Review

Strategies for speed optimisation in gas chromatography: an overview

Carl A. Cramers*, Piet A. Leclercq

Department of Chemical Engineering and Chemistry, Laboratory of Instrumental Analysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Abstract

An overview is given of existing methods to minimise the analysis time in gas chromatography being the subject of many publications in the scientific literature. Packed and (multi-) capillary columns are compared with respect to their deployment in fast gas chromatography (GC). It is assumed that the contribution of the stationary phase to peak broadening can be neglected (low liquid phase loading and thin film columns, respectively). The treatment is based on the minimisation of the analysis time required on both column types for the resolution of a critical pair of solutes (resolution normalised conditions). Theoretical relationships are given, describing analysis time and the related pressure drop. The equations are expressed in reduced parameters, making a comparison of column types considerably simpler than with the conventional equations. Reduction of the characteristic diameter, being the inside column diameter for open tubular columns and the particle size for packed columns, is the best approach to increase the separation speed in gas chromatography. Extremely fast analysis is only possible when the required number of plates to separate a critical pair of solutes is relatively low. Reducing the analysis time by reduction of the characteristic diameter is accompanied by a proportionally higher required inlet pressure. Due to the high resistance of flow of packed columns this seriously limits the use of packed columns for fast GC. For fast GC hydrogen has to be used as carrier gas and in some situations vacuum-outlet operation of capillary columns allows a further minimisation of the analysis time. For fast GC the columns should be operated near the conditions for minimum plate height. Linear temperature-programmed fast GC requires high column temperature programming rates. Reduction of the characteristic diameter affects the sample capacity of the 'fast columns'. This effect is very pronounced for narrow-bore columns and in principle non-existing in packed columns. Multi-capillary columns (a parallel configuration of some 900 narrow-bore capillaries) take an intermediate position. © 1999 Elsevier Science B.V. All rights reserved.

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*Corresponding author. Tel.: +31-40-2473024; fax: +31-2453762.
E-mail address: D.C.M.Tjallema-Dekker@tue.nl (C.A. Cramers)

1. Introduction

The principles and theory of fast gas chromatography were already established in the 1960s [1–3]. However, the application in daily routine remained limited in the past years. At recent international symposia a revival of interest in fast chromatography could be observed. Several sessions were entirely devoted to fast GC.

Separations on a second to minute time scale were shown, using either packed or (multi-)capillary columns. In some situations flow programming or extremely fast temperature programming was applied. Evaluation of the results is difficult because of the widely different conditions in the examples that were given.

In this work an overview is given which will allow a thorough evaluation of the advantages and disadvantages of several approaches to fast gas chromatography. It includes a comparison of capillary, multi-capillary and packed columns, based on reduced (dimensionless) parameters, which characterise the chromatographic and flow phenomena.

2. Theory

In order to compare the potentialities of the different approaches, it is necessary to turn back to chromatographic theory. It is obvious that an analysis requiring only 1000 theoretical plates can be carried out much faster than the separation of a really complex mixture. In order to compare the kinetic conditions for optimum speed attainable with different column types, it is essential to start with the concept of resolution normalised conditions. This means that in the comparison the required number of theoretical plates, N_{req}, for a given separation problem is considered to be constant.

The main criterion for selecting the proper chromatographic conditions is the separation of a critical pair of components. When the critical pair is separated, so will be all peaks in the chromatogram. The actual analysis time will be the time needed for the separation of the critical pair multiplied by $(1 + nk)$. Where n is the ratio of the retention factor of the last eluting peak and the k value of the second peak of the critical pair of solutes [4–6]. From basic GC theory it follows that the required plate number N_{req} to obtain a certain resolution R_s can be expressed as:

$$N_{req} = 16 R_s^2 \left[\frac{1 + k}{k} \right]^2 \left[\frac{\alpha}{\alpha - 1} \right]^2 \qquad (1)$$

with a resolution measured experimentally as:

$$R_s = \frac{\Delta t_R}{4\sigma} \qquad (2)$$

For peaks of equal size baseline separation is achieved at $R_s > 1.5$.

Δt_R is the difference in retention time; σ is the standard deviation of the second eluting peak of a critical pair of solutes expressed in time units; α is the relative retention $\alpha = k_2 / k_1$; k_2 is the retention factor of the latter eluting peak.

