Turbulent flow in capillary gas chromatography

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TURBULENT FLOW IN CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

The possibilities of turbulent flow capillary gas chromatography for increasing the speed of analysis were examined by use of previously developed sample introduction, detection and registration systems, which are compatible with peak widths in the millisecond range. Existing theoretical models for axial turbulent dispersion in capillary columns were evaluated experimentally. Substantially decreases in reduced plate heights were obtained ($h < 1$) for unretained components at an average linear velocity of 15 m/s for column diameters of 320 μm . Unfortunately, the plate height increased greatly with increasing solute capacity factor (by a factor 15 from $k = 0$ to $k = 1$). Comparison with theoretical models shows that this effect is mainly due to mobile phase mass transfer. Therefore, the gain in analysis speed is limited to low capacity factors. In addition the pressure drop required is considerably higher than for a comparable improvement in speed obtained by decreasing the column inside diameter.

INTRODUCTION

An efficient way to increase the speed of analysis in capillary gas chromatography (GC) is a reduction of the column diameter¹. However, the lack of compatible instrumentation has been a serious obstruction so far for the successful application of narrow-bore columns (I.D. < 100 μm). Recently, we have developed and evaluated sample introduction, detection and registration systems compatible with peak widths in the millisecond range^{2,3}. Very rapid separations are possible, *e.g.*, nine components separated in 0.5 s, with column diameters down to 10 μm I.D. However, the minimum useful column diameter is strongly limited by the detector sensitivity. Moving towards smaller column diameters, the sample capacity decreases more rapidly than the minimum detectable amount, thus reducing the dynamic range of the column detector system. At the column diameter where the minimum detectable amount is equal to the sample capacity, a further reduction of the column diameter is useless, unless more sensitive detectors become available. With currently available detectors this point is reached at a column diameter of about 5–10 μm . In practice the column diameter must be well above these values dependent upon the required dynamic range. It is clear that this limits the gain in analysis speed.

A reduction in the column diameter lowers the contribution of the velocity profile (C_m term) to the chromatographic dispersion. The chromatographic dispersion can also be lowered by changing the velocity profile.

A possible way to change the velocity profile is coiling the column into a helix, which induces a secondary flow. This effect is extensively described by Tijssen *et al.*^{4,5} for GC and liquid chromatography (LC). Another way is to create turbulent flow. With turbulent flow the velocity profile is largely flattened, thus decreasing flow inequalities; further, the effective diffusion coefficient of the component is considerably increased by convective contributions. As a consequence, peak broadening in the mobile phase due to the velocity profile is expected to be largely reduced. This has in fact been observed in chemical engineering studies of gas as well as liquid flow in pipes⁶. Reduced plate heights down to 0.5 are obtained at Reynolds numbers, Re , of $2 \cdot 10^4$ for unretained components. The Reynolds number is defined here as

$$Re = ud_c/\nu$$

where u = linear velocity, d_c = column diameter and ν = kinematic viscosity.

In this paper the possibility of using turbulent flow in capillary GC to increase the speed of analysis is studied. Normal bore columns are used (320 μm I.D.) because of their advantages of a good dynamic range (being the ratio of the sample capacity and the minimum detectable amount) and relatively easy column technology. Only a few experimental results on turbulent flow in GC have been reported, dating back to some 20 years ago^{7,8}. The results were not as promising as expected, possibly due to instrumental contributions or a significant influence of the stationary phase. Furthermore, the theoretical models on turbulent dispersion reported give rather different results which do not agree well with experimental results.

In this work recently developed instrumentation for narrow-bore columns was used, which is suitable for peak widths of a few milliseconds. Stationary phase effects were minimized by selecting a suitable thin film column. The experimental data were compared with those obtained by the different theoretical models. The potential of turbulent flow to increase the analysis speed was evaluated and compared with that of a reduction in column diameter.

THEORETICAL

Turbulent flow is a well known phenomenon in chemical engineering. In a study of gas flow in pipes Flint and Eisenklam⁶ have reported experimental and theoretical results for turbulent dispersion of unretained components as a function of the Reynolds number, Re . Curves of the reduced plate height, $h = H/d_c$, versus Re are characterized by a maximum at the transition from laminar to turbulent flow (Re approximately 2300) and thereafter a pronounced lowering of h down to 0.5 at $Re = 2 \cdot 10^4$.

Flint's theory was in good agreement with the experimental results, but it is emphasized that different velocity profiles have to be used, especially for the regime $Re < 6000$, where the most radical changes in the form of the velocity profile occur. Although the foregoing applies only for unretained components, it suggests that an high gain in analysis speed is possible with turbulent flow in GC. The theory of GC in

open tubular columns with laminar flow leads to the generally accepted Golay-Giddings plate height equation. Under turbulent conditions, this expression is no longer valid since the radial velocity profile is no longer parabolic and becomes velocity dependent. In addition radial mass transfer is enhanced by convection.

