Anal. Chem. **2002,** *74,* 246−252

Selectivity Enhancement for High-Speed GC Analysis of Volatile Organic Compounds with Portable Instruments Designed for Vacuum-Outlet and Atmospheric-Pressure Inlet Operation Using Air as the Carrier Gas

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A tandem ensemble of two 4.5-m-long × 0.25-mm-i.d. capillary columns with the first using a 0.50-μm film of nonpolar dimethyl polysiloxane and the second using a 0.25-μm film of polar trifluoropropylmethyl polysiloxane is operated with atmospheric pressure air as the carrier gas and an outlet pressure of 50.5 kPa established using a small vacuum pump. A thicker stationary-phase film is used in the first column to increase retention for very volatile compounds. This significantly increases the resolution of these compounds. The thicker film in the first (nonpolar) column decreases the polarity of the tandem column ensemble and, thus, changes its selectivity. A low-dead-volume valve, connected between the column junction point and a source of atmospheric pressure air, is used to obtain pulsed modulation of the carrier gas flow through the column ensemble. When the valve is open, the ensemble inlet pressure and the junction-point pressure are nearly the same, and carrier gas flow nearly stops in the first column, and flow in the second column increases. Enhanced resolution of a component pair that is separated by the first column but coelutes from the column ensemble can be obtained if the valve is opened for a few seconds after one of the components has crossed the junction and is in the second column, but the other component is still in the first column. A sequence of appropriately timed pulses is used to obtain enhanced resolution of several pairs of components that coelute from the column ensemble. These methods enabled the complete separation of an 18-component vapor mixture of common solvents in air in 3.5 min.

Field-portable GC instruments designed for high-speed analyses of air-borne organic vapors often sacrifice resolution for speed by using relatively short capillary columns.[1−3] Although microbore columns (i.d. ≤ 0.1 mm) can obtain fast separations with relatively small losses in resolution, sample capacity is reduced, and this results in poorer powers of detection.[4,5] Renewed efforts aimed at the miniaturization of GC instruments for vapor analysis by microfabrication techniques[6−8] must contend with column length constraints imposed by the limited column space available in these instruments. Improved performance of these instruments can be achieved by paying greater attention to column selectivity.

Recent work aimed at reducing the size and weight of portable GC instruments and achieving autonomous operation of microfabricated vapor monitoring instruments has explored the use of vacuum-outlet GC with atmospheric pressure air as the carrier gas in order to eliminate the need for tanks of compressed gas.[9−13] The low diffusivity and high viscosity of air relative to more common carrier gases result in lower optimal linear carrier gas velocities and more rapid losses in column efficiency at higher than optimal velocities[9,10]. This further restricts the column length and resolving power. To reduce vacuum pump size and weight, vacuum-outlet pressures of ≥0.5 atm are desirable.[13] This further reduces the maximum column length if carrier gas velocities near the optimal value are to be achieved with atmospheric pressure air at the column inlet. An additional issue is the poor resolution obtained for weakly retained (highly volatile) components. Some highly volatile compounds, such as acetone and low-molecular-weight alcohols are of considerable interest in air-quality monitoring.

Two approaches are under development for reducing the effects of the poorer resolving power associated with the use of relatively short capillary columns. First, arrays of low-dead-volume solid-state sensors that can differentiate components in some mixtures of organic vapors by pattern recognition techniques can

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10.1021/ac010879g CCC: $22.00
Published on Web 11/28/2001

obviate the need for complete chromatographic separation as well as provide data for vapor identification.[14−16] Second, a series-coupled (tandem) ensemble of capillary columns using different stationary phases and having adjustable carrier gas pressure at the column junction point can be used to tune[17−19] and program[11,12,20,21] selectivity for specified sets of target analytes.

Enhanced selectivity has been achieved with tunable tandem-column ensembles by controlling the carrier gas pressure at the column junction point using a precision pressure controller. If the junction-point pressure is increased, carrier gas flow rate decreases in the first column in the ensemble and increases in the second column. This increases analyte residence times in the first column and decreases residence times in the second column. The result is increased influence of the first column in determining the ensemble selectivity. On-the-fly junction-point pressure changes are used to achieve programmable selectivity. Although this approach can result in significant reductions in analysis times for some mixtures, excessive dead volume in the pressure controller limits its ability to produce rapid pressure changes at the column junction point. In addition, the use of a precision pressure control is not practical for completely microfabricated instruments.

In recent studies,[22,23] pulsed modulation of the carrier gas pressure at the column junction point has been used to obtain programmable selectivity with series-coupled column ensembles. A low-dead-volume valve connects the column junction point to a ballast chamber containing carrier gas. The ballast chamber pressure is controlled by an absolute pressure controller. Enhanced resolution can be obtained for a component pair that is separated by the first column but coelutes from the column ensemble by opening the valve for a few seconds when one component of the pair has crossed the junction and is in the second column, but the other component is still in the first column.

