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High-Speed Analysis of Complex Indoor VOC Mixtures by Vacuum-Outlet GC with Air Carrier Gas and Programmable Retention

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A pressure-tunable, series-coupled column ensemble was used with atmospheric pressure air as carrier gas for the vacuum-outlet GC analysis of 42 volatile and semi-volatile organic compounds commonly encountered as indoor air pollutants. Separation strategies applicable to a field-portable instrument that will employ a dual-stage preconcentrator and a microsensor array as the detector were developed, where coelution of certain analytes can be tolerated. The capillary column ensemble consists of a 4.5-m segment of nonpolar dimethyl polysiloxane followed by a 7.5-m segment of polar trifluoropropylmethyl polysiloxane. Good long-term thermal stability of the column ensemble was observed for continuous operation in air at temperatures up to 210 °C. A computer-driven pressure controller at the column junction point is used to adjust vapor retention for specified sets of target compounds. The compounds were divided into two groups according to retention order, and high-speed analysis conditions were determined for the two groups individually as well as for the entire mixture. The earlier eluting group of 21 compounds was analyzed isothermally at 30 °C in about 160 s using a single, on-the-fly junction-point pressure change during the separation. The later eluting group of 21 compounds was analyzed in about 200 s with temperature programming and a constant (tuned) junction-point pressure. The entire mixture was analyzed in about 400 s using a two-step temperature program and a three-step pressure program, with minimal overlap in eluting peaks. Separations are adequate for analysis by a sensor array capable of discriminating among small groups of coeluting vapors on the basis of their response patterns.

Introduction

The assessment of exposures to volatile and semi-volatile organic compounds (VOCs and SVOCs) in residential and nonindustrial working environments and the establishment of meaningful exposure limits are particularly challenging problems (*1*−*3*). Among the sources of (S)VOCs in such environments are building materials, furniture and floor finishes, personal care products, carpeting, cleaning products, and microbes (*4*, *5*). More than 350 anthropogenic and microbial compounds have been detected in residential and/or commercial indoor air at greater than 1 ppb (*4*). However, it is rare to find more than 60 identifiable compounds in a single location at such concentrations. Still, the complexity of indoor air−contaminant mixtures places constraints on monitoring options. For practical reasons, most studies focus on the 20−30 predominant compounds, which typically range in concentration from about 1 to 100 ppb (*6*−*8*).

Because of the wide range and low concentrations of (S)-VOCs potentially encountered, virtually all investigations of these compounds in building air rely on adsorbent or whole-air sampling followed by GC/MS analysis (*6*, *9*). In some cases, multi-adsorbent samplers are used because of the need to capture vapors covering a wide range of volatility (*9*, *10*). The costs of analysis and delays between sampling and analysis limit the quality and quantity of data obtainable. Having portable instrumentation capable of near-realtime determinations of (S)VOC profiles would greatly aid indoor air quality (IAQ) assessments and interventions.

Portable gas chromatographs (GC) can provide selective measurement of multiple individual airborne vapors, and handheld GCs are currently available commercially, some with high-resolution capillary columns and even temperature-programming capabilities (*11*, *12*). However, separation and detection schemes are limited by the conventional designs and technologies used in these instruments. Complex mixtures may not be adequately resolved, and vapor identification relies on retention time determined with a non-specific detector.

This paper describes the separation strategies intended for a field-portable instrument currently under development in which ambient air at atmospheric pressure will be used as the carrier gas, and the burden of analytical selectivity is shared among a dual-bed preconcentrator, a separation-column ensemble with tunable and programmable retention characteristics, and a detector comprising an array of polymer-coated surface acoustic wave (SAW) sensors. A set of 42 (S)VOCs was selected, with the goal of optimizing separations while constraining the total analysis to <10 min.

