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Journal of Chromatography A, 892 (2000) 3–13

JOURNAL OF  
CHROMATOGRAPHY A

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# Fast gas chromatography: packed column solvating gas chromatography versus open tubular column gas chromatography

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## Abstract

Packed capillary column solvating gas chromatography (SGC) and open tubular column gas chromatography (GC) were compared with respect to their potentials for fast separations. A recently introduced “universal” peak capacity equation was used to compare the performance of these two methods. The effects of various factors on peak capacity were investigated. Results demonstrate that retention factor and column efficiency are the main factors affecting peak capacity for fast separations. Packed columns produce both high retention factors and high selectivities. While high efficiencies and high peak capacities can be demonstrated by both techniques, open tubular column GC can surpass packed capillary column SGC in both measurements, except for the case of the analysis of simple mixtures in short analysis times, where retention factor and selectivity become important. Practical aspects such as pressure drop and sample capacity are compared for SGC and open tubular column GC. It was found that packed column SGC demonstrates higher sample capacities, but requires much higher column inlet pressures than open tubular column GC. A variety of mobile phases can be used for packed column SGC, which can provide high solvating power for large and polar compounds. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Gas chromatography; Fast chromatography; Open tubular columns; Packed capillary columns; Capillary columns; Peak capacity; Solvating gas chromatography; Sample capacity; Diesel fuel; Hydrocarbons; Phenols; Diesel

## 1. Introduction

Since the introduction of gas chromatography (GC) in 1941 by Martin and Synge [1], fast GC has been widely investigated using both packed and open tubular columns. A breakthrough in GC performance was the invention of open tubular columns by Golay in 1957 [2]. Five years later, Desty et al. [3,4] pioneered fast gas chromatographic separations using narrow-bore open tubular columns. They showed, both theoretically and experimentally, that decreasing

the column inner diameter is necessary to obtain the required efficiency to perform fast separations. This approach was further investigated by Gaspar [5,6] and Schutjes and co-workers [7,8]. The lack of adequate instrumentation seriously delayed the application of narrow-bore columns (<100  $\mu\text{m}$  I.D.) because the input band width, the amount of injected sample, and the detection limits are all critical factors. van Es et al. [9] improved the sampling system and successfully separated nine hydrocarbons in 0.7 s using a 30 cm $\times$ 50  $\mu\text{m}$  I.D. capillary column. Tijssen et al. [10] and Hail and Yost [11] further showed the theoretical and practical aspects of fast separations using short capillary columns. Recently, multicapillary column GC has proven to be an

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attractive technique for fast separations because of its ability to improve sample capacity as well as to provide high column efficiency [12–14]. Other strategies involving rapid temperature programming [15,16], vacuum outlet [17], and turbulent flow [18] have also been reported for fast open tubular column GC.

Another approach to fast GC is to use packed columns. Between 1960 and 1980, several groups investigated the potential of packed column GC using microparticulate packing materials [19–21]. In 1979, Lu et al. [22] separated nine compounds in 10 s using columns packed with 7  $\mu\text{m}$  silica particles and carbon dioxide as mobile phase. In 1982, Jonker et al. [23] significantly improved the detection and injection systems for fast separations, and the separation time was decreased to 0.15 s for four compounds using a 3.2 cm column packed with 10  $\mu\text{m}$  porous silica particles. Recently, solvating mobile phases including carbon dioxide and organic solvents have been used in packed capillary column GC, leading to high column efficiencies and fast analyses [24,25]. Researchers studying packed column GC emphasized that packed columns containing microparticles provided both higher column efficiency per unit length and higher sample capacity than open tubular columns. However, the rapid development of open tubular column technology eclipsed studies and applications of packed column GC. The excellent permeability of open tubular columns made it possible to use long columns with small column diameters for fast separations. Furthermore, column preparation was simplified with open tubular columns. Today, the fundamental question is still debated: which technique is better for fast separations, open tubular or packed column GC?

In order to attempt an answer to this question, an accurate and fair measurement should be used to compare the speed of fast separations. Efficiency per unit time has been widely used as the measurement for fast separations [9,23,24]. Fig. 1 shows two fast separations using two different lengths of columns [24]. It can be seen that although the plates per second ( $N_t$ ) in Fig. 1A are approximately twice those in Fig. 1B, the separation in Fig. 1B is acceptably faster because it shows similar resolution but shorter separation time. The average retention factors for the separation in Fig. 1B are higher than those in Fig.

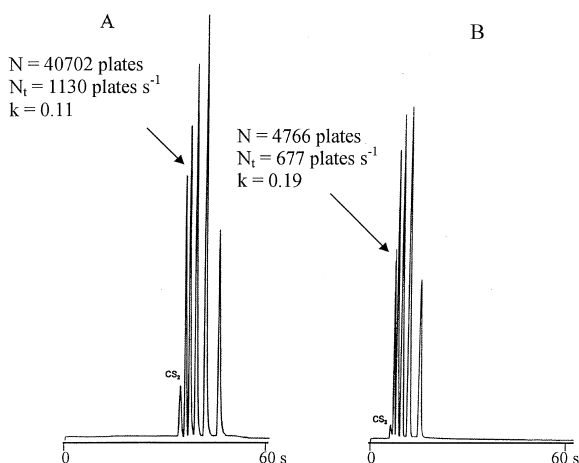


Fig. 1. Examples of fast SGC separations. Conditions: (A) 57 cm  $\times$  250  $\mu\text{m}$  I.D. capillary packed with 3  $\mu\text{m}$  nonporous ODS particles, 130°C, 170 atm (1 atm =  $1.01 \cdot 10^5$  Pa),  $\text{CO}_2$ , (B) 20 cm, 95 atm; other conditions as in (A). Reprinted with permission from Ref. [24].