In 1966 Pretorius and Smuts⁹ reported a theoretical model for turbulent dispersion, based on the Aris general dispersion theory, which allows for a non-parabolic velocity profile and a variable diffusion coefficient. In their calculation, different empirical velocity profiles from literature data were used together with radial diffusion profiles (convection superimposed on molecular diffusion), derived from the velocity profiles.

For a capacity factor $k = 0$, the calculated plate height for different Re numbers agreed well with the foregoing results of Flint and Eisenklam. The calculation was also performed for the chromatographically more interesting case of $k=1$. Here h also decreases with Re down to a value of about 2 at $\text{Re} = 2 \cdot 10^4$. The ratio between h for $k=0$ and for $k=1$ was about the same for turbulent as for laminar flow. From this theoretical study Pretorius and Smuts⁹ concluded that turbulent flow in GC may improve the analysis speed by a factor of 10, compared with laminar flow. In 1982 Martin and Guiochon¹⁰ calculated the peak broadening under turbulent flow conditions according to the Aris general dispersion theory. They used a fixed (theoretical) velocity profile throughout the whole turbulent region. Furthermore a radial diffusion profile derived from literature data was assumed. The results of their calculation differ substantially from those of Pretorius and Smuts. First, a plot of h versus Re shows an increase in h with increasing Re for all capacity factors. This is conflict with prior experimental data^{6,8}. Presumably this arises from the use of a fixed velocity profile throughout the whole turbulent region.

A second remarkable difference is the large influence of the capacity factor on h . Although for $k=0$ the calculated h is very low ($h=0.25$, $\text{Re}=2 \cdot 10^4$), it increases by a factor of 100 on going from $k=0$ to $k=1$. The few experiments made with turbulent flow in capillary GC also showed a significant increase in h with increasing k (refs. 7 and 8). Contrary to Pretorius and Smuts, Martin and Guiochon concluded that the potential of turbulent flow in GC is limited. In 1979, Tijssen¹¹ also derived an equation for turbulent dispersion in a systematic study of axial dispersion in helically coiled columns. It starts with a mass balance and assumes a turbulent velocity profile (see Fig. 1)

$$\frac{u}{\bar{u}} = \frac{6}{5} \left[1 - \left(\frac{r}{R} \right) \right]^{10} \quad (1)$$

where u = local velocity, $\bar{u}$ = average velocity, r = radial coordinate and R = column radius.

Neglecting axial diffusion and resistance to mass transfer in the stationary phase, this finally leads to

$$C_m = \frac{R^2}{D_R} \frac{1 + 14k + 55k^2}{168(1 + k)^2} \quad (2)$$

Fig. 1. Laminar turbulent velocity profiles: 1, parabolic; 2, 10th power (eqn. 1); 3, perfectly flat.

C_m = term describing the resistance to mass transfer in the mobile phase and D_R = average turbulent diffusion coefficient.

In the derivation no radial diffusion profile is used, but an average overall turbulent diffusion coefficient, D_R , is assumed. Although there exists a finite laminar sublayer in which interphase mass transfer is governed by molecular diffusion, it is assumed that this contribution is negligible for turbulent flow at sufficiently high Re numbers.

A remarkable property of eqn. 2 is the large influence of k on C_m . The latter increases by a factor of 17.5 on going from $k=0$ to $k=1$, which is much less than Martin and Guiochon have calculated (factor of 100), but is still significantly more than for optimum laminar flow (factor of 2). For the theoretical case of a perfectly flat velocity profile, Giddings¹² and Tijssen¹¹ have found the following:

$$C_m = \frac{R^2}{4D_R} \left(\frac{k}{1+k} \right)^2 \tag{3}$$

Contrary to expectation, the C_m term is only zero for $k=0$; it has a finite value for all other k values.

The discrepancies between the existing theories for turbulent dispersion are summarized in Table I. For comparison, the values under optimum laminar flow

TABLE I
DISCREPANCIES BETWEEN EXISTING THEORIES FOR TURBULENT DISPERSION
 $Re = 10^4$.

	$h = H/d_c$	
	$k=0$	$k=1$
Pretorius	0.6	3
Guiochon	0.2	65
Tijssen	0.8	12
Golay	0.3	0.6
(optimum laminar)		

conditions are also presented. It seems that the high capacity factor dependence of turbulent dispersion is an intrinsic property of turbulent flow, which arises from the shape of the velocity profile.

