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PRECONCENTRATION OF VOLATILE ORGANOSULPHUR COMPOUNDS FROM THE ATMOSPHERE ON SELECTED POROUS POLYMERS

ANDRZEJ PRZYJAZNY

Institute of Inorganic Chemistry and Technology, Technical University of Gdańsk, 11/12 Majakowski St., 80-952 Gdańsk (Poland)

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SUMMARY

The breakthrough volumes for vapours of eleven organosulphur compounds (thiols, sulphides, disulphides, thiophenes) on selected porous polymers (Chromosorb 102, XAD-2, XAD-4, XAD-7, Tenax GC) have been determined using an indirect method based on extrapolation of the $\log V_B = f(1/T)$ dependence to 20°C. The sorption capacity was determined by the surface areas, XAD-4 being the best porous polymer for preconcentration of the investigated compounds from the atmosphere. Fairly good linear correlations have been found between the logarithm of the breakthrough volume and the boiling point, the carbon number and the logarithm of the saturated vapour pressure. These relationships may be useful for estimating breakthrough volumes of other compounds of similar structure.

INTRODUCTION

Volatile organic sulphur compounds constitute a significant source of both biogenic and anthropogenic air pollution. The natural sources are primarily of biological origin. Dimethyl sulphide (DMS) is believed to be the main sulphur carrier in the global sulphur cycle¹. Challenger² found that DMS is produced by some species of marine algae. The main anthropogenic sources comprise petrochemistry, agrochemistry, wood-pulp treatment and pharmaceutical industry.

The main organic sulphur derivatives, thiols, sulphides, disulphides and thiophenes, are toxic^{3,4}. However, only a few toxicological studies have so far been carried out. The threshold limit values for methanethiol, ethanethiol, dimethyl sulphide, dimethyl disulphide and thiophene are 0.5, 0.4, 20, 5 and 6 ppm, respectively, while the maximum immission concentrations for long-term exposure are of the order of 0.01–0.06 ppm⁵.

The development of procedures for the determination of volatile organosulphur compounds is essential for atmospheric pollution control. However, direct analysis of these compounds is usually impossible due to their low concentration, generally below the ppm level. For this reason, a preconcentration step must be included in the analytical procedure. Among the procedures employed for this pur-

pose, trapping of sulphur compounds in organic solvents chilled by means of solid carbon dioxide should be mentioned^{6,7}. Final determination is carried out by injection of the solvent into a gas chromatograph. Thiols and sulphides can also be concentrated by chemical reactions with various compounds, primarily mercury salts, followed by their liberation through acidification and gas chromatographic (GC) determination⁷⁻⁹.

However, the most frequently used preconcentration method involves sorption on solid sorbents, generally activated charcoal, silica gel, alumina, molecular sieves, graphitized carbon black or porous polymers. The last group has found particularly broad application due to their high affinity for organic compounds, minimum adsorption of water and other inorganic compounds and chemical inertness. In addition, thermal desorption of the trapped components is easier in the case of porous polymers than for other solid sorbents.

Although numerous investigations of sorption of organic compounds on solid sorbents have been carried out, few studies have been devoted to organic sulphur compounds. Amongst those, the trapping of methanethiol, dimethyl sulphide and dimethyl disulphide on silica gel at -78.5°C , followed by thermal desorption at 125°C and 0.2 mmHg should be mentioned¹⁰. The preconcentration of thiols, disulphides and isothiocyanates on Porapak Q and Tenax GC has been reported by Cole¹¹. Steudler and Kijowski¹² collected reduced sulphur gases, COS, H_2S , MeSH, CS_2 , Me_2S and Me_2S_2 , in a trap packed with molecular sieve 5 A and Tenax GC and determined them by GC.

