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EVALUATION OF THE SUITABILITY OF SELECTED POROUS POLYMERS FOR PRECONCENTRATION OF VOLATILE ORGANIC COMPOUNDS

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SUMMARY

Breakthrough volumes on six porous polymers (Chromosorb 101, 103, 107 and Porapak N, Q, T) have been determined for vapours of 25 volatile organic compounds (amines, chlorinated hydrocarbons, etc.). The volumes were determined by a direct method, which seems to be simpler compared to the indirect estimation of breakthrough volume on the basis of such chromatographic parameters as retention volume, number of theoretical plates and peak width. The effect of the concentration of a model compound (acetone) in the gas mixtures on breakthrough volume was also determined on all investigated sorbents.

The investigations were carried out in a specially designed apparatus employing the method of diffusion tubes for the generation of model gaseous mixtures.

INTRODUCTION

Preconcentration constitutes an essential step in the analysis of organic air pollutants which usually occur in concentrations below the detection limit of the detector used. This step is also important for the determination of time-weighted average concentrations.

A number of sorbents such as active carbon[1,2], Al_2O_3[3,4], graphitized carbon black[5,6] and the primarily porous polymers Tenax-GC[7–13], Chromosorb Century Series[14–16], Porapaks[17–19] and XAD resins[20–23] have been employed for preconcentration of organic air pollutants. Preconcentration on solid sorbents is sometimes

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combined with cooling of a sorbent-containing tube[3,6,13,17,24,25]. Recently, devices for concentration of atmospheric pollutants became available commercially[11,26,27]. The concentrated compounds are liberated by thermal desorption and introduced via a stream of carrier gas either directly onto an analytical column or, prior to it, into a capillary trap followed by its rapid heating. Spirals made of Fe–Ni alloy can be used for the heating tubes packed with sorbent in order to speed up the desorption process[28]. Solvent extraction can also be employed for the liberation of retained components[1,2]. However, this technique is very difficult to automate and, additionally, extraction results in dilution of the sample since only a fraction of the extract can be introduced onto an analytical column[6].

The course of the adsorption process on a solid sorbent[29,30] is shown schematically in Fig. 1. Initially, concentration occurs in a manner similar to frontal chromatography (curve A). Subsequently, an equilibrium is established between adsorption and desorption processes (curve B). The equilibrium zone moves along the tube with the sorbent and traces of compounds can appear at its outlet (curve C). The breakthrough curve will have a shape similar to curve D. Knowledge of the breakthrough volume, V_B, is essential in analytical practice. It can be defined as the volume of gas which must be passed through a sorbent bed before the investigated compound begins to be eluted from the container with the sorbent. Passing larger volume of gas results in loss of compound and decrease of the recovery. It is usually assumed that the breakthrough of the sorbent bed occurs when the concentration of a

