

# Comparison of Empirical Peak Capacities for High-Efficiency Capillary Chromatographic Techniques

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**Experimental peak capacities for capillary gas chromatography (GC), capillary liquid chromatography (CLC), and capillary electrochromatography (CEC) were compared. To obtain a meaningful comparison, the following constraints were applied. First, the same sample (mixture of alkylbenzenes) was used as a test mixture for all three techniques; second, the same packing material and column diameter were used in CLC and CEC; and third, isothermal conditions were used in GC, while isocratic conditions were used both in CLC and in CEC. Comparison of peak capacities for the same total column efficiency (~36 000 plates) showed that the peak capacity of GC is greater than those of the liquid-phase separation techniques. Comparison of CEC and CLC for constant retention factor was also carried out. For this condition, the results depend on the particle size used; for 3- $\mu\text{m}$  porous particles, CEC had a peak capacity larger than CLC due to higher efficiency from the flow profile generated by electroosmotic flow. However, when 1.5- $\mu\text{m}$  nonporous particles were used, the peak capacities were approximately the same for both techniques. The effect of linear velocity on peak capacity was also studied for all three techniques. Practical conditions aimed at increasing peak capacities of liquid-phase separation techniques are discussed.**

Column efficiency ( $N$ ), reduced plate height ( $h$ ), and peak capacity ( $n$ ) are the most quoted parameters to express the potential separation power of a chromatographic technique. Efficiency is reported relative to either a retained or nonretained compound. Due to the fact that efficiency depends on several parameters such as particle size and/or column diameter, reduced parameters have been introduced to allow for comparisons among different chromatographic systems. Both efficiency and reduced plate height strictly refer to a *single* peak in the chromatogram. However, because chromatography almost always involves the separation of at least two compounds, peak capacity is a more useful<sup>1–5</sup> measurement to evaluate the overall separation potential of a chromatographic system.

Peak capacity is defined as the maximum number of components that can be separated at a specified resolution,  $R_s$ , within a given separation time window,  $\Delta t$

$$n = \Delta t / wR_s \quad (1)$$

where  $w$  is the width at the base of the peak. In practice, a value of  $R_s$  equal to 1.0 is considered sufficient for the separation of two adjacent peaks. Therefore, this resolution value of unity has been adopted as the standard resolution for the evaluation of peak capacity in column chromatography.<sup>1</sup> A practical difficulty in the calculation of peak capacity using eq 1 is that  $w$  is not constant for all peaks over the separation time, especially when long analysis times are involved. Therefore, eq 1 should be expressed in its differential form,<sup>6</sup>

$$dn = dt/dw \quad (2)$$

and integration of eq 2 over the desired separation time window yields the peak capacity:

$$n = \int_{t_1}^{t_2} dt/dw \quad (3)$$

Recently, Shen and Lee<sup>7</sup> found that, under nonprogrammed conditions, a linear relationship exists between the peak width at half-height,  $w_{1/2}$ , and the retention time,  $t$ , of a homologous series. This relationship can be expressed as

$$w_{1/2} = at + b \quad (4)$$

where  $w_{1/2}$  is related to  $w$  by the equation<sup>8</sup>

$$w = 1.699w_{1/2} \quad (5)$$

By substituting eqs 4 and 5 into eq 3, the following relationship is obtained

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$$n = 1/1.699 \int_{t_1}^{t_2} dt/at + b \quad (6)$$

where  $t_1$  and  $t_2$  are the retention times of the first and the last peaks used as bracketing compounds for the evaluation of the peak capacity of a given system. Upon integration of eq 6, an expression for peak capacity is obtained:

$$n = \frac{1}{1.699a} \ln \frac{at_2 + b}{at_1 + b} \quad (7)$$

Note that only one assumption has been made with this derivation, namely, the existence of a linear relationship between  $w_{1/2}$  and retention time.

Studies have been published on the peak capacities for various chromatographic techniques, such as capillary gas chromatography (GC),<sup>9</sup> supercritical fluid chromatography,<sup>7</sup> solvating gas chromatography,<sup>10,11</sup> and liquid chromatography.<sup>12–14</sup> However, to our knowledge, there have been no reports on the peak capacity for capillary electrochromatography (CEC).