An essential step in the selection of a suitable sorbent for preconcentration of organic compounds is the determination of its adsorption capacity. A measure of the adsorption capacity of a sorbent layer is the breakthrough volume, V_B , which can be defined as the volume of gas passed through a sorbent bed before the investigated compound begins to be eluted from the container. Passage of larger volumes of sample results in a loss of compound and a decrease in recovery. The breakthrough volumes of 90 organic vapours, including methanethiol, dimethyl sulphide and disulphide and thiophene, have been determined on Tenax GC¹³. The authors attempted to correlate the logarithm of the breakthrough volume with the boiling point, its reciprocal, the molecular weight and the carbon number in order to estimate breakthrough volumes of other compounds having similar structure. However, the study was limited to one sorbent and comprised only four sulphur compounds. More systematic work involving the determination of the breakthrough volumes of eight mercaptans, two sulphides and one disulphide on nine porous polymers and on Carbosphere was carried out by Torres *et al.*¹⁴. Although providing many valuable data, the paper does not list breakthrough volumes exceeding $15\text{ dm}^3/\text{g}$ of sorbent and the V_B values were determined for concentration levels considerably exceeding those encountered in practice, 240–1380 ppm (v/v), whereas it is known that breakthrough volumes decrease sharply with increasing vapour concentration¹⁵. Therefore, the published data do not provide an insight into the true suitability of the investigated sorbents for preconcentration of organosulphur compounds at low concentrations.

The purpose of the present work was to determine breakthrough volumes for a number of sulphur compounds from four groups, thiols, sulphides, disulphides and thiophenes, on porous polymers chosen to provide a variety of monomer compositions and surface areas. Furthermore, an attempt was undertaken to correlate the

experimental V_B values with some fundamental physicochemical parameters of organosulphur compounds in order to predict the affinity of any organic solute for sorbents using only these parameters of the analyte. The prediction is useful as a guide for estimating the ratio of sorbent to sample size required for the preconcentration of organic compounds from the atmosphere.

EXPERIMENTAL

Apparatus

A Carlo Erba Model Fractovap 2200 gas chromatograph equipped with a flame ionization detector was used for the determination of breakthrough curves. Glass sorption tubes (50×4 mm) packed with the investigated sorbents (0.9–1 g, 0.23 g in the case of Tenax GC) were installed in place of conventional GC columns. Argon at $60 \text{ cm}^3/\text{min}$ was used as the carrier gas and for generation of standard gaseous mixtures of the organosulphur compounds studied. The apparatus for the generation of standard gaseous mixtures by the permeation method was connected to the gas chromatograph through a sampling valve. A schematic diagram of the entire experimental set-up for the generation of model mixtures and the determination of breakthrough curves is shown in Fig. 1.

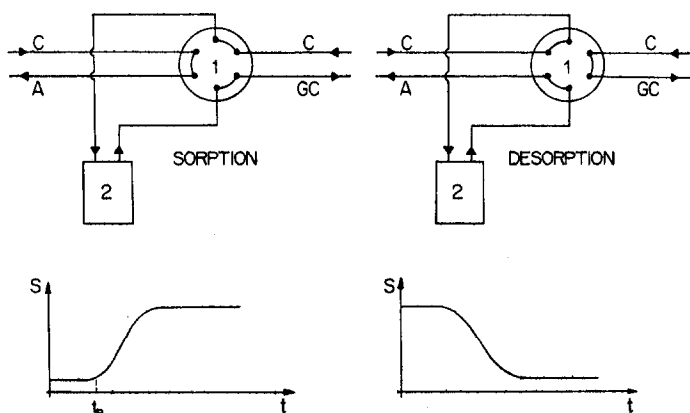


Fig. 1. Schematic diagram of the apparatus for the determination of breakthrough volumes, and the respective curves. 1 = Six-port sampling valve; 2 = chamber with permeation vessel; C = carrier gas; A = atmosphere; GC = sorbent bed placed in a GC thermostat; S = GC detector signal; t = time; t_B = breakthrough time.

