Exploration of a Multicapillary Column for Use in Elevated Speed Gas Chromatography

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EXPLORATION OF A MULTICAPILLARY COLUMN FOR USE IN ELEVATED SPEED GAS CHROMATOGRAPHY

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Elevated speed gas chromatography with a multicapillary column (MCC) was explored using mixtures of volatile alkanes and aromatic hydrocarbons with a 160 mm long MCC at 27°C. The van Deemter curves showed broad minima with volumetric flows from 10–60 mL/min (average linear velocities of 12–70 cm/s) and HETP values of 0.5–3 mm; corresponding retention times were 10–200 s. In comparison, a 2.89 m fused silica capillary column exhibited narrower minima with volumetric flows of 5–20 mL/min (average linear velocities of 105–418 cm/s) and HETP values of 2–70 mm; retention times were 10–60 s at 41°C. The MCC exhibited symmetry factors of ca. 1.3 at 10 ng and this rose to ca. 2.0 at 100 μg; greater loadings may be possible but were precluded here by limitations in the injector rather than the column. Comparison in the separation of volatiles in gasoline showed comparable performance with the conventional fused-silica capillary column. A first examination of the MCC suggests that major advantages exist with respect to low sensitivity in separation efficiency towards carrier gas flow rates and sample loading to at least 10 μg. The mechanical advantages of a MCC were also exploited revealing the simplicity of connecting it to other parts of a GC system.

Keywords: Multicapillary column (MCC), elevated speed GC, photoionization detection (PID), comparative studies

INTRODUCTION

Interest in using gas chromatography (GC) for on-site or in-field analyses has arisen through concerns regarding the integrity of samples when transported to an off-site laboratory, and from the delays and costs associated with a permanent laboratory. As a result, on-site screening of samples with portable gas chromato-

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graphs is an emerging theme in environmental analysis[1-5] even though small, rugged gas chromatographs have been commercially available for decades. Causes for the slow developments or delays with in-field analytical methods by GC are speculative but might be associated with the quality, cost, and inconvenience of commercially available instrumentation which, until recently, had lacked the refinements of laboratory instruments with respect to resolution, column efficiency, and molecular weight range covered. Consequently, the current developments for portable GC for on-site analysis concern the reliability and comparability of results obtained from field GC methods with findings from in-laboratory measurements. Another potential barrier to the advancement of GC for on-site screening could be the analyses times required for high resolution separations with capillary columns. Even analyses times of 5 to 10 minutes might be perceived as limitations, and separations in the 1–100 s range, through high-speed or elevated speed gas chromatography, would be advantageous for on-site measurements. Thus, high speed GC has undergone a resurgence in the 1990s with a comparatively large scope of development; the motivation common to this development seems to be on-site, rapid screening of industrial or environmental samples. Some of the areas emphasized in explorations of high speed GC during the last several years include principles[6,7], actual applications[8-12], advanced detectors[13,14], control of carrier gas pressure[15,16], manufacture of columns in silica[17], and sample injectors or injection methods[18-22]. A notable absence in all of these activities has been the subject of column technology where there have been few or no significant advances.

Columns performance with high speed GC has benefited from the general advances since the late 1970s throughout gas chromatographic technology with the maturation of manufacture of flexible, fused-silica, bonded-phase capillary columns. Such columns which are characterized by low bleed and high thermal stability form the basis for virtually all high speed GC owing to their intrinsic chromatographic properties and to the mechanical strength and flexibility of fused silica. Nonetheless, selecting column length and operating conditions is based upon the compromises in conflicting demands of speed versus resolution and of sample amounts versus column capacity. The solutions to these predicaments are generally to accept the state of art in separations, use readily available flexible capillary columns in short lengths and develop advanced detectors[13] or to exploit column performance through the use of low pressures or controlled-pressure regimes to maximize performance[15,16]. Extended ranges for molecular weights, solved in laboratory gas chromatographs through temperature programming, invites engineering difficulties for field instrumentation and particularly for hand-held gas chromatographs[13]. Two of the difficulties noted above, sample capacity and mechanical packaging, might be alleviated by

bonded-phase multicapillary columns (MCC), recently disclosed as a development from the military establishment of the former USSR.