This approach has several significant advantages. First, use of the valve obtains more rapid pressure changes at the column junction point. Second, the valve is closed for most of the analysis time, and the carrier gas flow rate in the ensemble is the same as would occur without additional connections to the junction point. This results in shorter ensemble holdup time and greater ensemble efficiency than would occur if the junction-point pressure were maintained at substantially higher or lower pressure for an appreciable portion of the analysis time. Third, pulsed flow modulation targets particular component pairs without significantly changing the resolution of other component pairs in the mixture.

A particularly useful implementation of pulsed-flow modulation involves using a ballast chamber pressure equal to the GC inlet pressure. When the valve is open, the pressure drop along the first column in the ensemble is zero, and carrier gas flow stops in this column. Stop-flow operation has been used to enhance the separation of pesticide mixtures[24] and essential oils.[25] In the present study, a very simple implementation of stop-flow operation is achieved by connecting the column junction point through a valve to a source of atmospheric pressure air. This obviates the need for the ballast chamber and the pressure controller and results in an instrumental configuration suitable for lightweight portable and microfabricated instruments. Design considerations and performance data are presented. The use of a thicker stationary-phase film in the first column is considered for increasing resolution of early-eluting components. Application to the high-speed analysis of air-borne vapors of volatile organic compounds is described.

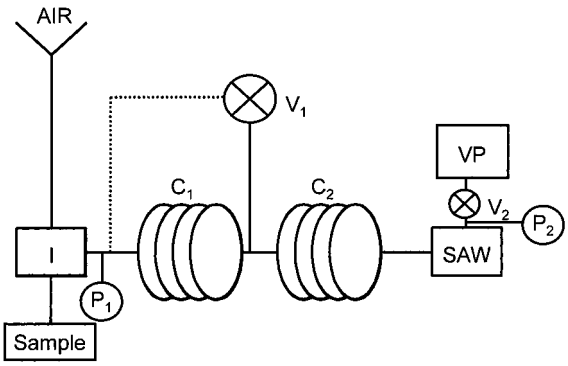

Figure 1. Experimental system used for stop-flow programmable selectivity with vacuum-outlet GC: C_1, nonpolar column; C_2, polar column; I, cryofocusing inlet; SAW, surface-acoustic-wave detector; VP, vacuum pump; V_1, stop-flow valve; V_2, outlet-pressure control valve; P_1, head pressure gauge; and P_2, outlet pressure gauge.

EXPERIMENTAL SECTION

Apparatus. The laboratory-based vacuum-outlet GC used for this study is illustrated in Figure 1. The oven of a Varian 3700 GC (Varian Instruments, Walnut Creek, CA) was used as an experimental platform. Sample injections were made using cryofocusing inlet I (Chromatofast, Inc., Ann Arbor, MI), which quantitatively collects and focuses organic vapors from air samples and injects them into the column ensemble as vapor plugs typically 5−10 ms in width. Although this inlet system is unsatisfactory for portable instrumentation, it is very useful for the study of other components of the portable and microfabricated instruments under development.

Detection is provided by a low-dead-volume, polymer coated surface acoustic-wave (SAW) sensor. The detector was designed and fabricated at Sandia National Laboratories[26] and graciously provided for this work. The detector dead volume is ~2 μL. The nominal operating frequency is 389 MHz, and the sensor was spray-coated with polyisobutylene (PIB) to a frequency shift of 1.1 MHz, corresponding to a coating thickness of ~65 nm. Details of detector design and operation can be found elsewhere.[26] Properties of the sensor and application to the analysis of volatile organic vapors in air samples with vacuum-outlet GC have been

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described.[13] Neither the inlet nor the detector results in significant extra-column band-broadening in this study.

The series-coupled column ensemble consists of two 4.5-m lengths of 0.25-mm-i.d. fused-silica capillary column. Column C_1 uses either a 0.25-μm- or a 0.50-μm-thick film of nonpolar dimethyl polysiloxane (DB-1, J&W Scientific, Folsom, CA). Column C_2 uses a 0.25-μm-thick film of polar trifluoropropylmethyl polysiloxane (Rtx-200, Restek, Bellafonte, PA). The column junction point is connected to a low-dead-volume pneumatically actuated valve, V_1 (MOPV-1/50, SGE, Austin, TX). The other end of the valve is either connected to the GC inlet (dotted line in Figure 1) or open directly to the atmosphere. The pneumatic valve is operated with a compressed-air source (50−55 psig) via an electronically actuated solenoid valve (GH3412, Precision Dynamics, Phoenix, AZ). When the valve is open, the pressure drop along C_1 is small, and carrier gas flow nearly stops in C_1; however, carrier gas flow increases substantially in C_2.

