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Note

Open-tubular columns support-coated *in situ* with cross-linked SE-54 stationary phase

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Glass capillary columns with immobilized stationary phases have become very popular, and many applications are described in the literature. The main advantage of immobilized stationary phases over the conventional ones is their insolubility in organic solvents, which makes them easy to regenerate by simple rinsing with solvents.

Several methods and procedures for the preparation of these columns have been reported[1–6], but up to now the immobilized coatings have been applied only to wall-coated open-tubular (WCOT) columns and no data have been reported for support-coated open-tubular (SCOT) columns. Although the separation efficiency of WCOT columns seems to be superior to that of SCOT columns, our main objectives were to prepare capillary columns with higher sample capacities and suitable for trace analysis.

Here we describe the preparation of SCOT columns coated *in situ* with cross-linked SE-54 stationary phase. RSil SCOT and Aerosil silica were used as support materials for the stationary phase which was immobilized by addition of benzoyl peroxide in a modification of the procedure described by Sandra *et al.*[7]. In addition, we prepared WCOT columns with immobilized SE-54 by the same method in order to compare both types of columns. Chromatographic results are presented to illustrate the performance of the columns with different samples.

EXPERIMENTAL

Borosilicate glass tubing (1.5 m × 7 mm O.D.) was successively rinsed with a sulphuric acid–chromate mixture, water and acetone prior to extrusion. After drying, 0.28 and 0.38 mm I.D. glass capillaries were drawn with a Shimadzu GDM-1B glass-drawing machine. A Shimadzu MCT-1A microcolumn treatment stand was used for the coating of the glass capillaries, and the columns were tested in a Perkin-Elmer Sigma 3B gas chromatograph equipped with a flame ionization detector.

The glass capillaries were deactivated by silanization with dimethyldichlorosilane–trimethylchlorosilane–carbon tetrachloride (5:2:45). Five per cent of the column length was filled with the above solution, and the column was then heated

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to 100°C for 12 h after sealing its ends with a micro-flame. Subsequently the capillaries were washed with dry methanol and dichloromethane.

Column preparation

All columns were 12 m long. The 0.38 mm I.D. glass tubing was used for the SCOT columns and the 0.28 mm I.D. tubing for the WCOT columns. In order to obtain comparable results, both tubings were coated by the same static method[8], but using a different concentration of the stationary phase coating solution. Two fumed silica gels were used as supports for the SCOT columns: RSil, 2–4 μm (Alltech Assoc.) and Aerosil (Hoechst).

The SCOT columns were made by a two-step process[9]. In the first step, a 20 mg/ml suspension of RSil SCOT or Aerosil in chloroform–acetone (9:1) was sonicated for 2 min, and a plug of this suspension (20% of the column length) was passed through the tubing at 370 cm/min. A short dummy column was attached to the column to avoid end disturbances. After the liquid had been expelled, the column was dried with a nitrogen flow for 10 h. In the second step, the commercially available SE-54 (Alltech Assoc.) stationary phase was statically coated on the deposited silica bed with a solution comprising 4 mg/ml SE-54 in dichloromethane–pentane (1:1) to which 0.2 mg/ml of benzoyl peroxide (Merck) in dichloromethane were added. After the static coating, the column was heated at 180°C for 1 h by programming from 50°C at 2°C/min and with an air flow of 0.5 ml/min. Finally the columns were rinsed six times with 3 ml of dichloromethane, and then conditioned overnight at 200°C.

The WCOT columns were prepared by statically coating the 0.28 mm I.D. capillaries with a solution containing 6 mg/ml SE-54 in dichloromethane–pentane (1:1) to which 0.3 mg/ml of benzoyl peroxide in dichloromethane had been added. The immobilization step was also made under an air flow and with the same conditions as used for the SCOT columns.

