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Short communication

Langmuirian parameters for Tenax GC adsorption of airborne organohalogen compounds

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Abstract

A study of the sampling conditions of diverse trihalomethanes, alkyl, alkenyl and aromatic chlorinated and brominated compounds and one chloroalcohol adsorbed on Tenax GC showed that the chromatographic behavior of these volatile organohalogen compounds can be modeled with a Langmuir isotherm. The equations derived from this model allow a description of the dependence between breakthrough volumes and atmospheric phase concentration of the adsorbates. They also indicate the breakthrough volumes at infinite dilution and the concentration thresholds requiring the application of Langmuir isotherms to avoid important quantitative sampling errors. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

As shown in previous studies, the retention behavior of airborne volatile organic compounds (VOCs) on solid-phase adsorption packings can be described with Langmuir isotherms [1,2]. This adsorption model provides a realistic description of the breakthrough volumes (V_b) for VOCs in the range of 1–500 mg/m³ which is the concentration interval of interest for many emission regulations and occupational safety guidelines. In contrast, the linear isotherm is useful for the description of the retention behaviour at low concentrations (<0.5–1 mg/m³), such as those encountered in ambient atmospheres.

The Langmuir equation shows a dependence between V_b and analyte concentration (c):

$$V_b = bm_{\max}/(1 + bc) \quad (1)$$

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where b is the distribution coefficient between the gas- and solid-phases and m_{\max} is the maximum mass that can be retained to form a monolayer on the adsorbent surface.

The linear model can, in fact, be described as a specific case of the Langmuir isotherm because V_b becomes independent of c when $bc \ll 1$.

In any case, the practical use of the Langmuirian model for prediction of adequate sampling conditions requires the knowledge of the constants defining the adsorption isotherms for the analyte–adsorbent systems of interest. Unfortunately, these are rarely available in the literature.

In the present study, the constants corresponding to a group of volatile organohalogen compounds adsorbed with Tenax GC are reported. The selected compounds are representative cases of solvents or intermediate reaction products of current use involving halomethanes (chloroform and bromochloromethane), alkyl and alkenyl derivatives (1,2-

dichloroethane, 1,2-dibromoethane, 1,1,2-trichloroethane, trichloroethylene, 1,1,2,2-tetrachloroethane, tetrachloroethylene, bromoethane, 1,2,3-trichloropropane and 1,4-dichlorobutane), aromatic compounds (chlorobenzene, bromobenzene and 1,2-dibromobenzene) and one alcohol (2-chloroethanol). The retention behavior of hydrocarbons and oxygenated compounds is reported elsewhere [3].

These constants have been calculated experimentally using a generator of dynamic atmospheres with known composition of individual VOCs [1,4]. For each compound, air flows with different concentrations were generated. These air masses were subsequently sampled with cartridges packed with this adsorbent and the breakthrough volumes were determined by direct mass spectrometric measurement of the air eluting from the cartridges. Adequate m/z ratios corresponding to the molecular mass of the compounds under study were selected in each case. The resulting curve fitted lines allowed to calculate the isotherm parameters at 20°C and confirmed that this group of compounds effectively follows a Langmuirian behavior on adsorption on Tenax GC. The changes in retention time volumes for multicomponent VOC mixtures are considered elsewhere [1].

2. Experimental

2.1. Generation of atmospheres with known VOC composition

The equipment designed for the generation of dynamic atmospheres containing known amounts of organochlorine compounds has been described elsewhere [4]. A circular oven equipped with a natural gas burner and a primary air entrance was used to generate a current of hot air (ca. 1000°C) that was diluted with ambient air. The resulting gas mixture was cooled in a heat exchanger (ca. 200°C) and received known amounts of organochlorine compounds that were introduced with a Chromatem 380 high-performance liquid chromatographic pump. The compounds were pumped through a 1 mm I.D. PTFE tubing into a sprayer situated at the base of a vertical 5 m × 29 cm I.D. pipe. This pipe homogenized and channelled the airstream (average flow-rate 300 m³/

h), which was subsequently released to the outside with an extraction fan. The fan was keeping all the system below atmospheric pressure (600 Pa). The pipe was equipped with three type K thermocouples for the control of the temperature at the top and at the base. The stream flow was measured with a Pitot tube connected to a capacitive electronic micromanometer (Furness Controls FCO-14). This micromanometer was used in a range of 0–10 Pa with time constant fitting. A sampling probe situated at 50 cm below the top of the pipe allowed the introduction of a portion of the spiked air into a glass dilution chamber (see diagram in Ref. [4]) where it was mixed with nitrogen (1:10). The dilution ratio was controlled with two oxygen analyzers situated before and after the air–nitrogen mixing device. Water condensation was avoided by external heating at 150°C.

