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Pressure-Tunable Column Selectivity for High-Speed Vacuum-Outlet GC

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A pressure-tunable ensemble of two series-coupled capillary columns operated at subambient outlet pressure is described. The ensemble consists of a 4.5-m length of nonpolar dimethyl polysiloxane column followed by a 7.5-m length of polar trifluoropropylmethyl polysiloxane column. Air at an inlet pressure of 1.0 atm is used as carrier gas, and a vacuum pump is used to pull the carrier gas and injected samples through the column ensemble. Detection is provided by a photoionization detector operated at a pressure of 0.3 psia. Ensemble selectivity is controlled by means of an electronic pressure controller located at the junction point between the columns. The minimum pressure step size is 0.1 psi, and 50 different set-point pressures can be used, each one producing a different pattern of peaks eluting from the column ensemble. Measured ensemble retention factors for a set of target compounds produce straight lines when plotted versus the ratio of the calculated holdup time of the first column in the ensemble to the total ensemble holdup time. A component band trajectory model is used to describe the effects of ensemble junction-point pressure on the elution patterns generated by the ensemble. Ensemble retention times predicted by the model are in good agreement with values obtained from chromatograms. The use of on-the-fly set-point pressure changes during a separation (selectivity programming) is demonstrated and used to improve the quality of the separation of a 19-component test mixture.

Vacuum-outlet gas chromatography (GC) involves the use of a vacuum pump to pull carrier gas and injected samples through a capillary separation column.[1–4] Vacuum-outlet techniques are useful for increasing analysis speed and for reducing detector dead time for some closed-cell detectors.[5–7] When the outlet of a column is connected directly to the ion source of a mass spectrometer, the column outlet pressure is typically less than 10^{-4} Torr. However, conventional GC/MS is conducted using relatively long capillary columns. For long columns, the improvement in analysis speed obtained with vacuum-outlet operation is small compared to the same column operated with atmospheric pressure at the column outlet.

Vacuum-outlet GC obtains its speed advantage from the increased gas-phase binary diffusion coefficient values for the sample molecules in the carrier gas at reduced carrier gas density. Larger gas-phase diffusion coefficient values improve mass transport in the gas phase. This shifts the optimal carrier gas velocity u_{opt} to larger values and results in significantly smaller plate height for average carrier gas velocities greater than u_{opt}. The improvement in analysis speed can be large when the column-inlet pressure is less than 1 atm.[3] However, as the column length increases and as the diameter decreases, the inlet pressure required to achieve suitable average linear carrier gas velocity values increases, and subambient inlet pressure is not practical. Thus, most studies designed to achieve increased analysis speed by the use of vacuum-outlet techniques have used relatively short, wider bore columns.

Carrier gas acceleration from the inlet to the outlet end of a column is much greater under vacuum-outlet conditions relative to the same column operated with atmospheric outlet pressure. The resulting very high local velocity of the carrier gas as it exits the column can be useful for reducing the dead time associated with closed-cell detectors including the thermal conductivity detector[7] and the photoionization detector (PID).[4,5] The high carrier gas velocity in the detector results in the detector cell volume being swept more quickly, and detector response time can be substantially reduced, which is very useful for high-speed GC (HSGC).

The range of column dimensions and operating conditions for which vacuum-outlet operation obtains a substantial speed advantage (shorter columns, wider bore columns), results in relatively low column resolving power. Thus, the use of vacuum-outlet HSGC has been restricted to demonstrations using simple mixtures.

In recent studies, vacuum-outlet HSGC has been used to obviate the need for cylinders of compressed carrier gas.[5,8] These studies were aimed at reducing size and weight of field-portable GC instruments. To this end, atmospheric pressure air was used as carrier gas, and a vacuum pump was used to pull the carrier gas and injected samples through a GC/PID system using 6–12-m-long, 0.25-mm-i.d. columns. The separations obtained for these studies yielded theoretical plate numbers in the range 12 000–44 000. These values are inadequate for complex mixtures, and thus, more attention must be paid to column selectivity if these

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instruments are to find broad-based application.

The enhanced selectivity needed for HSGC with atmospheric outlet pressure and flame ionization detection has been achieved by the use of pressure-tunable, series-coupled ensembles of two capillary columns using different stationary-phase chemistries.[8-12] By adjusting the carrier gas pressure at the junction point between the coupled columns, the ratio of the column holdup times can be changed. This changes the relative contributions that each of the columns makes to the ensemble selectivity. If the stationary-phase chemistries of the two columns are sufficiently different for a specified set of target compounds, changes in the pressure at the column junction point can produce large changes in the pattern of peaks eluting from the ensemble. When air is used as the carrier gas, the selection of columns used in the pressure-tunable ensemble is limited by the stability of the stationary phases in air at elevated temperatures.