1A. This implies that efficiency per unit time does not necessarily take into account the influence of retention factor on separation.

Resolution per unit time has also been used to compare the performance for fast GC separations [26,27]. However, resolution is usually only applicable to two components and it does not reflect the total separation power of a column. The peak capacity is a more useful measurement, as it gives the number of peaks separable with a resolution of unity within a specific time interval. Recently, Shen and Lee [28] introduced a more general peak capacity equation under isothermal and isobaric conditions:

$$n = 1 + \frac{\sqrt{5.54}}{4a} \cdot \ln \frac{at_n - b}{at_1 - b} \quad (1)$$

where  $n$  is the peak capacity, and  $t_1$  and  $t_n$  are the retention times of the first and  $n$ th peaks, respectively. The constant  $a$  equals  $(5.54/N_\infty)^2$ , where  $N_\infty$  is the theoretical plate number when the retention time approaches infinity. The constant  $b$  represents the influence of retention factor on  $N$ . In this study, we used the dead time  $t_0$  as  $t_1$ . It can be seen from Eq. (1) that within a given separation time,  $t_n$ , the peak capacity is dependent on the column efficiency, the  $b$  value, and the dead time of the column. The former

two factors are, in turn, affected by retention factor. In this work, we first investigated the effects of various factors on peak capacity. Then, we compared the potentials of open tubular column GC and packed column solvating GC (SGC) for fast separations. Furthermore, sample capacity, solvating power, and pressure drop for open tubular column GC and SGC were considered. Finally, exemplary fast separations were performed for comparison of the two techniques.

## 2. Experimental

### 2.1. Materials

Spherical porous silica (5  $\mu\text{m}$  and 10  $\mu\text{m}$ , 80  $\text{\AA}$ ) ODS and 5  $\mu\text{m}$  bare silica (60  $\text{\AA}$ , 300  $\text{\AA}$ ) particles were purchased from Alltech (Deerfield, IL, USA). Spherical porous ODS (80  $\text{\AA}$ ) particles of 3  $\mu\text{m}$  diameter were purchased from Phase Separations (Norwalk, CT, USA). Fused-silica capillary tubing was purchased from Polymicro Technologies (Phoenix, AZ, USA). Fused-silica capillary columns (50, 100, and 200  $\mu\text{m}$  I.D., 0.2  $\mu\text{m}$  DB-5) were purchased from J&W Scientific (Folsom, CA, USA). A porous-layer open tubular (PLOT) column (Carboxen 1006, 320  $\mu\text{m}$  I.D.) was obtained from Supelco (Bellefonte, PA, USA). Hexamethyldisilazane (HMDS), various phenol derivatives and normal hydrocarbons were purchased from Aldrich (Milwaukee, WI, USA). Light hydrocarbons ( $\text{C}_1$ – $\text{C}_4$ ) were purchased from Airgas (Radnor, PA, USA). Light hydrocarbons (methane, ethane, ethylene and ethyne) were purchased from Supelco. All other chemicals were purchased from Sigma (St. Louis, MO, USA).

### 2.2. Packed column SGC and GC

Polyhydrosiloxane (United Chemicals, Bristol, PA, USA) was used to encapsulate the 5  $\mu\text{m}$  (300  $\text{\AA}$ ) silica particles. The detailed procedure can be found in the literature [29,30]. All columns were packed using a  $\text{CO}_2$  slurry method as previously described [31].

SGC and GC experiments were carried out using a

Lee Scientific Model 501 SFC instrument with SFC grade  $\text{CO}_2$  (Scott Specialty Gases, Plumsteadville, PA, USA) for SGC, and helium for packed column GC. Column connections were made using zero dead-volume unions (Valco Instruments, Houston, TX, USA). A manual liquid injector (Valco Instruments) with a rotor volume of 0.06  $\mu\text{l}$  was used for introduction of samples. Detection was accomplished using a flame ionization detection (FID) system.

### 2.3. Open tubular column GC

Open tubular column GC experiments were carried out using a Hewlett-Packard 5890 Series II gas chromatograph with FID. Helium and hydrogen were used as mobile phases at various split ratios. All other open tubular columns were purchased as listed in Section 2.1.

