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## APPLICATION OF FUSED-SILICA CAPILLARY MICRO-PACKED COLUMNS IN GAS CHROMATOGRAPHY–MASS SPECTROMETRY

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### SUMMARY

It has been shown that the efficiency of fused-silica capillary micro-packed columns is nearly the same when they are installed in either a chromatograph–mass spectrometer or a gas chromatograph. Some practical examples of their analytical application are described.

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### INTRODUCTION

At present, packed and open-tubular columns are generally applied in gas chromatography–mass spectrometry (GC–MS)<sup>1–3</sup>. It should be noted, however, that the conventional packed columns are characterized by low efficiency. The classical capillary columns, *i.e.*, the smooth wall columns, cannot be employed for the analyses of low-boiling compounds and trace analyses because of their low sorption capacity and consequently the small sample size.

Averill<sup>4</sup> showed that porous-layer open-tubular (PLOT) columns allow the determination of larger samples by GC–MS, their separation power being not less than that for wall-coated open-tubular columns.

Besides the columns listed above, packed columns with a small diameter are also employed<sup>5,6</sup>. Bruner *et al.*<sup>6</sup> emphasized the high sorption capacity, the small value of the mass-transfer coefficient, *C*, and the possibility of the direct connection of such columns to the ion source of a mass spectrometer. For the analysis of polar compounds, those authors employed the 0.6 mm I.D. glass columns packed with Carbowax B and C (100–120 mesh), coated with a liquid phase.

It is known, however, that glass is characterized by higher adsorption and catalytic activity in comparison with fused silica. In addition, certain experience is required when working with a glass column.

Fused-silica capillary micro-packed columns (CMPCs) possess a high efficiency and a high sorption capacity<sup>7–9</sup>. For such columns with inner diameters less than

0.4 mm packed with microparticles (at most 50  $\mu\text{m}$ ), it was shown that the specific efficiency can be up to 30 000 theoretical plates per metre, the coefficient  $C$  is small (about  $10^{-4}$  s) and the maximum sample size is 2  $\mu\text{g}^{7-9}$ .

The purpose of our investigation was to evaluate the potential of fused-silica CMPCs for GC-MS. Taking into account the direct insertion of the CMPC into the mass spectrometer, it was of interest to examine the affect of the vacuum outlet pressure on the efficiency of the CMPC.

## THEORETICAL

For columns characterized by a high pressure drop, the dependence of the height equivalent to a theoretical plate (HETP),  $H$ , on the linear carrier gas velocity from the column outlet,  $u_0$ , is described by the equation derived by Giddings *et al.*<sup>10</sup>

$$H = \left[ A + \frac{B^0}{u_0} + C_g^0 u_0 \right] f_1 + C_s u_0 f_2 \quad (1)$$

where  $A$  and  $B^0$  correspond to the eddy and longitudinal diffusion respectively,  $C_g^0$  and  $C_s$  denote the mass-transfer coefficients for the gaseous and stationary phases respectively,  $f_1$  and  $f_2$  are the compressibility correction factors and the zero indices correspond to the column outlet conditions.

The expressions derived for viscous flow can roughly be applied to a micro-packed column due to the vacuum outlet pressure. However, the pressure at a CMPC inlet is high, *e.g.*, up to 25 atm<sup>7,8</sup>, and it is expected that effusion would prevail over the viscous flow in the very short tail-end of a column.

On differentiating eqn. 1, the optimum linear carrier gas velocity,  $u_{0,\text{opt}}$ , and the minimum HETP,  $H_{\text{min}}$ , are given as:

$$u_{0,\text{opt}} = \sqrt{\frac{B^0 f_1}{C_g^0 f_1 + C_s f_2}} \quad (2)$$

$$H_{\text{min}} = A f_1 + 2\sqrt{B^0 C_g^0 f_1^2 + B^0 C_s f_1 f_2} \quad (3)$$

Bearing in mind the vacuum outlet conditions, it is more expedient to replace the outlet linear velocity by the average linear velocity,  $\bar{u}_{\text{opt}}$ . Further, the inverse of  $\bar{u}_{\text{opt}}$  will be used to evaluate the contributions of different terms:

$$\frac{1}{\bar{u}_{\text{opt}}} = \frac{1}{\bar{u}_{0,\text{opt}} f_2} = \sqrt{\frac{C_g^0}{B^0 f_2^2} + \frac{C_s}{B^0 f_1 f_2}} \quad (4)$$