Multicapillary columns or bundles of small capillaries in a single small tube formed the early models for Golay's experiments in the late 1950s, and his comments in the mid–1970s[23] seemed to have initiated a flurry of interest in MCC[24–27]. These reports were dominated by discussions about the theoretical aspects of MCC and practical difficulties in the manufacture of the capillary bundles from glass. Some experimental results were reported, but the studies had seemingly been abandoned in view of the difficulties in creating uniform coatings of a stationary phase throughout hundreds or thousands of small capillaries. These workers recognized that inconsistencies in phase thickness between neighbouring capillaries in a bundle would degrade peak shape. However, the conundrum of manufacturing multicapillary columns or bundles was not satisfactorily solved[26–27]. Shortly thereafter, these problems had been overcome apparently through a previously unpublicized development program. Multicapillary columns with lengths of 300 mm were created for use originally in the former Red Army, at the present Institute for Applied Physics[28–29], and MCC have become commercially available with a range of stationary phases[30]. The stationary phases are conventional bonded silicones, though the manufacture of the bundles and bonding remain proprietary and patented. A cross-sectional photograph of a multicapillary column, shown in Figure 1, reveals a capillary bundle of over 1000 individual capillaries of inner diameter of 43 μm. In a first public description of these columns[31], retention times were short (< 40s), and the number of theoretical plates per column was high enough (5000 per meter) to merit further evaluation. The size of these columns, 50-300 mm in length and 3 mm in bundle diameter with potentially high volumetric flows are attractive for packaging portable instruments such as GC-ion mobility spectrometers[13].

Little else was known about the performance of these newly available multicapillary columns, and a preliminary assessment of chromatographic performance and retention properties was deemed helpful in gauging future usefulness of such columns. Thus, the objectives for this study were to gain a rapid characterization of one MCC and to provide a first look at feasibility with high-speed or elevated-speed portable GC analyzers. Mixtures of aromatic hydrocarbons including benzene, toluene, and xylene (isomer mixture) and of alkanes from n-pentane to n-octane were selected as an environmentally relevant set of test chemicals. The goal was to subject a multicapillary column to a series of measurements with varied carrier gas flow and sample amount. Another goal was to ascertain the behaviour of the stationary phase and determine standard terms such as height equivalent of a theoretical plate (HETP). Complete optimization for high speed chromatography was not of immediate concern in these studies.

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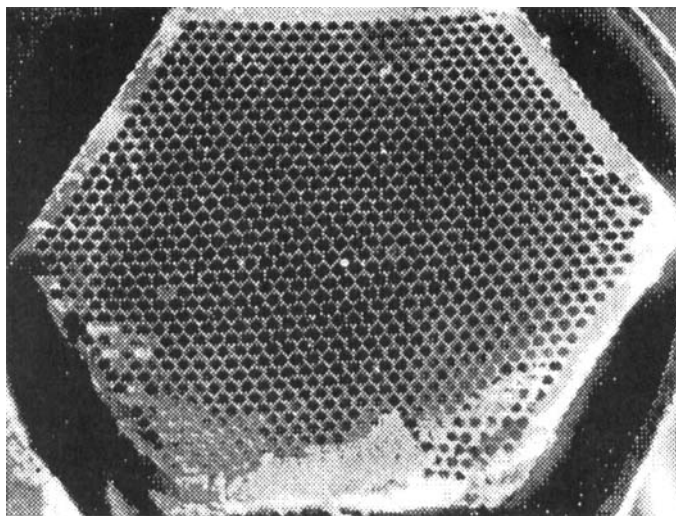
A

Cross section of the column (×43)
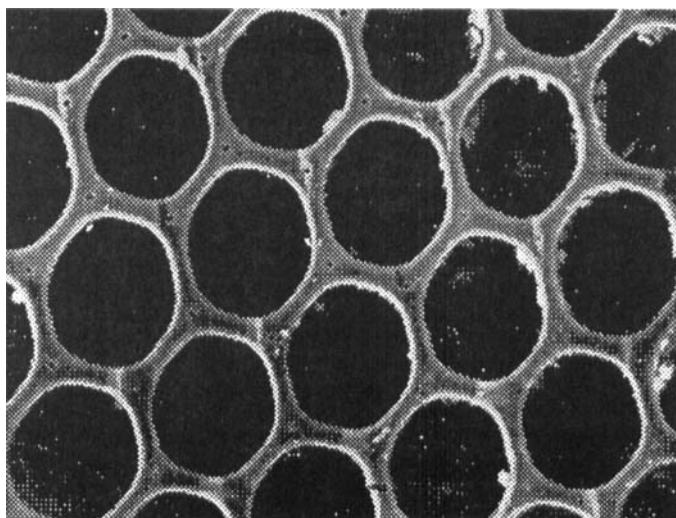
B

Column capillaries (×480)

