the systematic deviation between model and experimental results. There is no apparent general trend of the model to under- or overestimate the loss. The size of the prediction error is given by the average absolute differences of the calculated and experimental desorption losses. With the exception of pentane, the deviations could result from imprecision in the determination of the different ratios.

In the early studies of this computer model, the relative standard error of the prediction of effective uptake rates was determined to be 8% [7]. The average experimental desorption loss in the present study was 15%. The losses calculated by the computer program differed, on average, from the experimental value by 6% of the whole (Table 3). In a study of sample loss due to reversible adsorption, using trichloroethylene at 25 ppm and activated charcoal [14], the random error for the deviation between model and experimental results during the desorption period was 6%.

The largest deviation between model and experimental results in Table 3 is found for pentane on Tenax TA, where the loss is overestimated by more than 10%. This is the weakest combination of adsorbent/adsorbate in this study. It indicates a deficiency in the model when used to describe either the transport from the adsorbent to the air, or the transport within the adsorbent bed, when high concentrations of

Table 1
Experimental and calculated results from exposure of Tenax TA

Compound	C [ppm (v/v)]		Exposure time (min)	W_{exp} (μ g) (R.S.D.)	U_{eff}/U_{id}	Desorption time 1 (min)	W_1/W_{exp} (R.S.D.)	Calc W_1/W_{exp}	Desorption time 2 (min)	W_2/W_{exp} (R.S.D.)	Calc W_2/W_{exp}
	Exp	Calc									
Pentane	34	33	180	5.7 (5%)	0.51	147	0.81 ^d (8%)	0.69	417	0.65 (6%)	0.54
Pentane ^a	51	54	131	7.2 (2%)	0.54	179	0.71 ^d (2%)	0.62	361	0.65 (3%)	0.52
Hexane	0.46	0.3	635	0.39 (4%)	0.78	300	0.91 (7%)	0.88	530	0.80 (5%)	0.84
Hexane	7.8	7.6	240	2.8 ^d (4%)	0.74	180	0.88 ^d (5%)	0.83	360	0.74 ^d (8%)	0.76
Hexane	15	13	246	4.5 ^d (4%)	0.70	182	0.87 (5%)	0.82	371	0.68 (5%)	0.74
Hexane	16	10	120	1.9 (3%)	0.81	182	0.81 (4%)	0.80	360	0.74 (4%)	0.73
Hexane	134	165	180	35.8 (7%)	0.58	–	–	–	480	0.74 (8%)	0.61
Heptane	4.5	3.0	240	2.0 ^d (6%)	0.97	183	0.97 (7%)	0.95	363	0.92 ^d (7%)	0.93
Heptane	29	26	115	5.9 ^d (4%)	0.90	175	1.02 (8%)	0.90	360	0.94 (5%)	0.87
Heptane	180	154	176	41 (7%)	0.67	183	0.76 (15%)	0.83	364	0.77 ^d (8%)	0.78
Toluene	0.35	0.2	312	0.15 ^d (1%)	1.0	251	1.02 ^d (6%)	1.0	1252	0.90 ^d (7%)	0.98
Toluene	0.4	0.25	971	0.54 (4%)	0.97	240	0.94 (4%)	0.98	739	0.85 ^d (6%)	0.96
Toluene ^b	12	12	178	4.6 ^d (8%)	0.95	363	0.89 ^d (10%)	0.90	1130	0.80 ^d (11%)	0.83
Toluene ^c	241	299	182	94 ^d (1%)	0.74	181	0.76 (2%)	0.83	354	0.73 ^d (4%)	0.76

^a $T = 23.5^\circ\text{C}$.

^b $T = 27.0^\circ\text{C}$.

^c $T = 27.5^\circ\text{C}$.

^d $n = 3$, all others $n = 4$.

C = Concentration of the analyte in air. Exp/Calc = measured experimental concentration/calculated concentration according to computer program, collected mass and exposure time. W_{exp} = mass of analyte taken up by the adsorbent and relative standard deviation (R.S.D.). U_{eff}/U_{id} = the effective uptake rate calculated according to the computer program/the ideal uptake rate according to the computer program. W_1/W_{exp} = the mass of the analyte on the adsorbent after the desorption period, x (1 or 2), divided by W_{exp} . W_x/W_{exp} , R.S.D. = relative standard deviation of the ratio, approximated as the square root of the sum of the relative variances of the respective measurements. Calc W_1/W_{exp} = the mass of the analyte on the adsorbent after clean air exposure, as calculated in the computer program, divided by W_{exp} .

analyte are present. The highest equilibrium concentration used for calculating the adsorption isotherm for pentane on Tenax TA was approxi-

mately 30 ppm [7]. The experiments in this study have thus been performed near the upper limit of the described adsorption isotherm, and an

Table 2
Experimental and calculated results from exposure of Chromosorb 106

Compound	C [ppm(v/v)]		Exposure time (min)	W_{exp} (mg) (R.S.D.)	U_{eff}/U_{id}	Desorption time 1 (min)	W_1/W_{exp} (R.S.D.)	Calc W_1/W_{exp}	Desorption time 2 (min)	W_2/W_{exp} (R.S.D.)	Calc W_2/W_{exp}
	Exp	Calc									
Pentane	12	12	290	5.5 (5%)	0.88	215	0.81 (8%)	0.90	395	0.77 (5%)	0.84
Pentane ^a	51	45	122	9.7 (8%)	0.92	354	0.85 (9%)	0.81	539	0.79 ^d (9%)	0.76
Hexane	0.40	0.38	760	0.58 (3%)	0.99	390	1.01 (5%)	0.98	715	1.01 (8%)	0.97
Hexane	132	160	200	63 (11%)	0.95	235	0.79 (14%)	0.92	740	0.79 (14%)	0.84
Toluene	1.3	1.8	312	1.3 ^d (3%)	1.0	692	0.94 ^d (4%)	1.0	1172	0.88 ^d (3%)	0.99
Toluene	241	227	180	94 (2%)	0.98	182	1.01 ^d (10%)	0.96	353	0.94 ^d (2%)	0.94

See Table 1 for explanation of headings and footnotes.