When the primary demand for a specific resolution between a critical pair of components is fulfilled, a second aim is to obtain the analysis in a minimum of time. The equation for the retention time, to be minimised, is given by

$$t_R = t_0(1 + k) \qquad (3)$$

where t_0 is the time required to elute an unretained component:

$$t_0 = \frac{L}{\bar{u}} = \frac{L}{u_o f_2} \qquad (4)$$

with L the column length; $\bar{u}$ the average linear gas velocity; u_o the velocity at the column outlet; f_2 a gas compressibility correction factor (defined in Table 1). L can be replaced by NH with $H = L/N$ being the theoretical plate height, leading to:

$$t_R = [N(1 + k)]\left[\frac{H}{u_o f_2}\right] \qquad (5)$$

Combining Eqs. (1) and (4) the analysis time t_R can be expressed as:

$$t_R = 16R_s^2\left[\left(\frac{(1 + k)^3}{k^2}\right)\left(\frac{\alpha}{\alpha - 1}\right)^2\right]\left[\frac{H}{u_o f_2}\right] \qquad (6)$$

For baseline separation $R_s = 1.5$, Eq. (6) yields:

$$t_R = 36\left[\left(\frac{(1 + k)^3}{k^2}\right)\left(\frac{\alpha}{\alpha - 1}\right)^2\right]\left[\frac{H}{u_o f_2}\right] \qquad (7)$$

Eqs. (5)–(7) contain two parts. The first term of the right-hand side is equal to the required number of plates multiplied by $1 + k$. This part reveals the importance of optimising k (between 1.7 and 3 [5,6]) and maximising the relative retention α by proper selection of the stationary phase. The retention factor k can be tuned by selecting appropriate liquid phases, varying phase ratios, and column temperatures. This thermodynamic treatment will not be discussed in this paper.

The second part $H/\bar{u} = H/u_o f_2$ is the Purnell

Table 1
Gas compressibility correction factors: $P = p_i/p_o$

	$P = 1$	$P \gg 1$
$f_1 = \dfrac{9}{8} \cdot \dfrac{(P^4 - 1)(P^2 - 1)}{(P^3 - 1)^2}$	1	9/8
$f_2 = \dfrac{3}{2} \cdot \dfrac{(P^2 - 1)}{(P^3 - 1)}$	1	3/2P
$f_3 = \dfrac{1}{2} \cdot (P + 1)$	1	1/2P
$f_2 f_3$	1	3/4

criterion [7] or the plate duration [8], i.e. the time spent by the carrier gas to traverse one theoretical plate. Minimising the analysis time for a given required plate number is equivalent to minimising the peak duration. This gives the highest speed for N_{req} (N_{req}, not L is kept constant). Evaluation of the peak duration is difficult, because it is a complex function of retention factors, gas velocities, pressure drops, particle/column dimensions and solute diffusion coefficients.

2.1. Normalised resolution optimisation; packed versus capillary columns (negligible contribution of the stationary phase term to the plate height)

Two types of basic equations are needed for the calculation of the numerical value of $H/\bar{u}$ to compare packed and capillary columns.

(a) Plate height equations which describe the dependence of the experimental plate height upon carrier gas velocity and column parameters, e.g. the Horváth–Lin equation [9] for packed columns and the Golay–Giddings equation [10,11] for capillary columns.

(b) Flow equations, e.g. the Kozeny–Carman [12] and Hagen–Poiseuille [13] equations for packed and capillary columns, respectively.

These theoretical relationships can be considerably simplified, if they are expressed in terms of reduced parameters (dimensionless numbers) as proposed by Giddings [14]. In this way the dependence of H on $\bar{u}$ can be approximated by a single curve in reduced parameters for packed columns and another one for capillary columns. This, irrespective of particle size or column inside diameter, nature of the mobile phase or nature of the components, respectively. Identical curves can be expected only [2], if the following conditions are fulfilled:

(1) Contribution to plate height of the stationary phase is negligible (small liquid phase loading in packed columns and thin film open tubular columns). A more concise treatment including arbitrary film thickness in capillary columns can be found in Ref. [8].

(2) Structure of the packing in a packed column is independent of particle size.

The reduced, dimensionless parameters are defined in Table 2, where d is the characteristic diameter and

Table 2
Definition of reduced parameters

Reduced plate height	$h = H/d$
Reduced carrier gas velocity	$\nu = \dfrac{u_o d}{D_{m,o}}$
Column resistance factor	φ (see text, Eq. (8))
Retention factor	$k = \dfrac{t_R - t_0}{t_0}$
Reduced pressure	$P = p_i / p_o$

equals the particle size d_p in packed columns and the inside column diameter d_c for open tubular columns; u_o and $D_{m,o}$ represent the linear gas velocity and the binary solute/carrier gas diffusion coefficient at column outlet pressure p_o; p_i is the column inlet pressure, and φ is the dimensionless flow resistance parameter:

$$\varphi = \frac{1}{\langle \nu \rangle} \cdot \frac{d^2}{\eta} \cdot \frac{\Delta p}{L} \qquad (8)$$

with $\langle \nu \rangle$ the mean cross-sectional fluid flow velocity [15].