Electronic control of the junction-point pressure has been used to obtain very reproducible and computer-selectable ensemble selectivity.[13-15] A pressure controller with a step size of 0.1 psi (0.69 kPa) and a set-point repeatability of ±0.01 psi has been shown to be very satisfactory. For a junction-point pressure range of 10 psi, 100 different set-point pressures are available, each one producing a unique pattern of peaks eluted from the column ensemble.

With computer control of the column junction-point pressure, on-the-fly set-point pressure changes can be implemented during a separation. This provides a means for obtaining ensemble selectivity programming.[16,17] With selectivity programming, the initial column junction-point pressure is set to give the desired elution peak pattern for the early-eluting mixture components. Sometime after sample injection, the set-point pressure is changed in order to facilitate the separation of the later-eluting components.

This report considers the use of a pressure-tunable column ensemble for vacuum-outlet GC. A vacuum-outlet HSGC instrument designed for use with atmospheric pressure air as carrier gas[6] was modified for this study. The unique challenge here is the control of the column junction-point pressure at subambient values. A computer model is used to predict sample band trajectories through the column ensemble. The model is used to compare pressure-tunable column ensembles for vacuum-outlet operation to systems designed for atmospheric pressure operation. The model is also used to predict elution pattern changes caused by changes in the set-point pressure initiated during a separation (pressure programming).

EXPERIMENTAL SECTION

Apparatus. The vacuum-outlet instrument modified for these studies has been described in detail.[5,6] Figure 1 presents a simplified drawing of the system showing the series-coupled column ensemble C_1 and C_2, the column junction-point pressure control system EPC, and a vacuum vent line R used to extend the selectivity tuning range and to prevent contamination of the pressure controller. All components are mounted on a Varian 3700 GC (Varian, Walnut Creek, CA). The instrument uses a cryofocusing inlet system CI[18,19] (Cryointegrator model L, Chromatofast, Ann Arbor, MI), which delivers to the column ensemble sample vapor plugs that are 5–10 ms in width. This contributes no significant extracolumn band broadening for the retention time range considered in this study.

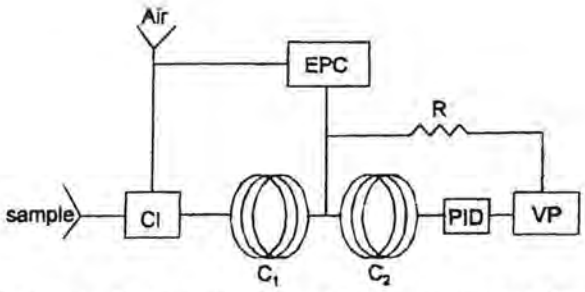

Figure 1. Vacuum-outlet GC with pressure-controlled column selectivity. C_1, nonpolar column; C_2, polar column; PID, photoionization detector; VP, vacuum pump; EPC, electronic pressure controller; R, capillary pneumatic restrictor used as vent line; CI cryofocusing inlet system.

A PID (model PI 52-02A, HNU Systems, Newton, MA) equipped with a 10.2-eV lamp and operated at a pressure of 0.3 psia (2.1 kPa) was used for all measurements. The detector cell volume is less than 100 μL. At this pressure, the detector contributes no significant extracolumn band broadening. This low detector pressure is provided by a laboratory vacuum pump VP (CENCO, model HYVAC 14, Central Scientific Co., Chicago, IL), which is connected directly to the detector outlet.

The column ensemble consists of a 4.5-m length of nonpolar dimethyl polysiloxane (DB-1, J&W Scientific, Folsom, CA) followed by a 7.5-m length of trifluoropropylmethyl polysiloxane (Rtx-200, Restek, Bellafonte, PA). These column lengths were chosen to obtain nearly equal carrier gas holdup times for the two columns in the absence of any additional connections at the column junction point. This length ratio reflects the greater carrier gas velocity in the second column resulting from decompression along the ensemble length and provides the largest symmetric tuning range. Both columns have 0.25-mm i.d. and use 0.25-μm-thick bonded stationary phases.

Column junction-point pressure control is provided by an absolute pressure capacitance–manometer device EPC (model 640A, MKS Instruments, Andover, MA). The control range is 0–100 psia in 0.1 psi steps. Repeatability typically is ±0.01 psi. Tank air for carrier gas is supplied to the pressure controller as well as to the cryofocusing inlet after purification with filters for water vapor and hydrocarbons. The tank delivery pressure is adjusted to provide a head pressure for the first column in the ensemble of 1.0 standard atmosphere (101 kPa). The column head pressure and detector pressure are monitored by means of digital pressure gauges (not shown in Figure 1).