In order to assess the differences in the values of  $H_{\text{min}}$  and  $1/\bar{u}_{\text{opt}}$  at the atmospheric outlet pressure and the vacuum outlet pressure, the terms in eqns. 3 and 4 can be expressed as follows (see, for example, refs. 11-13)

$$A = 2\lambda d_p \quad (5)$$

$$B^0 = 2\gamma D_0 \quad (6)$$

$$C_g^0 = b_1 \cdot \frac{k^2}{(1+k)^2} \cdot \frac{d_D^2}{D_0} \quad (7)$$

$$f_1 = \frac{9}{8} \cdot \frac{(P^4 - 1)(P^2 - 1)}{(P^3 - 1)^2} \approx \frac{9}{8} \quad (8)$$

$$f_2 = \frac{3}{2} \cdot \frac{P^2 - 1}{P^3 - 1} \approx \frac{3}{2} \cdot \frac{1}{P} \quad (9)$$

where  $\lambda$ ,  $\gamma$  and  $b_1$  are constants,  $d_p$  is the sorbent particle diameter,  $D_0$  is the solute diffusivity in the gas phase,  $k$  is the capacity factor,  $d_D$  is the average diffusion path in the gas phase and  $P$  is the inlet/outlet pressure ratio,  $P_1/P_0$  (for CMPC,  $P \gg 1$ ). Sorbents lightly loaded with liquid phases and sorbents without liquid phase have generally been used with fused-silica CMPCs<sup>7-9</sup>. In this case, the coefficient  $C_s$  can be written as<sup>12,13</sup>

$$C_s = b_2 \cdot \frac{k}{(1+k)^2} \cdot \frac{l_p^2}{D_s} \quad (10)$$

where  $b_2$  is a constant,  $l_p$  is the pore length and  $D_s$  is the intrinsic diffusivity in the sorbent particle.

From eqns. 5-10, the terms in expressions 3 and 4 can be expressed:

$$Af_1 = \frac{9}{4} \lambda d_p \quad (11)$$

$$B^0 C_g^0 f_1^2 = \frac{81}{32} \cdot \frac{k^2}{(1+k)^2} \cdot \gamma b_1 d_D^2 \quad (12)$$

$$B^0 C_s f_1 f_2 = \frac{27}{8} \cdot \frac{k}{(1+k)^2} \cdot \gamma b_2 l_p^2 \cdot \frac{D_0 P_0}{D_s P_1} \quad (13)$$

$$\frac{C_g^0}{B^0 f_1^2} = \frac{2}{9} \cdot \frac{k^2}{(1+k)^2} \cdot \frac{b_1 d_D^2}{\gamma} \cdot \frac{P_1^2}{(D_0 P_0)^2} \quad (14)$$

$$\frac{C_s}{B^0 f_1 f_2} = \frac{8}{27} \cdot \frac{k}{(1+k)^2} \cdot \frac{b_2 l_p^2}{\gamma} \cdot \frac{P_1}{D_s D_0 P_0} \quad (15)$$

In eqns. 11-15, the values of  $\lambda$ ,  $d_p$ ,  $k$ ,  $\gamma$ ,  $b_1$ ,  $d_D$ ,  $b_2$ ,  $l_p$ ,  $D_0 P_0$  and  $D_s$  are independent of the pressure. The term of  $D_0 P_0$  is constant as  $D_0 P_0 = D_{\text{atm}} P_{\text{atm}}$ . The value of  $D_s$  is assumed also independent of the pressure as the pathlength of the carrier gas molecules is smaller than the pore diameter,  $\Phi_p$ , only in case of high pressure. This pressure is 13 atm at most for the case when  $T = 400$  K,  $\Phi_p = 100$  Å and the effective molecule diameter is 3 Å.

In the case of columns with high hydrodynamic resistance the value of  $P_1$  varies little when  $P_0 \leq 1$  atm. This can be demonstrated by the combined solution of eqn. 2 and Poiseuille's equation.

On the basis of an examination of eqns. 11–15, it is expected that the values of  $H_{\min}$  at  $P_0 = 1$  atm and at the vacuum outlet pressure will be equal. This is also true of  $\bar{u}_{\text{opt}}$ .

For open-tubular columns, Cramers *et al.*<sup>14</sup> calculated theoretically that  $H_{\min}$  at the vacuum outlet pressure is 9/8-times higher than that at  $P_0 = 1$  atm. The equality of the  $H_{\min}$  values was shown experimentally by connecting an open-tubular column to a chromatograph–mass spectrometer as well as to a gas chromatograph<sup>14,15</sup>.

## EXPERIMENTAL

### Columns

Polymer-coated fused-silica capillaries manufactured in the U.S.S.R. and by Scientific Glass Engineering (Australia) were used. Their lengths varied from 100 to 120 cm, the inner diameter being 0.25 or 0.38 mm. The sorbents was Pellosil HC, 30–40  $\mu\text{m}$  (Reeve Angel, Clifton, NJ, U.S.A.) coated with 1% of a stationary liquid phase. The sorbent bed was immobilized at both ends of a column with gas permeable partitions made of a granular material and a binder<sup>16</sup>. The columns were resistant to pressures up to 25 atm: 1, 115 cm  $\times$  0.25 mm I.D., Pellosil HC with 1% Carbowax 20M; 2, 100 cm  $\times$  0.38 mm I.D., Pellosil HC with 1% 1,2,3-tris(2-cyanoethoxy)propane; 3, 120 cm  $\times$  0.25 mm I.D., Pellosil HC with 1% Carbowax 20M.

