Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1086 (2005) 151–159
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Band acceleration device for enhanced selectivity with tandem-column gas chromatography

Mark Libardoni, Megan McGuigan, Young J. Yoo, Richard Sacks *

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

Available online 11 July 2005

Abstract

An electrically heated and air cooled metal sheath surrounding the first 50 cm of the second column in a series-coupled, capillary-column ensemble of a non-polar and a polar column is used to obtain enhanced isothermal separation of component pairs that are separated by the first column in the ensemble but co-elute from the ensemble by virtue of the different selectivity of the two columns. As the first of the two components passes into the second column, a current pulsed through the metal sheath rapidly heats the first 50 cm of the second column thus accelerating the band for the first component. Ensemble retention-time shifts of several seconds are easily obtained. The device is then rapidly cooled to quiescent oven temperature by a flow of pressured air through the space between the metal sheath and the fused silica capillary column and an additional flow through a larger, co-axial plastic tube. Both heating and cooling require only a few seconds. If substantial cooling of the device occurs before the band for the second component enters the device, the band experiences less thermally-induced acceleration with the result that the separation of the two targeted components is enhanced in the ensemble chromatogram with no significant change in the pattern of peaks for the other mixture components. If the device is cooled to a temperature below oven temperature before the arrival of the band for the second component, this band will be slowed, and further enhancement of separation is achieved in the ensemble chromatogram. A band trajectory model, based on retention factor versus temperature data for the two components in the two columns, is used to predict peak separation and to aid in the selection of temperature-pulse initiation times.

Keywords: Gas chromatography; Temperature-programming; Modeling

1. Introduction

Tandem-column gas chromatography uses two capillary GC columns, often of similar length and the same internal diameter, but with different stationary phases to achieve a column ensemble with unique selectivity [1–3]. Changing the carrier-gas pressure at the junction point between the two columns changes the pattern of peaks eluting from the column ensemble. Pulsed pressure changes, typically lasting 1–5 s, have been used to target specific component pairs for enhanced separation and resolution [4,5]. These methods have been used to obtain order-of-magnitude reductions in analysis time for the separation of pesticides [6], citrus oils [7–10] and volatile organic compounds in air samples [11,12].

Comprehensive two-dimensional gas chromatography (GC × GC) [13,14] also uses two-columns connected in series. However, GC × GC generally uses two columns with different lengths and diameters that are connected in series through a concentration modulator. The modulator continuously traps, focuses and re-injects effluent from the primary column onto the second column for a rapid orthogonal analysis. Many modulators have been described in the literature and some are commercially available (for an overview see, e.g. [15]). Since its inception in the early 1990s, GC × GC has emerged as a powerful method for the separation of complex mixtures. Its application range covers environmental samples [16,17], forensic samples [18], petroleum products [19,20] and essential oils [21,22].

With a one-dimensional tandem-column ensemble, some compounds are separated in the first column and stay separated in the second column. Other compounds are not separated in the first column but are separated in the second

* Corresponding author. Tel.: +1 7346474865.
E-mail address: rdsacks@umich.edu (R. Sacks).

0021-9673/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2005.06.014

column. Often, some pairs or groups of components are separated by the first column but co-elute from the column ensemble because of the different selectivity of the two columns. For these components, enhanced separation often is possible by applying carrier-gas pressure pulses at the column junction point.

For a pair of components that are adequately separated by the first column but co-elute from the column ensemble, the pressure pulse is timed to occur when one of the components is in the second column while the other component is still in the first column. This results in a differential change in migration times for the two components in the two columns, and results in increased separation of these components in the ensemble chromatogram. An attractive feature of this method is that mixture components in the same column when the pressure pulse is applied show proportional shifts in ensemble retention times with the result that no significant change in the ensemble peak pattern is observed. Thus, specific component pairs can be targeted for enhanced separation without changing the relative positions of the other peaks in the ensemble chromatogram.

While pressure-pulse methods can be very effective, they require the use of mechanical devices including valves and pressure controllers. These devices can be maintenance intensive and would be difficult to incorporate in miniaturized and micro-fabricated GC instruments, which are under development in several laboratories [23,24]. In order to accommodate these needs, alternative methods for enhancing selectivity are required. The use of temperature pulses applied to one of the columns in a tandem-column ensemble for the purpose of increasing separation of targeted component pairs that are separated by the first column but co-elute from the column ensemble has recently been demonstrated [25]. In order to achieve rapid column heating, special columns were used incorporating at-column heating [25,26] to achieve heating rates of 800 °C/min. Convective cooling using cold nitrogen gas was used to obtain relatively rapid cooling.

While pulsed heating of one of the columns in the ensemble is effective for enhancing the separation of targeted component pairs, the need for special columns and cryo-cooled gas are significant limitations. In addition, temperature-pulse widths less than about 25 s are difficult to achieve. Since the entire second column is heated, peak-shape artifacts are produced if other mixture components enter or elute from the second column during a temperature pulse.

In order to overcome these limitations, a band acceleration device (BAD) was developed to very rapidly heat and cool the first 50 cm long segment of the second column in the ensemble. The BAD uses a resistively-heated and air cooled metal sheath surrounding the column. The BAD should not be mistaken for a modulator which is used in two-dimensional separations. A modulator is used continuously throughout a GC × GC analysis to trap, focus and re-inject effluent from the first column onto the second column. The BAD is used only at targeted times throughout the analysis to decrease retention factors of component pairs that would normally co-elute. While the BAD is not used as a thermal modulator, the electrical heating and gas cooling methods may be useful for future modulator development [27]. In this report, the design of the BAD and its operation are described. A spreadsheet-based model, which obtains plots of solute band position along the column ensemble axis versus time, is used to predict peak separation and to aid in the selection of temperature-pulse initiation times.

