CHROMSYMP. 2731

Retention characteristics of some volatile compounds on Tenax GR

K. Ventura, M. Dostál and J. Churáček*

Department of Analytical Chemistry, University of Chemical Technology, 532 10 Pardubice (Czech Republic)

ABSTRACT

Breakthrough volumes (maximum sample volumes, V_{max}) of low-molecular-mass compounds on graphite-filled Tenax have been measured. Using Tenax GR the sampling volumes are greater than with Tenax GC or Tenax TA. Tenax GR can be used in environmental analysis for trapping and enriching traces of low-molecular-mass organic compounds.

INTRODUCTION

Tenax TA (GC) is frequently used in environmental analysis as an adsorbent for enriching traces in the ppb (v/v) range [1–4]. Tenax GR is a new adsorbent for trapping low-molecular-mass organic compounds. It consists of Tenax matrix (poly-*p*-2,6-diphenylphenylene oxide) filled with 23% graphite.

To extend the usefulness of sorbents of the Tenax type, the effects of air flow-rate, pollutant concentration and other parameters have been investigated. The most important of these parameters is the estimated column capacity, *i.e.*, the volume of sampled air at which the compound being collected begins to be eluted from the sampling tube [5].

The column capacity depends on the retention time of the compound being sorbed at ambient temperature (using the Tenax stationary phases).

References to the properties and typical applications of Tenax GC and Tenax TA are given in refs. 4 and 6–8. The sources in the literature do not offer any information regarding the properties of Tenax GR.

EXPERIMENTAL

Apparatus

A Chrom 5 gas chromatograph with a flame ionization detector (Laboratorní přístroje, Prague, Czech Republic) was used.

All chemicals (*n*-alkanes, aromatics, alcohols, ketones, esters, amines and halogenated hydrocarbons; see Table I) were of analytical-grade purity and were obtained from Fluka, Merck and Janssen; helium was obtained from Messer Griesheim (Austria), nitrogen from Linde Technoplyn (Prague, Czech Republic), Tenax GR (60–80 mesh) was purchased from Chrompack (Middelburg, Netherlands). The U-shaped glass tested column, 3 mm I.D. with a bed length of sorbent 37 cm (mass 1 g), was homemade and was connected to the injection and detection ports of a gas chromatograph.

Procedure

The glass U column was filled with 1 g of Tenax GR and conditioned using helium as a carrier gas; after 0.5 h at a laboratory temperature the column temperature was programmed at a rate of 2°C min^{-1} from 22 to 250°C, then for 4 h at 250°C. Retention volumes and theoretical plates were determined by injection of 20–40 μl of the vapours of tested compounds saturated at 20°C, *i.e.*, in the

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* Corresponding author.

TABLE I

EXTRAPOLATED SPECIFIC RETENTION VOLUMES AND MAXIMUM SAMPLE VOLUMES FOR ORGANIC VAPOURS SAMPLED ON A 1.0-g TENAX GR ADSORBENT TUBE

A, B = empirical parameters of eqn. 3; N = number of theoretical plates; r = correlation coefficient; V_g^{20} = extrapolated specific retention volume at 20°C; $V_{max.}^{20}$ = maximum sample (breakthrough) volume at 20°C.

