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Pressure drop effects in packed capillary column supercritical fluid chromatography

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Abstract

The subject of column pressure drop has generated much controversy when using packed columns in supercritical fluid chromatography (SFC), since packed columns usually exhibit a significant pressure drop along the column. In this paper, the effect of pressure drop on the chromatographic behavior of capillary columns packed with small spherical silica particles in SFC was studied using neat carbon dioxide as mobile phase. The relationship between column pressure drop, column length, particle size, column diameter, column efficiency and resolution were experimentally measured and examined using a fixed linear restrictor. The influence of column pressure drop on resolution was obvious; however, the effect on column efficiency was insignificant.

Keywords: Pressure drop; Packed capillary columns; Capillary columns; Alkanes

1. Introduction

The effects of pressure drops in gas chromatography (GC) [1–3], liquid chromatography (LC) [4–6] and SFC [7–33] have been studied by a number of investigators. One commonality between GC, LC and open tubular column SFC is that the typical pressure drops experienced with these technologies have a small but measurable influence on retention and an insignificant influence on efficiency and resolution. However, for packed column SFC, the situation is not as simple. A number of authors [20–28,33] reported that column pressure drop had a profound effect on column efficiency, solute retention and resolution; they recommended that column pressure drop should be optimized by adjusting column length, column inner diameter and particle size to achieve optimum column efficiency. Other authors [10,29] found no efficiency losses or peak broadening and distortion, even with high pressure drops, when using small particle packings and long column lengths (up to 2.2 m by connecting a series of 11 conventional packed columns).

While most of the previous studies have been done with conventional or microbore columns, packed capillary columns have become more widely accepted and used in recent years because of their distinct advantages of sensitivity, efficiency, low mobile phase consumption and compatibility with mass sensitive detectors. However, no one has

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actually measured and examined the pressure drop effects for packed capillary columns.

In this paper, we report the effect of pressure drop in SFC using packed capillary columns. The relationships between column pressure drop and various column parameters such as particle size, column diameter and column length were experimentally measured. The effects of pressure drop on column efficiency and resolution were determined.

2. Experimental

2.1. Equipment and materials

The column preparation equipment and supercritical fluid chromatograph have been previously described [34,35]. Two modifications were made to the sample introduction system: first, a 60-nl instead of a 200-nl internal loop (Valco, Houston, TX, USA) was used and second, a flow-splitting tee (SGE, Austin, TX, USA) was employed to split the sample at a ratio of approximately 1:10. A Lee Scientific Series 600 SFC pump (Dionex, Salt Lake Division, Salt Lake City, UT, USA) was used to measure the column pressure. A standard analog high pressure gauge (calibrated by the manufacturer) was purchased from McMaster-Carr Supply Company (Santa Fe Springs, CA, USA) and used for calibrating the pressure transducers of the two SFC pumps. A micro-flow meter was purchased from Gilmont Instruments (Barrington, IL, USA) and used for measuring the mobile phase flow-rate at the end of column. It was calibrated using CO_2 gas with a soap bubble flow meter from Hewlett-Packard (Wilmington, DE, USA). Spectra-clean grade carbon dioxide was obtained from Airco (Riverson, NJ, USA) and used as mobile phase. Different internal diameter (50, 75, 100, 150, 200, 250, 300 and 400-μm) fused-silica capillaries were purchased from Polymicro Technologies (Phoenix, AZ, USA) for use as column materials. Spherical and irregular shape silica packing materials with mean particle sizes of 5, 10, 12, 20, 30 and 40 μm were kindly supplied by Keystone Scientific (Bellefonte, PA, USA). Hydrocarbon standards (*n*-alkanes from C_{12} to C_{18}) were obtained from Aldrich (Milwaukee, WI, USA) and used as test solutes.

2.2. Testing procedure.

The packed capillary columns were prepared and evaluated according to the procedures previously described [34,35]. Appropriate lengths of 10 μm I.D. fused-silica tubing were used as linear restrictors throughout this work because of their ease of use and reproducibility. It is very important to calibrate the two pumps simultaneously against a standard pressure gauge before any measurements are made. At least 20–30 min were allowed for pressure and temperature equilibrium before data were recorded. The reproducibility of the pressure measurements was 5% R.S.D..