The GC inlet pressure (head pressure of C_1) is monitored by gauge P_1 (px302-050AV, Omega Engineering, East Stamford, CT) and set at atmospheric pressure (101 kPa) by adjusting the air tank delivery pressure. Note that the cryofocusing inlet system contains several pneumatic restrictors (capillary tubing) in order to control flow rates in the device. The pressure drops along these restrictors necessitates the use of a tank delivery pressure greater than one atmosphere to obtain a column ensemble head pressure of one atmosphere. For some experiments, the column head pressure was set at ambient (barometric) pressure. A vacuum pump P (UN84.3 ANI, KNF, Neugerber, Inc., Treton, NJ) located downstream from the SAW sensor is used to drive the separation. The sensor pressure (column outlet pressure) was set at 0.50 atm (50.5 kPa) by means of needle valve V_2 (55-4 μ_BG, Nupro Co., Willoughby, OH) and measured by gauge P_2 (px304-050AV, Omega Engineering). For some studies comparing the 0.25-μm and the 0.50-μm stationary-phase film for C_1, the outlet of C_1 was connected directly to the SAW sensor, and the detector pressure was set at 79.7 kPa. This is the normal pressure at the column junction point, as determined by previously described calculations,[27,28] in the series-coupled column ensemble when the ensemble outlet pressure is 50.5 kPa.

Instrument control was provided using a PC and a 16-bit A/D board (CIODAS 1602, Computer Boards, Inc., Mansfield, MA) using Labtech Notebook software (Laboratory Technologies, Inc., Wilmington, VA). The SAW sensor was placed in the feedback loop of a dual-stage wide-band amplifier (B447D.001, Hewlett-Packard, Palo Alto, CA). The output frequency was monitored by a frequency counter (53131A, Hewlett-Packard) via an HPIB interface and a second PC using Benchlink Meter software (Version 1.0, HP). The sampling rate was 18 Hz. Chromatograms were processed with Grams/32 software (Galactic Industries, Salem, NH).

Materials and Procedures. Sample vapor mixtures were prepared by injecting 5 μL of each component into a 4-L glass sampling bottle and diluting with dry nitrogen. Table 1 lists the mixture components and their saturation vapor pressures at 25 °C. Complete evaporation occurs in the sampling bottle for all target solutes. A 0.25-mm-i.d. deactivated fused-silica tube was used to connect the sample bottle to the inlet of the cryofocusing system. For each injection, a small vacuum pump in the inlet system was used to pull about 1 cm^3 of sample gas into the cryofocusing trap tube. The tube was cooled to about −80 °C for sample collection and heated to ∼250 °C for vapor plug injection. All chromatograms were obtained isothermally at 30 °C.

Table 1. Compounds, Vapor Pressures and Retention Factors for Test Mixture

no.	name	vap. press. (kPa)[a]	k DB1 (0.5 μm)	k RTX 200
1	2-propanol	13.40	0.393	0.249
2	acetone	33.72	0.341	0.627
3	ethyl acetate	16.00	1.295	1.121
4	2-butanone	14.39	1.044	1.388
5	benzene	14.39	2.172	0.862
6	1-butanol	3.74	2.311	1.178
7	trichloroethylene	11.22	2.911	0.930
8	*n*-heptane	7.60	3.250	0.599
9	2,5-dimethylfuran	9.07	3.288	1.109
10	2,4-dimethylhexane	5.14	4.466	0.901
11	3-methyl-1-butanol	2.44	4.607	2.165
12	toluene	4.79	5.677	2.135
13	2-methylheptane	3.74	6.102	1.145
14	tetrachloroethylene	3.36	8.310	2.221
15	octane	2.81	8.640	1.461
16	hexanal	2.35	8.760	6.734
17	butyl acetate	2.81	10.236	6.676
18	chlorobenzene	2.44	11.475	4.592

[a] At 30 °C.

Retention factors for the target compounds were obtained separately for each column using measured values of retention time and calculated values of holdup time.[9,13] The retention factor values at 30 °C are given in Table 1. Note that DB-1 retention factors are for the column using the 0.50-μm-thick stationary phase. These retention factors were used in a previously described spreadsheet model,[27,28] which produces plots of solute band position along the column ensemble axis versus time.

RESULTS AND DISCUSSION

Film Thickness Considerations. Relatively thick stationary-phase films are often used to increase retention for the capillary GC analysis of very volatile compounds. For compounds with small retention factors at the column operating temperature, the increased interaction with the stationary phase obtained with thicker-film columns more than offsets the reduced column efficiency from increased resistance to mass transfer in the stationary phase. The result is increased resolution for early eluting components and in some cases, poorer resolution for strongly retained compounds. The use of a thicker stationary-phase film also will alter the selectivity of the column ensemble. The ensemble selectivity is dependent on the analyte retention factors for the two columns. When the stationary phase film thickness is increased for either column, retention factors for that column increase proportionally, and the contribution that the column makes to the ensemble selectivity will increase. This will alter the pattern of peaks eluting from the ensemble.