Organic compound	Boiling point (°C)	A	B	r	V_g^{20} (l)	N	$V_{max.}^{20}$ (l)
Hexane	68.4	3231.01	−6.55	0.9998	29.4	185	25.1
Heptane	98.3	3607.01	−7.32	0.9995	95.7	250	83.6
Benzene	80.5	3054.62	−5.83	0.9999	39.3	290	34.7
Toluene	110.8	3290.36	−6.01	0.9994	252.3	288	222.6
Xylene(s)	138–144	3827.24	−6.89	0.9974	1464.2	285	1290.7
Dichlormethane	40.7	2342.32	−4.70	0.9994	2.1	390	1.9
Trichlormethane	61.5	2679.50	−5.33	0.9974	7.9	325	7.0
Tetrachlormethane	76.7	2935.44	−5.74	0.9999	18.5	159	15.6
1,2-Dichlorethane	84.1	2917.04	−5.20	0.9989	49.5	405	44.6
Trichloroethylene	86.9	3042.63	−5.50	0.9962	49.0	484	44.5
Tetrachloroethylene	121.0	3262.83	−5.66	0.9992	292.0	561	267.3
Chlorobenzene	131.7	3547.92	−6.50	0.9999	402.6	362	360.3
Ethanol	78.5	2205.99	−4.50	0.9974	1.1	530	1.0
1-Propanol	97.2	2611.49	−5.10	0.9978	6.5	482	5.9
1-Butanol	117.5	3020.85	−5.72	0.9980	38.0	431	34.3
Acetone	56.3	2695.87	−5.58	0.9969	4.4	466	4.0
Methyl-isobutyl ketone	118.0	3714.12	−7.22	0.9993	279.6	131	230.8
Ethylacetate	77.1	3042.94	−6.00	0.9987	23.9	410	21.5
Propylacetate	101.6	3477.10	−6.69	0.9978	149.5	351	133.5
Butylacetate	126.5	3879.96	−7.42	0.9990	646.1	304	572.0
Propylamine	47.8	2471.95	−4.93	0.9947	3.2	442	2.9
Butylamine	77.8	2892.02	−5.54	0.9966	21.0	308	18.6
Pentylamine	104.0	3182.70	−5.90	0.9961	91.3	318	81.1
Diethylamine	56.3	2617.37	−5.10	0.9923	6.8	349	6.1
Dipropylamine	110.0	3491.30	−6.58	0.9974	194.1	264	170.2
Dibutylamine	160.0	4126.93	−7.53	0.9978	3521.0	191	3011.5
Epichlorhydrine	116.5	3062.74	−5.69	0.9997	57.9	949	54.1

range 10^{-6} to 10^{-7} g per injection, at a carrier gas (nitrogen) flow-rate of 20 ml min^{-1}.

Solute retention times were measured at a different temperatures ranging from 160 to 220°C.

RESULTS AND DISCUSSION

Determination of the maximum sample volume

The trapping tubes filled with Tenax GR may be regarded as chromatographic columns. At a given temperature, the vapour of each compound being eluted through the trapping tube is quantitatively adsorbed inside the trap until the gas volume flowing through the tube is equal to the retention volume of that substance less the volume corresponding to the elution of half of the solute band obtained in elution analysis. The maximum sample volume ($V_{max.}$) is given by the following equation [9–11]:

$$V_{max.} = V_R \left(1 - \sqrt{\frac{4}{n}} \right) \qquad (1)$$

To apply this equation, it is necessary to know the retention volume (V_R) and the number of theoretical plates (n) for each substance at trapping temperature.

Combining eqn. 1 with the equation for specific retention volume, the relationship for $V_{max.}$ reads:

$$V_{max.} = \frac{V_g \cdot w_L \cdot T_E \cdot 101.32}{p_B \cdot 273.15} \cdot \left(1 - \sqrt{\frac{4}{n}} \right) \qquad (2)$$
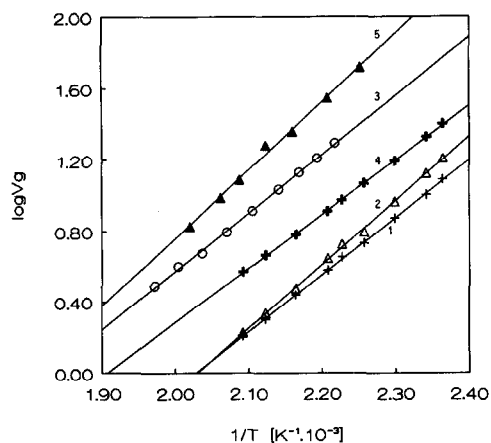
Fig. 1. Plot of log V_g versus reciprocal absolute temperature for hexane (1), heptane (2), toluene (3), benzene (4) and xylene(s) (5).