2. Experimental

2.1. Apparatus

The complete system is shown in Fig. 1. All experiments were performed with an HP 5890 GC equipped with two flame ionization detection (FID) systems and a split inlet I. The column ensemble consisted of two 0.18 mm I.D., 0.20 μm thick stationary phase fused silica capillaries with the 6.5 m long upstream column C_1 using a 5% phenyl–95% dimethyl polysiloxane phase (Rtx-5, Restek, Bellefonte, PA, USA) and the 5.7 m long downstream column C_2 using a polar polyethylene glycol phase (Rtx-Wax, Restek). The junction point between the columns is connected to FID_1 via a 30 cm long segment of 0.05 mm I.D deactivated fused silica tubing. About 10% of the effluent from the first column is split to this detector by means of an all-glass splitter in order to monitor the course of the separation from C_1.

2.2. BAD design

A 50 cm segment of C_2 is housed inside a 50 cm × 1.57 mm O.D. × 1.34 mm I.D. piece of metal-alloy tubing (Inconel 600, Huntington Alloys, Huntington, WV, USA) (T in Fig. 1) consisting primarily of Ni, Co, Cr and Fe and equipped with custom fabricated stainless steel tee adaptors (F) at each end. The column is centered through

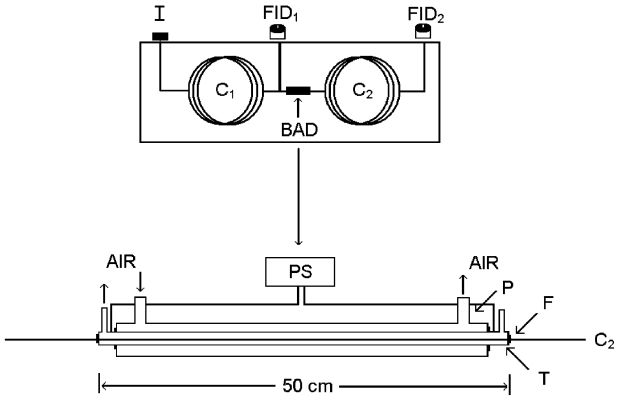

Fig. 1. Diagram of the complete GC system and detail of the band acceleration device. C_1, non-polar column; C_2, polar column; I, split inlet; FID_1 and FID_2, flame ionization detectors; B, band acceleration device; PS, power supply; T metal tube housing a 50 cm length of C2; P, plastic cooling sheath; F, gas-tight end fittings.

each tee adaptor with graphite ferrules. A 24 cm long segment of C_2 extends from the up-stream tee adaptor to the all-glass splitter. This length was needed for fabrication and mounting convenience. This portion of C_2, as well as the downstream portion beyond the BAD is always at the oven temperature. The metal-alloy tubing is housed inside a 48 cm long, 1/8 in. I.D., 1/4 in. O.D. segment of PTFE tubing (P in Fig. 1) (Aldrich, Milwaukee, WI, USA) with 1/4 in PTFE tee connectors at each end. The metal-alloy tubing is centered through the PTFE tubing via graphite ferrules at each end.

Located inside the GC oven, the BAD is independently heated relative to the GC oven and rapidly cooled with compressed house air without significantly affecting the temperature of the GC oven. Resistive heating of the BAD (1.6 Ω) is provided by 100 W, 8 A, dc power supply PS (Astrodyne International, Taunton, MA, USA) attached via alligator clips to the exposed ends of the metal-alloy tubing. Control of the power supply and cooling air is provided by a 330 MHz personal computer (Dell, Optiplex GX1, Round Rock, TX, USA) equipped with a 16-bit A/D interface board (PCI-DAS 1602, Computer Boards, Mansfield, MA, USA). Compressed house air at 80 psig is supplied through a computer controlled valve (GH3412, Precision Dynamics, Phoenix, AZ, USA) and directed into one end of the PTFE tee fitting as well as the opposite end of the metal-alloy tee fitting. This countercurrent flow of air allows for rapid and uniform cooling of the BAD both inside and outside the metal-alloy tubing. The exiting cooling air is routed out the opposing tee connectors through 1/4 in PTFE tubing and vented outside the GC oven compartment. The peak BAD temperature and the width of the heating/cooling pulse is controlled by means of the duration of the current pulse used for heating and the delay between the start of the heating pulse and the start of the cooling gas flow.

The BAD temperature was measured with a type J thermocouple and gauge (Model DP 116, Omega, Stamford, CT, USA). Thermocouple wire diameter is 0.01 in. A segment near the center of the metal tube was coated with polyimide resin and cured to provide an insulating layer. The thermocouple junction was sandwiched between this layer and a polyimide tube, which was cured to encapsulate the junction. The wire leads were passed out through the exit cooling gas line.