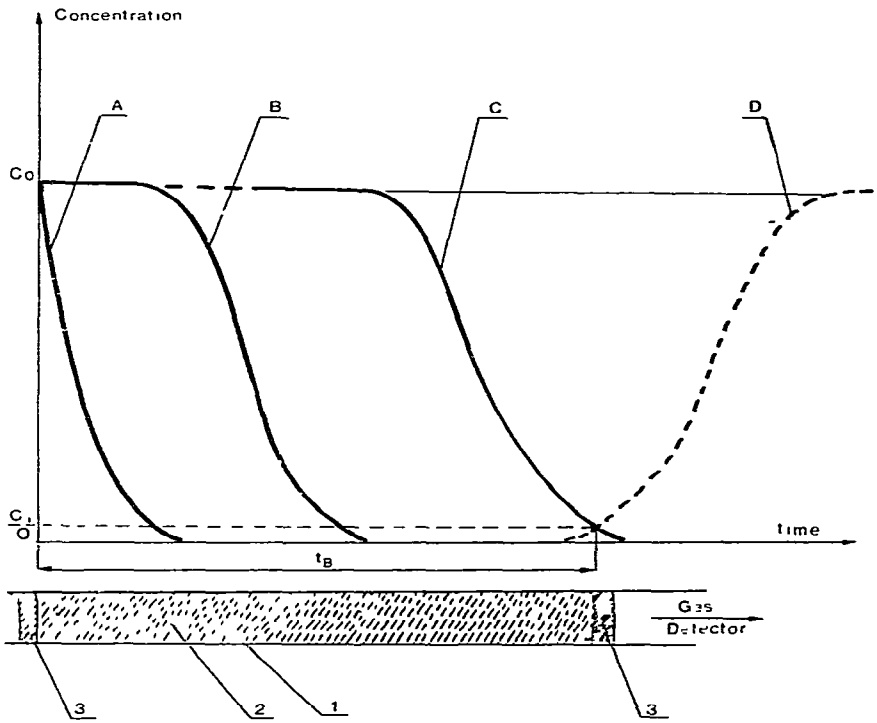

Fig. 1. The course of the adsorption process on a layer of solid sorbent. 1 = Tube; 2 = layer of solid sorbent; 3 = quartz wool plug; t_B = breakthrough time.

compound at the outlet of the container, C_t, reaches 50%[31], 5%[29,32] or 1%[33–35] of the concentration at the inlet, C_0, or, alternatively, when C_t reaches the detection limit for a given detector[36,37]. Another quantity related to V_B is the breakthrough time, t_B[33,34]. In order to use breakthrough volumes for comparison of the adsorption capacity of various sorbents, V_B should be expressed in units of gas volume per unit mass of adsorbent. Attempts have been made[30,34,38,39] to determine the dependence of V_B or t_B on such parameters as the concentration of the investigated compound, temperature, co-adsorption, sorbent particle size, gas flow-rate, gas humidity, properties of the adsorbent and adsorbed compound and the number of adsorption–desorption processes. The effect of these various factors on the breakthrough volume can then be taken into account by means of appropriate correction terms[38]. The resulting value is called the "safe sampling volume".

Breakthrough parameters (V_B or t_B) can be determined from theoretical calculations[33,34,40,41] (Wheeler, Dubinin–Radushkevich and Mecklenburg equations), by an estimation of the retention volume[38,42–46] or by direct measurements[32–39,47]. In the last case a stream of gas (flow-rate 0.05–9.0 l/min) containing known concentrations (20–8200 ppm) of the investigated organic compound is passed through a tube packed with a known amount of a given sorbent. The compound is then detected in the effluent from the tube directly by a flame-ionization detector (FID)[32–35,38,39,47] or a flame photometric detector[35] or indirectly by an IR detector after catalytic oxidation of the compound to CO_2 and removal of interfering combustion products from the gas stream[36,37]. Gravimetry can also be used as an auxiliary technique for evaluation of breakthrough parameters[39].

Values of the breakthrough volume for 71 organic compounds on Tenax-GC were published in 1979[38]. Data for other solid sorbents, equally widely used for preconcentration of volatile organic air pollutants, are considerably less extensive. This gap requires to be quickly filled so that the most effective sorbent for a given compound can be selected on the basis of breakthrough volume. Such a sorbent should ensure quantitative concentration of organic pollutants from a sample of possibly large volume.

The present paper describes a continuation of our previous work[36,37] aimed at the selection of the most effective solid sorbent, not only for the determination of time-weighted average concentrations of individual compounds liberated by thermal desorption but also for the determination of the total content of individual elements occurring in concentrated organic pollutants. Such parameters as total organic carbon (TOC)[48–52] and the total contents of other elements will permit overall characterization of the degree of pollution, whereas the determination of elemental ratios (C:H, C:N, etc.) will give essential information concerning the type of compounds constituting the pollutants. This type of procedure is used in classical elemental analysis[53,54] and is also possible in the analysis of air pollutants by combined gas chromatography–emission spectroscopy with a microwave plasma detector[55].

The purpose of our investigations was to determine the breakthrough volumes on six porous polymers (Chromosorb 101, 103, 107 and Porapak N, Q, T) for over twenty volatile organic compounds. Most of the compounds are chlorinated hydrocarbons and amines which are carcinogenic. In our method, a stream of nitrogen containing a known concentration of the volatile organic compound is passed through a specially designed thermostatted container[37] packed with a known amount

of solid sorbent. The effluent from the container is then analyzed by a FID. The change of the base line on the recorder chart indicates breakthrough of the sorbent layer and appearance of trace amounts of the volatile organic compound at the outlet of the container. The container is heated to thermally desorb the retained compound.