## 3. Results and discussion

### 3.1. How fast is fast?

In order to simplify the calculation of a meaningful separation time for a sample that contains  $n$  components, the conventional peak capacity equation can be used:

$$n = 1 + \int_1^n \frac{\sqrt{N}}{4} \cdot \frac{dt}{t} = 1 + \frac{\sqrt{N}}{4} \cdot \ln \frac{t_n}{t_0} \quad (2)$$

where  $t_n = t_0(k_n + 1)$ . The separation time for the  $n$ th component can be found from Eq. (2):

$$t_n = t_0 \exp[4(n-1)/N^{0.5}] \quad (3)$$

It can be seen that the separation time is mainly determined by column efficiency and peak capacity or the number of compounds that are to be separated. The later two factors are related to retention characteristics of these components. Table 1 shows the theoretically expected minimum separation time for samples with different numbers of components. It can be seen that if a mixture of five compounds could be separated in 0.4 s using a column packed with 10  $\mu\text{m}$  particles, the separation could be considered fast. Similarly, if a mixture of 300

Table 1  
Theoretically expected minimum separation times for packed column GC<sup>a</sup>

$n$	$k_n$	$N_{\text{req}}$	$d_p$ ( $\mu\text{m}$ )	$L$ (cm)	$t_n$
5	2	210	10	0.7	0.4 s
50	10	6700	10	22	48 s
300	20	154 000	10	510	36 min

<sup>a</sup> It was assumed that  $N_{\text{max}} = 30\,000$  plates  $\text{m}^{-1}$ ,  $u = 5$  cm  $\text{s}^{-1}$ ,  $N$  is independent of  $t_R$ . The  $k_n$  values were arbitrarily chosen, which are typical values in SGC. From Eq. (3) and  $t_n = t_0(1 + k_n)$ , it can be found that  $t_n/t_0 = 1 + k_n = \exp[4(n-1)/N^{0.5}]$ . Thus,  $N_{\text{req}} = [4(n-1)/\ln(1+k_n)]^2$ . Column length  $L$  was estimated from  $N_{\text{req}}$  and  $N_{\text{max}}$ . The  $t_0$  value was found from column length  $L$  and linear velocity  $u$ . Finally,  $t_n$  was calculated from the equation  $t_n = t_0(1 + k_n)$ .

compounds could be separated in 36 min, it would also be called a fast separation. Therefore, fast is a relative quantity that is difficult to precisely define. In this study, we selected samples with various levels of complexities, so that the separation speeds of SGC and open tubular column GC could be properly compared.

### 3.2. Factors affecting peak capacity

In order to optimize the separation conditions for fast SGC and open tubular column GC, we first

investigated the effects of various factors on peak capacity. When the conventional peak capacity Eq. (2) was derived, an assumption was made that the efficiency of each solute band should be independent of retention time. However, the plate number is closely related to retention, especially for fast separations where retention factors are usually less than 5. A more ‘‘universal’’ equation, such as Eq. (1) should be used, which takes into account the dependence of column theoretical plate number on retention.

#### 3.2.1. Retention factor

The constant  $b$  in Eq. (1) represents the influence of retention factor on  $N$ ; however, no direct relationship has been found between the retention factor and the  $b$  value. Fig. 2 shows the effect of the retention factor ( $k_n$ ) for the  $n$ th component on the  $b$  value. An empirical relationship can be found from experimental results:

$$b = \alpha + \beta \ln k_n \quad (4)$$

where  $\alpha$  and  $\beta$  are experimental constants. From Eqs. (1) and (2) it can be seen that peak capacity increases with increasing retention factor ( $k_n$ ) of the  $n$ th component and, thus, with increasing  $b$  value. In SGC, column retention factors can be tuned by

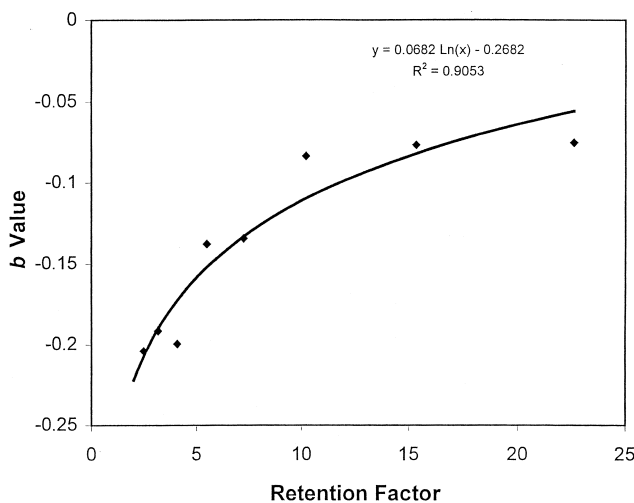


Fig. 2. Relationship between retention factor and  $b$  value in SGC. Conditions: 30 cm  $\times$  250  $\mu\text{m}$  I.D. capillary packed with 5  $\mu\text{m}$  porous (300  $\text{\AA}$ ) silica particles encapsulated with 10% (w/w) polyoctylhydrosiloxane, 100–150 $^{\circ}\text{C}$ , 160 atm,  $\text{CO}_2$ ,  $n\text{-C}_8$  as test solute for determination of retention factors;  $n\text{-C}_8$ ,  $n\text{-C}_9$ ,  $n\text{-C}_{10}$ ,  $n\text{-C}_{11}$  and  $n\text{-C}_{12}$  as standards for determination of  $b$  values.

