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## WHISKER-WALLED OPEN-TUBULAR GLASS COLUMNS IN GAS CHROMATOGRAPHY

### II. CHROMATOGRAPHIC PERFORMANCE

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#### SUMMARY

A variety of parameters relating to column efficiency (including the plate height, effective plate height, number of effective plates per unit time, phase ratio, sample capacity, performance index and percentage utilization of the theoretical efficiency) have been determined experimentally for whisker-walled open-tubular glass columns, and compared with values pertaining to other types of open-tubular columns.

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#### INTRODUCTION

We have previously reported<sup>1,2</sup> a method by which silica whiskers can be grown on the inner surface of open-tubular glass columns and used as a support for the liquid stationary phase. Preliminary experiments indicated that these whisker coatings have considerable promise as a means of obtaining high performance. In this paper we report more extensively on this aspect.

#### EXPERIMENTAL

Columns were drawn as described previously<sup>2</sup> from borosilicate glass (Pyrex, J. A. Jobling & Co., Staffs, Great Britain) to an O.D. of 0.1 cm, an I.D. of 0.020–0.035 cm and a length of 45–50 m. Whisker coatings were grown<sup>2</sup> on the inner surfaces of the columns; a typical portion of the surface obtained is shown in Fig. 1. The whiskers are *ca.* 10  $\mu\text{m}$  long and 1  $\mu\text{m}$  in diameter with a density of *ca.* 25 whiskers per 100  $\mu\text{m}^2$ . From these data, the surface area is estimated to be 8–9 times that of a smooth surface.

The surface of freshly grown whiskers is extremely active and can be de-activated, before coating with stationary phase, in a variety of ways, as reported elsewhere<sup>3</sup>. One method of de-activation, which was adequate for the present purpose, employs a 0.2% (w/v) solution of benzyltriphenylphosphonium chloride (BTTPC) in chloroform. Excess of solution was removed by washing with pure chloroform.

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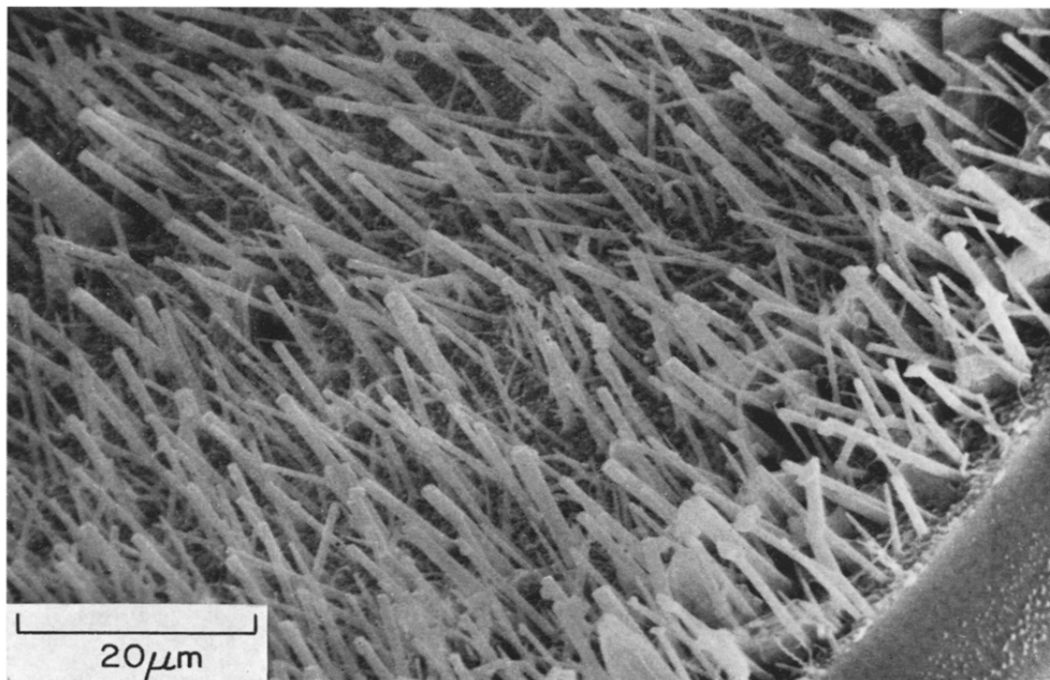


Fig. 1. A typical portion of the surface of a whisker-walled open-tubular column.

