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Langmuirian behaviour of smelly volatile organic compounds on air sampling with solid adsorbents ☆

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Abstract

A study of the sampling conditions of methylamine, trimethylamine, methanethiol, acetaldehyde, ethanethiol, dimethyl sulphide and dimethyl disulphide adsorbed on Carboxen-569 and HayeSep Q showed that the chromatographic behaviour of these volatile organic compounds (VOC) in these packings can be modelled with a Langmuir isotherm. The equations derived from this model allow the relationship between breakthrough volumes and atmospheric phase concentration of the adsorbates to be described. They also predict, for each adsorbent–adsorbate system, the breakthrough volumes at infinite dilution and the VOC concentration thresholds requiring the application of Langmuir isotherms to avoid important quantitative errors.

1. Introduction

The effective control of the emission of volatile organic compounds (VOC) to the atmosphere has been a primary objective of the recent years. Unfortunately, the currently available air pollution monitoring systems, namely adsorption on solid surfaces, have essentially been developed in ambient atmospheric studies [1–5]. Hence the operational conditions already known can only be extrapolated to emission source measurements with caution.

In the range of concentrations of both emission sources and occupational safety guidelines, it has been demonstrated that the breakthrough volumes (V_b) corresponding to VOC adsorption on solid surfaces are concentration dependent and follow a Langmuirian behaviour [6]. The V_b of one compound can be defined as the accumulated air volume eluting from the adsorbent at which detectable amounts of this compound start to elute from the tube. Accordingly, the relationship between V_b and atmospheric phase concentration (c) can be described by the following equation:

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

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.

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Using a generator of dynamic atmospheres, the equation of the Langmuir isotherm has been observed to describe accurately the chromatographic behaviour of benzene, toluene and styrene and their binary and ternary mixtures adsorbed on Tenax GC [6].

This study is an extension of this previous work [6] which is focused on the determination of the sampling conditions for the correct determination of smelly VOC in the range of concentrations found at emission (1–200 mg/m^3). The compounds of interest encompass amines (methyl- and trimethylamine), thiols (methane- and ethanethiol), sulphides (dimethyl sulphide and dimethyl disulphide) and an aldehyde (acetaldehyde). Two atmosphere generators were used to produce atmospheres containing individual known concentrations of these smelly compounds and these were used to determine the V_b of two adsorbents, Carboxen 569 and HayeSep Q. These two packings can be grouped as Type III adsorbents (localized negative charges) of low polarity [7]. This approach enabled us to test the validity of the Langmuir model for the description of the retention behaviour of these compounds with these adsorbents and allowed us to calculate the corresponding isotherm constants, b and m_{max}.

2. Experimental

2.1. Generation of atmospheres with known VOC composition

The equipment designed for the generation of dynamic atmospheres of the nitrogen- and sulphur-containing compounds consists of compressed nitrogen cylinders containing typically 50 ppm of the individual VOC to be studied (Fig. 1). The desired concentration is then obtained by nitrogen dilution in a mixing chamber. The equipment used to produce atmospheres with known concentrations of acetaldehyde has been described elsewhere [8]. Acetaldehyde was mixed with 20% of water before introduction. Once the system is in a steady-state condition, the average VOC concentration does not exhibit any significant drift (<1%) during the time of one experiment. The evaluation of the linearity between amount of compounds introduced in the air flow and concentration measured at the