Vapour-gas diffusion was employed for the preparation of model mixtures of known concentration[42,43,56–58]. The mixtures had concentrations lower or close to the level quoted in TLV (threshold limit value) standards elaborated by the US Occupational Safety and Health Organization[59,60] and other organizations[61].

EXPERIMENTAL

Apparatus

A schematic diagram of the device employed for the preparation of model gas mixtures by use of diffusion tubes is shown in Fig. 2. The theory of the method of diffusion tubes and their application for dynamic generation of model mixtures has been discussed previously[42,56,57]. The theoretical equation used for calculation of the diffusion rate is very complicated, and in practice the tubes are calibrated by weight loss over an extended period of time during which the tube is held at a constant temperature with a small flow of gas across it to remove any of the diffused material. Generally, a semimicro balance is employed to measure these weight losses. The tubes used in the present investigations were calibrated in the following manner. A glass ampoule (1) was filled with the volatile organic compound and then connected to a

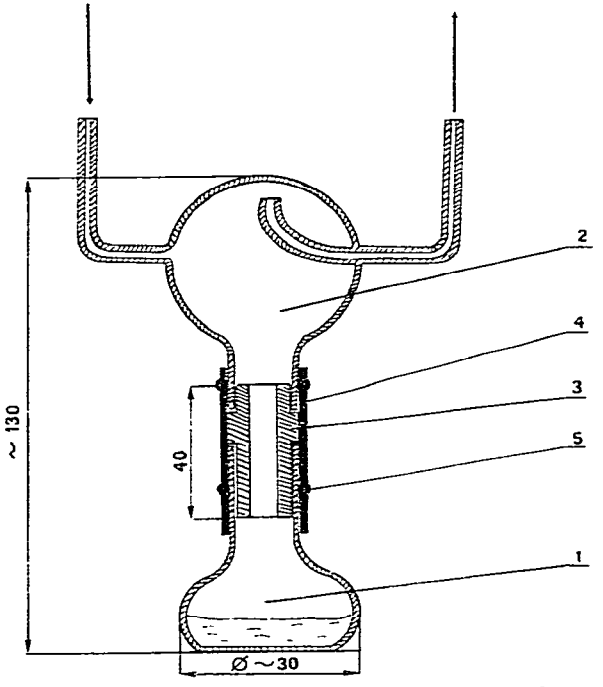

Fig. 2. Schematic diagram of device for preparation of gas mixtures by the diffusion method. 1 = Ampoule with volatile organic compound; 2 = mixing chamber; 3 = diffusion tube; 4 = piece of silicone rubber tubing; 5 = metal clamp. Dimensions in mm.

mixing chamber (2) through a PTFE diffusion tube (3) of exactly known diameter. The connection was tightened by means of a piece of silicone rubber tubing (4) and metal clamps (5). Subsequently, the entire device was thermostatted at 20 ± 0.1°C for 4–5 h. A stream of nitrogen was passed through the diffusion device at a flow-rate of *ca.* 50 ml/min. After it had reached thermal equilibrium, the device was removed from the thermostat, the ampoule was disconnected, wiped to dryness, plugged with a PTFE stopper and weighed on a semimicro balance. Immediately after weighing the ampoule was again connected to the device which was placed in the thermostat for *ca.* 24 h. Then the ampoule was reweighed and the diffusion rate (ng/min) was calculated. Similar measurements were carried out for each organic compound using diffusion tubes (3) of diameters ranging from 1.0 to 7.0 mm, thus allowing the preparation of model mixtures of various constant concentrations of a given organic compound while keeping constant the remaining parameters affecting the diffusion rate[42,56]

The ampoule (1) was also filled with aqueous solutions of highly volatile organic compounds (formaldehyde, methylamine, dimethylamine, trimethylamine and ethylamine). In order to calculate the diffusion rate of these compounds, a glass absorber filled with granulated magnesium perchlorate, which absorbs water diffusing from the ampoule together with the organic compound, was connected to the outlet of the diffusion device. The diffusion rate in aqueous solutions was then calculated from the difference between the weight loss of the ampoule and the gain in weight of the absorber containing $Mg(ClO_4)_2$.

