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COLLECTION AND ANALYSIS OF TRACE ORGANIC VAPOUR POLLUTANTS IN AMBIENT ATMOSPHERES

THE PERFORMANCE OF A TENAX-GC ADSORBENT TUBE

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SUMMARY

The technique by which organic contaminants in ambient air are analysed by adsorption on porous polymers and subsequent thermal desorption into a gas chromatograph is gaining in popularity. We present here an analysis of the adsorption characteristics of one of the commonly used adsorbents, Tenax-GC. The capacity of this adsorbent to collect a variety of organic vapours has been investigated with respect to changes in sampling flow-rate, temperature, vapour concentration and humidity. Safe sampling volumes are tabulated for 71 organic compounds, and a plot is presented for the interpolation of estimated values for unlisted compounds.

INTRODUCTION

Because of the relatively low concentrations of organic contaminants in ambient air, most chromatographic methods for the measurement of these contaminants require a concentration step before the actual analysis. The most frequently used methods for organic vapours are solvent scrubbing, cryogenic concentration, and adsorption on solid adsorbents. Because of dilution, most solvent-scrubbing techniques are insufficiently sensitive for analyses in the parts per billion (10^9) range. Cryogenic methods tend to collect large quantities of water vapour, which presents a major problem in the subsequent chromatographic analysis. Consequently, most attention has been given in the past to solid adsorption methods.

Two basic types of solid adsorbent are used for vapour collection. The more traditional collection method, used in most NIOSH procedures[1], utilises charcoal or silica gel as the adsorbent, followed by solvent desorption in conjunction with gas chromatographic analysis. A newer method, which evolved from gas adsorption on chromatographic support-coated packings[2,3], uses a porous polymer adsorbent and direct thermal desorption into the gas chromatograph[4–19]. The advantages of the latter technique are, principally, high sensitivity and an absence of solvent peak in the analysis. The technique has therefore gained wide acceptance in a variety of applications, including environmental trace analysis[7,8], industrial hygiene[2,5], stack sampling[9],

water analysis by direct sorption[12] or gas stripping[9], head-space analysis of biological fluids[8] or biological specimens[14], odour analysis[5] and the trapping of gas chromatographic effluents[17].

A number of different porous polymers have been employed as adsorbents, including the Chromosorb Century series[5,7], the Porapak series[4,14], Ambersorb XE-340 (see ref. 16) and others. However, the most popular adsorbent has been Tenax-GC[4–6,8–10,12,15,17,19]. This is a polymer of 2,6-diphenyl-*p*-phenylene oxide, the physical properties of which have been well described[20–22]. Its main advantages over other porous polymers are its high temperature stability and hence low bleed on thermal desorption and its relative insensitivity to the effects of water vapour, for which it has an extremely low affinity.

Some variants of the basic technique use charcoal rather than a porous polymer for adsorbent[23–25], or alternatively use a porous polymer but desorb with solvent[26–29]. Charcoal may be used when porous polymers have insufficient sampling capacity, and solvent desorption for very high boiling compounds (*e.g.*, polycyclic aromatics[26]) that are not readily desorbed thermally. Solvent desorption may also be used for analyses with an electron-capture gas chromatographic finish (*e.g.*, polychlorinated biphenyls[27], ethylene glycol dinitrate[28,29]) where the increased sensitivity of electron-capture over flame ionisation detection balances the dilution effect of solvent extraction.

In view of the popularity of Tenax and the thermal-desorption technique, it is perhaps surprising that little has been published on the chromatographic properties of the sorbent, particularly with regard to the safe sampling volumes of an adsorbent tube and the effects of parameters such as sampling flow-rate, temperature, vapour concentration and humidity on these volumes. This paper provides data on some of these aspects.

Safe sampling volumes

It is important to the user of a porous polymer sampling tube to know the safe sampling volume of the tube. This is the volume of air containing a particular vapour contaminant that may be sampled over a variety of circumstances without significant breakthrough. To determine this quantity, we determine experimentally the breakthrough volume of a particular compound on the tube. This we have defined as the point at which a continuous atmosphere drawn through the adsorbent tube appears in the tube effluent[2,30]. The breakthrough volume varies with such parameters as vapour concentration and sampling flow-speed, so the safe sampling volume must contain a safety margin to allow for changes in these parameters within certain limits.