### Apparatus

The investigations were carried out on a gas chromatograph–mass spectrometer. A monopole mass spectrometer and a turbo-molecular pump (U.S.S.R.) were used. The characteristics of the mass spectrometer were as follows: mass scales from  $m/e$  1 to 200 and from 2 to 400; minimum measured partial pressure of nitrogen,  $10^{-12}$  mmHg; chamber pressure, about  $10^{-6}$  mmHg.

The outlet carrier gas flow was from 1.5 to 4  $\text{cm}^3/\text{min}$  under normal conditions. Due to the low flow-rate the fused-silica CMPCs were directly coupled to the mass spectrometer. The other end of the CMPC was connected to a splitter. The inlet carrier gas pressure was up to 6 atm.

The characteristics of the fused-silica CMPCs were also determined using an LKhM-8MD gas chromatograph (Khromatograf Plant, Moscow, U.S.S.R.) with a flame-ionization detector and a splitter.

## RESULTS AND DISCUSSION

As seen from Table I, the efficiency of the fused-silica CMPCs installed in a chromatograph–mass spectrometer was slightly lower than those installed in a gas chromatograph. The values of  $P_1$  and  $\bar{u}_{\text{opt}}$  were equal for the two situations. The experimental data, therefore, conform to the theoretical assumptions.

Due to their higher sorption capacity the fused-silica CMPCs were applied to the GC–MS analyses of low-boiling compounds and mixtures. A mixture of diethyl ether, ethyl formate, ethyl acetate, *tert.*-butanol and methyl propyl ketone was completely separated on column 1. The analysis time was 60 s ( $T = 125^\circ\text{C}$ , helium carrier gas,  $P_1 = 4.5$  atm). The sorption capacity of fused-silica CMPC was sufficient for

TABLE I  
HEIGHTS EQUIVALENT TO A THEORETICAL PLATE OF FUSED-SILICA CMPCs

Temperature: 130°C. Carrier gas: helium;  $\bar{u} = 2\bar{u}_{opt} = 8.5$  cm/s.

Column	Substance chromatographed	H (min)	
		Gas chromatograph	Chromatograph-mass spectrometer
1	Ethyl acetate	0.38	0.40
3	Pseudocumene	0.35	0.37

this analysis. In particular, the value of  $k$  was 1.6 for ethyl acetate. In comparison, an open-tubular column, namely, a glass column coated with Carbowax 20M, 23 m  $\times$  0.25 mm, did not separate the mixture under the same conditions ( $k = 0.2$ ).

Column 1 was also applied to the analyses of the following mixtures: (1) chloroform, dichloroethane, nitromethane, 2-nitropropane and pyridine, (2) C<sub>6</sub>-C<sub>9</sub> aro-

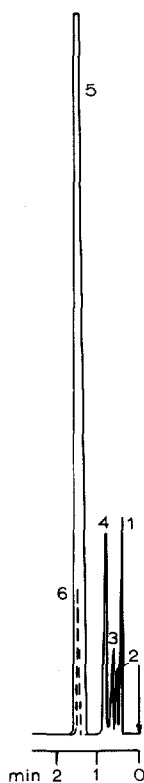


Fig. 1. GC-MS determinations of a mixture containing compounds of different classes. Column: 3, fused silica, 120 cm  $\times$  0.25 mm I.D., Pellosil HC, 30-40  $\mu$ m, coated with 1% Carbowax 20M,  $P_1 = 5.5$  atm. Temperature: 128°C. Peaks: 1 = diethyl ether; 2 = *n*-hexane; 3 = acetone; 4 = ethyl acetate; 5 = toluene; 6 = methyl propyl ketone (4%, w/w).

matic hydrocarbons; (3) aliphatic and alicyclic ketones from acetone to cyclohexanone and 2-octanone.

Admixtures of xylenes (about 0.01%, w/w) in C<sub>6</sub>–C<sub>8</sub> hydrocarbons were determined on column 2.

The difference in mass spectra permits the determination of chromatographically unresolved compounds. In particular, when the mixture of oxygen-containing compounds and hydrocarbons was analysed using column 3, the dominant component (toluene, mass spectral peaks at *m/e* 91 and 92) was masked completely by a minor component (methyl propyl ketone, *m/e* 41 and 43), as is seen in Fig. 1.

It can be concluded that the use of fused-silica CMPCs provides a high separation power as well as a high speed of analysis of admixtures and low-boiling compounds, and thus extends the range of application of GC–MS.

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