Previous work has shown that gas chromatography performed with atmospheric pressure air as carrier gas, where a vacuum pump is used to draw the carrier gas and injected samples through the system at reduced pressure, can provide effective separation of VOCs (*13*). Previous work also has shown that the components of mixtures of 3−4 VOCs can be reliably identified with an array of 3−6 polymer-coated SAW sensors provided that the response patterns of the component vapors are sufficiently unique (*14*−*16*). The separation strategies described in this paper have been developed to minimize separation time and maximize separation/resolution, while recognizing that coelutions of up to 3 or 4 analytes may be tolerable. The tunable and programmable retention capability (*13*, *17*−*19*) can be used to ensure that the components present in any overlapping peaks can be differentiated by the sensor array using pattern recognition methods.

The dual-bed adsorbent preconcentrator also under development for this instrument is intended to collect VOCs and SVOCs in two more-or-less separate fractions determined by the structures and volatilities of the compounds and by the temperatures of the two adsorbent beds. Trapped components can be thermally desorbed from the two beds either sequentially or simultaneously. In the former case, the components in the two fractions would be determined

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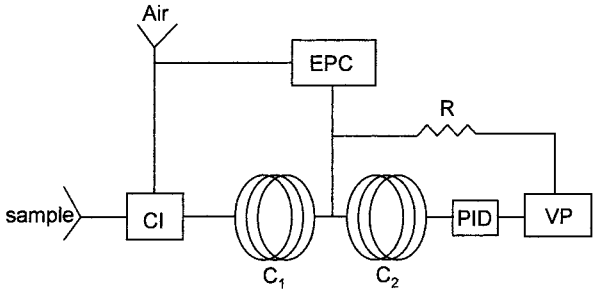

FIGURE 1. Vacuum-outlet GC with pressure-tunable column selectivity and photoionization detection. C_1, nonpolar column; C_2, polar column; CI, cryofocusing inlet system; EPC, electronic pressure controller; PID, photoionization detector; VP, vacuum pump; R, capillary pneumatic restrictor.

sequentially, and in the latter case all trapped components would be determined in a single, longer chromatographic run.

Experimental Section

Apparatus. To evaluate separation strategies using the pressure-tunable, dual-column ensemble with atmospheric pressure air as carrier gas, a laboratory GC system designed for high-speed operation was used. The system employs a cryogenic trap for sample preconcentration and focusing (*20*) and a photoionization detector (PID). The schematic diagram in Figure 1 shows the key components of the system, which has been described in detail elsewhere (*13*). All components are mounted on a Varian 3700 GC (Varian, Walnut Creek, CA), but only the Varian temperature-programmed oven is used for these studies. A croyfocusing inlet system CI (Cryointegrator model L, Chromatofast, Ann Arbor, MI) designed for high-speed GC is used to inject sample-vapor plugs with widths in the range of 5−10 ms. This inlet system also provides a precise zero-time reference for use with pressure programming.

The pressure tunable column ensemble consists of a 4.5-m-long nonpolar dimethyl polysiloxane capillary column C_1 (DB-1, J&W Scientific, Folsom, CA) followed by a 7.5-m-long polar trifluoropropylmethyl polysiloxane column C_2 (RTX-200, Restek, Bellafonte, PA). This column length ratio gives equal holdup time values for the two columns when the system is operated with an ensemble junction-point pressure equal to the pressure that would exist at the column junction point in the absence of the pressure controller or other connections (natural pressure) and with atmospheric pressure air as the carrier gas. Both columns are 0.25 mm i.d. and use 0.25-μm-thick bonded stationary phases.

The electronic pressure controller (EPC) at the column junction-point consists of an absolute pressure capacitance manometer (model 640A, MKS Instruments, Andover, MA) that can produce a 0.1 psi set-point step size with ±0.01 psi repeatability. Previous studies with pressure-tunable column ensembles using this pressure controller showed that very stable patterns of component peaks are obtained with shot-to-shot retention time variations less than 0.1%. The vent line restrictor R connected between the vacuum pump and the pressure control point provides more rapid pressure equilibration when the set-point pressure is reduced. It also increases the useful range of junction-point pressures while eliminating the risk of contamination of the controller by injected samples (*13*, *19*). Operation with junction-point pressures lower than the natural pressure results in sample being split between the second column and the vent line. This results in some loss of peak area.