Our method of direct measurement of breakthrough volume is essentially that of Pellizzari *et al.*[11], except that the sampled atmosphere is maintained at constant concentration rather than decreasing in concentration during the sampling. The method is more convenient than sampling on several tubes in series and analysing the "back-up" tubes[15], but is nevertheless very time-consuming and was used only to confirm the validity of the indirect method for a selected number of compounds. The indirect method derives the breakthrough volume from a measurement of the retention volume of an organic vapour on the adsorbent tube; the retention volume is defined here as the point at which a single injection of vapour emerges from the tube. This is the value measured at the peak maximum in conventional gas chromato-

graphy. Some authors[13,15,31,32] have used retention volume as synonymous with breakthrough volume. However, in general the breakthrough volume (as we have defined it) will be less than the retention volume, because the column efficiency of the adsorbent tube must be taken into account. Breakthrough volumes may be readily calculated from a knowledge of retention volume and adsorbent tube theoretical plates, by means of a summation of integrals method outlined by Cropper and Kaminsky[2]. Fig. 1 gives a summary of these calculations in the form of a plot of breakthrough volume as a fraction of the retention volume as a function of adsorbent tube theoretical plates.

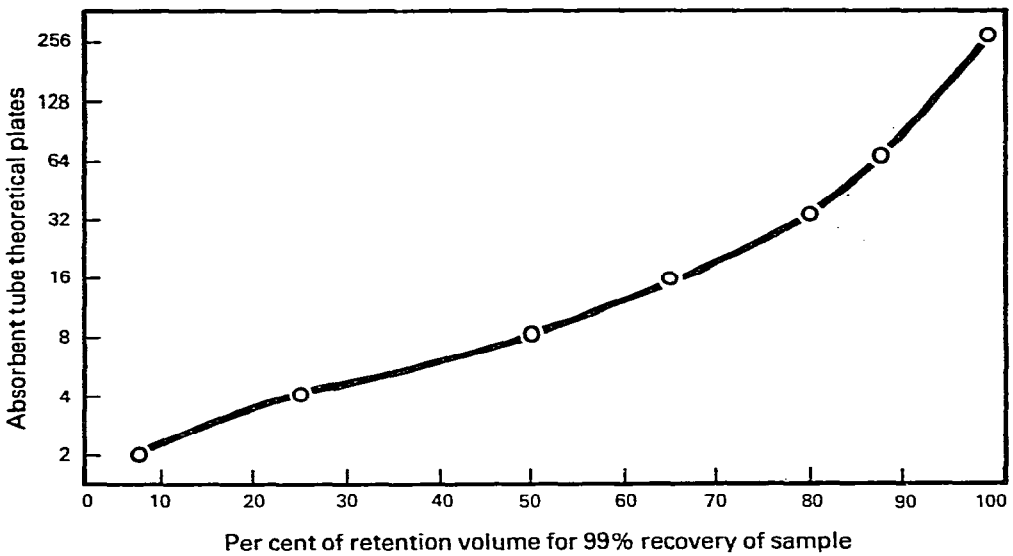

Fig. 1. Plot of sampling volume as percentage of retention volume as a function of adsorbent tube theoretical plates of Cropper and Kaminsky[2].

EXPERIMENTAL

Adsorbent tube

The adsorbent tube used in these studies was constructed of stainless-steel tubing (75 mm × 4.5 mm I.D.) and contained 0.13 ± 0.01 g of Tenax-GC (40–60 mesh). The adsorbent was held in place with small plugs of silanised glass wool and stainless-steel gauze discs, and the tube was sealed at each end with standard metal pipe fittings with polytetrafluoroethylene (PTFE) ferrules. Before use, the tubes were conditioned under nitrogen at 250° for 16 h.

Direct measurement of breakthrough volumes

Breakthrough volumes were measured directly by drawing a standard atmosphere of the organic compound through an adsorbent tube and monitoring the effluent with a continuous flame ionisation detector. Standard atmospheres were generated dynamically by syringe injection of liquid into a metered flow of air as described by Simmons[33]. For some atmospheres, a second dilution stage was introduced. The

humidity of the final atmosphere could be adjusted by introducing a train of water bubblers to the incoming air at the first or second dilution stage. The flame ionisation detector was adjusted to give full-scale deflection on the recorder for the generated atmosphere by inserting an empty adsorbent tube in the apparatus. The response time of the detector was *ca.* 15 sec.