A vent line consisting of a 1.0-m length of 0.25-mm-i.d. fused-silica tubing R is connected from the outlet of the pressure

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Table 1. Compounds and Boiling Points for Text Mixtures

no.	name	bp (°C)
1	acetone	56.2
2	ethyl acetate	77.1
3	benzene	80.1
4	isopropyl alcohol	82.4
5	trichloroethylene	86.7
6	2,5-dimethylfuran	93
7	heptane	98.4
8	2,4-dimethylhexane	109
9	toluene	110.6
10	1-butanol	117.6
11	2-methylheptane	118
12	tetrachloroethylene	121.1
13	octane	126
14	butyl acetate	126.1
15	chlorobenzene	130
16	hexanal	131
17	ethylbenzene	136.2
18	p-xylene	138.3
19	m-xylene	139.1

controller to the vacuum pump. This line prevents contamination of the pressure controller when the set-point pressure is less than the pressure at the column junction point in the absence of any external connections (natural junction-point pressure). The vent line also provides a low-restriction path to vent the internal volume of the pressure controller and the connecting plumbing. This results in more rapid pressure equilibration when the set-point pressure is changed.[17] When the set-point pressure is less than the natural junction-point pressure, sample and carrier gas from the first column in the ensemble is split between the second column and the vent line. This results in reduced peak areas in the chromatograms from the column ensemble. The quantitative aspects of sample splitting are not considered in this work.

Materials and Procedures. Table 1 lists the compounds and their boiling points used to prepare test mixtures. It contains common solvents and widely used organic compounds that are of interest in indoor air monitoring.[20] Vapor samples were prepared in a 3.8-L Tedlar gas sampling bag (Chromatography Research Supplies, Inc., Addison, IL) and diluted with clean, dry air. Pure liquid compounds (reagent grade or better) were mixed in the desired ratio, and an aliquot of the mixture was injected into the bag. After equilibration, the entire sample is in the vapor phase. A small vacuum pump on board the cryofocusing inlet system draws ~0.5 mL of the sample into a chilled capillary metal trap tube for focusing and subsequent injection into the column ensemble.

Data acquisition and junction-point pressure control were obtained with a 350-MHz Pentium II computer through a 16-bit A/D board (C10-DAS1602/16, Computer Boards, Inc., Middleboro, MA). Chromatograms were recorded with a sampling rate of 100 Hz. Labtech Notebook software (Laboratory Technologies Corp., Wilmington, MA) was used for interface control. Recorded chromatograms were processed with Grams/32 software (Galactic Industries Corp.). It was difficult to obtain reliable ensemble holdup time measurements with the PID, and without a second detector to monitor the effluent from the first column, holdup times for the individual columns could not be obtained. Thus, holdup times were calculated using standard gas-dynamic equations.[21] Excel spreadsheets were used for all calculations.

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RESULTS AND DISCUSSION

Comparison of Tandem-Column Operation with Atmospheric Pressure Outlet and Vacuum Outlet. When columns are combined in tandem so that all sample components pass through both columns, holdup times as well as retention times for the individual columns are additive, and ensemble values of holdup time t_{mo}, retention time t_{Ro}, and retention factor k_o for every mixture component can be defined.

$$t_{Ro} = t_{R1} + t_{R2} = t_{m1}(k_1 + 1) + t_{m2}(k_2 + 1) \quad (1)$$

$$k_o = (t_{Ro} - t_{mo})/t_{mo} = f_1 k_1 + f_2 k_2 \quad (2)$$

Here, subscripts 1 and 2 refer to the corresponding columns in the ensemble and f_1 and f_2 are weighting factors corresponding to the fractional contribution that each column makes to the ensemble value k_o. Values of f_1 and f_2 are equal to the fractions of the ensemble holdup time that can be attributed to the respective columns.

$$f_1 = t_{m1}/t_{mo} \quad \text{and} \quad f_2 = t_{m2}/t_{mo} \quad (3)$$

In previous work[16,17] with tandem column ensembles operated with atmospheric outlet pressure and flame ionization detection, two detectors were used so that t_{m1} and t_{mo} could be measured for every experiment. For the vacuum-outlet system using PID detection, direct measurement of these values was not practical, and holdup time values for the individual columns were calculated by the use of eq 4, where η is the carrier gas viscosity, L is the

$$t_m = [32\eta L^2(P^3 - 1)]/[(3/4)d^2 p_o(P^2 - 1)^2] \quad (4)$$

column length, d is the column diameter, P is the inlet-to-outlet pressure ratio (p_i/p_o), and p_o is the column-outlet pressure. For these calculations, the viscosity of air at 30 °C was used. The inlet pressure for the first column was assumed to be 1.0 atm, since the pressure was adjusted to this value for each experiment, and the outlet pressure was the column junction set-point pressure. The junction set-point pressure was also used as the inlet pressure for the second column, and the detector pressure value of 0.3 psia was used as the outlet pressure.