FIGURE 1 Cross sectional view of the multicapillary column (MCC)

EXPERIMENTAL

Instrumentation

Multicapillary column apparatus

The experimental apparatus consisted of a multicapillary column (Code N5 from the Institute of Applied Physics, Novosibirsk, Russia) with a photoionization detector (PID) and a rudimentary injector as shown in Figure 2. The length of the column, carrying a 0.25 μm thick stationary phase in the capillaries, was 16 cm. The MCC was connected to the PID which was equipped with a 10.6 eV photoionization discharge lamp (Polytech, Waldbronn, Germany). A set of metal rings, under voltage bias, was used with the detector in anticipation of a later expansion of the detector to a full GC-IMS instrument[32]. A flow of nitrogen gas (99.999%) was provided to the column via a Swagelock Tee union and to the detector at a rate of 110 mL/min. The detector electronics were created in the laboratory to provide power to the PID and amplify signal. Signals of 1×10^{-9} A were transformed to 0-5 V. Signals were collected and manipulated using a Intel 80486 based computer with a 32 bit ADC board (Keithly-Metrabyte Corporation, Taumton, MA) and software developed with Test Point for Windows (Capital Equipment Co., Burlington, MA). The column was held in a protective block to prevent mechanical stress and was left at ambient temperature which was practically constant at 27°C in a climate controlled laboratory. No special consideration was given to optimized performance in any particular set of measurements nor was special effort given to electronic time constants. Thus, the findings do not represent ultimate performance for the MCC columns, but may be useful for the intendend application of MCC's for in-field investigations.
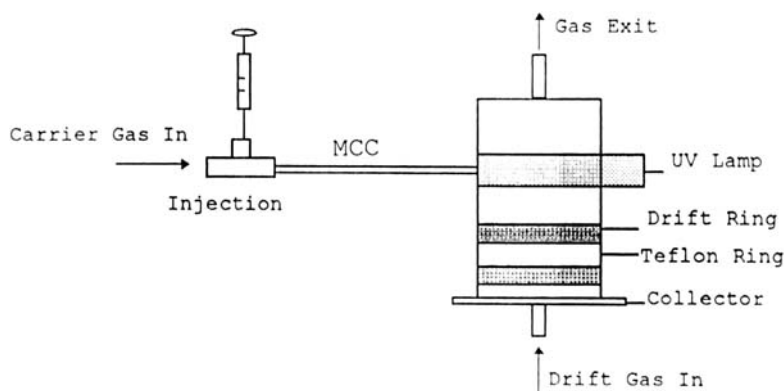

FIGURE 2 Experimental set-up for the MCC with photoionization detector (PID)

GC-PID with conventional bonded capillary column

A reference chromatographic system was based on a model 5890A gas chromatograph (Hewlett-Packard (HP) Co., D–76337 Waldbronn, Germany) equipped with a 2.89 m length of 1.05 µm thick phase HP–5 (5% phenylmethyl silicone bonded phase) fused silica column with 0.32 mm ID (HP Co.) and a photoionization detector (model 4430 PID from O.I.-Analytical, College Station, TX). The injector was operated in splitless mode, and the injector temperature was ambient to resemble the conditions used with the MCC. The column temperature was slightly elevated to 41°C, the lowest temperature that could be controlled in the equipment used.

Reagents and Chemicals

All reagents were analytical grade and used without further treatment, except for n-heptane which was obtained in chromatographic grade (99.7%) from Fluka Chemicals (Fluka-Chemie, D–89231 Neu-Ulm, Germany). All carrier gases were 99.999% and used without further treatment.