Stationary phase was coated on to the whiskers using the dynamic coating method<sup>4</sup>. Squalane was chosen as the stationary phase solely because data that are needed for estimating the phase ratio ( $\beta$ ) of the column are accurately known. A short plug (ca. 10% of the column volume) of a solution of squalane in chloroform (2.5–5%, w/v) was forced through the column using dry nitrogen as a propellant, at a linear velocity of 3 to 4 cm·sec<sup>-1</sup>. Excess of solvent was then removed by continuing the nitrogen flow for 24 h at room temperature. The column was then conditioned by increasing the temperature slowly to 130° and maintaining it there for a further 24 h. The internal diameter of the column was estimated by filling a short length, e.g., 35 cm, with distilled water and weighing it. As a check, a short length of the column was viewed end-on using a scanning electron microscope. The value of the internal diameter obtained in this way was within 4% of that obtained by weighing.

Columns were installed in a Varian Aerograph Model VA 1800 gas chromatograph that was modified by adding a splitter similar to that described by Ettre<sup>5</sup> and connections for make-up gas<sup>5</sup>. The outlet of the column was fed to a flame-ionization detector. Heat-shrinkable PTFE tubing (Raychem, Olifantsfontein, South Africa) was used to make the connections between the columns and the remainder of the system. The column temperature was maintained at 81°. *n*-Heptane was used as a test sample and methane as an "air peak".

#### CHROMATOGRAPHIC PERFORMANCE

A single, overall parameter describing column performance is still lacking and

a number of alternative parameters have been used. Numerical values of these parameters that were obtained in this study are summarized in Table I. Values of the mass distribution coefficient,  $k$ , were determined from the measured retention times of the solute and methane peaks<sup>5</sup>. The phase ratio,  $\beta$ , was estimated from the equation<sup>5</sup>

$$K = k \cdot \beta$$

where the concentration distribution coefficient,  $K$ , is 152 for the present system<sup>6</sup>;  $S$  in Table I refers to the percentage (w/v) of the stationary phase in the coating solution.

TABLE I

## SUMMARY OF CHROMATOGRAPHIC PERFORMANCE OF FOUR WHISKER-WALLED OPEN-TUBULAR GLASS COLUMNS

Parameter	Column			
	1	2	3	4
Length (m)	55.4	52.9	44.8	44.8
Radius (cm)	0.016	0.016	0.012	0.012
Stationary phase	Squalane	Squalane	Squalane	Squalane
Temperature (°C)	81	81	81	81
$S$ (%)	2.5	5	5	5
Phase ratio, $\beta$	125	90	80	80
$B_0$ (cm <sup>2</sup> ) (experimental)	$198 \cdot 10^{-7}$	$198 \cdot 10^{-7}$	$245 \cdot 10^{-7}$	—
$B_0$ (cm <sup>2</sup> ) (calculated)	$320 \cdot 10^{-7}$	$320 \cdot 10^{-7}$	$180 \cdot 10^{-7}$	$180 \cdot 10^{-7}$
Carrier gas	N <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub>	He
Sample	<i>n</i> -Heptane	<i>n</i> -Heptane	<i>n</i> -Heptane	<i>n</i> -Heptane
$k$	1.2	1.7	1.85	1.85
$H_{min}$ (cm)	0.04	0.045	0.025	0.030
$h_{min}$ (cm)	0.13	0.11	0.06	0.075
$\bar{u}_{opt}$ (cm·sec <sup>-1</sup> )	7.5	10	12.5	22.5
$N \cdot m^{-1}$ (max)	2630	2270	3880	3130
$N_{eff} \cdot m^{-1}$ (max)	780	900	1635	1320
$N_{eff} \cdot sec^{-1}$ (max)	100	57	90	130
$\bar{u}^*_{opt}$ (cm·sec <sup>-1</sup> )	21.5	26	22.5	30
$B$ (cm <sup>2</sup> ·sec <sup>-1</sup> )	0.143	0.207	0.197	0.2580
$C$ (sec)	$32 \cdot 10^{-4}$	$29 \cdot 10^{-4}$	$17.5 \cdot 10^{-4}$	$10.0 \cdot 10^{-4}$
$C_L$ (sec)	$6.5 \cdot 10^{-4}$	$8.0 \cdot 10^{-4}$	$5.0 \cdot 10^{-4}$	$5.0 \cdot 10^{-4}$
$C_G$ (sec)	$25.5 \cdot 10^{-4}$	$20.5 \cdot 10^{-4}$	$12.5 \cdot 10^{-4}$	$5.0 \cdot 10^{-4}$
$PI$ (poise)	0.4	0.40	0.65	—
$UTE$ (%) ( $a = 0.1$ )	62	55	71	58
Sample capacity ( $\mu$ g per component)	1.5–2.5	1.5–2.5	0.5–1.5	0.5–1.5
$TZ$ ( $I = 600$ – $700$ )	29.0	28.5	36.5	—

