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Optimization of post-column reactor radius in capillary high performance liquid chromatography Effect of chromatographic column diameter and particle diameter

Hongjuan Xu and Stephen G. Weber^{*}

Department of Chemistry, University of Pittsburgh, 219 Parkman Avenue, Pittsburgh, PA 15260, USA

Abstract

A post-column reactor consisting of a simple open tube (Capillary Taylor Reactor) affects the performance of a capillary LC in two ways: stealing pressure from the column and adding band spreading. The former is a problem for very small radius reactors, while the latter shows itself for large reactor diameters. We derived an equation that defines the observed number of theoretical plates (N_{obs}) taking into account the two effects stated above. Making some assumptions and asserting certain conditions led to a final equation with a limited number of variables, namely chromatographic column radius, reactor radius and chromatographic particle diameter. The assumptions and conditions are that the van Deemter equation applies, the mass transfer limitation is for intraparticle diffusion in spherical particles, the velocity is at the optimum, the analyte's retention factor, k' , is zero, the post-column reactor is only long enough to allow complete mixing of reagents and analytes and the maximum operating pressure of the pumping system is used. Optimal ranges of the reactor radius (a_r) are obtained by comparing the number of observed theoretical plates (and theoretical plates per time) with and without a reactor. Results show that the acceptable reactor radii depend on column diameter, particle diameter, and maximum available pressure. Optimal ranges of a_r become narrower as column diameter increases, particle diameter decreases or the maximum pressure is decreased. When the available pressure is 4000 psi, a Capillary Taylor Reactor with 12 μm radius is suitable for all columns smaller than 150 μm (radius) packed with 2–5 μm particles. For 1 μm packing particles, only columns smaller than 42.5 μm (radius) can be used and the reactor radius needs to be 5 μm .

Keywords

Post-column reactor; Theory; Band spreading; Capillary chromatography; Taylor-Aris

1. Introduction

It is well-known that post-column reactions can improve sensitivity and selectivity in liquid chromatographic analysis [1–3]. In just the past couple of years, papers using post-column reactions for a variety of bioanalytical applications have appeared, including amino acids and peptides [4,5], for fatty acid hydroperoxides in MEKC [6], for japonicus/polysaccharide [7], for glucosylated flavonoids [8], for acetyl-CoA esters [9], for phosphorylated peptides [10], for drugs (competitive binding) [11], for glucose and insulin [12], for bradykinin [13], for drugs [14], for lipoproteins [15], for tocopherols [16], for phosphorylated sugars [17], for peptides [3,18–21]. One should include the preparation of MALDI plates as a post-column reaction

^{*} Corresponding author. Tel.: +1 412 624 8520; fax: +1 412 624 1668. E-mail address: sweber@pitt.edu (S.G. Weber)..

[22]. Recent applications in environmental chemistry using post-column reactors include glyphosate [23], iodate and bromate [24], thiourea [25], anions [26] and ion chromatography [27]. However, post-column reactors come with some disadvantages. The most obvious are the additional hardware and reagents required, and the band spreading associated with the additional mixing following the separation.

The band spreading issue, as it is treatable theoretically, has been addressed. Huber et al. [28] considered the problem of using rather slow chemical reactions following the separation. They concluded that a packed bed reactor was superior to an open tubular reactor. In their work, they assumed that mixing, as opposed to reaction, was instantaneous. On the other hand, Kucera and Umagat [29] considered the case of post-column reactors for microbore columns. With smaller peak volumes than in 4.6 mm I.D. (inside diameter) columns, *microbore* columns pose more of a challenge for post-column reactor design. These workers considered a fast reaction, *o*-phthalaldehyde with amino acids and primary aliphatic amines. They proposed a simple tubular reactor. Special attention was paid to creating a low-volume mixing 'tee'. Peak variances depended linearly on the square of the reactor diameter, showing that the chromatography was compromised. In other words, they did not employ a reactor diameter small enough to make the additional band spreading from the reactor negligible. With 50 cm $\times$ 1 mm columns operating at 35 μ L/min, and with an equivalent post-column reagent flow rate, they used post-column reactor tubing in the 180–250 μ m I.D. range.