Procedures

Generation of Test Gas Mixtures

Since the injection ports were unheated, samples were generated as vapors in a dilution apparatus. Microliter amounts of neat liquid were injected into a 5 L glass bottle equipped with a cap that had been modified with a Swagelock union. After adding a known amount of liquid with syringes in volumes from 1 to 100 µL, the mixture was left for one hour; a sample was withdrawn through the Swagelock union using a gas tight syringe. Sample volumes were 1–250 µL, but commonly 10 or 100 µL. Two sets of mixtures were created: the alkane mixture containing n-pentane, n-hexane, n-heptane and n-octane in approximately equal amounts and the aromatic hydrocarbon mixture containing benzene, toluene, and xylene (isomer mixture) in approximately equal amounts.

Column Studies with varying Flow and Amount of Sample

Test mixtures of alkanes and aromatic hydrocarbons were used with the MCC apparatus and the HP–5 fused silica column under isothermal conditions, and either flow rate or sample loading were altered between extremes to measure column performance. The flows were changed between 1 to 100 m/min under ambient temperature for the MCC and slightly warmed for the HP–5. The sample loading for heptane was varied from 1 ng to 100 µg. This was done under conditions of carrier gas flow of 13 mL/min for the MCC and 8 mUmin for the HP–5.

Heptane was chosen for the high purity that was available commercially and the clean chromatogram obtained to allow interference-free measurements of peak broadening.

Evaluation of Retention Characteristics of the Stationary Phase

The stationary phases available with the MCC columns are purported to be conventional phases which are cross linked, however uncertainties existed over possible alterations of the phase through the yet unknown manufacturing process. Consequently, characterization of the liquid phase with a set of probe compounds was made, and the probes are shown in Table 1. The list contains a selection of volatiles, sufficient to provide an insight into the phase properties but incomplete to make a Rohrschneider or McReynolds calculation[33].

TABLE I Listing of Kovats numbers for a range of chemicals for MCC and HP-5 (to compare stationary phase properties)

chemical	MCC	HP-5
benzene	658	659
toluene	761	768
m-xylene	854	888
ethanol	499	419
1-propanol	579	552
1-butanol	681	674
acetone	513	476
3-pentanone	694	700
trichloroethene	698	699
tetrachloroethene	814	819

Resolution with a Complex Mixture

A preliminary measure of the performance of the MCC with a complex mixture was sought, and unleaded gasoline was chosen owing to the environmental importance of fuel spills or leaks and the complexity of these mixtures. Gasoline was obtained locally in Dortmund and used without pre-treatment. Thirty microliters of gasoline were injected into the 5 L bottle for vaporization; vapor samples for analysis were 80 µL for the MCC and 50 µL for the HP–5 column.

RESULTS AND DISCUSSION

Effects of Flow Rate on HETP and Retention Times

The effects of carrier gas flow on column efficiency for the MCC column and the narrow bore column of 2.89 m in length used to reference performance of the

MCC, are shown in Figure 3 as plots of HETP against volumetric flows and lin-
ear velocities. In Frame A, curves are shown for alkanes and aromatics and were
selected for k' values (capacity ratios) of 2-10 at ambient temperature. Optimum
performance for these columns occurred over a significant range of nearly
20 mL/min or more at volumetric flows of 10 to 30 mL/min for alkanes and 10 to
80 mL/min for aromatics. These values correspond to average linear velocities of
12 to 36 cm/s and 12 to 96 cm/s, respectively.

Linear Velocity in cm/s (Upper Axes)

