The effect of column characteristics on the minimum analyte concentration and the minimum detectable amount in capillary gas chromatography

The Effect of Column Characteristics on the Minimum Analyte Concentration and the Minimum Detectable Amount in Capillary Gas Chromatography[1)]

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Summary

The need for faster and more efficient separations of complex mixtures of organic compounds by gas chromatography has led to the development of small inner diameter open tubular columns. Owing to their decreased plate height, extremely narrow peaks are obtained. When differently sized columns with equal plate numbers are compared, injection of a fixed amount of a solute will give the highest detector signals for the smallest bore columns. When P is defined as the ratio of the column inlet and outlet pressures, it can be seen from theory that under normalized chromatographic conditions the minimum detectable amount (Q_o) for a mass flow sensitive detector increases proportionally to the square of the column diameter for P=1. In the situation of greater interest in the practice of open tubular gas chromatography where P is large, a linear relationship is derived between Q_o and the column diameter.

It is a widespread misunderstanding, however, that narrow bore capillary columns should be used for this reason in trace analysis. If a fixed relative contribution of the injection band width to the overall peak variance is allowed, a decreased plate height drastically restricts the maximum sample volume to be injected. It is shown that the minimum analyte concentration in the injected sample (C_o) is inversely proportional to the column inner diameter when a mass flow sensitive detector is used. For actual concentrations less than C_o, sample preconcentration is required. The effect of peak resolution and selectivity of the stationary phase in relation to C_o and Q_o will be discussed as well. The validity of the given theory is experimentally investigated. Minimum analyte concentrations and minimum detectable amounts are compared using columns with different inner diameter.

1 Introduction

Because of its high sensitivity and separation power, capillary gas chromatography has become a widespread analytical technique for complex mixtures of volatile organic compounds. As can be seen from the Golay-Giddings equation [1], the separation efficiency and the speed of analysis are both favored by decreasing the column inner diameter.

In the early sixties, *Desty et al.* [2] separated several organic compounds within a few seconds on a 35 μm inner diameter column. A much more complicated chromatogram was presented by *Schutjes* [3], who analyzed a natural gas condensate using a 95 m length of a 65 μm i.d. capillary column, having a theoretical plate number of 10^6. The increased plate number per unit of column length results in extremely narrow peaks: peak widths of 0.2–1 second are common for 50 μm i.d. capillary columns of 5–10 m length. Consequently, narrow bore capillary GC makes high demands on the injection technique, the detector electronics, and the data acquisition sampling rate. Large time constants here will destroy the column efficiency and will give erroneous retention times and peak area values if too small a sampling frequency is used. The same goes for tubing and the column connections, where void volumes will disturb the peak shape.

Manufacturing narrow bore capillary columns is a delicate procedure [4] and, as the total amount of stationary phase is restricted, column overload easily occurs, resulting in a limited linear working range [2].

As a consequence, 100 μm i.d. capillaries are the smallest diameter columns commercially available at this time.

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However, besides efficiency and analysis time, the detectability is favored as well, since narrow peaks result in a better signal to noise ratio, when a fixed amount of solute is introduced. This gave rise to the misunderstanding that for this reason in trace analysis narrow bore capillary columns should be employed. It is a well-known fact that the injected sample volume is restricted when a fixed contribution of the injection band width to the overall peak broadening is allowed. Therefore, the minimum analyte concentration in the sample is no longer proportional to the minimum detectable amount.

In this work a relationship between the column inner diameter and the minimum detectable amount (Q_o) as well as the minimum analyte concentration (C_o) is derived. The effect of the selectivity of the stationary phase, peak resolution, plate number, the solute capacity ratio and the injection band width will be discussed too. In the experimental section the validity of the theory is evaluated.

