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Dependence of the efficiency of a multicapillary column on the liquid phase loading method

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Abstract

One of the main approaches employed to reach fast chromatographic separation is based on using columns containing up to 1000 capillaries with the diameter size down to 10–100 μm . The efficiency of such columns depends on the dispersion of the capillary radius and on the way of the liquid-film loading. We present general equations describing these effects. Specifically, we show theoretically and experimentally that the separation efficiency can be improved by using the loading methods specially designed in order to take into account correlation between the film thickness and capillary radius. © 2001 Published by Elsevier Science B.V.

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1. Introduction

The development of fast gas chromatography is of high current interest (see a recent review by Cramers and Leclercq [1]). One of the most promising approaches aimed at this goal is to use a multicapillary column. In such columns, one can employ capillaries with the diameter size down to 10–100 μm . This guarantees high efficiency of a column, because with decreasing the capillary diameter the resolution is well known to increase [2]. Using a set of capillaries (up to 1000) allows to employ a relatively high flow-rate and accordingly simplifies the gas injection and detection. Although the very idea of this approach is old (to our knowledge, it can be tracked at least to the paper by Golay [3]), its practical implementation [4–7] became possible only

with the design of new technologies for manufacturing the required capillaries with a very narrow diameter distribution (this condition is crucial for successful performance of multicapillary columns). Nowadays, the multicapillary columns are commercially available (see, for example, Ref. [8]). The understanding of the physical principles which can be used for optimization of the performance of such columns is, however, still limited.

The resolution of a multicapillary column cannot obviously be better than that corresponding to a single capillary {the latter one is discussed in detail in the textbooks on gas chromatography (see, for example, Ref. [2])}. In practice, this upper limit can hardly be achieved, i.e. the efficiency of multicapillary columns depends rather on the distribution of capillaries over the radius and also on the way how the liquid phase is loaded on the walls of capillaries. In our patent [5], it was shown theoretically and experimentally that the performance of a multicapil-

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lary column could be improved by using correlation between the thickness of the liquid film and the capillary radius. Recently, this problem was also briefly analyzed in Ref. [9] in the case when the capillaries are coated statically (in this case, the retention factor of a capillary is independent of the capillary radius).

The goal of our present paper is to treat in detail the influence of the way of the liquid phase loading on the column efficiency and also to outline and compare some experimental approaches which can be employed in this field.

2. Theory

The efficiency of a conventional chromatographic column is characterized by using the number of theoretical plates or the height equivalent to a theoretical plate. These quantities are defined, respectively, as (see Eqs. (23) and (26) in Ref. [2]):

$$N = t_R^2 / \sigma^2 \quad (1)$$

and

$$H = L/N \quad (2)$$

where t_R and σ^2 are, respectively, the retention time and variance of a peak, and L is the capillary length. These definitions are phenomenological in the sense that to employ them there is no need to know what we have inside a column (one should be able only to measure the profile of an output signal). For this reason, Eqs. (1) and (2) are applicable to multicapillary columns as well. In the latter case, one should however bear in mind that the measured output signal is superposition of signals of single capillaries. Thus, to calculate N and H for a multicapillary column, we have to use properly averaged quantities taking into account the distribution of capillaries over the radius.

For a single capillary of the radius r , the standard expression for the retention time is well known to be (see, for example, Eq. (11) in Ref. [2]):

$$t(r) = L[1 + k(r)]/u(r) \quad (3)$$

where $k(r)$ is the retention factor, and $u(r)$ the carrier-gas velocity.