Indirect measurement of breakthrough volumes

Breakthrough volumes were measured indirectly from a consideration of retention volumes and the theoretical plates of the adsorbent tube. An adsorbent tube was connected to the injection and detection ports of a conventional gas chromatograph with flame ionisation detection by means of narrow-bore PTFE tubing. Retention volumes and theoretical plates were determined by injecting 1 ml of standard vapour atmosphere at 20° under a known carrier-gas flow and monitoring the effluent. Retention volumes were measured in experiments run with the adsorbent tube above ambient temperature and were extrapolated to room temperature by means of a plot of log (corrected retention volume) against reciprocal absolute temperature; they were also corrected for the retention volume of air. Theoretical plates were determined at temperatures as near 20° as practicable.

RESULTS

Extrapolation of retention volume data

The extrapolation of the log (retention volume) against reciprocal absolute temperature, examples of which are given in Fig. 2, may not be strictly valid. Tanaka[34] has observed some deviations from linearity for some chlorinated hydrocarbons on

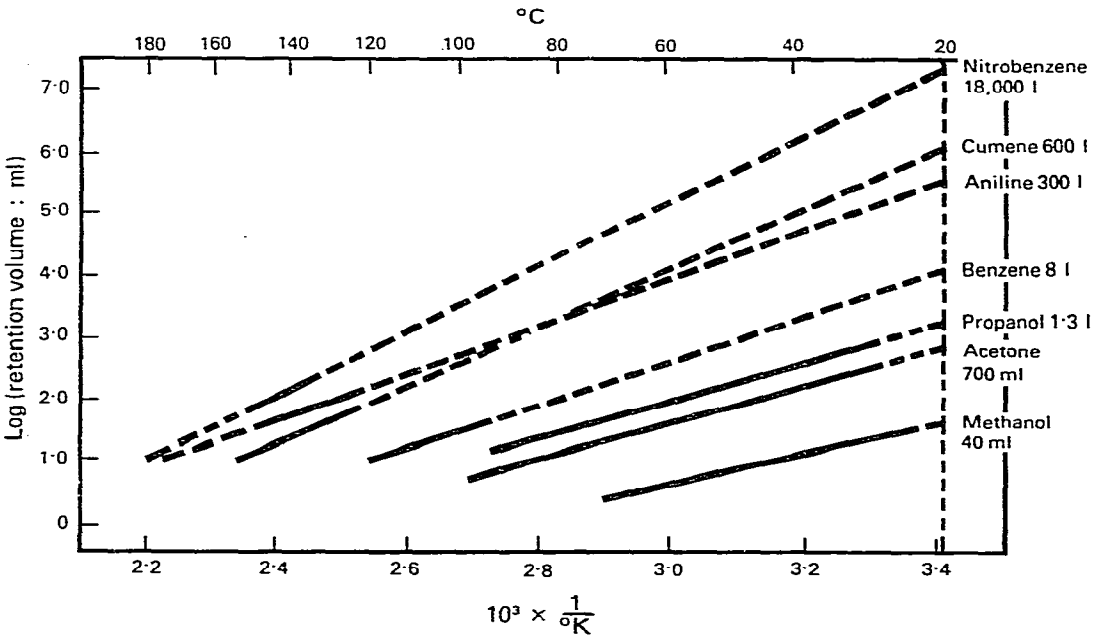

Fig. 2. Extrapolation of plot of log (retention volume) against reciprocal absolute temperature.

Tenax. However, we have observed only slight deviations from linearity for a wide range of compounds, in line with the findings of Butler and Burke[30].

