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Capillary gas chromatography with graphitized carbon black

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ABSTRACT

The outstanding properties of fused-silica capillary columns coated with graphitized carbon black impregnated with liquid phases are described together with the details of their preparation. HETP vs. \bar{u} curves are reported, together with some separations of industrial and environmental interest. Fast and more effective analyses may be achieved with such columns.

INTRODUCTION

The technology of capillary columns has reached highly sophisticated levels and the main research in the field of capillary gas chromatography (GC) is addressed toward two main aspects: extremely high performance in terms of HETP¹, and a search for very selective stationary phases and the development of high-temperature GC².

We have been studying selective stationary phases for GC through the development of columns containing graphitized carbon blacks (GCB) coated with suitable percentages and quality of stationary phases^{3,4}.

The success of this technique, called gas-liquid-solid chromatography (GLSC), is due to the peculiar properties of GCB and to the particular working mechanism, involving adsorption and interaction with the liquid stationary phase³. Further, linear elution and a low HETP are obtained for polar compounds using polar stationary phases. Very selective packed columns have been developed, which are nowadays widely used in environmental and industrial analysis⁴.

In the last few years, our efforts have been devoted to the preparation of fused-silica capillary columns with the aim of coupling the high separation factors of GLSC with the large number of theoretical plates achievable in capillary chromatography. In early works^{5,6} we showed that high performance and fast analysis can be achieved with these columns. In a recent paper⁷ we also showed that very high reproducibility can be obtained in the preparation of these columns.

In this paper we report further progress made in the preparation of fused-silica capillary columns with GCB, which is mainly due to the use of an extremely fine particle size.

EXPERIMENTAL

The preparation of the columns is based on a two-step procedure that can be summarized as follows: (a) preparation of a slurry where the adsorbent (GCB) and the liquid phase (SP1000) are mixed together in a suitable solvent and sonicated; (b) coating of the capillary columns by means of a static method.

Step (a) has been greatly modified with the aim of obtaining a slurry with a very fine particle size. This can be accomplished by considering that the maximum power of the sonicator is obtained when the slurry solvent is water and that a high sonication power is required when an organic solvent is used. The GCB (Carbopack B in this instance) is wet-sieved via a multi-stadium sieving cascade using water as medium. The material of finest particle size ($< 20 \mu\text{m}$) is sonicated in water by means of high-power sonicator (Model 450, Branson, Danbury, CT, U.S.A.) for 30 min. The slurry is then dried by means of a vacuum pump and methylene chloride-*n*-pentane (50:50) containing 35% (w/w) (with respect to the carbon black) of SP1000 is added. The container is shaken and sonicated again for 30 min.

The coating step (b) does not differ substantially from that described previously⁴, which is a modification of the method of Xu and Vermeulen⁸ (free-release static coating) for the preparation of glass capillaries. Essentially the slurry is pushed into the capillary by heating the slurry reservoir at 60°C and the solvent is then evaporated while the column is kept at a temperature higher than the boiling point of the solvent mixture⁴.

Two types of column with different I.D. (0.25 and 0.53 mm) were tested. A Carlo Erba Model 5160 Mega chromatograph equipped with both split-splitless and on-column injectors and a Dani Model 8510 chromatograph equipped with a PTV injector were used. Fused-silica tubing and Carbopack B were kindly supplied by Supelco (Bellefonte, PA, U.S.A.).

RESULTS AND DISCUSSION

Fig. 1 shows scanning electron micrographs of the carbon black layer on the inner wall of the fused-silica capillary. The particle dimensions cannot be easily evaluated but they seem to be in the region of $10^{-2} \mu\text{m}$. With the procedure described previously dimensions of about two orders of magnitude larger were obtained⁴. The graphite layer appears to be homogeneous.

In Fig. 2 the Van Deemter plots of three columns with two different inner diameters (0.53 mm for columns A and B and 0.25 mm for column C) are shown. The columns contained Carbopack B coated with SP1000 to different extents. The surface coverage values (Θ), obtained by using a method described in detail elsewhere⁷, are 1.2 for column A and 4.5 for columns B and C. The obvious difference in the *B* term of the Van Deemter equation for columns of different diameter is shown by the large difference in both the value of the minimum HETP (H_{min}) and of the resistance to mass transfer term, *C*. Column B shows a lower H_{min} than column A but a higher value of *C*. The latter may be due to the lower homogeneity of the adsorbing layer containing a small amount of stationary phase, but the former is more difficult to explain.