The concentration of organic compound in a gas mixture[58] was calculated from

$$C = \frac{RK}{F}$$

where C = concentration in ppm (v/v), R = diffusion rate in ng/min, K = reciprocal vapour density in nl/ng and F = nitrogen flow-rate in ml/min. The value of K can be calculated from

$$K = \frac{22.4}{M} \cdot \frac{T}{273} \cdot \frac{760}{p}$$

where 22.4 = molar volume of gas at STP, M = molecular weight of material, T = temperature in °K and p = pressure in Torr.

A schematic diagram of the apparatus for the determination of breakthrough volumes for volatile organic compounds on solid sorbents is shown in Fig. 3. A stream of nitrogen (315 ml/min) from a tank (1) was purified (to remove traces of oxygen) by means of a layer of copper placed in a reactor heated to 300°C. In case of visible oxidation of copper, a stream of hydrogen (20 ml/min) was passed through the heated reactor in order to reduce the copper oxide formed. The nitrogen was dried in an absorber (4) packed with granulated KOH. Four three-way cocks (6) allow streams of gases to be directed to a FID as follows: 1, a stream of pure nitrogen in order to establish the base line on a recorder chart [nitrogen does not flow through the diffusion device (7) and the container with sorbent (9), both placed in a thermostat]; 2, a stream of nitrogen containing a known concentration of volatile organic com-

pound (open flow through thermostatted diffusion device and closed flow through container with sorbent); 3, a stream of nitrogen containing a known concentration of volatile organic compound in order to determine the breakthrough volume on a known amount of sorbent in the container (nitrogen flows through diffusion vessel and container with sorbent); 4, a stream of pure nitrogen in order to thermally desorb the retained compound [closed flow through diffusion device and open flow through container with sorbent placed in electric heater (11)] until the base line was re-established at the initial level.

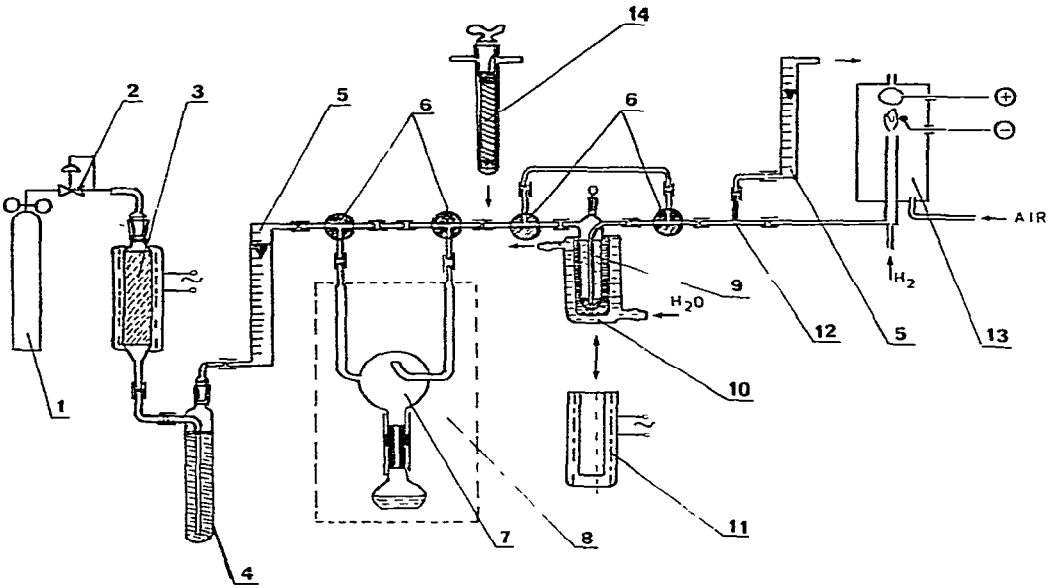

Fig 3 Diagram of apparatus for the determination of breakthrough volumes. 1 = Nitrogen tank; 2 = flow regulator; 3 = heated reactor packed with metallic copper wire; 4 = absorber filled with granulated KOH; 5 = rotameters; 6 = three-way cocks; 7 = diffusion device; 8 = water thermostat; 9 = container with sorbent; 10 = water thermostat; 11 = electric heater; 12 = stream splitter; 13 = FID; 14 = absorber packed with granulated $Mg(ClO_4)_2$.

Streams of gases were fed to the detector at a flow-rate of 50 ml/min using a stream splitter (12). An example of a recorder trace is shown in Fig. 4.

