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## Evaluation of a new graphitized carbon black employed in sampling volatile organic compounds

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### Abstract

A new adsorbent, high-surface-area graphitized carbon black (HSGCB), with a surface area of 560 m<sup>2</sup>/g, superior to that of commonly traded graphitized carbons, was studied. The evaluation was performed in terms of breakthrough volumes and thermal desorption recoveries of substances representative of the main classes of organic compounds. HSGCB was found to be an interesting alternative to activated charcoal for volatile compounds in that it can be used in thermal desorption. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Graphitized carbon black; Adsorbents; Sample preparation; Thermal desorption; Breakthrough volumes; Volatile organic compounds

### 1. Introduction

One of the most convenient and widely employed preconcentration methods for the evaluation of trace volatile pollutants in the environment and in the workplace is adsorption on a solid adsorbent. Generally made of glass or metal tubing, the so-called 'trap' holds the compounds to be analysed in a precise air volume. The desorption step can be performed by heating (thermal desorption) or by solvent extraction [1–14]. The choice of the adsorbent(s) is critical and requires a good knowledge of the adsorbent properties [14–18].

In the present study a new high-surface-area graphitized carbon black (HSGCB, 560 m<sup>2</sup>/g) was evaluated in terms of breakthrough volumes (BTVs), desorption recoveries of substances representative of

the main classes of organic compounds and effect of water on retention and on desorption recoveries. The ability of this graphitized carbon black to trap compounds of different volatility and polarity, especially low-boiling compounds, led us to suppose that it could be a good substitute for other commonly employed materials such as Carbosieve and activated charcoal. In fact, many of the compounds examined are released from HSGCB by the thermal desorption method with satisfactory recoveries.

On the contrary, thermal desorption of analytes from activated charcoal presents some difficulties due to the catalytic activity of activated carbons, which may cause some decomposition of analyzed compounds, and to the slow desorption of analytes because of specific sorbent–solute interactions. As a consequence of this latter phenomenon, some compounds could be irreversibly adsorbed and the temperature required for desorption could be so high as to cause many compounds to decompose. As a

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consequence, the desorption step must usually be performed with solvent extraction, in most cases with carbon sulphide. With this method the sample analysis can be repeated [3], which can be particularly useful for the analysis of unknown samples. However, very volatile compounds can evaporate during the extraction step or be covered by the solvent peak. Polar and less volatile compounds can be so strongly adsorbed that the solvent is unable to extract them, and polar compound recoveries are affected by water [19]. The method is less sensitive than thermal desorption because the use of solvent implies sample dilution.

Therefore, this new trapping material can be employed, followed by thermal desorption, for organic compounds too volatile for traditionally used adsorbents such as Tenax or graphitized carbon blacks.

## 2. Experimental

### 2.1. Gas chromatographic measurements of breakthrough volumes

Retention volumes were determined with a DANI

86.10 gas chromatograph equipped with a flame ionization detector (FID) and connected to a glass column (1 m×2 mm I.D.) packed with 1.76 g of HSGCB (0.250–0.170 mm) supplied by Carbochimica Romana (experimental samples) or with 1.19 g of Carbo-pack B (0.250–0.170 mm) from Supelco (Bellefonte, PA, USA). Both adsorbents were conditioned for 48 h at 300°C before use with nitrogen gas flowing through at 25 ml/min. The compounds tested and the corresponding BTVs are reported in Table 1.

For acetylene, ethylene and ethane the BTV values were measured directly at 20°C and calculated as the retention volumes ( $V_g$ ) [20]. For the other compounds examined the BTVs were calculated as the retention volumes at 20°C extrapolated from the plot of  $\log V_g$  vs.  $1/T$  [18,21,22]. Three determinations were repeated at six different temperatures ranging from 40°C to 320°C. The difference between the maximum and minimum temperature used was at least 50°C.