2 Theory

In the theoretical concept presented here, it is assumed that the chromatographic process is performed isothermally at the optimum carrier gas velocity. When the resistance to mass transport in the stationary phase can be neglected, the optimum carrier gas velocity as well as the corresponding minimum plate height value are obtained by differentiation of the Golay-Giddings equation [1].

$$u_{o,opt} = \frac{8D_{m,o}}{d_c\sqrt{F(k)}} \tag{1}$$

$$H_{min} = \tfrac{1}{2} d_c f_1 \sqrt{F(k)} \tag{2}$$

$$\bar{u}_{opt} = f_2 \cdot u_{o,opt} \tag{3}$$

where $u_{o,opt}$ is the optimum carrier gas velocity at the column outlet, $\bar{u}_{opt}$ is the average optimum carrier gas velocity, $D_{m,o}$ is the solute diffusion constant in the mobile phase at column outlet conditions, d_c is the column diameter, F(k) is a function of the capacity ratio:

$$F(k) = \frac{11k^2+6k+1}{3(1+k)^2} \tag{4}$$

and f_1 and f_2 are pressure correction factors as introduced by *Giddings et al.* [5] and *James* and *Martin* [6]:

$$f_1 = \frac{9}{8}\,\frac{(P^4-1)(P^2-1)}{(P^3-1)^2} \tag{5}$$

$$f_2 = \frac{3}{2}\,\frac{P^2-1}{P^3-1} \tag{6}$$

where P is the ratio of column inlet and column outlet pressures, p_i/p_o.

2.1 Retention Time

After introduction of the integrated form of Darcy's law, *Schutjes et al.* [7] expressed the retention time of a compound as:

$$t_R = \left[\frac{F(k)(1+k)}{16\,D_{m,o}}\,\frac{f_1}{f_2}\,N_{max}\right] d_c^2 \tag{7}$$

where N_{max} is the maximum theoretical plate number of a column of length L:

$$N_{max} = \frac{L}{H_{min}} \tag{8}$$

For columns operated at a minimum pressure drop, *i.e.* $P \approx 1$, and f_1 and f_2 both approach unity, equation (7) becomes:

$$t_R = \left[\frac{F(k)(1+k)}{16\,D_{m,o}}\,N_{max}\right] d_c^2 \tag{9}$$

In the case of greater practical interest where $P \gg 1$, f_1 approaches the value of 9/8 and f_2 equals 3/2 P; this equation (7) is rearranged to give:

$$t_R = \left[\frac{9}{16}\,F(k)(1+k)\sqrt{\frac{2\eta}{P_o D_{m,o}}}\,N_{max}^{3/2}\right] d_c \tag{10}$$

where η is the dynamic viscosity of the carrier gas at the column temperature.

2.2 Minimum Detectable Amount

For a mass flow sensitive detector the minimum detectable amount, defined as the mass of a compound to be introduced onto the column in order to give a detector signal of 4 times the noise level, is given by:

$$Q_o^m = \sqrt{2\pi}\,\frac{4R_n}{S}\,\sigma_t \tag{11}$$

and for a concentration sensitive detector:

$$C_o^c = \sqrt{2\pi}\,\frac{4R_n}{S}\,\sigma_t F_d \tag{12}$$

where R_n is the detector noise, S is the detector sensitivity, σ_t is the actual standard deviation of the Gaussian shaped peak, and F_d is the volumetric gas flow rate through the detector cell. When N_t is the actual total plate number including all additional peak broadening contributions, the equations (11) and (12) can be rewritten as:

$$Q_o^m = \sqrt{2\pi}\,\frac{4R_n}{S}\,\frac{t_R}{\sqrt{N_t}} \tag{13}$$

$$C_o^c = \sqrt{2\pi}\,\frac{4R_n}{S}\,\frac{t_R}{\sqrt{N_t}}\,F_d \tag{14}$$

If it is assumed that the injection of the sample is the only source of extra-column peak broadening, then according to the rule of additivity of variances:

$$\sigma_t^2 = \sigma_c^2 + \sigma_i^2 \tag{15}$$

where σ_c^2 and σ_i^2 are the variances of the chromatographic process and the injection respectively. When σ_i is b times as large as σ_c (see **Figure 1**), then

$$\sigma_t = \sqrt{1+b^2}\ \sigma_c \tag{16}$$

and so:

$$N_t = \frac{N_{max}}{1+b^2} \tag{17}$$

The b factor has an effect on both the peak resolution and the detector response:

$$R_s = \frac{\Delta t_R}{4\sigma_t} = \frac{\Delta t_R}{4\sigma_c\sqrt{1+b^2}} \tag{18}$$

and:

$$R_{max} = F_c C_i S \frac{\sigma_i}{\sigma_t} = F_c C_i S \frac{b}{\sqrt{1+b^2}} \tag{19}$$

where F_c is the column flow rate and C_i is the injected solute concentration.