The PID is equipped with a 10.2-eV lamp and has a cell volume <100 μL (model PI 52-02A, HNU Systems, Newton, MA). The PID and the downstream end of the vent line are maintained at a pressure of 0.3 psia (2.1 kPa) with vacuum pump VP (CENCO, model HYVAC 14, Central Scientific Co., Chicago, IL). Previous work has shown that when operated at this pressure the detector contributes no significant dead time for the chromatographic conditions used in this study (*13*).

TABLE 1. Compounds and Boiling Points for Test Mixture

label	name	BP (°C)	label	name	BP (°C)
1	acetone	56.2	22	*o*-xylene	144
2	ethyl acetate	77.1	23	styrene	145.2
3	2-butanone	79.6	24	2-heptanone	150
4	benzene	80.1	25	nonane	150.8
5	isopropyl alcohol	82.4	26	isopropylbenzene	151
6	trichloroethylene	86.7	27	heptanal	153
7	2,5-dimethylfuran	93	28	α-pinene	155
8	heptane	98.4	29	mesitylene	165
9	2,4-dimethylhexane	109	30	β-pinene	167
10	toluene	110.6	31	3-octanone	168
11	1-butanol	117.6	32	2-butoxyethanol	171
12	2-methylheptane	118	33	*p*-dichlorobenzene	173.4
13	tetrachloroethylene	121.1	34	1-octen-3-ol	174
14	octane	126	35	3-octanol	175
15	butyl acetate	126.1	36	*d*-limonene	175.5
16	chlorobenzene	130	37	D4	175.5
17	3-methyl-1-butanol	130	38	D5	210
18	hexanal	131	39	dodecane	216.3
19	ethylbenzene	136.2	40	naphthalene	218
20	*p*-xylene	138.3	41	tridecane	235.4
21	*m*-xylene	139.1	42	4-phenylcyclohexene	250

Materials and Procedures. A 350-MHz Pentium II PC equipped with a 16-bit A/D board (C10-DAS1602/16, Computer Boards, Inc., Middleboro, MA) running Labtech Notebook software (Laboratory Technologies Corp., Wilmington, MA) was used for data acquisition and instrument control. Chromatograms were processed with Grams/32 software (Galactic Industries Corp., Salem, NH). Because of pneumatic restrictors in the inlet system, compressed tank air was delivered to the inlet, and the pressure was adjusted to give a column head pressure of 1 atm (14.7 psia). Tank air was passed through a series of traps to remove water vapor and hydrocarbons and then supplied to the cryofocusing inlet and to the junction-point pressure controller. Humidified carrier gas was not considered in this study since the final field-portable instrument will use a desiccant to remove water vapor form the atmospheric pressure air used as carrier gas. The column head pressure is monitored with a gauge located between the GC inlet and the first column and is manually adjusted to 1 atm.

The 42 compounds selected for analysis are listed in Table 1. They are among the most common VOCs and SVOCs found in residential and building environments (*21*). Of course, this is a subset of the possible vapors that might be encountered in a given environment, but an effort has been made to make it representative of the range of compounds expected. The list contains compounds covering a 10^4-fold range of vapor pressures from 0.08 (naphthalene) to 231 Torr (acetone). The compound list includes aliphatic and aromatic hydrocarbons, chlorinated aliphatics and aromatics, oxygenated compounds, terpenes, and a few special chemicals associated with particular sources. Octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) are cyclic compounds used in personal care products, such as deodorants and antiperspirants (*21*). The four vapors 3-methyl-1-butanol, 1-octen-3-ol, 3-octanol, and 3-octanone are considered "signature" VOCs emitted from common indoor fungi and bacteria (*5*, *22*, *23*).

