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Dependence on sampling rates of Radiello® diffusion sampler for BTEX measurements with the concentration level and exposure time

Anne Pennequin-Cardinal[a,*], Hervé Plaisance[a], Nadine Locoge[a], Olivier Ramalho[b], Séverine Kirchner[b], Jean-Claude Galloo[a]

[a] *Ecole des Mines de Douai, LCSQA, Département Chimie et Environnement, 941 rue Charles Bourseul, BP 838, 59508 Douai, France*
[b] *Centre Scientifique et Technique du Bâtiment, Marne la Vallée, France*

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Abstract

Radiello® diffusive samplers filled with a thermally desorbable adsorbent (graphitised charcoal Carbograph 4) have been tested for the monitoring of BTEX. The sampling rates have been estimated under various controlled atmospheres in order to evaluate the effects of two factors (exposure time, concentration levels and their interaction) on the performances of the Radiello® sampler. Experiments have been carried out under various atmospheres in exposure chamber. A total of 174 Radiello® samplers were exposed while varying two conditions: exposure time (1, 3, 7 and 14 days) and BTEX concentrations (low, medium and high levels). The results show that the sampling rates of benzene and toluene decrease for exposure of 14 days and especially for high concentration levels: decrease of 30% at 10 $\mu g\,m^{-3}$ for benzene and 14% at 30 $\mu g\,m^{-3}$ for toluene.

To try to explain the variations of these sampling rates, the breakthrough volumes (V_B) of BTEX on Carbograph 4 have been determined at different temperature and concentration conditions in order to evaluate the Langmuir parameters and their adsorption enthalpy ($-\Delta H_{ads}$) using the Van't Hoff equation. With regard to these adsorption characteristics, the dependence of sampling rates with concentration level and exposure time were analysed and discussed.

Keywords: Diffusive sampler; BTEX; Sampling rate; Breakthrough volume

1. Introduction

Volatile organic compounds (VOC) are ubiquitous in air. We breathe an air volume containing a multitude of components that can cause a variety of adverse health effects. Among these pollutants, aromatic hydrocarbons, BTEX (benzene, toluene, ethylbenzene, xylenes), are particularly abundant in indoor environment [1–3] and one of them (benzene) is suspected to be carcinogenic [4,5]. The BTEX sources are very diverse and the contents of these compounds vary a lot according to the environment, whether indoor or outdoor. Thus vehicular exhausts and industrial emissions are considered to be the major sources of ambient and indoor BTEX [6–8]. Occasionally, consumer product emissions and tobacco smoke, but also construction materials, heating, solvents and adhesives may increase BTEX concentrations in indoor environments [9].

In this context, a simple method of measurement could be interesting to investigate many places. This approach can be overcome by the use of diffusive sampling methods because of their simplicity of implementation [10–12]. Indeed, a method that is already fully used for ambient air monitoring of benzene [13] in several countries is to sample by using diffusive Radiello® samplers [14]. This sampler is a cartridge containing a graphitised charcoal inserted in a diffusive body. The cartridge is thermally desorbed and analysed by gas chromatography.

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* Corresponding author. Tel.: +33 3 27 71 26 55; fax: +33 3 27 71 29 14.
E-mail address: cardinal@ensm-douai.fr (A. Pennequin-Cardinal).