3. Results and discussion

3.1. Total pressure drop along the column

3.1.1. Pressure drop across the frits

Since porous ceramic frits were used to support the packed bed, the pressure drop contribution from the support frits should be counted as part of the total column pressure drop. The relationship between column inlet pressure and column pressure drop for an empty 200 μm I.D. column with only support frits at both ends was experimentally measured and is shown in Fig. 1 (curve a). Throughout the entire

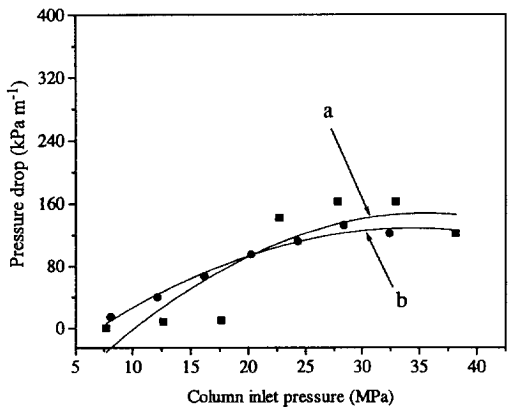

Fig. 1. Relationship between column inlet pressure and pressure drop. Conditions: (a) 1.25 m×200 μm I.D. empty capillary column with frits at both ends, (b) 10 m×50 μm I.D. SB-biphenyl-30 coated open tubular column; 40°C, 45 cm×10 μm I.D. linear restrictor.

pressure range from 7.6 to 40.5 MPa, the pressure drop ranged from 0 to 0.2 MPa. Compared to the inlet pressure, the pressure drop caused by the frits and empty tubing for this 200 μm I.D. capillary was less than 0.5% which cannot be distinguished from pump drift errors. This demonstrates that the frit used in this study did not contribute significantly to the column pressure drop.

3.1.2. Pressure drop across a typical open tubular column

In order to verify the reliability of the system for pressure drop measurement and to compare both packed and open tubular columns with each other, a typical open tubular SFC column (10 m×50 μm I.D. coated with 0.125 μm SB-Bipenyl-30 from Dionex) was also examined. The relationship between column inlet pressure and column pressure drop for this column is shown in Fig. 1 (curve b). The pressure drop along the column was in the range of 0 to 0.12 MPa/m . It can be seen that the open tubular column did exhibit some pressure drop, however, the pressure drop was very low (within the range of 0.1 ~1.2 MPa for a 10-m long column at a CO_2 flow-rate from 1 to 7.5 ml min^{-1}). The average pressure drop was approximately 0.4% of the column inlet pressure. These measured pressure drop data were compared with theoretically calculated data for open tubular columns [16], and comparable agreement was found.

3.1.3. Pressure drop along packed capillary columns with different column diameters

A variety of packed capillary columns can be prepared by either changing the column diameter or the particle diameter. In order to make a complete evaluation of the pressure drop profiles of packed capillary columns, all configurations should be tested. Based on 10-μm, 60 Å pore size silica packing material, different packed capillary columns were prepared with fused-silica tubing diameters ranging from 50 to 200 μm I.D. The relationship between column pressure drop and column diameter at 40°C is presented in Fig. 2. The changes in column pressure drop with column diameter were relatively small when the column diameters were larger than 100 μm while the changes were much more rapid

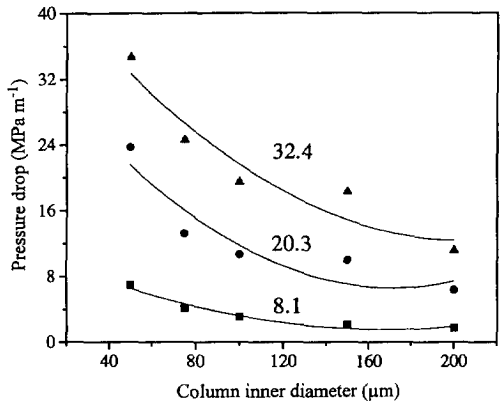

Fig. 2. Relationship between column pressure drop and column diameter for constant particle size. Conditions: 10-μm spherical silica packing material, 40°C, 45 cm×10 μm I.D. linear restrictor. The numbers (8.1, 20.2 and 32.3) indicate the column inlet pressure in MPa.

