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Articles

Programmable Selectivity for GC with Series-Coupled Columns Using Pulsed Heating of the Second Column

Joshua Whiting and Richard Sacks*

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

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A series-coupled ensemble of a nonpolar dimethyl polysiloxane column and a polar trifluoropropylmethyl polysiloxane column with independent at-column heating is used to obtain pulsed heating of the second column. For mixture component bands that are separated by the first column but coelute from the column ensemble, a temperature pulse is initiated after the first of the two components has crossed the column junction point and is in the second column, while the other component is still in the first column. This accelerates the band for the first component. If the second column cools sufficiently prior to the second component band crossing the junction, the second band experiences less acceleration, and increased separation is observed for the corresponding peaks in the ensemble chromatogram. High-speed at-column heating is obtained by wrapping the fused-silica capillary column with resistance heater wire and sensor wire. Rapid heating for a temperature pulse is obtained with a short-duration linear heating ramp of 1000 °C/min. During a pulse, the second-column temperature increases by 20−100 °C in a few seconds. Using a cold gas environment, cooling to a quiescent temperature of 30 °C can be obtained in ∼25 s. The effects of temperature pulse initiation time and amplitude on ensemble peak separation and resolution are described. A series of appropriately timed temperature pulses is used to separate three coeluting pairs of components in a 13-component mixture.

Series-coupled column ensembles using stationary phases with significantly different polarity and programmable carrier-gas pressure at the column junction point are proving useful in reducing GC analysis time for applications that include pesticides,[1] essential oils,[1−3] and air-borne organic vapors.[4−6] Reduced analysis time is obtained by using relatively short columns and structuring the ensemble chromatograms to more efficiently use the available peak capacity.

Recently, pressure pulses have been used to enhance the separation of targeted component pairs that are separated by the first column but coelute from the column ensemble because of the different selectivities of the two columns. The pressure pulse, which usually is a few seconds in duration, is applied when one of the targeted components has crossed the column junction point and is in the second column while the band for the other component is still in the first column. For the duration of the pressure pulse, the carrier gas flow rates in the two columns change differentially. That is, the flow rate in one of the columns increases and the flow rate in the other column decreases. The result is the enhanced separation of the component pair in the ensemble chromatogram.

An important advantage of pulsed carrier gas flow modulation is that the pulse does not significantly effect the separation of components that are in the same column during the pulse. Thus, mixture components that are adequately separated without the pressure pulse usually remain separated with the pulse. A pulse can be used to target a specific component pair for enhanced separation. An appropriately timed sequence of pulses can result in enhanced separation of several peak pairs or groups of peaks that coelute from the column ensemble.

Pressure pulses at the column junction point are obtained by connecting the junction point through a low-dead-volume valve to a carrier gas source at some preset pressure. Mechanical valves can be relatively high maintenance, and alternative approaches would be useful. Microfabricated versions of this technology are under development for autonomous air monitors.[7] However, low-power, normally closed microfabricated valves remain a challenge for fabrication engineers. To obviate these problems, and to develop useful new techniques for tuning and programming the selectivity of series-coupled column ensembles, the use of temperature pulses rather than pressure pulses is under development.

For component pairs that are separated by the first column in the ensemble but coelute from the ensemble, the second column can be rapidly heated when one of the targeted components is in the second column and the other component is still in the first

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* Corresponding author. E-mail: rdsacks@umich.edu.

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(7) Wireless Integrated Micro Systems (WIMS), Engineering Research Center (ERC) at the University of Michigan, Ann Arbor, MI 48109.

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column. During the pulse, migration rates of bands in the second column increase. If the second column cools, partially or completely, to its quiescent temperature prior to the second component of the targeted pair reaching the column junction point, enhanced separation of the targeted component pair will be obtained in the ensemble chromatogram.

The effectiveness of temperature pulses for obtaining enhanced ensemble separation of targeted component pairs depends on the heating and cooling rates of the second column and on the timing of the temperature modulations. Convection ovens are too slow for this application, but recently available heating methods using at-column resistive heating can obtain sufficiently rapid heating and cooling.[8−13]

This report describes the use of very rapid column heating and relatively fast cooling of the second column in the ensemble for enhanced separation of targeted component pairs in the nominally isothermal separation of a 13-component mixture of interest in atmospheric monitoring. The use of a sequence of temperature pulses is demonstrated for targeting several component pairs that coelute from the column ensemble. Air is used as carrier gas to more closely simulate the conditions to be used in the portable and microfabricated GC instruments for which these selectivity-enhancing technologies are being developed.

EXPERIMENTAL SECTION

Apparatus. The dual-column ensemble consists of 4.5-m lengths of 0.25-mm-i.d. wall-coated fused-silica columns. The first column uses a 0.50-μm-thick bonded film of nonpolar dimethyl polysiloxane (Rtx-1, Restek Corp., Bellefonte, PA), and the second column uses a 0.25-μm-thick bonded film of moderately polar trifluoropropylmethyl polysiloxane (Rtx-200, Restek). This pair of phases was chosen because of its suitability with air as a carrier gas.[14]

The complete apparatus is shown in Figure 1. High-speed heating and cooling are achieved by wrapping the individual columns with a heater wire and a sensor wire. This is shown in the inset of Figure 1. Each assembly is wound into a coil ~7 cm in diameter, and the coils are wrapped with metal foil. The column assemblies were manufactured by RVM Scientific (Santa Barbara, CA). Controller boards that interface to a PC are provided by the manufacturer. The columns also are provided with independently heated interface lines to minimize cold spots.

