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Effect of particle size distribution on the separation efficiency in liquid chromatography

Krisztián Horváth[a,*], Diána Lukács[a], Annamária Sepsey[b], Attila Felinger[b,c]

[a] Department of Analytical Chemistry, University of Pannonia, Egyetem utca 10, H-8200 Veszprém, Hungary
[b] MTA–PTE Molecular Interactions in Separation Science Research Group, Ifjúság útja 6, H-7624 Pécs, Hungary
[c] Department of Analytical and Environmental Chemistry and Szentágothai Research Center, University of Pécs, Ifjúság útja 6, H-7624 Pécs, Hungary

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ABSTRACT

In this work, the influence of the width of particle size distribution (PSD) on chromatographic efficiency is studied. The PSD is described by lognormal distribution. A theoretical framework is developed in order to calculate heights equivalent to a theoretical plate in case of different PSDs. Our calculations demonstrate and verify that wide particle size distributions have significant effect on the separation efficiency of molecules. The differences of fully porous and core–shell phases regarding the influence of width of PSD are presented and discussed. The efficiencies of bimodal phases were also calculated. The results showed that these packings do not have any advantage over unimodal phases.

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1. Introduction

The particle size distribution (PSD) of the chromatographic stationary phase particles is in a longstanding interest among chromatographers [1]. The effect of the PSD on column efficiency is a frequent investigated problem from the beginning of the 1970s. Halász and Naefe were the first ones who examined this effect in detail with particles that were larger than 50 μm. They came to the conclusion that in case of batches with relatively broad PSDs (±40% deviation from the average size) no decadence can be experienced in the chromatographic efficiency [2]. This concept was confirmed further on by other studies too [3].

That time the particle size of the chromatographic packing materials rapidly decreased. This is shown by the investigation of particles with 3.3 and 6 μm in similar manner two years after Halász's work and particles of the size 1–10 μm were tested too [4]. They observed that there is no change in the permeability and in the chromatographic efficiency as long as the particles are about the same average size and also the reduced plate height remains the same as the PSD becomes broader. One decade after Endele's work, Dewaele and Verzele prepared columns packed with mixtures of different compositions of reversed phase particles of 3 and 8 μm and investigated the effect of the PSD on the column efficiency [5]. By their experience, no effect was detectable at the optimal velocities on the HETP values.

The introduction of sub-2-μm particles made the researchers to investigate the effect of the PSD on the chromatographic efficiency and this time there were several new consequences to encapsulate to the field of chromatography. Billen et al. obtained that the breadth of the distribution of the stationary phase particle sizes has no effect on the chromatographic efficiency as long as no fines are present, because these fines decrease the efficiency of high account [6]. Beside this, they drawn attention to the fact that one can make several conclusions about the goodness of a chromatographic column depending on the definition used for the particle size. According to this, one should always be careful when dealing with the results of former studies, because it is very important to know what definition the comparison is based on.

Cabooter et al. inquired into the effect of the PSD on the chromatographic efficiency for sub-2-μm particles by analyzing kinetic plots in 2008 [7]. In their work, they placed great emphasis on the fact that not the PSD is important, but the number of theoretical plates one wants to achieve, because the greatest the achievable N is, the more effect the PSD has on the separation efficiency. In their study, they mention several times that they obtained better results using a column with a narrower PSD than using a column of the

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[*] Corresponding author. Tel.: +36 88624485.
E-mail address: raksi@almos.uni-pannon.hu (K. Horváth).

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same average particle size but of a broader PSD. However, every time they mention this, they note that the difference observed in the PSDs is not enough to explain the difference in the packing quality.

Bruns et al. [8,9] studied the packing morphology of capillaries packed by fully porous and core–shell phases with different PSDs. According to the authors, the bed disorder caused by wall effect has a significant influence on column efficiency. The results did not show direct correlation between the packing density and the particle size distribution. Cabooter et al. [10], however, observed nearly linear correlation between the width of the particle size distribution of commercially available HPLC particles (including fully porous and superficially porous) and the minimum reduced plate height, the A-term and the minimum reduced separation impedance.

A recent work in this field was the study of Gritti et al. in 2011 [3]. In that study, they deduced new theoretical aspects from the general rate model of chromatography and they used it to interpret the results. However by using this novel model they were able to specify the constant multipliers of the HETP curves, the result was the same as 40 years ago: in the optimal range of velocities there is no decrease in the efficiency if the relative standard deviation of the PSD is under 40%. Despite these a major emphasis is placed on the decrease of the PSD of the chromatographic stationary phase particles in the industry. The reason of this can be searched in the homogeneity. According to Gritti's work, the chromatographic efficiency of the columns can be optimized if a small amount of greater particles is added to the sub-3 μm particles which leads to better homogeneity. Manufacturers practice matches these, because on their confession they add a small amount of larger particles to the bathes to optimize the pressure drop along the column.

