Relationship Between the Optimum Flow Rate and the Column Temperature in Capillary Column Ion Chromatography

Dongjin Pyo,* Hohyun Kim, and Purnendu K. Dasgupta*

Department of Chemistry, Kangwon National University, Chuncheon 200-701, Korea
**Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409-1061, USA*
Received October 2, 1998

Ion chromatography (IC) is a high-performance version of ion-exchange chromatography, that has become the method of choice for routine anion analysis and has many applications in cation analysis as well. Ion chromatography was first introduced in 1975,[1] when it was shown that anion or cation mixtures can be readily resolved on HPLC columns packed with anion-exchange or cation-exchange resins. However, the separation efficiency of IC is somewhat lower than that of high performance liquid chromatography (HPLC). The reason for that is separations in IC are based on the charge-charge interactions during the separation process. One of the goals of this study is to develope the best means of achieving high separation efficiencies in IC. There are two general ways to improve the column efficiency in liquid chromatography; one is to use a small diameter column and another is to elevate the column temperature.

There is now a great deal of research interest in the use of small bore columns to improve liquid chromatographic column efficiency. This is because that both experimental[2] and theoretical data[3] demonstrate it is possible to achieve very high plate efficiencies (up to nearly 10^6) using small bore columns, either small bore packed columns, packed capillary columns, or open tubular capillary columns. Among these small bore columns, open tubular columns offer several unique advantages such as a high efficiency, a high speed and a good permeability.

Open tubular columns in LC were first investigated by Ishii, Tsuda, and coworkers[4-6] following pioneering work by Nota, *et al.*[7] In theory, as shown by Knox and Gilbert,[8] the bores of such columns must be in the range of 10-30 μm if they are to compete with packed columns in terms of speed and performance generally. However, thereafter, some authors[9,10] reported that the optimum internal diameters in open tubular capillary LC columns would be less than 10 μm to realize acceptable analysis time and high resolution. Such small i.d. open tubular columns are, however, very difficult to work with, since their volume is less than 1 μL, which is extremely high demand on instrumentations, such as injection, pumping, connection and especially detection. On column electrochemical detectors are used to obtain small detection volumes and fast response.[11] Although the chief advantages of 1-10 μm i.d. columns have been demonstrated,[12,13] practical problems mentioned above have limited the wide use of aforementioned small i.d. columns. These practical problems arise because of the very low volumes of the eluted peaks which demand injection and detection systems which themselves produce exceedingly small extra-column band broadening. To data, these technical problems have limited to the bores to about 50 μm.[3,14] Steenackers and Sandra[14] reported that they could get a high efficiency separations for some polar solutes including proteins using 50 μm i.d. open tubular columns.

The effect of high column temperature on separation efficiency has been investigated both experimently[15,16] and theoretically[17] by many authors. Diffusion coefficient (D_m) of the analyte in the mobile phase is increased with increasing temperature, and an increase in D_m improve the efficiency. It is reported[18] that high temperature is beneficial for both packed column chromatography and 50-100 μm i.d. open tubular column LC. Liu *et al.*[2,19] recently demonstrated that high temperature (100-200 °C) operation with 50 μm and 100 μm i.d. open tubular columns could make extremely high efficient separations(up to 10^6) for organic compounds.

Despite of all advantages of small bore open tubular columns, reports on capillary column ion chromatography are rarely found in the literature, although Muller, Simon and his co-workers[12,13] used 2.3 μm and 4.6 μm i.d. open tubular column to separate inorganic anions and cations with their specially designed on-column electrochemical detectors. In this study, a 50 μm i.d. silica capillary coated with Latex particles (diameter : about 360 nm) was used as a column. The optimum flow rates for capillary column ion chromatography were calculated using the Golay equation and compared with experimental values.

Experimental Section

The open tubular column ion chromatography instrument used in this study was constructed in the laboratory. A schematic diagram of the instrument is shown in Figure 1. It consisted of a Shimazu GC-8A oven for the control of the column temperature, a Dionex 2000I pump, a Rheodyne Model 7000 injector(injection volume : 5 μL), two split tees (Valco 1/16 inches, 0.75 mm bore), a UV detector (Isco, Inc. Lincoln, NE, Model CV^4), a 50 μm i.d. capillary column (length : 1 m) and a 20 μm i.d. capillary restrictor (length : 1 m).

