The Role of Wall-Coated Capillary Columns in GC-MS Techniques

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Summary
The sensitivity of a capillary column gas chromatography-mass spectrometry connection was investigated with respect to low stationary phase bleed, high efficiency, and low sample capacity of wall-coated capillary columns. Direct coupling, and connection via a two-stage jet separator, were compared, and the inertness of the stainless steel interface, in relation to cholesterol, was tested.

Introduction
The combination of gas chromatography with mass spectrometry is an analytical instrumental method which has an important role in research in both chemical and biological sciences. When wall-coated capillary columns are connected to a mass spectrometer they increase the power and versatility of the system. The low flow-rate of carrier gas into a mass spectrometer and the high separation power of capillary columns have been recognised recently as distinct advantages for the GC-MS connection. Other important features of combining capillary columns with GC-MS, such as faster analyses, higher sensitivity of the system and less background noise, with more easy interpretation of mass spectra still await recognition. This article discusses these features of Capillary Columns-GC-MS combination (CC-GC-MS) which make it possible to take full advantage of the high separation efficiency, sensitivity and speed of the CC-GC-MS method.

Materials and Methods
Wall-Coated, Open Tubular columns (WCOT), 25 m long, are a commercial product. Twenty five columns of each stationary phase, SE 30 and SP 1000, were measured after 18 hours conditioning at temperatures of 290°C and 240°C, respectively. Parameters of the SE 30 columns were measured with the hydrocarbon mixture, n-C15 to C19, and two polar substances, 2,6-xylene and 2,6-xylidine, at 120°C. SP-1000 columns were measured at 150°C. n-C15 to C19 hydrocarbons were used together with 2,6-xylene and 2,6-xylidine. Nitrogen was used for test runs of the column. Results are in Table I.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SE 30</th>
<th>SP 1000</th>
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<tbody>
<tr>
<td>Diameter mm</td>
<td>0.32 ± 0.03</td>
<td>0.38 ± 0.03</td>
</tr>
<tr>
<td>Capacity factor k'</td>
<td>12.3 ± 0.6</td>
<td>7.1 ± 0.3</td>
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<tr>
<td>Number of plates N</td>
<td>79 000 ± 5 000</td>
<td>53 300 ± 6 000</td>
</tr>
<tr>
<td>Coating efficiency %</td>
<td>90 ± 6</td>
<td>69 ± 8</td>
</tr>
<tr>
<td>RI of 2.6-xylene</td>
<td>1086.8 ± 0.6</td>
<td>1919 ± 1.7</td>
</tr>
<tr>
<td>RI of 2.6-xylidine</td>
<td>1145.7 ± 0.6</td>
<td>1870 ± 1.5</td>
</tr>
</tbody>
</table>

Analyses were performed on the LKB 2091-GC-MS instrument, with two-stage jet separator, and provision for mixing additional He with the column effluent. The instrument was equipped with a four-channel Multiple Ion Detector (MID) for detection of selected mass fragments which were specific for the substances analysed. Polycyclic aromatic hydrocarbons and coal tar vapours were analysed on a new, 25 m, SE-30 column, with an initial temperature of 160°C for five minutes, and programme rate of 2°C min⁻¹ to 320°C. Results are in Figs. 1a and 1b. The trace represents the total ion current record. The bis-heptfluorobutyryl derivative of tryptamine (Fig. 2), was analysed on a 12.5 m column, with OV-1 stationary phase. The column was stabilized before use for quantitative analyses by conditioning for 100 hours at 320°C (during nights). The reaction mixture (1 mm³) of tryptamine and heptfluorobutyric acid anhydride (HFBA) was injected via a glass-splitter with a split ratio of 1:2. Column temperature was 150°C for 4 minutes, then programmed 20°C min⁻¹ to 300°C. Carrier gas (He) at 150°C was 34 cm sec⁻¹, or 2 cm³ min⁻¹. The picture is an MID trace of an m/e = 339 fragment, recorded with three-channel UV oscilloscope. The relative sensitivity of the traces is 1:10:100. DDT analyses were made on a 1.5 m packed column, with 3% SE-30 on GasChrom Q, and a 12.5 m SE-30 coated capillary column. Results are shown in Figs. 3 and 4, respectively. Packed column analysis was made at 240°C, with He flow of 20 cm³ min⁻¹. Capillary column analysis conditions were: splitless injection at
300 ~

Fig. 1a

- Mixture of polycyclic aromatic hydrocarbons.

ACE = Acenaphthylene; AC = Acenephtene; F = Fluorene; 
PH = Phenanthrene; A = Anthracene; 1-MePH = 1-methylphenanthrene; 3.6-DMPH = 3.6 Dimethylphenanthrene; FT = Fluoranthene; P = Pyrene; BaF = Benzo (a) fluoranthene; 
BbF = Benzo (b) fluoranthene; BaA = Benzo (a) anthracene; 
C = Chrysene; BkFT = Benzo (k) fluoranthene; BaP = Benzo (a) pyrene; BeP = Benzo (e) pyrene; PER = Perylene.

300 ~

Fig. 1b

- Coal tar extract.

MePH = mixture of methylphenanthrenes and methylantracenes

a column temperature of 180 °C for 5 min. Then, programmed temperature of 15 °C min⁻¹. He velocity at 180 °C was 70 cm sec⁻¹, which corresponds to 4 cm³ min⁻¹.

Mass spectra of cholesterol were scanned from samples introduced both via the direct inlet (Fig. 5a) and the capillary column (Fig. 5b). Conditions for capillary column analysis were as follows: splitless injection of 2 mm³ cholesterol solution in acetone (12 ppm) onto the column at 180 °C. Isothermal period 7 min, then temperature programme 15 °C min⁻¹. Elution temperature of cholesterol was 270 °C. He velocity at 180 °C was 120 cm sec⁻¹ – 7 cm³ min⁻¹. Ion-source temperature was 220 °C, ionization energy 70 eV.

Results and Discussion

High quality capillary columns are necessary for successful work. Their manufacture requires detailed knowledge of the physical and chemical properties of the materials involved [5–7], and also precise control of the coating conditions.

Columns of low quality very often have a quasi-stable film of stationary phase. Solvent injection or temperature increase in such a column results in the shrinkage of the stationary phase and deterioration of the column. This phenomenon has often been incorrectly interpreted as an inherent feature of capillary columns, giving rise to a rumour about the low loadability of wall-coated columns.

Thermodynamically stable columns do not suffer from this disadvantage, and can be loaded with several mm³ of solvent, as has been demonstrated by Grob [8].

The quality of capillary columns can be measured very conveniently in terms of “coating efficiency” [9], defined as

\[ C_{\text{eff}} = \frac{100 \, \text{HETP min}}{\text{HETP}} \% \]  

(1)

where

\[ \text{HETP}_{\text{min}} = \tau \sqrt{\frac{1 + 6k' + 11k^2}{3(1 + k')^2}} \]

HETP is the height equivalent to theoretical plate, measured for the tested column at optimal carrier gas velocity, and k' is the capacity factor of the measured peak. \( C_{\text{eff}} \) is not dependent on column diameter and type of stationary phase, making it possible to compare the quality of different types of columns.

Results in Table I demonstrate that the industrial production of capillary columns may result in a quality close to the theoretical value. Shorter analysis times for the separation of mixtures, and longer life of the columns, are consequences of this fact.

Capillary columns are often criticised, in connection with mass spectrometry, for low sample-capacity, and

1) For explanations of common chromatographic symbols see standard chromatographic textbooks, e.g. [10].