The behaviour of the 0.53-mm I.D. columns is more like that of a packed than a capillary column. The only advantage of these large-bore capillary columns seems to

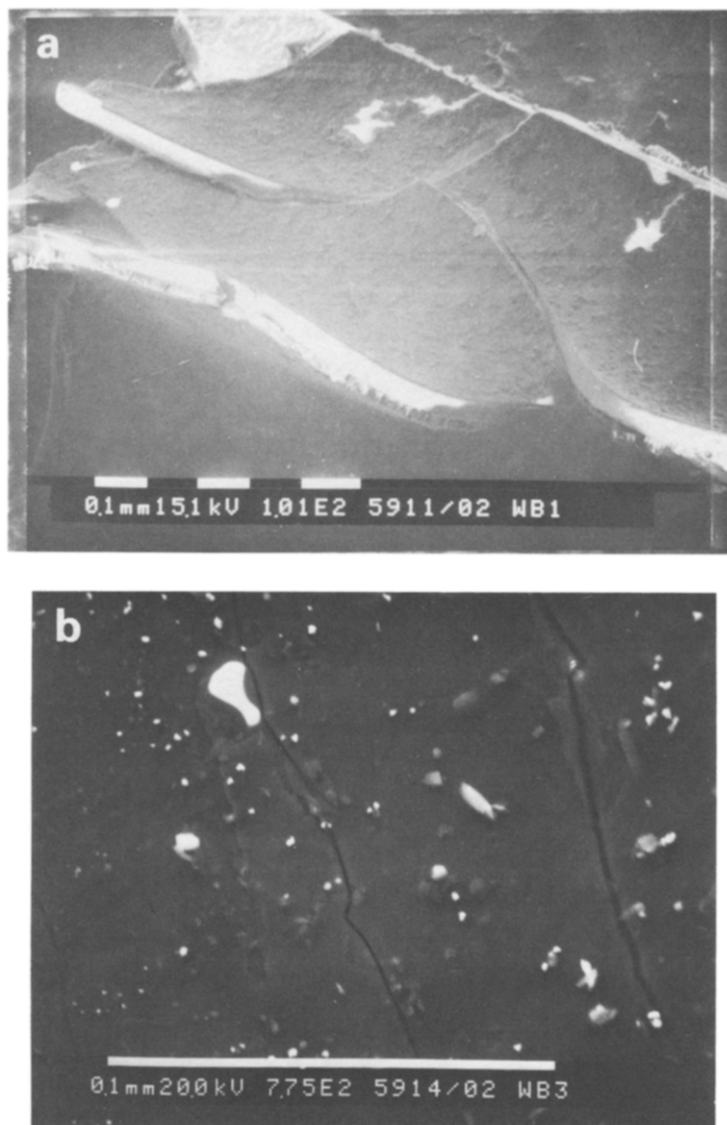


Fig. 1. Scanning electron micrographs of the inner wall of fused-silica capillary columns (C and A, see Fig. 2) coated with Carbopack B + SP1000.

be that the inlet pressure is of course much lower than for a packed column, with the possibility of making longer columns. There is also an increase in sample capacity owing to the larger surface area, which is, however, difficult to evaluate.

Further, as these columns are used in GLSC, where the mechanism is controlled by adsorption, the advantages of using wide-bore columns are even less important than in conventional capillary gas-liquid chromatography (GLC). It is concluded,

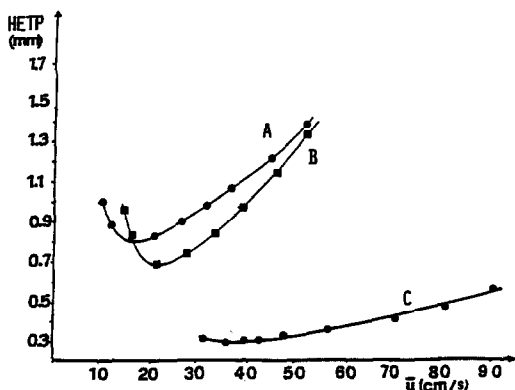


Fig. 2. Van Deemter plots obtained with three fused-silica capillary columns coated with Carbopack B + SP1000: (A) 33 m \times 0.53 mm I.D.; (B) 33 m \times 0.53 mm I.D.; (C) 24 m \times 0.25 mm I.D. Sample, *n*-dodecane ($k' = 7$); carrier gas, hydrogen.

from a theoretical and kinetic point of view, that wide-bore columns seem not to represent progress in capillary chromatography.

Column C shows outstanding properties from the kinetic point of view. H_{\min} occurs at about 40 cm/s and shows a coating efficiency of about 80% with a measured H_{\min} of 0.29 mm.