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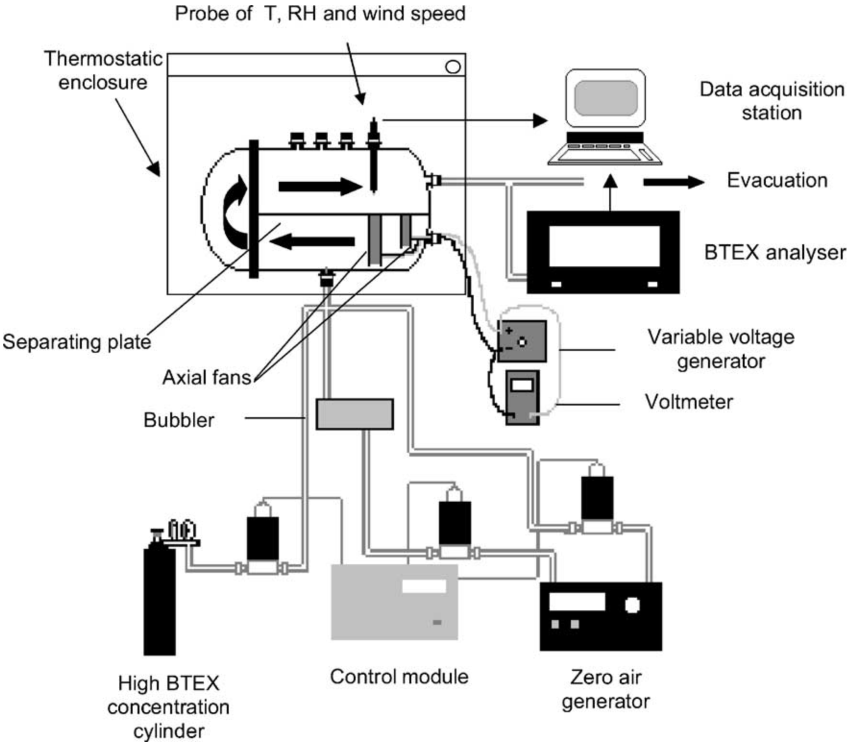

Fig. 1. Schema of the exposure chamber system.

In order to use Radiello® diffusive sampler to assess ambient or indoor air concentrations of these pollutants, several parameters must first be known: individual sampling rate and the respective dependence according to the exposure time and the concentration level. In this work, 174 samplers have been exposed to three concentration levels (low, medium and high) and for four durations (1, 3, 7 and 14 days).

To complete sampler experiments, the adsorbent characteristics were evaluated. In these topics, some adsorption properties (surface area, adsorption enthalpies, Langmuir parameters) were determined and discussed as regard to experiment results found in the exposure chamber.

2. Experimental

2.1. Diffusive samplers

BTEX are collected in Radiello® diffusive sampler, patented by the Foundation *Salvatore Maugeri* (FSM). The BTEX sampler consists of an adsorbent cartridge inserted in a microporous polyethylene membrane (code 120-2). The surface of diffusion is a 50 mm length microporous cylinder, with an external diameter of 16 and 5 mm thick. The stainless steel adsorbing cartridge is 60 mm long, 4.8 mm in diameter, filled with 300 mg of 40–60 mesh Carbograph 4 (a graphitised charcoal). The compounds diffuse through the membrane towards the cartridge where there are adsorbed by Carbograph 4. As the diffusion is parallel to the cartridge radius, the device has been called a radial diffusive sampler. During measurement, the membrane is fixed onto a triangular polycarbonate supporting plate.

The adsorption suitability for a passive sampling of VOCs with thermal desorption is directly related to the physical characteristics of sorbent, i.e. its surface area and the microporous volume. The higher the specific area of an adsorbent is, the better its adsorption capacity [15]. The higher the microporous volume of adsorbent material, the more difficult it will be for the compounds retained on the sampler to be entirely desorbed [15]. To correctly evaluate the surface area and the microporous volume of Carbograph 4, the surface characterization method using BET (Brunauer, Emmet and Teller) plots was employed. Table 1 compares the surface area and the microporous volume of Carbogaph 4 with those of several other adsorbents [15,16]. Carbograph 4 seems to be a good compromise for the thermal desorption because it provides a high surface area and a low microporous volume.

After exposure, the BTEX concentrations can be calculated by applying Fick's first law from the pollutant masses

Table 1
BET surface areas and total microporous volume of few adsorbents [15,16]

Adsorbent	S_{BET} ($\mathrm{m^2\,g^{-1}}$)	V_{micro} ($\mathrm{mL\,g^{-1}}$)
Tenax TA	26	6.7
Active charcoal	1250	341
Carbograph 1 g	76	0.7
Carbograph 4 g	129	0.5

Table 2
Values of different concentrations (μg m^{-3}) of BTEX tested in the exposure chamber

	0.4 LV	1 LV	2 LV
Benzene	2	5	10
Toluene	6	15	30
Ethylbenzene	1.3	3.5	7.5
m/*p*-xylene	3	7	15
o-xylene	1.7	4	9

retained on the cartridge [17,18]:

$$C = \frac{m_\mathrm{d} - m_\mathrm{b}}{d \times \mathrm{SR} \times t} \qquad (1)$$

where m_d is the adsorbed mass of compound (μg) sampled during the time t (min) under the concentration in air C (μg m^{-3}), d is the desorption efficiency, m_b the mass of compound (μg) on a non-exposed cartridge (a blank) and SR is the sampling rate of the compounds (m^3 min^{-1}).