Other workers have optimized post-column reactors experimentally. The sheath-flow approach has proven suitable for CE of DNA [30]. Optimization of post-column conditions for chemiluminescence detection has been achieved [31]. Hollow fiber membrane systems have been optimized to minimize band spreading [32]. The virtue of inducing secondary flow for improving radial mixing has been shown by Selavka et al. [33]. Contributions to band spreading were evaluated in a post-column reactor for photochemical reactions [34] and for saccharides [35]. Much of this work is dated, and applies to columns with typical dimensions of 4.6 mm I.D., 10–20 cm long with 5 μ m diameter particles.

Recently, our group has developed a mixer that is well-suited to mix reagents with effluent from a *capillary* column [1,36,37]. This mixer, in conjunction with a fused silica Capillary Taylor Reactor (a simple, open tube long enough to permit diffusional relaxation of radial concentration gradients [1,37]), creates a very simple post-column reaction device that does not increase band spreading under the conditions used [1]. In this system, diffusion-controlled reactions occurred in times on the order of 1 s, in physical volumes on the order of 10 s of nL [1,37]. Kinetically controlled reactions require longer reactors [37].

The magnitude of the inside diameter or radius of the post-column reactor is an important variable. It controls the reactor's contribution to band spreading; smaller reactor radii are preferred from this perspective. However, as the HPLC column defines the flow rate, the pressure in the post-column reactor (of constant length) increases in inverse proportion to the *fourth power* of the radius. Thus, there is clearly an optimal value for reactor radius. This paper determines that optimum, and demonstrates its dependence on column diameter and particle diameter.

2. Assumptions and limitations

In chromatographic theory, there are many variables. If the number of variables can be reduced, the essence of the theory is often made clearer. However, there is also a sacrifice in the breadth of applicability of the results from putting limitations on the system. Thus, it is important to state and discuss the limiting nature of the assumptions.

We will set the value of three significant parameters by allowing them to depend on other freely chosen variables. One is the chromatographic velocity. We have set the velocity equal to the optimum velocity. Kennedy and Jorgenson [38] have shown that the optimum velocity in capillary columns is a function of the column diameter. In this paper, we have not taken that subtlety into account. Further, there are several formulations of H versus v curves [39]. We have chosen to use the van Deemter equation (the expression is shown later), which works acceptably near the optimum velocity. Another parameter that is set is the post-column reactor length. Both theory [40] and experiment [1,37] show that if the reaction is fast enough, it will be completed in a length of cylindrical tubing that depends upon the reagents' diffusion coefficients, the tubing radius and the velocity. Furthermore, the velocity in the reactor depends on the chromatographic velocity (which we fix) and geometrical parameters. Finally, we have taken the k' (the retention factor) of a solute to be zero.

The limitations that accompany these decisions are as follows. Setting the velocity at the optimum means that the analysis will favor total number of theoretical plates over theoretical plates per unit time. We analyze both in this paper. Setting the length of the post-column reactor means that the detector will give a 'full signal' for fast enough reactions, but not for kinetically slow reactions. Finally, the restriction on k' will make the reactor's relative (to the column) contribution to band spreading larger than it would be for a retained solute. A retained solute has a k' -dependent variance (time units). By using $k' = 0$ in the formulations, we ignore this. The result is that the chromatography seems more sensitive to the presence of extracolumn band spreading than it would be for $k' > 0$.

Finally, we assume that the chromatographic system operates at the maximum pressure of the pumping system. The ultimate limitation to chromatographic throughput is pressure [41]. As the velocity is fixed at the optimum, we control the length of the chromatographic column to use the available pressure.