Because of internal heat sources and variable ambient temperature conditions, the field-portable instruments under development in this laboratory will operate with minimum column

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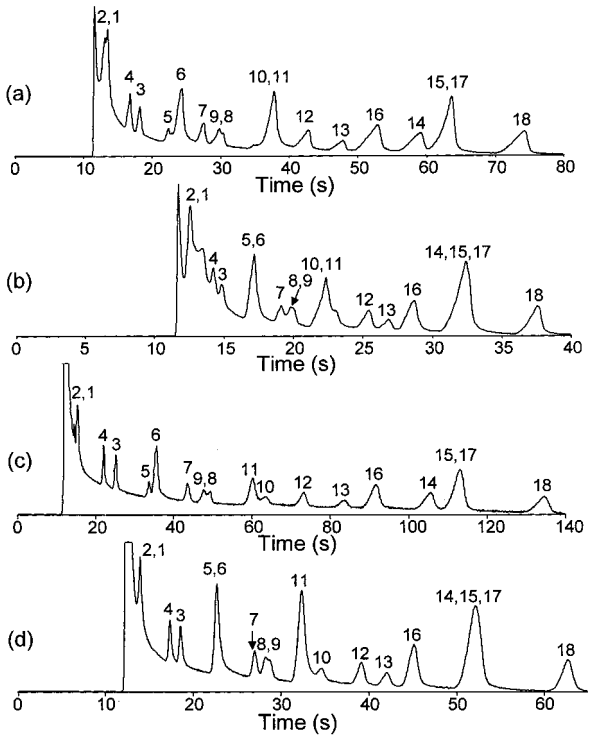

Figure 2. Chromatograms from the nonpolar column C1 using a 0.25-μm stationary-phase film at 30 (a) and 50 °C (b) and using a 0.50-μm stationary-phase film at 30 (c) and 50 °C (d). Air at 101 kPa was used as the carrier gas with an outlet pressure of 50.5 kPa. Peak numbers refer to the compound numbers in Table 1.

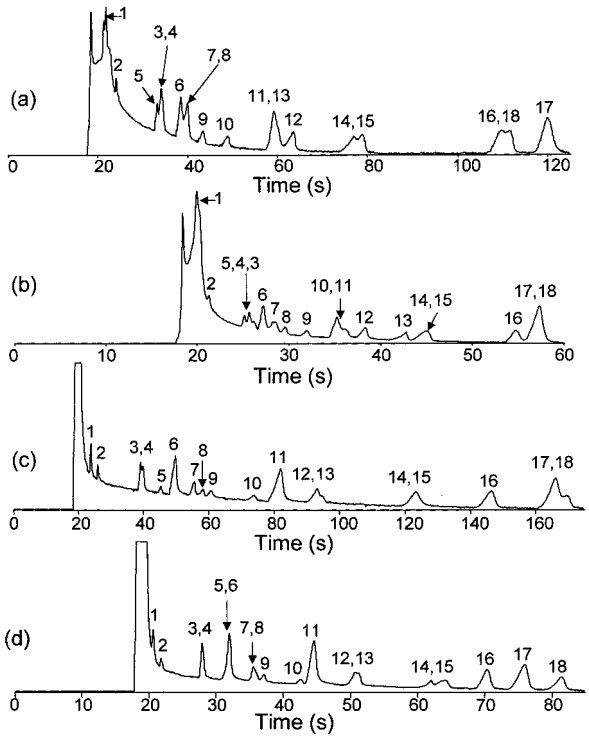

Figure 3. Chromatograms from the column ensemble with the nonpolar column C1 using a 0.25-μm stationary-phase film at 30 (a) and 50 °C (b) and using a 0.50-μm stationary-phase film at 30 (c) and 50 °C (d). Air at 1.0 atm was used as the carrier gas with an outlet pressure of 0.50 atm. Peak numbers refer to the compound numbers in Table 1.

temperatures of ≥30 °C. The two most weakly retained compounds from the target list (Table 1), isopropyl alcohol and acetone, have retention factors of <0.20 and at 30 °C with the thinner film (0.25 μm) nonpolar column used in this study. This results in insufficient resolution of these analytes.

The use of pulsed junction-point pressure modulation to enhance the separation of targeted component pairs requires adequate resolution of the component bands in the first column. Preliminary work with this mixture showed that components 1 (isopropyl alcohol) and 2 (acetone) can be adequately separated by the column ensemble, but components 3 (ethyl acetate) and 4 (2−butanone) coelute in the ensemble chromatogram.

