

Application of solid sorbents to the trace analysis of alkyl esters of acrylic acid in air

K. Ventura^{a,*}, P. Příhoda^b, J. Churáček^a

^a*Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, 532 10 Pardubice, Czech Republic*

^b*Vodohospodářský rozvoj a výstavba Ltd., 150 56 Prague, Czech Republic*

Abstract

Ten sorbents (Tenax GC, Porapak R and S, Chromosorb 102 and 105, DVB–1,4-DMN, Separon SE, CHN and SDA, and Synachrom E5) were tested for (pre)concentration of acrylates present in air. From a study on the applicability and the conditions to be used for both thermal desorption and GC separation, as well as evaluation on the factors influencing these two steps, optimum conditions for both concentration and separation have been estimated. Practical applications of the method for the analysis of the working atmosphere are demonstrated.

1. Introduction

Preconcentration is a basic step in the trace analysis of organic substances in the surrounding air. Trapping of the substances of interest on solid sorbents, especially on porous chromatographic polymers, is of considerable importance [1]. A survey of sorbents used for this purpose has been published by Namiešník [2]. Based on hygiene criteria, methods have to be developed for the determination of gaseous pollutants in the working environment within the concentration range either of 10^{-3} – 10^{-7} g m⁻³, or of 1 – 10^{-4} g m⁻³, depending on the type of the pollutant.

For the selection of the sorbent to be used for the preconcentration of gaseous organic contami-

nants, a high sorption capacity, which determines the maximum sample volume, is not the only criterion. Factors influencing both the course of the sorption process together with the method and results of the analytical determination should also be taken into account [2,3].

Recently, gas chromatography combined with mass spectrometry has become the method of choice for the analysis of acrylic acid esters, when preconcentration is needed [4–7]. The effect of the conditions of the exposure to acrylates and the sorption capacities of Tenax GC [8,9], other polymer sorbents [10,11] and silica gel [12,13] have been studied in actual working environments. Moreover, the determination of low concentrations of acrylic acid esters in air, trapped on chromatographic sorbents covered with a liquid phase, has been described in Refs. [14–17]. Recently a new sorption–derivatization–concentration technique has been described for C₁–C₈ acrylic acid esters [10].

* Corresponding author.

2. Experimental

2.1. Apparatus

A Chrom 5 gas chromatograph equipped with a flame ionization detector (Laboratorní přístroje, Prague, Czech Republic), an Apex chromatographic integrator (DataApex, Prague, Czech Republic), a glass-packed column, 2.5 m × 3 mm I.D., with 10% SP-1000 on Supelcoport 80–100 mesh (Supelco, Bellefonte, PA, USA), a 50- μ l gas-tight microsyringe (Hamilton Reno, NE, USA), Series 222 personal air sampler/low-flow pumps (SKC, PA, USA), thermal desorption equipment (University Pardubice) [18], glass sample tubes (61 × 3 mm I.D.), and U-shaped glass test columns, 3 mm I.D., were used throughout this study.

2.2. Chemicals

The specifications and suppliers of the sorbents and chemicals used are as follows: Tenax GC, 60–80 mesh, Chromosorb 102, 100–120 mesh, Chromosorb 105, 80–100 mesh (Serva Feinbiochemia, Heidelberg, Germany); Porapak R, 80–100 mesh, Porapak S, 120–150 mesh (Waters, Milford, MA, USA); DVB–1,4-DMN copolymer of divinylbenzene with 1,4-di-(methacryloyloxymethyl)naphthalene [19], 200–250 μ m (Institute of Chemistry, M.C.S. University, Lublin, Poland); Separon SE, 200 μ m,

Separon CHN, 200–300 μ m, Separon SDA, 90–125 μ m (Tessek, Prague, Czech Republic); Synachrom E5, 125–160 μ m (Lachema Brno, Czech Republic).

The acrylates were synthesized at the Faculty of Chemical Technology, University of Pardubice.