An essential element of the apparatus is a glass chamber with a permeation vessel (Fig. 2) through which argon is passed. The permeation vessel of my own design is characterized by a strictly defined permeation area (PTFE membrane). The diffusion rate through the membrane can be varied by changing the temperature of the vessel and/or the membrane thickness. It is very easy to change the membrane. The chamber was placed in a thermostat and maintained at constant temperature. The permeation rate, R , was determined gravimetrically. The concentrations of compounds in a mixture leaving the chamber were calculated from

$$c = RK/F \quad (1)$$

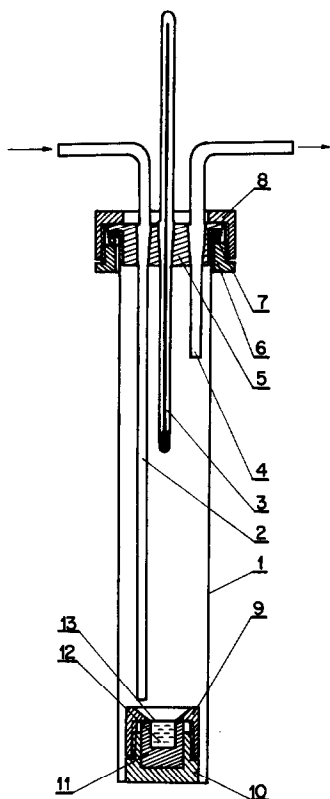


Fig. 2. Chamber with a permeation vessel for the generation of gaseous mixtures of sulphur compounds. 1 = Glass cylinder with flange; 2 = carrier gas inlet; 3 = thermometer; 4 = outlet tube; 5 = plexiglass head; 6 = tightening ring; 7 = O-ring with washer; 8 = cover; 9 = aluminium nut; 10 = permeation vessel body; 11 = PTFE insert; 12 = investigated sulphur compound; 13 = PTFE membrane.

where c is the concentration in ppm (v/v), R is the permeation rate in ng/min, F is the argon flow-rate in cm^3/min and K is the reciprocal of the vapour density in nl/ng

$$K = \frac{22.4}{M} \cdot \frac{T}{273} \cdot \frac{760}{p} \quad (2)$$

where 22.4 is the molar volume of gas at standard temperature and pressure, M is the molecular weight of the compound, T the temperature in $^{\circ}\text{K}$ and p the pressure in Torr.

Materials

The sorbents used in the preconcentration study were Chromosorb 102 (Johns-Manville, Denver, CO, U.S.A.), XAD-2, XAD-4 and XAD-7 (Rohm & Haas, Philadelphia, PA, U.S.A.) and Tenax GC (Enka, The Netherlands). They were cleaned by successive 8-h extractions with methanol, acetonitrile and diethyl ether in a Soxhlet extractor followed by heating for 2 h at 200 or 150 $^{\circ}\text{C}$ (XAD-7) in a stream of argon.

All organic sulphur compounds used to prepare the standard gaseous mixtures were of analytical reagent grade (E. Merck, F.R.G.).

Procedure

The determination of breakthrough volumes involves a number of steps, each corresponding to a different path in the apparatus taken by the generated model mixture. Initially, pure argon carrier gas was passed through a sorbent tube installed in the thermostat of the gas chromatograph (sampling valve in Desorption position, Fig. 1) until a stable baseline was achieved on the chart of the recorder connected with the detector placed at the column outlet. At the same time, a separate stream of pure argon was passed through the permeation chamber (Fig. 2). The flow-rates of both gas streams should be identical, $F = 60 \text{ cm}^3/\text{min}$. Subsequently, the sampling valve was switched to the sorption position, which initiates continuous passage of a model mixture through the sorbent bed (Fig. 1). Initially, the compound is completely retained by the sorbent and the position of the baseline on the recorder chart remains unchanged. After a certain time, depending on the type and amount of sorbent, the character and concentration of sorbate, flow-rate of the mixture, geometry and temperature of the sorbent bed, a so-called breakthrough of the bed occurs and the concentration of the sorbate in the outlet mixture begins to increase from zero to the value corresponding to the inlet mixture. The time dependence of the mixture composition at the column outlet observed as the detector signal on the recorder chart is called the breakthrough curve. A tangent to this curve at the inflection point intercepts the abscissa at the breakthrough time, t_B , and the product of t_B and the flow-rate yields the breakthrough volume. After determining the breakthrough curve, the sampling valve was switched back to the initial position and the process of desorption occurred. This process can be considerably accelerated by raising the bed temperature, which is easily accomplished since the sorption tube is installed in the GC oven.