The retention time Eq. (5) can now be written in terms of reduced parameters:

$$t_R = N_{req} \cdot \frac{h}{\nu} \cdot \frac{d^2}{f_2 D_{m,o}} \cdot (1 + k) \qquad (9)$$

The flow equations in their reduced form read:

$$\Delta p = p_i - p_o = \frac{N_{req} h \nu \varphi \eta D_{m,o}}{f_3 d^2} \qquad (10)$$

where η is the mobile gas phase dynamic viscosity.

Combining Eqs. (9) and (10) it follows:

$$\Delta p t_0 = \frac{N_{req}^2 h^2 \varphi \eta}{f_2 f_3} \qquad (11)$$

$h^2 \varphi = E$ is defined as the separation impedance, which represents the elution time per plate (plate duration) for an unretained solute times the pressure drop per plate, corrected for viscosity.

For ideal gases the relevant compressibility correction factors f_2 and f_3 are given in Table 1.

Using Eqs. (9) and (10) the appropriate dimensionless numbers h, ν and φ have to be included. In Table 3 the approximate values under optimum separation conditions are given. The consequences of working at higher than optimum values of the reduced velocity will be discussed later.

3. Discussion

Some interesting conclusions can be drawn from Eqs. (9)–(11). These equations show a complex pressure dependence. The optimum conditions can only be calculated numerically. Only under boundary conditions, such as a very low or very high inlet to outlet pressure ratio and a negligible influence of the stationary phase, explicit relationships can be obtained.

3.1. Low pressure drop (slow analysis, low plate number columns); P = 1

The compressibility correction factors f_2 and f_3 approach a value of 1. Including the dimensionless numbers relevant for packed and open tubular columns, it follows from Eq. (9) that the analysis time can be reduced proportional to d_p^2 for packed columns or to d_c^2 for open tubular columns. As shown by Eq. (10) the price is a proportionally increasing pressure drop.

Comparing the separation impedance E for packed (≈ 4000) and capillary (20) columns, it can be concluded that if both column types are operated

Table 3
Approximated values of the reduced parameters under optimal conditions

	Packed column	Packed capillary column	Capillary column
Reduced plate height, h	2	2	0.8
Reduced velocity, ν	3	3	5
Column resistance factor, φ	≈ 1000	≈ 500	32
Separation impedance, E	≈ 4000	≈ 2000	20

with the same pressure drop Δp a capillary column will allow a $200\times$ faster analysis. The influence of the selection of the carrier gas on speed of analysis (Eq. (9)) is given in Table 4 for $P=1$, showing the advantage of using hydrogen. As demonstrated above chromatographic performance in terms of speed of analysis for a fixed plate number can be substantially improved by miniaturisation: decreasing the characteristic diameter and increasing the pressure drop proportionally. Therefore in fast gas chromatography, especially for larger required plate numbers, N_{req}, the assumption $P=1$, $f_2=f_3=1$ becomes invalid.

3.2. High pressure drop (fast analysis, higher plate number columns); $P \gg 1$

As can be seen from Table 1, f_2 can now be replaced by $3/2P$ and $f_2 f_3$ equals $3/4$. Substitution of these values now leads to the following expressions:

$$t_R = N_{req}^{3/2} \cdot \frac{h^{3/2}\varphi^{1/2}}{\nu^{1/2}} \cdot d\left(\frac{\eta}{D_{m,o}p_o}\right)^{1/2}(1+k) \qquad (12)$$

$$\Delta p = \frac{4}{3} \cdot \frac{N_{req}^{1/2}(h\nu\varphi)^{1/2}(\eta D_{m,o}p_o)^{1/2}}{d} \qquad (13)$$

$$\Delta p t_0 = \frac{4}{3} \cdot N_{req}^2 h^2 \varphi\eta = \frac{4}{3} \cdot N_{req}^2 E\eta$$