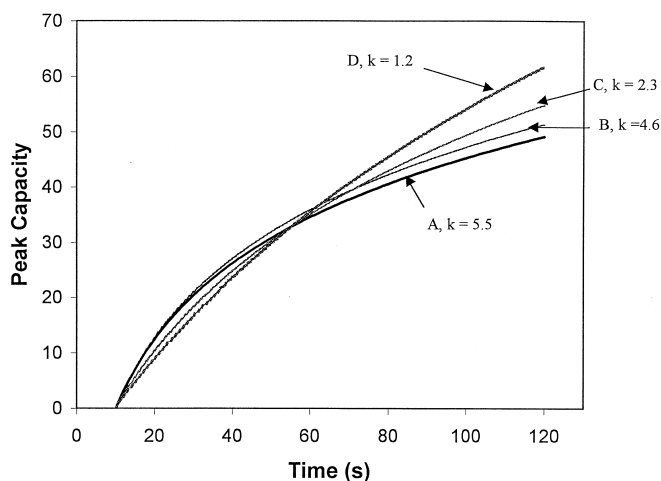


Fig. 3. Effect of retention factor on peak capacity at constant  $t_0$  in SGC. Conditions: 30 cm  $\times$  250  $\mu$ m I.D. capillary packed with 5  $\mu$ m porous (300  $\text{\AA}$ ) silica particles encapsulated with 10% (w/w) polyoctylhydrosiloxane, 160 atm,  $\text{CO}_2$ ,  $n$ - $\text{C}_8$  as test solute, (A) 100°C, (B) 110°C, (C) 150°C, (D) 200°C.

changing temperature and pressure or by using different stationary phases.

Fig. 3 shows the effect of retention factor on peak capacity in a time range of 0–120 s. The peak capacities were determined using the same column at the same inlet pressure. The dead time ( $t_0$ ) was constant under the experimental conditions because it was found that temperature had little effect on the linear velocity at temperatures higher than 100°C and at 160 atm (1 atm =  $1.01 \cdot 10^5$  Pa). It can be seen that the peak capacity increases with increasing column retention factor when the retention time is less than a certain value ( $\sim 60$  s) and decreases when the retention time is higher than this value. This suggests that an increase in the column retention factor favors fast separations of low retained compounds. Fig. 3 also suggests that raising the temperature favors fast separations of more retained compounds.

### 3.2.2. Column efficiency

The term  $N_{\infty}$  in Eq. (1) can be considered to be the effective plate number when the retention factor approaches infinity [32]. The effective plate number proportionally increases with an increase in column efficiency. Fig. 4 gives theoretical plots that show the effect of column efficiency on peak capacity for constant  $t_0$ . It can be seen that peak capacity is

significantly influenced by column efficiency when retention factor (thus,  $b$  value) and dead time ( $t_0$ ) are kept constant.

Fig. 5 shows the effect of column diameter on peak capacity in open tubular column GC. The peak capacity greatly increases when the column diameter decreases from 200 to 50  $\mu$ m I.D. Obviously, columns with small diameters are favored for fast separations. Here, column efficiency was the greatest contribution to peak capacity, although retention factors vary with column diameter.

### 3.2.3. Dead time

Theoretical plots showing the effect of dead time ( $t_0$ ) on peak capacity are shown in Fig. 6. If column efficiency and retention factor are kept constant, peak capacity increases with a decrease in dead time because the separation window increases. This result suggests that short columns packed with small particles would provide high peak capacities and be preferred for fast separations in SGC.

Other factors such as pressure can produce additional effects on peak capacity in SGC. Changing the column inlet pressure can cause changes in column efficiency, linear velocity (thus, dead time), and retention factor. These changes are complicated and not easily optimized for peak capacity and speed.

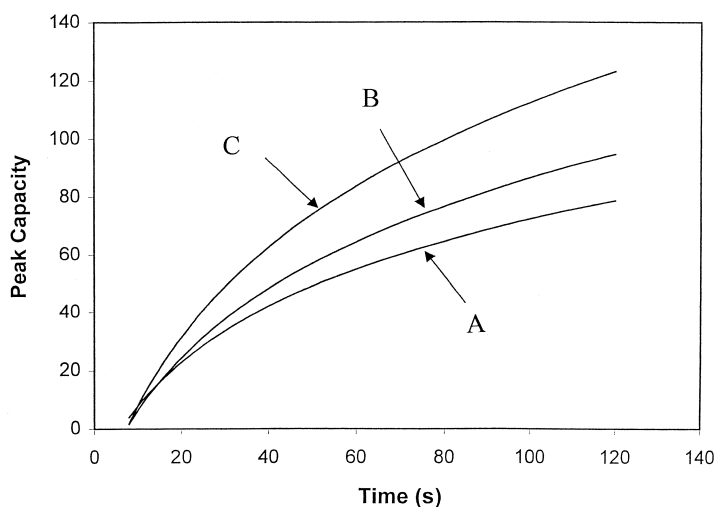


Fig. 4. Effect of column efficiency on peak capacity at constant  $t_0$  and  $b$  value. Conditions:  $t_0 = 10$  s,  $b = -0.2$ ,  $N_{\infty}$  = (A) 30 000 plates, (B) 50 000 plates, (C) 80 000 plates.