2.2. Exposure chamber

For validation, sets of Radiello® diffusive samplers were placed in a dynamic chamber, which allowed pollutants concentration, temperature, humidity and wind velocity to be controlled. The exposure system is presented in Fig. 1. It consisted of a glass cylinder with a capacity of 35 L (length: 50 cm and diameter: 30 cm). The pollutants were generated from a dilution of high BTEX concentrations (10.6 ppm of benzene, 31.5 ppm of toluene, 5.1 ppm of ethylbenzene, 10.2 ppm of *m*/*p*-xylene and 6 ppm of *o*-xylene) contained in a cylinder. For the tests in the exposure chamber, three concentration levels have been tested. The medium value is taken as the limit value (LV), i.e. 5 μg m^{-3} for benzene. For the other compounds, the ratios encountered in ambient air have been considered. The values of the different concentrations tested in the exposure chamber are presented in Table 2. In order to neglect the BTEX masses retained on the Radiello® sampler compared to the ambient masses in the exposure chamber, the air zero flows are raised, about 14 L min^{-1}. To obtain the concentrations presented in Table 2, the dilution of BTEX cylinder was between 3000 and 16,000. Two bubblers supplied with air zero were used to regulate humidity in the exposure chamber at 50%. Wind velocity was controlled by three fans installed inside the chamber and was regulated at 0.5 m s^{-1}. The exposure chamber was placed in a thermostatic enclosure maintaining a constant temperature at 20 °C for the tests.

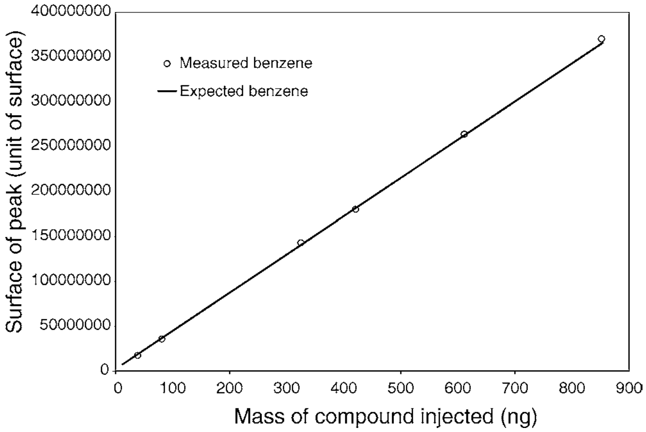

Fig. 2. Recovery rate of doped benzene on Radiello® cartridges.

The ambient conditions in the exposure chamber were continuously monitored and recovered by means of temperature, humidity and wind velocity multifunction probe (Testo). The BTEX concentrations were continuously measured at the exit of the chamber by a BTEX analyser (VOC 71M Environment SA). This analyser was beforehand frequently and calibrated from a cylinder having high concentration in BTEX. This cylinder was certified at the laboratory by using a reference GC-FID (VOC-AIR Chrompack system) calibrated with a diluted reference propane standard COFRAC. The answer of a FID detector is linked to the effective carbon number (ECN) in the molecule [19], and thus the response coefficient k_i of each compound i can be calculated from the response coefficient of propane, the ECN of propane and the compound i.

2.3. Analysis

The cartridges of Radiello® sampler were analysed with the Perkin Elmer automated thermal desorber ATD 400 associated with a gas chromatograph coupled with a flame ionisation detector (FID). Analytical conditions are given in Table 3. Before each analysis series, successive calibrations were carried out from doped cartridges. To do so, a standard solution of benzene, toluene, ethylbenzene and xylenes (BTEX) were prepared in methanol. Different dilutions of this solution were vaporised by a heated injector (250 °C) and adsorbed with a carrier gas from the vapour phase on Radiello® cartridges. Masses measured from these doped cartridges (values measured) are compared with those obtained

