

## Sorbent evaluation for diffusive monitoring of environmental contaminants

C. Prado<sup>a,\*</sup>, J.F. Periago<sup>a</sup>, A. Sepúlveda-Escrivano<sup>b</sup>

<sup>a</sup>*Instituto Nacional de Seguridad e Higiene en el Trabajo, E-30120 El Palmar, Murcia, Spain*

<sup>b</sup>*Departamento de Química Inorgánica, Universidad de Alicante, E-03080 Alicante, Spain*

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### Abstract

The adsorption characteristics of several adsorbate–adsorbent systems were analysed to obtain a better understanding of the parameters involved in the selection of adequate sorbents for diffusive sampling. Nitrogen adsorption was used to establish the porous texture of the adsorbent. Gas–solid chromatography and immersion calorimetry were used for studying the adsorption interactions of benzene and *n*-hexane with the adsorbent surfaces. In this way, specific retention volumes, isostatic heats of adsorption at low surface coverage and immersion heats for benzene and *n*-hexane were determined. The results obtained showed the important role of micropore volumes for a strong interaction of the adsorbents with the adsorbates. Chromosorb 106 and activated carbon were the best adsorbents for benzene and *n*-hexane when tube-type samplers and thermal desorption–gas chromatography were used.

### 1. Introduction

Diffusive monitoring has become one of the most important sampling techniques for measuring volatile organic compounds in industrial workplaces and indoor air atmospheres [1,2]. The time-weighted average concentration of the contaminant in the workplace environment can be calculated from the sampler collection time and the recovered mass on the sampler, if the uptake rate of the sampler is known. This uptake rate must be a constant, dependent only on the geometry of the sampler (cross-sectional area and diffusion length) and the contaminant diffusion coefficient in air (e.g., [2]). However, it has been reported that adsorption rates decrease

with exposure time when dealing with tube-type samplers for thermal desorption [3–5]. This occurs because of an underestimation of the contaminant collected (breakthrough or incomplete desorption), caused by an inadequate selection of the adsorbent, as effective adsorption would depend on the interactions that occur at the contaminant–adsorbent interface. Hence it is necessary to select the appropriate adsorbent for each particular contaminant.

The analysis will be carried out by means of thermal desorption and gas chromatography. Hence it must be taken into account that the sorption should be strong enough to ensure that the contaminant concentration at the gas–solid interface is zero, but not excessively strong in order to allow desorption under reasonable conditions of temperature and time.

Data on contaminant–adsorbent pairs useful

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\* Corresponding author.

for thermal desorption are sparse in the literature, and there have been few studies in which the parameters affecting good optimization for adsorbate–adsorbent systems were analysed [3,6–9].

The aim of this work was to evaluate the adsorbent–adsorbate interactions in order to have a better understanding of the parameters involved in the correct selection of an adequate sorbent for a given pollutant. Because of their potential toxicological risk, benzene and *n*-hexane were chosen as representative adsorbates of aliphatic and aromatic compounds, respectively.

## 2. Experimental

### 2.1. Adsorbents

The following adsorbents were used: Tenax-TA (SKC, Valley View, PA, USA), Tenax-GR (Alltech Associates, Deerfield, IL, USA), Chromosorb 106 and 102 (SKC), Porapak Q (Perkin-Elmer, Beaconsfield, UK), Spherocharb (Field Analytical, Surrey, UK) and an activated carbon. All of these were 60–80 mesh, except the active carbon, which was crushed and sieved to a particle size ranging from 0.35 to 0.84 mm.

Tenax-TA is a porous polymer based on 2,6-diphenyl-*p*-phenylene oxide and is used as both a column packing material and trapping adsorbent. Tenax-GR is the result of coprecipitation of graphitized carbon with Tenax-TA polymer. It contains 30% graphitized carbon. Chromosorb porous polymers are cross-linked resins of polyaromatic type; Chromosorb 102 type is slightly polar and 106 is non-polar. Porapak Q is an ethylvinylbenzene–divinylbenzene copolymer and is weakly polar. Spherocharb is a spherical carbon molecular sieve. The activated carbon used was a granular type obtained from olive stones by steam activation and kindly supplied by Dr. Rodríguez-Reinoso of Alicante University.

### 2.2. Surface characterization

The porous texture of the adsorbents was characterized by physical adsorption of nitrogen

at 77 K in an Autosorb-6 volumetric system (Quantachrome, Syosset, NY, USA). Samples were first degassed at 423 K and  $10^{-5}$  Torr for 4 h and then introduced into the adsorption system, where the volume adsorbed at each equilibrium pressure was recorded.