Test atmospheres of the vapors were prepared in 3.8-L Tedlar gas sampling bags (Chromatography Research Supplies, Inc., Addison, IL) by preparing a mixture of the liquid

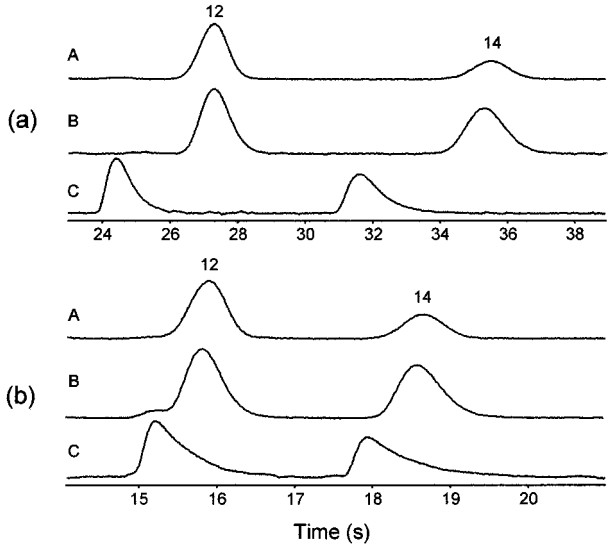

FIGURE 2. Chromatograms showing thermal stability of (a) dimethyl polysiloxane and (b) trifluoropropylmethyl polysiloxane using air as carrier gas. A, initial chromatograms at 30 °C; B, chromatograms at 30 °C following operation at 210 °C; C, chromatograms at 30 °C following operation at 230 °C. See Table 1 for peak identification.

components (reagent grade or better), injecting an aliquot of the mixture into a bag, and diluting with purified air. Vapor concentrations typically were in the range of 15−80 ppm (v/v). While these concentrations are relatively high as compared to those normally of interest for IAQ, the focus of this study was on separation strategies rather than ultimate detection limits. The sample bag was connected to the inlet system via a short (<1 m) 0.25 mm i.d. deactivated fused silica capillary. For each experiment, 0.5 mL of the test atmosphere was drawn into the cryofocusing inlet system by a small vacuum pump onboard the inlet system.

Results and Discussion

Column Ensemble Stability. Since air is used as the carrier gas for the work reported here, the stability of the columns at elevated temperatures is a major concern. It has been shown that bonded phases of dimethyl polysiloxane and trifluoropropylmethyl polysiloxane can be operated continuously in air at temperatures as high as 110 °C for at least 1 week without significant deterioration (*13*). However, higher temperatures are required for the lower vapor pressure compounds in the target mixture, and stable, long-term operation in air is required for robust, low-maintenance field-portable instrumentation.

The two column types used here were evaluated at temperatures in the range of 30−230 °C. The evaluation involved operating the columns under a continuous flow of air for the first week at 30 °C, the second week at 50 °C, and so on at 20 °C intervals until the final week at 230 °C. The total duration of this study was 11 weeks, and the columns were operated in air for the entire time. At the start of each week, the oven temperature was reduced to 30 °C, just long enough to record a chromatogram of a known test mixture. Comparison of the chromatograms was used to evaluate column deterioration.

Chromatograms labeled A in Figure 2 were obtained at the initial 30 °C temperature. Chromatograms labeled B and C were obtained at 30 °C following operation at 210 and at 230 °C, respectively. Note that 120 °C was the highest temperature used in the analytical studies reported here. The set of chromatograms labeled a is for the dimethyl polysiloxane column, and the set labeled b is for the trifluoropropylmethyl polysiloxane column. The peak numbers correspond to the component numbers in Table 1.

For both columns, retention times, peak shapes, and peak widths are nearly the same for chromatograms A and B. For set a, the peak widths (full width at half-maximum height) for peak 12 are 0.93 and 0.85 s for A and B, respectively, and for peak 14 they are 1.23 and 1.14 s, respectively. For set b, the values for peak 12 are 0.52 and 0.47 s for A and B, respectively, and for peak 14 they are 0.57 and 0.53 s, respectively. Thus, both columns appear to be stable up to 210 °C in air. After operation in air for 1 week at 230 °C (chromatograms C), retention times are shifted to significantly lower values, and very asymmetric peaks are observed with severe tailing. Note that the tailing is more severe for the trifluoropropylmethyl polysiloxane column.

