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Note

Preparation and efficiency of polar support-coated open tubular columns

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The many advantages and great superiority of glass open tubular columns are well known and described in detail in the literature. A comprehensive selection can be found in the proceedings of the recent Hindelang Symposia[1,2]. Until recently, however, problems in the preparation of stable, high efficiency columns delayed their wide scale application. In particular, polar stationary liquids were known to give problems of spreading and stability. Since the late sixties, methods have been developed to overcome these problems[3–9]. The recent work of Schomburg and Husmann[10] is noteworthy.

Making glass columns compatible for coating with polar phases requires the roughening of the inside surface, more rigorously than is the case with apolar and medium polarity phases. The most widely used methods for achieving this are based upon the deposition of a layer of small particles on the inside surface of the column, either by a chemical reaction ("etching") or by coating with a suspension of the particles[11–14].

Recently we reported on the chromatographic properties of these support-coated open tubular (SCOT) columns with different support materials and presented data on column efficiency, reproducibility and temperature–time stability[14]. That study was limited mainly to columns coated with apolar stationary phases. Our method, although fully satisfactory with apolar liquid phases, showed serious shortcomings when applied to polar SCOT columns. Silanized materials such as Silanox 101 were found to be unsuitable as supports for polar liquids[14–16], so a more polar, diatomaceous earth type support was chosen. However, the columns obtained were not as efficient as those prepared with apolar liquid phases. It was presumed that the low density of the support material on the column wall did not result in an even distribution of the liquid film.

In the present study we report on additional experimental work and dem-

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onstrate the usefulness of a slightly modified method in the preparation of high-efficiency polar SCOT columns. Further, a comparison is made between the SCOT columns and glass capillary columns prepared after modification by reaction with hydrochloric acid[10].

EXPERIMENTAL

Preparation of the columns

Pyrex glass capillaries (0.25 and 0.40 mm I.D.), prepared on a Hupe and Bisch drawing machine, were rinsed with acetone and ethanol, but without further pretreatments. As stated before, Chromosorb R 6470-1 (Johns-Manville, Denver, Colo., U.S.A.), a diatomaceous earth material, was chosen, because a slightly polar support is preferred for a polar liquid phase. The diatomaceous earth was not silanized. After grinding, a fraction with a mean particle size of *ca.* 2 μm was obtained by sedimentation. A suspension of the the support material was prepared by adding 3 g of Chromosorb R 6470-1 to 100 cm^3 of ethanol. Ethanol was chosen as the suspending solvent because in less polar solvents, such as tetrachloromethane and chloroform, conglomerates of support particles were formed. In spite of the low density of ethanol, the suspensions were sufficiently stable during the coating procedure. A balanced density slurry[17] consisting of 1,1,2,2-tetrabromoethane, dioxane and tetrachloromethane, as commonly used in packing liquid chromatographic columns, is not suitable because it effects an excessive pressure drop, while complete solvent evaporation is difficult and time consuming. The suspension was homogenized by treating it in an ultrasonic bath.

The columns were prepared according to a two-step dynamic procedure[14]. First, a plug of the suspension whose volume was *ca.* 20% of the column volume was forced through the column by nitrogen pressure, while the plug velocity was held constant at *ca.* 4 cm/s. To keep the suspension from clogging a short wetting-plug of pure ethanol was used. A short dummy-column behind the separation column of about the same length as the suspension plug prevented a sharp increase in the speed of the plug when leaving the separation column. After the plug had left this dummy-column the nitrogen pressure was increased to give a flow-rate of *ca.* 5 cm^3/min and the column was thoroughly dried. In the second step the columns were coated with the polar-liquid phase. A cyanopropylmethyl–phenylmethyl silicone, OV-225, was used as the stationary phase. A solution of 5% (w/v) OV-225 in tetrachloromethane was prepared. A plug whose volume was *ca.* 20% of the column volume was forced through the column at a velocity of *ca.* 4 cm/sec. After thorough drying, the columns were mounted in the gas chromatograph and conditioned by programming the temperature up to 250° at a rate of 0.5°/min.

Gas chromatography

A Hewlett-Packard (Type 5710; Avondale, Pa., U.S.A.) gas chromatograph, adapted for glass capillary columns and equipped with an all-glass solid injector[18] and a Perkin-Elmer (Type F17; Beaconsfield, Great Britain), as used. A Pue Unicam Series 104 gas chromatograph (Pye Unicam, Cambridge, Great Britain), equipped with a ^{63}Ni electron capture detector was used for the ultra trace analysis of pesticides.