It comes from the relation between the theoretical plate height and the particle size that if the PSD of chromatographic stationary phase has some kind of limited variance, then the theoretical plate height – what can be derived from the particle size – has similar kind of distribution too.

Rather contradictory information can be found in the literature about the relation between the PSD and the plate height of chromatographic column. Some results show that the large particle size variance has no influence on column efficiency, but according to other data, the wide PSD decreases the efficiency of chromatographic separation. The contradictions are explained by that the column quality of column filling can be significantly different when we work with stationary phases which have different PSDs. So it can be seen that the column efficiency is influenced by the quality of column packing procedure too. In this case, theoretical models provide more accurate insight than the practical measurements, because these do not take into consideration the variability of the column filling. Daneyko et al. [8,9] simulated the effect of PSD on longitudinal and transverse dispersion in chromatographic beds under non-retained conditions employing a fixed packing protocol. The authors studied wide PSD, narrow PSD and monodisperse packing. Results showed that the influence of the PSD on dispersion is negligible. The density of packing had a much more significant effect on column efficiency. The authors used the lattice-Boltzmann method that required high performance computing and the application of supercomputer (1024 processors) for data generation that took hundreds of hours.

The goal of this work is to develop a general theoretical framework for the analysis of effect of particle size distribution on the separation efficiency in liquid chromatography. By applying the proposed model, efficiencies of fully porous, core–shell and bimodal packing materials are studied for different sizes of molecules.

2. Theory

The spatial variance, μ_2, of a band at the outlet of the column can be calculated as the sum of spatial variances of independent processes taking place in the column as the band migrates through the column step-by-step.

$$\mu_2 = \mu_{2,(1)} + \mu_{2,(2)} + \cdots + \mu_{2,(n)} = \sum_{i=1}^{n} \mu_{2,(i)} \tag{1}$$

where $\mu_{2,(i)}$ is the variance of ith migration step, and n the total number of migration steps take place in the column.

By applying the definition of the height equivalent to a theoretical plate [11], Eq. (1) can be rewritten as

$$\mu_2 = \sum_{i=1}^{n} H_{(i)} \Delta z \tag{2}$$

where Δz is the length of one migration step, and $H_{(i)}$ is the local height equivalent to a theoretical plate at the ith migration step.

Considering that Δz is equal to the ratio of column length, L, and the number of migration steps, Eq. (2) can be simplified as

$$\mu_2 = \frac{L}{n} \sum_{i=1}^{n} H_{(i)} = L H_{\mathrm{col}} \tag{3}$$

where H_{col} is the mean of local HETPs, or in other words the observable HETP of the column. It can be calculated in the knowledge of the probability density function of local heights equivalent to a theoretical plate, f_H, as

$$H_{\mathrm{col}} = \int_0^{\infty} H f_H \, \mathrm{d}H \tag{4}$$

According to the general rate model of chromatography [12], the height equivalent to a theoretical plate is the function of the radius of the packing material particles.

$$H = g(r_{\mathrm{p}}) = \frac{2D_{\mathrm{L}}}{u} + 2\left(\frac{k_1^2}{1+k_1^2}\right)\left(\frac{u\, r_{\mathrm{p}}^2}{15FD_{\mathrm{p}}} + \frac{u\, r_{\mathrm{p}}}{3Fk_{\mathrm{f}}}\right) \tag{5}$$

where r_{p} is the radius of the packing material particles, D_{L} the axial dispersion coefficient, u the linear interstitial velocity of the eluent, k_1 the capacity ratio, F the phase ratio, D_{p} the diffusion coefficient of the solute in the particle pores, k_{f} the external mass transfer coefficient. Note that both D_{L} and k_{f} depend on r_{p}. Since the size of stationary phase particles has a certain distribution, $f_{r_{\mathrm{p}}}$, the local H values also varies.

The number particle size distribution can be described by log-normal distribution [13]. One of the main advantages of using log-normal distribution is that it is defined only for positive variables. This distribution can be used well for the description of PSDs with positive skew. Accordingly, the number PSD of the packing material is

$$f_{r_{\mathrm{p}}}(r_{\mathrm{p}}; m, s) = \frac{1}{r_{\mathrm{p}}\sqrt{2\pi s^2}} \exp\left(-\frac{(\ln(r_{\mathrm{p}}) - m)^2}{2s^2}\right) \tag{6}$$

where m and s^2 are the location and the scale parameters of the log-normal distribution, respectively. Note that both the mean and variance of Eq. (6) depend on m and s. A log-normal distribution with mean $\mu_{r_{\mathrm{p}}}$ and variance $\sigma_{r_{\mathrm{p}}}^2$ has the following parameters:

$$m = \ln\left(\frac{\mu_{r_{\mathrm{p}}}^2}{\sqrt{\mu_{r_{\mathrm{p}}}^2 + \sigma_{r_{\mathrm{p}}}^2}}\right) = \ln \mu_{r_{\mathrm{p}}} - \frac{1}{2}s^2 \tag{7}$$

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