EXPERIMENTAL

Experiments under turbulent flow conditions were performed with fused-silica columns having an internal diameter of $320\text{ }\mu\text{m}$, lengths ranging from 25 to 5 m and a stationary phase film thickness of $0.12\text{ }\mu\text{m}$ CP-Sil 5 CB (Chrompack, Middelburg, The Netherlands). The sample introduction system consisted of a pneumatically actuated Valco four-port valve (VICI AG; Valco, Schenkon, Switzerland) with an internal rotor (6 nl) which allows input band widths as low as 1 ms (ref. 3). The valve was mounted on top of a Carlo Erba 4160 gas chromatograph (Carlo Erba, Milan, Italy).

The carrier gas (nitrogen) pressure was controlled with a Tescom 44-1100 high pressure regulator (up to 100 bar) (Tescom, Minneapolis, MN, U.S.A.). Flame ionization detection could not be used due to extinguishing of the flame. Therefore, a low cell volume ($40\text{ }\mu\text{l}$) photoionization detector (HNU Systems, Newton, MA, U.S.A.) was used throughout all experiments. The amplifier was modified to lower the time constant to about 2 ms. Considering the high column flow-rates involved ($>1\text{ l/min}$), peak broadening due to the cell volume will be negligible. Since ordinary chartspeed recorders are far too slow, chromatograms were recorded on a digital storage oscilloscope (Nicolet, Madison, WI, U.S.A.), capable of sampling at a maximum rate of 1 MHz.

RESULTS AND DISCUSSION

Plots of $\log h$ versus $\log \text{Re}$ both for $k=0$ and $k=1$ are shown in Fig. 2. The transition from laminar to turbulent flow occurs at a Re of about 2300. Before this critical Re is reached, some incipient turbulent phenomena reduce the plate height, as reported in the literature⁵. Beyond the critical Re a pronounced decrease in the plate height is observed. For $k=0$, h reaches a value of about 0.8 at $\text{Re} = 1.5 \cdot 10^4$. This curve is in good agreement with earlier theoretical and experimental results for unretained components⁶. The gap between the two curves in Fig. 2 is a measure of the ratio between h for $k=0$ and $k=1$.

It is clear that for laminar flow beyond the optimum this gap becomes constant, on the other hand with turbulence this gap increases considerably with increasing degree of turbulence. This behaviour is also shown in Fig. 3, where the reduced plate height is plotted versus the capacity factor at $\text{Re} = 6200$. By comparing the experimental curve with the Tjissen theory (eqn. 2) and with laminar flow, both normalized at $k=0$, it is seen that the experimental results are fitted reasonably well with the function of k in eqn. 2. From $k=0$ to $k=1$ the experimental value of h changes by a factor of 19, whereas a factor of 17.5 was calculated. Under optimum laminar conditions these h values differ by only a factor of 2.1. These results are in contradiction with the theory of Martin and Guiochon¹⁰. They calculated this difference to be 100-fold under turbulent conditions.

Using eqn. 2, an absolute value for h can be calculated, provided that the

Fig. 2. Turbulent dispersion *versus* Reynolds number, for $k = 0$ ($\square$) and $k = 1$ (+).

Fig. 3. Turbulent dispersion *versus* capacity factor ($Re = 6200$): $\square$, experimental; +, with turbulence; $\diamond$, with laminar flow.

turbulent diffusion coefficient is known. According to empirical relationships¹⁰ the turbulent diffusion coefficient is

$$D_R/D_m^\circ = 1 + 0.009\text{Re}^{0.84} \cdot \text{Sc} \quad (4)$$

where D_R = average cross-sectional turbulent diffusion coefficient, D_m° = molecular diffusion coefficient, $\text{Sc} = \nu/D_m^\circ$, and ν = kinematic viscosity.

Calculation with eqns. 2 and 3 at $\text{Re} = 1.5 \cdot 10^4$ gives for $k=0$ and $k=1$, respectively, $h=0.8$ (experimental $h=0.8$) and $h=12$ (experimental $h=13$). It must be noted that the fit is less close at lower Re numbers. Obviously, the results depend upon the accuracy of the velocity profile, which changes with Re, particularly for lower Re numbers. In the theory of Tijssen a 10th power profile was used (eqn. 1). In the literature, however, a 7th power profile is often proposed as an approximation for the velocity profile in the range $6 \cdot 10^3 < \text{Re} < 10^5$ (ref. 13). Using this profile, we calculated according to the theory of Tijssen:

$$C_m = \frac{R^2}{D_R} \frac{0.85 + 10.3k + 34.5k^2}{100(1+k)^2} \quad (5)$$

This gives $h=1$ and $h=15$ for $k=0$ and 1 respectively. Comparing this with the former profile, the results differ only slightly.