2.3. Procedure

The U-shaped test columns (TC) and the sample tubes (ST) of identical I.D. differed only in their lengths. The mass of the sorbent filling and the length of its bed are given in Table 1. All sorbents were conditioned. Their thermal stability was investigated by recording the ionization current at the programmed increasing temperature. The maximum sample volumes (V_{\max}) of the tested sorbents were determined by an indirect method [3,18,20,21], based on the specific retention volumes and the number of theoretical plates, followed by extrapolation and calculation. The tested acrylates were fed as calibrated vapours using a gas-tight syringe.

Retention volume measurements were performed by determination of the number of theoretical plates using the test U-column; the height equivalent to the theoretical plate was calculated as well. The plate number of the trapping tube thus found was confirmed actually on the trapping tube at 50°C, a flow-rate of 60 ml min⁻¹ and a load of 4.5 · 10⁻⁷ g g⁻¹.

Table 1

Parameters of test columns and sampling tubes, thermal stability of sorbents, and desorption temperature, BA specific retention volumes at TD, extrapolated specific retention volumes and maximum BA sample volumes at 20°C

	TC m (g) / l (cm)	ST m (g) / l (cm)	TS TD (°C)	V_{μ}^{110} (1 g) BA (ml)	V_{μ}^{20} (1 g) BA (l)	V_{\max}^{20} (1 g) BA (l)	V_{\max}^{20} (ST) BA (l)
Tenax GC	0.7170 61.8	0.0661 5.7	380 200	9.3	1638.9	1583.4	71.2
Porapak R	1.2847 60.5	0.1210 5.7	250 200	99.7	6669.4	6367.3	591.1
Porapak S	0.9540 37.6	0.1446 5.7	250 200	79.3	2151.7	2011.3	220.6
Chromosorb 102	1.5633 57.0	0.1562 5.7	235 200	46.8	1185.4	1122.9	139.7
Chromosorb 105	1.5087 59.0	0.1457 5.7	235 190	91.8	1475.1	1307.5	130.0
DVB–1,4-DMN	1.1395 61.7	0.1053 5.7	250 200	36.0	2495.2	2321.9	166.5
Separon SE	1.5004 53.2	0.1608 5.7	230 190	19.8	1146.8	1032.6	118.4
Separon CHN	0.6005 48.0	0.0713 5.7	225 190	86.3	4828.8	4633.6	223.0
Separon SDA	1.3400 62.0	0.1231 5.7	220 190	21.2	509.4	479.7	43.8
Synachrom E5	0.59225 40.2	0.0840 5.7	195 170	313.3	37637.0	36388.0	2232.3

For trapping of acrylates in real samples from the surrounding air, Tenax GC (0.0661 g) and Separon SE (0.1608 g) were used at a flow-rate of 20 ml min^{-1} . The sample volume was 250–750 ml, at $20 \pm 2^\circ\text{C}$, and the desorption temperature was 190°C .

3. Results and discussion

The sorbents were selected on the basis of experience and literature data with respect to parameters influencing the sorption capacity and their desorption properties, i.e. particularly with respect to polarity, specific surface area and chromatographic background.

From the many commercially available sorbents, Tenax GC was selected, being the most frequently used sorbent with a low chromatographic background, useful for thermal desorption, together with Porapak R and S, Chromosorb 102 and 105 and DVB–1.4-DMN. The locally produced sorbents Separon SE, CHN and SDA and Synachrom were also investigated.

The thermal stability of the sorbents is given in Table 1. It was verified that, with insufficient conditioning, the plot of $\log V_g$ versus the reciprocal of the absolute temperature is not linear and the values of V_g are lower; at the same time the level of the chromatographic background is higher.

For preliminary testing of the properties of the sorbents used, butyl acrylate (BA) was selected from its homologous series. Retention volumes were measured at temperatures between 120 and 220°C (Fig. 1). By extrapolation to the sampling temperature, i.e. 20°C , values for the specific retention volume, V_g^{20} , were obtained. Comparison of the sorbents in terms of V_g^{20} as measured under comparable conditions for flow-rate and sorbent loading is given in Table 1.