Validity of indirect approach to determination of breakthrough volumes

Direct determinations of breakthrough volumes were made with acetone, dichloromethane, *n*-propanol and acrylonitrile; 1% breakthrough volumes observed were 515, 438, 860 and 750 ml, respectively. Volumes calculated by the indirect procedure were 515, 416, 901 and 757 ml, respectively, *i.e.*, values closely similar to the directly determined values. However, these comparisons disguise the fact that breakthrough volumes vary markedly with concentration, flow-rate of sampling and temperature and that here they have been determined under conditions that were closely matched to minimise these variations. Further comparisons were therefore made in a more detailed study of the effects of individual parameters on breakthrough volumes.

Influence of flow-rate on breakthrough volumes

No significant variation of retention volume with change of flow-rate was noted, although the number of theoretical plates of the adsorbent tube did vary significantly with flow-rate (Fig. 3), as expected from the Van Deemter equation[35]. Fig. 3 shows some experimental data for dichloromethane, acetone and propylamine. Propanol, acetic acid and acrylonitrile were also examined and gave efficiencies between those of dichloromethane and propylamine.

Fig. 3 indicates that there is an optimal sampling rate for adsorbent tubes, which for this type and geometry is about 50 ml/min. However, the breakthrough volume is still at least half the retention volume over a wide range, with a minimum of 5 ml/min and a maximum of 600 ml/min. These, limits, appropriately adjusted for

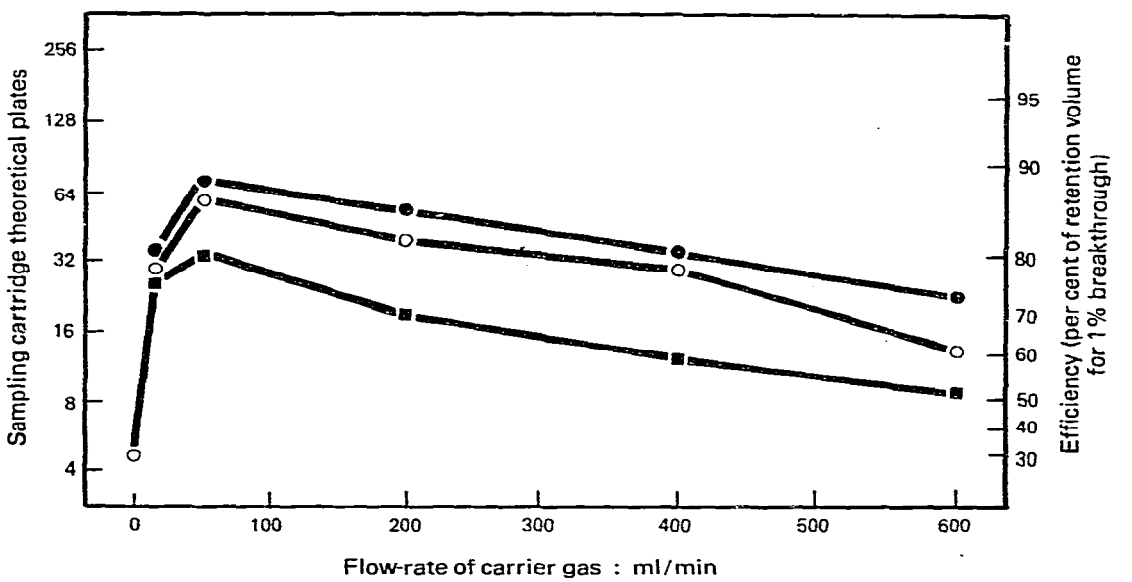

Fig. 3. Sampling parameters of Tenax adsorbent tubes as a function of flow-rate for dichloromethane (●), acetone (○) and propylamine (■).

tube diameter, should be borne in mind when a sampling pump at low flow is used for full-shift monitoring and when a hand-bellows pump or syringe is used for "snap" sampling. The maximum flow measured with a "Draeger" hand-bellows pump and adsorber tube was 600 ml/min. It is particularly important to avoid using very low flow-rates of sampling, as this produces poor theoretical plates (four for acetone at 1 ml/min) and, also, passive sampling may occur in addition to the dynamic sampling.

In order to confirm that breakthrough volumes could be reliably calculated from retention volumes and theoretical plates, results obtained for acetone were compared with direct observations of the effect of sampling flow-rate on breakthrough. Fig. 4 indicates acceptable agreement.