Although at lower Re values appropriate velocity profiles can be found, the Tijssen concept will probably no longer be valid. It assumes an overall turbulent diffusion coefficient, whereas at lower Re the influence of a laminar sublayer with molecular diffusion can probably no longer be neglected.

So far the resistance to mass transfer in the stationary phase has been neglected. Considering the high carrier gas velocities involved (up to 15 m/s), the reliability of this assumption must be verified. The resistance to mass transfer in the stationary phase is not affected by the flow profile in the mobile phase^{10,11}. Assuming a liquid diffusion coefficient, $D_L = 5 \cdot 10^{-6} \text{ cm}^2/\text{s}$ (ref. 14), $k=1$ and $\bar{u}=15 \text{ m/s}$, the reduced plate height of the resistance to mass transfer in the stationary phase is calculated to be $h_s=0.22$. This may be considered negligible in the foregoing results.

In order to answer the question of whether turbulent flow can increase the analysis speed, the ratio $H/\bar{u}$ has to be considered. For a fixed (required) plate number and capacity factor, the analysis time is proportional to the ratio $H/\bar{u}$. Under turbulent conditions this ratio was determined according to the experimental results at the highest Re in Fig. 1 ($\text{Re} = 1.5 \cdot 10^4$, $\bar{u}=15 \text{ m/s}$) by incorporating the experimental dependence of h on k in Fig. 2. For laminar flow the theoretical $H/\bar{u}$ at the optimum was taken, using a molecular diffusion coefficient, $D_m = 0.1 \cdot 10^{-4} \text{ m}^2/\text{s}$ (carrier gas nitrogen)¹⁵.

The resulting gain, G , in analysis speed with turbulent flow relative to laminar flow is given in the first column of Table II for different capacity factors. The second column gives an estimate of the gain in analysis speed in the (theoretical) case of a very narrow bore column requiring the same pressure drop as under turbulent conditions. In Fig. 4 a typical separation under turbulent conditions is presented. This clearly demonstrates again the high dependence of h on k . Another aspect which has to be

TABLE II

GAIN, G , IN ANALYSIS SPEED

First column: between turbulent ($Re = 10^4$) and optimum laminar flow for different capacity factors, k , carrier gas, nitrogen; $D_m = 1 \cdot 10^{-5} \text{ m}^2/\text{s}$; column, $L = 5 \text{ m}$, I.D. = 0.32 mm; $d_t = 0.12 \mu\text{m}$. Second column: when using a narrow bore column requiring the same pressure drop as under turbulent conditions ($\Delta p = 50 \text{ bar}$, I.D. $3 \mu\text{m}$).

k	G (turbulent)	G (laminar)
0	13	100
0.5	4	100
1	3	100
2	3	100
4.5	3	100

considered is the pressure drop associated with turbulent flow. The inlet pressure required for a given Re can be calculated¹⁰ from

$$p_i^2 - p_o^2 = \frac{316.4\eta^2 \cdot Re^{7/4} LRT}{Md_c^3} \quad (6)$$

where p_i, p_o = inlet and outlet pressures, η = dynamic viscosity, L = column length, R = gas constant, T = column temperature and M = molecular weight of the carrier gas. For example, a $5 \text{ m} \times 0.32 \text{ mm}$ column requires an inlet pressure of 36 bar (nitrogen) to obtain $Re = 10^4$. For He or H_2 as the carrier gas the pressure drop would even be larger. The gain in analysis speed is insufficient to compensate for the larger pressure drop. The same gain can be obtained more easily under laminar flow conditions by using hydrogen as the carrier gas, and/or applying a vacuum at the column outlet¹⁶ and/or a reduction of the column diameter¹⁵.

CONCLUSIONS

Low reduced plate heights can be obtained under turbulent conditions especially for unretained components ($h = 0.8$ at $Re = 1.5 \cdot 10^4$). Unfortunately, the dependence of the plate height on the capacity factor is significantly higher than under laminar

Fig. 4. Representative chromatogram of an hydrocarbon headspace sample under turbulent flow conditions. Column: $L = 5 \text{ m}$, I.D. = 0.32 mm; $d_t = 0.12 \mu\text{m}$; $p_i = 50 \text{ bar}$.

conditions. Consequently, the gain in analysis speed is limited in practice. Taking into account that an high pressure drop is required for turbulent flow, a reduction of the column diameter is a better approach to increase the analysis speed. From the theoretical models on turbulent dispersion reported in the literature, only the Tijssen theory gave acceptable agreement with the experimental plate heights at various capacity factors. In this theory the resistance to mass transfer in the mobile phase is calculated with a turbulent velocity together with an overall turbulent diffusion coefficient. Therefore, the large influence of the capacity factor on the plate height is an intrinsic property of turbulent flow, which can be explained from the shape of the velocity profile.

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