The demands of a sufficiently large resolution and a maximum response are incompatible. Although the optimum compromise very much depends upon the specific analytical problem, in general the product of R_s and R_{max} should be maximized. This maximum is achieved for b = 1 (cf. **Figure 2**).

The expressions for the minimum detectable amount [eqs. (13) and (14)] can now be rearranged using the equations (9), (10), and (17). For P = 1:

$$Q_o^m = \left[\frac{\sqrt{2\pi}}{4}\frac{R_n}{S}\frac{F(k)(1+k)}{D_{m,o}}\sqrt{N_t}\ (1+b^2)\right] d_c^2 \tag{20}$$

$$C_o^c = \left[\frac{\pi\sqrt{2\pi}}{2}\frac{R_n}{S}\sqrt{F(k)}(1+k)\sqrt{N_t}\ (1+b^2)\right] d_c^3 \tag{21}$$

when F_d is equal to the column flow ($F_d = F_c = \pi/4\ d_c^2 \cdot u_{o,opt}$), and for $P \to \infty$:

$$Q_o^m = \left[\frac{9}{4}\sqrt{2\pi}\frac{R_n}{S}F(k)(1+k)\sqrt{\frac{2\eta}{P_o D_{m,o}}}\ N_t\ (1+b^2)^{3/2}\right] d_c \tag{22}$$

$$C_o^c = \left[\frac{9\pi\sqrt{2\pi}}{2}\frac{R_n}{S}\sqrt{F(k)}\ (1+k)\sqrt{\frac{2\eta D_{m,o}}{P_o}}\ N_t\ (1+b^2)^{3/2}\right] d_c^2 \tag{23}$$

$$C_o = \frac{Q_o}{V_{inj}} \tag{24}$$

where V_{inj} is the injected sample volume (at the same temperature and pressure as C_o). When a Gaussian input band is considered,

$$V_{inj} = F_c\sqrt{2\pi}\ \sigma_i \tag{25}$$

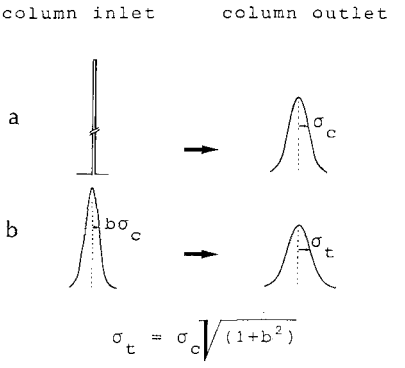

Figure 1

Representation of the progress of peak broadening in the chromatographic column.
a) sharp pulse injection.
b) gaussian shaped injection band ($\sigma_i = b\ \sigma_c$).

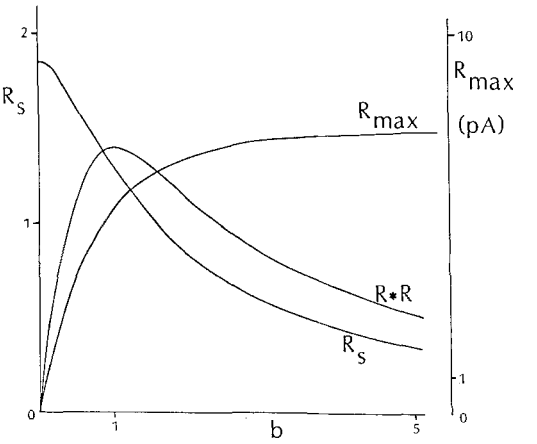

Figure 2

Peak resolution, detector response (FID) and their product as a function of the b factor.
(d_c = 100 µm, C_i = 100 ng/ml, S = 10^{-2} As/g, N_c = 100,000, k = 4, α = 1.030).