In the case of generation of gas mixtures by diffusion of a volatile organic compound from an aqueous solution (see Fig. 3), an absorber (14) packed with granulated $Mg(ClO_4)_2$ was connected to the outlet of the diffusion device as shown in the figure.

Before the investigations the containers[37] packed with 2.50 g of the studied sorbents were conditioned for 24 h at the maximum allowable temperature (see thermal stability in Table I) in a stream of nitrogen (50 ml/min). The determination of breakthrough volumes was carried out at 20 $\pm$ 0.1°C. Desorption temperatures and properties of the investigated sorbents are listed in Table I. A flame-ionization detector from a Hewlett-Packard Model 5700 A gas chromatograph was used for the analysis of the effluent from the container packed with the sorbent. The detector was

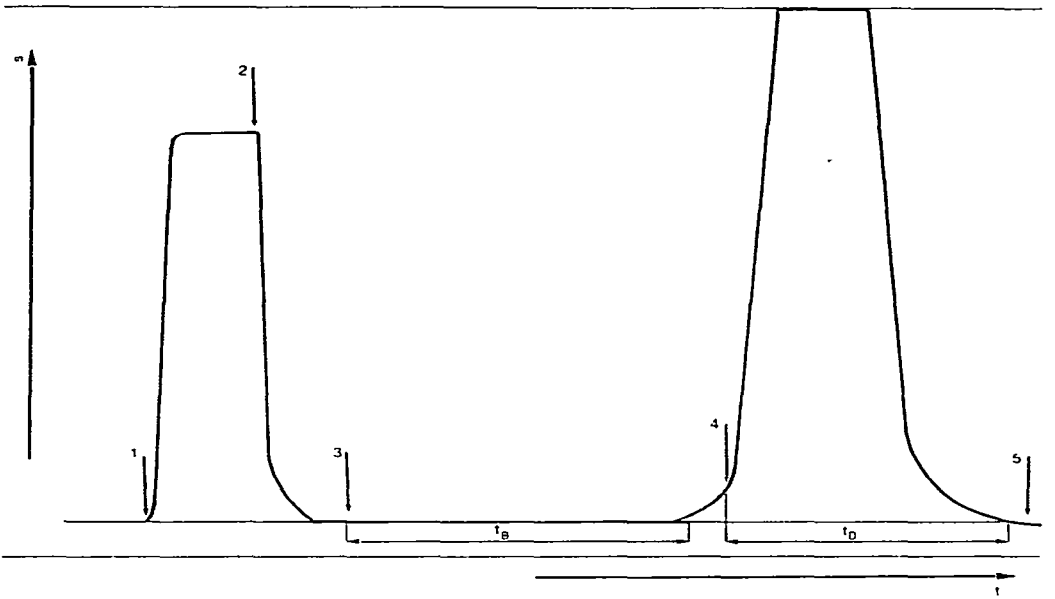

Fig. 4 Example of recorder trace. 1 = Gas mixture of nitrogen with vapours of volatile organic compound passed directly to detector; 2 = closure of nitrogen flow through the diffusion device, 3 = opening of flow through the diffusion device and passage of gas mixture to detector through the container with sorbent; 4 = beginning of thermal desorption of sorbed compound and stoppage of flow through the diffusion unit, t_B = breakthrough time, t_D = time of thermal desorption; 5 = beginning of cooling of the container with sorbent to room temperature in flow of pure nitrogen.

operated under the following conditions: hydrogen flow-rate, 40 ml/min; oxygen flow-rate, 50 ml/min; detector temperature, 250°C.

Reagents

Porous polymers used for preconcentration of vapours of volatile organic compounds from a stream of gases (characterized in Table I) were obtained as follows: Chromosorb 101, 103, 107 (Johns-Manville, Denver, CO, U.S.A.); Porapak N (Varian, Palo Alto, CA, U.S.A.); Porapak Q and T (Waters Assoc., Milford, MA, U.S.A.).

All volatile organic compounds used for the preparation of model mixtures were of Analytical Reagent grade. Aqueous solutions of highly volatile organic compounds of the following concentrations were used: formaldehyde, *ca.* 36%; methylamine, *ca.* 35%; dimethylamine, *ca.* 40%; trimethylamine, *ca.* 25% and ethylamine, *ca.* 70%.