2.3. Spreadsheet calculations

A band trajectory model that generates plots of solute band position along the column ensemble as a function of time has been previously described [28]. This model uses a series of standard equations to calculate carrier gas velocity, carrier gas viscosity, retention factors and migration times for 1 cm long segments along the length of the column ensemble. These values are all assumed to be constant in each 1 cm interval. By plotting the cumulative sums (integral) of the segment migration times versus position along the column axis, solute band trajectory plots are obtained. These plots allow for the selection of heating-pulse initiation times for enhancing the separation of targeted pairs or groups of components that coelute from the column ensemble.

Model input includes column dimensions, ensemble inlet and outlet pressures, column temperatures and the time-dependent BAD temperature T_b. Retention factors k in the BAD are calculated based on Van't Hoff plots of $\ln k$ versus $1/T_b$ for all sample components on each column. For the work reported here, the temperature of C_1 and C_2, except for the 50 cm long region of C_2 in the metal heating and cooling sheath, are equal to the isothermal oven temperature, which was 70 °C.

Data from the thermocouple used to measure the temperature of the BAD also is input into the model. The temperature pulse is approximated as a triangle, where the upward slope is the heating rate and the downward slope is the cooling rate. Using the temperature pulse triangle and the Van't Hoff plot coefficients, retention factor values for solute bands in the BAD are calculated as the temperature changes during heating and cooling pulses.

2.4. Materials and procedures

Hydrogen carrier gas was used after purification with filters for water vapor, hydrocarbons and oxygen. Column head pressure was 17.5 psig for all experiments. All chemicals used in test mixtures are reagent grade or better. Table 1 lists

Table 1
Components, boiling points and retention factors for test mixtures

Compound	Boiling point (°C)	k at 70 °C (C_1)	k at 70 °C (C_2)	Peak label
5-Methyl-2-hexanone	144	2.01	2.15	1
2-Heptanone	150	2.59	2.66	2
5-Methyl-1,3-heptanone	159	3.81	2.65	3
2,6-Dimethyl-4-heptanone	168	4.78	2.31	4
Decane	174	5.74	0.76	5
2-Chlorotoluene	159	4.09	5.37	6
3-Octanone	168	5.26	4.26	7
Heptanol	176	5.12	14.75	8
2-Bromotoluene	182	7.69	10.47	9
5-Nonanone	187	10.51	5.37	10

the compounds, their boiling points and their retention-factor values on both columns at 70 °C. Sample injection size was 1.0 μL with a split ratio of 100:1. The injector and detector temperature was 250 °C. During a heating pulse, an 8.0 A current is delivered to the metal tube. The cooling-air flow was 1.0 L/s, and about 3 L is consumed for each heating/cooling cycle.

3. Results and discussion

3.1. Temperature–pulse requirements

For two components that co-elute in the ensemble chromatogram, if the ensemble retention time of one of the peaks is shifted by 1.5 peak widths (base width, 4σ), the resolution will be 1.5 in the ensemble chromatogram. This is adequate for most applications. For the column ensemble and the operating conditions used in this study, peak widths are in range from less than 0.6 s for an ensemble retention factor of 1.0–3 s for an ensemble retention factor of 10. This is a typical range of retention factors for many isothermal applications. The BAD is located at the upstream end of column C_2, and calculations using standard equations for gas flow in capillary columns [29] give an average carrier gas velocity in the BAD at an oven temperature of 70 °C of about 140 cm/s. The resulting hold-up time t_m for the 50 cm long device is about 0.4 s. For compounds with C_2 retention factors (k_2) in the range 1–10, their residence time in the device (BAD retention time) with no heating or cooling pulse range from 0.8 to 4.4 s [$t_m(k_2 + 1)$].

For many volatile organic compounds, a 15–20 °C increase in column temperature results in a two-fold decrease in retention factors. If the BAD temperature is increased by 100 °C, retention factors typically will be reduced by more than a factor of 30. This results in decreases in BAD residence times and thus ensemble retention times of about 0.4 s for a compound with a k_2 value of 1 at the oven temperature to about 4 s for a k_2 value of 10 at the oven temperature.

Fig. 2 shows BAD temperature versus time data for heating pulses with heating current durations of 2–7 s for traces A–F, respectively. In all cases, the valve controlling the cooling gas was opened 1.0 s prior to the end of the heating pulse. This was found to produce a pulse of nearly triangular shape, which is well suited for use with the band-trajectory model. For pulses A–E, the cooling gas flow duration was 3.0 s, and for pulse F, the flow duration was 4.0 s. Note that a small temperature undershoot may occur at the end of the heating pulse depending on the pulse amplitude and the duration of the cooling gas flow. Careful adjustment of the flow duration can nearly eliminate the undershoot with the BAD temperature returning rapidly to it quiescent value of 70 °C (oven temperature).

For pulse D, a peak temperature of 160 °C is reached in about 4 s. The pulse is complete in about 6 s. The insets in Fig. 2 show the rising and falling portions of pulse D. The straight lines superimposed on the actual traces are the approximations used to estimate the BAD temperature for the spreadsheet calculations of solute band position versus time. The heating and cooling rates (slopes) are 28.3 and 46.7 °C/s, respectively. The straight-line approximations are reasonably good with r^2 values of 0.993 and 0.982, respectively. At sufficiently high BAD temperatures, the solute residence times in the 50 cm long BAD are at least an order of magnitude smaller than the width of the heating pulse, and the temperature change during the passage of the solute band is relatively small.