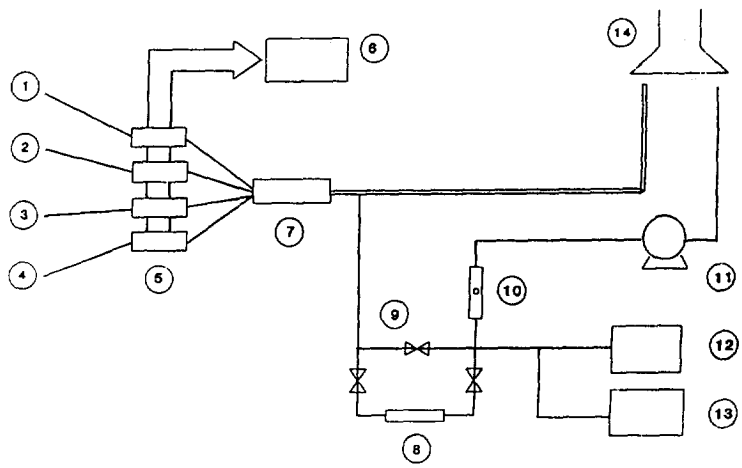

Fig. 1. Equipment designed for the generation of dynamic atmospheres with known concentrations of smelly nitrogen- and sulphur-containing compounds. 1–3 = Compressed cylinders containing the VOC standards diluted in nitrogen; 4 = nitrogen cylinder; 5 = mass flow meters; 6 = electronic command unit; 7 = jet mixing chamber; 8 = adsorption tube; 9 = bypass; 10 = flow meter; 11 = volume meter; 12 = mass spectrometer; 13 = flame ionization detector; 14 = gas extraction hood.

sampling site showed a straight line with a regression coefficient of 0.999 [8].

2.2. Sampling with solid adsorbents

The adsorption system is composed of 11.5 cm × 4 mm I.D. glass tubes (Supelco, Bellefonte, PA, USA) filled with Carboxen-569 (Supelco) [7] or HayeSep Q (Hayes Separation, Bandera, TX, USA) situated between glass-wool plugs, 350 and 150 mg, respectively. The air from the diluted stream was passed through the filled tubes (100 ml/min). The air volumes were measured with a Schlumberger precision volume meter. The analysis of the tube effluent was performed on-line using either a Cosma RS-55 flame ionization detector or a Balzers 420 mass spectrometer equipped with a heating capillary for atmospheric sampling. These two instruments were used to determine the concentrations of the VOC in the gas eluting from the tubes and therefore to determine the V_b values. The same detectors were also used for the direct analysis of the stream by appropriate switching of two three-way valves connected to a bypass tube.

2.3. Adsorption packings

Carboxen-569 has a mesh size of 20–45, a surface area of 485 m^2/g and a density of 0.58 g/ml [7]. Adequate desorption and regeneration temperatures are 300 and 350°C, respectively. The functional range for this packing is C_2–C_5. HayeSep Q is a divinylbenzene polymer with a surface area of 582 m^2/g and a density of 0.351 g/ml. Typical desorption and regeneration temperatures are 200°C. The maximum operating temperature is 275°C. According to the manufacturer, the retention properties of this polymer are interchangeable with those of Porapak Q.

3. Results and discussion

Methylamine, trimethylamine, methanethiol and acetaldehyde were retained with Carboxen-569. The adsorption of the other compounds, ethanethiol, dimethyl sulphide and dimethyl disulphide, with this packing gave rise to V_b that were too large for analysis. These compounds were collected with HayeSep Q, which, in turn, exhibited a poor retention capacity for the VOC included in the first group.

3.1. Linear expression of the Langmuir isotherm

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

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

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

Further, this equation provides a useful criterion for establishing 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. 2, where the least-squares straight lines corresponding to three representative cases, methylamine and acetaldehyde with Carboxen-569 and ethanethiol with HayeSep Q, are shown. In all cases, the agreement between experimental points and the fitted line is good.

Eq. 2 was therefore used to calculate the Langmuir constants of the smelly compounds included in this study. The results of these calculations are summarized in Table 1. The regression coefficients corresponding to the fit of this equation to the experimental V_b values are also given. These coefficients show fairly good agreement between the experimental results and the Langmuirian model, 0.97–0.998, being similar to those found previously for the adsorption of benzenes and alkylbenzenes with Tenax GC, 0.991–0.9999 [6].