when the column diameters were less than 100 μm. The pressure drop of a 50 μm I.D. column was almost 4 times higher than that of a 200 μm I.D. column of equal length. In contrast, the CO_2 volume flow-rate of a 50 μm I.D. column was 4 times less than that of a 200 μm I.D. column. The changing of column temperature did not change this relationship.

3.1.4. Pressure drop along capillary columns packed with particles of different diameters

In this series of experiments, the column internal diameter was fixed at 200 μm and spherical silicas ranging from 5- to 40-μm were selected as packing materials. The column length was selected to be approximately 1 m. The relationship between pressure drop and particle diameter for different column inlet pressures is shown in Fig. 3. There was a significant pressure drop when the particle size was smaller than 10 μm. A pressure drop as high as 17.2 MPa was observed at an inlet pressure of 40.5 MPa for the column packed with 5-μm silica. The column packed with 40-μm silica gave almost no pressure drop; only a few hundred kPa was measured at the highest column inlet pressure (42 MPa).

3.1.5. Pressure drop along packed capillary columns of different lengths

In order to examine the effects of pressure drop on column performance for different column lengths,

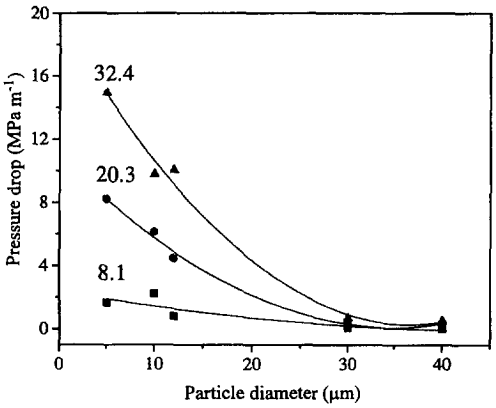

Fig. 3. Relationship between column pressure drop and particle diameter for constant column dimensions. Conditions: 200 μm I.D. capillary column, 40°C, 45 cm×10 μm I.D. linear restrictor. The numbers (8.1, 20.2 and 32.3) indicate the column inlet pressure in MPa.

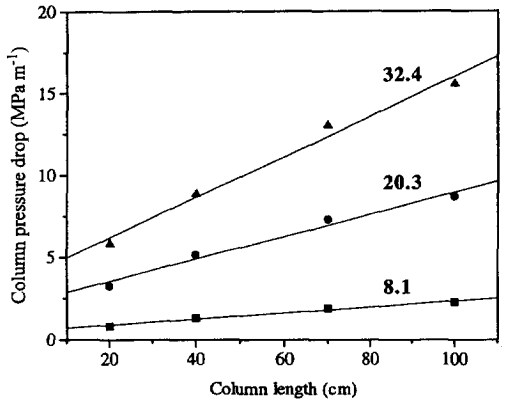

Fig. 4. Relationship between column pressure drop and column length. Conditions: 5-μm spherical silica packing material, 200 μm I.D. capillary column, 40°C, 45 cm×10 μm I.D. linear restrictor. The numbers (8.1, 20.2 and 32.3) indicate the column inlet pressure in MPa.

Berger and Deye [29] connected up to 11 columns in series. Using this approach, variations from column to column and dead volumes between columns were experienced. To avoid these problems in this study, a single long capillary column (1 m) packed with 5-μm spherical silica was prepared. Various pressure drops were realized by cutting off certain lengths of this column, followed by sealing the column inlet end with a frit. The relationship between column pressure drop and column length for different column inlet pressures is shown in Fig. 4. The column pressure drop increased linearly with an increase in column length. For a short column (20 cm), the pressure drop ranged from 0.8 to 6.1 MPa, depending on the inlet pressure applied (from 8.1 to 40.5 MPa). For a long column (100 cm), the pressure drop could be as high as 18.2 MPa at an inlet pressure of 40.5 MPa.