Equation 7 indicates that the peak capacity of a given system depends on its chromatographic efficiency (terms containing the constant  $a$ ), the linear velocity and the nature of the sample used (as they affect  $t_1$ ), and a constant ( $b$ ). Therefore, factors affecting efficiency such as column diameter, particle size, linear velocity, column length, and film thickness also affect peak capacity. The purpose of this study was to compare the experimental peak capacities for three high-resolution techniques: GC, capillary liquid chromatography (CLC), and CEC. To obtain a meaningful comparison, the following constraints were applied. First, the same sample (mixture of alkylbenzenes) was used as a test mixture for all three techniques; second, the same packing material and column diameters were used in CLC and CEC; and third, isothermal conditions were used in GC, while isocratic conditions were used both in CLC and CEC.

## EXPERIMENTAL SECTION

**Materials.** Porous spherical ODS1 particles ( $3 \mu\text{m}$ ,  $80 \text{ \AA}$ ) were purchased from Phase Separations (Norwalk, CT), and  $1.5\text{-}\mu\text{m}$  nonporous spherical ODS1 particles were kindly donated by Dr. Peter Myers of Xtec (Cheshire, U.K.). Fused-silica capillary tubing was purchased from Polymicro Technologies (Phoenix, AZ). Open tubular GC columns were purchased from J&W Scientific (Folsom, CA). Alkylbenzenes (benzene to  $n$ -nonylbenzene) were purchased from Aldrich (Milwaukee, WI), and all chemicals used in the preparation of mobile phases for the liquid-phase separations were purchased from Fisher (Fair Lawn, NJ). SFC-grade carbon dioxide (for column packing) and compressed nitrogen were obtained from Airgas (Salt Lake City, UT).

**Preparation of Packed Capillary Columns.** Fused-silica capillary columns ( $75 \mu\text{m}$  i.d.  $\times$   $360 \mu\text{m}$  o.d.) for CEC and CLC were packed using a modified carbon dioxide slurry packing

method.<sup>15</sup> The initial packing pressure was 900 psi ( $6.20 \times 10^3$  kPa). Then, the pressure was raised periodically ( $10\text{--}15 \text{ atm min}^{-1}$ ) to maintain a constant packing rate until the column was completely filled. The final packing pressure was 15 000 psi ( $1.03 \times 10^5$  kPa). This process was performed with the column placed in a sonicator bath. The column was then left to depressurize gradually. Once depressurization through the frit at the column outlet slowed, the residual pressure in the column was released gradually by opening a vent valve. Complete depressurization usually required 24 h. Inlet and outlet frits and a window for on-column UV detection were prepared using a resistive heating device (InnovaTech) while water was pumped through the column.<sup>16</sup>

**CLC System.** The detailed experimental apparatus and procedures used to perform CLC have been previously described.<sup>16</sup> Briefly, a double-head gas-driven liquid pump (model DSHF-302, Haskel, Burbank, CA) with a piston area ratio (gas-driven area to liquid piston area) of 346 was used to generate the necessary liquid pressures. For safety, the system is provided with a pressure shutoff valve. If the system were to leak, the valve could be shut down immediately. Furthermore, due to the fact that liquid mobile phases are practically incompressible, the pressure in the system would decrease rapidly if a leak occurred. Finally, pressures lower (e.g., 40 kpsi) than the limit (52 kpsi) are always used. We have not had any safety problems during the two years that this system has been in use. The internal volume of the pump head was 4.5 mL. Compressed nitrogen was used to drive the pump. The outlet of this pump was connected to a home-built injection system for static-split injection. Following injection, the desired column pressure was applied, the main valve to the column was opened, and data acquisition was initiated. A model 501 UV/visible detector from Lee Scientific was used to monitor on-column UV absorbance. Data were acquired with ChromQuest version 2.5.1 (ThermoQuest, Sunol, CA) and processed with a Pentium II 266-MHz computer.

**CEC System.** The CEC system used in this study was a home-built instrument as described in detail elsewhere.<sup>17</sup> Briefly, the computer-controlled system was equipped with a Spellman model SL60PN30 high-voltage power supply (Hauppauge, NY) with voltage capabilities up to  $\pm 60$  kV and a ThermoSeparations model UV 3000 detector (Sunol, CA). As a safety precaution, the holder assemblies and the CEC column were contained in a Plexiglas box to isolate the high voltage. This box was provided with a closed-contact device, so that whenever the box is open, the voltage automatically turns off. A home-written program was used to control the high-voltage power supply and to set the injection and analysis voltages and times.