A simple model and computational procedure were recently described for obtaining sample band migration plots (band position along the column axis vs time) for series-coupled column ensembles using pressure-tunable selectivity.[17] The model considers the changes in local carrier gas velocity in the ensemble resulting from acceleration along the column axis and from programmed changes in the pressure at the column junction point. The model also considers the changes in retention factors as sample components migrate across the column junction point.

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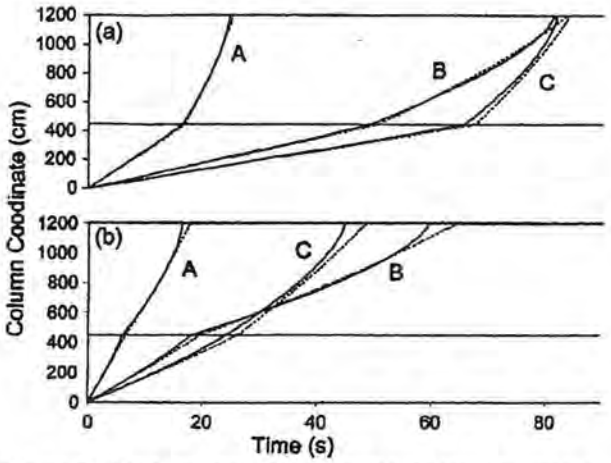

Figure 2. Band migration plots comparing atmospheric pressure-outlet (broken lines) and vacuum-outlet operation (solid lines) for conditions giving holdup time contributions of the first column of 67.4% (a) and 36.7% (b). See text for details. A, unretained component; B, $k_1 = 2.0$ and $k_2 = 3.0$; C, $k_1 = 3.0$ and $k_2 = 1.0$.

The carrier gas velocity profile along the axis of a column is described by

$$u_x/u_o = 1/[P^2 - (x/L)(P^2 - 1)]^{1/2} \quad (5)$$

where u_x is the local carrier gas velocity at column coordinate x and u_o is the column-outlet gas velocity.

$$u_o = (d^2/32)(P^2 - 1)p_o/2\eta L \quad (6)$$

For the model, the column is divided into 1.0-cm-long intervals, and the local carrier gas velocity is computed for each interval. From these values and the component retention factor on the column, the time required for the band to traverse each interval is computed. Summation of these times from the inlet end of the column to any column coordinate x gives the time required for the band to reach coordinate x.

Figure 2 depicts the migration of bands with various retention factors versus time for operation at atmospheric-outlet pressure (broken lines) and vacuum-outlet operation (solid lines) at 0.3 psia. The horizontal line at a column coordinate of 450 cm represents the junction point between the 450-cm-long nonpolar first column and the 750-cm-long polar second column. For the vacuum-outlet case, the inlet pressure was 1 atm (14.7 psia), and for the atmospheric pressure-outlet case, the inlet pressure was 26.0 psia. This latter value is the inlet pressure required to give the same average linear carrier gas velocity as for the vacuum-outlet case for a 12-m column with a 0.25-mm i.d. The carrier gas was air at 30 °C.

The upper plots (a) are for junction-point pressures of 24.4 and 13.0 psia for the atmospheric pressure-outlet case and the vacuum-outlet case, respectively. For these values, the first column contributes 67.4% to the ensemble holdup time, and the second column contributes 32.6%. These values correspond to the contributions that the respective columns make to the ensemble selectivity. The lower plots (b) are for junction-point pressures of 21.7 and 10.0 psia for the atmospheric pressure-outlet case and the vacuum-outlet case, respectively. Here the first column contributes 36.7% to the ensemble holdup time, and the second column contributes 63.3%. Note that if the column order in the ensemble is reversed, the fractional contributions change significantly due to the effects of carrier gas decompression along the column axis.

Plots labeled A are for an unretained band. Note that for case (a) the migration velocity increases sharply as the band migrates across the column junction. This is because the junction-point pressure is greater than the pressure that would occur at this point along the ensemble axis in the absence of any external connections. The opposite situation occurs for case (b). In all cases, the band trajectories for the atmospheric pressure and vacuum-outlet cases are quite similar except for the last 200 cm of the ensemble where the vacuum-outlet band trajectories show rapid acceleration.