2.3 Minimum Analyte Concentration

The minimum analyte concentration in the injected sample is related to the minimum detectable amount by:

Combination of the relationships (11), (12), (16), (22), and (23) finally yields for both types of detectors:

$$Q_o^m = \frac{2}{\pi} \frac{R_n}{S} \frac{\sqrt{F(k)}}{D_{m,o}} \frac{\sqrt{1+b^2}}{b} \frac{1}{d_c} \quad (26)$$

$$C_o^c = \frac{4R_n}{S} \frac{\sqrt{1+b^2}}{b} \quad (27)$$

2.4 Concept of Normalized Chromatographic Conditions

The main criterion for selecting the proper chromatographic conditions is the separation of a critical pair of compounds. The separation depends upon plate number, capacity ratios, and the selectivity of the stationary phase. The resolution can be expressed as:

$$R_s = \frac{1}{4} \frac{k}{k+1} \frac{\alpha-1}{\alpha} \sqrt{N_t} \quad (28)$$

where k is the capacity ratio of the second of both compounds and α is the relative retention. Once the stationary phase and the GC oven temperature have been selected a specific plate number is required to establish a certain separation.

In the following discussion, the chromatographic conditions are normalized assuming a fixed actual plate number, required to separate a "critical pair".

2.5 Influence of the Plate Number

When a particular separation problem requires a larger plate number, a longer column should be employed if all the other parameters are kept constant (*i.e.* d_c, k, α, and b).

Figure 3 shows the influence of the plate number on the minimum detectable amount and the minimum analyte concentration, which is similar for both detector types.

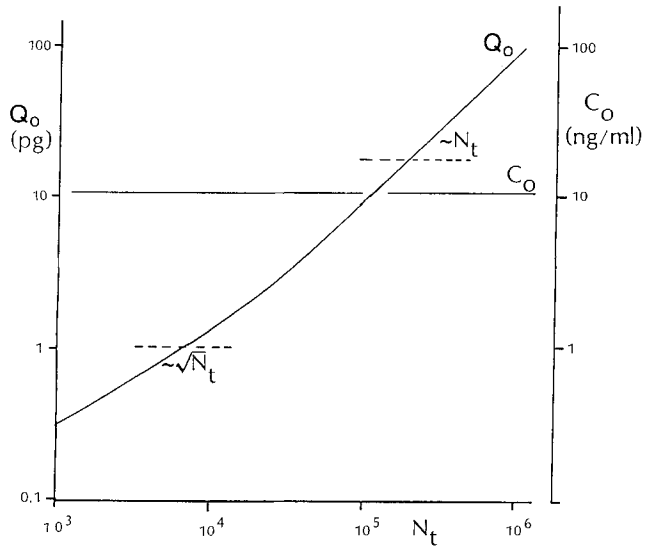

Figure 3

Influence of the total plate number on the minimum detectable amount (Q_o) and the minimum analyte concentration (C_o).
(d_c = 100 μm, k = 4, b = 0.1; FID: S = 10^{-2} As/g, R_n = 2 × 10^{-14} A).

Depending upon the pressure drop Q_o first increases proportionally to the square root of N_t and then linearly with N_t. Although C_o is not affected by the column length, excessive plate numbers should be avoided because of the corresponding needlessly long analysis times [cf. eqs. (9) and (10)]. Separation of the critical pair at a small plate number is enabled by the application of a highly selective stationary phase. Furthermore, the peak resolution should not be better than baseline separation, because of the undesired effect on t_R and Q_o.

2.6 Influence of the Capacity Ratio

The detectability of trace compounds is unfavorably influenced by large k values. **Figure 4** shows the increase of Q_o and C_o with increasing k for a mass flow sensitive detector. When a concentration sensitive detector is used the effect is less pronounced: C_o is unaffected, whereas Q_o increases according to $\sqrt{F(k)}(1+k)$.

The GC oven temperature and the stationary phase film thickness should be selected in such a way that the smallest possible k values are obtained. However, it must be remembered that the resolution rapidly drops when k is less than 2, resulting in a larger plate number required to establish a certain resolution. As discussed previously, this counterbalances the advantage of a small k value.

