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Considerations of Speed and Efficiency in Capillary Gas Chromatography

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

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Summary

The analysis time for a given resolution is a complex function of stationary phase selectivity, column radius, and thickness of the stationary phase film. Variation of these parameters has a large effect not only on analysis time, but also on the column inlet pressure and other instrumental requirements. The minimum amount that can be reliably detected as well as the maximum sample capacity of a column are strongly related to the selected column dimensions.

1 Introduction

Recent developments in column technology in capillary gas chromatography point in three directions:

- Improving the selectivity of the phase systems used: synthesis of new polar phases; tuning of polarity by coupled column systems; highly specific, *e.g.* chiral, liquid phases; the use of adsorbents (PLOT-Al_2O_3, Mol Sieve, Porapak columns).
- Narrow bore thin film columns (typically 50-100 μm inside diameter; 0.05-0.1 μm film thickness) having large plate numbers and a high generation speed of plates per unit time.
- Wide bore thick film columns. These columns with typical dimensions of 0.5 mm inside diameter and film thicknesses of 5-10 μm (bonded phases) have a low generation speed of plates per unit time. However, they offer a large sample capacity and the large carrier gas flows involved enable their use in combination with heat conductivity cells and FT-IR techniques.

The performance of capillary columns as a function of column diameter, film thickness, and phase selectivity will be discussed. Changing these parameters has a large effect on column efficiency, analysis time, pressure drop, minimum detectable amount, sample capacity and range, and instrumental requirements.

The treatment is based on the Golay-Giddings theory of capillary columns. For the derivation of the equations, reference is made to [1-4].

2 Theory

2.1 Analysis Time for a Given Resolution

The basic equation for the analysis time t_R needed for the isothermal separation of two components (most critical pair) was derived by *Ettre* [5]:

$$t_R = \frac{NH}{\hat{u}}(1+k) = 16\frac{(1+k)^3}{k^2}\frac{\alpha^2}{(\alpha-1)^2}R^2\frac{H}{\hat{u}} \quad (1)$$

where R is the resolution between two subsequently eluting peaks; k is the capacity ratio of the last eluting compound; and $\alpha = k_1/k_2$ is the relative retention. The plate number $N = L/H$, where H stands for the column plate height, and $\hat{u}$ is the average linear carrier gas velocity. $H/\hat{u}$ is a complex function of operating conditions and column dimensions. Basically, it contains pressure drop correction factors as well as terms describing the resistance to mass transfer in gas phase (C_m) and stationary phase (C_s).

2.2 Thin Film Columns; Influence of Column Diameter

For thin film columns the contribution of C_s can be neglected. The value of $H/\hat{u}$ [eq. (1)], under optimal chromatographic conditions, can be derived from the Golay-Giddings equation and the Poiseuille-Hagen equation for laminar flow through open pipes.

Two situations can be distinguished:
a. Columns having a limited number of theoretical plates and thus showing a small pressure drop ($P = p_i/p_o$, being the ratio of inlet-to-outlet pressure approaches a value of $P = 1$). The analysis time t_R [eq. (1)] is given by [1]:

$$t_{R_{P=1}} = \frac{4}{3}\frac{(1+k)(11k^2+6k+1)}{k^2} \times$$
$$\times R^2 r^2 \frac{\alpha^2}{(\alpha-1)^2}\frac{p_o}{p_1 D_{m,1}} \quad (2)$$

$D_{m,1}$ is the solute-carrier gas diffusion coefficient at unit pressure p_1 and r is the column radius. Thus for low pressure drop (low plate number columns or wide bore

columns) t_R is proportional to r^2. Increasing the column diameter has a large negative effect on the analysis time attainable.

b. For columns with high plate numbers, hence with large pressure drops, $P = p_i/p_o$ is always large. Under optimum gas chromatographic conditions the following equation can be derived [1]:

$$t_{R_{P\to\infty}} = 24 \frac{(1+k)^2 (11k^2+6k+1)}{k^3} \times \times \frac{\alpha^3}{(\alpha-1)^3} R^3 r \left[\frac{2\eta}{p_1 D_{m,1}}\right]^{1/2} \quad (3)$$

where η is the dynamic viscosity of the carrier gas. The retention time for a given resolution is proportional to r, showing the advantage of narrow bore columns.

For situations between P = 1 and P→∞ the reader is referred to a computer program described in reference [2].

Several interesting conclusions can be drawn from eqs. (2) and (3):

- Hydrogen should be used as carrier gas, because of its low $D_{m,1}$ or $\eta/D_{m,1}$ ratio. Helium and nitrogen are respectively 50% and 250% slower than hydrogen.

- Because of the second to third power dependence of t_R on $\alpha/(\alpha-1)$ the stationary phase must be carefully chosen.

- An unnecessarily large resolution R should be avoided. In practice this means selection of an appropriate temperature program and not using longer columns than strictly necessary.