Fig. 3. Plot of log V_g versus reciprocal absolute temperature for ethyl acetate (1), propyl acetate (2), butyl acetate (3), ethanol (4), 1-propanol (5) and 1-butanol (6).

in which $V_{max.}$ is the volume of sampled gas (= breakthrough volume, often non-accurately called safe sampling volume), V_g is the specific retention volume, T_E is the absolute temperature of exposition (K), p_B is the atmospheric pressure (kPa) and w_L is the mass of sorbent in column tube (g).

It is necessary to apply another model [12] for very low plate numbers.

The maximum sample volumes were then found indirectly from measured solute retention times and the theoretical plates of the adsorbent tube. The amount of vaporized sample injected into the gas chromatograph system was selected in such a way
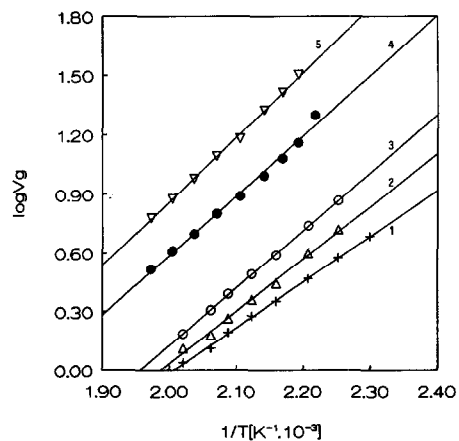
that the relationship between V_R was independent of sample volume (concentration) in the range studied (10^{-6} to 10^{-7} g).

Specific retention volumes at 20°C were estimated by extrapolation from temperature dependence using measured values for temperatures of 160–220°C:

$$\log V_g = \frac{A}{T} + B \qquad (3)$$

where A and B are empirical parameters (see Table I).

Measured dependences for different homologous series of compounds are given in Figs. 1–5. Good

Fig. 2. Plot of log V_g versus reciprocal absolute temperature for dichloromethane (1), trichloromethane (2), tetrachloromethane (3), trichloroethylene (4) and tetrachloroethylene (5).
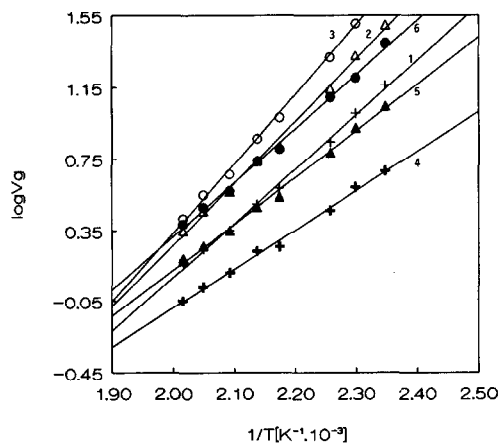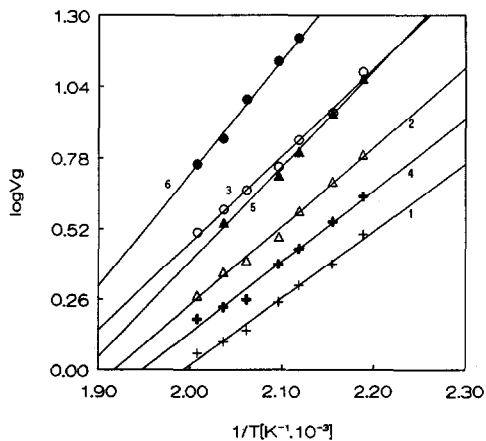