For the earliest eluting components, greater resolution on the nonpolar column is obtained using the 0.50-μm film column. This is shown by the chromatograms in Figure 2. Chromatograms a and b are for the 0.25-μm-film column at 30 °C and 50 °C, respectively, and c and d are for the 0.50-μm-film column at the same temperatures, respectively. For this study, the nonpolar column (C_1) was connected directly to the SAW detector at an outlet pressure of 79.7 kPa. Peak numbers correspond to the compound numbers in Table 1. The first peak in the chromatograms is from water vapor, which is present in the sample bottle and is collected and focused in the cold trap tube of the inlet systems, and traces of methyl alcohol injected into the sampling bottle along with the analytes. This peak is often distorted, showing two local maxima and varies somewhat in shape from shot to shot.

For chromatogram a, both components 1 and 2 show unacceptable overlap with the water/methyl alcohol peak. In addition, significant peak fronting is observed, probably from column overload. Chromatogram c, obtained with the thick film column at 30 °C, shows significant improvement in resolution and peak shapes. Peaks 1 and 2 elute lower on the water/methyl alcohol peak tail. Components 3 and 4 are separated by about 4 s, and components 5 and 6 show significantly increased resolution with the thicker film column.

For the chromatograms acquired at 50 °C, retention times for all components are substantially reduced particularly for the more retained components, which have larger retention factors. At the higher temperature, peak fronting is reduced for both the 0.25-μm- and 0.50-μm-film columns. However, reduced resolution is observed for early eluting peaks, and with the thinner film column, components 1−4 all coelute with the water/methyl alcohol peak. Selectivity changes also are observed at the higher temperature. In particular, component pair 5/6 coelutes at the higher temperature.

Figure 3 shows chromatograms for the same conditions as for Figure 2 except that series-coupled column ensembles were used, and the ensemble outlet pressure was reduced to 50.5 kPa (0.5 atm). This gives the same outlet pressure for the first column (79.7 kPa) and, thus, the same average linear carrier gas velocity and elution times for the first column as in Figure 2. In general, peak fronting is reduced with the column ensemble relative to Figure 2 using only the nonpolar column. In addition, the increased resolving power of the column ensemble and the difference in selectivity, relative to the nonpolar column only, results in complete separation of peaks 1 and 2.

The chromatogram for the series-coupled column ensemble using the thinner film nonpolar column at 30 °C (a) shows

overlapping clusters of peaks for components 3, 4, and 5 and for 6, 7, and 8. In addition, peak 1 coelutes with the water/methyl alcohol peak. At 50 °C (b), a significant selectivity change is observed. In particular, note peak groups 3/4/5, 6/7/8, and 10/11/12/13.

For the column ensemble using the thicker film nonpolar column at 30 °C, components 1 and 2 are very well separated, and the interference from the water peak is less significant than for any of the other chromatograms. Components 3 and 4 show appreciable overlap, but because they are well-separated by the first column (Figure 2c), the complete separation of these peaks should be possible by stopping the flow on C_1 after component 4 has crossed the column junction but while component 3 is still in C_1. Peak 6 (1−butanol) shows considerable tailing, which is characteristic of alcohols with this series-coupled column ensemble. For chromatogram d at 50 °C, components 1 and 2 elute higher on the water/methyl alcohol peak tail, and quantitation, particularly for peak 1, would be more difficult. In addition, components 5 and 6 coelute from the column ensemble, and they are not adequately separated in C_1 for the implementation of C_1 stop-flow operation. On the basis of these studies, all further work used the 0.50-μm-thick stationary phase for column C_1 and an oven temperature of 30 °C.

Enhanced Resolution with C_1 Stop-Flow. Previous work with programmable selectivity using C_1 stop-flow operation involved a ballast chamber and a precision electronic pressure controller to stop the carrier gas flow in the first column. These components are relatively large and expensive for the portable instrumentation under development and completely unacceptable for microfabricated instrumentation. The system shown in Figure 1 is much simpler, requiring only a single normally closed valve and uncoated fused-silica tubing for connection. Because the instruments under development will use ambient (atmospheric pressure) air as the carrier gas, it should also be possible to use ambient air at the column junction point to stop the flow in C_1.

Figure 4 illustrates the use of C_1 stop-flow to enhance the separation of components 3 and 4 in chromatogram 3(c). The plots show the positions along the column ensemble axis of the analyte bands for components 1−6 without stop-flow operation (a) and with a 2.0-s (nominal) stop-flow pressure change initiated 19 s after injection (b). The spreadsheet-based model used to generate these plots of band position vs time has been described previously.[27,28] Injection occurs at the lower left corner of each set of plots (zero time), and elution occurs along the top horizontal line corresponding to a band position of 900 cm (ensemble length).

The horizontal line at 450 cm corresponds to the column junction point. The local slope of any plot gives the band migration velocity at that point in the column ensemble. Discontinuous slope changes across the 450-cm line are the result of the different selectivities of the two column types as well as retention changes from the stationary-phase film thickness difference for the two columns.