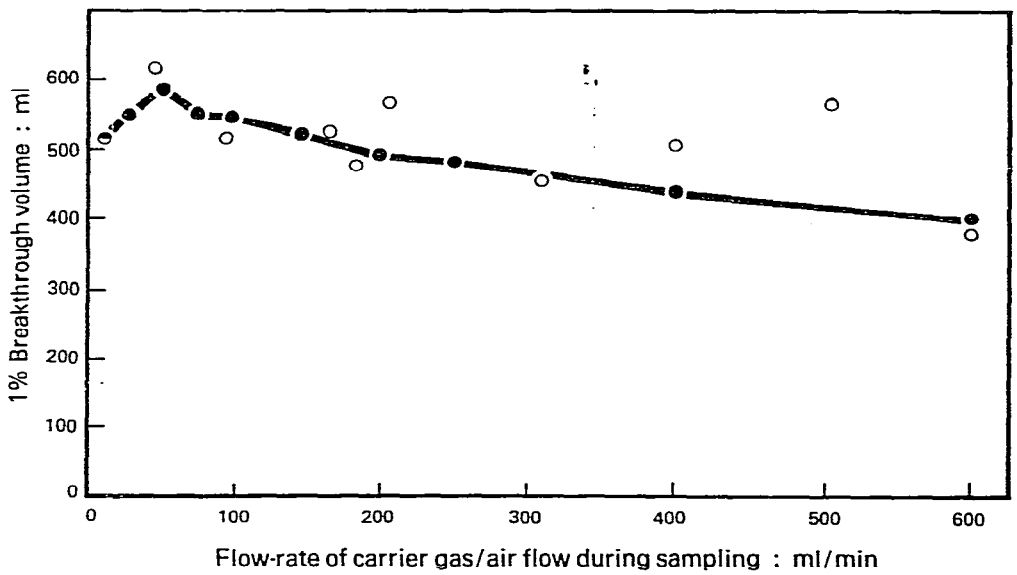

Fig. 4. 1% Breakthrough of acetone on Tenax adsorbent tubes as a function of sampling rate: calculated (●); observed (○).

Influence of vapour concentration on breakthrough volumes

It is known that Tenax used as an analytical column produces unusual peak shapes for many organic compounds, particularly at high sample loading[20,21], Both retention time and tube theoretical plates might therefore be expected to vary with sample size. Results obtained for acetone are presented in Fig. 5, both for calculated and observed breakthrough volumes. They show, however, that there are discrepancies between the volumes obtained by the two methods. Breakthrough volumes calculated from experiments with a single injection of acetone vapour suggest that there is little effect below about 5000 ppm. The values observed by direct experiment deviate significantly from the calculated values; premature breakthrough was observed above 100 ppm. This is because overloading of the adsorbent occurs more rapidly with a continuous atmosphere than with a single aliquot at the same concentration. However, the Tenax method is primarily a concentration technique and is most likely to be used to sample vapour concentrations below 100 ppm; in this region, the observed volumes