Gas standard (100  $\mu$ l) was injected into the gas chromatograph. The gas standard was prepared by loading a 0.5-l glass flask, previously evacuated with a rotary pump, with 2.5  $\mu$ l of each liquid compound or with 250  $\mu$ l of gaseous compounds. Before use,

Table 1  
Approximate breakthrough volumes of organic vapours measured at 20°C with the direct and GC methods

Compound	HSGCB (0.250–0.170 mm)		Carbo-pack B (0.250–0.170 mm)	
	$V_g$ (l g <sup>-1</sup> )		$V_g$ (l g <sup>-1</sup> )	
	GC	Direct	GC	Direct
Acetylene	0.020	0.021	NR	NR
Ethylene	0.045	0.051	NR	NR
Ethane	0.080	0.104	NR	NR
Propane	2.4 <sup>a</sup>	2.70 <sup>a</sup>	0.16 <sup>c</sup>	0.14
Ethanol	3.6 <sup>a</sup>	–	0.24 <sup>c</sup>	0.48 <sup>c</sup>
Propylene oxide	11.0 <sup>a</sup>	–	0.78 <sup>c</sup>	0.52 <sup>c</sup>
Acetonitrile	3.4 <sup>a</sup>	–	0.22 <sup>c</sup>	0.50 <sup>c</sup>
Methanol	0.6 <sup>a</sup>	–	0.02	–
Acetone	55.0 <sup>a</sup>	–	1.6 <sup>a</sup>	–
Vinyl chloride	4.2 <sup>a</sup>	4.80 <sup>a</sup>	0.14	0.22
Pentane	–	3.2·10 <sup>3a</sup>	11 <sup>a</sup>	–
Hexane	–	3.0·10 <sup>4a</sup>	1252 <sup>c</sup>	50 <sup>c</sup>
Pentane <sup>b</sup>	–	5.6·10 <sup>2a</sup>	–	–
Hexane <sup>b</sup>	–	4.7·10 <sup>3a</sup>	–	–

<sup>a</sup> Extrapolated to 20°C

<sup>b</sup> Compounds were injected simultaneously.

<sup>c</sup> See [18].

NR, not retained.

the glass flask was brought to atmospheric pressure with nitrogen.

## 2.2. Direct measurements of breakthrough volumes

BTVs were measured by drawing a standard atmosphere of each organic compound through the GC column at a flow-rate of 50 ml/min and monitoring the effluent with a FID. Retention volumes were determined with a DANI 86.10 GC equipped with a FID and connected to a glass column (1 m×2 mm I.D.) packed with 1.76 g of HSGCB (0.250–0.170 mm) or with 1.19 g of Carbopack B (0.250–0.170 mm). For pentane and hexane with HSGCB, a metal tube (10 cm×2 mm I.D.) filled with 200 mg of adsorbent was used instead of the 1-m column. Both the column and the metal tube were conditioned before use at 300°C for 48 h with nitrogen gas flowing through at 25 ml/min. Standard atmospheres of acetylene, ethylene, ethane, propane and vinyl chloride were generated by drawing the carrier gas (ultrapure nitrogen) containing 10 ppm (parts per million v/v) of each compound to be monitored directly into the column. The cylinders containing 10 ppm of each compound were prepared upon our request by Rivoira (Florence, Italy). The column or the tube containing the adsorbent and maintained at

20°C was first supplied with pure nitrogen, after which a two-way valve was switched and a known flow of nitrogen (30 ml/min) containing the compounds to be examined was used to substitute the carrier gas. The time that elapsed from the moment the valve was switched to the inflection point of the detector response curve was taken as the breakthrough time which, multiplied by the flow-rate, gave the breakthrough volume.

For pentane and hexane the standard atmospheres were generated using permeation tubes [23].

## 2.3. Desorption recoveries

A Carlo Erba 4300 gas chromatograph equipped with a flame ionization detector was employed. A model 890 thermal desorber manufactured by Dynatherm Analytical Instruments for Supelco was connected to the GC column with a capillary tube (transfer line) maintained at 230°C.