Fig. 4. Plot of log V_g versus reciprocal absolute temperature for propylamine (1), butylamine (2), pentylamine (3), diethylamine (4), dipropylamine (5) and dibutylamine (6).
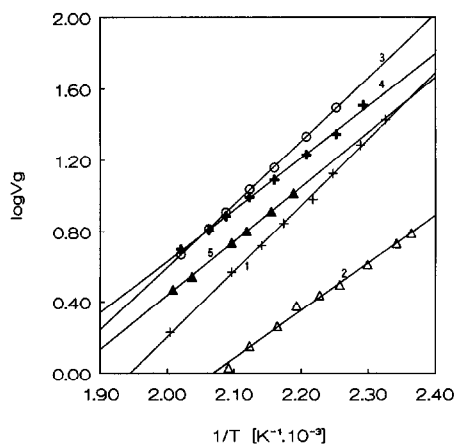
Fig. 5. Plot of log V_g versus reciprocal absolute temperature for methyl isobutyl ketone (1), acetone (2), chlorobenzene (3), 1,2-dichloroethane (4) and epichlorhydrine (5).
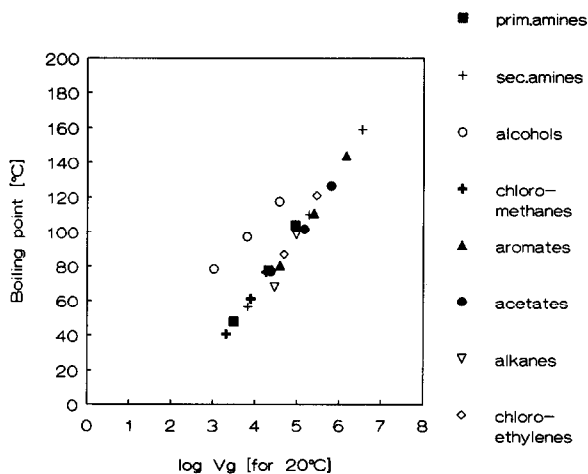

Fig. 6. Log V_g for Tenax GR as a function of boiling point.

linearity was obtained for all investigated compounds, as shown in Table I. Correlation coefficients are better than 0.997 for most of the compounds.

There is a good correlation between the logarithm of specific retention volumes and boiling points [8] of investigated compounds. The correlation for most compounds fits the straight line (Fig. 6), with the exception of aliphatic alcohols.

The flow-rate in the range 10–100 ml min^{-1} did not affect the retention volumes significantly. A flow-rate of 20 ml min^{-1} is sufficient (the minimum of the van Deemter equation is less than 5 ml min^{-1}).

CONCLUSIONS

The maximum sample volumes (V_{max}) for organic vapours of low-molecular-mass compounds on Tenax GR sorption tubes have been measured. Quantitative sample enrichment is limited by the minimal detectable amount of the compounds which must be at least trapped, and thus by the breakthrough volume of the least-retained compound of the sample mixture.

This paper shows the possible use of graphitized Tenax as a trapping material. It has been observed that relatively large sample volumes can be used at ambient temperature for compounds of similar vapour pressure and at very low concentrations. This is usually valid for a great number of atmospheric pollutants. When the sampling volumes of most of the compounds used in the present work are compared with Tenax GC(TA) [4,13], values nearly twice as high are obtained. All the advantages of "Tenax", for example good thermal desorption, are retained.

REFERENCES

1 T. Class and K. Ballschmiter, Fresenius' Z. Anal. Chem., 325 (1986) 1.
2 K. Sakodynsky, L. Panina and N. Klinskaja, Chromatographia, 7 (1974) 339.
3 R. van Wijk, J. Chromatogr. Sci., 8 (1970) 418.
4 I. Maier and M. Fieber, J. High Resolut. Chromatogr. Chromatogr. Commun., 11 (1988) 566.
5 F. C. Poole and S. A. Schuette, Contemporary Practice of Chromatography, Elsevier, Amsterdam, 1984.
6 G. Mac Lead and J. Ames, J. Chromatogr., 355 (1986) 393.
7 A. J. Núñez, L. F. González and J. Janák, J. Chromatogr., 300 (1984) 127.
8 R. H. Brown and C. J. Purnell, J. Chromatogr., 178 (1979) 79.
9 A. Raymond and G. Guiochon, J. Chromatogr. Sci., 13 (1975) 173.
10 T. Tanaka, J. Chromatogr., 153 (1978) 7.
11 J. Namieśnik, Talanta, 35 (1988) 567.
12 P. Lövkvist and J. A. Jönsson, Anal. Chem., 59 (1987) 818.
13 J. F. Pankow, Anal. Chem., 60 (1988) 950.