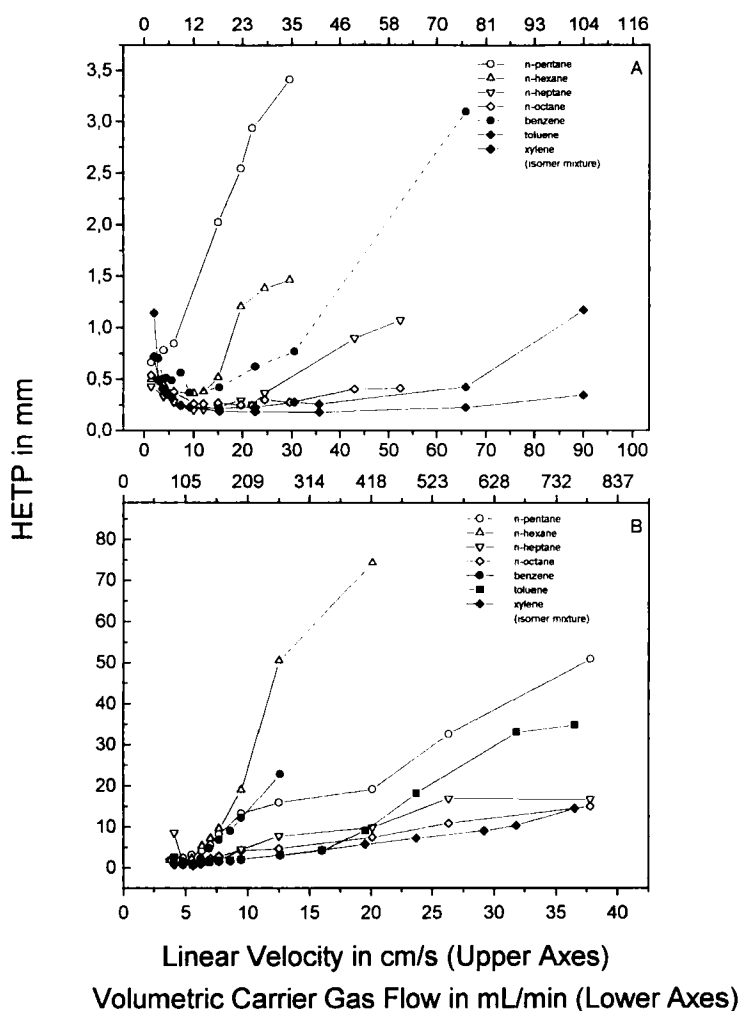**Volumetric Carrier Gas Flow in mL/min (Lower Axes)**

FIGURE 3 Plot of HETP versus flow rate for MCC (Frame A) and a short length of conventional
bonded-phase capillary column (Frame B)

Representative chromatograms from these studies illustrating the peak shapes under these conditions are shown in Figure 4. Peak shapes for chromatograms of 100 s showed smooth profiles from large numbers of measurements. Since the ADC rates were not optimized for each run time to yield a similar number of data points for every run, chromatograms of 20 s showed pronounced distortion. This was regarded, however, as acceptable for the objectives of the study: a broad evaluation of MCC rather than optimized performance.

The results from the reference column are shown in Frame B of Figure 3. The plots for the alkanes showed optima from 2-5 m/min with HETP values roughly 2-3 times those for the MCC and with a steep rise in HETP for large flows. The plots for aromatics showed broad minima compared to those for alkanes though these curves were also more sensitive to flow rate as compared with the MCC.

These results suggest certain practical ramifications including robust performance without care toward flow control and operation with flow rates greater than those employed for traditional columns; this might simplify slightly the design of detectors for which flows of 20–30 mL/min are optimum, as is the case for a flame ionization detector. More than these advantages counts the possibility of drawing substantial volumes of a gaseous sample through the column when on-column preconcentration is employed. The limitation is that of dilution of a deposited band of finite mass with large volumes of carrier gas during elution and separation.
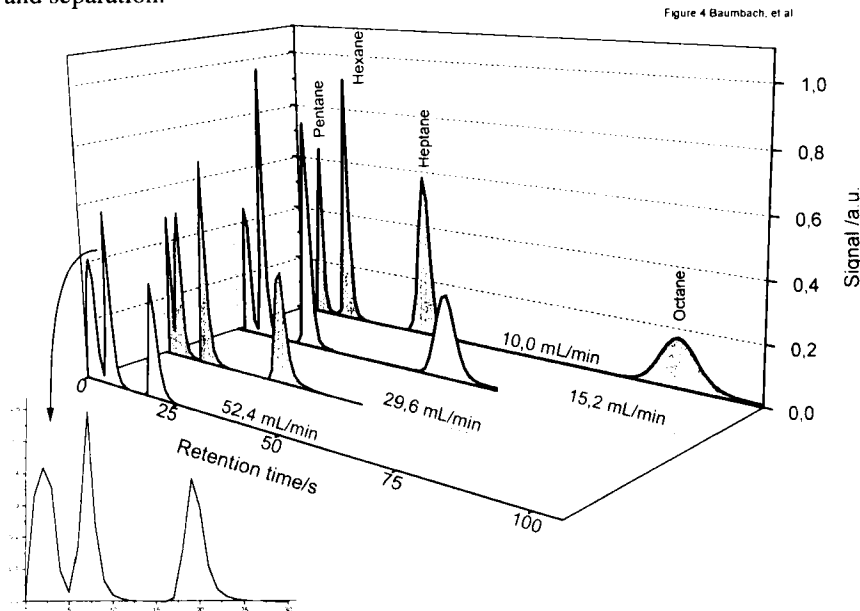