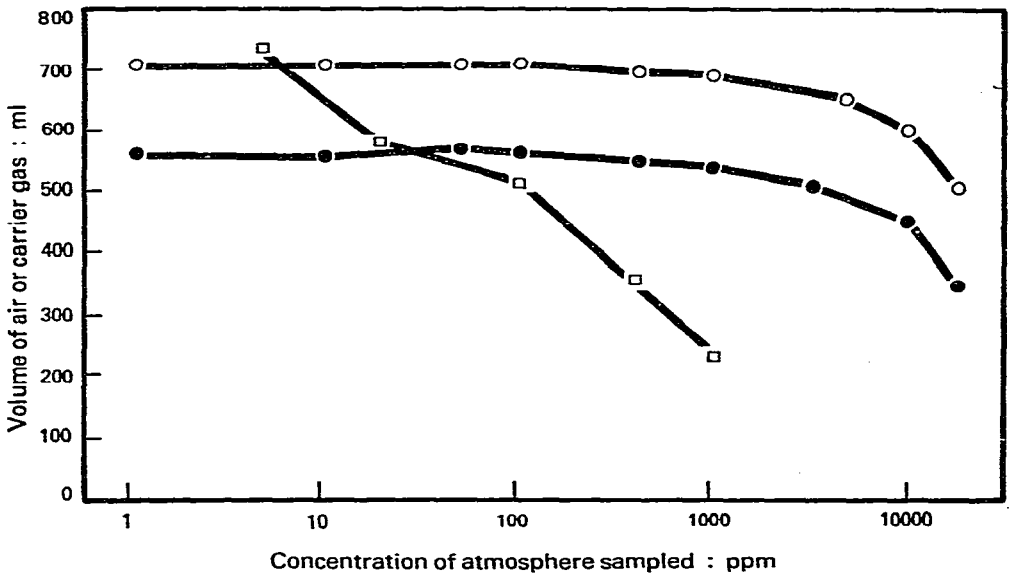

Fig. 5. Sampling parameters of Tenax adsorbent tubes as a function of acetone vapour concentration; calculated retention volume (○); calculated breakthrough volume (●); observed breakthrough volume (□).

exceed the theoretical, so that the calculated breakthrough volume remains a safe practical limit. The calculated value, incidentally, is based on the assumption that the peak shape is Gaussian, which is not true at very high or very low sample concentration. Results similar to those represented in Fig. 5 were obtained for *n*-propanol and dichloromethane.

The effect of temperature on breakthrough volumes

Temperature has only a small effect on theoretical plates and peak asymmetry[22], and, for this reason, determinations were carried out at as near ambient as practicable. It has a much more serious effect on retention volume, which we have already noted varies inversely with temperature (Fig. 2). This plot may be used to determine retention volume and hence breakthrough volume at any given temperature. To a first approximation, retention times are doubled for each 10° decrease in temperature. Fig. 2 may also be used to determine suitable desorption temperatures for the thermal desorption of samples. An extrapolation to high temperature will give the retention volume of a compound. This volume is increased to take account of tube theoretical plates, and from this volume is calculated the desorption time at a given flow-rate. Note that the desorption temperatures given in Table I refer to a desorption volume of 50 ml. In practice, due to poor thermal transfer, nominal desorption temperatures for a thermal-desorption apparatus may need to be higher than these values.

The effect of humidity on retention volumes

High ambient humidity has a much smaller adverse effect on retention volumes on Tenax than it has on those for other porous polymer adsorbents. Janak *et al.*[36] have examined the effect of water vapour in the carrier gas on retention times. They

observed no significant effect with acetone, ethyl acetate, benzene or propanol; ethanol and methanol showed slightly reduced retention volumes, but in any event these have breakthrough volumes too low for practical sampling on Tenax. Pellizzari *et al.*[15] observed that up to 92% relative humidity had no significant effect on breakthrough volumes of acrolein, diethyl sulphate, propylene oxide, methyl ethyl ketone, nitromethane, glycidaldehyde and bis(chloromethyl) ether. We have confirmed no significant effect for acetone and acrylonitrile (high humidity breakthrough within ±5% of low humidity breakthrough) by direct determination.

Determination of safe sampling volumes

We have defined the safe sampling volume as the volume of air containing a particular vapour contaminant that may be sampled over a variety of circumstances without significant breakthrough occurring on a sample tube. If, for the adsorbent tube described, we limit sampling flow-rate to between 5 and 600 ml/min, vapour concentrations to below 100 ppm, temperatures to up to 20° and relative humidity to up to 95% at 20°, we find from the results presented above that the breakthrough volume is not less than 50% of the measured retention volume for each vapour. Thus, experimentally, we need to determine only the retention volume of an organic species at 20° and, under the defined circumstances, the safe sampling volume will be at least 50% of this value. On this basis, Table I lists measured retention volumes, calculated safe sampling volumes and also the derived functions safe sampling volume per gram of adsorbent and desorption temperature.