Rapid cooling of the second (polar) column is achieved with a stream of cold nitrogen gas obtained by passing house nitrogen through a $^3/_8$-in-i.d. Cu cooling coil immersed in liquid nitrogen. The end of the tube was connected to a fitting with a $^1/_2$-in. exit i.d. A fine metal screen over the end of the fitting was used to prevent droplets of liquid nitrogen from hitting the foil wrapper on the column. This gas source was positioned along the axis of the column coil and ~20 cm from the plane of the coil.

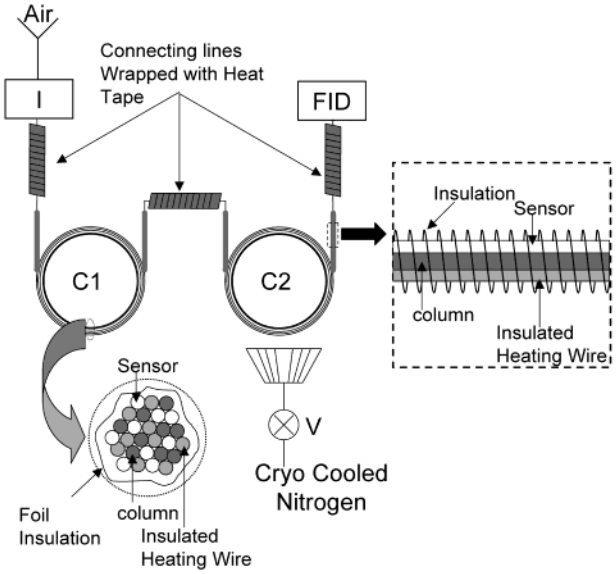

Figure 1. Series-coupled ensemble of a nonpolar column C_1 and a polar column C_2. The columns use at-column heating to achieve high-speed temperature programming and independent temperature control of the two columns. Heating pulses are applied to the second column, and cold nitrogen gas is used to obtain more rapid cooling of the second column: I, split inlet; FID, flame ionization detector; V, cooling-gas control valve. Independently heated connecting lines are used to eliminate cold spots. The insets show the fused-silica capillary column and the heater wire and sensor wire used to obtain rapid column heating and the independently heated connecting lines.

Samples are introduced into the column ensemble with an inlet splitter from a Varian 3700 GC. Ensemble chromatograms were detected with a Varian flame ionization detector (FID). The FID current was monitored with an electrometer/amplifier built in-house and having a time constant of less than 10 ms. The electrometer was interfaced to a PC (Gateway, GP6-350, Souix Falls, ND) with a 16-bit A/D board (CIO-DAS 1602, Computer Boards, Inc., Mansfield, MA).

Materials and Procedures. Compressed air was used as carrier gas at an inlet pressure of 20 psig. All chromatograms were obtained with 30 °C isothermal operation of the first column. The second column was operated with an initial temperature of 30 °C. At selected times after sample injection, the second column was rapidly heated (1000 °C/min nominal) until the temperature as monitored by the sensor wire reached a preset value. A negative temperature ramp of 1000 °C/min was then used to return the set-point temperature to 30 °C. The actual heating rate was in the range 800−900 °C/min. The cooling rate is dependent on the temperature difference between the column and the ambient environment. Typical cooling rates for this study were 80−150 °C/min.

Table 1 lists the compounds used for this study. These compounds are of interest in ambient air monitoring.[15,16] Retention factors on the two columns at 30 °C are also listed. These values were obtained from measurements with the individual columns. Test samples were prepared as mixtures of the pure substances.

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Table 1. Compounds and Boiling Points for Test Mixtures

label	name	k on C_1	k on C_2	bp (°C)
1	2-propanol	0.38	0.26	82.4
2	acetone	0.34	0.63	56.2
3	2-butanone	1.04	1.39	79.6
4	ethyl acetate	1.29	1.15	77.1
5	benzene	2.17	0.86	80.1
6	1-butanol	2.12	1.19	117.6
7	heptane	3.52	0.69	98.4
8	trichloroethylene	3.13	0.94	86.7
9	2,5-dimethylfuran	3.48	1.20	93.0
10	2,4-dimethylhexane	4.89	0.98	109.0
11	3-methyl-1-butanol	4.79	2.27	130.0
12	toluene	5.71	2.26	110.6
13	2-methylheptane	6.78	1.22	118.0

The compounds were reagent grade chemicals from Aldrich (Milwaukee, WI) except for isopropyl alcohol (Fisher Scientific, Fair Lawn, NJ) and benzene (Burdick and Jackson Laboratories, Muskegon, MI). Sample injections were 0.1 μL. The inlet split ratio was 400:1. Injector and detector temperatures were 200 °C.

Spreadsheet calculations were used to model the effect of temperature pulse initiation time and amplitude on the ensemble retention times and peak separation for a pair of target compounds. In the model, the column ensemble is divided into 1.0-cm-long intervals, and the time required for a solute band maximum to migrate through each interval is computed. These times are summed over the column-ensemble length to determine retention times. The model, which has been described in detail,[17,18] uses as input the column dimensions, inlet and outlet pressures, carrier gas viscosity at the column temperature, and retention factor versus temperature data. Retention factors (k) were measured over a range of second-column temperatures (T_c), and slope and intercept values from plots of ln(k) versus $1/Tc$ were used as input to the spreadsheet calculations. Retention time accuracy for the model is typically 1−2 s.

RESULTS AND DISCUSSION

Heating Pulse Characterization. Figure 2a shows the heating pulses with ambient-air cooling (A) and with cooling provided by a flow of cold nitrogen (B) for a peak pulse (set-point) temperature of 70 °C. Figure 2b shows heating pulses for peak set-point temperatures of 50 (A), 70 (B), 90 (C), and 120 °C (D) using cold nitrogen gas to achieve more rapid cooling. In all cases, the initial and final column temperatures were 30 °C.