Plots labeled B are for a mixture component having retention factors of 2.0 and 3.0 on the nonpolar and the polar columns, respectively. Plots labeled C are for a component having retention factor values of 3.0 and 1.0, respectively. For case (a), components B and C nearly coelute from the column ensemble. While the retention times are shifted to earlier values for the vacuum-outlet case, the peak separation is nearly the same as for the atmospheric pressure-outlet case. For case (b), much larger peak separation is obtained, and larger differences are observed in the band trajectories for the vacuum-outlet and the atmospheric pressure-outlet cases. This is because of the greater contribution (lower local carrier gas velocity) of the second column for case (b). Here, the shift to smaller retention times for the vacuum-outlet case is considerably larger than for case (a). Again, the peak separation is not appreciably effected by the use of vacuum-outlet operation.

Note that the band migration plots for the atmospheric-outlet and the vacuum-outlet cases cross twice in the second column for components A and B. This is observed for both values of junction-point pressure and is the result of the differences in the carrier gas velocity profiles for the different outlet pressure values and the small differences in the time at which these components enter the second column for the two different pressure regimes.

The practical range of junction-point pressures for vacuum-outlet operation using the instrument and column lengths described here extends from 8.0 to 13.0 psia. Higher pressures resulted in some peak doubling. This appears to be an artifact of the cryofocusing inlet system. While pressures lower than 8.0 psia could be used, excessive sample splitting to the vent line resulted in inadequate sample reaching the detector for the concentrations used in this study. This pressure range corresponds to a range of contributions of the first column from 24.9% to 67.4%. Since the minimum pressure step size is 0.1 psi for the controller used in this work, a total of 50 unique set-point pressures can be used, and each of these results in a somewhat different pattern of eluted peaks.

Selectivity Tuning for Vacuum-Outlet GC. Figure 3 illustrates the degree of control over peak positions that can be obtained with a pressure-tunable column ensemble used with vacuum-outlet conditions. Peak numbers correspond to the compound numbers in Table 1. For the three component peaks

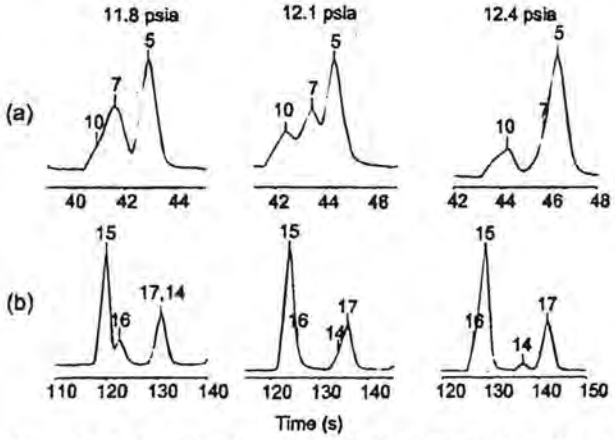

Figure 3. Chromatograms of two component groups from Table 1 using different values of junction-point pressure.

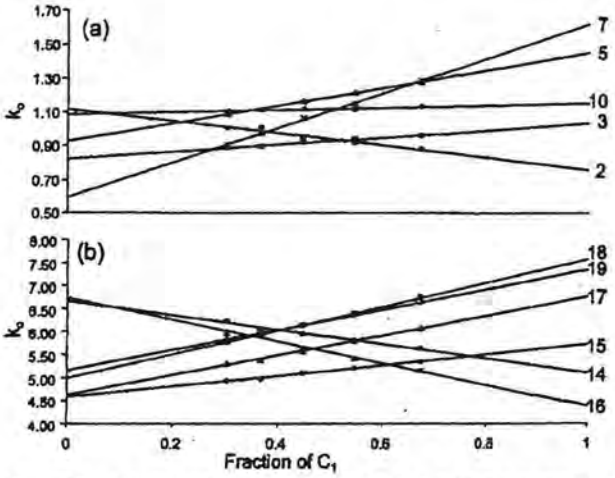

Figure 4. Plots of ensemble retention factors k_0 vs the calculated holdup time fraction for column C_1. Numbers next to the plots correspond to compound numbers in Table 1. Extrapolations to fraction values of 1.0 and 0 give the corresponding retention factors on C_1 and C_2, respectively.

shown in Figure 3a, peak 10 appears as a shoulder on the left flank of peak 7 for a junction-point pressure of 11.8 psia. When the pressure is increased to 12.1 psia, the elution order of components 7 and 10 changes, and the resolution is improved. For a pressure of 12.4 psia, peak 7 now elutes on the left flank of peak 5. This example clearly shows the ability to shift the retention order of components in a mixture.