In this paper, we determine how the system dimensions influence chromatographic performance as judged by the number of theoretical plates, N , and the number of theoretical plates per time. The results will show that there is an optimum in reactor radius that is dependent on the particle diameter and the column radius. Very small reactor radii lead to excessive pressure in the reactor, diminishing chromatographic performance by forcing a shortening of the column (remember, total pressure is fixed). Very large reactor radii lead to excessive band spreading in the reactor.

3. Equation derivation

3.1. Reactor requires pressure

The total pressure in the system is given by Eq. (1).

$$P_m = \frac{\phi \eta v_c L_c}{d_p^2} + \frac{8 \eta v_r L_r}{a_r^2} \quad (1)$$

Here, P_m is the maximum pressure of the HPLC pump, η is the viscosity of the mobile phase, L_c and L_r represent the length of the column and the reactor, respectively, v_c and v_r are the average linear velocities in the column and the reactor, respectively, d_p is the diameter of the packing particles, a_r is the radius of the capillary used to make the reactor and ϕ is the column's permeability. The left-hand term on the right side is the pressure drop in the column [41] while the right-hand term is the pressure drop in the reactor. We will now use the assumptions described above with the van Deemter equation to remove some of the variables.

3.2. Average velocity is the optimum velocity

$$H_c = \frac{2D}{v} + \lambda d_p + \frac{d_p^2}{gD} v \quad (2)$$

In the van Deemter equation, Eq. (2), H_c is the height equivalent to a theoretical plate for the chromatographic column, D is the solute's diffusion coefficient in the mobile phase, v is the average mobile phase velocity, d_p is the packing particle diameter, and λ and g are numerical, geometry-dependent constants (values of such parameters are discussed below). We choose the optimal velocity as the column velocity.

$$v_c = v_{opt} = \sqrt{2g} \frac{D}{d_p} \quad (3)$$

v_r is a function of v_c and the ratio of a_c , the radius of the column and a_r . The factor b in Eq. (4) below is equal to $\epsilon_c + (1 - \epsilon_c)\epsilon_i$, where ϵ_c is extraparticle porosity and ϵ_i is intraparticle porosity.

$$v_r = v_c b \left(\frac{a_c}{a_r} \right)^2 \quad (4)$$

3.3. Reactor length is the length required for significant diffusional mixing

L_r , the length of the reactor, is given by Eq. (5) [1,37,40]. We fix L_r based on capillary Taylor theory [1,37]. The numerical factor represents the degree of mixing by diffusion. A larger number means more complete mixing. We choose 2.5 here, which means the length of the reactor is just enough for complete mixing. Kinetic factors are not considered here, thus extent of mixing is equivalent to the extent of reaction.

$$L_r = \frac{2.5 v_r a_r^2}{D} \quad (5)$$

3.4. Revised pressure expression

After substituting Eqs. (3)–(5) into Eq. (1), we obtain Eq. (6):

$$P_m = \frac{\sqrt{2g} \phi D \eta L_c}{d_p^3} + \frac{40 g D \eta b^2 (a_c / a_r)^4}{d_p^2} \quad (6)$$

The first term on the right-hand side of Eq. (6) is still the pressure drop across the column (P_c) while the second term is that across the post column reactor (P_r). This equation can be recast into a dimensionless ratio of column pressure to available pressure to give Eq. (7). In Eq. (7), the dimensionless second term of the right-hand side is the fraction of the available pressure needed by the reactor.

$$\frac{P_c}{P_m} = \frac{P_m - P_r}{P_m} = 1 - \frac{40 g D \eta b^2 (a_c / a_r)^4}{d_p^2 P_m} \quad (7)$$

3.5. Reactor adds band broadening

Band spreading occurs in the reactor, but it may not be significant if the chromatographic peaks are broad. Thus, we must compare the extent of broadening from both sources. We have already shown experimentally that the mixer portion of the mixer/reactor adds no measurable

broadening [1]. The variance (in units of time squared) for the column (at the optimum velocity) is given by Eq. (8).