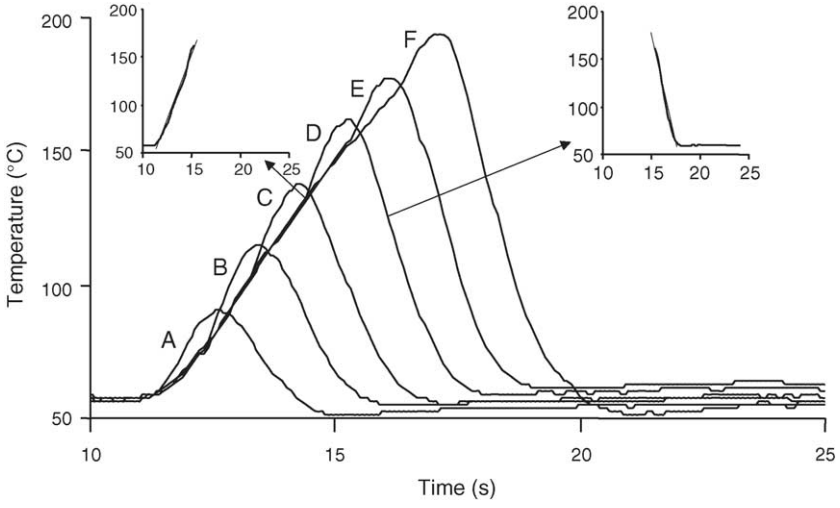

Fig. 2. Heating pulses for heating current durations of 2 s (A), 3 s (B), 4 s (C), 5 s (D), 6 s (E) and 7 s (F). The cooling gas flow begins 1.0 s before the termination of the heating current and lasts for 3.0 s for pulses A–E and for 4.0 s for pulse F. The insets to the left and right of the temperature waveforms shows the heating and cooling portions of pulse D and the straight-line approximations used in the spreadsheet model to obtain solute band trajectories through the column ensemble.

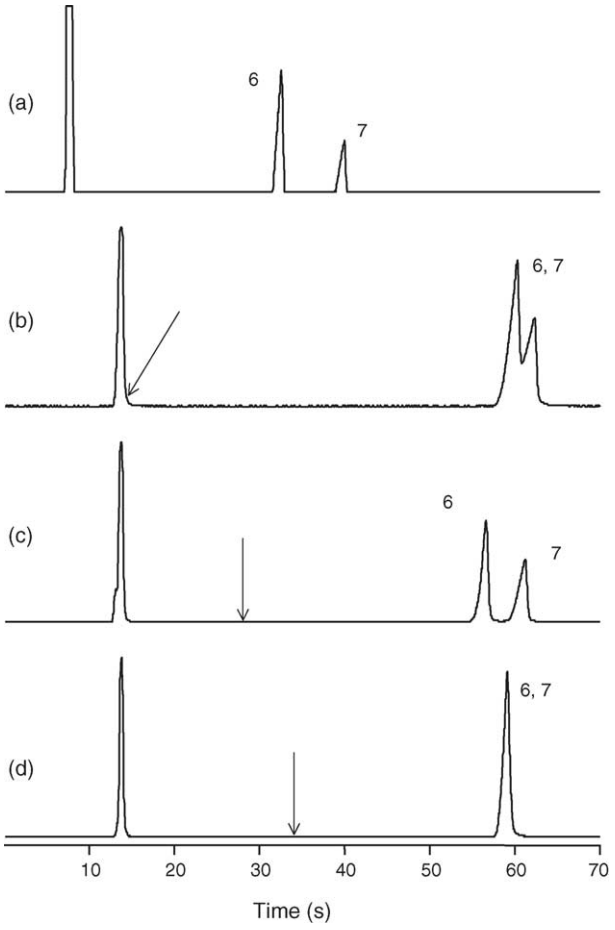

Fig. 3. Chromatograms illustrating the operation of the BAD for enhanced separation of a component pair that is separated by the first column in the ensemble but co-elutes from the column ensemble. Peak numbers correspond to compound numbers in Table 1. (a) Chromatogram from FID_1 monitoring a portion of the effluent from the first column; (b) chromatogram from FID_2 monitoring the column ensemble with a heating pulse initiated 15 s after sample injection; (c) chromatogram from FID_2 with a heating pulse initiated 28 s after sample injection; (d) chromatogram from FID_2 with a heating pulse initiated 33 s after sample injection. Vertical arrows indicate the heating pulse initiation time.

3.2. BAD operation

Fig. 3 shows chromatograms for a pair of solutes that are completely separated by the first column but are not adequately separated in the ensemble chromatogram. Peak numbers correspond to compound number in Table 1. Chromatogram (a) is from FID_1, which monitors about 10% of the effluent from the first column. Chromatogram (b) shows the ensemble chromatogram for the case when a heating pulse (pulse D in Fig. 2) is initiated 15 s after sample injection. Pulse initiation time is indicated by a vertical arrow. Both components are in the first column during the duration of the pulse, and no change is seen in the ensemble chromatogram relative to the case without a BAD temperature pulse (not shown in Fig. 3).

For chromatogram (c), the BAD heating pulse was initiated 28 s after sample injection. This is just prior to solute band 6 entering the device, and the band is in the device at the time of peak temperature. The result is a decrease in the ensemble retention time for component 6 of about 3.5 s. Note that there is no change in the ensemble retention time for peak 7. The result is more than adequate separation of the two peaks. For chromatogram (d), the temperature pulse is initiated 34 s after injection. At this time, component 6 has passed through the BAD, and the temperature pulse has no effect on its ensemble retention time. The band for component 7, however, passes through the device at about the time of peak temperature, and the peak is shifted to shorter ensemble retention time. The result is that peak 7 is shifted into peak 6, and complete co-elution occurs.