Prior to use, all buffers and solvents were filtered through a  $0.22\text{-}\mu\text{m}$  Durapore membrane filter (Millipore, Bedford, MA) and degassed thoroughly. Likewise, samples were degassed and filtered through a  $0.2\text{-}\mu\text{m}$  poly(tetrafluoroethylene) (PTFE) syringe filter (Chromacol, Trumbull, CT) before use. Both CEC and CLC separations were performed under isocratic conditions. The mobile phase for CLC separations consisted of different concentrations of acetonitrile in water (containing 0.1% v/v TFA). For CEC, Tris (50 and 20 mM) was used as a buffer. The sample was dissolved

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Table 1. Linear Relationship between Peak Width ( $w_{1/2}$ ) and Solute Retention Time ( $t$ ) in CLC, CEC, and GC

technique <sup>a</sup>	experiment 1	experiment 2
CLC	$w_{1/2} = 0.0127t - 0.0009$ $R^2 = 0.997$	$w_{1/2} = 0.0153t - 0.0122$ $R^2 = 0.997$
CEC	$w_{1/2} = 0.0117t - 0.0022$ $R^2 = 0.996$	$w_{1/2} = 0.0111t - 0.0121$ $R^2 = 0.980$
GC	$w_{1/2} = 0.0115t + 0.0012$ $R^2 = 0.999$	$w_{1/2} = 0.009t + 0.0078$ $R^2 = 0.998$

<sup>a</sup> Conditions: A mixture of 10 alkylbenzenes (benzene to *n*-nonylbenzene) was used for all experiments. (CLC) Experiment 1: 33 cm  $\times$  75  $\mu$ m i.d. fused-silica capillary packed with 3- $\mu$ m ODS1; ACN/H<sub>2</sub>O (70:30) mobile phase, UV detection at 210 nm; 3000 psi ( $2.06 \times 10^4$  kPa). Experiment 2: same column as used in experiment 1, 3700 psi ( $2.55 \times 10^4$  kPa); ACN/H<sub>2</sub>O (65:35) mobile phase. (CEC) Experiment 1: 25 cm  $\times$  75  $\mu$ m i.d. fused-silica capillary packed with 3- $\mu$ m ODS1; ACN/Tris buffer (80:20, 50 mM, pH 8.2) mobile phase, UV detection at 210 nm; 5 kV, 1 s electrokinetic injection; 15 kV applied voltage. Experiment 2: 33 cm  $\times$  75  $\mu$ m i.d. fused-silica capillary packed with 3- $\mu$ m ODS1; 30 kV applied voltage; other conditions are the same as in experiment 1. (GC) Experiment 1: 10 m  $\times$  200  $\mu$ m i.d. DB-5 fused-silica capillary column; He carrier gas, 100 °C oven temperature; FID detection. Experiment 2: 13 m  $\times$  200  $\mu$ m i.d. DB-5 fused-silica capillary column; 120 °C oven temperature; other conditions are the same as in experiment 1.

in a small volume of mobile phase to a concentration of 2  $\mu$ L mL<sup>-1</sup> per component.

**GC System.** Open tubular column GC experiments were carried out using a Fisons 8000 Series gas chromatograph (ThermoQuest, Milan, Italy) with FID detection. Capillary columns (DB-5, 10 and 13 m, 200- $\mu$ m i.d., 0.2- $\mu$ m film thickness) were used. Helium was used as the mobile phase, and the injector split ratio was set at 1:100. Separations were made under isothermal conditions. For GC analysis, the alkylbenzenes were dissolved in CS<sub>2</sub> at a concentration of 200 ppm.