Table 3
Analytical conditions of ATD 400–GC MS

ATD 400	Autosystem GC
Cold trap: Carbopack B + Carbosieve III	Carrier gas: Helium (column flow: 1.25 mL min^{-1})
Desorption temperature: 290 °C	Column: CP-Sil 8 CB 50 m × 0.32 mm × 0.25 μm
Desorption time: 10 min	Column temperature program: 10 min at 35 °C; 5 °C min^{-1} to 140 °C; 15 °C min^{-1} to 250 °C; 3 min at 250 °C
Trap temperature: 10–290 °C	Detector: FID, 250 °C
Split flow: 10 mL min^{-1}	

Table 4
BTEX recovery rates (%) on Carbograph 4

Compound	Recovery rate (mean ± SD)
Benzene	101 ± 3
Toluene	99 ± 4
Ethylbenzene	98 ± 4
m/*p*-xylene	97 ± 3
o-xylene	97 ± 4

by directly injecting the same solutions into the chromatograph injector (values expected). For the two methods, the analysis was made with the same split flow, which is presented in Table 3. Results are shown for benzene in Fig. 2. The recovery is the ratio between values measured and values expected. In Fig. 2, it can be seen that a linear and quasi 100% recovery rate was obtained for this compound at these concentrations. Table 4 gathers the values of BTEX recovery rate. The results are close to 100% recovery rate; the techniques of doping are thus validated and the thermal desorption is thus considered nearly whole.

3. Results and discussion

3.1. Determination of the blank value and detection limits

To determine blank values, batches of unexposed samplers (seven cartridges) were analysed 1 day after conditioning and 28 days after, with storage at 4 °C. As there is no significant difference between the two storage durations, the mean blank values are used to be subtracted from the sampler mass in order to determine experimental sampling rates, for the exposed samplers.

The detection limits for a compound is defined as three times the standard deviation of blank values. The results of the detection limits obtained for BTEX Radiello® sampler from supplier's sampling rates are gathered in Table 5. The detection limits are relatively weak (0.03 $\mu g\,m^{-3}$ of benzene for 7 days exposure), which will allow precise analysis even in the range of background concentrations of BTEX. Indeed, its values represent only 1.5% of the weakest concentrations imposed in exposure chamber (2 $\mu g\,m^{-3}$ of benzene).

Table 5
Average blank values (ng) and deviation standard of BTEX Detection limits ($\mu g\,m^{-3}$) of the BTEX Radiello® sampler for 1 and 7 days sampling

Compound	Average blank value ± standard deviation	Detection limit for 1 day sampling	Detection limit for 7 days sampling
Benzene	5.2 ± 2.5	0.2	0.03
Toluene	2.8 ± 1.4	0.1	0.01
Ethylbenzene	1.7 ± 3.5	0.3	0.04
m/*p*-xylene	2.5 ± 2.2	0.2	0.02
o-xylene	1.6 ± 2.9	0.2	0.03

Table 6
Range of BTEX concentrations ($\mu g\,m^{-3}$) Comparison between experimental and supplier's (FSM) sampling rates (SR) ($cm^3\,min^{-1}$)

Compound	Range of BTEX concentrations	Experimental SR ± standard deviation	SR given by the constructor
Benzene	1.9–10.5	27.9 ± 2.3	27.8
Toluene	6.9–39.3	28.1 ± 1.8	30
Ethylbenzene	1.2–7.7	24.9 ± 2.4	25.7
m/*p*-xylene	2.6–15.9	22.0 ± 2.3	26.6
o-xylene	1.4–9.6	22.3 ± 2.2	24.6

3.2. Determination of BTEX sampling rates

To estimate the BTEX sampling rates, sets of six diffusive samplers were exposed under the standard conditions: relative humidity = 50% ± 3%, temperature = 20 °C ± 2 °C, wind velocity = 0.5 $m\,s^{-1}$ ± 0.1 $m\,s^{-1}$ for 7 days and 1 LV. One unexposed sampler is analysed before each analysis series to check the conditioning system and the analysis. Table 6 gives the sampling rates found in these tests in exposure chamber and those given by Foundation Salvatore Maugeri (FSM). On the one hand, for benzene, toluene and ethylbenzene, values found in exposure chamber are close to those given by the supplier. On the other hand, for xylenes, experimental values are weaker of roughly 10–20% compared to the values indicated by FSM.