With ambient-air (20−22 °C) cooling, ∼250 s is required for the column to reach the starting temperature of 30 °C (trace A, Figure 2a). The cold nitrogen cooling provides a local temperature near the column of ∼0 °C, and the column temperature returns to the starting value of 30 °C in ∼25 s (trace B, Figure 2a). Column cooling is exponential with time, but if the set-point temperature at the end of the cooling cycle is substantially above the temperature in the column environment (local temperature), cooling to the final set point (30 °C) is much more rapid and more nearly linear with time.

For spreadsheet calculation of retention time with second-column heating pulses, the second-column temperature during a pulse was approximate by a triangle (linear temperature increase and linear temperature decrease). Note in Figure 2b that, as the peak set-point temperature for the heating pulse increases, the time required for the second column to cool to the final set-point temperature of 30 °C increases substantially, and the cooling is less linear with time.

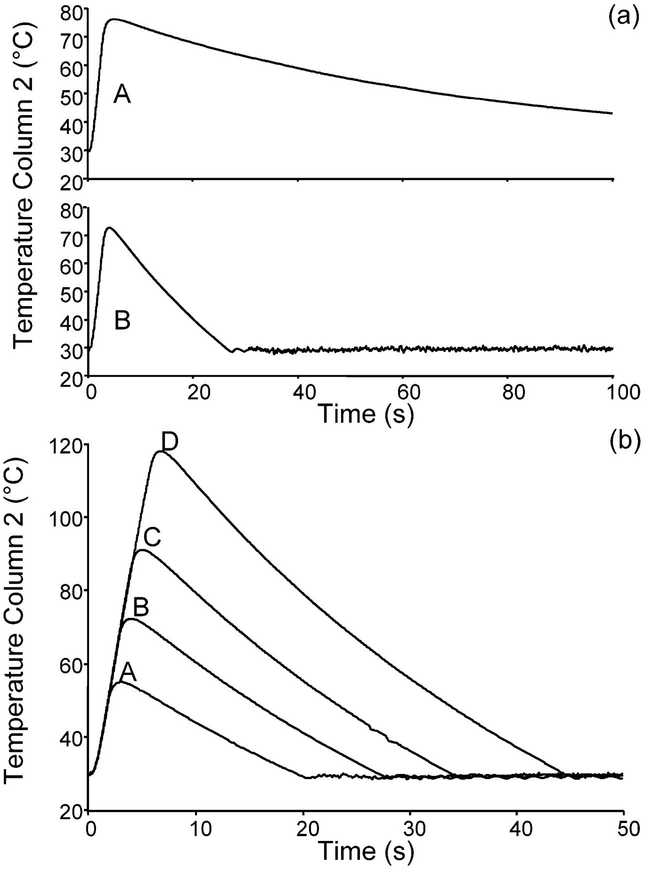

Figure 2. (a) Second-column heating pulses with peak set-point temperature of 70 °C and cooling in ambient air (A) and in cold nitrogen gas (B); (b) second-column heating pulses using cold nitrogen cooling and peak set-point temperatures of 50 (A), 70 (B), 90 (C), and 120 °C (D). In all cases, the set-point temperature before and after the heating pulse was 30 °C.

Heating Pulse Initiation Time. Ethyl acetate and 2-butanone were chosen as test compounds because they are well separated by the first (nonpolar) column but coelute from the column ensemble. This situation, which is very common in separations with tandem column ensembles, is the result of one of the compounds having greater retention on one of the columns and the other compound having greater retention on the other column. The compounds were injected separately so that the peak retention times and shapes could be easily defined even for cases where ensemble retention times for the two compounds are very similar.

Figure 3 shows chromatograms of ethyl acetate (solid lines) and 2-butanone (dashed lines). The chromatograms are overlays of the two peaks. For chromatogram a, no heating pulse was used, and the entire separation was conducted isothermally at 30 °C. The two compounds have the same ensemble retention times and thus would coelute if injected together. Note that the small peak to the left of the 2-butanone peak is from an impurity.

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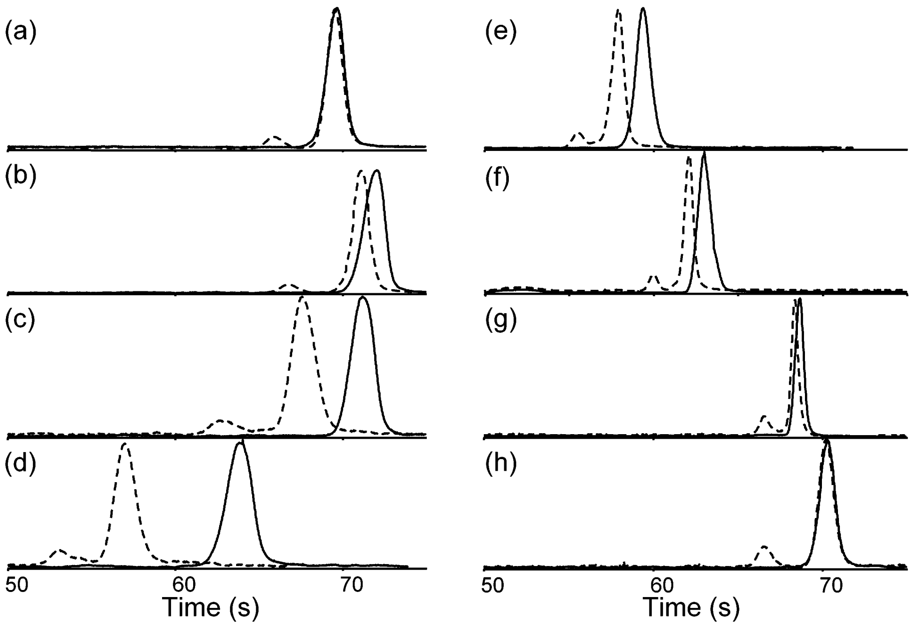

Figure 3. Overlays of ensemble chromatograms for ethyl acetate (solid lines) and 2-butanone (dashed lines) with no second-column heating pulse (a) and with heating pulses beginning 0 (b), 15 (c), 25 (d), 35 (e), 50 (f), 65 (g), and 75 s (h) after sample injection. In all cases, the initial and final second-column temperature was 30 °C, and the peak set-point temperature during the pulse was 70 °C.