The constants in Table 1 corresponding to adsorption on Carboxen-569 lie in a limited

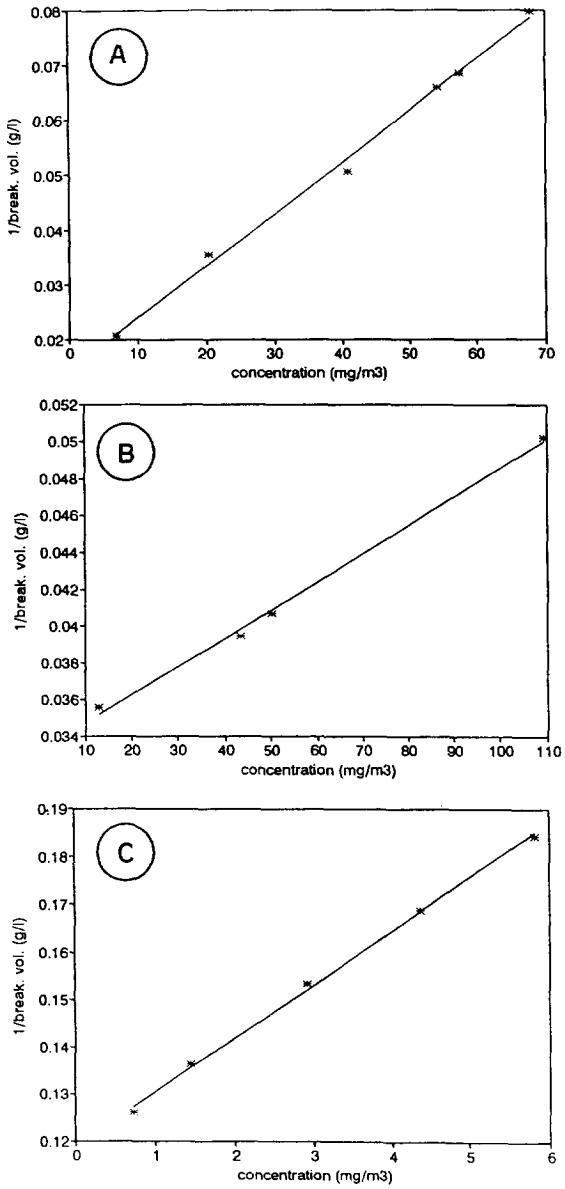

Fig. 2. Straight lines corresponding to least-squares curve fitting of Eq. 2 to the experimental breakthrough volumes determined with the generator of dynamic atmospheres with known VOC composition. (A) Methylamine on Carboxen-569; (B) acetaldehyde on Carboxen-569; (C) ethanethiol on HayeSep Q.

range, 1.1–6.5 mg/g for m_{max} and 0.012–0.046 m^3/mg for b. This cluster shows that general conditions for the joint sampling of these compounds can easily be obtained. Conversely, the constants corresponding to the examples of adsorption on HayeSep Q range over more than two orders of magnitude, 0.088–36 for m_{max} and 0.0067–0.95 for b, showing that the sampling conditions are more compound dependent with this packing. In this respect, it is worth mentioning that this packing exhibits a strong difference between the retention capacity of the lower (ethanethiol and dimethyl sulphide) and higher (dimethyl disulphide) molecular mass sulphur-containing VOC.

3.2. The Langmuir equation

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 all compounds considered in this study are shown in Fig. 3. As indicated by the correlation coefficients (Table 1), the agreement between the experimental and theoretical points is fairly good.

The Langmuir constants listed in Table 1 can be used for the calculation of the V_b corresponding to high c values and comparison with empirical results obtained in other studies. Accordingly, the constants in Table 1 were used for the calculation of V_b for ethanethiol, dimethyl sulphide and dimethyl disulphide at the concentrations tested in one previous study [9], 668, 602 and 239 ppm (v/v), respectively, in which Porapak Q was considered and the standard mixtures were generated with diffusion tubes. Whereas these V_b are relatively similar in the case of dimethyl disulphide (10 and 33 l/g for the experimental study [9] and the value derived from Table 1 constants, respectively), there is a strong discrepancy (about one order of magnitude) for the other two compounds. The concentrations tested in this previous study were fairly high, 934 (dimethyl disulphide) and 1550 (dimethyl sulphide) mg/m^3, in comparison with the ranges used for the calculation of the Langmuir constants in the present study, 2.5–12.5 and 10–230 mg/m^3, respectively. The large dis-