Fig. 4 shows a plot of peak separation in the ensemble chromatogram versus heating pulse initiation time for the compounds (6 and 7) and conditions used for Fig. 3. Points labeled b–d correspond to chromatograms (b–d) in Fig. 3. For pulse initiation times of less than 25 s, the pulse is over before either of the solute bands enters the device, and no significant change in ensemble peak separation is observed. For pulse initiation times in the range 26–31 s after sample injection, the band for component 6 passes through the BAD during the heating pulse, and the peak separation is nearly constant at about 4.5 s. Since the time window for pulse initiation is relatively large, precise control of pulse initiation time is not critical. For pulse initiation times in the range 33–38 s, solute band 7 passes through the BAD during the heating pulse, and no measurable peak separation is observed. For pulse initiation times in the range 38–41 s after injection, component 7 passes through the BAD during the end of the heating pulse, and its retention time shift in the ensemble chromatogram decreases, and the ensemble peak separation returns to its quiescent (no heating pulse) value of 2.0 s.

3.3. Enhanced targeted component pair separation

As mixture complexity increases, the probability of more than one component band passing through the BAD during a heating pulse increases, and thus the ensemble peak separation may change for peak pairs other than the targeted pair. An example is shown in Fig. 5 for the separation of a nine-component mixture. For simple cases such as illustrated in Fig. 3, plots of ensemble peak separation versus heating pulse initiation time such as shown in Fig. 4 are very useful for the determination of optimal pulse initiation time. However, for more complex situations, solute band trajectory plots from spreadsheet calculation are far more useful for the development of separation strategies.

Solute band trajectory plots of band position along the column axis versus time are shown in Fig. 5 for the case with no BAD heating pulse (a) and for the case of a single pulse (pulse F in Fig. 2) initiated 30 s after sample injection and timed to obtain enhanced separation of component pair 8/9. For each set of plots, the solid horizontal line at a column-axis coordinate of 6.5 m corresponds to the junction-point of the two columns in the ensemble. For many of the mix-

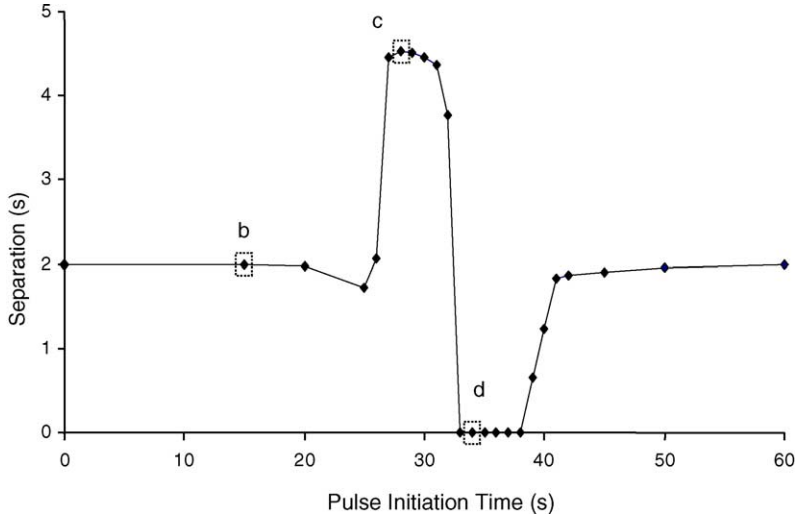

Fig. 4. Plot of peak separation vs. pulse initiation time for the compounds used in Fig. 3. Points labeled b–d correspond to chromatograms (b–d), respectively, in Fig. 3.

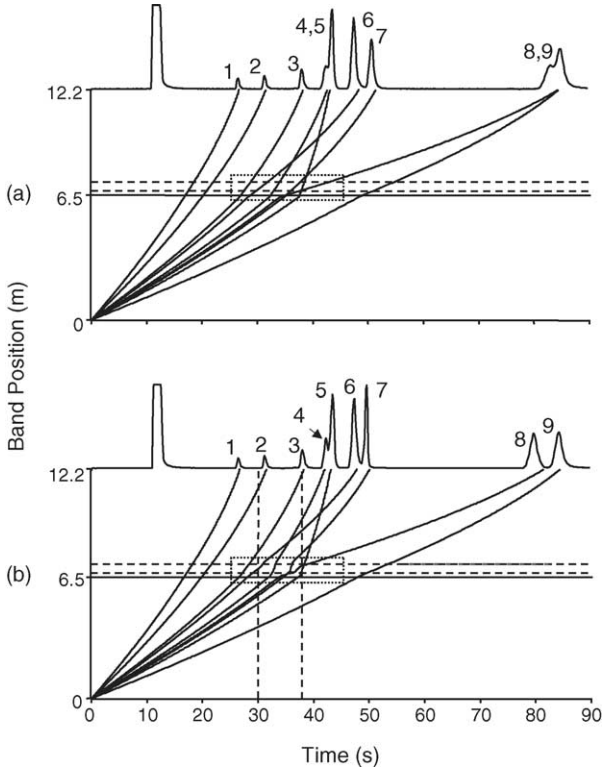

Fig. 5. Plots of solute band position in the column ensemble vs. time and chromatograms for a nine-component test mixture without a BAD heating pulse (a) and with a pulse initiated 30 s after sample injection and targeting component pair 8/9 for enhanced separation (b). The solid horizontal lines at column coordinate 6.5 m correspond to the column junction point, and horizontal dashed lines show the location of the BAD. Vertical dashed lines in (b) show the start and end of the temperature pulse. Peak numbers correspond to compound numbers in Table 1.