As the specific retention volume is significantly affected by the quantity of gaseous sorbate, a factor known as loading of the sorbent, Z (g g^{-1}), was applied, expressing the mass of a sorbate sorbed by the unit mass of the sorbent. The retention volumes were measured on all

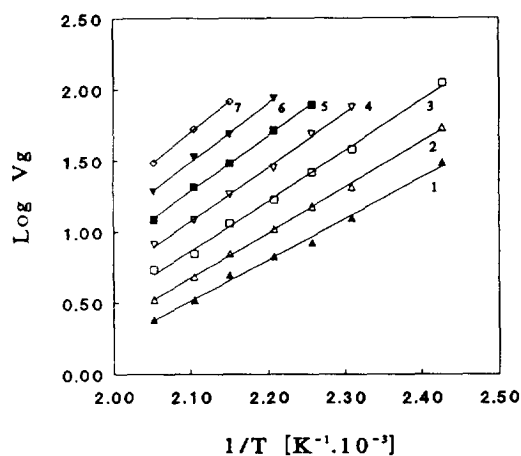


Fig. 1. Plot of $\log V_g$ versus the reciprocal of the absolute temperature for methyl acrylate (1), ethyl acrylate (2), propyl acrylate (3), butyl acrylate (4), pentyl acrylate (5), hexyl acrylate (6) and heptyl acrylate (7) on Separon SE.

sorbents at different sample volumes and, consequently, for different quantities of sorbate in the gas phase (Figs. 2 and 3, Table 2).

The results show that: the V_g^{20} values are almost constant up to $Z = 10^{-5} \text{ g g}^{-1}$; however, with Z increasing beyond this value the specific retention volume on all sorbents significantly decreases (Fig. 3).

The dependence of $\log V_g$ on the boiling points of the homologous series of acrylates is linear

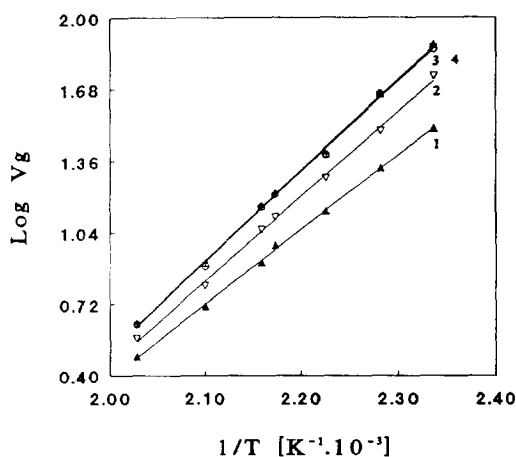


Fig. 2. $\log V_g = AT^{-1} + B$ for BA on Tenax GC as a function of sorbent loading factor (Z , g g^{-1}). Z -values: $3.80 \cdot 10^{-1}$ (1), $1.27 \cdot 10^{-2}$ (2), $1.27 \cdot 10^{-5}$ (3) and $8.16 \cdot 10^{-7}$ (4).