The retention time for a multicapillary column is a superposition of those of single capillaries. Assuming the contribution of a single capillary to the total signal to be proportional to the capillary cross section, i.e. to r^2 , we have:

$$t_R = \int t(r) r^2 P(r) dr / \int r^2 P(r) dr \quad (4)$$

where $P(r)$ is the radius distribution of capillaries. In our analysis, this distribution is considered to be Gaussian:

$$P(r) = \frac{1}{\sqrt{2\pi}\sigma_r} \exp\left[-\frac{(r - r_o)^2}{2\sigma_r^2}\right] \quad (5)$$

where r_o is the average radius, and σ_r^2 the variance. Substituting Eq. (5) into Eq. (4) expanding $t(r)$, $u(r)$, and r^2 into the Taylor series near r_o , and taking into account the zero-order terms of expansion, we obtain:

$$t_R = t(r_o) = (1 + k_o)L/u_o \quad (6)$$

where k_o and u_o are the retention factor and average carrier-gas velocity for the capillary with $r = r_o$.

Note that to get Eq. (6), we do not need explicit expressions of the dependence of $k(r)$ and $u(r)$ on r . In addition, it is appropriate to notice that Eq. (6) is independent of our assumption that the contribution of a single capillary to the total signal is proportional to r^2 . We might instead assume, e.g. that the contribution was proportional to $u(r)r^2$, and it would not change the result. The latter comment is applicable to Eq. (8) and accordingly to Eq. (15) below as well.

For σ^2 [Eq. (1)], we have:

$$\sigma^2 = \sigma_o^2 + \langle(\Delta t)^2\rangle_c \quad (7)$$

where σ_o^2 is the variance corresponding to a single capillary with $r = r_o$ (an explicit expression for this term is given by the famous Golay equation [2]), and

$$\langle(\Delta t)^2\rangle_c = \int [t(r) - t_R]^2 r^2 P(r) dr / \int r^2 P(r) dr \quad (8)$$

is the term taking into account the radius distribution.

The time $t(r)$ in Eq. (8) is given by Eq. (3). The latter equation depends on $k(r)$ and $u(r)$. To execute integration in Eq. (8), we need explicit expressions

for $k(r)$ and $u(r)$. According to the Poiseuille law, we have:

$$u(r) = u_o r^2 / r_o^2 \quad (9)$$

The retention factor is known to be proportional to the ratio of the volumes of the liquid and gas phases:

$$k(r) = KV_l / V_g \simeq K[2\pi r d_f(r)] / (\pi r^2) \\ = 2Kd_f(r) / r \quad (10)$$

where K is the distribution coefficient, and $d_f(r)$ the liquid film thickness. Often, the dependence of d_f on r can be represented in the power-law form (see, for example, Section 3):

$$d_f(r) = c_f r^\alpha \quad (11)$$

where c_f is a constant, and α the exponent dependent on the way of deposition of the liquid phase. Using the latter expression, we can rewrite Eq. (10) as:

$$k(r) = 2Kc_f r^{\alpha-1} \quad (12)$$

Substituting expressions (9) and (12) into Eq. (3) yields:

$$t(r) = \frac{Lr_o^2}{u_o r^2} \cdot \left[1 + k_o \left(\frac{r}{r_o} \right)^{\alpha-1} \right] \quad (13)$$

where $k_o = 2Kc_f r_o^{\alpha-1}$.

Expanding expression (13) in the series near r_o , one obtains:

$$\Delta t = t(r) - t_R \simeq - (L/u_o r_o) [2 + k_o(3 - \alpha)] \Delta r \quad (14)$$

where $\Delta r = r - r_o$.

Substituting expressions (5) and (14) into Eq. (8), expanding r^2 in Eq. (8) near r_o , and integrating over dr result in:

$$\langle (\Delta t)^2 \rangle_c = (L\sigma_r / u_o r_o)^2 [2 + (3 - \alpha)k_o]^2 \quad (15)$$

Inserting this expression into Eq. (7), we get:

$$\sigma^2 = \sigma_o^2 + (L\sigma_r / u_o r_o)^2 [2 + (3 - \alpha)k_o]^2 \quad (16)$$

Substituting Eqs. (6) and (16) into Eq. (1), we obtain the following general expression for the number of theoretical plates:

$$N = \frac{L^2(1 + k_o)^2}{u_o^2 \sigma_o^2 + (L\sigma_r / r_o)^2 [2 + (3 - \alpha)k_o]^2} \quad (17)$$