ture components, the band trajectory plots show abrupt slope changes as the bands migrate across the column junction. This is the result of the different migration rates associated with the different stationary phases in the two columns. The pair of horizontal dashed lines corresponds to the location of the BAD. Sample injection occurs at the lower-left corner of the plots, and elution from the column ensemble occurs at the end of the band trajectory plots corresponding to band position coordinate of 12.2 m (length of the column ensemble). Chromatograms are shown above the band trajectory plots. Peak numbers correspond to the compound numbers in Table 1. Note the good agreement between the actual and predicted retention times.

Without a BAD heating pulse [chromatogram (a)], coelutions are observed for component pairs 4/5 and 8/9. Note that the band trajectory plots for components 7 and 8 are nearly parallel in C_1, and thus these components could not be separated under these conditions using only the non-polar column C_1. Components 2–4 have nearly parallel band trajectories in column C_2, and thus these components could not be separated using only C_2. This is confirmed by the retention factor values in Table 1. For case (b), a single heating pulse with peak temperature of 180 °C is used to target component pair 8/9 for enhanced separation. The pulse initiation and completion times are indicated by the dashed vertical lines in Fig. 4b. The pulse is timed to accelerate the band for component 8. Since the pulse is complete before the band for component 9 enters the device, no acceleration occurs for component 9.

Solute bands from several compounds enter the BAD during the heating pulse, and the separations of several closely spaced peak pairs in the ensemble chromatogram are changed by the heating pulse. This is illustrated more clearly in Fig. 6, where the regions in the dotted-line boxes in Fig. 5 are shown in greater detail. Again, the solid horizontal line represents the column junction point, and the dashed horizontal lines

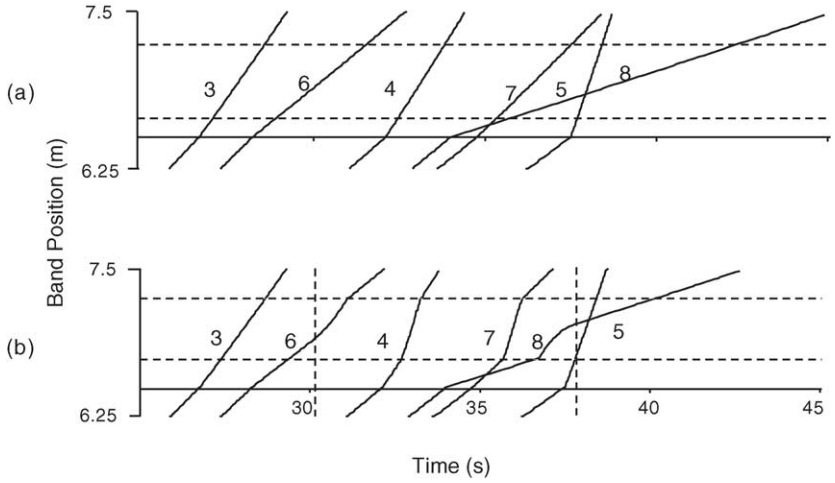

Fig. 6. Expanded view of the plots of solute band position vs. time from Fig. 5 corresponding to the regions of Fig. 5 in the dotted-line rectangles. The solid horizontal lines at column coordinate 6.5 m correspond to the column junction point, and horizontal dashed lines show the location of the BAD. Vertical dashed lines in (b) show the start and end of the temperature pulse. Plot numbers correspond to compound numbers in Table 1. See text for details.

indicate the location of the BAD. Fig. 6a is for the case with no temperature pulse, and Fig. 6b is with a single temperature pulse starting about 30 s after injection. Dashed vertical lines in Fig. 6b indicate the starting and ending times of the temperature pulse.

The heating pulse affects the band migration velocities for components 4, 6, 7 and 8. Component 6 enters the device prior to the start of the heating pulse, and the band velocity (local slope of the band trajectory plots) increases as the BAD temperature increases at the start of the heating pulse. The bands for components 4 and 7 enter and exit the BAD while it is hot, and their residence time in the device approaches the minimum value of about 0.4 s (BAD holdup time). Note that component 5 (*n*-decane) has very low retention on the polar polyethylene glycol column, and its band velocity through the BAD approaches the carrier gas velocity with the result that the band for *n*-decane would not undergo significant acceleration even if the BAD was hot. Component 8 has relatively large retention in the polar column, and thus retention time is shifted considerably even though the band enters the BAD near the end of the heating pulse, and the BAD temperature falls to the GC oven temperature before the band exits from the device.