For the compounds listed in Table 2A and C a glass column (2 m×2 mm I.D.) was employed, packed with Carbopack B AW (0.170–0.125 mm)+6.6% poly(ethylene glycol) (PEG) at the following conditions respectively: 30°C for 5 min then 10°C/min to 150°C; 30°C for 4 min then 30°C/min to 200°C. For the compounds listed in Table 2B, a glass

Table 2

Recovery (%) of organic compounds in dry atmosphere and in 80% relative humidity from HSGCB (0.250–0.170 mm) thermally desorbed at 300°C for 3 min

Column	Compound	0% Relative humidity		80% Relative humidity	
		Recovery (%)	R.S.D.(%)	Recovery (%)	R.S.D. (%)
A	Propylene oxide	93	1	83	15
	Acetone	100	3	89	6
	Methanol	100	1	102	4
	Ethanol	98	3	93	5
	Acetonitrile	100	3	95	4
	Methylethyl ketone	98	2	96	5
B	Benzene	100	2	90	4
	Toluene	99	2	91	3
	Ethylbenzene	98	4	89	4
	<i>o</i> -Xylene	100	3	98	5
C	Hexane	99	5	97	4
	$\alpha$ -Pinene	92	2	90	5
	1,3,5-Trimethylbenzene	90	4	93	4
	<i>n</i> -C <sub>10</sub>	100	9	99	6
	<i>n</i> -C <sub>12</sub>	84	12	86	10

**Table 3**  
Recovery (%) of organic compounds from HSGCB (0.250–0.170 mm) thermally desorbed at 350°C for 3 min at 300°C for 3 min or 6 min and at 200°C for 3 or 6 min

Compound	HSGCB											
	350°C, 3 min		300°C, 3 min		300°C, 6 min		200°C, 3 min		200°C, 6 min		+4% Carbowax 20M 200°C, 6 min	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
2-Methoxy ethanol	67	9	75	7	75	9	38	9	55	10	92	4
<i>t</i> -Butyl acetate	65	9	62	8	72	10	40	10	73	10	92	5
Ethyl acetate	101	5	81	7	105	5	46	8	75	8	92	4
Methoxypropanol	70	9	78	9	80	7	42	7	54	7	93	6
3-Methyl-2-pentanone	104	7	84	9	105	6	44	8	46	9	91	5
2-Ethoxyethyl acetate	45	10	74	8	85	7	37	7	52	9	100	3
2-Butoxyethanol	58	10	62	10	71	11	22	8	36	9	92	4

column (2 m×2 mm I.D.) packed with Carbo-pack C (0.170–0.125 mm)+0.2% PEG 1500 was employed at 150°C for 3 min then 20°C/min to 200°C. For compounds in Table 3, a graphite layer open tubular (GLOT) capillary column (30 m×0.53 mm I.D.) filled with Carbo-pack B+Carbowax 1500 [24] was employed. The oven temperature was 30°C for 3 min then 20°C/min to 160°C. The glass traps (11.8 cm×6 mm O.D.×3 mm I.D.) were laboratory-made out of glass tubing and filled with 300 mg of adsorbent (HSGCB). The traps were conditioned at 300°C for 48 h with nitrogen gas at a flow-rate of 25 ml/min, tested before use, then loaded by injecting 200 µl of a standard mixture at the concentration of 5 ppm under a 10 ml/min stream of nitrogen for 6 min and desorbed at 300°C for 3 min under a stream of nitrogen at 30 ml/min and 5 ml/min for the packed and capillary columns, respectively. The compounds reported in Table 2 were examined in a dry atmosphere and in 80% humidity. The gas standard was prepared by loading a 0.5-l glass flask, previously evacuated with a rotary pump, with 2.5 µl of each liquid compound or with 250 µl of gaseous compounds. Eighty percent humidity at 20°C was simulated by injecting 7 µl of water into the 0.5-l glass flask together with the compounds to be examined. Before use, the flask was brought to atmospheric pressure with nitrogen.