Tunable Retention. Retention selectivity is achieved by tuning the pressure at the junction point between the columns either before or during the separation. A unique feature of this study is the use of atmospheric pressure air as carrier gas. This requires that the junction-point pressure be controlled at subambient values. For the system described here the useful range of tuning pressure is 8.0−13.5 psia (*24*). Since the pressure controller has a 0.1 psi step size, about 55 unique pressure values can be used, each producing a somewhat different pattern of eluting peaks.

For a pressure-tunable column ensemble, an ensemble retention factor k_o can be determined for every mixture component:

$$k_o = (t_{Ro} - t_{mo})/t_{mo} \quad (1)$$

where t_{mo} and t_{Ro} are the ensemble holdup time and component retention time, respectively. The ensemble retention factor can be expressed as the sum of the retention factors for the individual columns weighted by the fraction of the ensemble holdup time attributable to each column:

$$k_o = (t_{m1}/t_{mo})k_1 + (t_{m2}/t_{mo})k_2 \quad (2)$$

$$k_o = (t_{m1}/t_{mo})(k_1 - k_2) + k_2 \quad (3)$$

where t_{m1} and t_{m2} are the holdup times for columns 1 and 2, respectively. Since it was not practical to measure the holdup times for the individual columns for the vacuum-outlet system used here, values were computed by the use of eq 4 (*13*):

$$t_m = [32\eta L^2(P^3 - 1)]/[(3/4)d^2 p_o(P_2 - 1)^2] \quad (4)$$

where p_o is the column outlet pressure, P is the inlet-to-outlet pressure ratio for the individual columns, η is the carrier gas viscosity, d is the column diameter, and L is the column length. For the first column, the inlet pressure was 1 atm, and the outlet pressure was the set-point pressure at the column junction-point. For the second column, the inlet pressure was also the set-point pressure, and the outlet pressure was the detector pressure (0.3 psia). The value of η used in eq 4 was adjusted for the oven temperature.

The quantity t_{m1}/t_{mo} corresponds to the fractional contribution that the first column makes to the ensemble retention pattern. From eq 3, a plot of k_o vs t_{m1}/t_{mo} should be linear with a slope equal to $k_1 - k_2$ and an intercept equal to k_2. Figure 3 shows these plots for the first 21 components in Table 1 at a temperature of 30 °C (panel a) and for the last 21 components at a temperature of 100 °C (panel b). These temperature values were chosen so that the maximum k_o values were about 7, since for typical values of t_{mo} this gives maximum retention times of about 200 s for each group of compounds. The range of t_{m1}/t_{mo} values shown on the plots (0.249−0.752) corresponds to the useful set-point pressure range (8.0−13.5 psia).

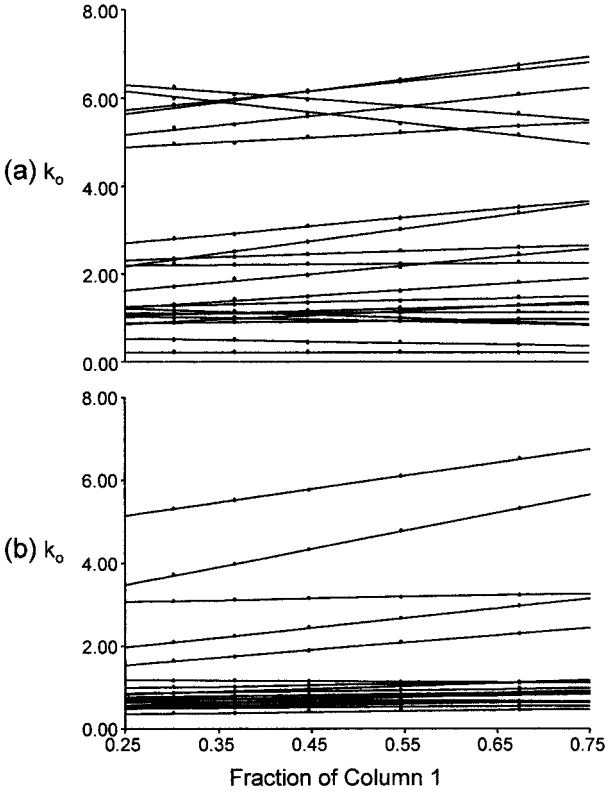

FIGURE 3. Plots of ensemble retention factors, k_o, vs holdup time fraction of column C_1, t_{m1}/t_{mo}, for (a) the first 21 components in Table 1 and (b) the last 21 components in Table 1.