$$= \text{constant at a given temperature} \qquad (14)$$

Under high pressure drop conditions ($P \gg 1$) the analysis time t_R now becomes linearly proportional to the characteristic diameter (d_c or d_p), instead of d^2 as in the low pressure situation. Again separation speed t_0 (t_R) is traded off against pressure drop Δp. A similar relationship for the analysis time (Eq. (12)) was reported by Tijssen [16] and Guiochon [4]. Knox and Saleem [2] published equations Eqs. (12)–(14) as early as 1969, which led them to the very

valuable remark: "The ultimate limitation on speed is inevitably set by the pressure which the apparatus can tolerate". The influence of the carrier gas type at $P \gg 1$ is reflected now in the mobile phase diffusion coefficient and the carrier gas viscosity (Eq. (12)). Using diffusion coefficients according to Fuller et al. [17] and dynamic viscosities [18] the relative analysis times are given in Table 4.

3.3. Speed of analysis by packed and capillary column systems

Some interesting conclusions can be drawn from Eqs. (12) and (13) about the speed of packed and capillary column systems. Substituting the optimum values of h and ν from Table 3, it follows that the ratio d_c/d_p at which the analysis times are equal is 29. Inserting the proper values of h and ν and $d_c=29d_p$ in Eq. (13) shows that under equal analysis time conditions the pressure drop of a packed column system is 200 times larger. The same conclusion also directly follows from the ratio of the separation impedances $E_{packed}/E_{capillary}$ (Eq. (14)).

Under optimum conditions the column length required to separate a critical pair is given by the product of N_{req} and H_{min} or:

$$L = N_{req}hd \qquad (15)$$

If N_{req} is assumed to have the same value for the packed and the open tubular system, it follows that under the equal analysis time conditions ($d_c/d_p=29$), using values for h_{min} and ν_{opt} from Table 3:

$$\frac{L_{capillary}}{L_{packed}} = 11.6 \qquad (16)$$

Fast separations of simple mixtures with packed columns were already achieved in the 1960s. An example of extreme speed has been published by

Table 4
Analysis time for different carrier gases relative to hydrogen

Carrier gas	$P=1$ ($\propto 1/D_{m,o}$, Eq. (9))	$P \gg 1$ ($\propto(\eta/D_{m,o})^{1/2}$, Eq. (12))
H_2	1	1
He	1.2	1.6
N_2	4.0	2.8
CO_2	5.6	2.8

Jonker et al. [19]. They showed a separation of four components in only 0.15 s with a 3.2-cm long column packed with 10-μm particles. The plate number was 650 with a pressure drop of 63 bar. The column was operated under the conditions $h = 4.9$ at $\nu = 6.4$ with He as the carrier gas.

Under optimum conditions ($h = 2$ and $\nu = 3$) this column would have yielded 1600 plates with an analysis time of 0.23 s ($k = 2$) and a pressure drop of 43 bar (according to Eqs. (12) and (13)). These equations also show that a capillary column can generate the same required plate number of 1600 using a 290-μm I.D. column with a length of 37 cm, and a pressure drop of only 0.21 bar. For this open tubular column, operated at atmospheric outlet pressure, however, the requirement $P \gg 1$ is not valid anymore (caused by the relatively low plate number in this case) and for the open tubular column Eq. (9) with $f_2 = 1$ becomes valid.

The column diameter d_c giving 1600 theoretical plates, a retention time of 0.23 s for a solute with retention factor of 2 can be calculated, if $D_{m,o}$ is included. It appears that an open tubular column with an inside diameter of 70 μm and a length of 9 cm gives exactly the same analysis time and plate number (see Table 5). The pressure drop (Eq. (10) $f_3 = 1$) is now only ≈ 0.1 bar. This example clearly illustrates the great superiority of capillary columns as compared to packed columns from the viewpoint of speed of analysis related to pressure drop.

It should be emphasised again that in the above treatment the stationary phase term in the plate

height equations is neglected. For capillary columns this means that thin film columns are considered.

For fast analysis this is obvious, since for thick film columns the (reduced) plate height is increased and the corresponding optimal (reduced) velocity is decreased considerably.

3.4. Alternative approaches to fast GC

3.4.1. Turbulent flow conditions

Another way to obtain very small analysis times in capillary GC is to create turbulent flow. Only a few experimental results on turbulent flow in GC are known, some dating from about 30 years ago. The results were not as promising as expected, possibly due to instrumental contributions or a not negligible influence of the stationary phase [20,21]. With turbulent flow the velocity profile is largely flattened. Furthermore, the effective radial dispersion is considerably increased by convective contributions.