For chromatogram b, a temperature pulse with peak set-point temperature of 70 °C was applied to the second column at the time of sample injection. The pulse is completely over 25 s after injection. Both compounds are in the first column for the entire duration of the pulse. The result is a small shift to later retention times for both components, which is caused by a pressure increase at the column junction point during the temperature pulse. This pressure increase is the result of the increase in viscosity of the carrier gas in the second column during the pulse. Use of a flow-controlled system rather than a pressure-controlled system should reduce the effects of this change in pressure. Note that the retention time shift is different for the two compounds, and some separation is observed.

For chromatogram c, the temperature pulse was initiated 15 s after injection. A small shift to earlier retention time (relative to case b) is observed for ethyl acetate (solid line), and a larger shift is observed for 2-butanone. The result would be the complete separation of these two components in a mixture. Significant peak broadening also is observed relative to (a) and (b). These trends continue for case d, where the temperature pulse is initiated 25 s after injection. Here a peak separation of ~7 s would be observed in the mixture chromatogram.

For chromatograms e−g, the temperature pulse was initiated 35, 50, and 65 s, respectively, after injection. In all these cases, both compounds have crossed the column junction point prior to the initiation of the temperature pulse, and the peak separation is reduced steadily with increasing pulse initiation time. Also note that peak widths decrease steadily with increasing pulse initiation time. This occurs because the pulse lasts ~25 s, and if a compound elutes from the column ensemble prior to the end of the pulse, the higher elution temperature results in reduced peak width. For case g, the pulse is applied just prior to elution of the two bands, and the high elution temperature results in very significant peak narrowing. For case h, elution of both components from the column ensemble occurs prior to pulse initiation, and the chromatograms are the same as for case a.

In Figure 4, the retention times for ethyl acetate (A) and for 2-butanone (B) are plotted versus temperature pulse initiation time for measured values (a) and for computer-generated values (b). The computer-generated values are based on a previously described band migration rate model.[16,17] Error bars for measured values indicate standard deviations for four replicate injections. For both plots, the tick marks on the vertical axis indicate the retention times if no temperature pulse is used. Note that both the shapes of the plots and the magnitude of the retention time shifts are in good agreement for the computer-generated values and the measured values.

Several regions of these plots can be defined. For pulse initiation times less than ~15 s, both solute bands are in the first column for the entire duration of the pulse, and only the change in pressure at the column junction point caused by viscosity changes of the carrier gas in the second column influences ensemble retention times.

In the region from about 15 to 30 s, both compounds enter the second column after the start, but prior to the end of the pulse, and the first compound to enter the second column (2-butanone) experiences a higher second-column temperature and thus is shifted more toward lower retention times than the second component to enter the second column. The result is increased peak separation.

If the temperature pulse is initiated more than 40 s after injection, both solute bands are in the second column when the pulse begins, and thus, both peaks are shifted to shorter retention times, with respect to their values without the temperature pulse, but with significantly less separation. In this region, as the pulse initiation time is increased, the solute bands elute from the column ensemble before the completion of the temperature pulse, and the retention time shifts gradually shrink until the pulse initiation

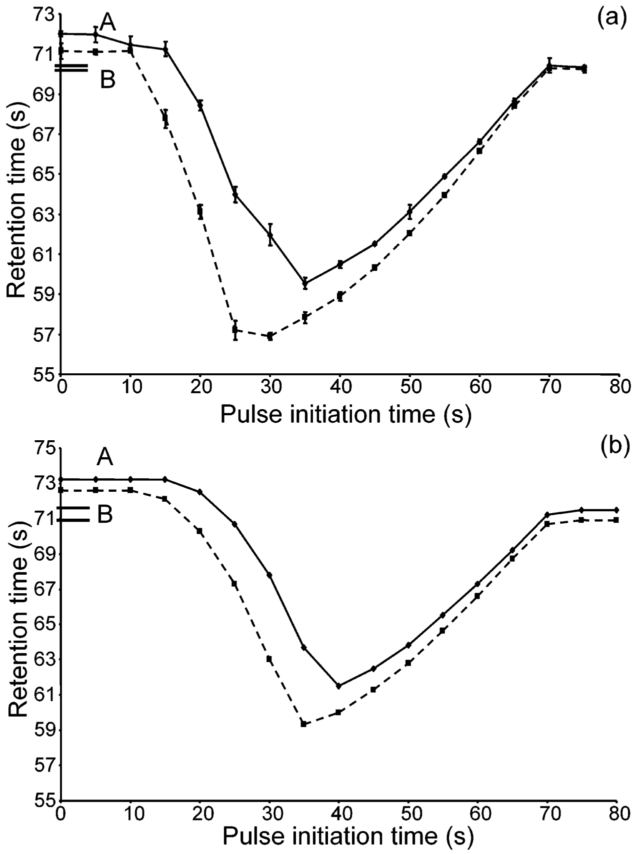

Figure 4. Ensemble retention times versus heating-pulse initiation time for ethyl acetate (plots A, solid lines) and 2-butanone (plots B, dashed lines). (a) average measured values for four replicate injections; (b) computer-generated plots assuming a triangular heating pulse. In all cases, the initial and final second-column temperature was 30 °C, and the peak set-point temperature during the pulse was 70 °C.