Table 3
Summary of the deviation between calculated and experimental results

Adsorbent and compound	Average experimental desorption loss (%)		Average (Calc - Exp) desorption loss (%)		Average Calc - Exp desorption loss (%)	
	Time 1	Time 2	Time 1	Time 2	Time 1	Time 2
<i>Tenax TA</i>						
Pentane	24	35	+11	+12	11	12
Hexane	13	26	+4	-3	4	5
Heptane	9	12	+2	+3	6	3
Toluene	10	18	-3	-6	3	6
<i>Chromosorb 106</i>						
Pentane	17	22	-3	+2	7	5
Hexane	10	10	-6	-1	8	4
Toluene	3	9	-2	-6	2	6
Average	12	19	+1	+0.4	6	6

Time 1/Time 2 = Shorter/longer desorption period in each experiment, see Table 1,2. Calc = calculated loss of analyte according to computer program. Exp = experimental loss of analyte.

expansion of the isotherm could solve some of the above problems.

When comparing C_{exp} and C_{calc} in Table 1 and according to Refs. [7,9], it seems possible to estimate the exposure concentration for the poor combination of pentane on Tenax TA in spite of the strongly reduced uptake rate. This could give a false impression of the possibility to analyze pentane using diffusive samplers packed with Tenax TA, since the possible errors due to reversible adsorption and concentration fluctuations, in this case, can be very high.

Table 1 shows that when pentane (33 ppm, Tenax TA) is present in the first 180 min of the 597 min (10 h) total sampling period (exposure + long desorption time) the sample loss equals 35%. For the whole sampling period of 597 min, the correct TWA concentration should be 10 ppm (v/v). Applying the computer program on the residual experimental mass after the end of the 597 min gives an estimated concentration of 9 ppm, a deviation of 10% from the correct TWA. If the exposure to pentane had been performed in the last, instead of in the first, part of the sampling period, the calculated concen-

tration would, instead, be 14 ppm, a deviation of 40%.

It is evident that the decrease in sampling rate resulting from the high concentration pulse in the beginning of the sampling period, has been reduced in the computer model by the prolonged total sampling period (exposure + desorption), thereby counterbalancing the effects of sample loss incurred by reversible adsorption. These factors have the opposite effect for a concentration pulse at the end of the sampling period. It is therefore possible to use Tenax TA for measuring pentane in a stable environment without fluctuating concentrations, provided that the adsorbent is not saturated during the exposure period. In an environment with unstable concentrations, it would be possible to estimate maximum sampling errors based on prior knowledge, or assumption, of the fluctuation pattern in the studied air.

It is interesting to note that a strong combination of adsorbent/adsorbate, such as toluene on Tenax TA, also suffers from sample loss due to high concentrations or long sampling times (Table 1). The resulting loss is not negligible and

should be considered when sampling toluene for several hours, or at high concentrations, utilising Tenax TA. However, the reduction in uptake rate is a minor problem compared with the potential net sample loss in an environment with strongly fluctuating concentrations.

The calculations of effective uptake rates and losses due to reversible adsorption are based on the measured adsorption isotherm of the adsorbent and the adsorbate in single combination [7]. This works well in single-component atmospheres where no interfering compounds are present. However, the adsorption isotherm for a particular compound may change if another compound is present at high concentrations. Vejrosta et al. [20] showed that the adsorption of 0.5 ppmv benzene, by Tenax GC, decreased even in the presence of about 10 ppbv of *o*-xylene. Increasing the concentration of *o*-xylene by three orders of magnitude decreased the partition coefficient of benzene by a factor of approximately 5. Co-adsorption could thus limit the applicability of these methods when interfering compounds are present in the sampled atmosphere. This study [20] was performed under equilibrium conditions. However, a prerequisite for a well functioning diffusive sampler is that equilibrium is never attained. More work has to be done to investigate the severeness of competitive adsorption during diffusive sampling.

4. Conclusion

For thick-bed diffusive samplers, the computer program [6] offers the possibility to calculate effective (reduced) uptake rates and estimate possible net sample loss due to reversible adsorption, provided that the adsorption isotherm for the adsorbent/adsorbate pair is known. It is then possible to calculate the effective uptake rates and also to estimate sample loss due to reversible adsorption during fluctuating concentrations of adsorbate. The errors can be estimated and compared with the need for accuracy of the measurement.

When screening for the presence of compounds in air, the demand of accuracy of a TWA

is less than 50% expressed as relative overall uncertainty [21]. If the adsorption isotherms are determined, thick-bed diffusive samplers could thus be used for the screening of many, weak bound, compounds. For instance, it could be possible to measure styrene with high accuracy with Tenax TA and at the same time performing screening measurement of hexane with a less, but estimated, accuracy.

The presence of co-adsorbing compounds in the air could however change the adsorption isotherm of the analyte on the sorbent [20]. This could severely limit the applicability of the suggested approach to describe the performance of the diffusive sampler.

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