If N depends primarily on the distribution of capil-

laries over the radius [i.e. σ_o^2 is negligibly small], one has:

$$N = \frac{r_o^2(1 + k_o)^2}{\sigma_r^2 [2 + (3 - \alpha)k_o]^2} \quad (18)$$

The latter equation can be rewritten as:

$$N = N_o \cdot \frac{4(1 + k_o)^2}{[2 + (3 - \alpha)k_o]^2} \quad (19)$$

where $N_o = r_o^2 / 4\sigma_r^2$ is the number of theoretical plates for the nonsorbing species.

Using Eq. (19), it is instructive to compare a few ways of deposition of the liquid phase:

(i) If the liquid film thickness is the same for all capillaries (i.e. $\alpha = 0$), we have:

$$N = N_o \cdot \frac{4(1 + k_o)^2}{[2 + 3k_o]^2} \quad (20)$$

In particular, $N = (4/9)N_o$ for $k_o \gg 1$.

(ii) For $\alpha = 1$, the number of theoretical plates:

$$N = N_o \quad (21)$$

is independent of k_o .

(iii) With increasing α , the efficiency of the multicapillary column increases and becomes equal to:

$$N_{\max} = N_o(1 + k_o)^2 \quad (22)$$

at $\alpha = 3$. With further increasing α , N_{\max} may be even higher, but then decreases. Thus, the film deposition with $\alpha \approx 3$ is optimal.

Finally, it is of interest to present a general equation describing the effect of the distribution of capillaries over the radius on the theoretical plate height. It can be derived by substituting expression (17) into Eq. (2), i.e.:

$$H = H_c + H_o \cdot \frac{[2 + (3 - \alpha)k_o]^2}{4(1 + k_o)^2} \quad (23)$$

where $H_c = u_o^2 \sigma_o^2 / [L(1 + k_o)^2]$ is the height for a single capillary, and $H_o = 4L\sigma_r^2 / r_o^2$ the height corresponding to the nonsorbing species in the case when $H_c \ll H_o$. Earlier, Eq. (23) was published (without derivation) in Ref. [5].

In the specific cases, Eq. (23) yields [cf. Eqs. (20)–(22)]:

$$H = H_c + H_o \cdot \frac{[2 + 3k_o]^2}{4(1 + k_o)^2} \text{ for } \alpha = 0 \quad (24)$$

$$H = H_c + H_o \text{ for } \alpha = 1 \quad (25)$$

$$H = H_c + H_o/(1 + k_o)^2 \text{ for } \alpha = 3 \quad (26)$$

3. Ways of the film loading

Experimental approaches to deposition of the liquid phase on the capillary walls are numerous. Below, we discuss and compare four of them (Fig. 1).

3.1. Static method

Conceptually, the simplest method of the film formation (Fig. 1a) is as follows: the column is filled with the liquid phase solution; one end of the column is sealed; then the solvent is evaporated through the open end by heating in the oven, while the high molecular phase rests as a film on the capillary walls. The advantage of this method is high reproducibility. The shortcoming is that the efficiency is relatively low. Indeed, the amount of the high-molecular phase per the unit column length is proportional in this case to r^2 . The wall area per unit length is proportional to r . The film thickness is accordingly proportional to r as well. This means that $\alpha = 1$ and $N = N_o$ [see Eq. (19) or (21)].

3.2. Dynamic method

At the dynamic loading, a liquid phase plug is forced through capillaries under excess pressure (Fig. 1b). According to experiments [10,11], the thickness of the remaining film of the liquid phase solution is in this case given by:

$$d_f = crU^\beta, \quad (27)$$

where c is a coefficient dependent on the properties of the liquid and surface, U the solution front velocity, and β the exponent equal to ≈ 0.5 in a wide range of velocities. According to the Poiseuille

law, the front velocity is proportional to the capillary radius multiplied by the pressure drop. Thus, the thickness of the film obtained after evaporation of the solvent is proportional to $r^{1.5}$, i.e. $\alpha \approx 1.5$. With this exponent, Eq. (19) yields $N \approx 1.8N_o$ provided that $k_o \gg 1$. This efficiency is two times higher than that of the static method.