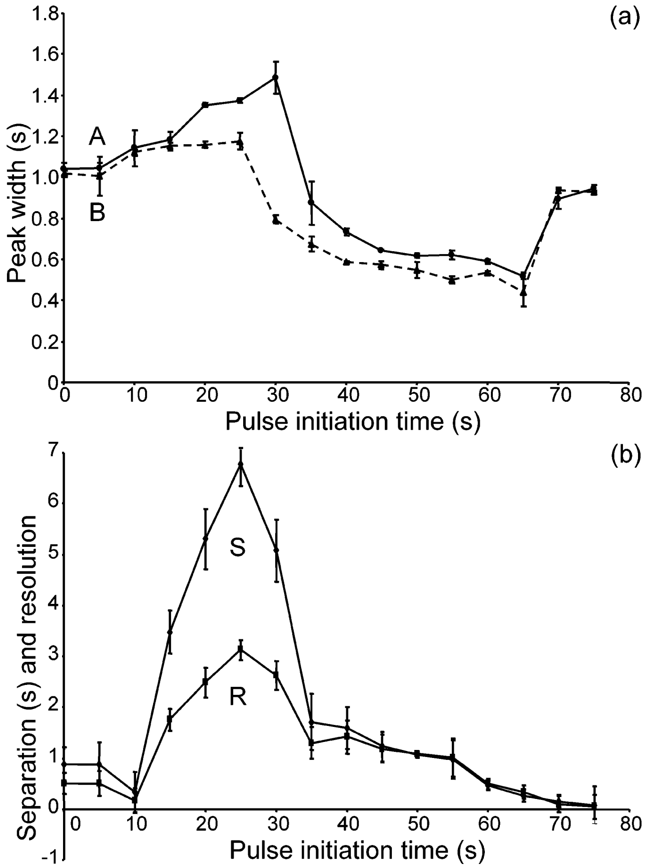

Figure 5. (a) Peak widths (full width at half-height) for ethyl acetate (plot A, solid line) and 2-butanone (plot B, dashed line) versus heating-pulse initiation time; (b) peak separation (*S*) and resolution (*R*) versus heating-pulse initiation time. In all cases, the initial and final second-column temperature was 30 °C, and the peak set-point temperature during the pulse was 70 °C.

time increases to more than ~70 s, at which time the solutes elute from the column ensemble prior to the start of the temperature pulse, and consequently, the pulse has no effect.

Figure 5 shows plots of peak width (full width at half-height) (a) versus the temperature−pulse initiation time for ethyl acetate (A) and 2-butanone (B) and plots of peak separation (*S*) and peak resolution (*R*) for the two components as functions of pulse initiation time. The heating pulse had a nominal peak temperature of 70 °C and a width of ~25 s. Since the elution times for the test compounds on the first column are 30−35 s, for pulse initiation times greater than 5 s, the solute bands will enter the second column prior to the end of the heating pulse, and the bands will accelerate as they enter the hotter second column with the result that the bands are stretched by the sharp temperature gradient across the column junction during the heating pulse. This band stretching is clearly seen in chromatograms a−d in Figure 3 as well as in the plots of Figure 5a.

If the solute bands enter the second column prior to the heating pulse, but elute from the second column after completion of the pulse, the elution temperature does not change, but reduced migration time in the second column results in reduced peak width. If elution from the column ensemble occurs prior to completion of the heating pulse, the elution temperature increases steadily with increasing pulse initiation time, and peak widths steadily decrease. This is seen in Figure 5a for pulse initiation times in the range 35−65 s. For pulse initiation times greater than 70 s, both compounds have eluted from the column ensemble prior to the start of the heating pulse, and the peak widths abruptly return to their 30 °C values.

The peak separation plot *S* and peak resolution plot *R* in Figure 5b are derived from the retention time plots in Figure 4a and the peak width plots in Figure 5a. Resolution was computed as the ratio of peak separation to the average base width (4σ) of the two peaks. Separation was computed as the time between peak apexes for the two compounds. For pulse initiation times greater than the component elution times of ~70 s, separation and resolution are near zero. A relatively broad maximum is observed in the resolution plot, and for pulse initiation times in the range 15−30 s, resolution greater than 1.5 is achieved with a peak value of ~3.0 for a pulse initiation time of 25 s. These data suggest that maximum resolution is achieved when the heating pulse begins just prior to the target solutes entering the second column so that the first band enters the second column at the beginning of the nearly linear cooling cycle.

Heating Pulse Amplitude. Figure 6 shows chromatograms for injections of ethyl acetate (solid lines) and 2-butanone (dashed lines) for heating pulse peak temperature set-point values of 50 (a), 70 (b), 90 (c), 110 (d), 130 (e), and 170 °C (f). In all cases, the heating pulse initiation time was 25 s, which corresponds to