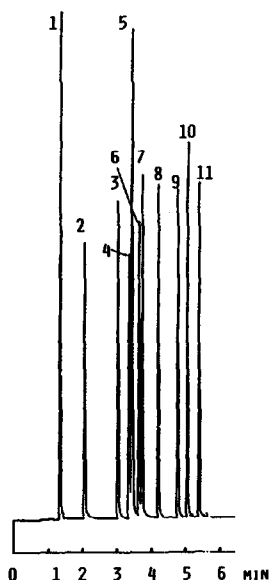


Fig. 3. Separation with a fused-silica capillary column (24 m \times 0.25 mm I.D.) coated with Carbopack B + 5% SP1000. Peaks: 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = *p*-xylene; 5 = *m*-xylene; 6 = isopropylbenzene; 7 = *o*-xylene; 8 = *n*-propylbenzene; 9 = 1,3,5-trimethylbenzene; 10 = *p*-cymene; 11 = *n*-butylbenzene. Column temperature: 1.5 min at 70°C, then heated at 20°C/min to 160°C and held to the end. Carrier gas, hydrogen; linear velocity, 40 cm/s; sample volume, 0.1 μ l; splitting ratio, 1:100; flame ionization detection (FID).

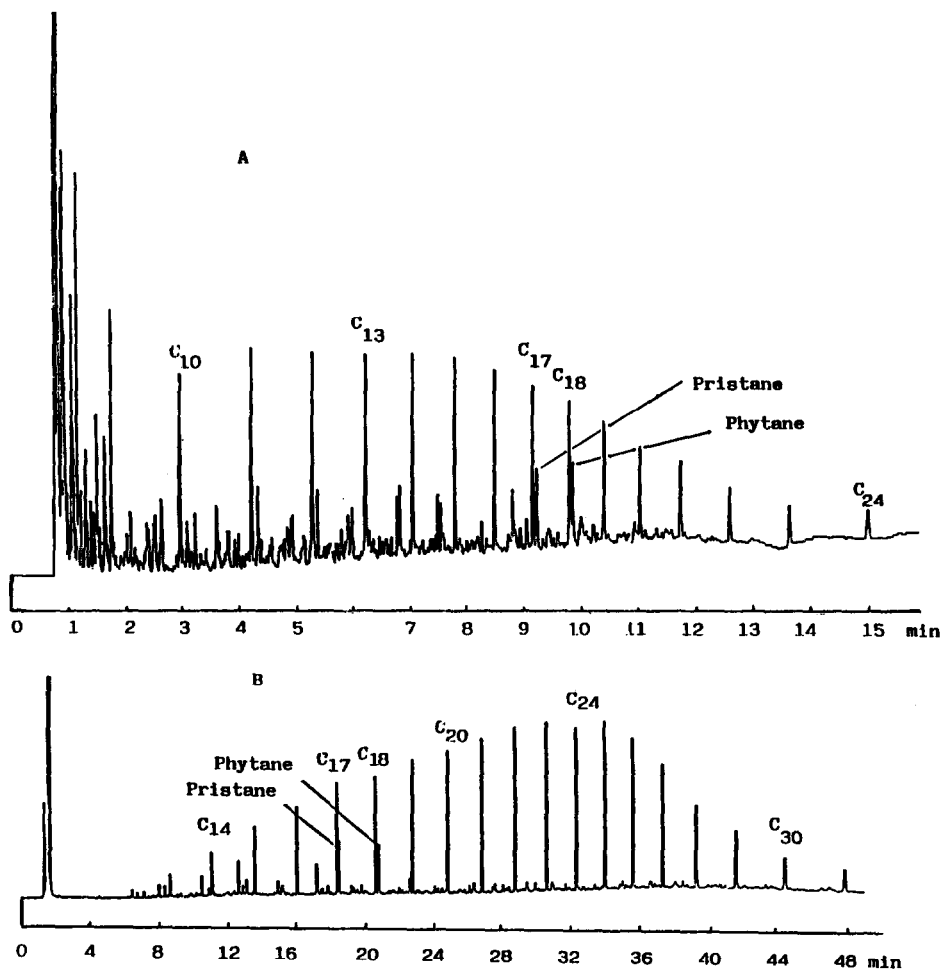


Fig. 4. (A) Separation with a fused-silica capillary column (24 m \times 0.25 mm I.D.) coated with Carbo-pack B + SP1000. Column temperature: 2 min at 60°C, then heated at 20°C/min to 230°C and held to the end. Carrier gas, hydrogen; linear velocity, 50 cm/s; sample, 0.05 μ l of Iran crude oil; splitting ratio, 1;100; FID ($8 \cdot 10^{-11}$ a.u.f.s.). (B) Separation with an SE-54 fused-silica capillary column (30 m \times 0.25 mm I.D.). Column temperature, 2 min at 100°C, then heated at 5°C/min to 270°C and held to the end. Carrier gas, hydrogen; linear velocity, 42 cm/s; sample, 0.1 μ l of crude shale oil; splitting ratio, 67:1; FID ($8 \cdot 10^{-11}$ a.u.f.s.).