Procedure

Determination of the effect of acetone concentration in a model mixture on breakthrough volumes. Acetone was chosen as a model compound, as in other work[38]. A stream of nitrogen was passed through the device for the preparation of model gaseous mixtures by a diffusion method (7 in Fig. 3). The prepared mixture of nitrogen–acetone vapours of known concentration was passed to the container maintained at 20°C (9 in Fig. 3), and was then directed through the stream splitter (12 in Fig 3) to

TABLE I
PROPERTIES OF INVESTIGATED POROUS POLYMERS
Sorbent mesh size 80–100 except for Porapak Q (50–80). All sorbents are hydrophobic.

Type of sorbent	*Structure*	*Pore diameter (μm)*	*Specific surface area (m^2/g)*	*Density (g/cm^3)*	*Thermal stability (°C)*	*Desorption temperature (°C)*
Chromosorb 101	Styrene–divinylbenzene	0.3–0.4	< 50	0.30	275	265
Chromosorb 103	Cross-linked polystyrene	0.3–0.4	15–25	0.32	275	265
Chromosorb 107	Cross-linked acrylic ester	0.009	400–500	0.30	250	240
Porapak N	Polyvinyl pyrollidone	0.012	225–350	0.38	190	180
Porapak Q	Ethylvinylbenzene–divinylbenzene	0.0075	500–600	0 34	250	240
Porapak T	Ethylene glycol	0 0091	250–350	0 38	190	180

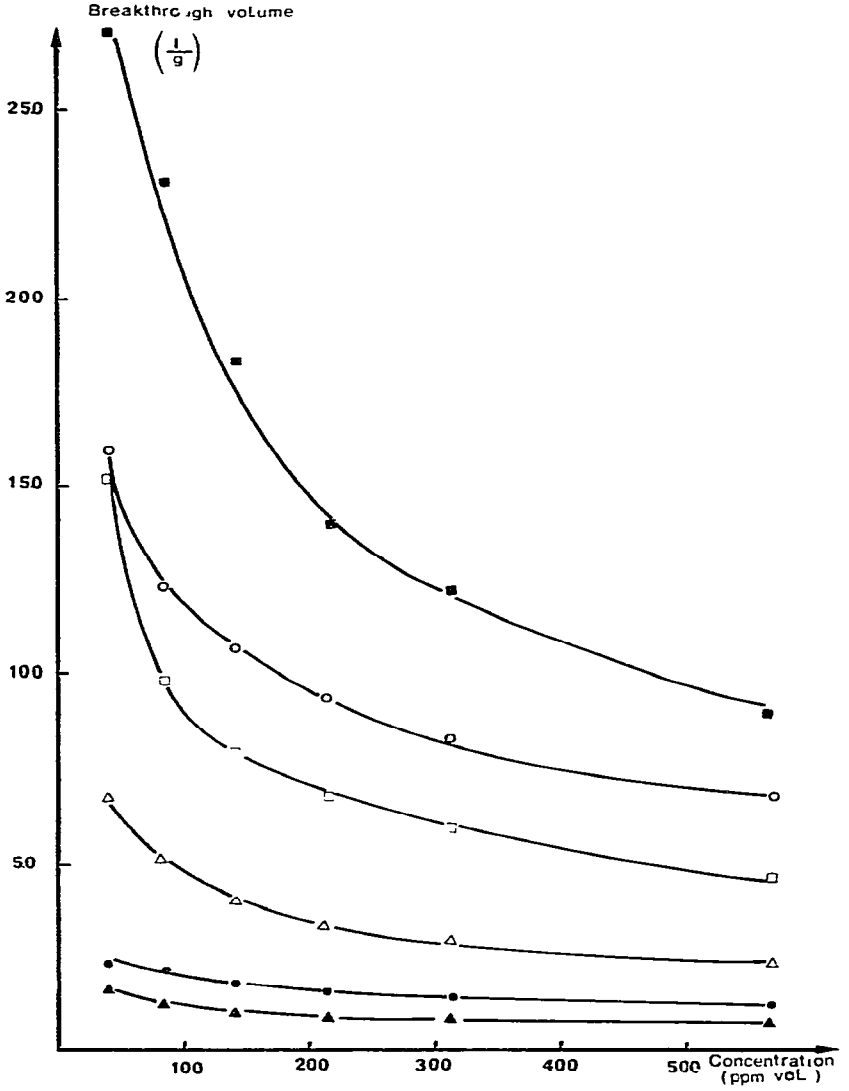

Fig. 5 The effect of concentration of acetone on breakthrough volumes of investigated sorbents in a stream of nitrogen. Sorbents: ●, Chromosorb 101; ▲, Chromosorb 103, ■, Chromosorb 107; ○, Porapak N; △, Porapak Q; □, Porapak T