## RESULTS AND DISCUSSION

**Relationship between Peak Width ( $w_{1/2}$ ) and Solute Retention Time ( $t$ ).** As was previously stated, a linear relationship must exist between  $w_{1/2}$  and solute retention time ( $t$ ) in order to use eq 7 for the calculation of peak capacity. A previous study<sup>7</sup> showed that different homologous series gave different values for  $a$  and  $b$  in eq 4. To eliminate this variability, the same standards were analyzed using all three separation techniques, and plots of  $w_{1/2}$  versus  $t$  could be directly compared. The equations obtained from fitting of the experimental data are given in Table 1. The high correlation coefficients ( $R^2 \geq 0.98$ ) demonstrate that the data are adequately fitted using linear equations. It can be inferred from eq 4 that the smaller the  $a$  value (small slope), the higher the efficiency of a chromatographic column. In practice, this prediction was found to be true in each instance; systems with higher efficiencies generated smaller  $a$  values. Table 1 also shows that  $b$  can have either positive or negative values. The particular sign for  $b$  should be included in the calculation of peak capacity when eq 7 is used. In all cases, column efficiency was dependent on the solute retention factor. When the average column efficiency was calculated from the efficiency values obtained using each of the 10 peaks in the chromatogram, a direct correlation was found between the relative standard deviation of the column efficiency and the  $b$  value. A larger  $b$  value was always related to a larger standard deviation.

**Comparison of Peak Capacities for Constant Column Efficiency.** Equation 7 shows that the peak capacity depends on several parameters. To obtain a meaningful comparison of peak capacities for different chromatographic techniques, some of these variables must be fixed, and then the effect of the remaining variables can be evaluated. Separations were first performed at equal total column efficiencies of  $\sim 36\,000$  plates for CLC, CEC,

and GC using the conditions given for experiment 1 in Table 1. The chromatograms are presented in Figure 1. To the naked eye, the early section of the GC chromatogram seems more crowded than that of CEC and CLC. However, peak resolutions for the first four consecutive pairs (compounds resolved in less than 1 min) are equal to, or larger than, those for the liquid-phase separation techniques. A total of 36 000 plates was an average value calculated using the retention times and peak widths for each of the 10 compounds in the mixture for each technique.

Table 1 shows that the slopes ( $a$  values) of the equations for all three techniques are similar. Values for  $a$  and  $b$  obtained from these experiments were used for the calculation of peak capacities according to eq 7. The retention time for benzene in each of the separation techniques was assigned to be the  $t_1$  value. Figure 2 shows the calculated peak capacities for different  $t_2$  values for the three techniques using eq 7. It can be seen that, for any given  $t_2$  value, GC has the highest peak capacity. Since  $a$  values are similar (approximately same column efficiency), the smaller  $t_1$  value is the reason for the largest peak capacity obtained for GC. This smaller  $t_1$  value makes the logarithmic term in eq 7 larger, thereby generating a larger peak capacity. At a  $t_2$  value of 60 min, the peak capacities for GC, CEC, and CLC are 251, 117, and 114, respectively. Amazingly, a GC peak capacity of 124 is calculated for a  $t_2$  value of only 5 min. Since the widths at the bases of the peaks for the 8 compounds eluted between 0.32 and 5 min range from 0.8 to 5.3 s, it is expected that indeed 124 compounds could be separated by GC in 5 min, if the compounds in the mixture aligned themselves one after other. In comparison, for the same  $t_2$  value of 5 min, not even the first compound eluted from either the CEC or CLC column. In other words, a GC peak capacity higher than 100 is obtained during the dead time of the liquid-phase techniques for a column packed with 3- $\mu$ m porous particles. On the basis of the same total column efficiencies, and under nonprogrammed conditions, GC has a fundamental advantage in peak capacity over liquid-phase techniques because the range of retention factors for a given set of homologues spans a much wider range.

These findings contradict previous claims<sup>18,19</sup> that the peak capacities of CEC should approach those of GC. Such statements are based solely on consideration of equal total column efficiencies. However, the results of this study demonstrate that the retention window also has a significant effect on peak capacity. The