Straight lines are observed in all cases. Linear regression correlation coefficients range from 0.971 to 0.999. Note that wherever a pair of these lines crosses, the corresponding pair of components will coelute. The utility of a pressure-tunable column ensemble is that the fractional contribution of the columns can be adjusted to provide a chromatogram that can best take advantage of the selectivity of the SAW sensor array detector. Note that the lower portion of Figure 3b is very congested, with many mixture components having $k_o < 1$. This suggested that it would be difficult to find isothermal conditions for the separation of these compounds that would provide adequate resolution of the early-eluting components in this group while maintaining an analysis time of under 200 s. The use of a lower starting temperature to increase retention and resolution of the early-eluting components and relatively fast temperature programming to reduce analysis time will be required.

Analysis of the Low Boiling Point Components. A window-diagram method was used to guide the selection of the junction-point pressure for the column ensemble. A window diagram consists of a plot of some separation quality parameter versus either the junction-point pressure or the holdup time fraction t_{m1}/t_{mo} or t_{m2}/t_{mo} (*15, 16, 25−29*). Values of the separation quality parameter are computed for all possible peak pairs, and the worst-case value, corresponding to the component pair that is most difficult to separate (i.e., the critical pair), is plotted.

Most previous work with window diagrams has used relative retention (α) as the separation quality parameter (*15, 25−29*):

$$\alpha = k_{oi}/k_{oj} \tag{5}$$

where k_{oi} and k_{oj} are the ensemble retention factors for mixture components i and j, respectively. For high-speed separations, k_o values are relatively small, and α is not a satisfactory measure of separation quality (*30*). The relative resolution R_{rel}, defined by eq 6, has been shown to provide useful window diagrams for any range of k_o values (*30*):

$$R_{rel} = \Delta k_o/(k_{oa} + 1) \tag{6}$$

where $\Delta k_o = k_{oi} - k_{oj}$, and k_{oa} is the average of the two ensemble retention factors.

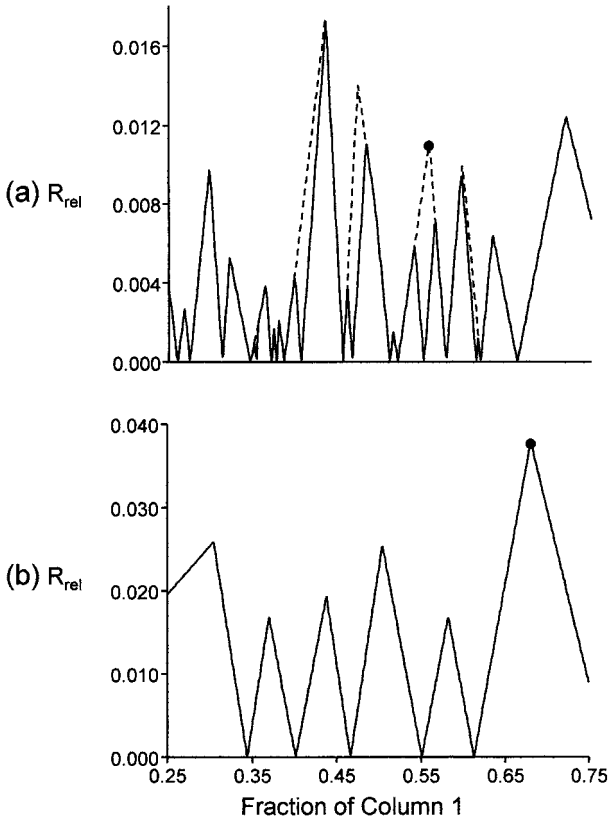

FIGURE 4. Relative resolution window diagrams for the first 21 components in Table 1: (a) solid-line plot for all 21 components and dashed-line plot for the first 15 components; (b) plot for the last 6 components. Circles on the plots indicate conditions used for the chromatograms in Figure 5.