### 2.3. Measurements of specific retention volumes and isosteric heats of adsorption

Gas–solid chromatography was used to determine the specific retention volumes and the isosteric heats of adsorption for benzene and *n*-hexane (both from Merck, Darmstadt, Germany) on the different sorbents [10,11]. The adsorption measurements were carried out using the system shown in Fig. 1. The sorbent (0.2 g) was packed into a stainless-steel column (89 mm × 6.4 mm O.D.) that was placed between the injector and the flame ionization detector of a Perkin-Elmer Model 3920 B gas chromatograph. The adsorptive vapours were generated by an on-line dynamic atmosphere containing a known concentration of the pollutant, and were injected into the column by means of a 5-ml manual valve. The amounts injected were about 0.1 μg, and nitrogen at a flow-rate of 30 ml/min was used as the carrier, except for the active carbon and Spherocharb, where an amount of about 1 μg and a flow-rate of 70 ml/min were necessary to obtain a detectable peak. Retention measurements were made over the temperature

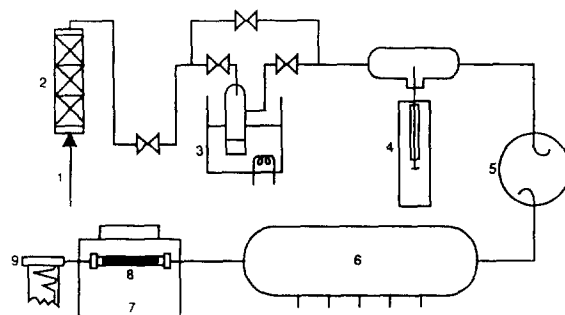


Fig. 1. Scheme of the system used to generate the controlled atmospheres and to obtain specific retention volumes: 1 = air intake; 2 = filter; 3 = humidifier; 4 = automatic syringe injector; 5 = mixing chamber; 6 = sampling chamber; 7 = gas chromatograph; 8 = packed sorbent tube; 9 = integrator.

range 348–583 K and a set of injections were made until the retention times were reproducible for consecutive injections.

The specific retention volumes,  $V_s$ , were calculated from the retention times measured, which were corrected for the retention time of air as a non-adsorbed gas.

Isosteric heats of adsorption ( $-\Delta H_i$ , kJ/mol) can be calculated from the plot of the logarithm of the measured retention volume against the reciprocal of the absolute temperature of the chromatographic column [12].

#### 2.4. Immersion calorimetry

The heats of immersion of the adsorbents in benzene and *n*-hexane were determined at 303 K with a conventional Tian–Calvet-type differential microcalorimeter (Model C 80D; Setaram, Caluire, France). The samples (about 0.1 g) were placed in a glass bulb with a brittle end and degassed at 423 K and  $10^{-5}$  Torr for 4 h; then, the bulb was sealed and introduced into the calorimeter cell containing 7 ml of the wetting liquid. Once thermal equilibrium had been achieved in the calorimeter block, the brittle end was broken and the liquid was allowed to enter the bulb, the heat flow evolution being monitored as a function of time. Thermal effects related to the breaking of the bulb and the evaporation of the liquid to fill the empty volume of the bulb with the vapour at the corresponding vapour pressure were calibrated by using empty bulbs of different volumes.

### 3. Results and discussion

Fig. 2 shows the nitrogen adsorption isotherms at 77 K for the seven adsorbents studied in order to establish the role of the porous texture in the contaminant–sorbent surface interaction. Table 1 gives the total micropore volumes (calculated by applying the Dubinin–Radushkevich equation to the adsorption data) and the BET surface areas [13].