$$\sigma_c^2 = \frac{H_c L_c}{v_c^2} \quad (8)$$

To get an expression for the variance, we will use the column length defined by pressure conservation (Eq. (9), from Eq. (6)),

$$L_c = \frac{P_m d_p^3}{\sqrt{2g\phi D\eta}} - \frac{20\sqrt{2g}b^2(a_c/a_r)^4 d_p}{\phi} \quad (9)$$

the optimal velocity (Eq. (3)) and the minimum value of H_c ($H_{\min}$, Eq. (10)) derived from the optimum velocity and the van Deemter equation (Eq. (2)).

$$H_c = H_{\min} = \left(2\sqrt{\frac{2}{g}} + \lambda\right) d_p \quad (10)$$

After substituting Eqs. (3), (9) and (10) into Eq. (8), we get the final description for the column variance.

$$\sigma_c^2 = \frac{2\sqrt{2/g} + \lambda}{(2g)^{3/2} D^3 \phi \eta} d_p^6 P_m - \frac{20(2\sqrt{2/g} + \lambda)b^2}{\sqrt{2g} D^2 \phi} \left(\frac{a_c}{a_r}\right)^4 d_p^4 \quad (11)$$

3.6. Variance in the reactor

The variance in the same units for the reactor is given by Eq. (12) [1].

$$\sigma_r^2 = \frac{H_r L_r}{v_r^2} = \frac{v_r a_r^2}{24D} \frac{2.5 v_r a_r^2}{D} \frac{1}{v_r^2} = \frac{2.5 a_r^4}{24D^2} \quad (12)$$

L_r is defined above, and H_r is the height equivalent to a theoretical plate in a reactor [1],

$$H_r = \frac{v_r a_r^2}{24D} \quad (13)$$

3.7. Total peak variance

The total peak variance is the sum of the column and reactor variances.

$$\begin{aligned} \sigma^2 &= \sigma_c^2 + \sigma_r^2 = \frac{2\sqrt{2/g} + \lambda}{(2g)^{3/2} D^3 \phi \eta} d_p^6 P_m + \frac{2.5}{24D^2} a_r^4 \\ &= \frac{M}{D^3 \eta} d_p^6 P_m - \frac{40gMb^2}{D^2} \left(\frac{a_c}{a_r}\right)^4 d_p^4 + \frac{2.5}{24D^2} a_r^4 \end{aligned} \quad (14)$$

Here, we define M as $\frac{2\sqrt{2/g} + \lambda}{(2g)^{3/2} \phi}$.

The band broadening arising from the reactor can be considered negligible when it contributes no more than 10% extra to the peak width in the absence of the reactor. This is the case if $\sigma_r^2/\sigma_c^2 \leq 0.21$.

3.8. Column efficiency

N is defined here as the number of theoretical plates from the column when using an ideal reactor that requires pressure but adds no band spreading. The column variance, Eq. (11), is used to generate Eq. (15). M is defined above.

$$N = \frac{t_{0c}^2}{\sigma_c^2} = \frac{L_c}{H_c} = \frac{P_m d_p^2}{4g^2 \phi^2 \eta DM} - \frac{10b^2(a_c/a_r)^4}{\phi^2 Mg} \quad (15)$$

However, with a post-column reactor, the retention time and the peak variance depend on more than just the column. The observed number of plates, N_{obs} , includes all effects of the reactor.

$$\begin{aligned} N_{obs} &= \frac{t_0^2}{\sigma^2} = \frac{(t_{0c} + t_{0r})^2}{\sigma_c^2 + \sigma_r^2} \\ &= \frac{[Jd_p^2 - 40b^2(a_c/a_r)^4 + 5\phi(a_r/d_p)^2]^2}{4gMJ\phi^2 d_p^2 - 160gM\phi^2 b^2(a_c/a_r)^4 + 0.4\phi^2(a_r/d_p)^4} \end{aligned} \quad (16)$$

where t_{0c} and t_{0r} are the dead time in the column and the reactor, respectively; M has the same definition as in Eq. (14); J represents the ratio $P_m/gD\eta$.