Column efficiencies and capacity ratios were measured for some carboxylic acid

methyl esters (methyl nonadecanoate and methyl tricosanoate) with nitrogen as the carrier gas. Phase ratios were calculated with the aid of the partition coefficient of β-methylnaphthalene, determined separately on a packed column. The resistance to mass transfer in the liquid phase, C_L, in the Golay equation, was calculated from the combined measurements of plate-height curves with helium and nitrogen as the carrier gases[14,19].

RESULTS AND DISCUSSION

In Table I are presented some characteristics of the OV-225 columns prepared according to the procedure described. By comparing these data with earlier results (ref. 14, Table IV), it can be seen that the new method results in a remarkable improvement of column performance. In contrast to the older method, 0.25 mm I.D. columns could be prepared without difficulty[6,14]. Low values for C_L ($<10^{-3}$ sec) indicate an even distribution of the liquid film on the column wall. Fig. 1. shows a scanning electron microscope (SEM) photograph of the column wall after the second coating step. As compared with previous experiments in which 5–10 μm Hyflo Supercel was used as a support[14], a much higher surface density of the support material on the column wall was obtained with Chromosorb R 6470-1. Therefore, a more even distribution of the stationary liquid can be expected. It should be noted that no coherent layer of support material was obtained. Therefore, the columns prepared are related to the hydrochloric acid-treated wall-coated open tubular (WCOT) columns[3] rather than to the conventional SCOT columns[20]. Table II gives some characteristics of an OV-225 column on prolonged use; these data indicate a good long-term temperature stability.

In Table III are presented some characteristics of the columns described above and of some current column types, as prepared in our laboratories, for comparison. In terms of plate height, the columns prepared according to Schomburg and Husmann[10]

TABLE I

CHARACTERISTICS OF CHROMOSORB OV-225 SCOT COLUMNS

A = Methyl nonadecanoate; B = methyl tricosanoate.

Property	*Column No.*			
	1	*2*	*3*	*4*
Length (m)	50	31	55	47
Internal diameter (mm)	0.40	0.40	0.24	0.25
Temperature (°C)	220	220	130	220
Capacity factor for B	3.1	5.4	3.0*	5.7
Phase ratio	580	330		350
Linear gas velocity (cm/sec)	8.8	8.4	9.3	7.6
Plate height for B (mm)	0.46	0.39	0.51*	0.44
Theoretical plates per metre for B	2180	2530	1950	2260
$C_L \cdot 10^4$ (sec)	7	2		
Separation number (A–B)	48	48		
Coating efficiency (%)	70	87	37	44

* β-Methylnaphthalene.