Values of the plate height,  $H$ , were obtained in the usual way from the chromatogram and are plotted against the mean carrier gas flow velocity,  $\bar{u}$ , in Fig. 2. The minimum values of the plate height,  $H_{min}$ , at the optimum mean carrier gas flow velocity,  $\bar{u}_{opt}$ , are listed in Table I. Values of the plate number per metre of column length,  $N \cdot m^{-1}$ , were calculated from  $N \cdot m^{-1} = 100/H$  ( $H$  measured in centimetres). The effective plate height was calculated using the equation<sup>7,8</sup>

$$h = \frac{(1 + k)^2}{k^2} \cdot H$$

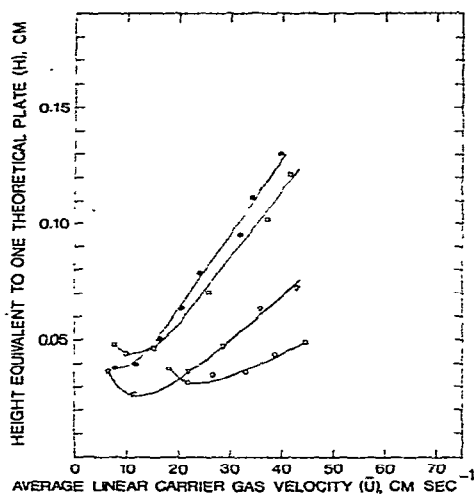


Fig. 2. Plate height ( $H$ ) versus mean carrier gas flow velocity. Solute: *n*-heptane. Stationary phase: squalane. ●,  $r = 0.016$  cm, nitrogen as carrier gas,  $k = 1.2$ ,  $\beta = 120$ , column length = 55.4 m; □,  $r = 0.016$  cm, nitrogen as carrier gas,  $k = 1.7$ ,  $\beta = 90$ , column length = 52.9 m; ▽,  $r = 0.012$  cm, nitrogen as carrier gas,  $k = 1.85$ ,  $\beta = 80$ , column length = 44.8 m, ○,  $r = 0.012$  cm, helium as carrier gas,  $k = 1.85$ ,  $\beta = 80$ , column length = 44.8 m.