Eq. (16) looks unwieldy. However, N_{obs} is only dependent on P_m and three size-related variables, d_p , a_c and a_r . The figures based on these equations are much clearer. First, we will show the effect of column radius on the reactor choice. Second, we will find the relationship between N_{obs} and the variables d_p and a_r to get the optimal reactor radius for P_m equal to 4000 psi and a_c equal to 50 μm . Finally, the effects of P_m on the reactor choice will be shown.

To display the effect of the reactor, we also calculate the number of theoretical plates of the column under the same conditions but without the reactor (N_0) as below. Here, the pressure available for the column is the maximum offered by the pump.

$$N_0 = \frac{P_m d_p^2}{\phi \eta D(4 + \lambda \sqrt{2g})} \quad (17)$$

3.9. Description of some empirical parameters

There are many parameters used in the calculations. Here, we list the parameters and discuss their origin and value.

ϕ , the column's permeability depends upon the method of packing and the particles for a packed column. For various columns, it ranges from 500 to 1000 [41]. We routinely obtain a value of 750 for 2.6–5 μm particle packings in 100 μm diameter columns. The effect of changes in ϕ on the results is negligible. λ and g are numerical, geometry-dependent constants. Typically, λ is 2 and g is 30 [39]. The value 2 comes from experiment and the simple random walk approach to eddy dispersion. The number 30 comes from assuming that the C -term is governed by diffusional relaxation within the spherical particle. The value for λ will never be far from 2. The value for g would give a C -term in the Knox equation of 0.033, which is close to the observed value from many systems of $C \sim 0.05$. D is the diffusion coefficient of the solute in the mobile phase. η is the viscosity of the mobile phase. In our final expressions of N_{obs} , N and N_0 , D and η always appear as the product $D\eta$ for a given solute and at constant temperature, this product, sometimes called the Walden product ($D\eta = RT/6\pi a$ where R is the gas constant, T is the temperature and a is the radius of the diffusing molecule), will remain fairly constant

as the solvent changes. We used $5.0 \times 10^{-10} \text{ m}^2/\text{s}$ as D and 0.001 N s/m^2 as η . These values are typical for solutes of a few hundred Daltons molar mass and aqueous eluents. As the Walden product is in the final expressions, the product of these values is suitable for other solvents (but not dramatically larger or smaller solutes). b is equal to $\epsilon_e + (1 - \epsilon_e)\epsilon_i$, where ϵ_e is extraparticle porosity and ϵ_i is the intraparticle porosity. Usually, both porosities are near 0.4 [39], so b is 0.64. This term is appropriate if the mean, not the extraparticle, velocity is used in the van Deemter equation. Of all of the parameters, the value of g is the most dependent on the particular system (particle shape, intra- versus interparticle mass transport limitation, diffusional versus kinetic stationary phase mass transfer limitation).