### 3.3. Open tubular column GC versus packed column SGC

#### 3.3.1. Peak capacity

Fig. 7 shows separations of light hydrocarbons using packed and open tubular columns. When a 4

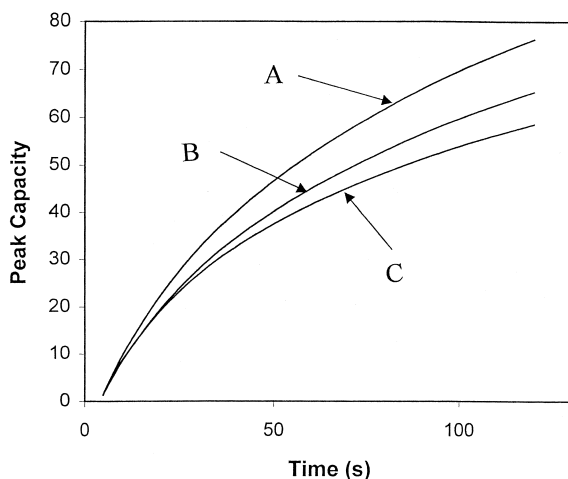


Fig. 5. Effect of column diameter on peak capacity at constant  $t_0$  in open tubular column GC. Conditions: (A) 2 m  $\times$  50  $\mu$ m I.D. capillary, DB-5,  $d_r = 0.2$   $\mu$ m, 120°C, He,  $N = 24$  000 plates, normal hydrocarbons ( $C_8$ – $C_{12}$ ) as test solutes; (B) 2 m  $\times$  100  $\mu$ m I.D. capillary, DB-5,  $N = 12$  000 plates; (C) 2 m  $\times$  200  $\mu$ m I.D. capillary, DB-5,  $N = 6000$  plates.

cm (5  $\mu$ m silica, 60  $\text{\AA}$ ) packed column was used, the four compounds were completely separated in less than 9 s (see Fig. 7A). When a 3 m  $\times$  50  $\mu$ m I.D. open tubular column was used, methane and ethane were not separated, as shown in Fig. 7B. All four compounds were separated using a 100 m  $\times$  250  $\mu$ m I.D. open tubular column; however, 6 min were required (Fig. 7C). Retention factors, column efficiencies, and dead times for these separations are listed in Table 2. It is obvious that the packed column provided much higher retention factors than

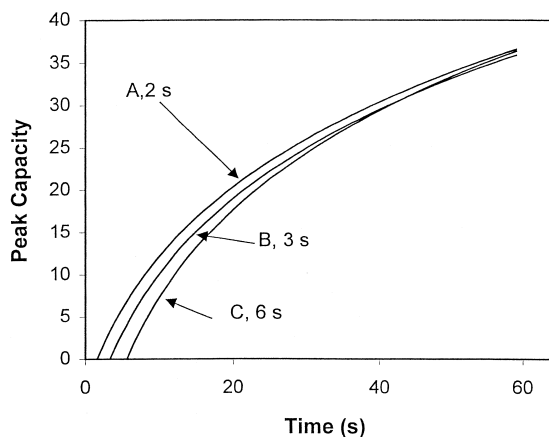


Fig. 6. Effect of dead time on peak capacity at constant  $N_{\infty}$  and  $b$  value. Conditions:  $N_{\infty} = 12$  000 plates,  $b = -0.3$ .

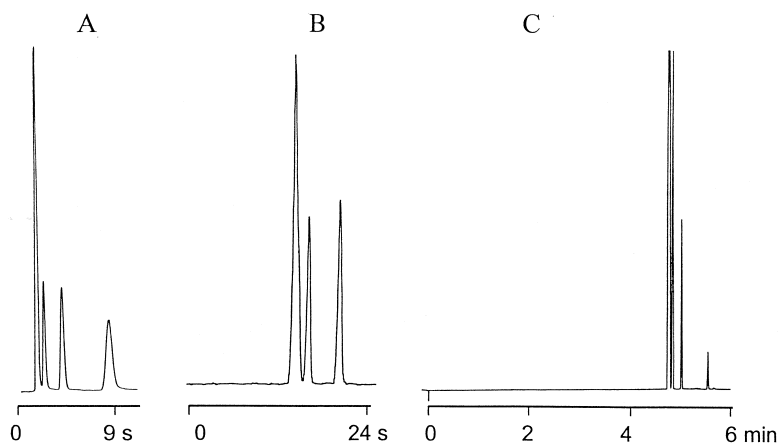


Fig. 7. GC separations of light hydrocarbons ( $C_1$ – $C_4$ ) using packed and open tubular columns. Conditions: (A) 4 cm  $\times$  250  $\mu$ m I.D. column packed with 5  $\mu$ m silica particles (60  $\text{Å}$ ), 30 atm.  $\text{CO}_2$ ; (B) 3 m  $\times$  50  $\mu$ m I.D. capillary, DB-5, He; (C) 100 m  $\times$  250  $\mu$ m I.D. capillary,  $\text{H}_2$ .

Table 2

Retention factors, column efficiencies, and dead times for separations of hydrocarbons ( $C_1$ – $C_4$ )

Column	Retention factor for $C_4$	Total column efficiency (plates)	Dead time (s)
4 cm, 5 $\mu$ m silica, 60 $\text{Å}$	8.2	1200	1.0
3 m $\times$ 50 $\mu$ m I.D., 0.2 $\mu$ m DB-5	0.48	20 000	16
100 m $\times$ 250 $\mu$ m I.D., 0.25 $\mu$ m polymethylsiloxane	0.20	450 000	280

the open tubular columns although the latter had much higher column efficiency. Therefore, retention factor has a major effect on peak capacity for these light hydrocarbons. In comparison, the column efficiency has a much less effect on peak capacity. This result is in agreement with that discussed in Section 3.2.1, that is, highly retained columns such

as packed columns can provide high peak capacity for low retained compounds.