3.3. Modified dynamic method

Further increase of the column efficiency is possible at a dynamic phase loading with incomplete column filling (Fig. 1c). In this case, the liquid phase solution first fills the column almost entirely (by about 90%), but so that it does not reach the second end of the column even in the widest capillaries. Then, the solution is displaced in the opposite direction under the gas-pressure drop. In this case, the length of the penetration of the liquid phase into a capillary is proportional to r , while its thickness is proportional to $r^{1.5}$ (see Section 3.2). Thus, the average amount of the liquid phase in a capillary is proportional to $r^{2.5}$, i.e. $\alpha \approx 2.5$. With this exponent, Eq. (19) yields $N \approx 16N_o$ at $k_o \gg 1$. [Note that Eq. (19) has been derived provided that the uniform film covers the capillary walls entirely, but actually it holds in the case of the nonuniform distribution of the liquid phase as well (in the latter case, one should employ the average film thickness for each capillary)].

3.4. Combination of static and dynamic approaches

According to our experience, one of the best methods of deposition of the liquid phase is based on combination of static and dynamic approaches (Fig. 1d). In this case, the column is first filled with the liquid phase solution, and then the solvent is evaporated through the column end by heating. As the column moves into the oven, the solution is pumped into the column. The solution velocity in wider capillaries is higher than in narrower ones. Therefore, the film is thicker in wider capillaries. Our experiments indicate that under such circumstances one can obtain the films with the optimal exponent $\alpha \approx 3$.