Nitrogen adsorption isotherms for active car-

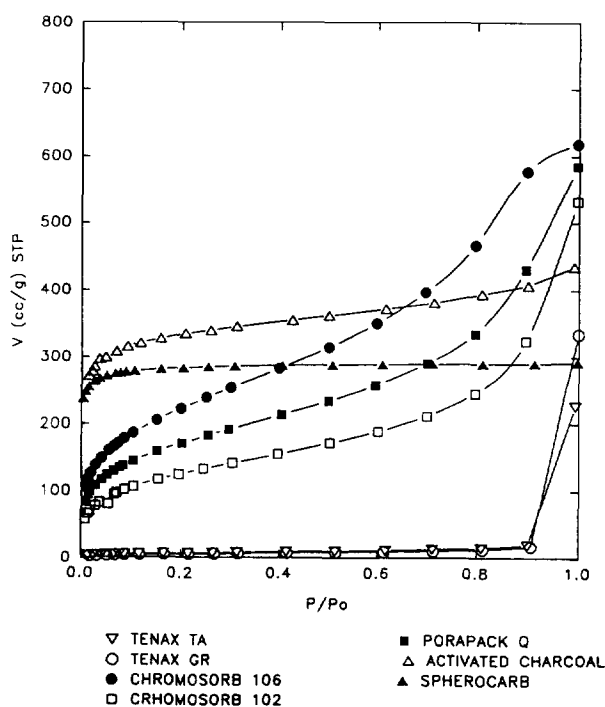


Fig. 2. Nitrogen adsorption isotherms at 77 K on the different adsorbents.

bon and Spherocharb are basically of type I, characteristic of microporous carbon. However, there are differences between them, as the isotherm for Spherocharb can be considered almost exclusively microporous with a very narrow microporosity, whereas active carbon presents a wider range of micropores, as can be deduced from the more open knee and a steeper linear branch.

Both Chromosorb 106 and 102 and Porapak Q

Table 1  
Physical properties of the adsorbents

Adsorbent	$S_{\text{BET}}(\text{N}_2)$ ( $\text{m}^2/\text{g}$ )	$V_{\text{micro}}$ (ml/g)	$T_{\text{max}}$ ( $^{\circ}\text{C}$ )
Tenax-TA	26	6.74	375
Tenax-GR	21	5.69	390
Chromosorb 106	800	197.73	250
Chromosorb 102	454	113.20	250
Porapak Q	615	153.84	250
Activated carbon	1250	341.24	400
Spherocharb	1000	288.92	225

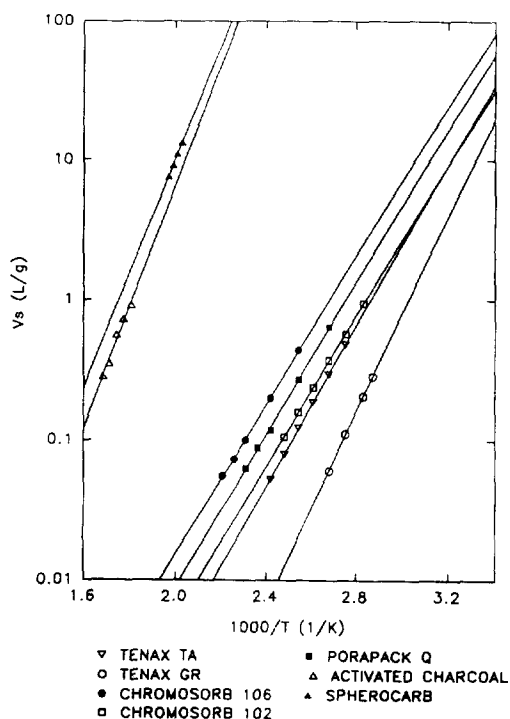


Fig. 3. Plots of  $\log V_s$  against  $1/T$  for benzene on different adsorbents.

show a very developed porosity in all ranges of pore sizes with a considerable mesoporosity ( $2 \text{ nm} < \phi < 50 \text{ nm}$ ). Tenax-TA and Tenax-GR

show very little microporosity, as can be deduced from the amounts adsorbed, being 90.5% of its total pore volume in the macropore region [14].

By comparison of the nitrogen adsorption isotherms and the specific surface areas and micropore volumes in Table 1, it can be seen that the set of adsorbents selected for this study have a very large range of porosity and pore size distribution.

The chromatograms obtained for the adsorbents with benzene and *n*-hexane were used to determine their retention times. These values (corrected for the gas hold-up time) were used to calculate the specific retention volumes. It should also be noted that the peaks obtained were symmetrical and independent of sample size and carrier flow-rate, which indicated that the measurements were carried out in the linear region of the isotherm [10,11].