3.3. Influence of exposure time and concentration levels on sampling rates

In these tests, 174 diffusion samplers were exposed under various combined conditions of time exposure and concentration levels to estimate the single effect of each factor and their interaction on the sampling rates. The following concentration levels and exposure times have been combined:

- exposure time: 1, 3, 7 and 14 days;
- concentration level: 0.4, 1 and 2 LV.

All the other parameters are fixed for the whole of the tests:

- relative humidity: 50% ± 3%;
- temperature: 20 °C ± 2 °C;
- wind speed: 0.5 $m\,s^{-1}$ ± 0.1 $m\,s^{-1}$.

For each combination (exposure time and concentration), two sets of six samplers and one blank were exposed in exposure chamber. The statistical analysis is performed on the variation of sampling rate (noted V_{SR}) with regard to the value found under the standard conditions. Figs. 3 and 4 present the response surface of benzene and toluene, respectively, obtained by fitting the experimental V_{SR} values according to the method proposed by Marquardt [20]. For benzene, sampling rate strongly decreases for long time exposure, particularly with high concentration: decrease of roughly 9% for 14 days at 2 $\mu g\,m^{-3}$ of benzene and of 31% for 14 days at 10 $\mu g\,m^{-3}$ of benzene. For toluene, the sampling rate decreases of roughly 14% for 14 days at 35 $\mu g\,m^{-3}$.

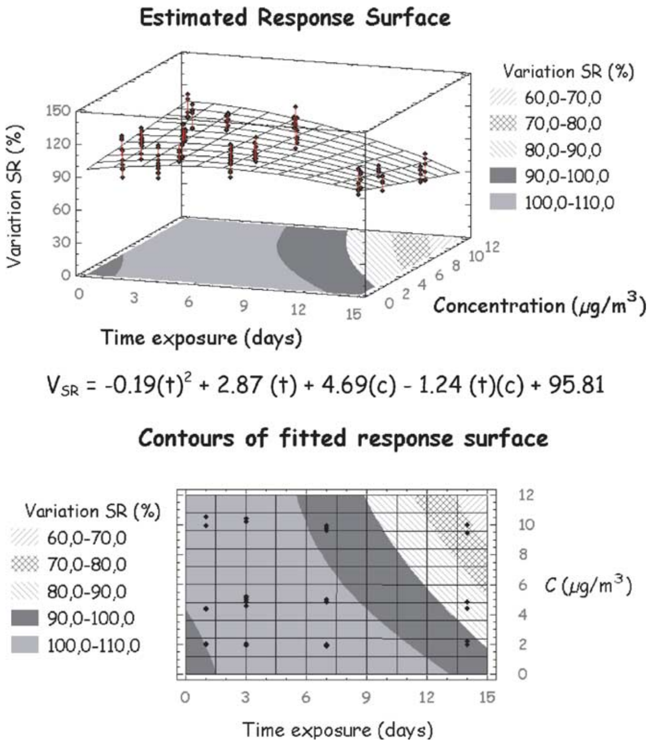

Fig. 3. Variation of sampling rate (noted SR) of benzene (%) vs. exposure time (days) and benzene concentration ($\mu g\, m^{-3}$) with the fitted response surface.