4. Results and discussion

4.1. Effect of column diameter: is a Capillary Taylor Reactor useful for large columns?

The introduction discussed cases in which the simple Capillary Taylor Reactor added measurable band spreading with 4.6 and 1 mm I.D. columns. Table 1 provides a view of this problem. Table 1 shows the effect of a Capillary Taylor Reactor on the maximum number of observed theoretical plates, $\text{Max } N_{\text{obs}}$, as a function of d_p and a_c (Eq. (16)). Values for N_0 , the number of theoretical plates generated by the capillary column without the reactor (Eq. (17)), are also given. The ' a_r range' is the range of reactor radii at which N_{obs} is at least 90% of N_0 . The reactor can have a significant deleterious effect on the column efficiency. For a column having a radius of 150 μm , the $\text{Max } N_{\text{obs}}/N_0$ ratio increases from 19.5 to 99.9% as the diameter of packing particles increases from 1 to 5 μm . The influence of the reactor is small for the 2–5 μm particles but significant for 1 μm particles. The larger the column diameter is, the more effect the reactor has on the column efficiency. The $\text{Max } N_{\text{obs}}/N_0$ ratio decreases as column radius increases. The a_r range in which N_{obs}/N_0 is larger than 90% becomes narrow or even disappears as column radius increases. Therefore, a small column is preferred when used with a Capillary Taylor Reactor especially when the column is packed with small particles. Specifically, the effect of the reactor is negligible when column radius is smaller than 150 μm for particle diameters greater than or equal to 2 μm .

4.2. Optimization of the reactor radius for capillary columns with various particle sizes

Fig. 1 gives the relationship between the number of theoretical plates (N or N_{obs}) and the radius of the reactor a_r for a 100 μm I.D. column ($a_c = 50 \mu\text{m}$). N is the number of theoretical plates observed with a hypothetical reactor that requires pressure but causes no extracolumn band spreading. N_{obs} is defined by Eq. (16). N and N_{obs} depend similarly on a_r at small values of a_r . N and N_{obs} sharply increase and then reach a plateau or maximum as a_r increases. Larger particles exhibit a significant plateau, while the smallest particle size, 1 μm , shows a maximum. As a_r increases beyond the maximum, N does not change at all while N_{obs} gradually decreases. The shape of Fig. 1 can be understood qualitatively by considering systems for large and small values of a_r .

There is a minimum value of a_r that can be derived from Eq. (7). This equation shows that all the pressure available is used by the reactor when both sides of the equation equal zero. As a_r is decreased towards this limit, $(40gD\eta b^2/(d_p^2 P_m))^{1/4} a_c$, more of the available pressure is used to push fluid through the reactor. To compensate, the column's length approaches zero, so N_{obs} approaches zero as well. Thus, the effect of the reactor on the column efficiency as a_r/a_c approaches $(40gD\eta b^2/(d_p^2 P_m))^{1/4}$ mostly comes from the pressure it steals. The pressure available to the column is increased with a larger diameter reactor, according to Eq. (7). For a large enough value of a_r , it will approach P_m . However, when a_r becomes large, the variance from dispersion within the reactor becomes significant and cannot be neglected compared to the variance caused by the column. N_{obs} gradually decreases as a_r increases as shown on the right-hand side of Fig. 1 because of the effect of the reactor variance (Eq. (12)).

Obviously, what we are most interested in is the middle part of Fig. 1 where the effect from the reactor is minimal and N_{obs} is the largest. Columns with larger packing particles have a larger column variance, so there is a wider region of conditions that allow the band broadening from the reactor to be negligible compared to that from the column. Therefore, columns with larger packing particles have a wider plateau.

Table 2 lists the range of reactor radii that give a value of N_{obs} that is larger than 90% of N_0 , which we used to define the acceptable region. The parameters ‘Max N_{obs} ’, ‘ a_r range’ and N_0 have the same definitions as in Table 1. t_0 is the retention time of an unretained solute. In addition, to determine whether it is possible to use a post-column reactor without significant sacrifice, Table 2 also compares Max N_{obs} with N_0 . Values of Max N_{obs} for particle sizes from 2 to 5 μm are all larger than 90% of N_0 . This is not the case with a 1 μm column, where Max N_{obs} is only 86.2% of N_0 . This means that there is no reactor size that will yield an observed number of theoretical plates greater than or equal to 90% of N_0 . The variance from a 1 μm column is quite small and the variance from the reactor is never negligible.