Two splitters were used to provide a fairly low flow rate (usually about 1 μL/min) for 50 μm i.d. open tubular capillary column. The first splitter in which a tube of 10 cm×20 μm i.d. fused silica capillary was used as the split tube, was placed between the pump and the preheating tube. The split

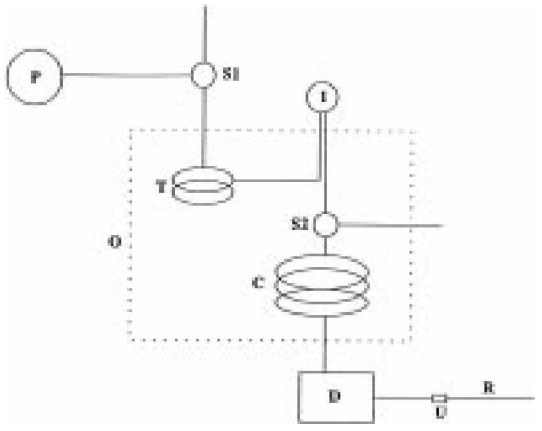

Figure 1. Schematic diagram of open tubular capillary column ion chromatographic system : **P**, IC pump; **S1**, first splitter; **S2**, second splitter; **I**, injector; **T**, preheating tube; **C**, column; **D**, detector; **R**, restrictor; **O**, GC oven; **U**, union.

ratio of the first splitter was about 1 : 10. The second splitter in which 1.3 m×75 μm i.d. fused silica capillary was used as the split tube giving a split ratio about 60 was placed inside the oven. To avoid the extra-column broadening due to a splitter, the column inlet was inserted into 20 cm×0.030 inches stainless steel tubing which connects between injector and the second splitter. A preheating tube (50 cm×0.25 mm i.d. stainless steel tube) was used to preheat the eluant before column and placed between the first splitter and the injector inside the oven.

A variable wavelength absorbance detector, a Model CV[4] (Isco, Inc. Lincoln, NE) was utilized to measure the absorbance at 210 nm. The detection was carried out by measuring the absorbance on the column at a position 15 cm from the end of the capillary tube. Latex particles used in this work were supplied by Dionex and have a very small diameter (about 360 nm) and carry the actual anion exchange groups. These particles are agglomerated to the silanol groups on the inner surface of fused silica capillary by electrostatic interaction. Before the capillary was treated with a solution of the latex particles, the capillary was cleaned with several reagents to produce the maximum number of active surface silanol groups. The coating procedure involved flushing the capillary with a solution of the latex particles.

Results and Discussions

In 1958, for an open tubular column, Golay[20] derived a equation in which the height equivalent to a theoretical plate (HETP) is given in the following :

$$H = \frac{2D_m}{u} + \frac{1 - 6k' + 11k'^2}{96(1+k')^2} \cdot \frac{d_c^2}{D_m} \cdot u + \frac{2k'}{3(1+k')^2} \cdot \frac{d_f^2}{D_s} \cdot u \quad (1)$$

where D_m is the diffusivity of the solute in the mobile phase (cm^2/s), D_s is the diffusivity of the solute in the stationary phase (cm^2/s), d_c is the column inner diameter (cm), d_f is the film thickness (cm), u is the velocity of the mobile phase (cm/s) and k' is the capacity factor of the solute. The first term is based on the contribution of longitudinal diffusion and the second and the third terms are based on resistance to mass transfer in the mobile phase and stationary phases, respectively. Since the columns used in this study, either bare silica capillary or Latex particle coated silica capillary have very small film thickness, the third term in eqn. (1) can be negligible. Therefore, the Golay equation can be expressed to the following :

$$H = \frac{2D_m}{u} + \frac{1 + 6k' + 11k'^2}{96(1+k')^2} \cdot \frac{d_c^2}{D_m} \cdot u \quad (2)$$

The optimum velocity (u_{opt}), at the minimum value of H can be calculated from eqn. (2) using the following equation.

$$\frac{dH}{du} = 0 \quad (3)$$

$$u_{opt} = \sqrt{\frac{2}{f(k')}} \cdot \frac{D_m}{d_c} \quad (4)$$

$$\left[\text{where } fk' = \frac{1 + 6k' + 11k'^2}{96(1+k')^2}\right]$$

u_{opt} can be estimated from equation (4) when D_m, d_c and k' are given. Here, it should be noted that the diffusivity of solute in the mobile phase, D_m is a function of temperature. It is clear that D_m increase with increasing temperature, resulting in higher optimum flow rates and flatter the Van Deemter curves. We have made some high temperature experiments to verify this phenomena in IC, and these experimently obtained u_{opt} data were compared with the calculated values (Table 1) using a nitrate ion as a solute. The diffusion coefficient of nitrate in water at room temperature was calculated from the ion mobility of nitrate, u_m, using the following relationship.[21]

$$u_m = \frac{z_m F D_m}{RT} \quad (5)$$

where z_m is the absolute value of the charge of nitrate, F is the faraday constant and R is the gas constant. The ion mobility of nitrate, u_m, at 25 is found as 7.404×10^{-4} cm^2/sec.[22] Using this value and equation (4), the diffusion coefficient of nitrate, D_m at 25 can be calculated as 1.901×10^{-4} cm^2/sec. To calculate the diffusion coefficients of nitrates at high temperatures, the following Stokes-Einstein equation was employed.

$$D_m = \frac{kT}{4\pi a\eta} \quad (6)$$

where k is the Boltzmann constant, a is the radius of nitrate and η is the viscocity of the eluant. The diffusion coefficients of nitrate in water at 75 °C, 110 °C and 150 °C were calculated as 5.243×10^{-5} cm^2/sec, 8.137×10^{-5} cm^2/sec and 10.929×10^{-5} cm^2/sec, respectively. As expected, the large difference in D_m was seen at different temperatures. Using these D_m values and eqn. (4), the optimum flow rate, u_{opt} for