Table 3 reports the recoveries obtained by desorbing a trap of HSGCB at 350°C for 3 min, 300°C for 3 min and 300°C for 6 min; the same trap at 200°C for 3 min, at 200°C for 6 min and from a trap containing the same amount of HSGCB covered with 4% Carbowax 20M desorbed at 200°C for 3 min. The compounds in Table 3 were cryo-focused ahead of the column with dry ice.

The loading procedure was carried out using the sample desorber apparatus switched to the sample preparation mode. The traps were immediately analysed and the recoveries calculated by comparison with 200 µl of the same sample injected into an empty glass tube in the thermal desorber connected to the gas chromatograph.

### 3. Results and discussion

Fig. 1a–c show the chromatograms of some

volatile compounds with the relative retention times and GC conditions.

The chromatographic column used for the separation of the mixtures examined was packed with the adsorbent to be tested, HSGCB (0.250–0.170 mm). From the retention times and from the GC conditions it is evident that even very volatile compounds were strongly retained, demonstrating the great adsorption capacity of the graphitized carbon black.

Table 1 reports the BTVs calculated on HSGCB and Carbo-pack B with GC and direct methods. The former are values at infinite dilution, that is, calculated under conditions that differ greatly from those occurring in real air sampling, but useful for a theoretical evaluation. The direct method gives values closer to real sampling conditions [25]. The concentration of standard used for direct measurements (5 ppm) was on the order of the concentration in the workplace. It can be noted that, as expected, HSGCB BTVs are higher. This is partly due to its greater surface area, but this is not sufficient to explain its greater sampling capacity, given the surface area ratio of 560/100=5.6, which is less than the BTV ratio for each compound on the two graphitized carbon blacks. Therefore, the greater adsorption capacity has to be attributed in part to the presence of chemically active atoms or to irregularities such as pores in the carbon surface [26]. In fact, the presence of such impurities, although reduced by heat treatment, is known to be responsible for the different BTVs of graphitized carbon blacks with the same surface area [18]. The difference in BTVs is particularly noteworthy for compounds such as vinyl chloride, methanol, acetonitrile, propylene oxide and propane. The BTVs of these compounds on HSGCB are large enough to allow the use of this material in air sampling instead of activated charcoal. It is interesting that even compounds such as acetylene, ethylene and ethane were slightly retained by this adsorbent. For pentane and hexane the BTVs were calculated both separately and together with the direct method to verify the variation found when both compounds were present in the gaseous atmosphere. As expected, the BTVs of pentane and hexane, when calculated separately for each compound, were greater than those obtained when both the compounds were present in a gaseous mixture [21].