2.2. Adsorption and analysis

The adsorption system was composed of 11.5 cm × 4 mm I.D. Supelco glass tubes filled with 150 mg of Tenax GC (35–60 mesh, Enka) situated between glass wool plugs. The tubes were kept at 20°C. The air from the diluted stream was passed through the filled tubes (150 cm³/min) by a membrane pump (Charles Austen, Capex 2D) working in impeller mode. The air volumes were measured with a Schlumberger precision volume meter. The analysis of the tube effluent was performed on-line using a mass spectrometer Balzers 420 equipped with a heating capillary for atmospheric sampling. This instrument was focused on mass fragment ions characteristic of the organochlorine compounds present in the airstream for the measurement of the V_b values. The same detection was also used for the direct analysis of the air stream by adequate switching of two three-way valves connected to a bypass tubing.

Repeated measurements of the concentrations of the spiked compounds showed a range of variation of 3–4% with respect to the mean. This dispersion was essentially introduced by the pulses of the chromatographic injection pump. Once the system was in a steady-state condition, the average VOC concentration did not exhibit any significant drift (<1%). The evaluation of the linearity between amount of com-

pound introduced in the air flow and concentration measured at the sampling site showed a straight line with a regression coefficient of 0.999 [4].

3. Results and discussion

3.1. The linear expression of the Langmuir isotherm

Eq. (1) can be linearized by transformation into the reciprocal form:

$$1/V_b = 1/(bm_{\max}) + c/m_{\max} \quad (2)$$

V_b and c are the respectively, dependent and independent variables in the experiments of generation and adsorption of atmospheres with known VOC composition. Thus, Eq. (2) can be used to determine the Langmuir constants for the VOCs of interest.

Furthermore, this equation provides a useful criteria for the estimation of the suitability of the Langmuirian model. If the compound–adsorbent system can be described with a Langmuir gas–solid isotherm, the experimental points must show a good fit to Eq. (2). This is illustrated in Fig. 1 where the least-squares straight lines corresponding to several representative cases, e.g., chloroform, 1,2-dichloroethane, 1,2-dibromoethane, 1,1,2-trichloroethane, trichloroethylene, 1,1,2,2-tetrachloroethane, tetrachloroethylene, 1,2,3-trichloropropane, chlorobenzene and bromobenzene, are shown. In all cases, the agreement between experimental points and fitted line is good.

As shown in Table 1, the regression coefficients corresponding to the fitting of this equation to the experimental V_b values are high, 0.96–0.9999, being similar to those previously found for the adsorption of benzenes and alkylbenzenes with Tenax GC, 0.991–0.9999 [1]. A Langmuirian behaviour for the solid-phase adsorption of some organohalogen hydrocarbons, e.g., chloroform, has even been observed when these compounds are isolated and concentrated in water samples [5].

Eq. (2) has been used to calculate the Langmuir constants of the organohalogen compounds included in this study. For this purpose, air mixtures containing known amounts of individual VOCs were

prepared with the equipment for the generation of dynamic atmospheres. The results corresponding to these calculations are also summarized in Table 1. The b constant ranges in a rather narrow interval, 0.0056–0.036 m³/mg, whereas the m_{\max} parameter exhibits values encompassing almost three-orders of magnitude, 0.0225–18 mg. Thus, the chemical differences of this wide group of organohalogen compounds are essentially reflected in significant changes in analyte load capacity of the adsorbent and not in the distribution coefficients between gas- and solid-phases [1,6]. These relatively uniform b values contrast with the high dispersion found in other groups of compounds (e.g., volatile thiols and sulphides [2]) and suggest a similar chromatographic process for the organohalogen compounds when retained with Tenax GC.

Obviously, the parameters determined from Eq. (2) can be used to represent V_b vs. c as defined in Eq. (1). This type of plot provides a direct comparison between the V_b – c dependence and the relationship predicted by the Langmuir isotherm. The plots corresponding to representative examples of the compounds considered in this study are shown in Fig. 2. As indicated by the correlation coefficient values (Table 1) the agreement between experimental and theoretical points is good.