Table 1. Experimentally measured and calculated optimum flow rates for open tubular capillary ion chromatography

Col. Temp.	Calculated U_{opt} (cm/sec)	Experimental U_{opt} (cm/sec)
75	0.124	0.179
110	0.199	0.191
150	0.276	0.240

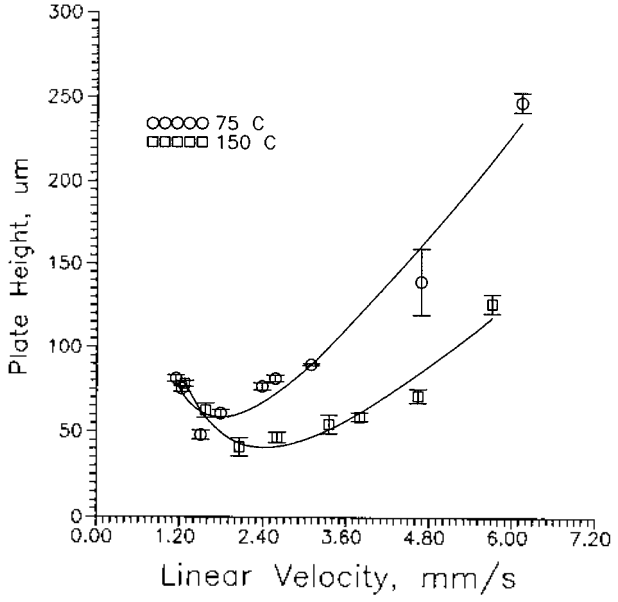

Figure 2. Van Deemter curves at 75 °C and 150 °C. (column : 1m×50 μm i.d. capillary coated with Latex particles, eluent : 1mM sodium sulfate, detector : UV detector at 210 nm).

the nitrate was calculated and shown in Table 1. We could also determine the optimum flow rates for nitrate experimently using 1m×50 μm i.d. Latex particle coated silica capillary. The Van Deemter curves for nitrate at 75 °C and 150 °C are shown in Fig. 2. The calculated optimum flow rates in 50 μm i.d. open tubular ion chromatography matches fairly well with actual experimental data (see Table 1).

Acknowledgment. This investigation was supported by a grant from KOSEF (98-0501-07-01-3). This work was also supported partially by Ministry of Education (BSRI-98-3425).

References

1. Small, H.; Stevens, T. S.; Baumann, W. C. *Anal. Chem.* **1975**, *47*, 1801.
2. G. Liu, G.; Djordjevic, N. M.; Erni, F. *J. Chromatogr.* **1992**, *592*, 239.
3. Knox, J. H. *J. Chromatogr. Sci.* **1980**, *18*, 453.
4. Tsuda, T.; Hibi, K.; Nakanishi T.; Takeuchi, T.; Ishii, D. *J. Chromatogr.* **1978**, *158*, 227.
5. Tsuda, T.; Novotny, M. *Anal. Chem.* **1978**, *50*, 632.
6. Ishii, D.; Tsuda, T.; Takeuchi, T. *J. Chromatogr.* **1979**, *185*, 73.
7. Nota, G.; Marino, G.; Buonocore, V.; Ballio, A. *J. Chromatogr.* **1970**, *46*, 103.
8. Knox, J. H.; Gilbert, M. T. *J. Chromatogr.* **1979**, *186*, 405.
9. Jorgenson, J. W.; Guthrie, E. J. *J. Chromatogr.* **1983**, *255*, 335.
10. Scott, P. W. *J. Chromatogr.* **1990**, *517*, 297.
11. Manz, A.; Simon, W. *J. Chromatogr.* **1987**, *387*, 187.
12. Muller, S. R.; Simon, W.; Widmer, H. M.; Grolimund, K.; Schomburg, G.; Kolla, P. *Anal. Chem.* **1989**, *61*, 2747.
13. Muller, S.; Scheidegger, D.; Haber, C.; Simon, W. *J. High Resolut. Chromatogr.* **1991**, *14*, 174.
14. Steenackers, D.; Sandra, P. *J. High Resolut. Chromatogr.* **1994**, *17*, 557.
15. Tsuji, K.; Goetz, J. F. *J. Chromatogr.* **1978**, *157*, 185.
16. Herbut, G.; Kowalczyk, J. S. *J. High Resolut. Chromatogr. Chromatogr. Commun.* **1981**, *4*, 27.
17. Antia, F. D.; Horvath, Cs. *J. Chromatogr.* **1988**, *435*, 1.
18. Erni, F. *J. Chromatogr.* **1990**, *507*, 141.
19. G. Liu, G.; Djordjevic, N. M.; Erni, F. *J. Chromatogr.* **1992**, *598*, 153.
20. Golay, M. *Gas Chromatography*; Desty, D. H., Ed.; Butterworths: London, 1958; p 36.
21. Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley & Sons: New York, 1980; p 135.
22. Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley & Sons: New York, 1980; p 67.