- The k containing term in eqs. (2) and (3) should be minimized ($k_{min} \approx 2$). Therefore, phase ratio and column temperature should be tuned in such a way that k values between 1 and 3 are reached for the components of interest.

2.3 Influence of Film Thickness

A complete theoretical treatment of thick film columns is very complex [2]. Both H_{min} and $\hat{u}_{opt}$ in eqs. (2) and (3) are affected by an increase in film thickness. The stationary phase mass transfer term C_s can no longer be neglected with respect to C_m. The ratio of $H_{min}/\hat{u}_{opt}$ is proportional to the sum C of the C_m and C_s terms.

On increasing the film thickness d_f, both C_m and C_s will be enlarged, increasing the plate height H_{min} and reducing $\hat{u}_{opt}$. Thick films give an additional decrease in analysis time attainable. (Wide bore) thick film columns should only be employed if special analytical requirements such as high sample capacity, *e.g.* needed in combination with large volume detectors (HWD or FT-IR), enforce their use.

3 Pressure Drop

Pressure drop and analysis time attainable for a given resolution between a critical pair are related through an approximate relationship (p→∞).

$$\Delta p t_R = \text{constant} \quad (4)$$

or

$$\Delta p r = \text{constant [eq. (3)]}$$

Thus if high plate numbers, up to a million theoretical plates, are required, a short analysis time (narrow bore columns) is accompanied by a large inlet pressure.

Typically one million theoretical plates requires an inlet pressure of 30 bar on a 70 m × 50 μm inside diameter column.

4 Minimum Detectable Amount, Sample Capacity, Working Range

Column and detector properties determine the *minimum amount*, φ_o, of a component that can be reliably distinguished from the background noise; two types of detectors have to be taken into consideration:

For a mass-flow dependent detector, such as an FID:

$$\varphi_o = 4\sigma \frac{R_n}{S} \sqrt{2\pi} \quad (5)$$

and for a concentration dependent detector, *e.g.* a hot wire detector (HWD):

$$\varphi_o = 4\sigma \frac{R_n}{S} \sqrt{2\pi} F \quad (6)$$

R_n is the noise level of the detectors; S is the detector sensitivity; σ is the second moment of the eluting peak; and F is the volumetric flow rate measured at the detector temperature and pressure.

φ_o is proportional to the peak width (second moment). For a given plate number N, φ_o is proportional to the retention time t_R. Therefore, for high plate number columns φ_o is linearly dependent on the column radius r [eq. (3)]. Very small quantities can be detected on narrow bore columns.

The *sample capacity*, φ_s, is the maximum amount of a component which can be injected on a column giving a limited (*e.g.* 10%) increased peak width (second moment). φ_s is assumed to be approximately proportional to the volume occupied by one theoretical plate and is for capillary columns, keeping the capacity factor k constant, proportional to the radius r^3. Hence varying the column diameter has a large effect on the sample capacity.

The full equation for φ_s reads [3]:

$$\varphi_s = \frac{MP_s}{R^* T_c} \sqrt{3\pi} (r - d_f) (1 + k) (LH)^{1/2} \quad (7)$$

where d_f represents the film thickness; r the column radius; L the column length; H the plate height; and M the molecular weight of the component; P_s the saturated vapour pressure at column temperature T_c and R* the gas constant.

The advantage of the use of wide bore thick film columns for the sample capacity is directly reflected in this equation. Note that $(LH)^{1/2}$ is proportional to the column radius r and that k includes the volume of the stationary phase related to the film thickness d_f.

The *working range*

$$W = \frac{\varphi_S}{\varphi_O} \qquad (8)$$

of a column should generally exceed the concentration ratio of the compounds in the sample to be analyzed. If not, the detector response for the trace compounds can only be distinguished from the noise level when the column is overloaded for the main peaks. This may obscure small peaks eluting next to the overloaded peaks [4].

In practice, for high plate number columns, W is proportional to r^2, a distinct advantage of wide bore columns.

The selection of a column inner diameter, therefore, often implies a compromise between speed of analysis and required working range. The largest working range is always obtained with wide bore thick film columns.

5 Sample Introduction

Extra column contributions to peak dispersion should be kept to a minimum. Therefore, the duration of the injection band, for a given high plate number, should be lowered proportionally to the analysis time and thus the column radius r [eq. (3)].

Extremely fast separations ($N/s = 10^4$) can only be executed with input band widths of the order of ms, requiring the use of special sample introduction systems (*e.g.* fluidic logic sample devices [6]).

Split mode injection allows sample band widths (second moment) between 50 ms and 0.1 s for gases and of the order of 1 s for high boiling liquid samples.

6 Time Constants of Detector (Electronics)

The time constant, T, of detection / data acquisition should be such that $T \leq 0.1\ \sigma$. Only for very fast (low plate number) separations does this become critical. Modern instrumentation offers time constants of the order of 0.1 s allowing separation speeds (second moments σ) of the order of 1 s. Narrow bore columns with high plate numbers ($> 10^5$) can be exploited without serious difficulties.

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