3.2. Langmuir vs. linear isotherms

Eq. (1) predicts that at infinite dilution there is a V_b beyond which the retained VOCs elute independently of the concentration of the adsorbate in the gas-phase. This volume is coincident with the retention volumes currently reported as guidelines for the chromatographic behavior of the VOCs in the diverse adsorbent systems [7–9]. The infinite dilution V_b corresponding to the organohalogen VOCs considered in this study are summarized in Table 2. These volumes range over a wide span, from 0.43 to 310 dm³ per 150 mg of adsorbent, which is consistent with the wide range of m_{\max} indicated above. In this respect, it has to be mentioned that even higher retention volume differences have been predicted for these compounds. Thus, whereas the maximum sampling volumes of Table 2 for 1,2-dichloroethane and 1,2-dibromoethane are 26 and 110 dm³, respectively, other studies based on tem-

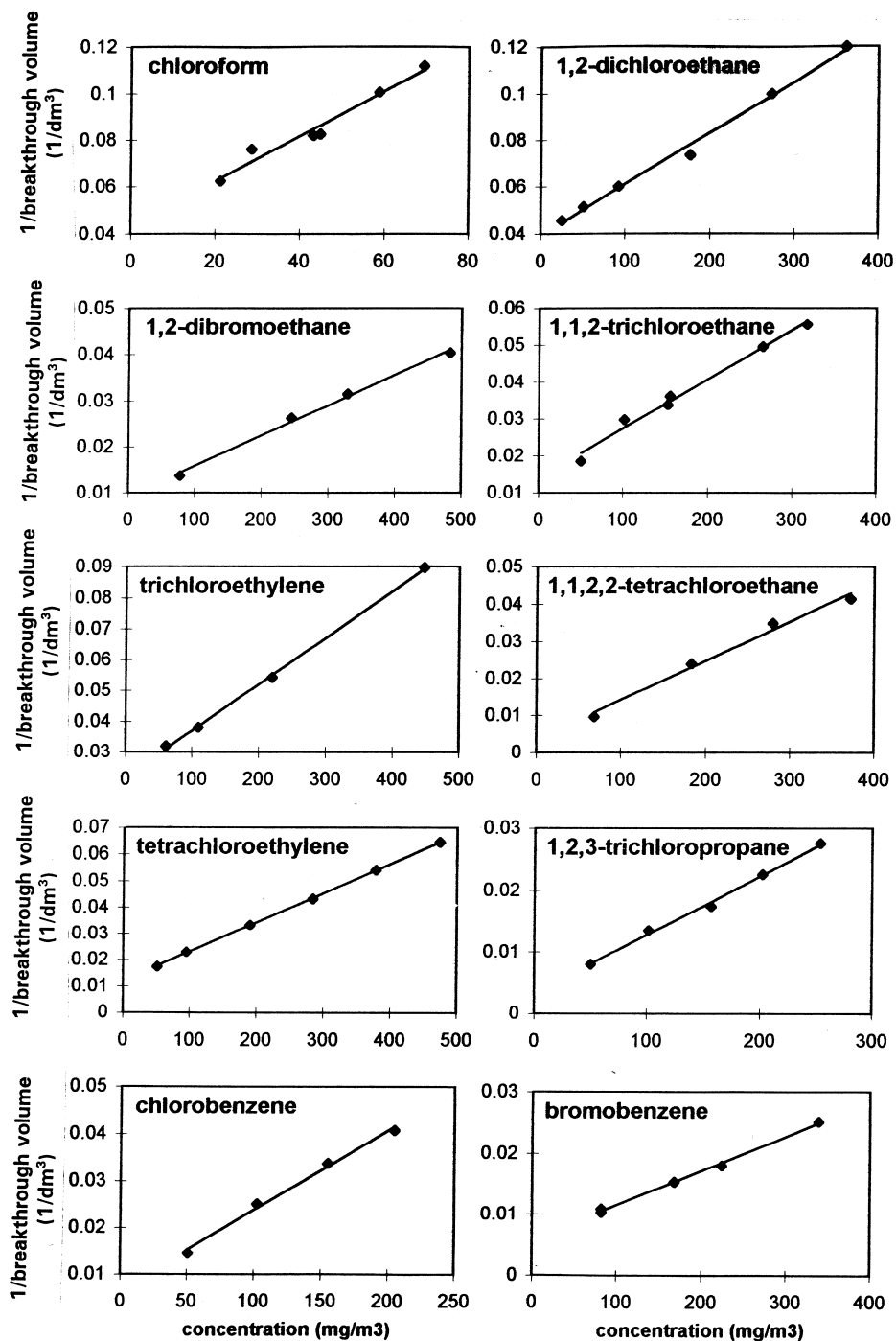


Fig. 1. Straight lines corresponding to least-squares curve fitting of Eq. (2) to the experimental breakthrough volumes determined with the generator of dynamic atmospheres with known VOC composition.