Maximum separation of component pair 8/9 occurs when the heating pulse is timed so that component 8 passes through the BAD at the time of peak temperature. This would require that the pulse be initiated about 34 s after sample injection. However, the band for component 7 enters the device before component 8 with the result that the peak for component 7 is shifted into the peak for component 6 in the ensemble chromatogram. If the pulse initiation time is reduced to about 30 as shown in Fig. 6b, component 6 is in the device at the start of the temperature pulse, and the peak for component 6 in the ensemble chromatogram is shifted sufficiently to prevent the co-elution of 6 and 7 in the ensemble chromatogram. Note in Fig. 5b that the separation of component pair 6/7 is smaller than in Fig. 5a but adequate to give a resolution of about 0.98, and component pair 8/9 has a resolution of 1.66. Also note that the band for component 4 passes through the BAD during the temperature pulse resulting in some improvement in the resolution of component pair 4/5 in the ensemble chromatogram.

3.4. Multiple temperature pulses

Fig. 7 shows how two sequential temperature pulses with a cooling interval between them can be used to separate three components that are all separated by the first column but co-elute in the ensemble chromatogram. Fig. 7a shows band position versus time plots and the corresponding chromatograms for the case with no temperature pulses applied to the BAD. Note that these solutes elute from the first column with separations of more than 10 s between adjacent bands. This should be more than adequate for enhancing their separation in the ensemble chromatogram.

In Fig. 7b, a single 8 s long heating pulse (dashed vertical lines) with amplitude of 195 °C (pulse F in Fig. 2) is used to accelerate the solute band for component 8. The pulse initiation time was adjusted so that the solute band for component 8 was in the BAD during the highest temperature portion of the pulse. This shifts component 8 to shorter ensemble retention time by about 3.6 s. Since the temperature pulse is completely over before component 9 crosses the column junction, the pulse has no significant effect on the ensemble retention time for components 9 and 10.

If a second heating pulse is used to shift peak 9 in order to separate components 9 and 10, peak 9 is shifted into peak 8 in the ensemble chromatogram. However, if the cooling air flow for the first temperature pulse is continued until the second pulse, the solute band for component 9 enters the BAD when its temperature is about 25 °C. This results in an increase in the retention factor for component 9 to a value of about 80, and this band slows dramatically shifting the peak to longer

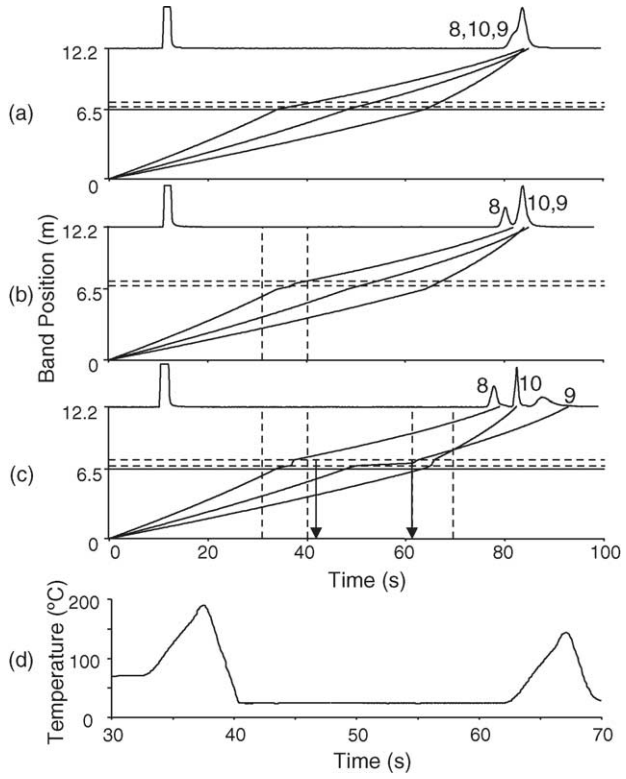

Fig. 7. Plots of solute band position in the column ensemble vs. time and chromatograms for a three-component test mixture without a BAD heating pulse (a), with a pulse initiated 30 s after sample injection and targeting component 8 for enhanced separation from components 9 and 10 (b), and with continued cooling followed by a second heating pulse initiated 61 s after injection to obtain the complete separation of components 8–10 (c). The BAD temperature profile used for chromatogram (c) is shown in (d). Vertical dashed lines in (b) show the start and end of the temperature pulses and vertical arrows show the cooling interval between the heating pulses. Peak numbers correspond to compound numbers in Table 1.

ensemble retention time. A second temperature pulse then is used to increase the separation of component pair 9/10. This is shown in Fig. 7c where the right pair of vertical lines indicates the beginning and end of the second temperature pulse. The vertical arrows in Fig. 7c indicate the BAD cooling interval. The BAD temperature versus time profile is shown in Fig. 7d. The relatively large error in the ensemble retention time for component 9 predicted by the model is the result of extrapolation error in the determination of the retention factor value at a temperature of 25 °C from a plot of ln(k) versus 1/T.

Note that the second temperature pulse is needed after termination of the cooling gas flow because the return to the oven temperature of 70 °C for the BAD is very slow (see Fig. 2), and this would shift the ensemble retention time of component 10 to a larger value thus decreasing the separation of component pair 9/10. In addition, the second temperature pulse is needed to shift the ensemble retention time of component 10 relative to component 9 in order to achieve baseline separation of this component pair.