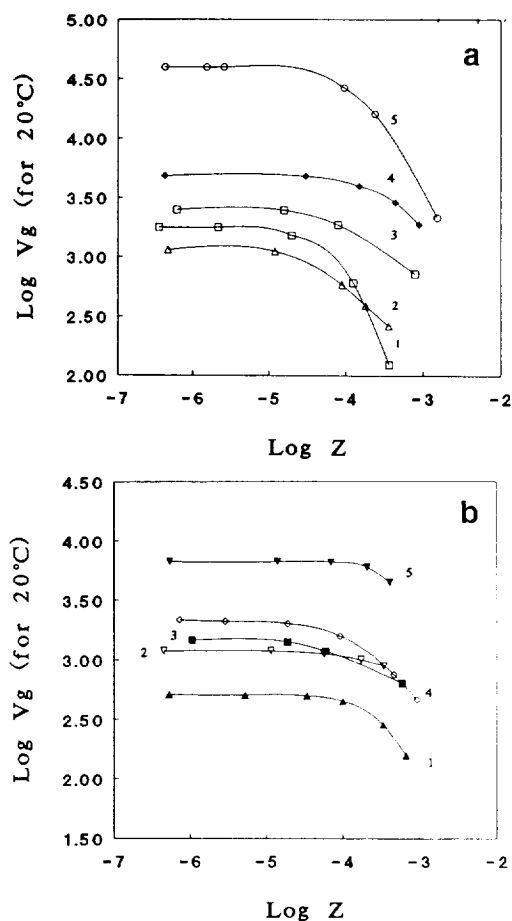


Fig. 3. (a) BA specific retention volume V_g^{20} as a function of sorbent loading factor Z for test sorbents Tenax GC (1), Separon SE (2), DVB-1,4-DMN (3), Separon CHN (4) and Synachrom E5 (5). (b) BA specific retention volume V_g^{20} as a function of sorbent loading factor Z for test sorbents Separon SDA (1), Chromosorb 102 (2), Chromosorb 105 (3), Porapak S (4) and Porapak R (5).

(correlation coefficient $r > 0.9965$), and this can be used to check and estimate the retention volume of the sorbents. The dependencies for Tenax GC, Separon SE and Separon CHN are shown in Fig. 4.

Maximum sorption is obtained at the "optimum linear flow-rate". The minimum of the Van Deemter dependence corresponds to low flow-rates and in all sorbents investigated it was less than 5 cm s^{-1} . Flow-rates in the range $10\text{--}100 \text{ ml min}^{-1}$ did not affect the retention vol-

umes significantly. The selected flow-rate of 60 ml min^{-1} permitted measurements under comparable conditions for all sorbents investigated, also for the higher members of the homologous series of acrylates, which had very long retention times with low flow-rates.

For the determination of V_{max} , a method based on measuring V_g and n [2,20–22] was selected. V_{max} values were determined for a completely filled sampling tube (ST) and for identical amounts of the sorbents (1 g; Table 1).

The number of theoretical plates of the sampling tube [$n(\text{ST})$] and of the column containing 1 g of sorbent [$n(1 \text{ g})$] was determined in a similar way. First of all, n was determined for the test column [$n(\text{TC})$], followed by measuring V_g^{20} , and the height equivalent to the theoretical plate, H . On this basis [$n(\text{ST})$] and [$n(1 \text{ g})$] values were determined.

The number of theoretical plates of the sampling tube [$n(\text{ST})$], with EA and BA as samples on Tenax GC and Separon SE, was verified by means of measurements on a bed of sorbent corresponding to that of the sampling tube. When identical conditions (sorbent load and carrier gas flow) were employed in the two procedures, the corresponding mean values for $n(\text{ST})$ showed differences within the limits of 10 and 20%.

To verify the calculated V_{max} values the maximum sample volumes of the sampling tube were measured using direct gas chromatographic measurement in the systems Tenax GC vs. EA and Separon vs. EA. Measurement was carried out at 50°C , because at lower temperatures chromatography was very slow due to the long retention times, and it was not possible to determine the exact breakthrough point. The calculated maximum sample volume for Tenax GC was 400 ml, as compared to a measured value of 535 ml; for Separon SE these values were 950 and 850 ml, respectively. If the maximum sample (breakthrough) volume is defined as the volume at which the sorbate starts to penetrate through the sorbent bed, then at a 10% breakthrough for EA the volume passed through corresponds to 1.7 times the V_{max} for Tenax GC and 1.5 times the V_{max} for Separon SE. Brown [10] gives a safe

Table 2
Number of plates of test column $n(\text{TC})$, height equivalent to a theoretical plate H , number of plates of sampling tube $n(\text{ST})$, number of plates of sampling tube with 1 g of sorbent $n(1 \text{ g})$, their maximum sample volumes $V_{\text{max}}(\text{ST})$, $V_{\text{max}}(1 \text{ g})$ at 20°C, specific retention volume V_g^{20} and these parameters as a function of sorbent loading Z for BA