Table 1
Calculated Langmuir constants for the organochlorinated compounds included in this study

Compound	m_{\max} (mg ^a)	b (m ³ /mg)	Regression coefficient	n	Range (mg/m ³)
Chloroform	1.0	0.0215	0.98	6	20–70
Bromochloromethane	0.11	0.014	0.96	5	30–150
1,2-Dichloroethane	4.6	0.0056	0.997	6	20–400
1,2-Dibromoethane	15	0.0072	0.997	4	80–500
1,1,2-Trichloroethane	7.5	0.0095	0.993	6	50–350
Trichloroethylene	6.6	0.0069	0.9996	4	60–450
1,1,2,2-Tetrachloroethane	9.45	0.029	0.993	4	60–400
Tetrachloroethylene	9.1	0.0091	0.9999	6	50–500
Bromoethane	0.0225	0.019	0.995	5	30–150
1,2,3-Trichloropropane	11	0.028	0.998	5	50–300
1,4-Dichlorobutane	0.11	0.036	0.98	5	100–200
Chlorobenzene	5.9	0.025	0.997	4	50–250
Bromobenzene	18	0.0094	0.998	5	80–350
1,2-Dibromobenzene	15	0.0072	0.997	5	80–500
2-Chloroethanol	0.20	0.010	0.98	5	20–150

^a These values refer to one cartridge filled with 1 g of Tenax GC.

perature extrapolations predict retention volumes of 4 and 450 dm³, respectively [10]. On the other hand, these Table 2 volumes are intermediate of others predicted from heat of adsorption considerations. Thus, retention volumes of 130 [11], 2400 [12] and 360 [13] dm³ have been predicted for chlorobenzene and the maximum sampling volume derived from Eq. (2) for this compound is 150 dm³ (Table 2).

Current sampling volumes for field analyses are 0.5–5 dm³. Thus, according to Table 2 values, in most cases the Tenax GC cartridges considered in this study could be useful for the analysis of low concentrations of these compounds. However, problems in the determination of bromoethane (0.43 dm³), bromochloromethane (1.5 dm³) and 2-chloroethanol (2 dm³) may be encountered. An obvious way to increase retention efficiency is the use of higher amounts of adsorbent in the cartridge since the m_{\max} parameter depends on the total solid-phase amount. Tables 1 and 2 values correspond to values normalized to 1 g of adsorbent which is a commonly used amount for operational reasons.

Another aspect to be considered is the threshold concentration above which the V_b become affected by the gas-phase concentrations of the adsorbate. This is an important parameter to understand whether the chromatographic system behaves according to linear conditions or non-linear isotherms. According to Eq. (1), the system starts to deviate from the linear

isotherm when the term $bc > 0$ and contributes significantly to $(1 + bc)$. Obviously, if b is constant the significance of this term depends on the gas-phase concentration (c).

Thus, for a relative error of 5%, the ratio 0.05/ b provides a reference concentration above which non-linear Langmuirian effects become significant. These ratios have also been calculated (Table 2). Consistently with the low dispersion of b values they range over a narrow span lying between 1.4 and 8.9 mg/m³. These threshold values can easily be lower than the concentrations usually encountered at emission or even occupational safety regulations [14]. Thus, the sampling strategies for these organohalogen VOCs must take into account Langmuirian effects which make the V_b smaller than those predicted by the linear theory. In addition to this, it must be pointed out that in multicomponent mixtures the real deviation volumes of each VOC also depend on the Langmuirian concentration effects of the other compounds [1].

4. Conclusions

The chromatographic behavior of organohalogen VOCs such as halomethanes, aliphatic, olefinic and aromatic chlorine and bromine compounds and chloroalcohols follow Langmuir isotherms when ad-