Experiments show that low plate heights can be obtained under very high speed conditions ($p_I = 50$ bar, $\bar{u} \approx 15$ m/s; Re $\approx 10^4$) [22]. Unfortunately, the dependence of the plate height on the retention factor is significantly higher than under laminar flow conditions, limiting the use of turbulence to solutes with a low retention factor. Also the instrumental requirements with respect to time constants of sample introduction and detection are very severe in turbulent gas chromatography.

Taking into account the high pressure drop required for turbulent flow, a reduction of the column diameter is a better approach to increase the analysis speed in capillary GC.

3.4.2. Vacuum outlet conditions

As demonstrated by Giddings in the 1960s [3,23] true time optimisation will require vacuum column outlet conditions. This can directly be concluded from Eq. (5). Under vacuum outlet conditions $P = p_i / p_o \gg 1$, f_2 can be replaced by $3/2P$ yielding:

$$t_R = \frac{2}{3} \cdot N_{req} \cdot \frac{h}{\nu} \cdot \frac{d^2}{D_{m,i}} \qquad (17)$$

where $D_{m,i}$ is the binary solute carrier gas diffusion coefficient at inlet pressure.

The largest value of $D_{m,i}$ will be obtained, if a

Table 5
Comparison of packed and capillary columns ($t_R = 0.23$ s for $k = 2$; $N = 1600$; carrier gas He)

Outlet pressure:	Packed column	Open tubular column	
	Atmospheric	Atmospheric	Vacuum
L (cm)	3.2	9	37
d (μm)	d_p 10	d_c 70	d_c 290
Δp (bar)	43	0.1	0.1
T (K)	373	215[a]	200[a]

[a] In the data presented in this table $k = 2$ is kept constant. For thin film open tubular columns this theoretical exercise leads to sub-ambient column temperatures. In the calculation of pressure drop by using Eq. (14) the accompanying change in carrier gas viscosity with temperature is accounted for.

given column is operated at vacuum outlet conditions generating N_{req} theoretical plates, where the absolute value of the column inlet pressure will be minimal.

The gain in speed of analysis by vacuum outlet pressure conditions compared to atmospheric outlet pressure conditions of a given column can be expressed by [24]:

$$G = \frac{p_{i,opt,atm}^3 - 1}{(p_{i,opt,atm}^2 - 1)^{3/2}} \tag{18}$$

Where $p_{i,opt,atm}$ is the absolute inlet pressure (in bar) under optimal conditions at atmospheric outlet pressure ($p_o = 1$ bar).

The optimum absolute inlet pressure under vacuum outlet conditions $p_{i,opt,vac}$ expressed in bar can be found from:

$$p_{i,opt,vac}^2 = p_{i,opt,atm}^2 - 1 \tag{19}$$

G is seen to increase with decreasing values of $p_{i,opt,atm}$ (Table 6). The largest gains are obtained with sub-atmospheric inlet pressures. Thus, vacuum outlet will be of particular interest for high permeability (open tubular) columns, with a large inner diameter and/or a short length.

For narrow-bore capillary columns and packed columns requiring high inlet pressures the gain in speed of analysis becomes negligible. The subject of vacuum outlet gas chromatography is extensively treated by the authors in Ref. [24].

As pointed out above under vacuum outlet conditions always the condition $P = p_i/p_o \gg 1$ is met and therefore Eqs. (12)–(14) have to be used. According to Eqs. (12)–(14) it appears that the same

Table 6
Gain in speed of analysis by vacuum outlet operation as a function of the optimum inlet pressure ($p_{i,opt,atm}$) at atmospheric pressure outlet

$p_{i,opt,atm}$ (bar,absolute)	$p_{i,opt,vac}$ (bar, absolute)	Gain G
1.01	0.14	10.6
1.05	0.32	4.8
1.1	0.46	3.4
1.5	1.12	1.7
2.0	1.73	1.35
3.0	2.83	1.15
4.0	3.87	1.08

analysis time as observed by Jonker on a packed column with microparticles ($N_{req} = 1600$, $t_R = 0.23$ s, $\Delta p = 43$ bar) can be produced by an open tubular column under vacuum outlet conditions, with the following dimensions: $L = 37$ cm; I.D., 290 µm; inlet pressure, 0.1 bar absolute (see Table 5).

Using the computer program [25,26] for time optimisation of capillary columns developed in the authors' laboratory, these conditions could be verified. This program is based on the underlying theory; no simplifications are made, except from the assumption of ideal gas behaviour.