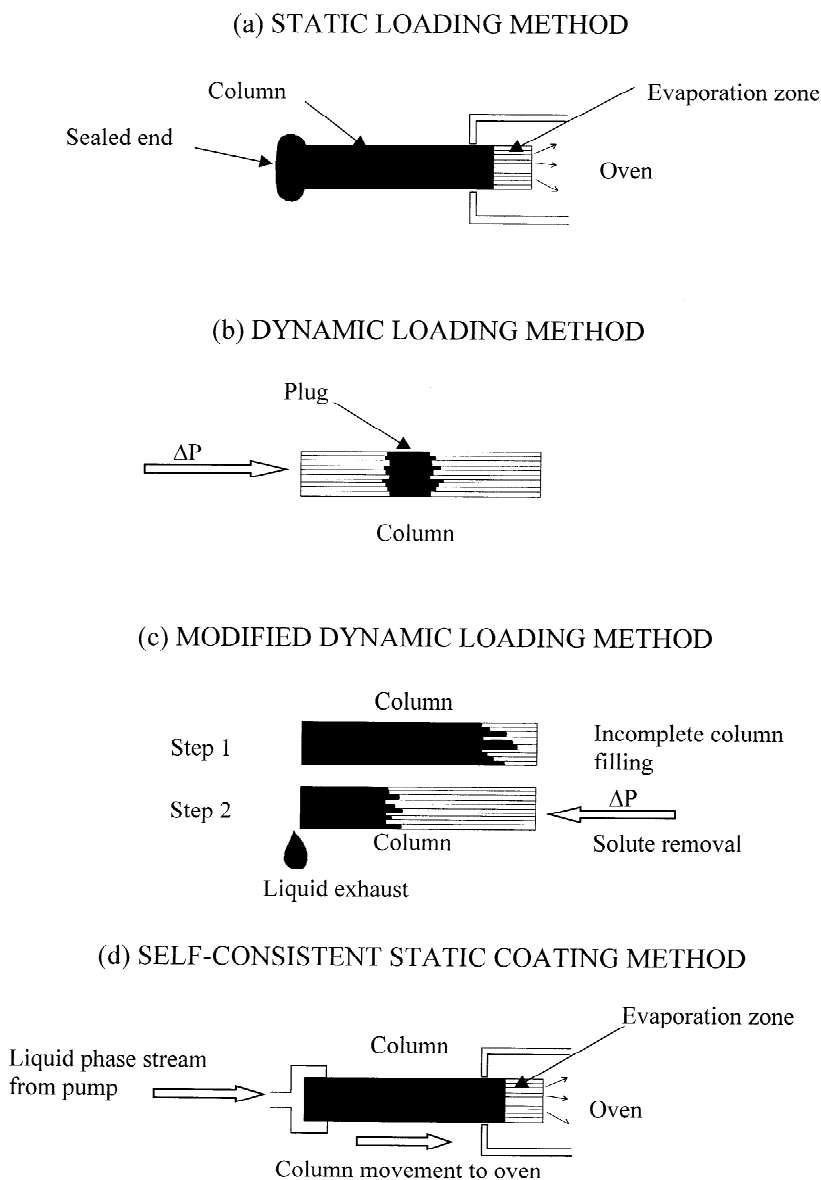


Fig. 1. Schemes of four methods of deposition of the liquid phase on the walls of a polycapillary column (for details, see Section 3).

4. Examples

The columns used in our group typically contain 1000 capillaries with the length from 20 cm to 1 m and the radius of 18 μm [4]. The radius dispersion of capillaries is from $\sigma_r/r_o = 0.014 \pm 0.0005$ to 0.020 ± 0.0005 (these data were obtained by employ-

ing the optical microscope). Injection of gases occurs via a specially designed injector [12] based on the Parker three-way skinner valve allowing us to reduce the injection time down to 20–50 ms. After separation, the effluent is analyzed by using the standard flame-ionization detector combined with (i) a laboratory-made electrometric amplifier with the response

time of 10^{-3} s and (ii) a specially designed 20-bit system of the signal processing with the digitalization rate up to 1000 samples per s.

To illustrate the dependence of the efficiency of the multicapillary column on the method of deposition of the liquid phase, we show two chromatograms (Fig. 2) exhibiting separation of the mixture of (1) *n*-pentane, (2) 2,2,4-trimethylpentane, (3) 2,5-dimethylhexane, (4) 2,3,4-trimethylpentane, (5) 3-methylheptane, and (6) *n*-octane (the carrier gas is nitrogen) in the column with the films obtained by using the static and combined methods, respectively. In both cases, the measurements were performed at the same temperature and with the same carrier-gas velocity. For the static method (with $\alpha = 1$), the separation is seen (Fig. 2b) to be not complete. In addition, one may notice that the numbers of theoretical plates are nearly equal (about 820–850 theoretical plates) for all the peaks. In other words, the numbers of theoretical plates is independent of the retention factor. This finding is in agreement with Eq. (21). For the combined self-consistent method (Fig. 2a), the separation is much better. Specifically, the number of theoretical plates of the first peak is

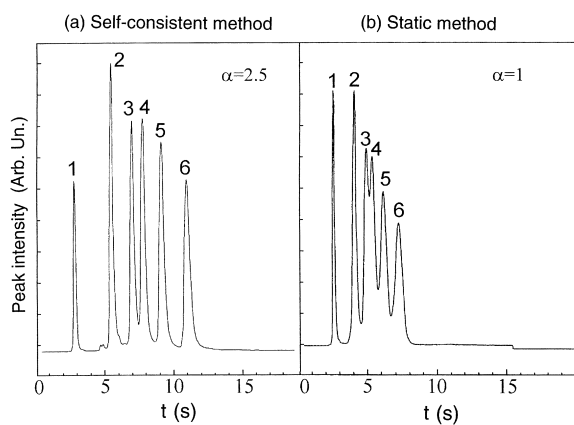


Fig. 2. Chromatograms of the mixture of (1) *n*-pentane, (2) 2,2,4-trimethylpentane, (3) 2,5-dimethylhexane, (4) 2,3,4-trimethylpentane, (5) 3-methylheptane, and (6) *n*-octane (the carrier gas is nitrogen) in the cases of the multicapillary column with the SE-30 liquid phase film loaded from chloroform solution by employing the (a) combined and (b) static methods, respectively. The column used contains 1200 capillaries with $L = 1$ m, $r_o = 18$ μ m, and $\sigma_e/r_o = 0.017 \pm 0.0005$. The carrier gas is nitrogen with the flow of 40 ml/min. The measurements were performed at 40°C.