The chromatograms above the plots were obtained using air as the carrier gas with a 101 kPa head pressure and a 50.5 kPa outlet pressure. The instrument was configured with a connection from the stop-flow valve (V_1 in Figure 1) to the head of the column ensemble (dotted line, Figure 1). For plots a, predicted retention times are less than the actual values by amounts ranging from

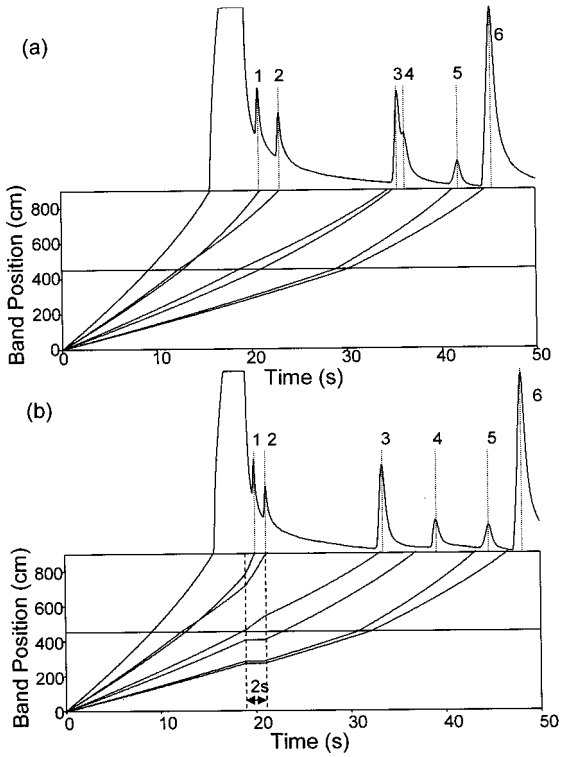

Figure 4. Plots of analyte band position along the column ensemble vs time without stop-flow operation (a) and with a 2.0 s (nominal) stop-flow interval beginning 19.0 s after injection (b) using the column conditions described in Figure 3c. For each set of plots, injection occurs at the lower left corner (zero time), and elution occurs along the top horizontal line. The middle horizontal line corresponds to the column junction point. The ensemble chromatograms are shown above the plots. Air at 1.0 atm was used as the carrier gas with an outlet pressure of 0.50 atm. Peak numbers refer to the compound numbers in Table 1.

0.03 to 2.1 s. The predicted peak pattern, however, is observed in the chromatogram. From the predicted band trajectories through the column ensemble, component 4 should reach the column junction point about 2.3 s after component 3.

For plots b, the junction point pressure was set to increase to 101 kPa at 19 s after injection and then dropped to the normal value at this point in the column ensemble (79.7 kPa) 21 s after injection. Note that when the valve is opened, component 3 has crossed the column junction, but component 4 is still in the first column. During the stop-flow interval, band velocities for components 1−3 increase, and velocities for components 4−6 are assumed to be zero. When the interval ends at 21 s, the velocities of bands in C_1 return to the values prior to the start of the interval. The result is a large increase in the separation of components 3 and 4 in the ensemble chromatogram, with relatively small changes in the separation of other adjacent peak pairs. The ensemble separation of components 1 and 2 is smaller with the stop-flow interval, but the peak widths are also reduced so that the change in resolution is small. However, the baseline curvature from the tail of the water/methyl alcohol peak in this region is greater with the stop-flow interval.

Chromatograms for a mixture containing components 3, 4, 8 and 9 are shown in Figure 5 for stop-flow intervals of 0 (a), 2 (b), 10 (c), 30 (d), and 60 s (e). When the length of the stop-flow interval is increased from 2 to 10 s, the separation of component

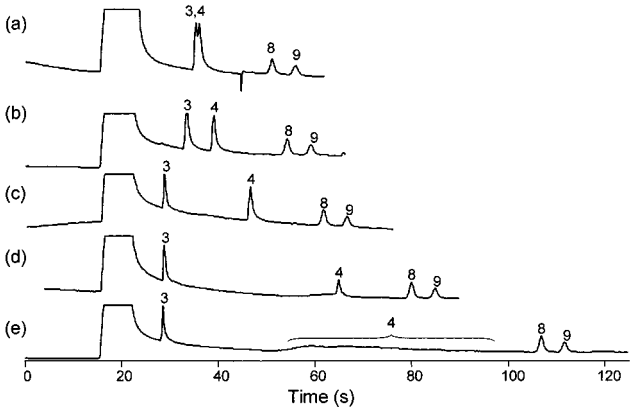

Figure 5. Ensemble chromatograms showing enhanced separation of components 3 and 4 using stop-flow operation: (a) no stop-flow, (b) 2-s, (c) 10-s, (d) 30-s, and (e) 60-s stop-flow. Column conditions are the same as for Figure 3c. In all cases, the stop-flow interval started 19 s after injection. Peak numbers refer to the compound numbers in Table 1.