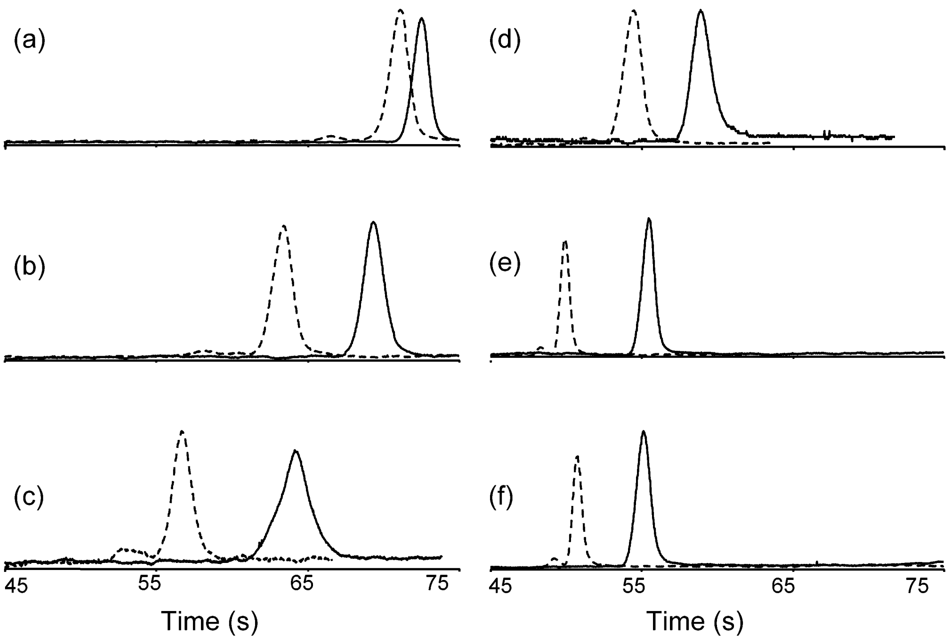

Figure 6. Overlays of ensemble chromatograms for ethyl acetate (solid lines) and 2-butanone (dashed lines) using heating pulses initiated 25 s after injection and using peak set-point temperature of 50 (a), 70 (b), 90 (c), 110 (d), 130 (e), and 170 °C (f). In all cases, the initial and final second-column temperature was 30 °C.

the case of maximum resolution in Figure 5b. The starting temperature was 30 °C, and the final set-point temperature after completion of the heating pulse was 30 °C.

As the peak heating pulse temperature increases from 50 to 90 °C, there is a decrease in retention times for both peaks, but the decrease in larger for 2-butanone (dashed lines) with the result that there is a corresponding increase in the peak separation. Substantial increases in peak width also are observed, particularly for ethyl acetate (solid lines). For heating pulses with peak temperatures greater than 90 °C, the peak separation decreases and then becomes nearly constant. The same is true for the peak widths. Note that the chromatograms for Figures 3 and 6 were obtained on different days, and a small change in column flow rate results in smaller retention times for both compounds in Figure 6b relative to Figure 3d even though the temperature pulse initiation time and amplitude are the same.

In Figure 7, the retention times for ethyl acetate (A) and for 2-butanone (B) are plotted versus temperature pulse amplitude (peak set-point temperature) for measured values (a) and for computer-generated values (b). In all cases, the pulse initiation time was 25 s. The computer-generated plots and the experimental data are in reasonable agreement both in the shape of the plots and in the magnitude of the retention time shifts. Significant deviations of the measured values of retention time relative to the computer-generated values are expected because of the assumption of a linear decrease in temperature after the peak pulse temperature. This assumption is less valid for the higher amplitude pulses (see Figure 2b).

The important point is Figure 7 is that the solute retention times remain nearly constant for peak pulse temperatures greater than ~130 °C. This is the result of the longer pulse duration for the cases with large peak temperature. For typical organic compounds, a 15–20 °C increase in column temperature results in a 2-fold reduction in retention factors (k). Since retention times are equal to $t_m(k + 1)$, where t_m is the column holdup time, for sufficiently high temperatures, retention factors are small, and retention times become relatively independent of the column temperature. For pulses with peak set-point temperature greater than ~130 °C, both components elute prior to the end of the pulse, and retention in the second column is relatively low for the entire residence time in the second column. Thus, the ensemble retention times are dominated by the retention times in the first column and are relatively independent of heating-pulse amplitude.

Figure 8 shows plots of peak width (full width at half-height) (a) for ethyl acetate (A) and 2-butanone (B) and plots of peak separation (S) and resolution (R) versus peak set-point temperature (pulse amplitude). Data for plots b were obtained from the data in Figure 7a and Figure 8a. The data for a peak set-point temperature of 30 °C is for the case where no pulse is used, and the entire separation is isothermal at 30 °C.

For both compounds, the peak widths increase with increasing pulse amplitude, reach maximum values for peak pulse temperatures of 70–90 °C, decrease with further increases in peak pulse temperature, and finally become nearly independent of peak temperature for values greater than 130 °C. The initial increase in peak width with increasing pulse amplitude is the result of band stretching as the component bands migrate into the hotter second column. For larger pulse amplitudes, the higher elution temperatures, which result from reduced retention and greater pulse duration, result in reduced peak widths, which become relatively constant as retention factors get small.

Both peak separation and resolution increase with increasing pulse amplitude until a maximum separation is observed for a peak set-point temperature of 70 °C above which the separation steadily decreases, but resolution becomes relatively constant. Note that the resolution is in the range from 3 to 4 for peak set-point temperatures greater than 70 °C.

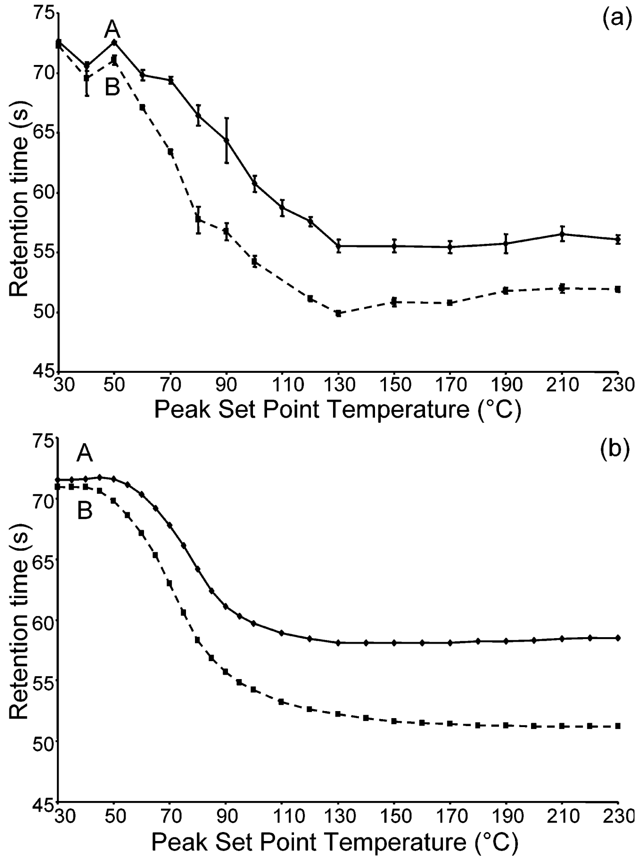

Figure 7. Ensemble retention times versus heating-pulse amplitude (peak set-point temperature) time for ethyl acetate (plots A, solid lines) and 2-butanone (plots B, dashed lines). (a) Average measured values for four replicate injections; (b) computer-generated plots assuming a triangular heating pulse. In all cases, pulse initiation time was 25 s after injection, and the initial and final second-column temperature was 30 °C.