FIGURE 4 Plot of chromatograms of a mixture of n-pentane (135 ng), n-hexane (114 ng), n-heptane (118 ng) and n-octane (112 ng) at various flow rates

The influence of flow rate on retention under isothermal conditions is shown in Figure 5 where gross retention times for the test mixtures are shown for a MCC column (27°C, Frame A) and the reference 2.89 m bonded phase capillary column (41°C, Frame B). For MCC, the retention time curves for the alkanes all showed similar profiles and reached a shallow slope at ca. 25-35 mL/min or 29-41 cm/s. A similar pattern was observed for the HP-5 column at ca. 10-15 mLmin or 209-314 cm/s (see Frame B). The pattern for the aromatics was also comparable for the two columns as shown in Frames A and B of Figure 5.
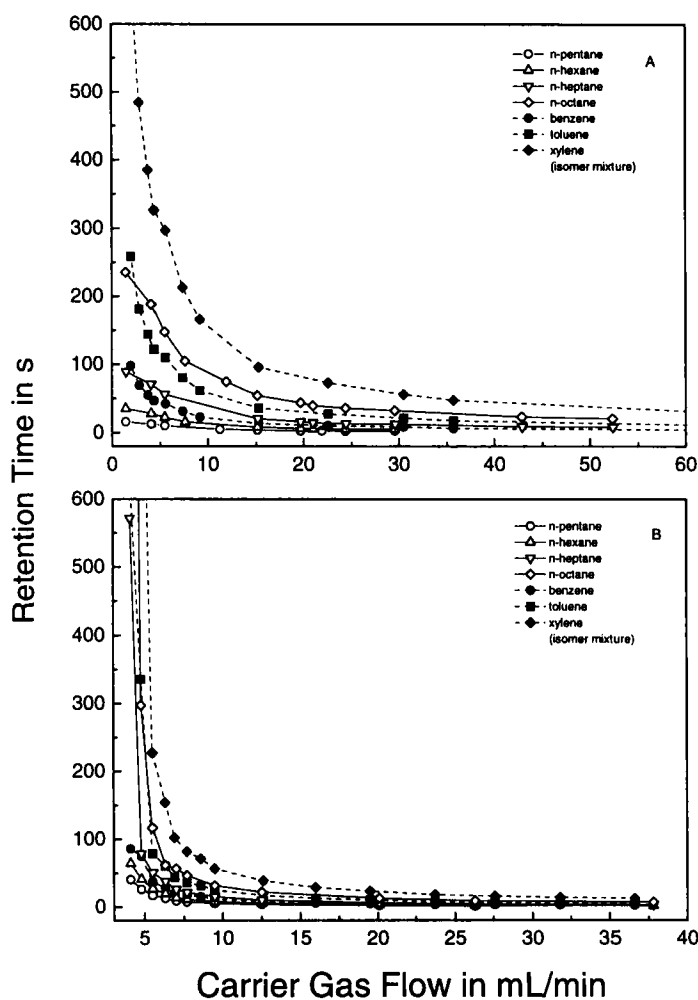

FIGURE 5 Plot of retention time versus flow rate of carrier gas for a MCC (27°C, Frame A) and a 2.89 m HP–5 column (41°C, Frame B)