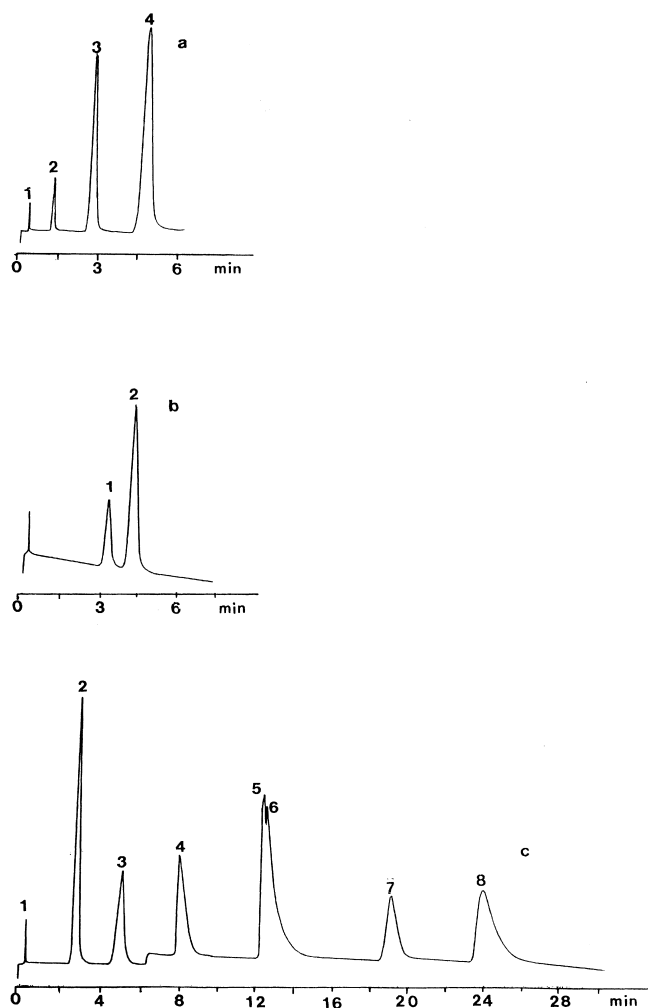


Fig. 1. Chromatographic separation of the following mixtures of volatile compounds on an HSGCB 0.250–0.170 mm (1 m×2 mm I.D.) column: (a) 1=methane, 2=acetylene, 3=ethylene, 4=ethane; column temperature: 30°C; (b) 1=propane, 2=vinyl chloride; column temperature: 120°C for 1 min, then to 150°C at 2°C/min; (c) 1=methane, 2=ethylene, 3=methanol, 4=propane, 5=ethanol, 6=acetonitrile, 7=propylene oxide, 8=acetone; column temperature: 30°C for 5 min then to 120°C at 25°C/min, then to 150°C at 2°C/min

The HSGCB was then tested in order to determine whether water was retained, which would affect retention behaviour. When two (or more) compounds simultaneously present in a mixture are both well retained by the same adsorbent, their BTVs change. The effect of mutual deactivation is similar to the well-known decrease in the capacity ratio,  $k'$ , with the percentage of the stationary phase observed in gas–liquid–solid chromatography with graphitized carbon blacks. Compounds with very low BTVs show a very slight deactivating effect which is only

present at extremely low concentrations of the eluted compounds, such as those occurring when the BTV is calculated from the retention volumes (GC method) and for compounds of low molecular mass [21]. The BTV of water calculated on HSGCB with the GC method was 0.003 l/g, which is very low [27]. The effect of water evaluated by examining the change in retention times of a mixture of volatile compounds before and after the injection of water is illustrated in Fig. 2, which shows the chromatograms obtained by injecting a mixture of methanol, ethanol,

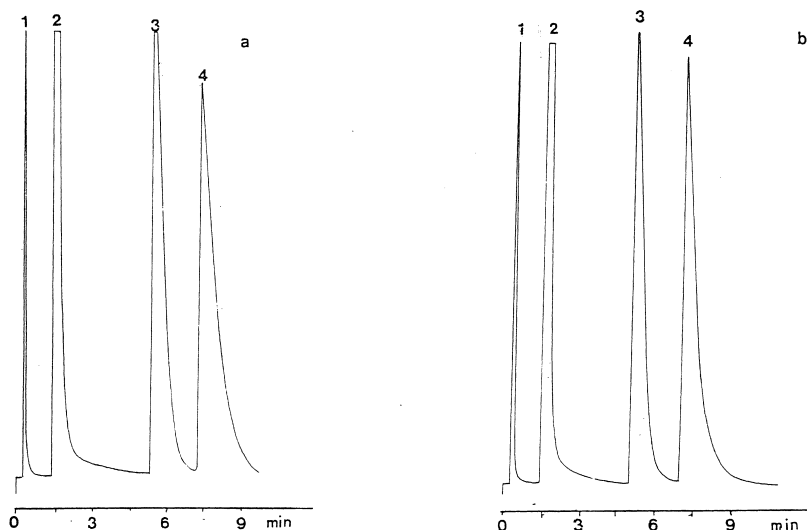


Fig. 2. Chromatographic separation of the following mixture of volatile compounds on an HSGCB 0.250–0.170 mm (1 m×2 mm I.D.) column before injection of 10 µl water: (a) 1=methanol, 2=ethanol, 3=propylene oxide, 4=acetone, column temperature: 120°C for 1 min then to 150°C at 2°C/min; (b) The same separation after injection of 10 µl of water.

propylene oxide and acetone before and after injection of 10 µl of water at 120°C for 1 min, then to 150°C at 2°C/min. The retention times for the mixture and, as a consequence, the BTVs did not change significantly. The propylene oxide peak probably underwent a partial decomposition after water injection due to reaction with the water. The same test was performed by injecting a mixture of acetylene, ethylene and ethane at 30°C in isothermal conditions before and after 10 µl of water. The retention times did not change significantly in this case either (Fig. 3).