3.1.6. Pressure drop along capillary columns packed with spherical and nonspherical particles

Fig. 5 shows experimental results of column pressure drops measured for spherical and irregular packing materials of the same particle size (40 μm). It can be seen that particles with a spherical shape lead to slightly higher pressure drops than those with irregular shape. Spherical particles have less surface area, they experience less resistance [36] from friction, and they can be packed more tightly and uniformly. Irregular particles can lodge together more easily in the column and result in lower packing density and higher permeability. The measured lower efficiencies of columns packed with irregular particles also support this proposed loosely packed structure [37].

3.2. Pressure drop versus resolution

Column pressure drop is proportional to column length under comparable conditions. Resolution was

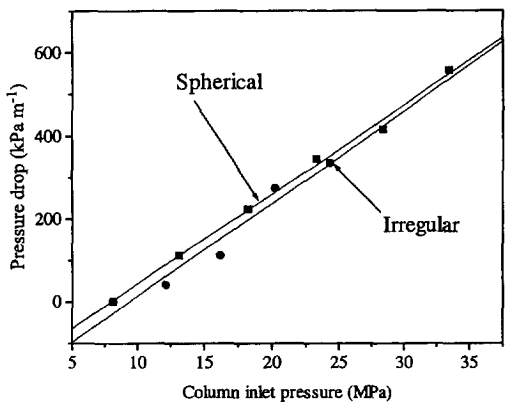

Fig. 5. Relationship between column inlet pressure and pressure drop for different particle shapes. Conditions: 40-μm silica packing material, 200 μm I.D. capillary column, 40°C, 45 cm×10 μm I.D. linear restrictor.

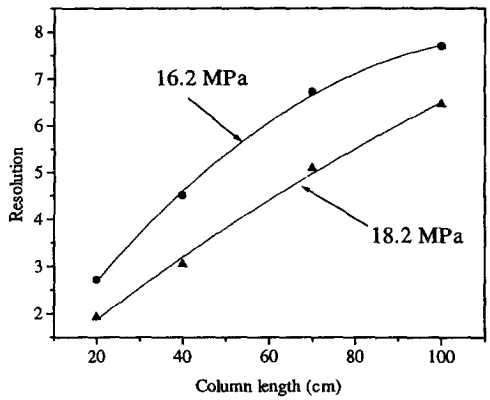

Fig. 6. Relationship between column length and resolution of *n*-hexadecane and *n*-heptadecane at different inlet pressures. Conditions: 5-μm spherical silica packing material, 200 μm I.D. capillary column, 100°C, 45 cm×10 μm I.D. linear restrictor, CO_2, FID.

calculated based on the retention times and peak widths at half height of two analytes, *n*-hexadecane and *n*-heptadecane. Fig. 6 shows plots of resolution versus column length at two different inlet pressures. It can be seen that resolution increased with an increase in column length, but decreased with an increase in column inlet pressure, the latter mainly due to a decrease in retention factor or a loss in selectivity as a result of the higher mobile phase density and linear velocity. This could be explained by the dependence of resolution on column total plate number, selectivity and retention factors.

3.3. Pressure drop versus column efficiency

Using the same linear restrictor, inner diameter and packing material, columns of different lengths were examined for column efficiency. Table 1 lists the efficiency data measured at optimum conditions. It is clear that all of the columns gave similar optimum linear velocities and efficiencies. The theoretical plate height or reduced plate height of each column did not change with column length. This means that the plate height is not affected by column length or column pressure drop.