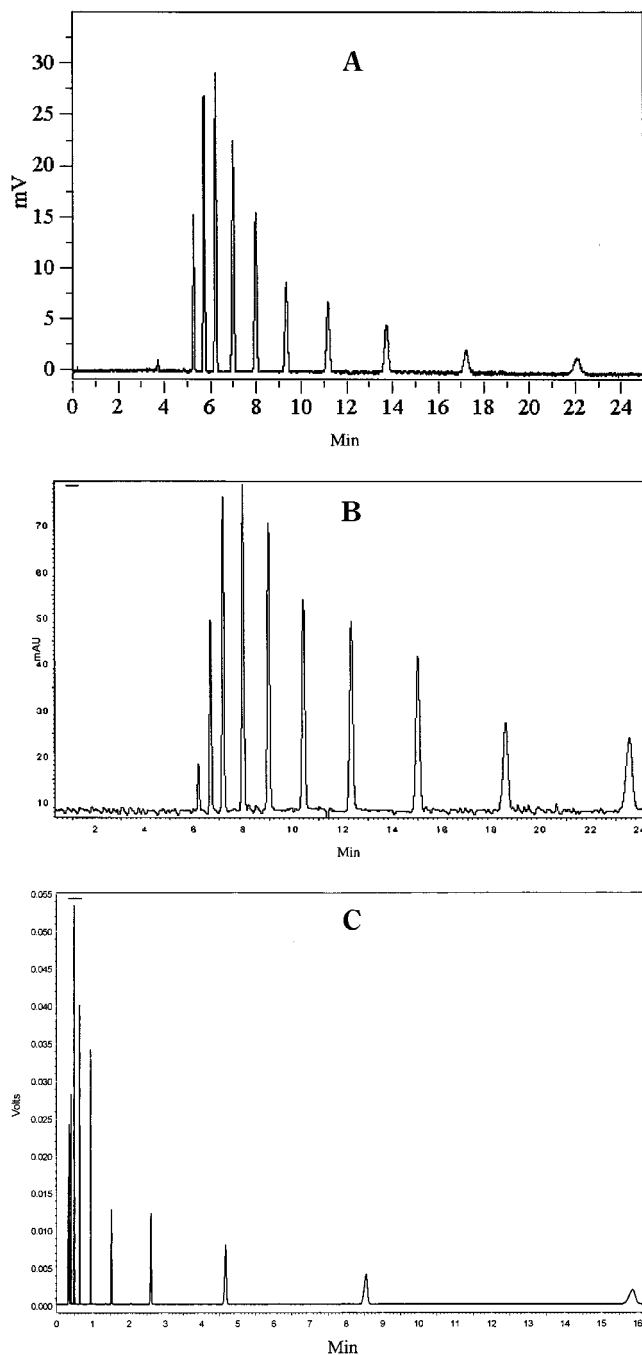


Figure 1. (A) CLC, (B) CEC, and (C) GC chromatograms of a mixture of alkylbenzenes (benzene to *n*-nonylbenzene) at an average column efficiency of  $\sim 36\,000$  total plates. Experimental conditions are given in Table 1 under experiment 1.

logarithmic term in eq 7 contains the ratio  $t_2/t_1$ , which is a ratio of retention times. At high values, this ratio approaches the retention factor ( $k$ ). Table 2 shows that GC has both the highest retention factors and the highest retention ratios for late-eluting compounds. Likewise, it also has the lowest retention factors for early-eluting compounds.

#### Comparison of Peak Capacities for Constant Retention Factor.

Comparison of peak capacities for similar retention factor

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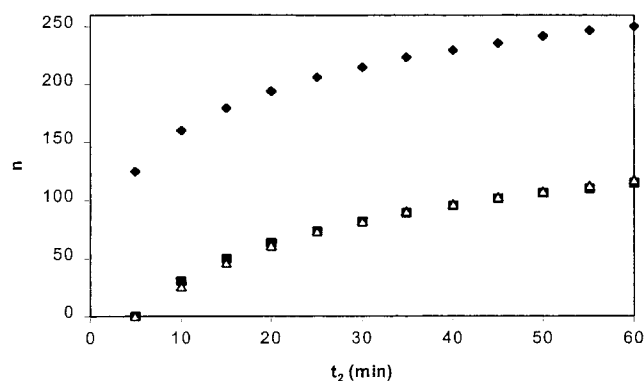


Figure 2. Calculated peak capacities ( $n$ ) for different  $t_2$  values for packed column CEC (■), CLC (△), and open tubular column GC (◆) according to eq 7. The constants  $a$  and  $b$  used for these calculations are those given in Table 1, under experiment 1. The  $t_1$  values used in eq 7 for CEC, CLC, and GC were 6.15, 5.28, and 0.32 min, respectively.