Finally, the effects of water were tested by evaluating, at 20°C and 80% humidity, the capacity of HSGCB to adsorb water [28]. The adsorption capacity for water was 10 mg/g, which is higher than those of traditional graphitized carbons (2–3 mg/g), but much lower than the adsorption capacity of molecular sieves.

In Figs. 1 and 2 the peaks of polar compounds show significant tailing, as expected. Each carbon sorbent, although graphitized, still presents some 'active sites'. It is probable that chemical heterogeneities present on the carbon surface are partially reformed during cooling after graphitization [14]. Therefore, for chromatographic purposes, a

liquid phase needs to be introduced as 'tail reducer' [29,30].

The aim of this work was the study of HSGCB as trapping material. The adsorbent needed to be tested to verify that such 'active sites' do not cause irreversible adsorption or decomposition of the compounds of interest when employed as trapping material. The HSGCB was also tested in terms of desorption recoveries, and the results obtained are reported in Tables 2 and 3. Table 2 also reports the

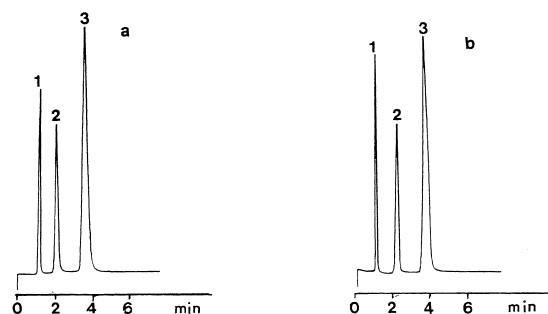


Fig. 3. Chromatographic separation of the following mixture of volatile compounds on an HSGCB 0.250–0.170 mm (1 m×2 mm I.D.) column before injection of 10 µl of water: (a) 1=acetylene, 2=ethylene, 3=ethane; column temperature: 30°C; (b) same separation after injection of 10 µl of water.

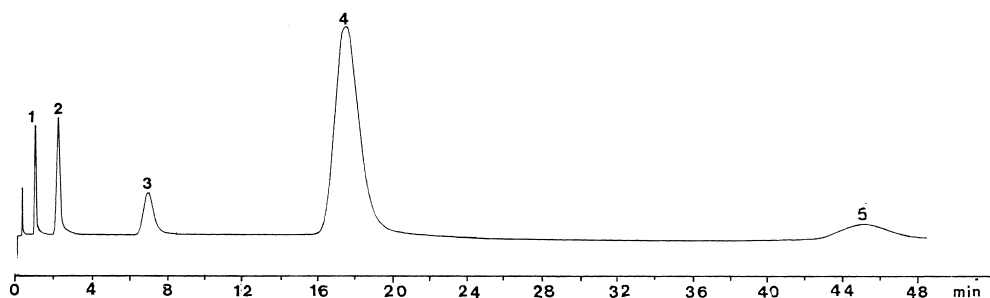


Fig. 4. Chromatographic separation of the following mixture of amines on an HSGCB (0.250–0.170 mm)+0.8% KOH+4% Carbowax 20M (1 m×2 mm I.D.) column: 1=*n*-butylamine, 2=*n*-pentylamine, 3=*n*-hexylamine, 4=*n*-heptylamine, 5=*n*-octylamine; column temperature: 200°C.

recoveries obtained by desorbing the same compounds from HSGCB in the presence of 80% humidity. Water did not affect the recoveries except for that of propylene oxide which probably partially decomposes in the presence of water, thus giving a lower recovery and a higher R.S.D.