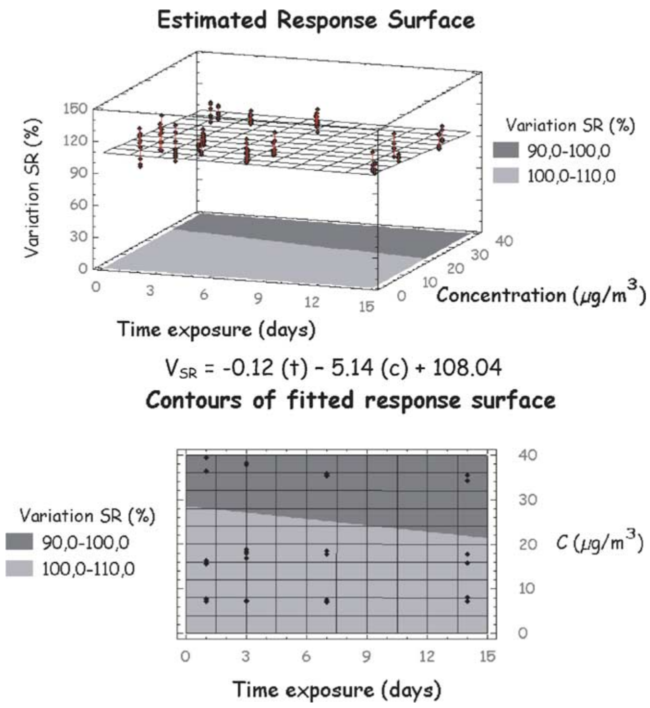

Fig. 4. Variation of sampling rate (noted SR) of toluene (%) vs. exposure time (days) and toluene concentration ($\mu g\, m^{-3}$) with the fitted response surface.

Otherwise, for ethylbenzene and xylenes, the deviations of sampling rates due to time exposure and concentration level remain weak (<5%). For all of the compounds, the increase of the concentration involves a weak decrease of the sampling rates.

Up to 7 days, the parameters weakly influence the sampling rates. Beyond (for exposure of 14 days), the passive sampler cannot be used anymore with a single value of sampling rate for benzene. In these conditions, the modelling obtained previously can be used to determine the sampling rate values adapted to various sites.

The decrease of the sampling rate of benzene seems to be related to the desorption of a part of molecules during the sampling. In previous works [21,22], similar studies on Perkin Elmer sampler with three different adsorbents (Tenax TA, Carbograph TD-1 and Chromosorb 106) showed that the sampling rate of benzene decreased exponentially with exposure dose. These decreases (from 10 to 15% for 14 days of exposure at 0.4 LV) are higher than the one of Radiello® sampler. This is explained by the fact that, the higher the ratio of sampling rate on sampling surface, the more quickly this phenomenon of sampling rate decrease will appear. However, Carbograph 4 has a high specific area and the Radiello® sampler a high sampling surface because of its geometry. The decrease of Radiello® sampling rate thus appears at higher doses than for Perkin Elmer sampler.

3.4. *Breakthrough volumes*

This phenomenon of sampling rate decrease could be due to a deficit of adsorption capacity of benzene on Carbograph 4. In order to check this assumption, the breakthrough volumes were determined. The breakthrough volume (V_B) can be defined as the volume of a gaseous sample that passes through an adsorbent bed before eluting a given fraction of the analyte from this adsorbent [23,24]. Different breakthrough volumes of a cartridge filled with 0.35 g of Carbograph 4 have been measured in accordance with temperature and concentration to determine the Langmuir adsorption parameters and the enthalpies of adsorption. Fig. 5 shows the experimental system setup used for the determination of V_B. Breakthrough volumes were measured by analysing continuously the BTEX concentration at the exit of the cartridge. The system was placed in a thermostatic enclosure, which allows maintaining the temperature constant during the determination of breakthrough volumes.

3.4.1. *Determination of Langmuir parameters*

The Langmuir model is based on several assumptions:

- maximum adsorption corresponds to the formation of a monolayer of molecules on a plane surface;
- the adsorption sites are equivalent and independent the ones of the others.

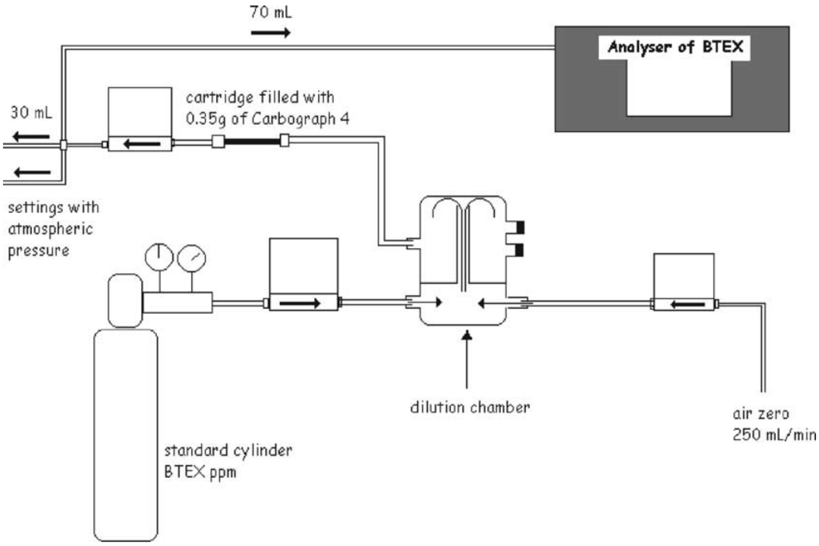

Fig. 5. Experimental setup for the determination of V_B.