For most compounds there is good correlation between retention volume and boiling point (Fig. 6); hence retention volumes (and derived safe sampling volumes) may be interpolated for compounds for which direct data are unavailable. The correlation coefficient for most compounds with respect to the line drawn in Fig. 6 is

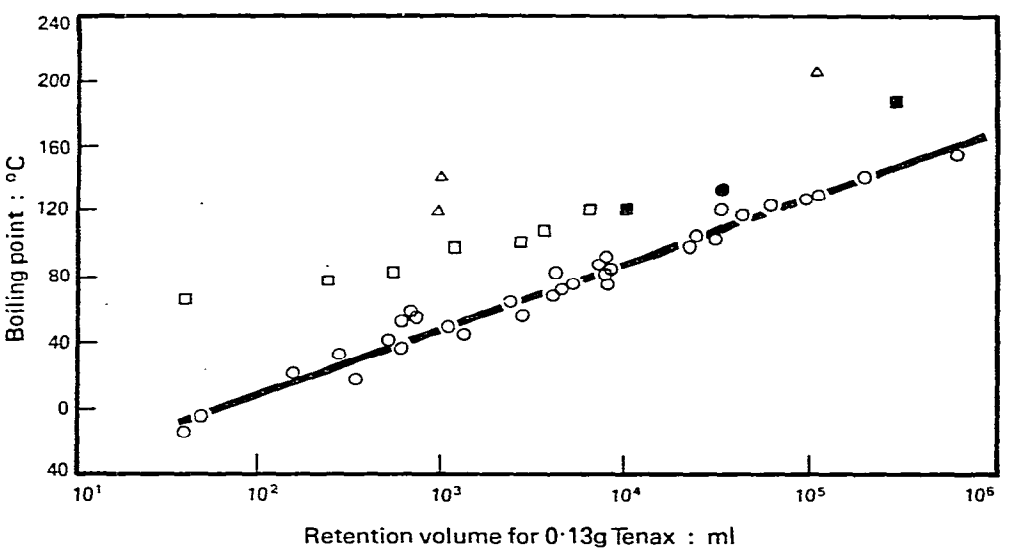

Fig. 6. Retention volumes for Tenax adsorbent tubes as a function of boiling-point of the organic vapour collected: most compounds (○); alcohols (□), acids and anhydrides (△); higher amines (■); chlorobenzene (●).

TABLE I

EXTRAPOLATED RETENTION VOLUMES AND SAFE SAMPLING VOLUMES FOR ORGANIC VAPOURS SAMPLED ON A 0.13-g TENAX ADSORBENT TUBE

Data are relevant to sampling parameters of flow-rate between 5 and 600 ml/min, vapour concentration below 250 mg/m³ and temperatures up to 20°. Retention volumes are given at 20°. Desorption temperatures refer to a desorption volume of 50 ml.

Organic compound	*Boiling point (°C)*	*Retention volume (l)*	*Safe sampling volume (l)*	*Safe sampling volume per g of adsorbent (l)*	*Desorption temperature (°C)*
Hydrocarbons					
Pentane	36	0.59	0.29	2.2	70
Hexane	69	4.3	2.1	16	90
Heptane	98	23	11	85	110
Octane	125	100	50	390	120
Benzene	80	8.0	4.0	31	100
Toluene	111	50	25	190	120
Xylene(s)	138–144	400	200	1500	140
Cumene	152	600	300	2400	140
Trimethylbenzene(s)	165–176	1800	900	8900	150
Styrene	145	400	200	1500	140
Methylstyrene	167	1600	800	6000	150
Butadiene	−4	0.16	Not applicable		
Chlorinated hydrocarbons					
Chloromethane	−24	0.01	Not applicable		
Dichloromethane	40	0.52	0.2	1.5	70
Chloroform	62	2.5	1.2	9.3	90
Carbon tetrachloride	76	8.0	4.0	31	100
Chloroethane	12	0.1	Not applicable		
1,1-Dichloroethane	57	1.8	0.9	7.0	90
1,2-Dichloroethane	84	7.1	3.5	27	100
1,1,1-Trichloroethane	74	5.0	2.5	19	100
1,1,2-Trichloroethane	114	45	22	170	120
1,1,1,2-Tetrachloroethane	130	100	50	390	130
1,1,2,2-Tetrachloroethane	146	220	110	850	130
Vinyl chloride	−14	0.04	Not applicable		
Vinylidine chloride	32	0.28	0.1	1.1	60
1,2-Dichloroethylene	55	1.4	0.7	5.4	90
Trichloroethylene	87	7.4	3.7	28	100
Tetrachloroethylene	121	63	31	240	130
Allyl chloride	45	1.3	0.6	5	90
Chlorobenzene	131	34	17	130	120
Other halogenated hydrocarbons					
Bromomethane	4	0.14	Not applicable		
Fluorotrichloromethane	24	0.04	Not applicable		
2-Chloro-2-bromo-1,1,1-trifluoroethane	50	0.2	0.1	0.8	50
1,2,2-Trifluoro-1,1,2-trichloroethane	48	0.03	Not applicable		