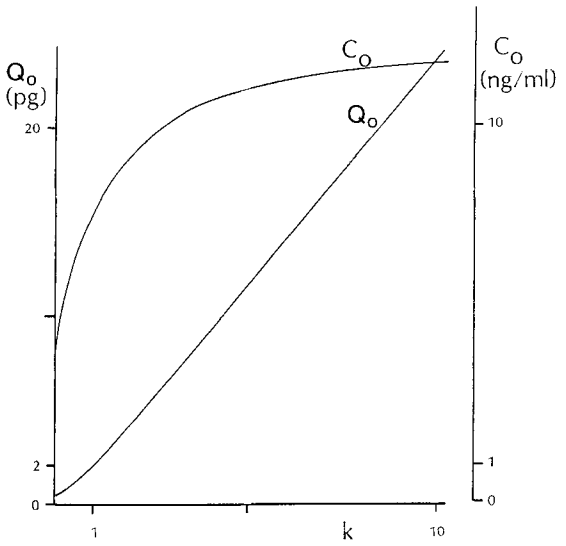

Figure 4

Influence of the capacity ratio on the minimum detectable amount (Q_o) and the minimum analyte concentration (C_o) for a mass flow sensitive detector.
(d_c = 100 μm, N_t = 100,000, b = 0.1; FID: S = 10^{-2} As/g, R_n = 2 × 10^{-14} A).

2.7 Influence of the Column Inner Diameter

A large effect of the column inner diameter on the minimum detectable amount is shown by the curves of **Figure 5**. A second to third power dependence exists for concentration sensitive detectors, whereas for mass flow sensitive detectors Q_o is proportional to d_c up to d_c^2. This relationship

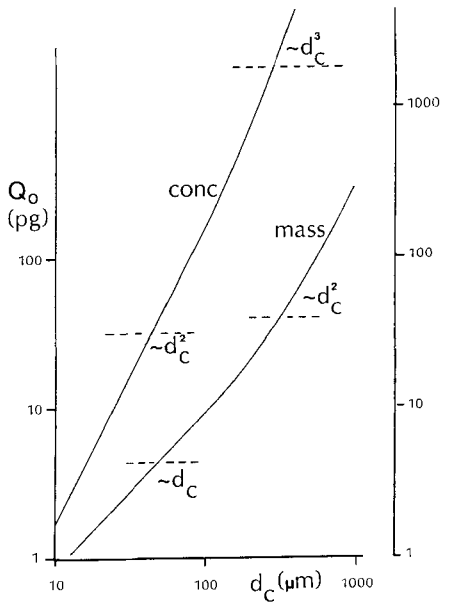

Figure 5

Influence of the column inner diameter on the minimum detectable amount for a FID ("mass") and a TCD ("conc") detector.
(N_t = 100,000, k = 4, b = 0.1; FID: S = 10^{-2} As/g, R_n = 2 × 10^{-14} A; TCD: S = 10^3 Vml/g, R_n = 5 × 10^{-6} V).

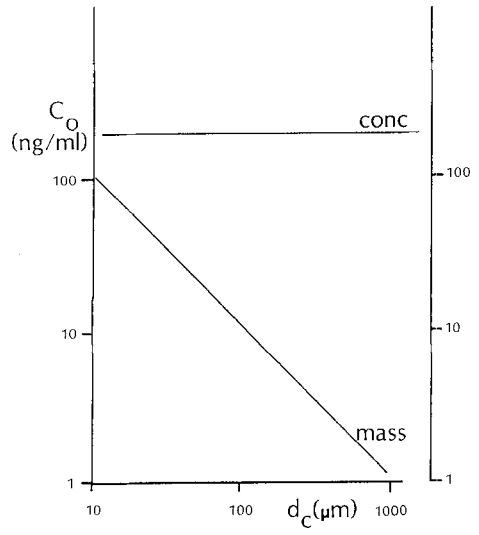

Figure 6

Influence of the column inner diameter on the minimum analyte concentration for a FID ("mass") and a TCD ("conc") detector.
(N_t = 100,000, k = 4, b = 0.1; FID: S = 10^{-2} As/g, R_n = 2 x 10^{-14} A; TCD: S = 10^3 V ml/g, R_n = 5 × 10^{-6} V).

has often been misinterpreted to mean that narrow bore columns should be used in trace analysis. However, because a fixed b value is assumed, the minimum analyte concentration is favored by large diameter columns in combination with a mass flow sensitive detector, and C_o is independent of d_c for concentration sensitive detectors (**Figure 6**).