3.4.3. Effect of carrier gas velocities larger than under optimum conditions ($\nu > \nu_{opt}$) for capillary columns

The theoretical relationships presented before proceed from the assumption of gas chromatography performed at the optimum carrier gas velocity. At higher velocities the analysis time is reduced, but simultaneously the column plate number will decrease due to a larger plate height. In order to restore the ensuing loss in peak resolution a longer column has to be selected, thus re-establishing the original plate number. However, this opposes the decreased analysis time. It can be concluded that the speed of analysis will be improved as long as the increased carrier gas velocity overrules the required column length increment. This subject was already recognised by Scott and Hazeldean in 1960, introducing the concept of 'optimum practical gas velocity' [27].

For thin film open tubular columns again two boundary conditions can be distinguished: $P = 1$ (Eq. (9) with $f_2 = 1$) and $P \gg 1$ (Eq. (12) with $f_2 = 3/2P$). Introducing the dimensionless quantities:

$$\xi = \frac{h}{h_{min}} \tag{20}$$

and

$$V = \frac{\nu}{\nu_{opt}} = \frac{u_o}{u_{o,opt}} \tag{21}$$

it follows from Eq. (9) for low pressure drop, thin film columns:

$$\frac{t_R}{t_{R,opt}} = \frac{h/\nu}{h_{min}/\nu_{opt}} = \frac{\xi}{V} \tag{22}$$

Starting from the Golay equation, it appears [28] that:

$$\xi = \frac{H}{H_{\min}} = \frac{1}{2} \cdot \left(V + \frac{1}{V}\right) \cdot \frac{f_1}{f_{1,\text{opt}}} \tag{23}$$

or for $P = 1$ (and for $P \gg 1$):

$$\xi = \frac{H}{H_{\min}} = \frac{1}{2} \cdot \left(V + \frac{1}{V}\right) \tag{24}$$

For $P = 1$ it follows from Eq. (23):

$$\frac{t_R}{t_{R,\text{opt}}} = \frac{\xi}{V} = \frac{1}{2V} \cdot \left(V + \frac{1}{V}\right) \tag{25}$$

When $V = 2$, $\xi = 1.25$. Thus the plate height is increased by 25%; if the required plate number is kept constant the column length has to be increased by 25%. The carrier gas velocity is, however, doubled, resulting in $t_R/t_{R,\text{opt}} = 0.625$. At $V = 4$, $t_R/t_{R,\text{opt}} = 0.53$.

For larger values of V the ratio ξ/V assumes a constant value of 0.5. Increasing the carrier gas velocity above $V = 4$ results in a proportional increase in the column length. The retention time will remain constant when N_{req} is kept constant.

Moreover, GC columns operated at very large carrier gas velocities will necessarily require a large pressure gradient making the assumption $f_2 = 1$ invalid. Furthermore, fast analysis of rather complex mixtures will require long columns with a small internal diameter and thus will operate under high pressure drop.

For large values of P Eq. (12) has to be used; including the defined values of ξ and V yields ($N_{\text{req}} = $ constant):

$$\frac{t_R}{t_{R,\text{opt}}} = \frac{\xi^{3/2}}{V^{1/2}} = \frac{\left[\frac{1}{2} \cdot \left(\frac{1}{V} + V\right)\right]^{3/2}}{V^{1/2}} \tag{26}$$

This function assumes a minimum value of 0.92 for $V = \sqrt{2}$ or $u_o = u_{o,\text{opt}}\sqrt{2}$ [29]. Compared to a column length L operated under optimal conditions an 8% faster analysis can be obtained ($N_{\text{req}} = $ constant) with a column of length $1.06L$ (as follows from Eq. (24) for $V = \sqrt{2}$: $H/H_{\min} = 1.06$). From this it follows that $\bar{u}_{\text{opt}}/\bar{u} \approx 0.87$ or $\bar{u} = 1.15\bar{u}_{\text{opt}}$.

Blumberg in a series of publications (among

others Ref. [8]) on the theory of fast capillary gas chromatography came to the same conclusions.

Using Eq. (26) it can be seen that the plate height and column length are already almost doubled for $V = 2$. Hence we can come to the following conclusion:

Fast narrow bore, thin film open tubular columns require a high pressure drop, $P \gg 1$. These columns should be operated close to or slightly above optimum conditions ($1 \leq V < 1.4$).

The validity of both boundary expressions Eqs. (25) and (26) were checked by comparing with experimental plate height data. Excellent agreement was observed between theory and experiment [28].