Fig. 8 shows selective separations of light hydrocarbons ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$ ) in packed column GC, PLOT column GC, and open tubular column GC. It can be seen that packed column GC provides the best selectivity among these techniques,

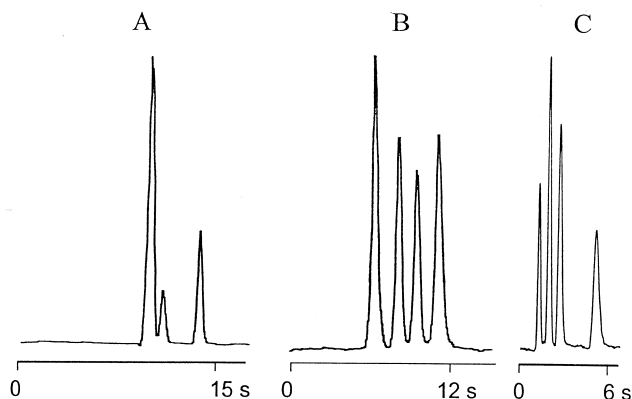


Fig. 8. Fast separations of light hydrocarbons ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$ ). Conditions: (A) 3 m  $\times$  50  $\mu$ m I.D. capillary, DB-5, 25°C, He; (B) 10 m  $\times$  320  $\mu$ m I.D., 175°C,  $\text{H}_2$ ; (C) 4 cm  $\times$  250  $\mu$ m I.D. capillary packed with 5  $\mu$ m porous silica (60  $\text{Å}$ ) particles, 80°C, 50 atm, He.

as illustrated in Fig. 8C. Open tubular column GC could not completely resolve the four compounds (see Fig. 8A) and PLOT column GC required a longer separation time compared to packed column GC (Fig. 8B). This result further indicates that selectivity and retention factor can have a significant effect on peak capacity.

Fig. 9 shows separations of normal hydrocarbons ( $C_8$ – $C_{12}$ ) in SGC and open tubular column GC. In order to make a reasonable comparison, we adjusted the optimum column efficiency, separation time, and dead time so that they were almost the same. It can be seen that a better separation was obtained in SGC for the first three compounds; in open tubular column GC, the last two compounds were better separated. The peak capacities were calculated from Fig. 9 and the results are plotted in Fig. 10. As is shown, for low retained compounds, the peak capacity for SGC is higher than for open tubular column GC.

Fig. 11 shows separations of a diesel fuel sample in SGC and open tubular column GC. Comparing

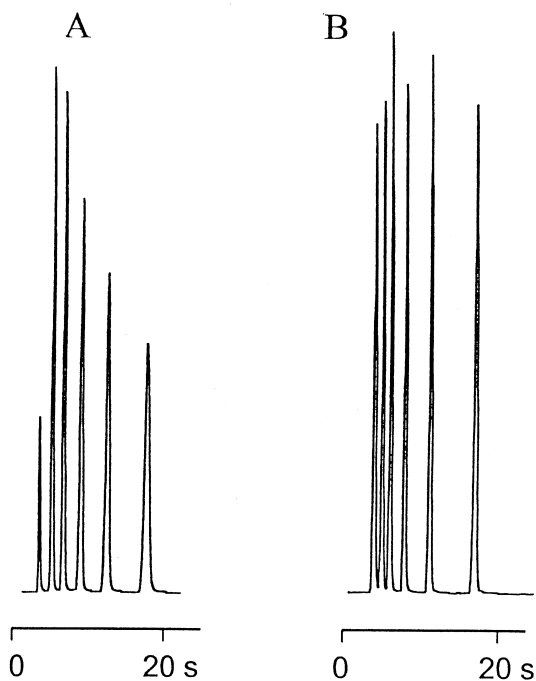


Fig. 9. Separations of normal hydrocarbons ( $C_8$ – $C_{12}$ ). Conditions: 120°C; (A) 11 cm  $\times$  250  $\mu$ m I.D. column packed with 3  $\mu$ m ODS, 240 atm,  $CO_2$ ; (B) 1 m  $\times$  50  $\mu$ m I.D. column, DB-5,  $H_2$ .

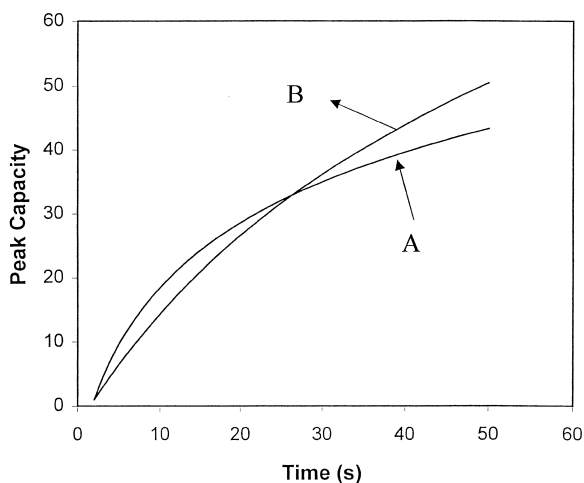


Fig. 10. Peak capacities for SGC and open tubular column GC. Conditions: (A) 11 cm  $\times$  250  $\mu$ m I.D. capillary packed with 3  $\mu$ m porous (80 Å) ODS particles, 120°C, 240 atm,  $CO_2$ ,  $u=5$  cm  $s^{-1}$ ,  $N=12$  000 plates, normal hydrocarbons ( $C_8$ – $C_{12}$ ) as test solutes; (B) 1 m  $\times$  50  $\mu$ m I.D. capillary, DB-5, 120°C, He,  $u=50$  cm  $s^{-1}$ ,  $N=12$  000 plates.