RESULTS AND DISCUSSION

The chloroform–acetone (9:1) mixture had an adequate density to stabilize both the Aerosil and RSil suspensions. A 15–20 mg/ml suspension of the above silicas proved to be appropriate for the formation of an homogeneous and regularly distributed porous layer on the internal surface of the capillary tubing. Fig. 1 shows a scanning electron microscope (SEM) photograph of the column wall after the Aerosil coating step.

The benzoyl peroxide was added both as a solid and as a solution to the coating solution, no differences in the performance of the resulting columns being observed. Although the concentration of the peroxide was varied between 2 and 8%, a concentration of 5% was found to be adequate.

Both Aerosil and RSil SCOT columns were prepared, but the former exhibited a very high activity and it was necessary to deactive it by silanization prior to use. After this, the two types of columns had very similar performances.

The phase cross-linking was first attempted with air alone, by heating the statically coated column at 300°C for 2 h under an air flow of 2 ml/min, but the resulting columns were too active to be used. In view of these results, benzoyl peroxide was

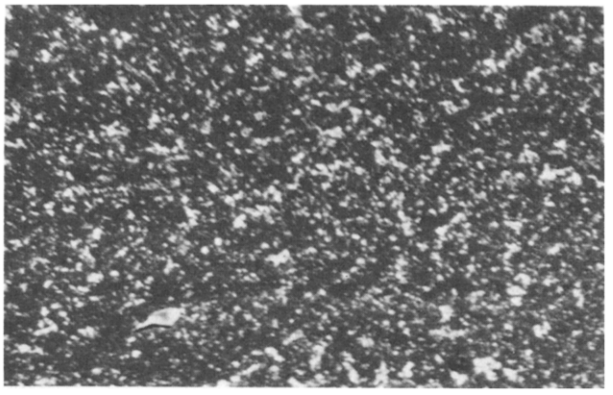
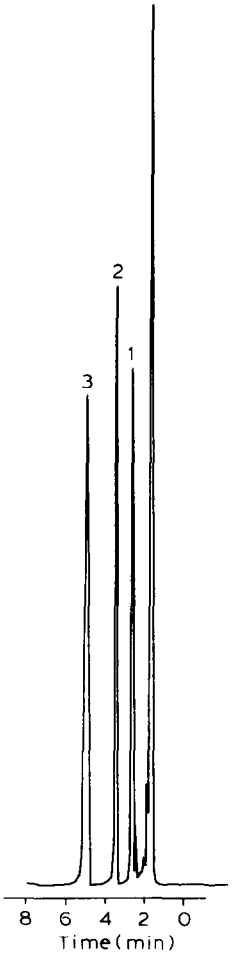


Fig. 1. Scanning electron microscope (SEM) photograph of a glass capillary coated with Aerosil. Magnification: × 1500.



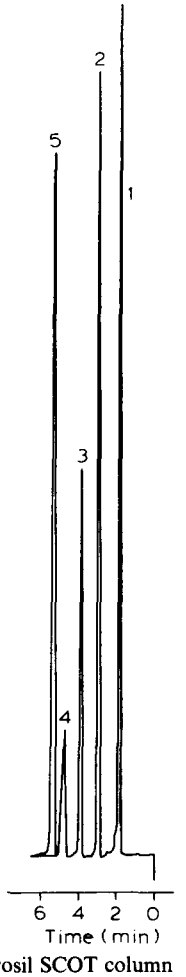


Fig. 2. Analysis of an alcohol mixture at 140°C. Column: 12 m × 0.38 mm I.D. Aerosil SCOT column with immobilized SE-54. Peaks: 1 = 1-hexanol; 2 = 1-heptanol; 3 = 1-octanol.

Fig. 3. Analysis of a phenol mixture at 155°C. Column: 12 m × 0.38 mm I.D. RSil with immobilized SE-54. Peaks: 1 = benzene; 2 = phenol; 3 = *m*-cresol; 4 = *o*-ethylphenol; 5 = *p*-ethylphenol.

added to the coating solution, but an air flow was used instead of the nitrogen flow employed in the concentional method[7].