Large values of N are often accompanied by long experimental time which is also shown in Table 2. To get a different perspective, we also looked at N_{obs} per unit time (N_{obs}/t_0) (Fig. 2). Fig. 2 displays how N_{obs}/t_0 changes with a_r . From Fig. 2, with a proper size reactor, the N_{obs}/t_0 of a column with 1 μm particles can be more than four times larger than that of a 2 μm column, and over 20 times greater than a 5 μm column. Therefore, smaller particles are better in faster separations, even with a post-column reactor.

Table 3 is analogous to Table 2, but for the number of observed plates per time. It displays the range of a_r that will yield N_{obs}/t_0 that is at least 90% of N_0/t_0 . Note that the range is only slightly different from that for N_{obs} . Similar to Table 2, columns with large particles have a wider plateau for N_{obs}/t_0 .

4.3. The special case of 1 μm particles: is a smaller column better when using a reactor?

As mentioned before, the reactor always affects the observed chromatographic efficiency when d_p is 1 μm (as shown in Fig. 1, there is no plateau there at $d_p = 1 \mu\text{m}$ and Table 2, N_{obs}/N_0 always smaller than 90%). This is because the column variance from a 1 μm column is extremely small so that the variance from the reactor cannot be neglected. The only way to minimize the variance from the reactor is to use small radius reactors, which will be accompanied by a sacrifice in available column pressure. However, Eq. (7) tells us that the pressure drop for the column will not change if a_c/a_r and d_p are constant. Therefore, for a given particle diameter, if the column diameter is scaled down as the reactor diameter is scaled down, the fraction of the maximum pressure available for the column should remain constant. That means when the column diameter is reduced, the reactor diameter should be reduced proportionally. Therefore, using a smaller column diameter might be helpful.

Fig. 3 shows curves of N_{obs} for 1 μm particle packing plotted against reactor radius with column radius as a parameter. In Fig. 3, the curves of N_{obs} versus reactor radius increase sharply, reach a maximum and then gradually decrease at larger reactor radii. The maximum value of N_{obs} increases more than two times and the optimum value of a_r becomes smaller as the column diameter changes from 100 to 25 μm . When the column radius is equal to or less than 42.5 μm , the Max N_{obs}/N_0 ratio starts to approach 90%, which means the reactor’s effect is negligible at the optimal radius of the reactor, which is 5 μm .

4.4. Maximum pressure (P_m) and optimal reactor radius

Results shown in Table 4 indicate the effect of P_m . Max N_{obs} , the maximum value of N_{obs} under optimal conditions, increases almost proportionally as P_m increases. The ‘ a_r range’

increases slightly as P_m increases. However, a_r , the reactor radius at which the maximal N_{obs} is achieved, is independent of P_m .

4.5. Conclusion

In this paper, the influence of the diameter of a Capillary Taylor Reactor on the performance of capillary liquid chromatography was studied. The reactor steals pressure from the column which in turn decreases the numbers of theoretical plates when small reactor diameters are used. At the same time, it adds some band broadening. The choice of the reactor radius actually depends on several factors such as packing particle size, maximal available pressure and column diameter. For packing particles larger than or equal to 2 μm , the Capillary Taylor Reactor is suitable for columns with radii not larger than 150 μm (for “suitable”, we defined as if $N_{obs}/N_0 > 90\%$). A reactor with about a 12 μm radius (i.e., the commercially available 25 μm I.D. capillary) works well under such conditions. For 1 μm particles, however, the requirements are more stringent. Only columns with smaller than 42.5 μm radii can be used and the optimal reactor radius is 5 μm , which is much smaller compared to those coupled with larger particle packing columns. The results above are obtained under a maximal pressure of 4000 psi. The limitations in the column diameter become less restricted when a higher maximum pressure is available.

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Fig. 1.