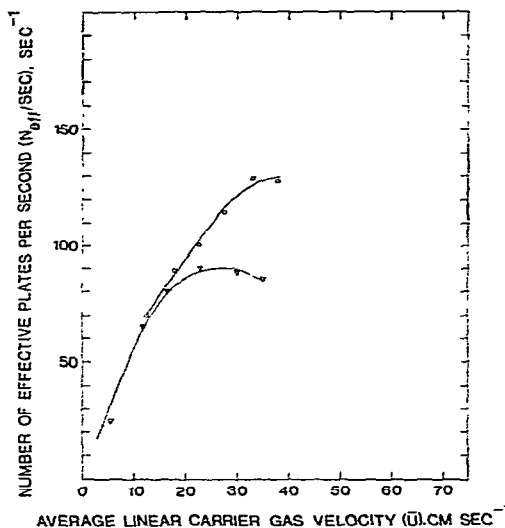


Fig. 3. Number of effective plates per second ( $N_{\text{eff}} \cdot \text{sec}^{-1}$ ) versus mean carrier gas flow velocity ( $\bar{u}$ ). Column length, 44.8 m; radius, 0.012 cm; solute, *n*-heptane ( $k = 1.85$ );  $\beta = 80$ . Carrier gas: ○, helium; ▽, nitrogen.

Values of the effective plate number per metre,  $N_{\text{eff}} \cdot \text{m}^{-1}$ , follow from the above two equations.

The maximum number of effective plates per second,  $N_{\text{eff}} \cdot \text{sec}^{-1}$  (max), refers to the highest value obtained when the effective plate number per second is plotted against flow velocity, as shown in Fig. 3.  $N_{\text{eff}} \cdot \text{sec}^{-1}$  is determined by dividing  $N_{\text{eff}}$  by the time required to elute the *n*-heptane;  $\bar{u}^*_{\text{opt}}$  is the linear gas velocity pertaining to  $N_{\text{eff}} \cdot \text{sec}^{-1}$  (max).  $B$ ,  $C$ ,  $C_L$  and  $C_G$  refer to the Golay equation<sup>5</sup>:

$$H = \frac{B}{\bar{u}} + C\bar{u}$$

where  $C = C_L + C_G$ ,  $B$  = longitudinal gaseous diffusion,  $C$  = total mass transfer,  $C_L$  = resistance to mass transfer in the liquid phase and  $C_G$  = resistance to mass transfer in the gas phase.  $B$  has been calculated<sup>6</sup> from

$$B = \frac{H_{\text{min}} \bar{u}_{\text{opt}}}{2}$$

and the data in Fig. 1.  $C$  was determined from the slopes of the plate height versus flow velocity graphs at high linear velocities.  $C_L$  was estimated by the method of Perrett and Purnell<sup>9</sup>, viz.

$$C_L = \frac{\Delta H}{\Delta u}$$

where  $\Delta H = H_{He} - H_{N_2}$ , *i.e.*, the difference of the plate height for a single component (*e.g.*, *n*-heptane) using helium and nitrogen as carrier gases at a flow velocity ratio that equals the ratio of the diffusion coefficients of the solute in the two carrier gases.  $C_G$  follows from the difference between  $C$  and  $C_L$ .

The performance index<sup>10</sup>,  $PI$ , was calculated from the equation

$$PI = \left( \frac{W_h}{t_r - t_m} \right)^4 \left( \frac{t_r - t_m}{t_r} \right)^4 \left( \frac{t_m}{t_r - 0.9375 t_m} \right) t_r \Delta P \text{ (poise)}$$

where  $W_h$  = peak width at half height (seconds),  $t_r$  = retention time of retarded peak (seconds),  $t_m$  = retention time of unretarded peak (seconds) and  $\Delta P$  = pressure drop across the column ( $\text{dyne}\cdot\text{cm}^{-2}$ ).

The percentage utilization of the theoretical efficiency (UTE, %)<sup>6</sup>

$$UTE = \frac{H_{\min} \text{ (theoretical)}}{H_{\min} \text{ (measured)}} \cdot 100$$

was calculated using the experimental data for  $H_{\min}$  (*cf.*, Table I) and the corresponding values of  $H_{\min}$  (theoretical) obtained from the extended Golay equation<sup>11</sup>:

$$\begin{aligned} H_{\min} \text{ (theoretical)} &\approx 2(BC_G)^{\frac{1}{2}} \quad (\text{ref. 6}) \\ &= r \left( \frac{1 + 6k + 11k^2}{3(1+k)^2} + \frac{8a}{3} + \frac{16ka}{3(1+k)^2} \right)^{\frac{1}{2}} \quad (\text{ref. 6}) \end{aligned}$$

where  $a$  is the ratio of the thickness of the whisker layer to the column radius, as determined from a scanning electron micrograph of the column<sup>2</sup>.