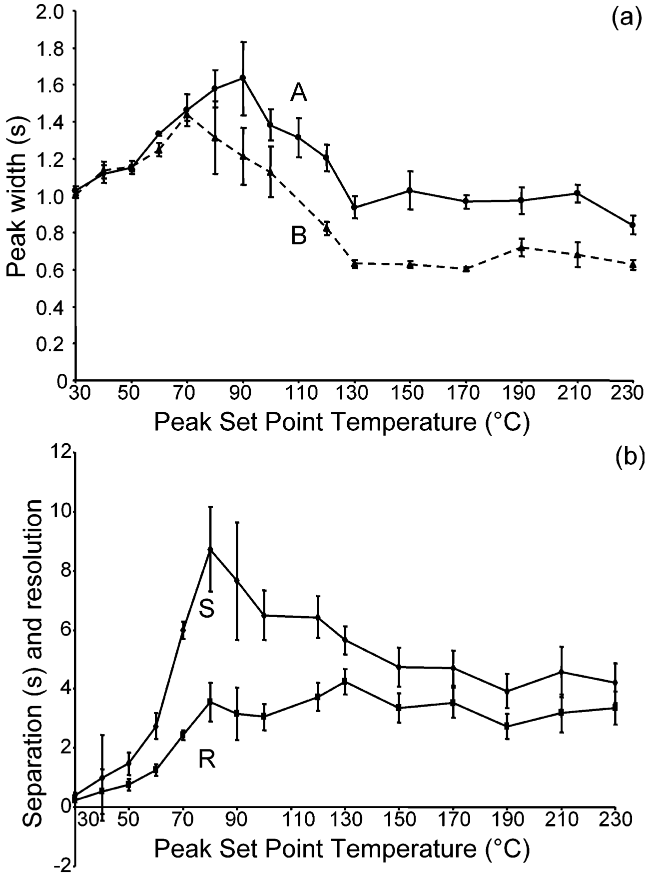

Figure 8. (a) Peak widths (full width at half-height) for ethyl acetate (plot A, solid line) and 2-butanone (plot B, dashed lines) versus heating-pulse amplitude (peak set-point temperature); (b) peak separation (*S*) and resolution (*R*) versus heating-pulse amplitude. In all cases, the pulse initiation time was 25 s after injection, and the initial and final second-column temperature was 30 °C.

Multiple Pulses for Mixture Analysis. An attractive feature of using second-column temperature pulses to achieve enhanced resolution of peak pairs that are separated by the first column but coelute from the column ensemble is that ensemble retention times for compounds that are in the first column during the entire heating pulse are only effected by the relatively small changes in first-column holdup time caused by viscosity changes in the second column. Thus, component pairs that are separated by the column ensemble without any heating pulses should remain separated with heating pulses. However, high-amplitude temperature pulses should be avoided because of the greater pulse width.

Figure 9a shows the separation of a 13-component mixture without the use of second-column heating pulses. Peak numbers correspond to compound numbers in Table 1. Small, unlabeled peaks are from impurities. The second-column temperature is shown below the chromatogram. Both columns were operated isothermally at 30 °C. The chromatogram is complete in less than 3 min, but only 7 of the 13 peaks are adequately separated for peak-area quantitative analysis. Note that, under these separation conditions, the *k* values listed in Table 1 predict that neither the first column nor the second column alone (assuming a column length equal to the ensemble length) would adequately separate all of the compounds, and multiple coelutions would occur as is seen for the column ensemble without temperature pulses in Figure 9a.

For chromatogram b, a single heating pulse was used to target component pair 3/4 for enhanced separation. The heating pulse with peak temperature of 90 °C is applied to the second column 33 s after injection. This is just prior to components 3 and 4 reaching the column junction point. Components 1 and 2 elute shortly after the start of the pulse and thus experience only a small portion of the pulse. The results are small shifts to slightly earlier retention times, a decrease in separation, and significant peak narrowing. Components 3 and 4 enter the second column just after the start of the pulse with the result that relatively large retention time shifts are observed, and the peaks are separated with a resolution of 2.2. Since peaks 3 and 4 elute before the end of the heating pulse, significant peak narrowing is observed. Components 5 and 6 enter the second column before the end of the pulse but elute after completion of the pulse. This results in some band stretching. Peaks 7−13 are in the first column during the entire pulse and are relatively unaffected by the pulse.