Complete recoveries were obtained for many compounds representative of the main classes of organic compounds. However, the compounds reported in Table 3 had lower recoveries. A higher desorption temperature (350°C) and a longer desorption time (6 min) were tested to verify that the desorption was complete. Two compounds, ethyl acetate and 3-methyl-2-pentanone, showed an improved recovery. However, the higher temperature may cause some decomposition. In fact, slightly lower recoveries were found for alkoxy compounds (2 methoxyethanol, methoxypropanol, 2-butoxyethanol) and *tert*-butyl acetate at 350°C than at 300°C. However, these compounds showed a slight increase in recovery with a desorption time of 6 min. An even longer desorption time did not yield further improvement. At 300–350°C some decomposition also occurred, as already observed for *tert*-butyl acetate on other graphitized carbon blacks [18]. This phenomenon was probably catalyzed by metal atoms or other impurities present on the adsorbent surface. Therefore, in order to reduce the decomposition phenomena a modified trap (see Table 3) was used in which the HSGCB was covered with 4% Carbowax 20M, a liquid phase which homogenized the carbon surface by covering active sites present on it. In this case, recoveries rose to about 90%.

The trap modified with Carbowax 20M was not

desorbed at temperatures higher than 200°C in order to avoid the liquid phase bleeding. The trap with HSGCB was desorbed at the same temperature (200°C) as the trap covered with Carbowax in order to verify that the better results were not due to a lesser degree of decomposition at lower temperatures.

As expected the recoveries at 200°C with a

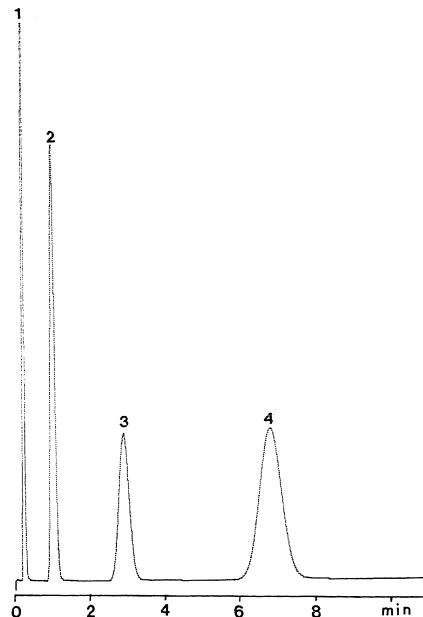


Fig. 5. Chromatographic separation of the following mixture of ketones on an HSGCB (0.250–0.170 mm)+4% Carbowax 20M (1 m×2 mm I.D.) column: 1=acetone, 2=methylethyl ketone, 3=cyclopentanone, 4=methylisobutyl ketone; column temperature: 150°C.



desorption time of 3 or 6 min were not complete and the 6 min desorption gave better recoveries. A longer desorption time did not give any improvement. A higher temperature was necessary. The effect of the liquid phase on the adsorbing isotherm is shown in Fig. 4 for a mixture of amines injected into a GC column packed with HSGCB (0.250–0.170 mm)+0.8% KOH+4% Carbowax 20M and in Fig. 5 for a mixture of ketones injected into a GC column packed with HSGCB (0.250–0.170 mm)+4% Carbowax 20M. Fig. 2 shows the worst, strongly tailed, peak shape obtained for acetone injected into a GC column packed with HSGCB (0.250–0.170 mm). With this latter column no amines were eluted. Irreversible adsorption and peak tailing phenomena were suppressed by the liquid phase, which linearized the adsorption isotherm by covering the ‘active sites’ of the adsorbent and homogenizing its surface, as already shown in the literature (see for example [31]).

#### 4. Conclusions

The results obtained indicate that HSGCB does not irreversibly adsorb the volatile and medium-boiling compounds (even polar ones) tested, is not affected by water and can substitute Carbosieve and activated charcoal in trapping volatile organic compounds such as methanol, vinyl chloride, acetone, ethanol, etc. Moreover, it can be used in a multilayer trap with other adsorbents when mixture of compounds of different polarity and volatility need to be examined [18].

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