a FID. The breakthrough time (t_B, see Fig. 4) of the acetone vapour on the sorbent layer was measured with a stop-watch. The breakthrough was detected by the observation of change in the base line on a recorder tracing. Subsequently, the retained acetone was desorbed by heating the container by means of a resistance heater. The time for quantitative thermal desorption (t_D, see Fig. 4) was measured with a stop-watch. The next cycle of measurements was initiated after cooling the container to 20°C. These operations were repeated three times and the average breakthrough volume was calculated. Utilization of diffusion tubes (3 in Fig. 2) of various diameters

TABLE II
BREAKTHROUGH VOLUMES OF VOLATILE ORGANIC COMPOUNDS ON POROUS POLYMERS

Compound	*Concentration (ppm, v/v)*	*Porous polymer*											
		Chromosorb 101		*Chromosorb 103*		*Chromosorb 107*		*Porapak N*		*Porapak Q*		*Porapak T*	
		Breakthrough volume (l/g)	*Desorption time (min)*	*Breakthrough volume (l/g)*	*Desorption time (min)*	*Breakthrough volume (l/g)*	*Desorption time (min)*	*Breakthrough volume (l/g)*	*Desorption time (min)*	*Breakthrough volume (l/g)*	*Desorption time (min)*	*Breakthrough volume (l/g)*	*Desorption time (min)*
1 Acetone	39	2.35	7	1.56	5	23.50	9	15.95	19	6.81	11	15.25	12
2 Benzene	16	>15	12	12.06	12	>15	16	>15	14	6.34	10	>15	12
3 *n*-Hexane	25	>15	8	3.42	6	>15	10	>15	13	>15	15	12 72	10
4 Methanol	24	0.27	5	0.68	7	3.25	10	2.83	9	1.12	5	3.60	7
5 Diethyl ether	99	1 61	8	0.75	8	10.69	11	12.82	9	6.05	6	6.30	7
6 Furan	110	0.86	10	0 46	6	6.01	10	5.71	10	2.49	6	3.91	9
7 Formaldehyde	9	8.04	10	5.95	10	>15	13	>15	9	5.34	6	>15	12
8 Methylamine	25	1.12	18	0.39	14	8.97	30	11.47	28	7.13	19	15.01	32
9 Dimethylamine	18	2.26	21	0.76	15	12.52	37	14.92	29	10.78	20	>15	35
10 Trimethylamine	20	6.94	19	1.16	11	>15	31	>15	20	>15	16	>15	28
11 Ethylamine	19	1.41	16	0.52	13	10.17	27	12.01	32	14.50	22	>15	29
12 Diethylamine	9	2 80	18	0.91	12	12.81	26	14.80	35	>15	21	>15	32
13 Triethylamine	11	>15	20	4.06	15	>15	29	>15	20	>15	18	>15	29

14 Dichloromethane	169	2.78	7	2.16	6	14.91	31	12.06	21	4.53	11	9.69	13
15 Chloroform	32	>15	18	6.84	9	>15	13	>15	13	>15	12	14.98	11
16 Carbon tetrachloride	23	>15	12	7.31	12	>15	13	>15	9	>15	7	>15	9
17 1,2-Dichloroethane	25	>15	23	>15	23	>15	21	>15	19	16.11	12	13.46	15
18 1,1,1-Trichloroethane	19	9.39	15	1.47	12	>15	15	>15	12	>15	8	>15	11
19 1,1,2-Trichloroethane	14	>15	18	>15	18	>15	20	>15	22	>15	14	>15	18
20 Trichloroethylene	13	>15	21	>15	25	>15	21	>15	13	>15	12	>15	14
21 Tetrachloroethylene	15	>15	33	>15	35	>15	30	>15	25	>15	15	>15	22
22 1-Chloropropane	66	5.59	14	3 76	14	>15	24	>15	17	9.25	8	8.09	13
23 1,2,3-Trichloropropane	13	>15	16	>15	19	>15	11	>15	35	>15	23	>15	33
24 2-Chlorobutane	29	14 65	20	6.52	17	>15	28	>15	14	14.92	10	11.45	13
25 *tert* -Butyl chloride	42	0.23	6	0.11	6	>15	20	>15	13	12.91	8	5.25	9