Since some of the investigated compounds were strongly retained on the sorbents employed, the breakthrough volumes were determined by extrapolation of a plot of $\log V_B$ against reciprocal absolute temperature to 20°C , the approximate temperature at which the columns would operate if they were used for sampling. The measurements covered at least a 20°C range of temperature.

RESULTS AND DISCUSSION

This research was carried out to evaluate the effectiveness of several commercially available porous polymeric sorbents. The adsorbents chosen provided a variety of monomer compositions and surface areas. Some properties of the porous polymers are listed in Table I.

The low concentrations and high affinities of some sulphur compounds for porous polymers made it impossible directly to determine the breakthrough parameters, since the breakthrough curve would be undistinguishable from the baseline in these cases. For this reason, the plot of $\log V_B$ against reciprocal absolute temperature was extrapolated to 20°C . An example of this dependence for methanethiol is shown in Fig. 3. This extrapolation may not be strictly valid. Tanaka¹⁶ has observed some deviations from linearity for selected chlorinated hydrocarbons on Tenax GC. How-

TABLE I
PROPERTIES OF POROUS POLYMERS USED

DPPPO = 2,6-Diphenyl-*p*-phenylene oxide; STY-DVB = styrene-divinylbenzene; MTC = methacrylate polymer.

Sorbent	Specific surface area, S (m^2/g)	Pore diameter (nm)	Temperature limit ($^{\circ}C$)	Chemical composition
Tenax GC	19	144	375	DPPPO
Chromosorb 102	300-400	8.5	250	STY-DVB
XAD-2	300	9	200-250	STY-DVB
XAD-4	849	5	200-250	STY-DVB
XAD-7	450	9	150	MTC

ever, only slight deviations were observed in the present study, as indicated by the high correlation coefficients, r , ranging from 0.987 to 0.999. These high r values show that the efficiency of the sorbent column depends only to a small extent on the temperature and that only adsorption, rather than both partitioning and adsorption, was occurring. The measurements covered a $20^{\circ}C$ range in temperature in $5^{\circ}C$ intervals, e.g., at 30 – $50^{\circ}C$ for Tenax GC and the most volatile compounds and at 100 – $120^{\circ}C$