If a fixed column length is used, a comparison of optimum conditions and conditions of $u_o = \sqrt{2}u_{\text{opt}}$ ($V = \sqrt{2}$) gives according to Eq. (12) with $(N^{3/2}h^{3/2}) = (N_{\text{req}}^{3/2}h^{3/2})_{\text{opt}}$:

$$\frac{t_R}{t_{R,\text{opt}}} = \frac{1}{\sqrt{V}} = \frac{1}{\sqrt[4]{2}} \approx \frac{1}{1.19} = 0.84.$$

A 16% reduction in analysis time is obtained at the cost of a 6% loss in efficiency (Eq. (24)).

3.4.4. Effect of carrier gas velocities larger than under optimum conditions ($\nu > \nu_{opt}$) for packed columns

In contrast to the situation for capillary columns no exact analytical plate height equation is available for packed columns. One of the expressions describing the H–u relation for packed columns was developed by Horváth and Lin [30]. For $k = 2$ and neglecting the stationary phase term the equation can be written in the reduced form:

$$h \approx 1.5 + \frac{1.4}{\nu} + 0.08\nu \tag{27}$$

or $h_{\min} = 2.2$ at $\nu_{\text{opt}} = 4.2$.

With $t_R \propto h^{3/2}/\nu^{1/2}$ the effect of increasing ν above values of ν_{opt} can be numerically approached for large values of P. The equation describing the situation for $P = 1$ is not relevant for packed columns, due to their intrinsically high inlet pressures.

The results are given in Table 7. For $V = 2.9$ the ratio $t_R/t_{R,\text{opt}}$ is minimal and approaches a value of 0.75. It can be concluded that packed columns can be operated under 3–4 times the optimum conditions,

Table 7
Packed columns with carrier gas velocities larger than ν_{opt} ($P \gg 1$)

ν	4.2	8.4	12.2	16.8	42
V	1	2	2.9	4	10
$t_R/t_{R,opt}$	1	0.77	0.75	0.77	1.05

but also here the gain in speed is marginal, approximately 25%. It should be kept in mind, however, that the required inlet pressure for packed columns is often already the limiting factor. Increasing the flow-rate and thus column length to keep N_{req} constant, is not an attractive approach.

3.5. Temperature-programmed conditions (constant-pressure mode)

In the foregoing treatment, analysis time optimisation was discussed for isothermal analysis. From the viewpoint of practical gas chromatography this assumption is too restrictive. It has been estimated that 80% of all GC users include temperature programming. In an extensive treatment Schutjes et al. [31] proved that the dependence of the analysis time on the column inside diameter for a capillary column or particle size in a packed column is the same in both isothermal and linear temperature-programmed analysis.

At $P = 1$ the analysis time, t_R, in the programmed mode will be proportional to d^2 (d_c or d_p), whereas at values of $P \gg 1$ a linear dependence on d will be found. For the programming rate r ($= \partial T/\partial t$) it followed:

$$r \propto \frac{1}{t_{0,iso}} \tag{28}$$

Or for columns that are operated with the same phase ratios, stationary phase and carrier gas:

$$r \propto \frac{1}{d^2} \text{ for } P = 1$$

$$r \propto \frac{1}{d} \text{ for } P \gg 1$$

Consequently, in linear temperature-programmed analysis the programming rate has to be significantly increased when using narrow-bore (or small particle) columns as compared to standard ones, requiring instrumentation offering these high programming

rates. The validity of this theory was confirmed by several experiments [31]. It should be emphasised here again, that extreme high speed of analysis both in isothermal and programmed-temperature analysis can only be obtained if N_{req} is relatively small (Eqs. (9) and (12)).

3.6. Sample capacity

Another important factor is the effect of characteristic diameter reduction on the sample capacity of fast columns. In principle this is not a problem for packed columns; the speed of analysis is related to d_p, but the sample capacity can be varied at will by increasing the column diameter. A large advantage in this respect for packed columns. In open tubular columns the speed as well as the sample capacity are related to the inside column diameter d_c.

In an extensive theoretical and practical study on the sample capacity of open tubular columns Ghijsen et al. [32] came to the following conclusion:

The maximum sample capacity, C_{max} for columns with an equal phase ratio leading to maximally 10% peak broadening is given by:

$$C_{max} \propto \beta d_c^3 \tag{29}$$

where β is a proportionality factor: $0.05 < \beta < 1.8$; $\beta \approx 1.8$ for solutes and stationary phases with similar structures; $\beta \approx 0.05$ for solutes and stationary phases with very different structure.

The sample capacity is thus drastically reduced [$\propto d_c^3$] for narrow-bore columns. This is a serious limitation for narrow-bore open tubular GC.