Table 2. Retention Factors ( $k$ ) and Retention Ratios ( $t_2/t_1$ ) for a Mixture of Alkylbenzenes in CLC, CEC, and GC at Constant Column Efficiency ( $N \sim 36\,000$ )<sup>a</sup>

compound	CLC ( $t_0 = 3.7$ min)		CEC ( $t_0 = 4.6$ min)		GC ( $t_0 = 0.3$ min)	
	$k$	$t_2/t_1$	$k$	$t_2/t_1$	$k$	$t_2/t_1$
benzene	0.43	1.00	0.35	1.00	0.10	1.00
toluene	0.55	1.09	0.46	1.08	0.27	1.15
ethylbenzene	0.68	1.18	0.56	1.16	0.54	1.39
<i>n</i> -propylbenzene	0.89	1.33	0.74	1.29	1.01	1.82
<i>n</i> -butylbenzene	1.16	1.51	0.96	1.46	1.98	2.70
<i>n</i> -amylbenzene	1.52	1.77	1.27	1.69	3.76	4.31
<i>n</i> -hexylbenzene	2.02	2.12	1.70	2.00	7.16	7.39
<i>n</i> -heptylbenzene	2.71	2.60	2.28	2.44	13.60	13.24
<i>n</i> -octylbenzene	3.65	3.26	3.06	3.02	25.72	24.22
<i>n</i> -nonylbenzene	4.97	4.18	4.15	3.83	48.56	44.93

<sup>a</sup> Conditions: Same as for experiment 1 in Table 1. Thiourea (CEC and CLC) and  $\text{CS}_2$  (GC) were used as nonretained compounds to determine  $t_0$  values. The retention time for benzene in each technique was assigned to be the  $t_1$  value.

( $k$ ) was possible only for CLC and CEC. Similar retention factors for CLC and CEC were obtained under the conditions given for experiment 2 in Table 1 using a column packed with  $3\text{-}\mu\text{m}$  nonporous particles for both experiments. Table 3 lists the retention factors for the 10 compounds for each technique. From these experiments,  $a$  and  $b$  values were obtained and used in eq 7 to calculate the peak capacities for these techniques for different  $t_2$  values. The results are presented in Figure 3. At a  $t_2$  value of 60 min, the peak capacities for CEC and CLC were 137 and 102, respectively. Since similar  $t_1$  values were used for the calculation of peak capacities, CEC generated a peak capacity higher than CLC due to higher efficiency (smaller  $a$  value in eq 7) from the pluglike profile. The total column efficiency for CEC was 58 000 plates versus 29 000 for CLC. Note that even though the efficiency for CEC is twice that for CLC, the peak capacity is higher only by  $\sim 35\%$ , which is due to the complex relationship between  $n$  and efficiency ( $a$ -containing terms) in eq 7.

The large difference in peak capacity (Figure 2) between GC and the liquid-phase separation techniques can be reduced by using particles with smaller diameters ( $1\text{--}1.5\ \mu\text{m}$ ), as this increases column efficiency. When a 26-cm column packed with

Table 3. Retention Factors ( $k$ ) for a Mixture of Alkylbenzenes in CLC and CEC ( $N_{CLC} \sim 29\,000$ ;  $N_{CEC} \sim 58\,000$ )<sup>a</sup>

compound	CLC $t_0 = 3.4$ min	CEC $t_0 = 2.9$ min
benzene	0.51	0.95
toluene	0.66	1.09
ethylbenzene	0.83	1.24
<i>n</i> -propylbenzene	1.09	1.46
<i>n</i> -butylbenzene	1.44	1.76
<i>n</i> -amylbenzene	1.91	2.16
<i>n</i> -hexylbenzene	2.56	2.70
<i>n</i> -heptylbenzene	3.49	3.46
<i>n</i> -octylbenzene	4.76	4.52
<i>n</i> -nonylbenzene	6.56	6.07

<sup>a</sup> Conditions: Same as for experiment 2 in Table 1. Thiourea was used as nonretained compound to determine  $t_0$  values.