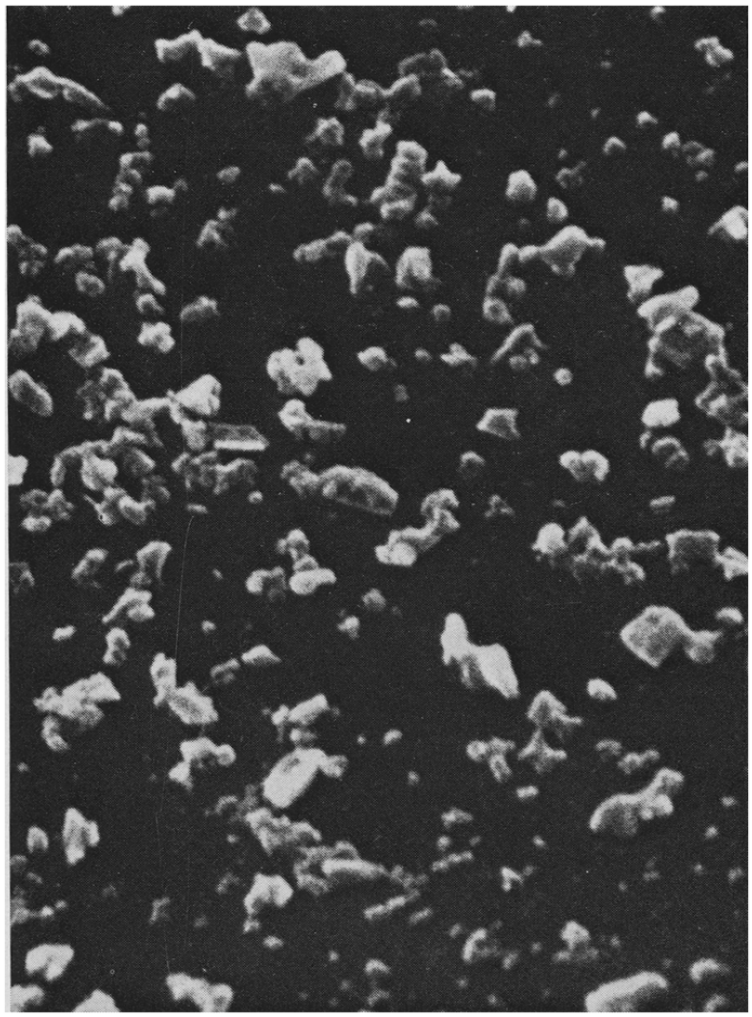

Fig. 1. Scanning electron microscope photograph of a SCOT column coated with Chromosorb R 6470-1 and OV-225. Magnification: 5000×.

TABLE II

CHARACTERISTICS OF A CHROMOSORB R 6470-1/OV-225 SCOT COLUMN UPON PROLONGED USE AT 220°

B = Methyl tricosanoate.

Property	*Week*		
	0	*4*	*8*
Capacity factor for B	3.2	2.7	2.7
Linear gas velocity (cm/sec)	8.8	9.8	9.9
Theoretical plates per metre for B	2120	1980	1960

TABLE III

CHARACTERISTICS OF SCOT AND WCOT OV-225 COLUNNS

B = Methyl tricosanoate.

Property	*Column type*			
	WCOT	*WCOT*	*SCOT*	*SCOT*
Coating procedure	Static[7]	Dynamic[10]	Dynamic	Dynamic
Internal diameter (mm)	0.25	0.25	0.25	0.40
Length (m)	30–50	30–80	30–50	30–50
Capacity factor for B	5–10	3–8	3–5	3–5
Theoretical plates per metre	2000–2800	3500–4500	2000–2500	2000–2500
$C_L \cdot 10^4$ (sec)		5	5	5
Coating efficiency (%)	50–80	70–90	40–60	50–90

are superior. Dynamically coated SCOT and WCOT columns prepared by a static coating procedure have equivalent characteristics. However, dynamically prepared columns are preferred because of the simple preparation technique. Owing to a higher density of the support material over the glass surface, an improvement in the efficiency of polar SCOT columns has been achieved which is now comparable to that obtained for the apolar SCOT columns[14].