3.7. Multi-capillary columns

A very interesting development in column technology is the introduction by Alltech [33] of the multi-capillary column. A parallel configuration consisting of 919 coated capillaries with an I.D. of 40 μm and a length of 1 m.

Speed and pressure drop are dictated by the 40-μm inside diameter. Flow-rate and sample capacity are, however, theoretically 919 larger because of the parallel operation.

From literature data [34,35], it follows that due to very slight inequalities in the parallel columns $h_{min} \approx$

1.8–2.0 instead of $h_{min} \approx 0.8$ for an ideal thin film open tubular column.

It should be emphasised here, however, that also for a single narrow-bore column with an I.D. of 50 μm or less, it is very difficult to obtain a minimum value of h of 0.8.

A real impact of the concept of multi-capillary columns can only be anticipated, if more flexibility can be offered. This applies to available column lengths, inside diameters and number of columns in the parallel configuration.

4. Conclusions

The basic principle of decreasing analysis times in gas chromatography is miniaturisation: a decrease of the particle size in packed columns or the column diameter in capillary column. This implies that for a given required plate number, N_{req}, the column diameter can be decreased proportional to the decrease in characteristic diameter. Reduction of the characteristic diameter heavily increases the demand on the pressure capability of the instrumentation. For packed columns this implies that higher plate numbers at high speed are outside reach.

It should be emphasised that it is assumed that the contribution of the stationary phase term to the plate height can be neglected (thin films/low liquid phase loading). This assumption is correct, when discussing fast gas chromatography.

The effect of characteristic diameter reduction on sample capacity is very pronounced for capillary columns and in principle non-existing in packed columns. Multi-capillary columns take in this respect an intermediate position.

Table 8 summarises the dependence of analysis time, pressure drop, sample capacity and volumetric flow-rate at column outlet conditions and linear temperature-programming rate on the characteristic diameter.

High speed GC involves high pressure drops if N_{req} is not too small, therefore, for this table the condition $P \gg 1$ is used (Eqs. (12) and (13)).

Turning back to Eq. (12) it appears that the analysis time is very dependent on the required plate number ($N_{req}^{3/2}$). Extremely fast analysis can only be obtained, if N_{req} is small. Minimisation of N_{req} is therefore always a primary task, this is done by proper stationary phase and column temperature selection ($k_{opt} \approx 2$); this optimisation is not subject of this paper.

For fast analysis hydrogen is the carrier gas of choice, with helium as second best (about 60% slower). Vacuum outlet operation also enhances the diffusivity in the carrier gas, since the column inlet pressure is lowest for $p_o \to 0$. This implies a larger average diffusion coefficient in the mobile phase and thus a shorter analysis time. This effect is most pronounced for wide bore and/or short columns. For longer narrow-bore columns the inlet (and average pressure) is hardly affected by a change in outlet pressure from atmospheric to vacuum and no gain in analysis time is obtained.

For a well-optimised column ($L = L_{req}$), just able to separate the critical pair, increasing of the carrier gas velocity to higher values than u_{opt} is counterproductive: the resolution will decrease.

Increasing the column length to counteract the loss in resolution will yield a marginal reduction of 8% faster analysis time. The general conclusion is that high-speed open tubular columns should be operated very close to the optimum conditions.

If a given column, e.g. offers a resolution of $R_s = 3$ for the critical pair, of course increase of the flow-rate above the optimum can drastically reduce the

Table 8
Dependence on characteristic diameter in high speed GC ($P \gg 1$)

	Capillary column	Multi-capillary column	Packed column
Analysis time	d_c	d_c	d_p
Pressure drop	$1/d_c$	$1/d_c$	$1/d_p$
Sample capacity[a]	d_c^3	nd_c^3	Column diameter
Volumetric flow rate[a]	d_c	nd_c	Column diameter
Temperature programming rate (r)	$1/d_c$	$1/d_c$	$1/d_p$

[a] n, number of parallel capillaries.

analysis time. Situations such as this are often described in the literature. However, a reduction of the length of that column to a value where the resolution is decreased to 1.5 would yield under optimum conditions the same analysis time as the (too long) column described above.

If linear temperature programming is used, the programming rate of the column has to be increased proportionally to the reduction in the characteristic diameter, requiring ovens that allow for very high programming rates.

On the instrumental side also the reduction of analysis times by miniaturisation must be accompanied by a proportional decrease of the time constants of the instrument (among others, detection and sample introduction systems). For very fast analysis this requires adapted instrumentation.

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