The mixture used for the chromatograms shown in the lower portion of Figure 3 contained four components. At 11.8 psia, components 14 and 17 coelute. If the junction-point pressure is increased to 12.1 psia, components 15 and 16 merge, and component 14 appears as a shoulder on the left flank of peak 17. If the pressure is increased to 12.4 psia, component 16 appears as a shoulder on the left flank of component 15, and components 14 and 17 are completely separated.

Figure 4 shows plots of ensemble retention factors k_0 versus the fractional contribution of the first column in the ensemble for two groups of components where pressure selectivity tuning can be useful in improving the quality of the separation. Numbers by the plots correspond to the compound numbers in Table 1. These

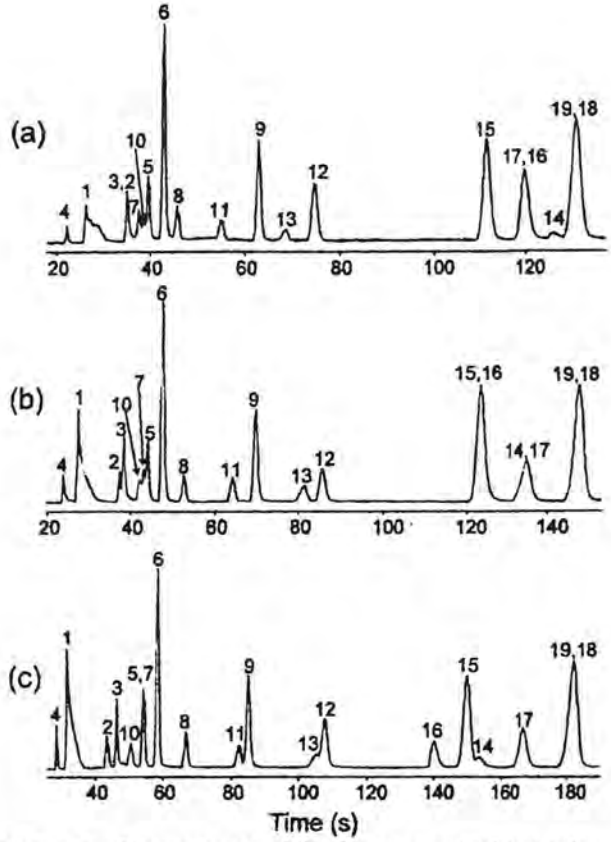

Figure 5. Chromatograms of the 19-component mixture using junction-point pressure values of 10.9 (a), 12.1 (b), and 13.1 (c) psia. Peak numbers correspond to compound numbersin Table 1.

retention factors were computed from measured values of ensemble retention times and calculated values of ensemble holdup times. The fraction values were computed from the ratio of the calculated holdup time for the first column to the calculated ensemble holdup time. Since retention times for the two columns are additive, a linear relationship is expected for each compound.[13,22] The lines shown in the figure are linear regression fits for each compound. Correlation coefficients are in the 0.98–0.9999 range for most of the compounds studied. For 1-butanol (plot 10), the correlation coefficient was 0.83 due to the very small slope value.

Note that the fraction value corresponding to any crossing point of a pair of plots in Figure 4 results in coelution of the corresponding component pair. No fraction value in the available tuning range results in adequate separation of *m*-xylene (plot 19) and *p*-xylene (plot 18). The examination of similar plots for all 19 of the mixture components reveals that, with either column alone, at least two nearly complete coelutions will occur not including the two xylene isomers.

Figure 5 shows complete chromatograms of the 19-component mixture using junction-point pressure values of 10.9 (a), 12.1 (b), and 13.1 (c) psia. The corresponding contributions from the first column are 43.8%, 55.8%, and 68.3%, respectively. The broad and distorted acetone peak (peak 1) is an artifact produced by the cyrofocusing inlet system and is related to the high volatility of

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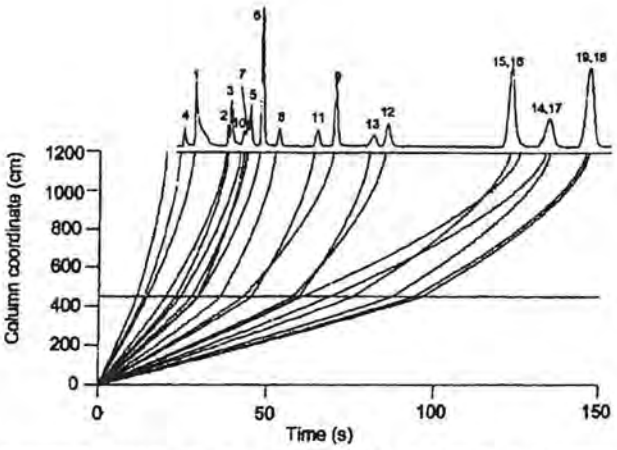

Figure 6. Band trajectory plots for the 19-comonent mixture using a junction-point pressure of 12.2 psia. Retention factor values for the two columns were found from the extrapolations of plots such as those in Figure 4 for all 19 mixture components. The chromatogram show above the plots was obtained at a junction-point pressure of 12.1 psia. Peak numbers correspond to the compound numbers in Figure 4.