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

Compound	Adsorbent	m_{max} (mg/g)	b (m^3/mg)	Regression coefficient	n	Range (mg/m^3)
Methylamine	Carboxen-569	1.1	0.065	0.996	6	8–70
Trimethylamine	Carboxen-569	2.9	0.047	0.997	5	15–130
Methanethiol	Carboxen-569	3.7	0.012	0.98	6	5–105
Ethanethiol	HayeSep Q	0.088	0.95	0.998	5	0.5–6
Dimethyl sulphide	HayeSep Q	0.77	0.012	0.97	4	2.5–125
Dimethyl disulphide	HayeSep Q	36	0.0067	0.993	4	10–230
Acetaldehyde	Carboxen-569	6.5	0.0046	0.997	4	12–110

crepancy for dimethyl sulphide corresponds to the case of the greatest difference between the concentrations evaluated in the two studies. In view of the low retention capacity of HayeSep Q for dimethyl sulphide, it is surprising that in the previous study such an elevated concentration was retained. Probably under these conditions the retention mechanism does not fulfil some of the Langmuir retention conditions, e.g., that only a monolayer of gas molecules should be adsorbed on the solid surface and that no interaction should occur between adjacent adsorbate molecules.

3.3. Langmuir vs. linear isotherms

Eq. 1 predicts that at infinite dilution there is a V_b beyond which the retained VOC 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 behaviour of the VOC in diverse adsorbent systems [1,2,10–12]. The infinite dilution V_b corresponding to the smelly VOC considered in this study are summarized in Table 2. These volumes cover a wide range, from 9.2 to 240 l/g of adsorbent. The values are higher than the usual sampling volumes collected in field analyses (0.5–5 l), showing that the adsorption methods selected in this study have sufficient retention power for the gas-phase monitoring of the above-described smelly VOC.

Another aspect to be considered is the threshold concentration above which the V_b becomes affected by the gas-phase concentrations of the adsorbate. This is an important parameter to evaluate in order to determine whether the system behaves according to ideal conditions or non-linear isotherms. According to Eq. 1, the system starts to deviate from the linear isotherm when the term $bc > 0$ and thus becomes an amount that contributes significantly to $1 + bc$. Obviously, if b is constant the significance of this term depends on the concentration. If a relative error of 5% is assumed, the ratio $0.05/b$ provides a reference concentration above which the non-linear Langmuirian effects become significant. These ratios are also listed in Table 2. Again they cover a wide range, between 0.053 and 11 mg/m^3. These threshold values can be below the concentrations usually encountered at emission. Hence the sampling strategies for these smelly VOC must take into account Langmuirian effects which make the V_b smaller than those predicted by the linear theory.

The odour thresholds of most of these compounds are well below the concentrations in Table 2, e.g., 0.0005 and 0.0042 mg/m^3 for trimethylamine and methanethiol, respectively [13]. However, for ethanethiol the odour threshold, 0.0025 mg/m^3 [13], is close to the concentration limit for non-linear effects. This case shows that for some compounds the non-linear adsorption effects are significant not only at emission levels but also at concentrations near to the odour threshold.