(Continued on p. 88)

TABLE I *(continued)*

Organic compound	*Boiling point (°C)*	*Retention volume (l)*	*Safe sampling volume (l)*	*Safe sampling volume per g of adsorbent (l)*	*Desorption temperature (°C)*
Esters					
Methyl acetate	57	0.7	0.3	2.7	80
Ethyl acetate	71	4.6	2.3	18	100
Propyl acetate	102	25	12	92	120
Isopropyl acetate	90	8.0	4.0	31	100
Butyl acetate	126	110	55	420	130
Methyl acrylate	81	8.3	4.1	32	100
Ethyl acrylate	100	31	15	120	120
Aldehydes and ketones					
Acrolein	53	0.62	0.3	2.4	80
Acetone	56	0.70	0.3	2.7	80
Methyl ethyl ketone	80	4.3	2.1	16	100
Methyl isobutyl ketone	118	35	17	130	120
3,5,5-Trimethylcyclohex-2-enone	214	7400	3700	28000	170
Acetaldehyde	21	0.16	Not applicable		
Alcohols					
Methanol	65	0.04	Not applicable		
Ethanol	78	0.24	0.1	0.9	50
n-Propanol	97	1.1	0.5	4.2	80
Isopropanol	82	0.55	0.3	2.1	70
n-Butanol	118	6.6	3.3	25	100
Isobutanol	108	3.7	1.8	14	100
sec.-Butanol	99	2.8	1.4	11	90
n-Octanol	180	1800	900	6900	140
Allyl alcohol	96	1.2	0.6	4.6	80
Acids and anhydrides					
Acetic acid	118	1.0	0.5	3.9	80
Acetic anhydride	140	1.0	0.5	3.9	80
Maleic anhydride	202	112	55	440	160
Amines					
Methylamine	−6.3	0.05	Not applicable		70
Ethylamine	17	0.35	0.15	1.2	80
Propylamine	48	1.1	0.5	4.2	80
Pyridine	116	10	5	39	130
Aniline	184	280	140	1100	170
Miscellaneous					
Acetonitrile	82	0.51	0.25	1.9	70
Acrylonitrile	78	0.89	0.45	3.5	80
Dimethylhydrazine	63	1.1	0.55	4.2	80
Epichlorhydrin	117	18	9	69	100
Ethylene oxide	14	0.06	Not applicable		
Ethyl mercaptan	35	0.9	0.45	3.5	80
Nitrobenzene	211	18000	9000	69000	180

0.98. However, there are important exceptions, *viz.*, alcohols, acids and anhydrides, higher amines and chlorobenzene.

In determining a suitable volume of air sample for subsequent analysis, care should also be taken to ensure that detector or amplifier overload does not occur in the analysis, particularly if thermal desorption of the whole sample into a gas chromatograph is intended.

CONCLUSIONS

Breakthrough volumes for organic vapours on Tenax adsorption tubes have been measured by both indirect and direct means. The methods give similar results, and, in general, the simpler indirect method has been employed.

Breakthrough on Tenax varies significantly with flow-rate of sampling. For the geometry of the tubes described here, sampling should ideally be at 50 ml/min, but should in any event be between 5 and 600 ml/min. Breakthrough also varies significantly with vapour concentration, although in the practical range for subsequent desorption (*i.e.* below 100 ppm) deviations are towards larger breakthrough volumes and hence calculated safe sampling volumes still apply. Temperature markedly affects breakthrough (to a first approximation, retention volumes are doubled for each 10° decrease in temperature), and this should be borne in mind when using Table I. Breakthrough is virtually independent of humidity (which is not so for other porous polymers).

Table I lists safe sampling volumes as 50% of the measured retention volume. This factor takes account of reasonable variations in the above parameters, except for temperatures over 20°. Retention volumes for unlisted compounds may be cautiously interpolated from Fig. 6.

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