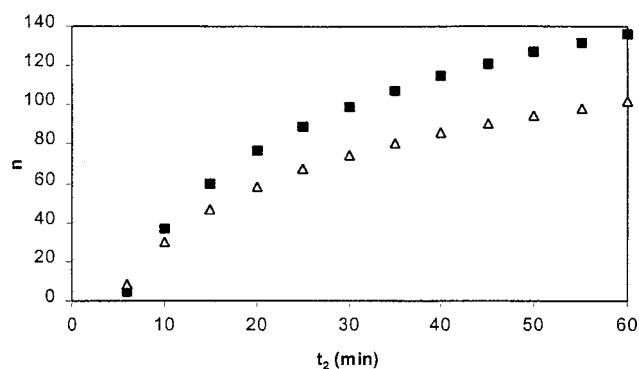


Figure 3. Calculated peak capacities ( $n$ ) for different  $t_2$  values for packed column CEC (■) and CLC (△), according to eq 7. The constants  $a$  and  $b$  used for these calculations are those given in Table 1, under experiment 2. The  $t_1$  values used in eq 7 for CEC and CLC were 5.66 and 5.13 min, respectively.

1.5- $\mu\text{m}$  nonporous particles was used, efficiencies for CEC and CLC became approximately the same because of a decrease in the effect of the hyperbolic flow profile in CLC. In addition, as this and other studies have demonstrated,<sup>20,21</sup> retention factors in CEC and CLC are similar under similar experimental conditions. For this column, peak capacities for CEC and CLC at a  $t_2$  value of 60 min were 139 and 148, respectively.

**Effect of Linear Velocity on Peak Capacity.** Several equations have been proposed for the calculation of peak capacity,<sup>1,3–5,7</sup> and all show a dependence of peak capacity on both efficiency and  $t_1$ . However, no systematic studies have been carried out on the effect of linear velocity on peak capacity. Even though linear velocity does not seem to be directly involved in eq 7 for the calculation of peak capacity, indeed, it plays a very important role. Linear velocity affects both column efficiency (according to the van Deemter equation) and, hence, the  $a$ -containing terms in eq 7, as well as the  $t_1$  value, which determines the width of the retention window. In practice, separations are carried out at linear velocities near, or higher than, the optimum velocity. Under these conditions, an increase in linear velocity generates two opposite effects; it reduces the efficiency (increasing  $a$  values in eq 7),

Table 4. Effect of Linear Velocity ( $u$ ) on Peak Capacity ( $n$ ) in CLC, CEC, and GC<sup>a</sup>

	CLC	CEC	GC
Experiment 1			
$u$	1.1 mm s <sup>-1</sup>	1.2 mm s <sup>-1</sup>	33.5 cm s <sup>-1</sup>
$t_1$ (min)	4.07	4.27	0.53
$N$ (plates)	48 000	34 000	39 000
$n$ (at 60 min)	148	120	248
Experiment 2			
$u$	2.2 mm s <sup>-1</sup>	1.8 mm s <sup>-1</sup>	55.5 cm s <sup>-1</sup>
$t_1$ (min)	2.15	2.58	0.33
$N$ (plates)	40 000	28 000	37 000
$n$ (at 60 min)	164	133	266

<sup>a</sup> Conditions: A mixture of 10 alkylbenzenes (benzene to *n*-nonylbenzene) was used for all experiments;  $t_1$  values were assigned from the retention time for benzene in each separation technique. (CLC) 26 cm  $\times$  75  $\mu\text{m}$  i.d. fused-silica capillary packed with 1.5- $\mu\text{m}$  nonporous ODS1 particles; ACN/H<sub>2</sub>O (65:35) mobile phase, UV detection at 210 nm. Experiment 1: 7500 psi (5.15  $\times$  10<sup>4</sup> kPa). Experiment 2: 15 000 psi (1.3  $\times$  10<sup>5</sup> kPa). (CEC) 25 cm  $\times$  75  $\mu\text{m}$  i.d. fused-silica capillary packed with 3- $\mu\text{m}$  porous ODS1; ACN/Tris buffer (80:20, 50 mM, pH 8.2) mobile phase, UV detection at 210 nm; 5 kV, 1 s electrokinetic injection. Experiment 1: 20 kV applied voltage. Experiment 2: 30 kV applied voltage. (GC) 10 m  $\times$  200  $\mu\text{m}$  i.d., DB-5 fused-silica capillary column; He carrier gas, 100 °C oven temperature; FID detection.