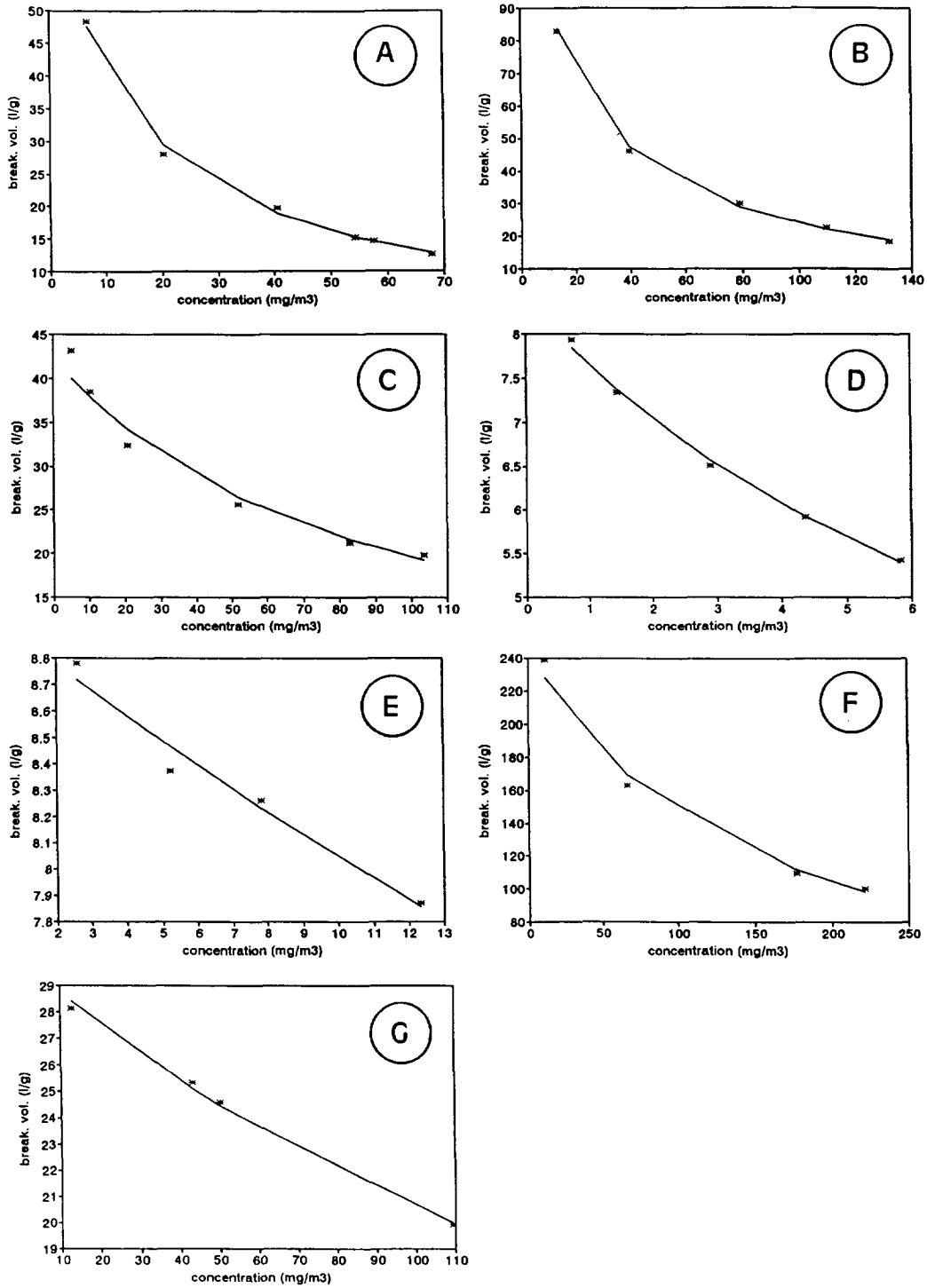

Fig. 3. Experimental (symbols) and Langmuirian (lines) breakthrough volumes for (A) methylamine, (B) trimethylamine and (C) methanethiol adsorbed on Carboxen-569, (D) ethanethiol, (E) dimethyl sulphide and (F) dimethyl disulphide on HayeSep Q and (G) acetaldehyde on Carboxen-569.

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

Compound	Adsorbent	Maximum sampling volume[a] (m_{max} b) (l/g)	Maximum analyte concentration[b] (0.05/b) (mg/m^3)
Methylamine	Carboxen-569	71.5	0.76
Trimethylamine	Carboxen-569	140	1.1
Methanethiol	Carboxen-569	44	4.2
Ethanethiol	HayeSep Q	84	0.053
Dimethyl sulphide	HayeSep Q	9.2	4.2
Dimethyl disulphide	HayeSep Q	240	7.5
Acetaldehyde	Carboxen-569	30	11

[a] At infinite dilution.
[b] For a 5% error with respect to the volume at infinite dilution.

4. Conclusions

The chromatographic behaviour of smelly VOC such as methylamine, trimethylamine, methanethiol and acetaldehyde follow Langmuir isotherms when adsorbed on Carboxen-569. Likewise, ethanethiol, dimethyl sulphide and dimethyl disulphide show Langmuirian behaviour when adsorbed on HayeSep Q. In relation to previous publications [6], this finding represents a considerable extension of the type of VOC and packings that can be described with these non-linear equilibrium equations, suggesting that the Langmuir isotherm may be a close approximation for the gas–solid distribution behaviour of VOC at concentrations up to 250 mg/m^3.

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