permitted preparation of gaseous mixtures of various acetone concentrations. The breakthrough volumes of gas mixtures having six different concentrations of acetone [39, 87, 137, 213, 310 and 561 ppm (v/v)] were determined for each of the six investigated polymers. The dependence of breakthrough volume (l/g) on the concentration of acetone in a stream of nitrogen (ppm, v/v), determined on the basis of experimental results, is shown in Fig. 5.

Determination of breakthrough volumes of volatile organic compounds. The breakthrough volumes of vapours of 25 volatile organic compounds on the studied sorbents were determined in the manner described above. The results are listed in Table II. The data represent the average of three parallel measurements. As described earlier[36,37], the exact value of the breakthrough volume was not determined for compounds characterized by strong retention on the sorbent. Such cases are represented in Table II by the expression $V_B > 15$ l/g. The concentrations of organic compounds in a stream of nitrogen were close to TLV standards[59–61].

RESULTS AND DISCUSSION

The breakthrough volumes for vapours of 25 volatile organic compounds on six porous polymers (Chromosorb 101, 103, 107 and Porapak N, Q, T) were measured by a direct method. The method has a great potential due to its simplicity. The value of the breakthrough volume depends on a large number of parameters, the effects of which have been investigated by other authors. The present studies were limited to the determination of the effect of concentration of a model compound on the breakthrough volume (Fig. 5). The breakthrough volume decreases considerably with increase in concentration of an organic compound, particularly in the cases of Chromosorb 107 and Porapak T. For the remaining sorbents the breakthrough volume decreases approximately by a factor of two with an increase of acetone concentration from 39 to 561 ppm (v/v). Similar results were obtained for Tenax GC[38]. For practical reasons, the range of concentrations below 100 ppm is of importance.

In some cases it was not possible to determine the breakthrough volumes of gas mixtures containing very low (< 50 ppm) concentrations of vapours of organic compounds. The investigated compounds differed considerably in volatility and, despite using diffusion tubes of various diameters (1–7 mm), for many compounds it was not possible to obtain sufficiently low diffusion rates (amount of compound diffusing through a tube into a stream of gas per unit of time) under the experimental conditions. On the other hand, it should be pointed out that the diffusion method of preparation of gaseous model mixtures is tedious and time-consuming due to the gravimetric calibration, especially for low diffusion rates. In the future, such investigations will be facilitated by utilization of commercially available devices for the preparation of model gas mixtures. Recently, such devices employing diffusion and permeation tubes have been introduced by Analytical Instrument Development Company[58,60].

On the investigated sorbents, the lowest breakthrough volumes were exhibited by methanol, 0.27–3.60 l/g. It can also be observed that, under the described conditions on Chromosorb 107 and Porapak N, breakthrough volumes larger than 15 l/g were found in 17 cases per 25, whereas on Chromosorb 101, 103, Porapak Q and T the breakthrough volumes exceeded this value in 10, 5, 12 and 15 cases respectively.

In order to account for the effect of various parameters on breakthrough volume, its value is appropriately reduced. The resulting value is termed the "safe sampling volume".

Desorption times of investigated compounds ranged from 5 to 35 min.

Among the studied adsorbents, Chromosorb 107 and Porapak N exhibit high adsorption capacity for various volatile organic compounds. Thus, these adsorbents and XAD-7[36,37] can be successfully employed for the concentration of volatile organic pollutants in air.

The ultimate goal of our investigations is the development of a simple method of determination of the total contents of individual elements occurring in organic pollutants (TOC, TON, TOS, etc.). Hence, it is necessary to select the best sorbent for preconcentration of volatile organic air pollutants and to determine the optimum conditions for desorption, the enrichment factor and the degree of adsorption of gaseous inorganic pollutants (CO_2, CO, H_2S, SO_2, H_2O, NO, NO_2) which can influence the experimental results. These investigations will be the subject of subsequent papers.

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