The prepared columns were tested with different types of samples which included alcohols, methyl esters, phenols, phthalates, hydrocarbons and pesticides. Some of the resulting gas chromatograms are shown in Figs. 2–4.

The characteristics of the best Aerosil and RSil SCOT columns with immobilized SE-54 stationary phase, as well as those of two WCOT columns prepared in this work, are presented in Table I. Plate heights and capacity factors were measured for pure C_8, C_9 and C_{10} *n*-alkanes. As seen from Table I, the performance of both types of immobilized SE-54 columns is similar, but the SCOT columns have a higher capacity which makes them more desirable for the trace analyses carried out in our laboratories.

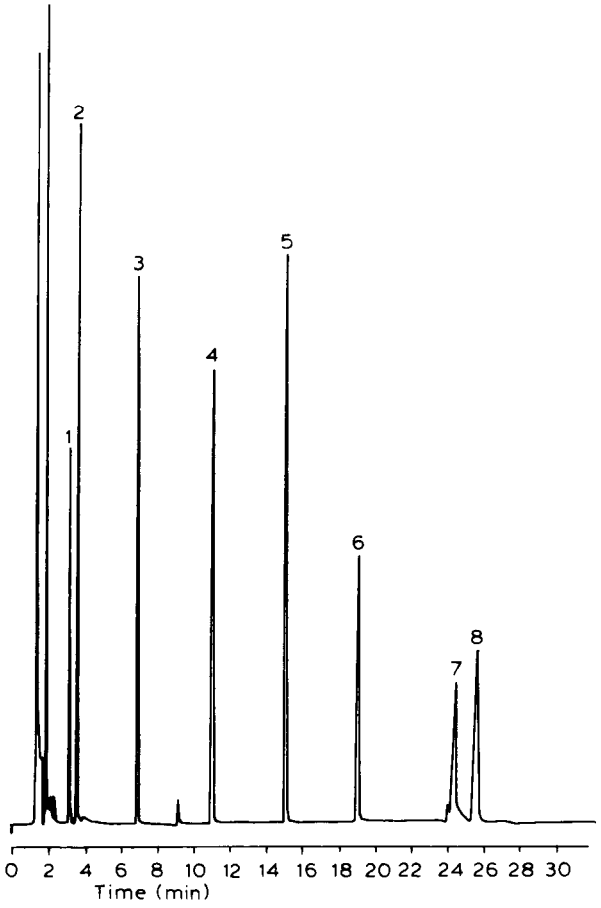


Fig. 4. Analysis of a methyl ester mixture. Column: 12 m × 0.38 mm I.D. RSil SCOT column with immobilized SE-54. Column temperature programmed from 130 to 220°C at 6°C/min. Peaks: 1 = caprylate; 2 = caprate; 3 = laurate; 4 = myristate; 5 = palmitate; 6 = linoleate; 7 = oleate; 8 = stearate.

TABLE I

CHARACTERISTICS OF THE AEROSIL AND RSil SCOT COLUMNS, AND WCOT COLUMNS WITH IMMOBILIZED SE-54

k_i = Capacity factors; N = number of theoretical plates.

	WCOT-1	*WCOT-2*	*Aerosil SCOT*	*RSil SCOT*
Phase concn. (mg/ml)	6	6	4	4
Length (m)	12	12	12	12
I.D. (mm)	0.28	0.28	0.38	0.38
k_1 (n-C_8)	1.1	1.5	1.5	1.7
k_2 (n-C_9)	2.2	3.0	3.2	3.5
k_3 (n-C_{10})	4.6	6.1	7.0	7.4
N_t (n-C_9)	28 368	35 995	27 715	31 933
N_{eff}/m	1053	2148	1431	1578
HEPT (mm)	0.42	0.33	0.43	0.38
Coating efficiency (%)	50	67	70	80

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