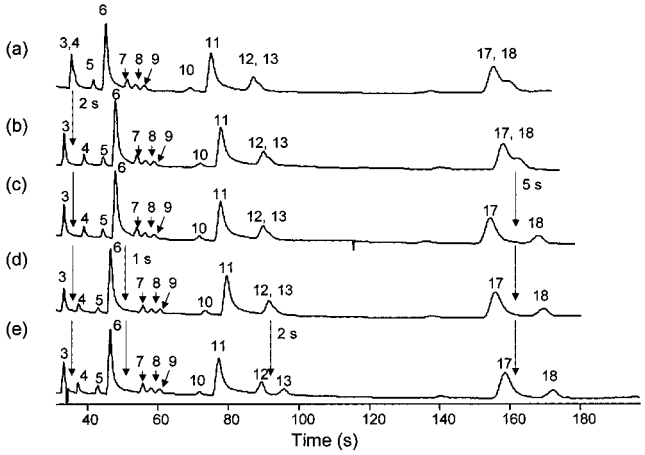

Figure 6. Ensemble chromatograms showing the use of multiple stop-flow intervals: (a) no stop-flow, (b) one stop-flow interval to separate components 3 and 4, (c) two stop-flow intervals to separate component pairs 3/4 and 17/18, (d) three stop-flow intervals to separate 3/4 and 17/18 and to increase separation for 6/7, and (e) four stop-flow intervals to enhance separation of pairs 3/4, 6/7, 12/13, and 17/18. Column conditions are the same as for Figure 3c. Peak numbers refer to the compound numbers in Table 1.

3 from the other mixture components increases accordingly, but peak widths and the separations for the other peak pairs change very little. For 30- and 60-s stop-flow intervals, peaks 8 and 9 are shifted to correspondingly later times, but their separation, peak widths, and peak areas are relatively unchanged. Peak 4, however, shows diminished area and an apparent baseline shift before the peak for the 30-s stop-flow interval and only a very diffuse and broad feature for the 60-s stop-flow interval.

Plots of retention time shift vs nominal stop-flow duration for components 4, 8 and 9 give straight lines with near-zero intercepts and an average slope of 0.91. This indicates that flow has not been completely stopped in C_1, but it has been reduced to about 9% of its original value with valve V_1 closed. This is the result of the pressure drop along the capillary tube connecting V_1 to the head of the column ensemble as well as along the tube connecting V_1 to the column junction. From the spreadsheet model, the velocity of the band for component 4 just prior to opening V_1 is 27.5 cm/s. With the valve open, the velocity drops to about 2.5 cm/s, but after 30 s, the leading portion of the band has reached the junction and slowly migrates across the junction, producing the apparent baseline increase and a diminished area of the main peak. For the 60-s stop-flow case, the entire band has migrated across the junction prior to the end of the interval. This results in the broad, diffuse feature seen in Figure 5e.

Because a stop-flow duration of 2 s is more than adequate for the complete separation of components 3 and 4, the implications of the slow band migration in C_1 during the stop-flow interval are minimal. Bands for components 8 and 9 are farther from the column junction at the start of the stop-flow interval, and they do not reach the junction, even with a 60-s stop-flow interval. Thus, their peak areas are unchanged.

Multiple Stop-Flow Intervals. For more complex mixtures, several component pairs may be adequately separated by C_1 but coelute from the column ensemble. For these cases, multiple stop-flow intervals can be used to obtain adequate separation of all of these component pairs. From Figures 2c and 3c, it is apparent that component pairs 3/4, 12/13, and 17/18 are adequately separated by C_1 but show substantial overlap from the column ensemble. Figure 6 shows portions of chromatograms containing these components. Chromatogram a was obtained without stop-flow operation. For chromatogram b, a single 2.0-s (nominal) stop-flow interval was used to separate components 3 and 4. Note that other components in the mixture show small shifts to later retention times in chromatogram b but no significant change in peak-pair separations.

For chromatogram c, a second, 5-s-long stop-flow interval is used to enhance the separation of component pair 17/18. Note that the initiation time of the second stop-flow interval must be delayed relative to the 40-s value predicted by Figure 2c because the first stop-flow interval delays the arrival at the column junction point of all of the components that are in C_1 during the first stop-flow interval. For chromatogram 6d, a third, 1-s long stop-flow interval is used to move peaks 7−9 away from the tail of peak 6. For chromatogram 6e, a fourth 2-s long interval is used to enhance the separation of components 12 and 13. Note that in chromatogram 6e, all of the components are adequately separated, with the analysis time increasing only by the sum of the stop-flow intervals (10 s nominal).