Z (g g^{-1})	$n(\text{TC})$	H (mm)	$n(\text{ST})$	$n(1 \text{ g})$	V_g^{20} (l)	$V_{\text{max}}(\text{ST})$ (l)	$V_{\text{max}}(1 \text{ g})$ (l)
<i>Tenax GC</i>							
$3.56 \cdot 10^{-7}$	288.2	2.14	26.6	402.0	1638.9	71.2	1583.4
$2.12 \cdot 10^{-6}$	286.5	2.16	26.4	399.6	1632.5	70.7	1576.7
$2.51 \cdot 10^{-5}$	257.8	2.40	23.8	359.6	1515.4	63.4	1454.8
$1.25 \cdot 10^{-4}$	226.2	2.73	20.9	315.5	606.7	24.2	577.8
$3.76 \cdot 10^{-4}$	197.9	3.12	18.2	276.0	123.0	4.6	116.1
<i>Separon CHN</i>							
$4.25 \cdot 10^{-7}$	214.2	2.24	25.4	356.7	4828.8	223.0	4633.6
$3.00 \cdot 10^{-6}$	186.9	2.57	22.2	311.2	4810.0	211.8	4577.0
$1.50 \cdot 10^{-4}$	156.3	3.07	18.6	260.3	3950.1	161.9	3713.8
$4.49 \cdot 10^{-4}$	123.7	3.88	14.7	206.0	2879.8	105.4	2660.0
$8.99 \cdot 10^{-4}$	92.1	5.21	10.9	153.4	1872.7	56.6	1685.2

sampling volume per gram of Tenax GC for MA (32 l) and EA (120 l). The values measured in our laboratories are lower: 22.7 l for MA and 80 l for EA (Table 3).

For comparison of sorbents with respect to their suitability for thermal desorption, specific retention volumes were determined for BA at the recommended desorption temperature, which ranged from 30 to 50°C below the value of

the thermal stability (Table 1). Before heating is started, air should be removed from the sorbent since, in the presence of oxygen, rapid degradation of otherwise thermally stable polymer sorbents occurs. The efficiency of desorption depends not only upon the type of the desorbed substances, but also on the quantity of analytes entrapped in the sorbent bed.

For liberating acrylates concentrated upon Synachrom E5, carbon disulphide desorption is preferable because of the high chromatographic background at thermal desorption. By using the method described, concentrations of 2-ethylhexyl acrylate [$V_{\text{max}}^{20}(\text{ST}) > 2232.3 \text{ l}$] in the air above unhardened floors (20–50 mg m^{-3}) and above hardened and mature floors (0.005–0.060 mg m^{-3}) were estimated. The relative standard deviation of the determination in five parallel samples was 15%.

The method was used in practice for checking ethyl acrylate concentrations in monomer storage facilities. With Tenax GC and Separon SE and thermal desorption, concentrations varying between 0.01 and 0.48 mg m^{-3} were obtained under various trapping conditions.

Sorption of acrylates from gas-phase trapping tubes filled with polymer sorbents with subsequent thermal desorption is also suitable for

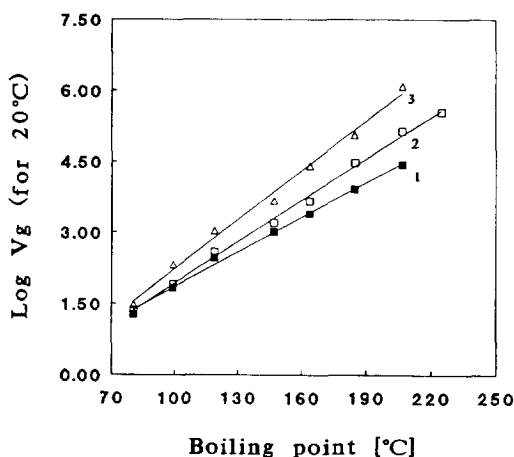


Fig. 4. $\text{Log } V_g$ for Separon SE (1), Tenax GC (2) and Separon CHN (3) as a function of boiling point.

Table 3

Maximum sample volumes of acrylates for 1 gram of sorbent and sampling tube: the upper value is V_{\max}^{20} (1 g) (l) and the lower value is V_{\max}^{20} (ST) (l)

	MA	EA	PrA	BA	PeA	HexA	HepA	OcA
Tenax GC	22.7 1.2	80.0 4.1	386.2 18.9	1583.4 71.2	4540.1 196.4	30075 1243.0	139916 5720.7	350722 13754
Separon SE	18.7 2.3	64.4 8.2	293.8 35.2	1032.6 118.4	2458.9 252.9	8204.2 815.4	27385 2555.8	
Separon CHN	30.3 1.7	207.9 11.7	1075.6 58.7	4633.6 223.0	25741 1165.2	116219 4745.7		

Experimental conditions: $F = 60 \text{ ml min}^{-1}$, $Z (10^{-7}; 10^{-6}) \text{ g g}^{-1}$

head-space analyses of aqueous acrylates solutions.