The logarithms of the derived specific retention volumes were then plotted against the reciprocal of the absolute column temperature. Representative plots for benzene are shown in Fig. 3. Straight lines were obtained over the temperature range studied. From these plots the specific retention volumes at 293 K [ $V_s(293 \text{ K})$ , l/g], were obtained by extrapolation, and are given in Table 2. These  $V_s(293 \text{ K})$  values were reproducible (the observed precision was 4.5%,

Table 2  
Benzene and *n*-hexane adsorption parameters on different adsorbents

Adsorbate	Adsorbent	$V_s(293 \text{ K})$ (l/g)	$-\Delta H_i$ (kJ/mol)	$Q_i$ (J/g)	$Q_i$ (J/ml <sub>micro</sub> )
Benzene	Tenax-TA	36.9	55.0	34	5.09
	Tenax-GR	37.8	62.2	27	4.67
	Chromosorb 106	88.9	51.0	70	0.35
	Chromosorb 102	34.1	51.5	44	0.39
	Porapak Q	65.9	53.0	57	0.37
	Activated carbon	$9.2 \cdot 10^6$	83.3	154	0.45
<i>n</i> -Hexane	Spherocarb	$5.9 \cdot 10^6$	79.0	142	0.49
	Tenax-TA	19.1	56.9	12	1.78
	Tenax-GR	21.7	66.7	10	1.75
	Chromosorb 106	110.3	53.4	62	0.31
	Chromosorb 102	43.2	55.1	38	0.34
	Porapak Q	88.9	55.5	47	0.31
	Activated carbon	$1.4 \cdot 10^8$	93.6	142	0.48
	Spherocarb	$3.0 \cdot 10^7$	83.8	138	0.42

$n = 5$ ), and were used as a measure of the intensity of the adsorption by the adsorbent at the temperature of interest, at which tube-type diffusive air samplers will be used in practice.

The amount of adsorbate injected was the smallest detectable and the measurements were in the Henry's law region. Hence the isosteric heat of adsorption at zero coverage could be calculated from the slope ( $\Delta H_i/2.303R$ ) of the plots mentioned above. These values are given in Table 2, where heats of immersion from calorimetric measurements are also included.

Table 2 shows that Tenax-TA and -GR and Chromosorb 102 have low specific retention volumes at 293 K, which means a weak adsorption character. The largest values of  $V_s$  (293 K) for benzene and *n*-hexane correspond to Spherocharb and active carbon, indicating that both contaminants are strongly retained by these sorbents. The plots in Fig. 4 show that maximum interaction occurs readily in micropores [15,16], and that porosity is the main parameter affecting the adsorption behaviour of the systems studied. This was confirmed by immersion calorimetry as shown in Fig. 5.

Immersion calorimetry measures the formation of a liquid–solid interface and heats of adsorption will mainly depend on the chemical nature of the surface, chemical nature of the immersion liquid, solid porosity and shape and size of the molecules [17–19]. As indicated by Fig. 5, interaction of the adsorbate with the solid surface increases with increase in microporosity of the sorbents. This is in agreement to Bansal et al. [18], who found that the heat of immersion was a function of micropore volume and pore-size distribution for a series of active carbons. Hence higher values were obtained for Spherocharb and active carbon, which have the greater micropore volume and the narrowest micropore size distribution. In order to see if there is another factor affecting the interaction with the sorbent surface,  $Q_i$  data were normalized with micropore volumes. As can be observed, the values calculated for Tenax-TA and -GR are high, which may be due to a specific interaction of the molecules with these adsorbents.

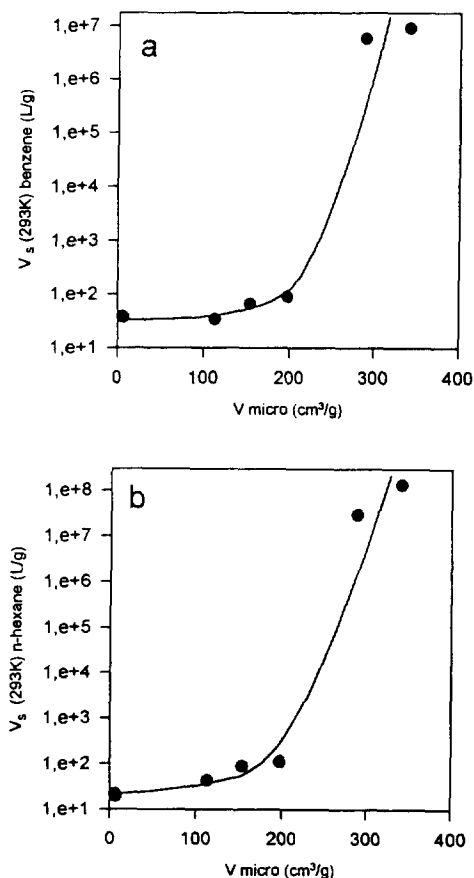


Fig. 4. Variation of the specific retention volumes at 293 K with micropore volumes of the adsorbents (a) benzene and (b) *n*-hexane.