Asymmetry and Sample Loading

One potential benefit of the MCC with an estimated volume loading of stationary phase of 5.4 mm^3 for a film thickness of 0.25 μm and 1000 capillaries of 43 μm ID and 16 cm length versus a 2.89 m HP–5 column of 0.32 mm ID and 1 μm film thickness (stationary phase estimated as 2,4 mm^3) is the increased capacity for sample loading. Heptane was chosen for this study owing to high purity and retention times of >20 s (k'>3) at flow rates of 13 mL/min (MCC, 27°C) and 8 mL/min (HP–5, 41°C), respectively, and results are shown in Figure 6 for peak asymmetry (expressed by the tailing factor[34]) and retention time. In the range of 10-1000 ng, the asymmetry for the 2.89 m long HP-5 column, at splitless injection, was nearly 3 times worse than that for the MCC because of peak tailing. For amounts of heptane greater than 5 μg peak distortion, front-skewing and tailing occur. Peak distortion could be influenced by extra-column effects, the injection port in this instance, voiding calculations of retention time or asymmetry terms. In contrast, the MCC provided suitable chromatograms for evaluation with amounts of heptane even higher than 5 μg, but injector contributions became noticeable here also. The tailing factors for the MCC were low throughout the range of sample loading, though results at 10 μg and greater should be considered unreliable owing to injector contributions. The points are shown here only to illustrate the robustness of the MCC towards amounts of up to 100 μg. The
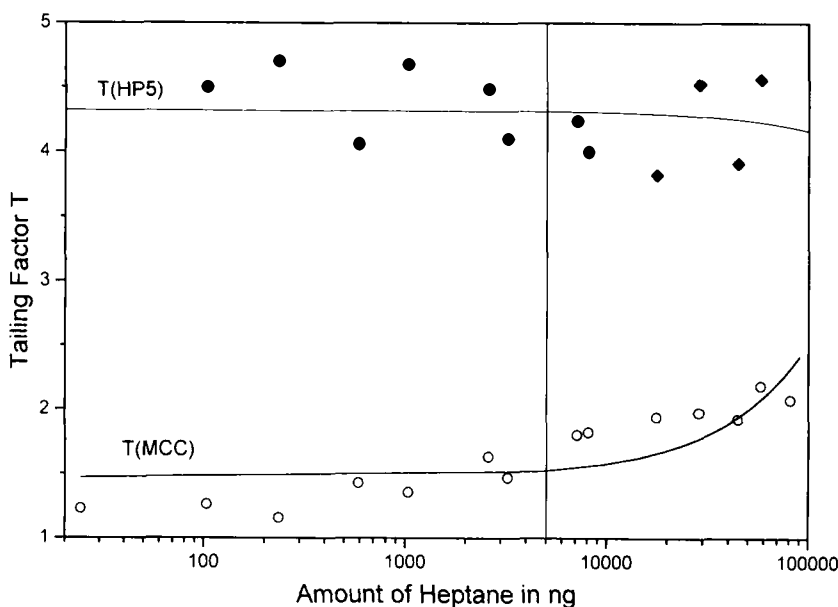

FIGURE 6 Plots of tailing factor versus sample amount for MCC (carrier gas flow 13 m/min) and HP–5 column (carrier gas flow 8 mL/min)
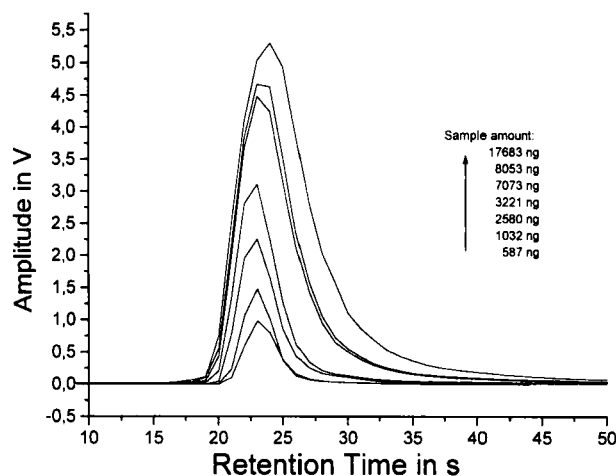
FIGURE 7 MCC peaks for n-heptane at various sample loads. The amounts of chemical were (in ng):
587, 1032, 2580, 3221, 7073, 8053, 17683 in ascending order

chromatographic profiles for the MCC are shown in Figure 7 where the effect of
increasing sample amount is shown in tailing. Eventually, contributions from the
injection port arise with a broad peak at increased retention times.

Stationary Phase Polarity

The column as received was an early production item, which had been selected
from existing and stored stock, and arrived with little documentation and with an
understanding that the phase was either 0% or 5% phenyl-methyl silicone,
though additional phases were becoming available. Thus, a characterization of
the phase was essential, and the results from the determination of Kovats reten-
tion indices are shown in Table I and comparison can be made between the MCC
and the HP–5 column (5% phenyl-methyl silicone). Comparison of the retention
indices in Table I, on the whole, suggests that the surface coating was a 5% phe-
nyl-methyl silicone, and that the manufacturing provided a stationary phase
remarkably like the ones in columns that have become industry standard.