Window diagrams were constructed using k_o values computed from the linear regression slopes and intercepts of the plots in Figure 3a. R_{rel} was calculated for all component pairs at each value of t_{m1}/t_{mo}, and the smallest R_{rel} value (i.e., the value for the critical pair) was plotted in the window diagram.

Figure 4a shows the relative-resolution window diagram for the 21-component mixture (solid line) and for the first 15 components to elute (broken line). Components 20 (*p*-xylene) and 21 (*m*-xylene) cannot be separated with any junction-point pressure value, and they were considered as a single component in construction of the window diagrams. Each zero-point in the window diagram corresponds to the complete coelution of a critical component pair. Because of the high density of peaks in the chromatograms, 18 different peak pairs become critical (18 zero points in the window diagram) over the useful junction-point pressure range. Each local maximum in the window diagram corresponds to a t_{m1}/t_{mo} value where two particular peak pairs share the role of critical pair because they have the same R_{rel} value. Usually, the junction-point pressure yielding the t_{m1}/t_{mo} value that corresponds to the largest local R_{rel} maximum in the window diagram is used for the analysis.

Previous studies (*30*) have shown that R_{rel} values of at least 0.035−0.040 are needed for complete separation (actual

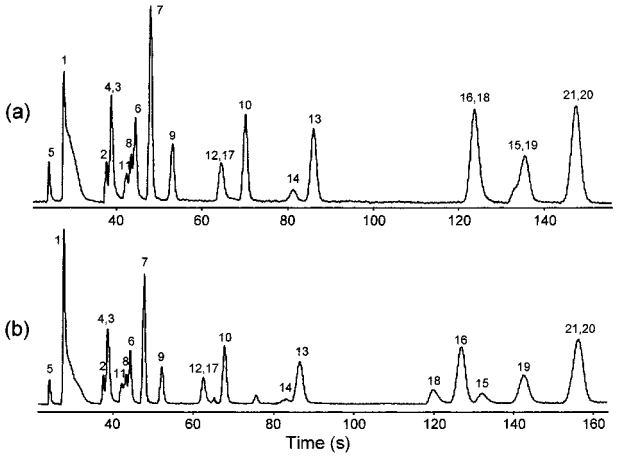

FIGURE 5. Isothermal chromatograms at 30 °C for the first 21 components in Table 1: (a) chromatogram using a junction-point pressure of 12.1 psia; (b) chromatogram using junction-point pressure programming from 12.1 to 13.1 psia 45 s after injection.

critical pair resolution $R > 1$) using a column ensemble with a resolving power comparable to the ensemble used in this study. It is clear from the solid-line window diagram in Figure 4a that no t_{m1}/t_{mo} value will result in a complete separation. Therefore, chromatograms were obtained with holdup time fraction values corresponding to each of several local maxima in the window diagram, and they were evaluated with respect to the total number of completely separated peaks, the number of mixture components in each multicomponent chromatographic feature, and the expected selectivity of the SAW sensor array for the components in each of these features (*14*−*16*).

If consideration is restricted (temporarily) only to the first 15 components to elute, the window diagram represented by the dashed line in Figure 4a is obtained, and improved separation is expected. The chromatogram shown in Figure 5a was obtained at 30 °C using a junction-point pressure of 12.1 psia, which corresponds to a t_{m1}/t_{mo} value of 0.558 indicated by the circle on the dashed-line of Figure 4a. This results in the largest number of completely separated peaks for the first 15 components. The nearly complete coelution of component pairs 3/4 (2-butanone and benzene) and 12/17 (2-methylheptane and 3-methyl-1-butanol) should not represent significant problems for the instrument under development, because these vapor pairs should be easily differentiated with the response patterns obtained with the SAW sensor array (*14*, *16*). The unusual shape of peak 1 (acetone) is an artifact of the inlet system, which has been discussed earlier (*13*).