For chromatogram c, a second pulse with peak set-point temperature of 60 °C is used to target component pair 7/8 for enhanced separation. The pulse was initiated 68 s after injection and results in the completed separation of components 7 and 8. For chromatogram d, a third temperature pulse was used to

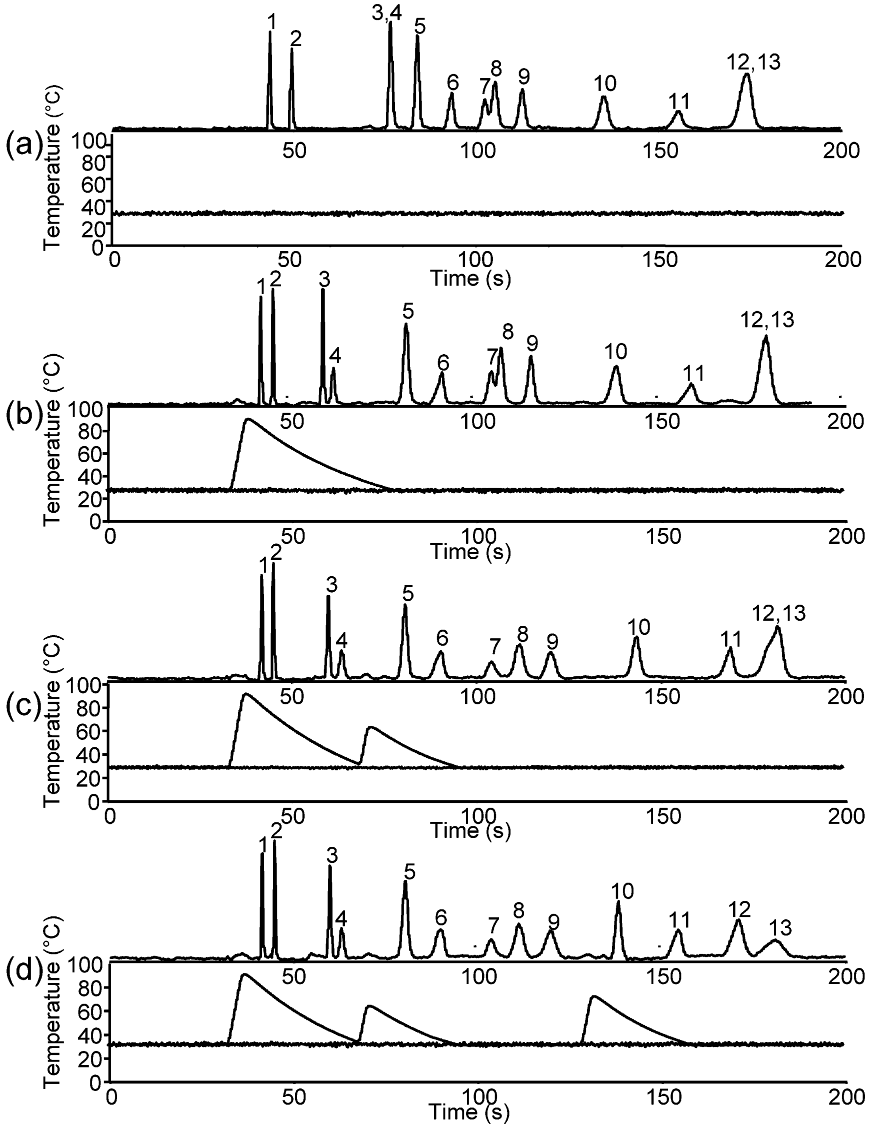

Figure 9. Separation of a 13-component mixture with no second-column heating pulses (a), with one pulse to enhances the resolution of component pair 3/4 (b), with a second heating pulse to enhance the resolution of component pair 7/8 (c), and with a third heating pulse to enhance the resolution of component pair 12/13 (d). See text for heating-pulse parameters. Peak numbers correspond to compound numbers in Table 1.

achieve complete separation of component pair 12/13. Thus, the use of three appropriately timed second-column heating pulses resulted in complete separation of the 13-component mixture while only adding a few seconds to the total duration of the chromatogram.

CONCLUSIONS

High-speed at-column heating of a low-thermal-mass column system combined with relatively rapid cooling in a 0 °C environment can obtain pulsed heating of the second column in a series-coupled ensemble of two columns using significantly different stationary phases. For component pairs that are separated by the first column in the ensemble but coelute from the ensemble by virtue of the different selectivities of the columns, enhanced separation can be achieved if the retention times for the two components are changed differentially by the heating pulse. A simple means to accomplish this is to apply a heating pulse to the second column just prior to the first component of the targeted peak pair entering the second column. In this way, both components enter the second column during the temperature decrease after the peak temperature is achieved. Determination of the pulse initiation time requires knowledge of the retention times of compounds in the first column. This can be determined for mixtures containing known analyte. Thus, pulsed heating of the second column is most useful for targeted analysis where the possible analytes are known.

In addition to changes in retention times, second-column heating pulses can alter peak widths by stretching solute bands if they enter the second column during the temperature pulse and by narrowing the peaks eluting from the column ensemble if they elute during a heating pulse. If the second column temperature changes appreciably in the time required for a solute band to cross the column junction and migrate into the second column or to elute from the column ensemble, band stretching is asymmetric, and distorted peaks are observed. However, these artifacts do not have a significant effect on the resolution of adjacent peaks in the ensemble chromatogram.

The heating pulse width in the studies reported here is determined primarily by the cool-down time of the second column. The cool-down time depends strongly on the difference between ambient temperature and the final set-point temperature after completion of the heating pulse as well as on the thermal mass of the second column. For the relatively low final set-point temperature of 30 °C, cold-gas cooling was needed to achieve sufficiently rapid cooling. For isothermal separations at higher column temperatures and for temperature-programmed operation, more rapid cool-down will be achieved, and cold-gas cooling may be eliminated. Studies under these conditions are in progress. Other studies are in progress where the heating pulse is applied only to the upstream end of the second column. This, and reduction in the thermal mass of the column to obtain more rapid cooling, will eliminate artifacts caused by heating-pulse-induced changes in ensemble elution temperatures. It is anticipated that temperature pulsing of the second column in a series-coupled column ensemble will be utilized to achieve programmable selectivity in low-power, portable, and microfabricated GC instruments used for environmental monitoring.

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