Application

The detection of gasoline in environmental matrices is one relevant application
of high-speed portable GC with photoionization detector that can be used to
probe actual resolution of the MCC. Results from chromatographic analyses of
vapors of unleaded gasoline are shown in Figure 8. The resolution of the MCC
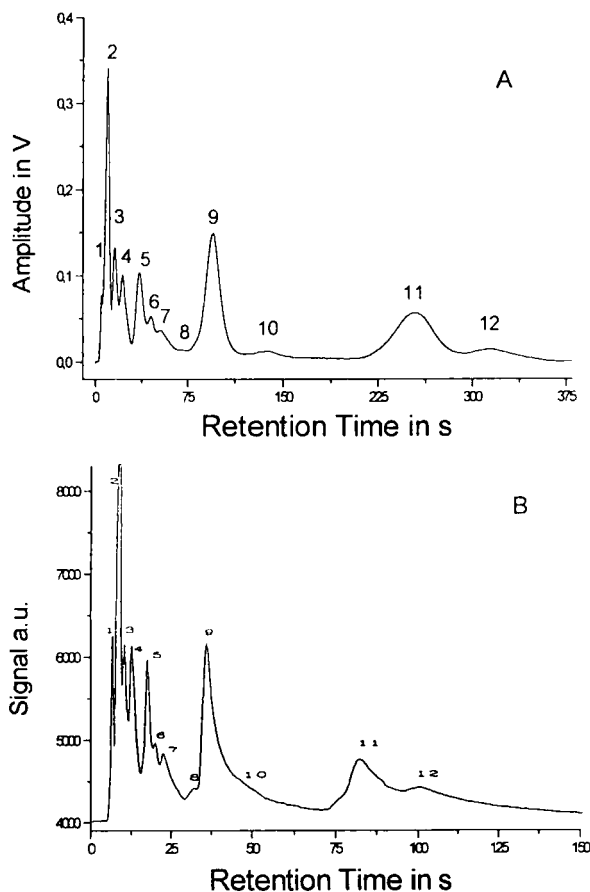
FIGURE 8 Chromatograms of gasoline test gas samples for MCC (carrier gas flow 6 mL/min, A) and HP-5 (carrier gaz flow 8 ml/min, B). Peak identification: 1: n-Butane; 2: n-Pentane; 3: not identified; 4: n-Hexane; 5: Benzene/Cyclohexane; 6: iso-Octane; 7: n-Heptane; 8: not identified; 9: Toluene; 10: n-Octane; 11: Xylenes; 12: not identified

and the 2.89 m HP-5 column were comparable though retention times for the MCC were up to 3 times longer than those for the HP-5. Thus, no startling increase in separation efficiency and speed was afforded with the MCC but suitable performance against a standard capillary column exhibited.

CONCLUSIONS

The multicapillary column allows separations to be carried out not at high speed but at elevated speed (>10s). It can be operated with increased carrier gas flows

that would be especially helpful if the column is being used with pre-enrichment strategies where the column serves as sampler and analyzer, or is combined with detectors that perform best at elevated flow rates, such as FID, PID and IMS (ion mobility spectrometer). Optimum chromatographic performance over a broad range of more than 20 mL/min would allow a high tolerance for control over the carrier gas to maintain best separations. The stationary phase tested here shows retention properties comparable to those for a commercial 5% phenyl-methyl silicone bonded phase column, supporting statements that MCC's are available with ordinary bonded stationary phases. The effects of sample loading were noticeable in the 10 ng to 10 µg range but could only provisionally be tested at truly high levels up to 100 µg, owing to simple injector arrangements and test gas generation procedures. The mechanical integrity was not formally tested, but convenience and informality of plumbing supported the expectations as to stable performance at flow rates of 30 mL/min or more. The chromatographic separation achieved with a complex mixture was comparable to that for a 2.89 m bonded-phase column. This first examination of a MCC, intended to mimic conditions on a simple, low-powered GC should now be enhanced with careful attention to heated, well-designed injection ports and to control of column temperature.

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