also about 830 theoretical plates, but with increasing the retention time (for peaks 2–6) the number of theoretical plates increases and reaches about 3400 theoretical plates for peak 6. The latter findings are in agreement with Eq. (19) with $\alpha \approx 2.5$. [The dependence of the number of theoretical plates on the retention time (Fig. 2) can easily be converted into the dependence of the number of theoretical plates on the retention factor, because the retention time is basically proportional to the retention factor. Here it is appropriate to note that the dependences of the number of theoretical plates on the retention factor, following from the data shown in Fig. 2, are not typical for the conventional chromatographic columns].

To demonstrate more explicitly application of the general equations derived above to experiment, we have measured the dependence of the theoretical plate height on the the retention factor for *n*-undecane. The results, obtained by using the static and modified dynamic film-deposition methods with $\alpha = 1$ and 2.5, respectively, are exhibited in Fig. 3

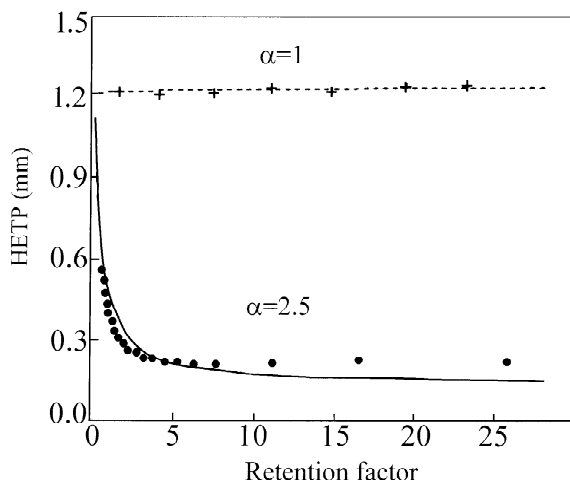


Fig. 3. Theoretical plate height (HETP) for *n*-undecane as a function of the retention factor for the multicapillary column with the liquid phase loaded by using the static and modified dynamic deposition methods with $\alpha = 1$ and 2.5, respectively. The plus signs and filled circles represent experimental data obtained by employing the same column as that described in the caption for Fig. 2. The retention factor was varied by increasing temperature from 40 to 140°C (the passage time of the nonsorbing species was measured by employing methane). The solid and dashed lines have been obtained by using Eq. (23) with $H_c = 1.9r_o$ (note that $H_c \ll H$).

together with the theoretical curves predicted by Eq. (23). The agreement between experiment and theory is seen to be reasonably good especially if one takes into account that the theoretical curves were constructed with no fitting parameters. Some relatively small difference between the experiment and theory at large values of the retention factor for the modified dynamic film-deposition methods might be connected with the fact that in the experiment α is not exactly equal to 2.5.

Finally, we may emphasize that the main goal of Figs. 2 and 3 is to illustrate how the efficiency of multicapillary columns depends on the method of the liquid-film loading. To reach this goal, we used the set of capillaries with a relatively large dispersion of radii. In our group, we have sets with slightly better dispersion and with the theoretical plate heights about two times smaller than that shown in Fig. 3. Such sets are available commercially as well [8]. From the commercial sources, one can however hardly find any description of the physical principles behind the possible ways of the liquid-film loading.

5. Conclusion

We have shown theoretically and experimentally that the efficiency of the multicapillary chromatographic columns can be improved by using the

loading methods specially designed in order to take into account correlation between the thickness of the liquid film and the capillary radius.

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