The separation number,  $TZ$ , was determined from the relationship proposed by Kaiser<sup>12</sup>:

$$TZ = \frac{1.699 t_R(z+1) - t_R(z)}{W_b(z) + W_b(z+1)} - 1$$

where  $t_R(z)$  and  $t_R(z+1)$  are the retention times of two consecutive peaks in a homologous series and  $W_b(z)$  and  $W_b(z+1)$  are the two corresponding peak widths.

The sample or load capacity refers to the maximum amount of solute that can be injected on to the column without appreciably (*e.g.*, 10%) affecting the band width, *i.e.*, the plate height.

The column permeability,  $B_0$ , was determined from the well-known equation<sup>5</sup>

$$\Delta P = \eta \frac{L \bar{u}}{B_0}$$

where  $\Delta P$  = the pressure drop across the column,  $\eta$  = the viscosity of the carrier gas,  $L$  = column length and  $\bar{u}$  = linear carrier gas velocity.

#### *Comparison with other types of surface-modified open-tubular columns*

For the purpose of comparison, it is convenient to classify open-tubular columns<sup>6</sup> into "classical" wall-coated open-tubular (WCOT) columns, in which the stationary phase is spread as a thin film on the inner surface of the column, and porous-layer open tubular (PLOT) columns, in which the inner surface is either chemically

## PERFORMANCE PARAMETERS OF VARIOUS TYPES OF MODIFIED OPEN-TUBULAR COLUMNS

Type of column	Workers	Reference	Modifying reagent/solid support	Column material	Column dimensions		$h$ (cm)	$\beta$	Sample capacity	Most polar stationary phase used	F
					Length (m)	I.D. (cm)					
Wall-treated open-tubular	Novotný and Tešárik	13-15	HCl (vapour)	Alkali-type glass	10-50	0.015-0.027	$H^* = 0.04-0.06$	-	-	Triethanol-amine	1.5-2
Alexander and co-worker	13, 16, 17	HCl (vapour)	Alkali-type glass	20	0.022	0.034 (0.28)	400	-	DEGA	1.5-2	
Novotný and Bartle	13, 18	HCl (vapour)	Alkali-type glass	50	0.5	0.05	-	-	-	SF-96	1.5-2
Schomburg <i>et al.</i>	13, 19	HCl (vapour)	Alkali-type glass	18	0.025	0.065	-	-	-	DEGS	1.5-2
Rijswick and Tešárik	13, 20	HF (vapour)	Borosilicate glass	15	0.018-0.022	0.0425	-	-	-	OV-101	1.1-1.3
Grob	21, 22	CH <sub>2</sub> Cl <sub>2</sub> (vapour)	Borosilicate	50	0.026	~0.07	-	-	-	XE-60, PPG	-
Schieke <i>et al.</i>	1, 2	HF (vapour)	Borosilicate	45	0.024	0.06 (0.06)	80	0.5-2 $\mu$ g/component	Carbowax 20M	Carbowax 20M	8-9
Porous-layer open-tubular	Horning and co-workers	23-26	Silanox	Glass	30-60	0.03	0.18	-	-	Silar-5CP	-
Nikely and Blumer	27-29	Silanox	Glass/stainless steel	11	0.05	0.19 (0.25)	50	5 $\mu$ g/component	PZ-176	FFAP, DEGS	-
Bertsch <i>et al.</i>	30	Silanox	Nickel	100-200	0.05	0.14	-	2-5 $\mu$ l of complex sample	Carbowax 20M	Carbowax 20M	-
Watanabe and Tonita	13, 31	NaCl crystals	Glass	5-20	0.056	0.032	-	-	OV-101	OV-101	1.5-2
Nota <i>et al.</i>	32	Graphite	Glass	14	0.05	$H^* = 0.07$	-	-	Carbowax 20M	Carbowax 20M	-
Grant	6, 33	Diatomaceous earth and LiCl	Glass	20	0.5	~0.2	-	-	Dilauryl phthalate	Dilauryl phthalate	5-10
Cronin	34	Diatomaceous earth and glass powder	Glass	36	0.05	0.15 (0.4)	150	-	Carbowax 20M	Carbowax 20M	-
Eltre and Purnell	6	Diatomaceous earth	Stainless steel	17	0.05	0.1 (0.1)	76	~10 <sup>-2</sup> $\mu$ l/component	DEGS	DEGS	30
Scientific Glass Engineering	35	Diatomaceous earth	Glass	50	0.05	0.16	-	-	Carbowax 20M	Carbowax 20M	-