Table 2. Predicted and Experimental Retention Times for the 19-Component Test Mixture

		12.1 psia		12.2 psia	
compound name	expt	pred	% diff	pred	% diff
unretained	19.80	19.32	2.43	19.68	0.60
isopropyl alcohol	24.16	23.49	2.81	23.92	1.01
acetone	28.21	27.52	2.46	27.95	0.91
ethyl acetate	37.60	37.08	1.40	37.68	−0.22
benzene	38.59	37.49	2.88	38.24	0.92
1-butanol	42.42	41.04	3.30	41.82	1.43
heptane	43.25	41.90	3.16	42.91	0.78
trichloroethylene	44.30	42.91	3.19	43.82	1.08
2,5-dimethylfuran	47.84	46.46	2.92	47.44	0.83
2,4-dimethylhexane	52.92	51.02	3.66	52.26	1.25
2-methylheptane	64.39	61.89	3.96	63.47	1.44
toluene	69.99	68.07	2.78	69.49	0.72
octane	80.80	78.22	3.25	80.31	0.60
tetrachloroethylene	85.74	82.95	3.31	84.92	0.96
chlorobenzene	123.29	120.21	2.53	122.69	0.49
hexanal	123.29	123.95	−0.53	125.70	−1.94
butyl acetate	135.05	131.38	2.75	133.46	1.19
ethylbenzene	135.05	131.84	2.41	134.77	0.21
m-xylene	147.18	142.70	3.09	145.84	0.91
p-xylene	147.18	143.55	2.49	146.80	0.26

acetone. From Figure 4, the coelution of components 16 and 17 is expected for the 10.9 psia junction pressure. Also, the near coelution of components 2 and 3 is predicted from the plots in Figure 4.

When the pressure is increased to 12.1 psia (Figure 5b), near coelution is seen for peak pairs 15/16 and 14/17. Again, this is consistent with the plots in Figure 4. Also note the elution order change for peak pair 2/3. The junction-point pressure value of 12.1 psia gives the best separation of the congested region of the chromatogram containing peaks 2, 3, 5, 7, and 10. While complete separation is not achieved, all five peak apexes are clearly seen. Note, however, that this junction-point pressure results in poor separation of components 14−17.

When the junction-point pressure is increased to 13.1 psia, the separation of components 14−17 is significantly improved. Also, components 2, 3, and 10 are completely separated. However, components 5 and 7 coelute, and components 12 and 13 show excessive overlap.

Extrapolation of the plots in Figure 4 to fraction values of 0 and 1.0 provides estimates of the component retention factors on the individual columns. These values were used in the band trajectory model for all 19 of the mixture components. Band trajectory plots were generated for junction-point pressure values of 12.0, 12.1, and 12.2 psia. The results are shown in Figure 6 for 12.2 psia. The ends of the band position versus time plots at column coordinate 1200 cm gives the predicted retention times for the mixture components. The chromatogram obtained at a junction pressure of 12.1 psia (Figure 5b) is shown above the band trajectory plots. This pressure value provides the best separation of the first 12 components.

The predicted elution order is correct for all components. The accuracy of predicted retention times is summarized in Table 2. Values of relative error range from −0.53% to 3.96% for the model using a junction-point pressure of 12.1 psia. If a junction-point pressure of 12.2 psia is used in the model, the accuracy of the predicted retention times is significantly improved. Note that this discrepancy of 0.1 psia is near the measurement and control