Fig. 2 shows a ultra trace analysis in the pg range of a standard pesticide mix-

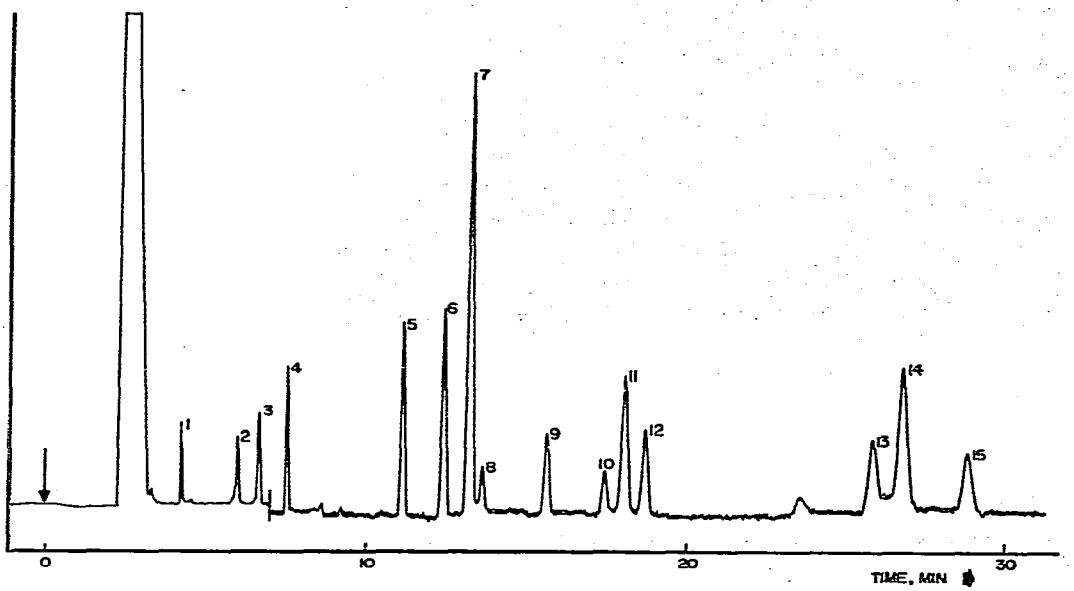

Fig. 2. Chromatogram of test mixtures of pesticides. Column (31 m × 0.40 mm I.D.): Chromosorb R 6470-1/OV-225; temperature: 225°; carrier gas: argon–methane (95:5, v/v); linear velocity: 12 cm/sec; detection: ^{63}Ni electron capture, 300°. Samples: 1 = hexachlorobenzene (1 pg); 2 = α-benzenehexachloride (α-BHC) (1 pg); 3 = aldrin (2 pg); 4 = γ-BHC (1 pg); 5 = *o,p'*-dichlorodiphenylethane (*o,p'*-DDE) (5 pg); 6 = α-endosulfan (5 pg); 7 = *p,p'*-DDE (10 pg); 8 = β-BHC (2 pg); 9 = dieldrin (2 pg); 10 = *o,p'*-dichlorodiphenyltrichloroethane (*o,p'*-DDT) (5 pg); 11 = endrin (10 pg); 12 = *o,p'*-dichlorodiphenyldichloroethane (*o,p'*-DDD) (5 pg); 13 = *p,p'*-DDT (10 pg); 14 = *p,p'*-DDD (10 pg); 15 = β-endosulfan (5 pg).

ture on a SCOT OV-225 column. Only a very small amount of catalytic decomposition of *p,p'*-DDT into *p,p'*-DDD is observed. Note also the good peakshape of the endrin peak.

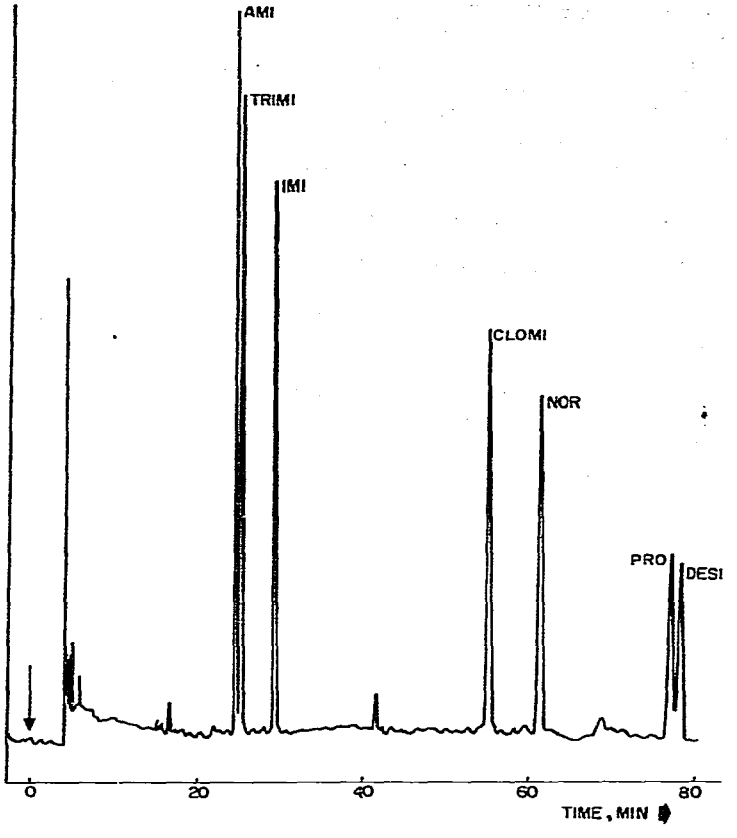

Fig. 3. Chromatogram of a standard mixture of tricyclic antidepressants. Column (50 m × 0.40 mm I.D.): Chromosorb R 6470-1/OV-225; temperature: 220°; carrier gas: helium; linear velocity: 22 cm/sec; detection: flame ionization. Samples: 25 ng each of HFB derivatives of nortriptyline (NOR), protriptyline (PRO) and desipramine (DESI); other components eluted as free bases are amitriptyline (AMI), trimipramine (TRIMI), imipramine (IMI) and clomipramine (CLOMI).

Fig. 3 shows the separation of a test mixture of tricyclic antidepressants, giving another indication of the separation capability of these columns. The choice of the ideal column for a given problem is however more than just a matter of plate heights. Simplicity and reproducibility of the column preparation are amongst the factors influencing the choice for a certain colomn type. To facilitate this choice more comparative data on the mentioned variables are required.

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