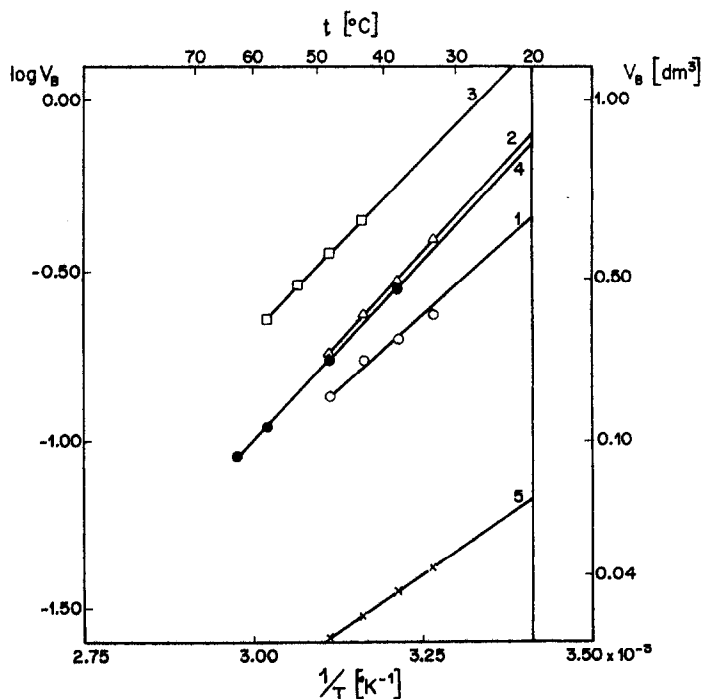


Fig. 3. Temperature dependence of the breakthrough volume of methanethiol on various sorbents: 1 (○) = XAD-2; 2 (△) = Chromosorb 102; 3 (□) = XAD-4; 4 (●) = XAD-7; 5 (×) = Tenax GC. Breakthrough volumes are given for the amount of sorbents used in the investigations.

for XAD-4 and the least volatile compounds. In the first case, the V_B values were also determined directly at 20°C and the agreement between the extrapolated values and those determined directly was good, the difference not exceeding 5%.

The values of the breakthrough volumes (dm^3/g) extrapolated to 20°C for eleven organosulphur compounds are listed in Table II. Each result is the average of three consecutive determinations. As expected, the V_B values increase with the molecular weights and boiling points of the studied compounds. The exceptions, *e.g.*, ethanethiol and *n*-propanethiol on XAD-4 or diethyl sulphide and diisopropyl sulphide on Chromosorb 102, can be attributed to the errors resulting from the indirect method of determination of V_B (extrapolation over different temperature ranges). Similar peculiarities can also be found in the paper of Torres *et al.*¹⁴, *e.g.*, the extremely low breakthrough volumes for dimethyl disulphide. Compounds of similar boiling points have similar V_B values, *e.g.*, dimethyl sulphide (b.p. 37.3°C) and ethanethiol (b.p. 35°C). This indicates that non-specific interactions (Van der Waals forces) play the main rôle in the adsorption process. However, when comparing aromatic and aliphatic compounds with similar boiling points, *e.g.*, dimethyl disulphide (b.p. 109.7°C) and 2-methylthiophene (b.p. 112.6°C), it is found that aromatic compounds have higher affinity for the sorbents than do aliphatic compounds. Finally, sulphides are more strongly retained on the investigated sorbents than are disulphides, *e.g.*, diethyl disulphide (b.p. 154°C) and di-*n*-propyl sulphide (b.p. 142.4°C).

From the data in Table II it is seen that XAD-4 has the best overall sample capacity for the organosulphur compounds, and Tenax GC has the worst. The remaining sorbents are roughly equivalent for preconcentration purposes. Taking into account the data in Table I, it can be concluded that the sorption capacity is determined by the surface area, the adsorbent with the greatest area having the highest capacity. For samples consisting of only high-boiling components, Tenax GC may be the adsorbent of choice, because of its thermal stability and relatively low breakthrough volumes. These characteristics would allow the sample components to be desorbed more rapidly from Tenax than from other sorbents. For samples containing

TABLE II

BREAKTHROUGH VOLUMES (dm^3/g) ON SOME POROUS POLYMERS

Values were extrapolated to 20°C from the linear regression curve: $\log V_B = b/T + a$, the parameters b and a being calculated on the basis of V_B values determined at four temperatures. $F = 60 \text{ cm}^3/\text{min}$.

Compound	Concentration (ppm, v/v)	Chromosorb 102	XAD-2	XAD-4	XAD-7	Tenax GC
Dimethyl sulphide	0.70	4.7	2.9	10.1	4.4	0.97
Diethyl sulphide	0.87	173	52	8600	304	9.9
Di- <i>n</i> -propyl sulphide	1.0	3140	50 000	> 100 000	36 900	674
Diisopropyl sulphide	0.22	139	26 800	15 900	19 000	15.1
Dimethyl disulphide	1.6	76	35	51	84	17.9
Diethyl disulphide	6.6	1110	290	761	150	158
Thiophene	11.5	35	28	622	332	26
2-Methylthiophene	9.0	71	79	1530	404	27
Methanethiol	7.9	0.79	0.45	1.3	0.75	0.29
Ethanethiol	7.3	4.8	2.7	25	3.6	0.97
<i>n</i> -Propanethiol	13.5	4.8	3.7	19	6.1	1.6