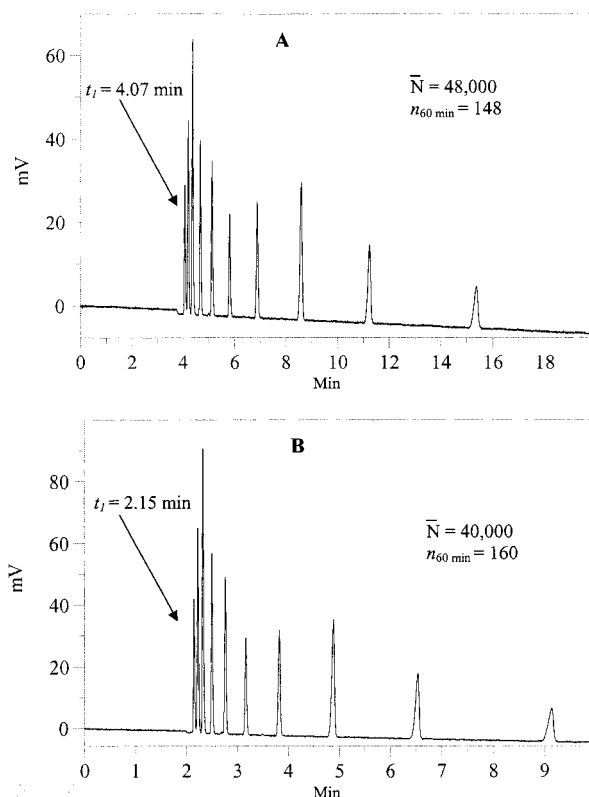


Figure 4. CLC chromatograms of a mixture of alkylbenzenes (benzene to *n*-nonylbenzene). Separations at (A) 7500 and (B) 15 000 psi. Experimental conditions are given in Table 4.

which reduces the peak capacity, but at the same time reduces  $t_1$ , which creates a wider retention window and, therefore, increases peak capacity. Experiments were carried out to study the net effect of linear velocity on peak capacity. These experiments were performed at values close to the optimum velocity for each technique and also at linear velocities roughly twice the optimum values. The results are presented in Table 4. As can be

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seen, an increase in linear velocity increases the peak capacity for all three techniques. In practice, separations should be performed at the maximum linear velocity allowed by the desired resolution. This will increase peak capacity and reduce analysis time.

Finally, we wanted to determine whether it is possible for the liquid-phase separation techniques to obtain peak capacities as high as that of gas chromatography, assuming equal total column efficiency. To maximize the efficiency of CEC and CLC, small particles must be used. Furthermore, since  $t_1$  values for GC typically are smaller than those of the liquid-phase separation techniques, very high voltages (CEC) or ultrahigh pressures (CLC) must be used to reduce  $t_1$ . Data from the chromatograms presented in Figure 4 show that almost a linear relationship exists between head pressure and  $t_1$  in CLC. Using a pressure of 7500 psi, a  $t_1$  value of 4.1 min was generated, while doubling the pressure reduced the  $t_1$  value almost by half. It is estimated that in order to obtain a  $t_1$  value similar to that found in GC in this

study (0.3 min) a pressure of  $\sim 95\,000$  psi would be required. Such a high pressure has been already achieved.<sup>22</sup> Results from this laboratory have demonstrated that the linear relationship between head pressure and  $t_1$  holds true at ultrahigh pressures,<sup>23</sup> and similar resolution and retention factors are obtained. In addition, van Deemter plots for columns packed with small particles are very flat, which allows the use of very high linear velocities without significant deterioration of column efficiency.<sup>16,22,23</sup>

In the case of CEC, as the second column of Table 4 and results from several research groups show,<sup>24,25</sup> the electroosmotic flow and linear velocity for a given column are proportional to the applied voltage. Therefore, it is estimated that in order to achieve a  $t_1$  value of 0.3 min using a 26-cm column packed with 1.5- $\mu\text{m}$  nonporous particles, a potential of  $\sim 300\,000$  V would be required. This obviously would be plagued with technical difficulties and safety issues. Bubble formation, due to generation of unusually high Joule heat, would be one of these problems. The use of CLC with ultrahigh pressures would be more feasible for the achievement of high peak capacities than CEC.

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