Figure 7 shows chromatograms without stop-flow operation (a) and with three stop-flow intervals (b) to obtain a complete separation of the same mixture as shown in Figure 6, except that the connection from V_1 to the head of the column ensemble was removed, and air in the GC oven was used directly as the stop-flow gas. The chromatograms in Figures 6e and 7b are similar except for artifacts in the baseline in Figure 7b. These are caused by the greater water vapor content in the ambient (GC oven) air introduced through V_1 during the stop-flow intervals.

Plots of retention time shift vs nominal stop-flow duration for the instrument configuration used for Figure 7 give straight lines with near-zero intercepts and slopes of about 0.80. This indicates that carrier gas flow in C_1 has been reduced to about 20% of the value with valve V_1 closed. This is considerably greater than for the case in which the valve is connected to the head of the column ensemble. Observation of the ensemble head pressure during stop-flow operation showed a significant increase in pressure during a

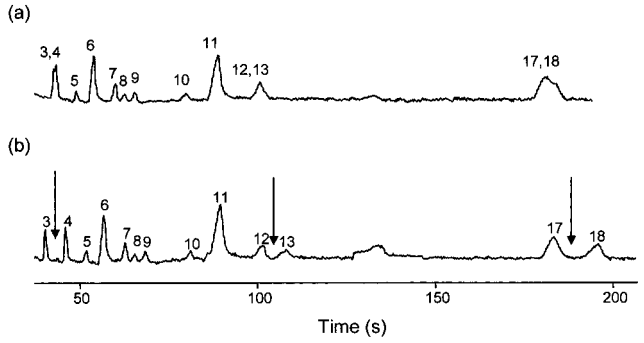

Figure 7. Ensemble chromatograms showing the use of multiple stop-flow intervals with the stop-flow valve (V_1) opening directly to ambient air: (a) no stop-flow, and (b) three stop-flow intervals to enhance separation of pairs 3/4, 12/13, and 17/18. Column conditions are the same as for Figure 3c. Peak numbers refer to the compound numbers in Table 1.

stop-flow interval when V_1 opens directly to the GC oven. This is the result of pneumatic restrictions in the cryofocusing inlet system, which will not be present in portable instruments incorporating these technologies and using ambient air as the carrier gas.

CONCLUSIONS

The combination of a thicker stationary-phase film for C_1 and multiple stop-flow intervals can be used to obtain the complete separation of an 18-component mixture of volatile organic compounds in air in less than 3.5 min using atmospheric pressure air as the carrier gas and vacuum-outlet column operation with an outlet pressure of 0.5 atm. The thicker stationary-phase film increases resolution of weakly retained components on the first column, and this facilitates the use of stop-flow operation for the separation of component pairs that are separated by the first column but coelute from the column ensemble. The thicker stationary-phase film also reduces the effects of the water/methyl alcohol peak on the earliest eluting target compounds.

The valve-operated stop-flow system described in this report is much simpler and less costly to implement than previously described systems using a precision pressure controller and a ballast chamber, and thus, it is more suitable for small, lightweight, portable and microfabricated instruments. However, because of pressure drops along the connecting lines, it may not be possible to obtain complete stop-flow conditions in the first column. This will impact on using the technique for component pairs that are just barely separated by the first column, because migration across the column junction of some of the analyte band from the second component during the stop-flow interval will be inevitable. However, preliminary studies with an instrument using ambient air both as the carrier gas and as the stop-flow gas indicate that band migration velocities in C_1 during stop-flow operation are $<5\%$ of the valves with the stop-flow valve closed. Portable and microfabricated instruments under development will use a sorption-based vapor preconcentrator and require a scrubber to remove water vapor from the ambient air used as the carrier gas. The pressure drops associated with these devices will need to be examined.

A limitation of the experimental system described in this report is the use of a pneumatically actuated valve for stop-flow operation. For portable instrumentation, which requires no compressed gas tanks, this valve will need to be replaced with a solenoid valve. Several commercial solenoid valves have been evaluated for this application, but dead volume in the valves increases pressure equilibration times after valve closing, and this degrades the system's performance. Alternative valve designs are under consideration. For a completely microfabricated instrument, which is under development at the University of Michigan, a normally closed, low-power microfabricated valve is a major challenge.

ACKNOWLEDGMENT

The authors express their appreciation to the following individuals: Dr. Mark Burns and Ms. Tincuta Veriotti of the University of Michigan; Dr. Gregory Frye-Mason, Dr. Patrick Lewis, and Dr. Richard Kottenstette of Sandia National Laboratories; and Dr. Jay Grate of Pacific Northwest Laboratories. Funding for this work was provided by Grant no. R01-OH03692 from the National Institute for Occupational Safety and Health of the Centers for Disease Control and Prevention (NIOSH-CDCP). Additional support provided by the University of Michigan Center for Wireless Integrated Microsystems (WIMS) through the Engineering Research Centers Program of the National Science Foundation under Award no. EEC-9986866 is also gratefully acknowledged.

Received for review August 6, 2001. Accepted October 7, 2001.

AC010879G