In a theoretical treatment, Giddings⁹ showed that for a highly porous and homogeneous adsorbent the C term should be as low as 10^{-7} , provided that the surface area of the adsorbent is very high (10^3 m²/g). In practice, however, an adsorbent with both of these properties is not available, but GCB represents a good compromise, being a non-porous and homogeneous adsorbent. In this instance it is reasonable^{4,9} to assume $C = 10^{-4}$. In fact, the value calculated from the Van Deemter plot is $2.2 \cdot 10^{-4}$, which is very close to the theoretical value. It should be pointed out that this value is hardly reached in GLC, so that GLSC capillary columns can yield a better resolution in a shorter time.

TABLE I
LIST OF PRIORITY POLLUTANTS SEPARATED

No.	Compound	No.	Compound
1	Chloromethane	19	<i>trans</i> -1,3-Dichloropropene
2	Dichlorodifluoromethane	20	Toluene
3	Bromomethane	21	Tetrachloroethylene
4	Vinyl chloride	22	<i>cis</i> -1,3-Dichloropropene
5	Trichlorofluoromethane	23	1-Chloro-2-bromopropane
6	1,1-Dichloroethylene	24	2-Chloroethyl vinyl ether
7	<i>trans</i> -1,2-Dichloroethylene	25	Bromodichloromethane
8	1,1,1-Trichloroethane	26	Ethylbenzene
9	Carbon tetrachloride	27	Chlorobenzene
10	<i>cis</i> -1,2-Dichloroethylene	28	1,1,2-Trichloroethane
11	1,1-Dichloroethane	29	Dibromochloromethane
12	Methylene chloride	30	1,4-Dichlorobutane
13	Benzene	31	Bromoform
14	Trichloroethylene	32	1,1,2,2-Tetrachloroethane
15	Chloroform	33	1,3-Dichlorobenzene
16	Bromochloromethane	34	1,4-Dichlorobenzene
17	1,2-Dichloropropane	35	1,2-Dichlorobenzene
18	1,2-Dichloroethane		

In Fig. 3 the separation of some aromatic compounds is illustrated and the high resolving power of the GLSC capillary column is shown. An almost baseline separation of the three xylenes is obtained in less than 6 min without any overlapping of possibly interfering compounds.

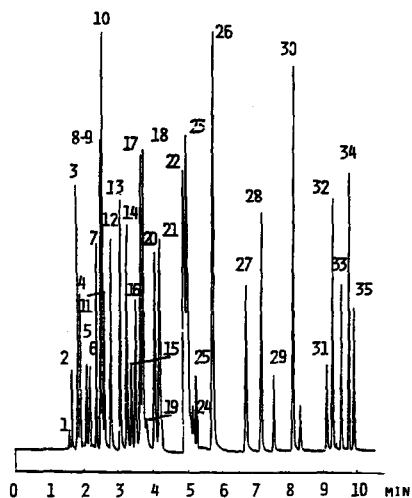


Fig. 5. Separation of 35 priority pollutants. Peak numbers as in Table I. Fused-silica capillary column (33 m \times 0.53 mm I.D.) coated with Carbowax B + SP1000. Column temperature, 2 min at 30°C, then heated at 20°C/min to 200°C and held to the end. Carrier gas, hydrogen; linear velocity, 30 cm/s; sample volume, 0.1 μ l; splitting ratio, 1:100; FID.

In Fig. 4 the separation of the components of a crude oil with the critical pairs $n\text{-C}_{17}$ -pristane and $n\text{-C}_{18}$ -phytane is shown and compared with that obtained with a GLC column with the same resolving power. The operating conditions were different as they were adjusted in each instance to obtain the best performance. The separation of interest is obtained more than twice as fast on the CarboPack B column. Of course, as our column is more retentive the overall analysis is stopped at C_{24} .

In order to show the high resolving power of these columns, a separation of 35 priority pollutants (Table I) is shown in Fig. 5. This separation, obtained in only 10 min, is one of the fastest and the most effective reported for this kind of mixture. The separations in Figs. 4 and 5 were obtained with columns A and B in Fig. 1, respectively.

In conclusion, the results given here represent the most recent achievements in GLSC with capillary columns and in our opinion provide the best demonstration that our aim of coupling a high value of α with a large number of theoretical plates has almost been achieved. More research with the use of different stationary phases is needed in order to achieve more complete results.

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