4. Conclusions

The electrically heated and air-cooled band acceleration device is very useful for enhancing the separation of component pairs that are separated by the first column in a one-dimensional series-coupled column ensemble but co-elute from the ensemble. The device is a viable alternative to the use of pulsed pressure or flow control at the junction point of two columns in a series-coupled ensemble. The BAD should not be mistaken for a modulator which is used in two-dimensional separations, although the electrical heating and gas cooling methods used with the BAD may be useful for future modulator development. Operation of the BAD is based entirely on rapid temperature changes and thus requires no mechanical devices other than the valve used to control the cooling gas. For micro-fabricated columns as well as for columns using low-thermal-mass at-column heating techniques very rapid heating and sufficiently rapid cooling can be obtained without the need for cooling gas. This is particularly attractive for low-power, autonomous instruments under development for environmental monitoring.

For simple cases where only a single solute band passes through the BAD during a heating pulse, precise timing of the pulse is not critical since the heating pulse width is much greater than the band residence time in the device. In addition, with sufficient heating pulse amplitude, band residence time in the device is nearly equal to the device holdup time, and modest pulse amplitude changes have relatively little effect on ensemble retention times.

For more complex situations, rapid heating and cooling are important in minimizing the number of component bands that are influenced by the temperature pulse. Ideally, the pulse should affect the ensemble retention time of only one component in the mixture so that a specific component pair can be targeted for enhanced separation without affecting the ensemble retention times of other mixture components. Since the holdup time in the BAD is only 0.4 s for the conditions described in this report, a heating pulse width of one second or less would be adequate and would substantially reduce the probability of more than one mixture component being affected by the device. Capacitive discharge heating of a low-thermal mass device is under investigation. Work in progress will emphasize the BAD for temperature programmed GC.

The BAD is most useful for targeted analysis including process monitoring, natural products analysis and some laboratory applications where the target compound list is known, and retention data can be readily obtained for all target compounds on both columns used in the ensemble. With this information, the solute band trajectory model can be used to develop separation strategies and determine heating pulse initiation times. While optimal temperature pulse initiation time can be determined from repeated trials as shown in Fig. 4, the use of a second detector to monitor a fraction of the effluent from the first column is useful for methods development since it provides a simple means for obtaining retention data from both columns.

References

[1] P. Sandra, F. David, M. Prood, G. Diricks, M. Verstappe, M. Verzele, J. High Resolut. Chromatogr. Chromatogr. Commun. 8 (1985) 782.
[2] M. Akard, R. Sacks, Anal. Chem. 66 (1994) 3036.
[3] M. Akard, R. Sacks, Anal. Chem. 67 (1995) 2733.
[4] T. Veriotti, M. McGuigan, R. Sacks, Anal. Chem. 73 (2001) 279.
[5] T. Veriotti, R. Sacks, Anal. Chem. 73 (2001) 813.
[6] T. Veriotti, R. Sacks, Anal. Chem. 73 (2001) 3045.
[7] T. Veriotti, R. Sacks, Anal. Chem. 73 (2001) 4395.
[8] T. Veriotti, R. Sacks, Anal. Chem. 74 (2001) 5635.
[9] T. Veriotti, M. McGuigan, R. Sacks, Perfume. Flavor. 72 (2002) 40.
[10] J.A. Pino, A. Rosado, J. Essent. Oil Res. 12 (2000) 675.
[11] J. Whiting, R. Sacks, Anal. Chem. 74 (2002) 246.
[12] A.J. Grall, E.T. Zellers, R. Sacks, Environ. Sci. Technol. 1 (2001) 163.
[13] J.B. Phillips, J. Beens, J. Chromatogr. A 856 (1999) 331.
[14] P. Marriott, R. Shellie, Trends Anal. Chem. 21 (2002) 573.
[15] J. Dallüge, J. Beens, U.A.Th. Brinkman, J. Chromatogr. A 1000 (2003) 69.
[16] J. Dalluge, L.L.P. van Stee, X. Xu, J. Williams, J. Beens, R.J.J. Vreuls, U.A.Th. Brinkman, J. Chromatogr. A 974 (2002) 169.
[17] H.J. De Geus, I. Aidos, J. de Boer, J.B. Luten, U.A.Th. Brinkman, J. Chromatogr. A 910 (2001) 95.
[18] G.S. Frysinger, R.B. Gaines, J. Forensic Sci. 47 (2002) 471.
[19] J. Blomberg, P.J. Schoenmakers, U.A.Th. Brinkman, J. Chromatogr. A 972 (2002) 137.
[20] G.S. Frysinger, R.B. Gaines, J. High Resolut Chromatogr. 23 (2000) 197.
[21] J.M. Dimandja, S.B. Stanfill, J. Grainger, D.G. Patterson, J. High Resolut Chromatogr. 23 (2000) 208.
[22] R. Shellie, P.J. Marriott, Flavour Fragr. J. 18 (2003) 179.
[23] C.J. Lu, J. Whiting, R.D. Sacks, E.T. Zellers, Anal. Chem. 76 (2003) 1400.
[24] E. Kolesar, R. Reston, IEEE Trans. Compon. Pack. Man. B. 21 (1998) 324.
[25] J. Whiting, R. Sacks, Anal. Chem. 75 (2003) 2215.
[26] E.U. Ehrmann, H.P. Dharmasena, K. Carney, E.B. Overton, J. Chromatogr. Sci. 12 (1996) 533.
[27] M. Libardoni, J.H. Waite, R. Sacks, Anal. Chem. 77 (2005) 2786.
[28] M. McGuigan, R. Sacks, Anal. Chem. 73 (2001) 3112.
[29] D. Grant, Capillary Gas Chromatography, Wiley, Chichester, New York, 1998.