Table 1
Experimental parameters and efficiency measurements for columns of different lengths[a]

L (cm)	ΔP (MPa)[b]	u_{opt} (cm s^{-1})	k	N	N m^{-1}	h
20	2.56	0.48	1.9	17 471	87 354	2.3
40	4.94	0.51	2.1	34 388	85 969	2.3
70	7.28	0.53	2.2	59 070	84 368	2.3
100	8.83	0.51	1.2	84 920	84 920	2.3

[a] Conditions: 5-μm bare silica packing material, 200 μm I.D. columns, 45 cm×10 μm I.D. linear restrictor, 100°C, CO_2, FID, n-C_{16} test solute.
[b] Measured at 20.3 MPa column inlet pressure.

There exist different opinions about the relationship between column pressure drop and efficiency. One view [24], based on Darcy's law, states that there is a maximum allowable column pressure drop or a maximum plate number. For 5-μm particles, the maximum allowable pressure drop is approximately 25 bar, and the highest column efficiency is approximately 2000 theoretical plates. For 4-μm particles, the optimum column length would be ca. 30–40 cm. Application of longer columns resulted in an unacceptably high pressure drop and band broadening [38].

For a packed column, Darcy's equation can be expressed as:

$$N = (\Delta P d_p^2)/(1000 \eta h \nu D_m) \quad (1)$$

where N is the total plate number, ΔP is the pressure drop along the column, d_p is the particle size, 1000 is the column permeability coefficient, η is the viscosity of the mobile phase, h is the reduced plate height, ν is the reduced linear velocity, and D_m is the diffusion coefficient of the solute in the mobile phase. At a practical operating column temperature (100°C) and pressure (>10.1 MPa), the conditions are quite removed from the immediate vicinity of the critical point, and the density of CO_2 does not vary considerably along the column length [23]. For constant particle size, reduced plate height and reduced linear velocity, the total theoretical plates are proportional to the column pressure drop. In other words, increasing the pressure drop will result in increasing the total plate number if the pressure drop is generated by increasing the column length. It is very difficult from only the Darcy equation (Eq. (1)) to see that there is a maximum allowable pressure drop, and a maximum column length. In our opinion, the maximum column length and pressure drop do exist, but are limited by the maximum

available pressure of the pump and the mechanical strength of the packing and column materials.

There is another explanation for the relationship between column efficiency and pressure drop. It has been considered that a large column pressure drop can cause a significant density gradient [22]. This density gradient can affect the solubility of certain compounds and cause undesirable sample discrimination effects [39]. However, several researchers [29–33] reported that density gradients, retention gradients, or solute velocity gradients apparently do not cause efficiency losses. Experimental observations found that under most conditions, efficiency losses have nothing to do with pressure drop; apparent efficiency sometimes appears to be higher and at other times lower than with no pressure drop. Clearly, the effect of pressure drop on column efficiency involves complex processes which are not fully understood. We found, in this study, that total plate numbers for both long and short columns are comparable and additive; long columns with high pressure drops gave similar reduced plate heights as short columns with low pressure drops under the experimental conditions explored (see Table 1 conditions). We believe that column efficiency is strongly related to mobile phase conditions and properties such as addition of modifier, concentration of modifier, density uniformity of the mobile phase throughout the column, temperature uniformity and so on, as well as to the uniformity of packing. It is also important to use a proper restrictor to keep the column outlet pressure high enough so that the entire column is operated under supercritical conditions [35]. Furthermore, the experimental conditions should be selected in such a way that they are removed from the vicinity of the critical point.