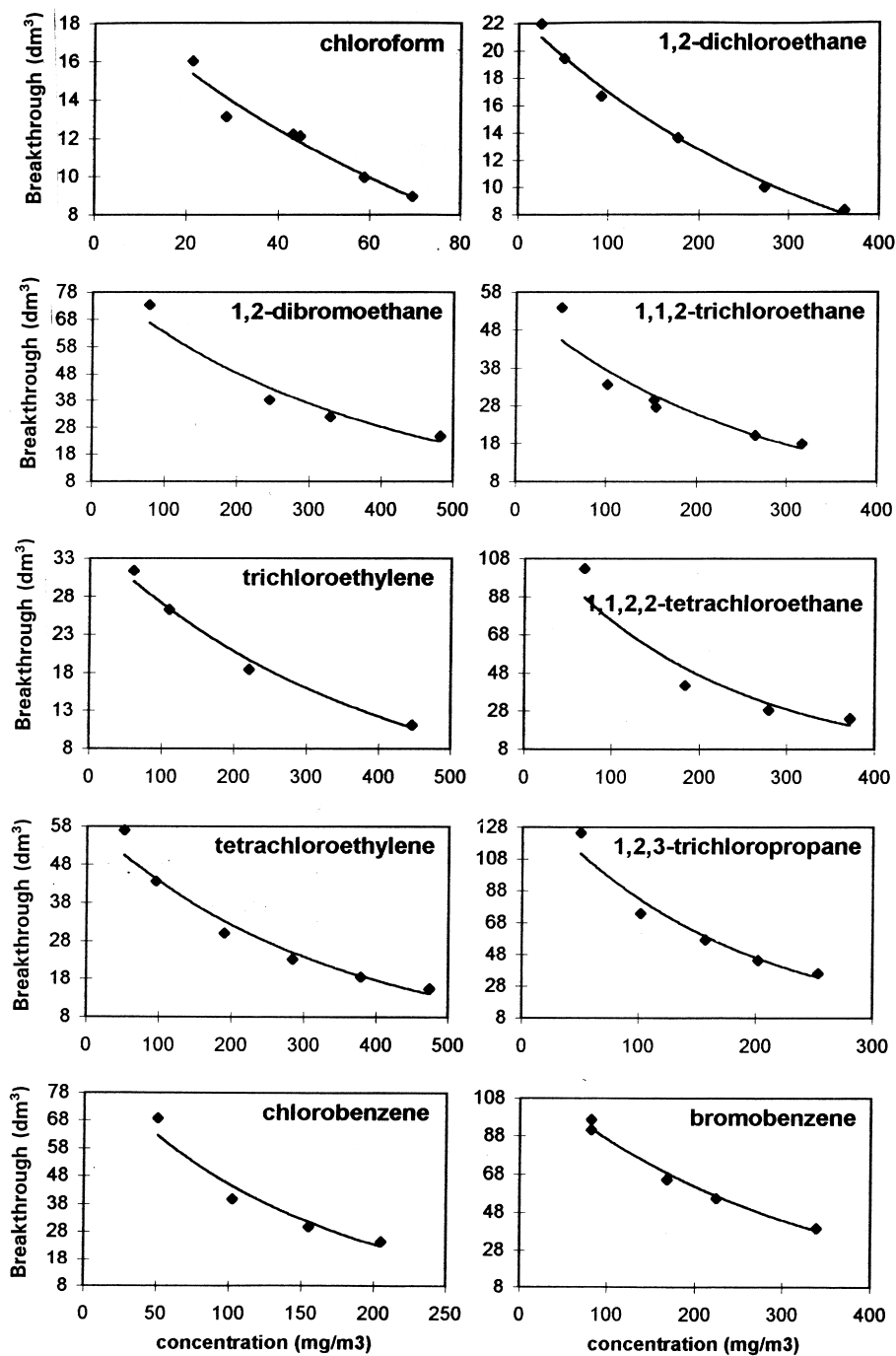


Fig. 2. Experimental (♦) and Langmuirian (—) breakthrough volumes for various organohalogen compounds adsorbed on Tenax GC.

Table 2
Sampling conditions defined by the Langmuir constants listed in Table 1

Compound	Max. sampling volume ^a ($m_{\max}b$) (dm ³)	Max. analyte concentration ^b (0.05/ b) (mg/m ³)
Chloroform	21.5	2.3
Bromochloromethane	1.5	3.6
1,2-Dichloroethane	26	8.9
1,2-Dibromoethane	110	6.9
1,1,2-Trichloroethane	71	5.3
Trichloroethylene	46	7.2
1,1,2,2-Tetrachloroethane	270	1.7
Tetrachloroethylene	83	5.5
Bromoethane	0.43	2.6
1,2,3-Trichloropropane	310	1.8
1,4-Dichlorobutane	4.0	1.4
Chlorobenzene	150	2.0
Bromobenzene	170	5.3
1,2-Dibromobenzene	110	6.9
2-Chloroethanol	2.0	5.0

^a At infinite dilution. These values refer to one cartridge filled with 1 g of Tenax GC.

^b Concentrations involving 5% breakthrough errors due to Langmuirian effects.

sorbed on Tenax GC from atmospheres were they are present in concentrations up to 70–500 mg/m³. The chromatographic behavior of these compounds on this adsorbent cannot be described with linear isotherms at air concentrations above 1–9 mg/m³. All compounds analyzed exhibit similar gas–solid-phase distribution coefficients (0.0056–0.036 m³/mg) and very different adsorption capacity values (0.0225–18 mg for 1 g of adsorbent). This difference suggests the occurrence of similar chromatographic adsorption interactions for all these organohalogen compounds when retained with Tenax GC.

Acknowledgements

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