these separations, it can be seen that the resolution at the beginning (ca. 5 min) of both separations is quite similar; however, for the rest of the separation, the peaks for open tubular column GC are narrower than those for SGC. Since temperature and pressure programs were used, the separation number (SN) was used to express the separation power:

$$SN = (t_2 - t_1) / [(w_{1/2})_2 - (w_2)_1] \quad (5)$$

The separation number for the  $n$ - $C_9$  to  $n$ - $C_{23}$  interval was calculated to be 500 for open tubular column GC compared to 300 for SGC. This indicates that open tubular column GC is the preferred technique for the separation of complex samples.

### 3.3.2. Solvating power

In SGC, various mobile phases can be used, such as carbon dioxide, organic solvents and water. Since temperatures higher than their boiling points are used, the physical states of the mobile phases vary throughout the column length. For example, water is a liquid at the column inlet (under high pressure) but it is a gas at the column outlet. These mobile phases can provide high solvating power and, thus, elute



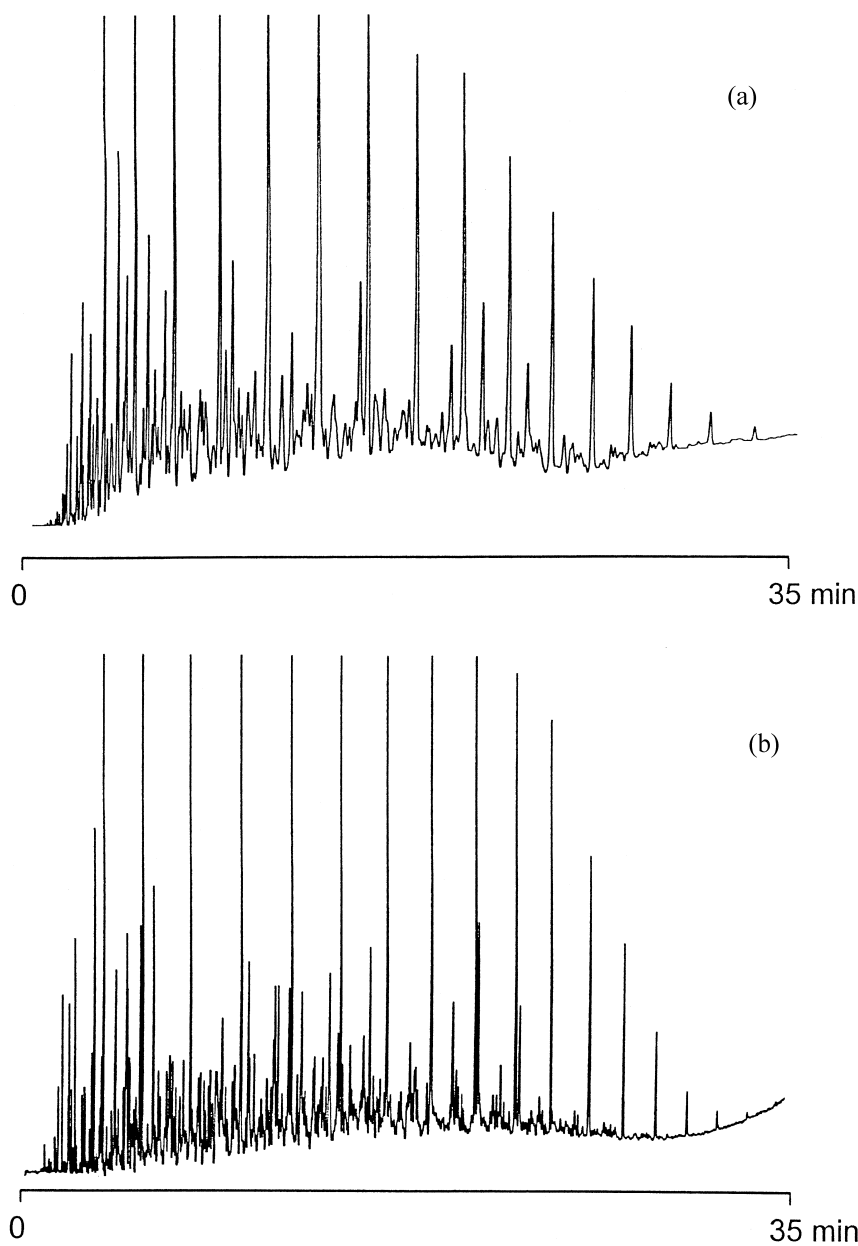


Fig. 11. Separation of a diesel fuel. Conditions: (A) 70 cm  $\times$  250  $\mu$ m I.D. column packed with 5  $\mu$ m (80  $\text{\AA}$ ) ODS particles, 60–260°C at 6°C min<sup>-1</sup>, 200–250 atm, at 1 atm min<sup>-1</sup>, CO<sub>2</sub>; (B) 10 m  $\times$  100  $\mu$ m I.D. capillary DB-5, 60–260°C at 6°C min<sup>-1</sup>, H<sub>2</sub>.