highly volatile compounds, XAD-4 should be employed for preconcentration purposes. However, in the case of methanethiol and dimethyl sulphide the obtained enrichment factor may still be insufficient. Therefore, it was decided to investigate the sorption of MeSH and Me₂S on the carbon molecular sieve Carbosphere (Alltech). The breakthrough volumes determined by the described method were *ca.* 3000 and 2830 dm³/g for methanethiol and dimethyl sulphide, respectively. Hence, the adsorption of both compounds on Carbosphere is very effective and this sorbent can be used for preconcentration of MeSH and Me₂S from atmospheres containing extremely low levels of these contaminants. However, thermal desorption from Carbosphere is very difficult due to the strong retention of sulphur derivatives and an alternative method, such as liquid extraction, is required in this case.

An attempt was undertaken to correlate the values of breakthrough volume with such parameters as the boiling point (b.p.), reciprocal of the boiling point (1/b.p.), molecular weight (MW), carbon number (C_n) and saturated vapour pressure, *p*⁰, of the investigated compounds. The results are shown in Table III. It follows from the correlation coefficients, *r*, listed that the best linear correlation for XAD-type resins is that between the logarithm of *V*_B and the carbon number, whereas for Chromosorb 102 and Tenax GC the best correlations are obtained between log *V*_B and the boiling point or log *p*⁰. Typical plot of log *V*_B vs. log *p*⁰ for Chromosorb 102 is shown in Fig. 4. These relationships can be used to predict the capacity of sorbents for any organic compound using only its fundamental physicochemical parameters. The prediction is useful as a guide for estimating the appropriate sample size in the

TABLE III

PARAMETERS OF VARIOUS REGRESSION CURVES, $\log V_B = a + bX$ FOR THE INVESTIGATED SORBENTS

Parameters were calculated for the eleven solutes, except on XAD-4, where *n* = 10 (without *n*-Pr₂S). Boiling points are expressed in °K.

Regression curve		Sorbent				
Form	Parameters	Chromosorb 102	XAD-2	XAD-4	XAD-7	Tenax GC
$\log V_B = a + b \cdot \text{b.p.}$	Intercept, <i>a</i>	-6.33	-8.44	-5.84	-7.53	-6.33
	Slope, <i>b</i>	0.022	0.028	0.023	0.026	0.020
	Correlation coefficient, <i>r</i>	0.948	0.832	0.769	0.826	0.938
$\log V_B = a + b \cdot 1/\text{b.p.}$	<i>a</i>	9.03	11.24	10.24	11.10	7.77
	<i>b</i>	-2615	-3364	-2792	-3215	-2403
	<i>r</i>	0.931	0.816	0.795	0.832	0.922
$\log V_B = a + b \cdot \text{MW}$	<i>a</i>	-1.98	-3.37	-1.65	-2.64	-2.26
	<i>b</i>	0.041	0.058	0.046	0.053	0.037
	<i>r</i>	0.936	0.901	0.818	0.876	0.906
$\log V_B = a + b \cdot C_n$	<i>a</i>	-0.145	-1.27	-0.369	-0.904	-0.654
	<i>b</i>	0.506	0.853	0.793	0.830	0.465
	<i>r</i>	0.784	0.902	0.922	0.935	0.778
$\log V_B = a + b \cdot \log p^0$	<i>a</i>	0.194	-0.151	0.877	0.281	-0.250
	<i>b</i>	-1.235	-1.620	-1.277	-1.493	-1.160
	<i>r</i>	0.951	0.886	0.822	0.836	0.940