It can be expressed as a linear equation relating V_B to the adsorption parameters b and m_{max} as:

$$\frac{1}{V_B} = \frac{1}{b \times m_{max}} + \frac{c}{m_{max}} \qquad (2)$$

where b ($m^3\,mg^{-1}$) is the distribution coefficient which is defined kinetically as the ratio of the adsorption rate constant k_{ads} on the desorption rate constant k_{des}, c ($mg\,m^{-3}$) is the adsorptive concentration in air, m_{max} ($mg\,g^{-1}$) is defined as the maximum mass that can be retained to form a monolayer on the adsorbent surface [24]. This parameter can be representative of the total number of adsorption available sites on the surface of the adsorbent [23].

From the regression line of the reverse of breakthrough volume according to concentration (Fig. 6), the Langmuir adsorption parameters can be deduced. These parameters are reported in Table 7. According to the m_{max}-calculated values, it seems that there is not a high number of adsorption sites suitable for benzene in comparison with the other compounds. This could explain the previously observed high decrease of the sampling rate of benzene for the 14 days exposure. Indeed, at high doses, for benzene, the available sites are more quickly filled because rare on surface.

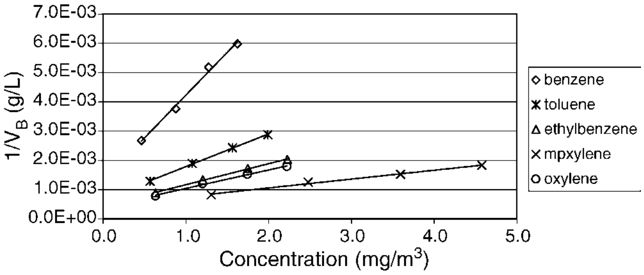

Fig. 6. Measured $1/V_B$ at 293 K vs. concentrations of BTEX.

Table 7
Langmuir adsorption parameters calculated from the experimentally measured V_B at 293 K

Compound	b ($m^3\,mg^{-1}$)	m_{max} ($mg\,g^{-1}$)	R^2
Benzene	2.2	0.3	0.994
Toluene	1.6	0.9	0.999
Ethylbenzene	1.4	1.4	0.998
m-xylene	1.2	1.7	0.996
p-xylene	1.2	1.7	0.996
o-xylene	1.5	1.7	0.997

In order to check this assumption, the ratios of masses sampled on m_{max} were determined. To do so, the masses sampled for a decrease of 10% were considered (corresponding to 14 days exposure at 2 $\mu g\,m^{-3}$ for benzene and 14 days exposure at 35 $\mu g\,m^{-3}$ for toluene). The results are presented in the form of percentages in Table 8. The results show that few sites are occupied when the sampling rates begin to decrease. Less than 1% of total number of available sites is involved in passive sampling in circumstances where the sampling rates remain constant.

In order to verify if the sampling rates decreases were related to the attraction forces weak in energy or on an affinity deficit, the adsorption enthalpies were determined.

Table 8
Masses and percentages of occupied sites for a decrease of 10% of sampling rates for benzene and toluene

	Compounds	
	Benzene	Toluene
m_d (ng)	122	1190
m_d ($mg\,g_{ads}{}^{-1}$)	3.49E−4	3.4E−3
m_{max} ($mg\,g_{ads}{}^{-1}$)	0.3	0.9
m_d (%age of m_{max})	0.1	0.4

3.4.2. Determination of adsorption enthalpies

The experimentally measured breakthrough volumes are also used to calculate the adsorption enthalpies values ($-\Delta H_{\text{ads}}$) of BTEX on Carbograph 4, b can be expressed as:

$$b = \frac{k_{\text{ads}}}{k_{\text{des}}} = \frac{N\theta}{N(1-\theta)}\frac{1}{c} \qquad (3)$$

where N is the total number of sites and $N\,(1-\theta)$ is the number of vacant sites.