This means that unless a sample preconcentration technique is employed, diluted samples can best be analyzed using a wide bore column, allowing the introduction of a relatively large sample. It should be noted that a large column inner diameter has the drawback of long analysis times.

2.8 Influence of the Injection Band Width

For a fixed relative contribution of the injection band width to the overall peak width the b value, defined as σ_i/σ_c, should be kept constant. As **Figure 7** shows, small values of b have a disadvantageous effect on C_o, whereas large b values drastically reduce the peak resolution (cf. Fig. 2). In general b should lie between 0.1 and 1.

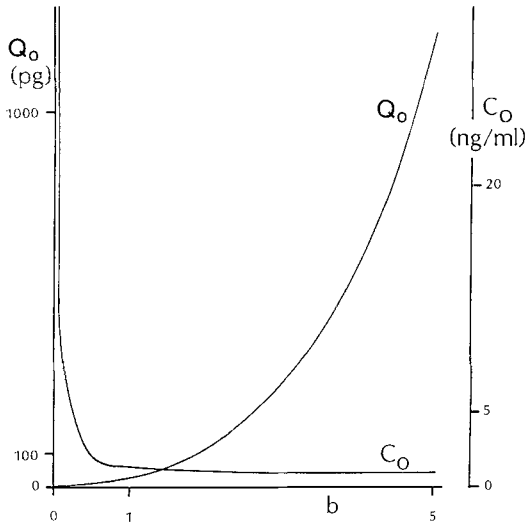

Figure 7

Minimum detectable amount (Q_o) and minimum analyte concentration (C_o) *versus* the b factor.
(N_t = 100,000, d_c = 100 μm, k = 4; FID: S = 10^{-2} As/g, R_n = 2 × 10^{-14} A).

3. Experimental

In order to evaluate the theory presented, two fused silica capillary columns with different inner diameters were used: a 50 μm i.d. narrow bore OV-1 capillary column (home made) and a 320 μm i.d. OV-1 wide bore capillary column (Hewlett Packard, Avondale, USA). The specific data and the experimental conditions for both columns are listed in **Table 1**. The chromatograph used was a Varian, Model 3400 (Varian Associates, Walnut Creek, USA) equipped with a Flame Ionization Detector. The electronics were specified to have a time constant of 50 ms. Chromatographic data were processed by a Shimadzu C-R 3A computing integrator (Shimadzu, Kyoto, Japan), sampling at a maximum frequency of 100 Hz. For accurate peak width measurements a Kipp recorder, Model BD40 was employed (Kipp & Zonen, Delft, The Netherlands) at a paper speed of

Table 1

Experimental data of the narrow bore and wide bore equipment.

	Narrow bore	Wide bore
Analytical column		
i.d.	50 μm	320 μm
length	7.5 m	25 m
stationary phase	OV-1	OV-1
film thickness	0.08 μm	0.52 μm
carrier gas	helium	helium
P	13.1	1.7
û	0.36 m/s	0.38 m/s
oven temperature	100°C	95°C
injection temperature	175°C	175°C
detection temperature	250°C	250°C
Dummy tube		
i.d.	0.32 mm	2.2 mm
length	5 m	1 m
material	fused silica	stainless steel
Restriction capillary		
i.d.	25 μm	100 μm
length	0.6 m	1 m
material	fused silica	fused silica
Splitter 1		
flow	1250 ml/min	260 ml/min
Splitter 2		
flow	0.4–27 ml/min	2.3–75 ml/min

10 mm/s. Because of the high inlet pressure required for narrow bore GC, the Varian carrier gas supply was by-passed using a Tescom Model 44-1123-24 pressure regulator (Tescom Corp., Minn., USA).

In the theory presented a Gaussian injection profile is assumed. In order to imitate this experimentally, the effluent of an empty tube installed after the splitter injector was flushed onto the capillary analytical column (**Figure 8**). They were interconnected by a home-made low dead-volume glass T-splitting device.