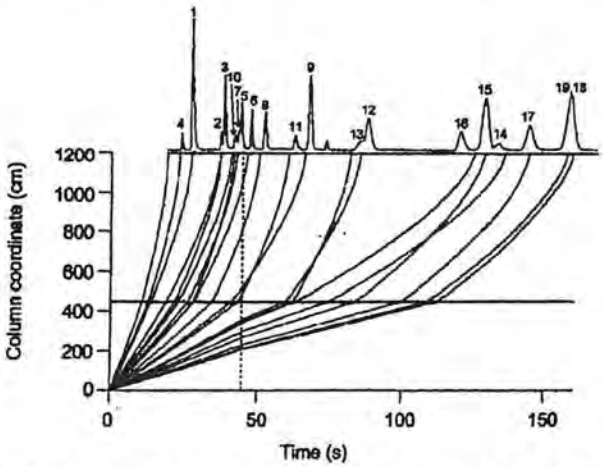

Figure 7. Band trajectory plots and chromatogram for the 19-comonent mixture using a junction-point pressure of 12.1 psia for the first 45 s of the chromatogram, and a pressure of 13.1 psia after 45 s. Retention factor values for the two columns were found from the extrapolations of plots such as those in Figure 4 for all 19 mixture components. Peak numbers correspond to the compound numbers in Figure 4.

resolution limit of the pressure controller and may reflect either control or measurement error as well as small differences between the actual column dimensions and those used in the model.

Selectivity Programming. The chromatograms shown in Figure 5 demonstrate that a junction set-point pressure of 12.1 psia (chromatogram b) provides the best separation of components 1−12 while a pressure of 13.1 psi results in significantly better separation of components 14−19. This suggests that a change in junction-point pressure (programmable selectivity) could be useful in improving the quality of the separation for the complete mixture. Figure 7 shows band trajectory plots for the 19 components for the case where the junction-point pressure is initially set at 12.1 psi, and 45 s after injection, the pressure is changed to 13.1 psia. This is indicated by the broken vertical line

in Figure 7. The chromatogram obtained with this pressure program is shown above the band trajectory plots.

Mixture components 1−5, 7, and 10 elute from the column ensemble prior to the pressure change, and their retention times and elution pattern are unaffected by the pressure change. Components 6, 8, 9, and 11 are on the second column when the pressure increase occurs, and their migration velocities increase slightly following the pressure change. The remainder of the components is still on the first column when the pressure change occurs, and significant decreases in migration velocities (slopes of the band trajectory plots in Figure 7) occur to the right of the broken vertical line.

Te elution pattern in the chromatogram for components 14−19 in Figure 7 is similar to the pattern seen in chromatogram (c) of Figure 5. Component peaks 12 and 13, however, show significantly more overlap than in the chromatogram of Figure 5c. Note that the chromatogram obtained with selectivity programming has fewer coelutions than could be obtained with any single selectivity. Adjustment of the time at which the pressure change is initiated and the final junction-point pressure may achieve further performance enhancements. In addition, multiple pressure changes may be useful for some mixtures.

The instrument used for these studies does not have inlet pressure control, and the inlet pressure was adjusted to 1.0 atm for each column junction set-point pressure used to demonstrate selectivity tuning. For the set-point pressure programming experiments, the inlet pressure was initially set to 1.0 atm (14.7 psia) for the initial set-point pressure of 12.1 psia. The inlet pressure increased to 14.9 psia when the set-point pressure was changed under program control. This may account for the somewhat poorer agreement between the model and the measured retention times for components 12−19 observed in Figure 7 compared to Figure 6 where no on-the-fly set-point pressure change was used.

CONCLUSIONS

Vacuum-outlet GC with a PID detector provides a means for the elimination of all compressed gas tanks for portable instruments. While the use of a vacuum pump will increase the power budget for the instrument, the intended use of the instrument is for indoor air-quality monitoring, and battery operation is not anticipated. Pressure-tunable tandem column ensembles are very useful for vacuum-outlet GC and will significantly aid in the development of lightweight, portable GC instruments, which will operate with atmospheric pressure air as carrier gas. Practical instrumentation, which will use a small on-board vacuum pump, will require operation at significantly higher outlet pressures than the 0.3 psia value used here. The absolute pressure capacitance manometer used in these studies should be satisfactory for higher outlet pressures, but with atmospheric pressure carrier gas at the inlet, the available tuning pressure range is limited. This will limit the maximum number of available set-point pressures.

The 12-m total column length (ensemble length) used in these studies is too long to take full advantage of vacuum-outlet operation of the column. Longer columns are needed with this complex mixture to get increased resolution. Also, with atmospheric pressure air as carrier gas, longer columns are needed to achieve average carrier gas velocity values closer to u_{opt}. This is particularly important with air because its large viscosity and smaller gas-phase binary diffusion coefficients relative to hydrogen and helium results in more rapid loss in efficiency for average carrier gas velocity values greater than u_{opt}.

Further work is needed to develop optimization algorithms and procedures for selecting the pressure program that will result in the most complete high-speed separation of a set of target compounds. Further work also is needed to develop detectors having small enough dead volumes to permit operation at significantly higher outlet pressures. Microfabricated surface acoustic wave detector and multichannel detector arrays are under development for these applications.[23,24]

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