highly retained compounds. Fig. 12 shows a separation of phenol derivatives using neat water as mobile phase. These polar compounds were rapidly separated at 200°C and 200 atm. Organic solvents

have been previously used for separations of large polycyclic aromatic hydrocarbons (PAHs) [25]. PAHs containing 6 to 8 aromatic rings, which are usually difficult to separate by conventional GC,

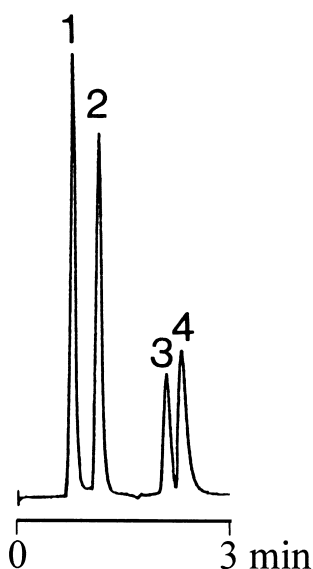


Fig. 12. SGC separation of phenol derivatives. Conditions: 50 cm $\times$ 250  $\mu$ m I.D. capillary packed with 3  $\mu$ m porous PBD zirconia particles, 200°C, 200 atm, water. Peak identifications: (1) phenol, (2) 4-chlorophenol, (3) 4-nitrophenol, (4) 3,5-dimethylphenol.

were resolved in 3 min when acetonitrile or hexane were used as mobile phases.

### 3.3.3. Sample capacity

Sample capacity is defined as the maximum amount of a compound that can be injected onto a column that leads to a specified percentage (usually 10%) increase in peak width. Table 3 lists sample capacities for SGC and open tubular column GC. Results show that packed column SGC has much higher sample capacity than open tubular column GC. This is mainly due to the fact that packed

Table 3

Comparison of sample capacities for packed column SGC and open tubular column GC<sup>a</sup>

SGC		Open tubular GC	
5 $\mu$ m (80 Å)	5 $\mu$ m (300 Å)	50 $\mu$ m I.D.	100 $\mu$ m I.D.
400 ng	280 ng	1.7 ng	4 ng

<sup>a</sup> Conditions: SGC, 5  $\mu$ m porous ODS, 120°C, 17 cm $\times$ 250  $\mu$ m I.D. fused-silica capillary (1:10 split ratio); GC, 2 m $\times$ 50  $\mu$ m I.D. capillary column, (1:3000 split ratio); and 2 m $\times$ 100  $\mu$ m I.D. column, (1:1270 split ratio). Both at 80°C and DB-5 as stationary phase.

columns have much higher surface areas than open tubular columns. The maximum sample capacity,  $C_{\max}$ , for columns with an equal phase ratio and a maximum of 10% peak broadening is given by [27]:

$$C_{\max} \propto \beta d_c^3 \quad (6)$$

where  $\beta$  is a proportionality factor. The sample capacity is significantly reduced for narrow-bore columns. This is a main factor that limits the application of these columns. We also found that high split ratios had to be used for the 50  $\mu$ m I.D. column, which can cause sample discrimination. Therefore, packed column SGC is more practical for fast separations in terms of sample capacity.

### 3.3.4. Pressure drop

Cramers and Leclercq [27] found that for high speed separations, there is a relationship between pressure drop ( $\Delta P$ ), required plate number ( $N_{\text{req}}$ ), and column diameter or particle size ( $d$ ):

$$\Delta P = c\phi N_{\text{req}}^{1/2}/d \quad (7)$$

where  $c$  is a constant which is widely different for packed and open tubular column GC, and  $\phi$  is the column resistance factor. The typical values for column resistance factor are 500 and 32 for packed capillary columns and open tubular columns, respectively [27]. If  $d_c/d_p=30$  for equal analysis times, the reduced velocities are 3 and 5, and reduced plate heights are 2 and 0.8 for packed capillary and capillary columns, respectively, and the pressure drop of a packed column is about 200-times higher than that of a capillary column. Open tubular columns have high permeability and can provide high total column efficiencies; thus, they can provide high peak capacities. Open tubular column GC is the preferred technique for fast separations of complex samples.

It should be pointed out that if a mobile phase without solvating power is used with packed columns, it is difficult to achieve an acceptable separation of a complex mixture. Since mobile phases with solvating power can overcome solute adsorption and speed up elution, total column efficiencies as high as 260 000 plates have been reached when a 3.36 m column was used at a pressure of 260 atm [32].

#### 4. Conclusions

For simple mixtures containing low retained components where retention factor and selectivity become important, packed column SGC is superior to open tubular column GC for fast separations. For complex samples containing highly retained solutes, where efficiency becomes significant, open tubular column GC is more suitable for fast separations. Packed column SGC provides higher sample capacities, but requires much higher column inlet pressure than open tubular column GC. A variety of mobile phases such as CO<sub>2</sub>, hot water, and organic solvents can be used for packed column SGC, which can provide high solvating power for large and polar compounds. Finally, SGC is a new approach to fast chromatography and much more work is needed to explore its theoretical and practical aspects.

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