\*  $H$  = theoretical plate height.

modified, *i.e.*, wall-treated (WTOT) columns, or a layer of support material is deposited on the inner surface [support-coated open-tubular (SCOT) columns]. Several of the performance parameters mentioned in the previous section are listed in Table II. The data were either obtained from the sources cited or were calculated from other available data. Where several values of a particular parameter were available, the best value is quoted.

It is important to note that performance parameters have been compared at similar values of  $k$  (*e.g.*,  $k = 2-5$ ) and  $K$ . This latter point is important because from the equation<sup>7,8</sup>

$$h = \left( \frac{\beta}{K} + 1 \right)^2 H$$

it is clear that a column with an intrinsically high  $\beta$  value may be made to appear spuriously effective by calculating  $H$  from the peak of a substance with a large  $K$  value. The unbracketed values of  $h$  listed in Table II refer to  $k$  values of 2-5; the  $K$  values vary over a large, and often unknown, range of values. Therefore, for the reasons just mentioned, an attempt has been made to correct the effective plate height to similar values of  $K$  ( $= 150$ ). This correction can be performed only if the phase ratio is known and furthermore it is assumed that  $H$  is not unduly affected by changes in  $K$ .

Table II also includes two quantities that are not efficiency parameters, but which nevertheless are related to column performance. The first relates to the spreading characteristics of the stationary phase on the support. A support surface is only useful in practice to the extent to which a variety of liquid stationary phases can be spread on it as a thin film without forming droplets. For this to be possible,  $\gamma_c^s$ , the critical surface tension of the surface, of the support surface must be higher than that of the stationary phase. Values of  $\gamma_c^s$  for the various types of open-tubular columns are sparse; as an alternative, the most polar stationary phase that has been reported to have been used successfully on a particular modified surface will be specified. This assumes that the surface tension of a stationary phase increases with its polarity<sup>16</sup>.

The second quantity is the  $F$  value, which has been defined by Golay<sup>11</sup> as the ratio of the surface area of the modified support to that of an unmodified open-tubular column of similar internal diameter. High  $F$  values enable low values of the phase ratio,  $\beta$ , to be obtained and at the same time, depending on the geometry of the surface, to spread the stationary phase in a thin uniform film.

## DISCUSSION

The data presented here suggest that in whisker-walled open-tubular (WWOT) columns band spreading is essentially determined by mobile phase effects. This is consistent with the fact that the plate height,  $H_{min}$ , decreases when either the column radius is decreased or the diffusivity of the solute in the mobile phase is increased, whereas a decrease in the phase ratio,  $\beta$ , does not significantly increase the plate height.

The effective plate height (at comparable  $K$  values) of WTOT columns is generally higher than that of SCOT columns; WWOT columns are exceptional in

this regard. This difference is basically ascribable to differences in the phase ratios.

All of the modified surfaces can successfully accommodate polar stationary phases and the surfaces can be deactivated sufficiently well so that peak tailing does not cause any significant problems. SCOT columns have larger  $F$  values than do WTOT columns, again with the exception of the WWOT columns.

The amount of sample that can be handled without significantly decreasing the column efficiency is, with the exception of WWOT columns, larger in SCOT columns than WTOT columns.

The data in Table II shows that WWOT columns combine the best performance characteristics of WTOT and SCOT columns. The fact that they are easily and cheaply constructed in long lengths and have been found to withstand relatively rough handling are further attractive features.

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