The carrier gas velocity through the dummy tube could be adjusted by a micro needle valve placed in the second split vent. In this way the widths of the Gaussian shaped injection bands were varied. The injection profile was monitored by introducing a small amount of the main split stream into the FID via a short narrow bore restriction (cf. Table 1).

Approximately 20 μl of *n*-decane headspace vapor was introduced by syringe injections.

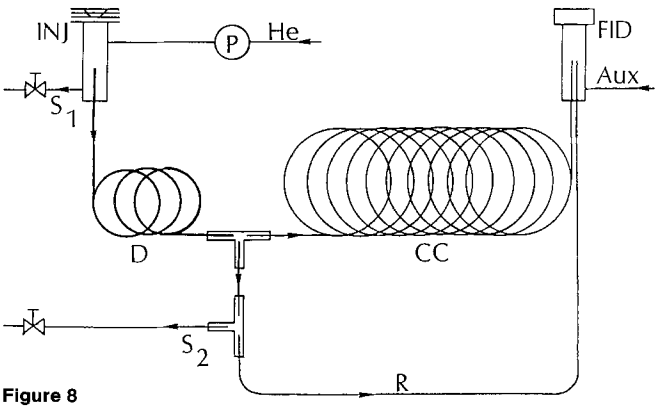

Figure 8

Experimental set-up.
CC = analytical capillary column, D = Dummy tube, R = capillary restriction, P = pressure regulator, S_1 = splitter 1, S_2 = splitter 2, Inj = injector, FID = Flame Ionization Detector, Aux = FID gases.

Table 2

Comparison of theoretical and experimental values of Q_o and C_o for a 50 μm i.d. and a 320 μm i.d. column.

			Calculated		Experimental	
	N_t (10^3)	b	Q_o (pg)	C_o (ng/ml)	Q_o (pg)	C_o (ng/ml)
50 μm i.d.× 7.5 m						
S = 10^{-2} As/g	63	0.40	2.9	1.8	3.2	2.2
R_n = 10^{-14} A	51	0.65	3.2	1.2	3.6	1.6
η = 2.28×10^{-5} Pa.s	35	0.98	3.6	0.94	4.4	1.2
$D_{m.o}$ = 3.0×10^{-5} m^2/s	21	1.59	5.2	0.78	5.9	0.88
k = 2.81	11.7	2.17	6.0	0.73	8.9	0.83
N_c = 73000						
CE = 0.42						
320 μm i.d.× 25 m						
S = 10^{-2} As/g	82	0.19	9.4	0.57	8.5	0.55
R_n = 10^{-14} A	80	0.44	11	0.26	8.9	0.25
η = 2.26×10^{-1} Pa.s	57	0.81	13	0.17	11	0.15
$D_{m.o}$ = 2.9×10^{-5} m^2/s	23	1.8	22	0.12	16	0.11
k = 2.76	8.8	3.1	32	0.11	26	0.10
N_c = 85000						
CE = 0.85						

4 Results and Discussion

In the practice of capillary gas chromatography, the theoretical H_{min} value [cf. eq. (2)] will seldom be attained because of several additional peak broadening contributions. In this paper all these effects, except the injection width, are corrected for by the introduction of a coating efficiency factor:

$$H_c = \frac{H_{min}}{CE} \tag{29}$$

and

$$N_c = N_{max} \cdot CE \tag{30}$$

where N_c and H_c are the column plate number and plate height respectively. The effect of the sample injection on the overall peak width was already expressed by the b factor (eq. (16)), and so

$$H_t = (1+b^2)\, H_c \tag{31}$$

and

$$N_t = \frac{N_c}{1+b^2} \tag{32}$$

Introduction of these corrections in the derived equations finally yields:

$$t_R = \left[\frac{F(k)(1+k)}{16 D_{m,o}}\, N_t \frac{1+b^2}{CE}\right] d_c^2 \qquad \text{for } P=1 \tag{9a}$$

$$t_R = \left[\frac{9}{16}\, F(k)(1+k) \sqrt{\frac{2\eta}{P_o D_{m,o}}}\, N_t^{3/2} \left(\frac{1+b^2}{CE}\right)^{3/2}\right] d_c \qquad \text{for } P\to\infty \tag{10a}$$