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References

[1] R.J. Laub, Anal. Chem., 56 (1984) 2115.
[2] J.C. Giddings, Anal. Chem., 36 (1964) 741.
[3] M.N. Myers and J.C. Giddings, Anal. Chem., 37 (1965) 1453.
[4] E. Katz, K. Ogan and R.P.W. Scott, J. Chromatogr., 260 (1983) 277.
[5] V.L. McGuffin and C.E. Evans, J. Microcol. Sep., 3 (1991) 513.
[6] R.P.W. Scott (Editor), Small Bore Liquid Chromatography Columns: Their Properties and Uses, John Wiley, New York, 1984.
[7] H.G. Janssen, H.M.J. Snijders, J.A. Rijks and C.A. Cramers, J. High Resolut. Chromatogr., 14 (1991) 438.
[8] M.L. Lee and K.E. Markides (Editors), Analytical Supercritical Fluid Chromatography and Extraction, Chromatography Conferences, Provo, UT, 1990.
[9] P.J. Schoenmakers and F.C.C.J.G. Verhoeven, Trends Anal. Chem., 6 (1987) 10.
[10] D.R. Gere, R. Board and D. McManigill, Anal. Chem., 54 (1982) 736.
[11] D.E. Martire, J. Liq. Chromatogr., 10 (1987) 1569.
[12] D.E. Martire, R.L. Riester, T.J. Bruno, A. Hussam and D.P. Poe, J. Chromatogr., 545 (1991) 135.
[13] X. Zhang, D.E. Martire and R.G. Christensen, J. Chromatogr., 603 (1992) 193.
[14] D.E. Martire, J. Chromatogr., 461 (1989) 165.
[15] H.G. Janssen, H.M.J. Snijders and C.A. Cramers, J. High Resolut. Chromatogr., 15 (1992) 458.
[16] M. Roth and A. Ansorgova, J. Chromatogr., 465 (1989) 169.
[17] S.M. Fields and M.L. Lee, J. Chromatogr., 349 (1985) 305.
[18] M. Jaremo, L. Karlsson, J.A. Jonsson and L. Mathiasson, Chromatographia, 38 (1994) 17.
[19] L. Karlsson, M. Jaremo, M. Emilsson, L. Mathiasson and J.A. Jonsson, Chromatographia, 37 (1993) 402.
[20] M. Novotny, W. Bertsch and A. Zlatkis, J. Chromatogr., 61 (1971) 17.
[21] J.A. Graham and L.B. Rogers, J. Chromatogr. Sci., 18 (1980) 75.
[22] P.J. Schoenmakers and F.C.C.J.G. Verhoeven, J. Chromatogr., 352 (1986) 315.
[23] P.J. Schoenmakers, P.E. Rothfusz and F.C.C.J.G. Verhoeven, J. Chromatogr., 395 (1987) 91.
[24] P.J. Schoenmakers and L.G.M. Uunk, Chromatographia, 24 (1987) 51.
[25] P.A. Mourier, M.H. Caude and R.H. Rosset, Chromatographia, 23 (1987) 21.
[26] K.D. Bartle, T. Boddington, A.A. Clifford and G.F. Shilstone, J. Chromatogr., 471 (1989) 347.

[27] F.P. Schmitz and E. Klesper, J. High Resolut. Chromatogr. Chromatogr. Commun., 10 (1987) 519.
[28] T.A. Berger and J.F. Deye, Chromatographia, 30 (1990) 57.
[29] T.A. Berger and J.F. Deye, Chromatographia, 31 (1991) 529.
[30] T.A. Berger, Proc. 14th Int. Symp. on Capillary Chromatography, Baltimore, MA, 1992, p. 734.
[31] T.A. Berger and W.H. Wilson, Proc. 14th Int. Symp. on Capillary Chromatography, Baltimore, MA, 1992, p. 783.
[32] T.A. Berger and W.H. Wilson, Anal. Chem., 65 (1993) 1451.
[33] T.A. Berger and L.M. Blumberg, Chromatographia, 38 (1994) 5.
[34] A. Malik, W. Li and M.L. Lee, J. Microcol. Sep., 5 (1993) 361.
[35] W. Li, A. Malik and M.L. Lee, J. Microcol. Sep., 6 (1994) 557.
[36] D. Tong, K.D. Bartle and A.A. Clifford, Proc. 16th Int. Symp. on Capillary Chromatography, Riva del Garda, Italy, 1994, p. 172.
[37] W. Li, D. Pyo, Y-Wan, E. Ibañez, A. Malik and M.L. Lee, J. Microcol. Sep., 8 (1996) 259.
[38] L.G. Blomberg, M. Demirbuker, I. Hagglund and P.E. Andersson, Trends Anal. Chem., 13 (1994) 126.
[39] H.E. Schwartz, LC·GC, 5 (1987) 14.