The values of  $-\Delta H_i$  indicate again higher energy sites on Spherocharb and active carbon. As is known, there is an enhancement of the energy of adsorption when the width of the pore is slightly larger than the diameter of the adsorbed molecules. This means that the micropore width of these sorbents is in the range of the diameters of benzene and *n*-hexane molecules. The heats of adsorption for both Tenax-TA and -GR are also higher than those for Chromosorb and Porapak Q, according to the immersion results mentioned above, thus pointing to a specific interaction.

Table 2 also shows that the  $-\Delta H_i$  and  $Q_i$  values are higher for *n*-hexane than for benzene, indicating that a linear conformation of the

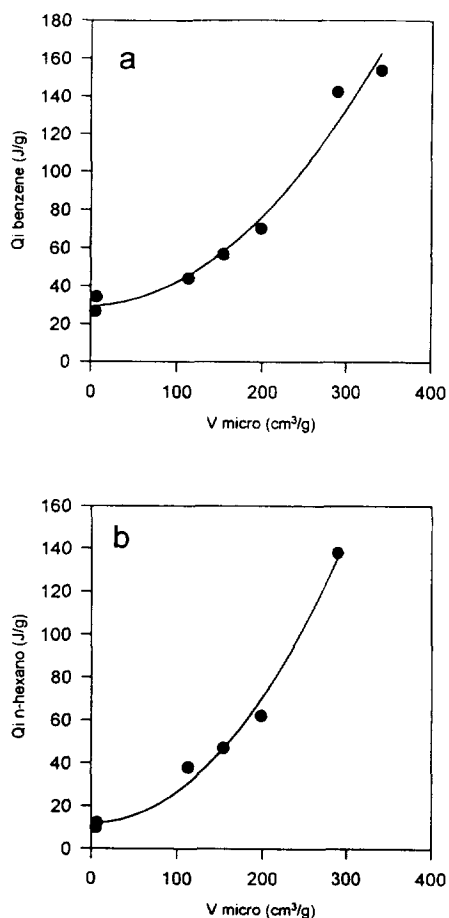


Fig. 5. Variation of the immersion heats ( $Q_i$ , J/g) with micropore volumes of the adsorbents (a) benzene and (b) *n*-hexane.

molecule will allow the greatest interaction between the surface and adsorbate [15].

From the results obtained, both Sphero carb

and the active carbon fulfil the first condition for a sorbent to be used in diffusive sampling, i.e., both of them show strong interaction with benzene and *n*-hexane. However, they must also be able of desorbing the contaminants with reasonably temperature and time conditions. Table 3 shows the specific retention volumes and the desorption time, calculated from  $\log V_s$  vs.  $1/T$  plots, at the maximum operating temperature, and for a usual carrier gas desorption flow-rate of 30 ml/min. The results for Sphero carb (73 min for benzene and 140 min for *n*-hexane) indicate that Sphero carb was unsuitable at the low operating temperature used, which is the maximum allowed for this adsorbent. However, it could be appropriate for trapping very volatile compounds, for which high desorption temperatures are not necessary.

The active carbon used here appears to be an adequate sorbent for benzene and *n*-hexane when desorption can be carried out at temperatures higher than 300°C. It must be noted that active carbons can currently be prepared with the porosity and surface chemistry adequate for each particular application [20]. Chromosorb 106 can also be used as a sorbent for both contaminants. In fact, constant uptake rates for benzene on this sorbent have been reported [21].

#### 4. Conclusions

The total micropore volume is the main parameter affecting the adsorbent–adsorbate interaction in the systems studied. Tenax-TA, Tenax-GR and Chromosorb 102 show a weak adsorp-

Table 3

Desorption conditions for benzene and *n*-hexane on Chromosorb 106, Sphero carb and active carbon

Adsorbent	$T_{\text{max}}$ (°C)	Benzene		<i>n</i> -Hexane	
		$V_s(T_{\text{max}})$ (l/g)	Desorption time (min)	$V_s(T_{\text{max}})$ (l/g)	Desorption time (min)
Chromosorb 106	250	0.009	0.06	0.007	0.05
Activated carbon	300	0.511	3.40	0.802	5.35
Sphero carb	225	10.970	73.00	20.974	140.00

tion character for benzene and *n*-hexane. Chromosorb 106 and the active carbon used are potential sorbents for tube-type diffusive sampling of benzene and *n*-hexane. Complete thermal desorption of benzene and *n*-hexane from Spherosorb is hindered by its low maximum operating temperature.

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