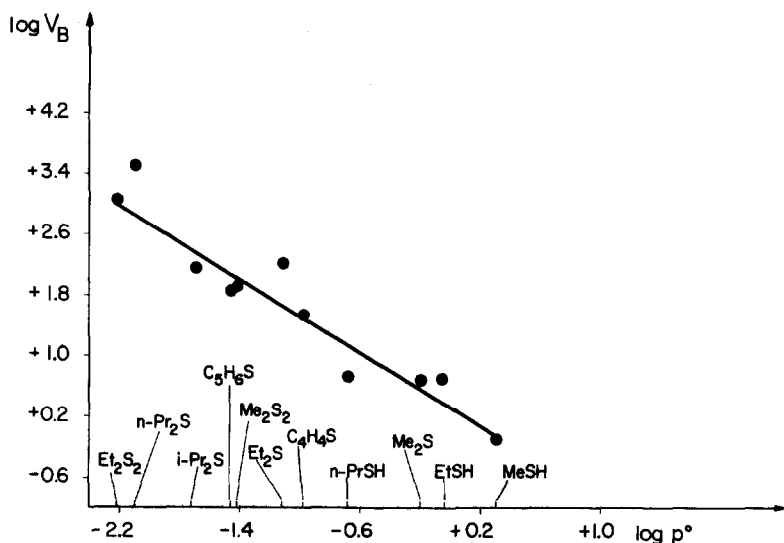


Fig. 4. The dependence of the breakthrough volume (in dm^3/g) on Chromosorb 102 on the saturated vapour pressure (atm) of the organosulphur compounds collected. $c = 0.2\text{--}13.5$ ppm (v/v); $F = 60$ cm^3/min ; $t = 20^\circ\text{C}$. Et = Ethyl; Me = methyl; Pr = propyl; i-Pr = isopropyl.

preconcentration of organic compounds from the atmosphere. Naturally, this is valid only for the case of non-specific interactions between the sorbent and the sorbate (physical adsorption), *i.e.*, primarily for non-polar and moderately polar sorbents.

The data obtained in the present study were compared with those of other authors. The breakthrough volumes determined by Kawata *et al.*¹³ for CH_3SH , $(\text{CH}_3)_2\text{S}$ and thiophene on Tenax GC were in good agreement with those determined in this work: V_B values (dm^3/g) were 0.2 vs. 0.29, 1.8 vs. 0.97 and 28 vs. 26 for CH_3SH , $(\text{CH}_3)_2\text{S}$ and thiophene, respectively. The discrepancy observed for dimethyl disulphide (38 vs. 18 dm^3/g) can be attributed to the difference in flow-rates (200 vs. 60 cm^3/min), the geometry of the sorbent bed and the amount of sorbent used (0.5 vs. 0.23 g) as well as to the difference in the methods of determination of the V_B values (direct vs. extrapolation). On the other hand, the data obtained in this study are in considerable disagreement with those obtained by Torres *et al.*¹⁴, the latter values being generally lower. Most probably, this can be attributed primarily to the substantially higher concentrations in the model gaseous mixtures (by approximately two orders of magnitude) employed by Torres *et al.* and also to the different geometry of the sorbent bed.

On the basis of the above discussion the following conclusions can be drawn.

(1) When direct determination of breakthrough volumes at ambient temperature is impossible due to strong retention of the concentrated sample components, there is a possibility of utilization of the $\log V_B = f(1/T)$ dependence, which shows good linearity for the investigated sorbents and organosulphur compounds.

(2) For the porous polymers of low and moderate polarity studied, the sorption capacity is determined by their surface area, which indicates that the sorption mechanism is based on physical adsorption.

(3) The most suitable sorbent for preconcentration of highly volatile organosulphur compounds is XAD-4.

(4) For the investigated sorbents and sorbates, the logarithm of the breakthrough volume showed fairly good linear correlations with the boiling point, the carbon number and the logarithm of the saturated vapour pressure. These relationships may be useful for estimating breakthrough volumes of other compounds of similar structure.

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