The constant of the thermodynamic balance of adsorption K_{ads} can be expressed in the same way as:

$$K_{\text{ads}} = e^{-\Delta H_{\text{ads}}/RT} = \frac{N\theta}{N(1-\theta)P_{\text{A}}} = \frac{N\theta}{N(1-\theta)}\frac{M}{cRT} \qquad (4)$$

Then the Eq. (2) gives:

$$\frac{1}{V_{\text{B}}} = \frac{1}{((K_{\text{ads}}RT)/M)m_{\max}} + \frac{c}{m_{\max}} \qquad (5)$$

For very diluted solutions (concentration closed to 0), the second term of this equation becomes negligible in front of the first.

$$-\text{Ln}(V_{\text{B}}) = \text{Ln}(e^{\Delta H_{\text{ads}}/RT}) + \text{Ln}\left(\frac{M}{RTm_{\max}}\right) \qquad (6)$$

The second term of this equation is considered as a constant compared to the first term. The adsorption enthalpies can then be deduced from the Van't Hoff equation:

$$\text{Ln}(V_{\text{B}}) = \frac{-\Delta H_{\text{ads}}}{RT} + k \qquad (7)$$

To estimate the breakthrough volumes at various temperatures, the system was placed in a thermostatic enclosure. The adsorption of BTEX on Carbograph 4 was analysed at four different temperatures in the range 283–303 K. Fig. 7 shows V_{B} measured versus temperature. Using these measured V_{B}, the adsorption enthalpies ($-\Delta H_{\text{ads}}$) for each studied concentration are calculated by the Van't Hoff expression (Eq. (7)). This equation is reported to be limited to a temperature range of approximately 5–10 K due to the temperature dependence of $-\Delta H_{\text{ads}}$ [25]. A linear relationship, for the first three points, between the calculated $-\Delta H_{\text{ads}}$ and the concentration was observed for each compound and the standard adsorption enthalpy $-\Delta H^0_{\text{ads}}$ was determined by extrapolating the linear equation to zero. Table 9 gathers the results of adsorption standard enthalpies obtained from Fig. 7. According to the values of adsorption enthalpies, the benzene has the best adsorption capacity on Carbograph 4, the decrease of the sampling rate of benzene is thus not due to an affinity deficit between this compound and adsorbent.

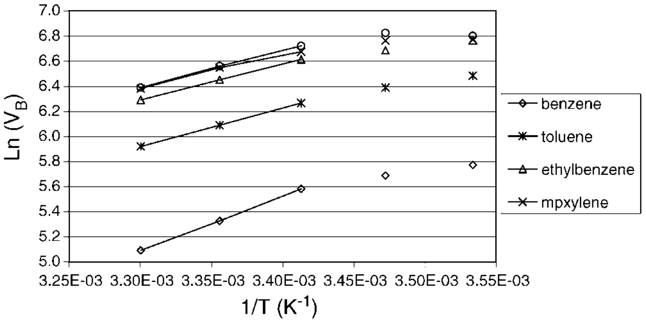

Fig. 7. Measured Ln (V_{B}) for BTEX vs. temperature.

Table 9
Calculated standard adsorption enthalpies of BTEX on Carbograph 4

Compound	$-\Delta H^0_{\text{ads}}$ (kJ mol^{-1})
Benzene	44.8
Toluene	24.4
Ethylbenzene	26.6
m/p-xylene	27.8
o-xylene	25.8

One possible explanation of the observations is that there is accumulation of pollutants on the adsorbent surface, until obtaining condensation points (micro-droplets) around the adsorption sites of pollutant. The compound molecules then pass into liquid phase [26]. A balance establishes between this liquid phase and the gas phase, with the vaporisation of a part of the condensed product quantity.

Moreover, benzene is the compound that vaporises most easily (it has the lowest boiling point). And so, one possible explanation for benzene is that, in spite of the fact that this compound had the best adsorption capacity on Carbograph 4, the possible formation of condensation points can appear more quickly where vaporisation is.

This aspect and the fact that Carbograph 4 had a low number of available sites for the retention of benzene could explain the decrease of the sampling rate of benzene observed for high doses of exposure.

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