Plot of N (dashed line) and N_{obs} (solid line) against the radius of reactor. Each curve corresponds to a different particle diameter. The highest curve is for $d_p = 5 \mu\text{m}$, and the lowest is for $d_p = 1 \mu\text{m}$. $a_c = 50 \mu\text{m}$; $P_m = 4000 \text{ psi}$; $D = 5.0 \times 10^{-10} \text{ m}^2/\text{s}$; $\eta = 0.001 \text{ N s/m}^2$; $b = 0.64$; $\phi = 750$; $g = 30$, $\lambda = 2$.

Fig. 2. N_{obs}/t_0 (s⁻¹) as a function of a_r . Conditions are the same as in Fig. 1.

Fig. 3. Plot of N_{obs} against the radius of the post-column reactor. $d_p = 1 \mu\text{m}$; a_c is altered from 25 to $100 \mu\text{m}$. The solid line represents N_{obs} while the dashed line represents N_0 . Other conditions are the same as in Fig. 1.

Table 1

Effect of the column radius on N_{obs}/N_0

d_p (μm) N_0	1 3770	2 15100	3 34000	4 60400	5 94300
$a_c = 150 \mu\text{m}$	735 Max N_{obs} a_r range (μm) Max N_{obs}/N_0	13600 12 90.1%	33400 9-25 98.2%	60100 8-38 99.5%	94200 7-52 99.9%
$a_c = 500 \mu\text{m}$	94 Max N_{obs} a_r range (μm) Max N_{obs}/N_0	3600 — 23.8%	25700 — 75.6%	55600 26-35 92.1%	91400 22-52 96.9%
$a_c = 1000 \mu\text{m}$	68 Max N_{obs} a_r range (μm) Max N_{obs}/N_0	535 — 3.5%	10000 — 29.5%	41600 — 68.9%	82000 — 86.6%

$P_m = 4000 \text{ psi}$; $D = 5.0 \times 10^{-10} \text{ m}^2/\text{s}$; $\eta = 0.001 \text{ N s/m}^2$; $b = 0.64$; $\phi = 750$; $g = 30$; $\lambda = 2$.

Table 2
Range of useful reactor radii with maximum N_{obs} as a criterion

d_p (μm)	Max N_{obs}	a_r range (μm)	N_0	Max N_{obs}/N_0 (%)	t_0 (s)
1	3250	—	3770	86.2	2.4
2	15000	4–14	15100	99.3	39
3	34000	3–25	34000	100	199
4	60400	3–38	60400	100	628
5	94400	3–53	94400	100	1533

$a_c = 50 \mu\text{m}$; other conditions are the same as in Table 1.

Table 3
Range of useful reactor radii with maximum N_{obs}/t_0 as a criterion

d_p (μm)	Max N_{obs}/t_0 (s^{-1})	N_0/t_0 (s^{-1})	a_r range (μm)
1	1530	1540	3–5
2	390	390	2–13
3	170	170	2–24
4	100	100	2–37
5	60	60	2–51

Conditions are the same as listed in Table 2.

Table 4

Effect of the P_m on the acceptable range of reactor radii when $a_c = 50\text{ }\mu\text{m}$

$d_p\text{ (}\mu\text{m)}$	1	2	3	4	5
$P_m = 2000\text{ psi}$	Max N_{obs}	7500	17000	30200	47200
	$a_t\text{ (}\mu\text{m)}$	5	10	12	14, 15
$P_m = 4000\text{ psi}$	$a_t\text{ range (}\mu\text{m)}$	—	4–22	3–32	3–45
	Max N_{obs}	3250	34000	60400	94400
	$a_t\text{ (}\mu\text{m)}$	5	10	12	14, 15
	$a_t\text{ range (}\mu\text{m)}$	—	3–25	3–38	3–53
$P_m = 8000\text{ psi}$	Max N_{obs}	7000	67900	121000	189000
	$a_t\text{ (}\mu\text{m)}$	5	10	12	14, 15
	$a_t\text{ range (}\mu\text{m)}$	5	3–29	3–44	2–61

Other conditions are the same as in Table 1.