V_{g}^{20} specific retention volume at 20°C (l)
 V_{\max}^{20} maximum sample (breakthrough) volume at 20°C (l)
 Z sorbent loading factor (g g^{-1})

Acknowledgements

This work was accomplished with the financial support of the Grant Agency of the Czech Republic, reg. number 203/93/2157.

List of symbols and abbreviations

BA butyl acrylate
 EA ethyl acrylate
 F flow-rate (ml min^{-1})
 H height equivalent to a theoretical plate (mm)
 HepA heptyl acrylate
 HexA hexyl acrylate
 l length (cm)
 m mass of sorbent (g)
 MA methyl acrylate
 n number of theoretical plates
 OcA octyl acrylate
 PeA pentyl acrylate
 PrA propyl acrylate
 ST sampling tube
 T temperature (K)
 TC test column
 TD maximum recommended desorption temperature ($^{\circ}\text{C}$)
 TS thermal stability ($^{\circ}\text{C}$)

References

- [1] A.J. Núñez, L.F. González and J. Janák, J. Chromatogr., 300 (1984) 127.
- [2] J. Namiešník, Talanta, 35 (1988) 567.
- [3] F.C. Poole and S.A. Schuette, Contemporary Practice of Chromatography, Elsevier, Amsterdam, 1984.
- [4] J.K. Haken and D. Srisukh, J. Chromatogr., 219 (1981) 45.
- [5] J.R. Ashes and J.K. Haken, J. Chromatogr., 111 (1975) 171.
- [6] A. Horna, J. Táborský, J. Churáček and O. Dufka, J. Chromatogr., 348 (1985) 141.
- [7] A. Horna, J. Táborský and J. Churáček, J. Chromatogr., 360 (1986) 89.
- [8] K.J. Krost, E.D. Pellizzari, S.G. Walburn and S.H. Hubbard, Anal. Chem., 54 (1982) 810.
- [9] R.H. Brown and C.J. Purnell, J. Chromatogr., 178 (1979) 79.
- [10] J. Churáček, H. Pechová, A. Horna, R. Kotrla and K. Ventura, J. Chromatogr., 557 (1991) 523.
- [11] J. Namiešník, L. Torres, E. Kozłowski and J. Mathieu, J. Chromatogr., 208 (1981) 239.
- [12] W.J. Vincent and V. Guient Jr., Am. Ind. Hyg. Assoc. J., 43 (1982) 499.
- [13] M.W. Bosserman and N.H. Ketcham, Am. Ind. Hyg. Assoc. J., 41 (1980) 20.
- [14] M.T. Dmitriev, E.A. Komrakova and J.P. Tichomirov, Gig. Sanit., 11 (1984) 59.
- [15] N.S. Podkovyrina, L.A. Shumkova and E.D. Tsybyshev, Gig. Tr. Prof. Zabol., 2 (1981) 45.

- [16] E.A. Komrakova and L.V. Kuznetsova, *Gig. Sanit.*, 1 (1981) 43.
- [17] G.N. Kotov, A.A. Evstratov, A.F. Tubolkin and A.I. Ginak, *Gig. Sanit.*, 5 (1982) 57.
- [18] K. Ventura, K. Svobodová, M. Dostál and J. Churáček, *Collect. Czech. Chem. Commun.*, 59 (1994) 2415.
- [19] B. Gawdzik and T. Matynia, *React. Polym.*, 5 (1987) 197.
- [20] K. Ventura, M. Dostál and J. Churáček, *J. Chromatogr.*, 642 (1993) 379.
- [21] M. Dostál, K. Ventura and L. Průdek, *Chem. Listy*, 87 (1993) 814.
- [22] A. Raymond and G. Guiochon, *J. Chromatogr. Sci.*, 13 (1975) 173.