$$Q_o^m = \left[\frac{\sqrt{2\pi}}{4}\, \frac{R_n}{S}\, \frac{F(k)(1+k)}{D_{m,o}} \sqrt{N_t}\, \frac{1+b^2}{CE}\right] d_c^2 \qquad \text{for } P=1 \tag{20a}$$

$$Q_o^m = \left[\frac{9}{4}\sqrt{2\pi}\, \frac{R_n}{S}\, F(k)(1+k) \sqrt{\frac{2\eta}{P_o D_{m,o}}}\, N_t \left(\frac{1+b^2}{CE}\right)^{3/2}\right] d_c \qquad \text{for } P\to\infty \tag{22a}$$

$$C_o^c = \left[\frac{\pi\sqrt{2\pi}}{2}\, \frac{R_n}{S}\, \sqrt{F(k)}\,(1+k) \sqrt{N_t}\, \frac{1+b^2}{CE}\right] d_c^3 \qquad \text{for } P=1 \tag{21a}$$

$$C_o^c = \left[\frac{9\pi\sqrt{2\pi}}{2}\, \frac{R_n}{S}\, \sqrt{F(k)}(1+k) \sqrt{\frac{2\eta D_{m,o}}{P_o}}\, N_t \left(\frac{1+b^2}{CE}\right)^{3/2}\right] d_c^2 \qquad \text{for } P\to\infty \tag{23a}$$

$$C_o^m = \left[\frac{2}{\pi}\, \frac{R_n}{S}\, \frac{\sqrt{F(k)}}{D_{m,o}}\, \frac{\sqrt{1+b^2}}{b}\right] \frac{1}{d_c} \tag{26}$$

$$C_o^c = \frac{4R_n}{S}\, \frac{\sqrt{1+b^2}}{b} \tag{27}$$

In order to allow the comparison of the experimental results the capacity ratios of *n*-C10 on both columns were equilized by adjustment of the GC oven temperature. At both temperatures the binary gas diffusion constant was determined following the procedure described by *Fuller et al.* [8]. The dynamic viscosity was obtained from tabulated values [9] corrected for deviating temperatures by:

$$\eta_t = \eta_{T_1} \left(\frac{T}{T_1}\right)^{0.7} \tag{33}$$

From separate investigations the column coating efficiency as well as the detector sensitivity were calculated, whereas the detector noise was determined during the described experiments. No difference in the detector performance was observed throughout this work. For the experimental evaluation, the amount of solute flushed onto the analytical column was calculated from the peak area measurements

$$Q_i = \frac{A}{S} \tag{34}$$

where A is the peak area. Together with the injection band width the maximum concentration at the column inlet was calculated

$$C_i = \frac{Q_i}{F_c \sqrt{2\pi}\, \sigma_i} \tag{35}$$

If C_i produces a signal of y times $4R_n$, C_o is given by $C_o = C_i/y$ and consequently $Q_o = Q_i/y$.

Table 2 shows the theoretically calculated and the experimentally determined values, together with the numerical values of the most important parameters. It should be noted that two columns of a fixed length are compared. Therefore, N_c is constant and N_t varies with different b-values.

The experimental results very well confirm the derived theoretical relationships. As predicted an approximately 6 times smaller C_0 value is observed, when the 320 μm i.d. column is compared with the 50 μm i.d. column for equal b. For Q_0 the dependence upon the column diameter is less obvious, as both b and N_t vary simultaneously.

5 Conclusions

It has been shown for a mass flow sensitive detector (FID), that the minimum analyte concentration decreases inversely proportional to the column inner diameter. Therefore, wide bore capillary columns should be used for the analysis of highly diluted samples, unless a sample pre-concentration technique is used. To obtain full benefit of the injection volume capacity of wide bore columns, the injection band width should be 10-100% of the chromatographic peak broadening (b = 0.1–1).

When an on-column sample enrichment technique is employed (*e.g.* cryogenic trapping) the detectability is favored by narrow bore columns, as the minimum detectable amount decreases more than proportionally with decreasing column inner diameter.

Furthermore, narrow bore capillary columns have the benefit of short analysis times, however, at the cost of high inlet pressures.

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