As shown in Figure 5a, the component pairs 16/18 (chlorobenzene and hexanal), 15/19 (butyl acetate and ethylbenzene), and 20/21 (*p*- and *m*-xylene) coelute near the end of the chromatogram. As noted above, coelution of *p*- and *m*-xylene occurs for all junction-point pressure values, so these components must be treated as unresolvable. A powerful feature of the tandem-column ensemble is the ability to begin an analysis using a junction-point pressure that is most satisfactory for the early-eluting mixture components and then change the junction-point pressure during the analysis (selectivity programming) to facilitate the separation of the later-eluting components. Figure 4b shows the window diagram for the last six components to elute. The window of greatest amplitude occurs for a junction-point pressure of 13.1 psia and has a maximum R_{rel} value of nearly 0.040. This should provide a complete separation of these components (not including the xylene isomers).

For Figure 5b, programmed, on-the-fly pressure tuning was used to improve the quality of the separation of the last six eluting components without sacrificing the quality of the separation of the first 15 components. For this chromatogram, the junction-point pressure was changed 45 s after injection from an initial value of 12.1 psia to a value of 13.1 psia. While the earlier portion of the chromatogram remains virtually the same, component pairs 16/18 and 15/19 now are completely separated. This illustrates the utility of programmable retention selectivity for increasing the number of completely separated peaks.

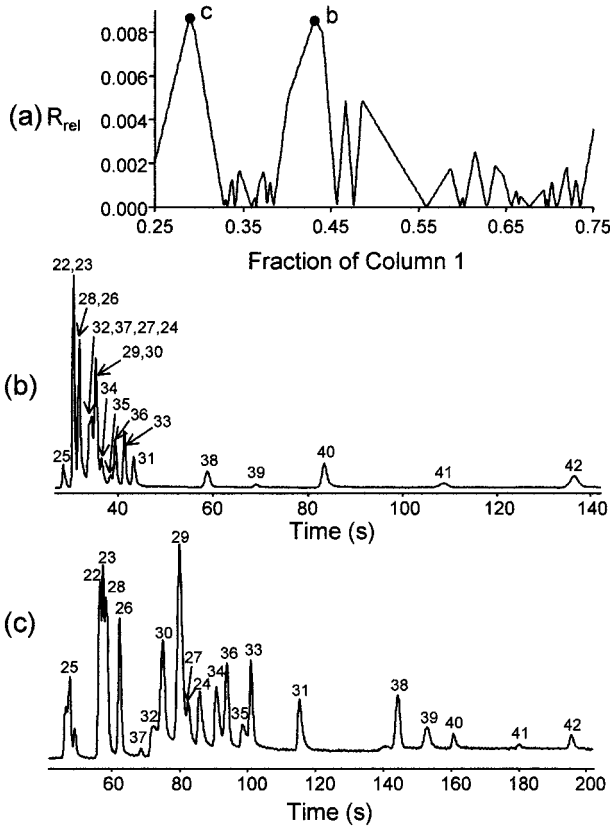

FIGURE 6. Window diagram and chromatograms for the last 21 components in Table 1: (a) window diagram for an isothermal separation at 100 °C; (b) isothermal chromatogram at 100 °C; (c) temperature-programmed chromatogram with an initial temperature of 60 °C and a 50 °C/min ramp to 120 °C beginning at the time of injection followed by isothermal operation at 120 °C until the end of the separation. For chromatogram b, the junction-point pressure was 10.9 psia, and for chromatogram c it was 8.8 psia. The corresponding t_{m1}/t_{mo} values are indicated by points labeled b and c on the window diagram.

Analysis of the Higher Boiling Point Components. The isothermal separation of the higher boiling point components is complicated by the fact that inadequate retention of the early-eluting components of this mixture occurs at a temperature of 100 °C. Figure 6a shows a window diagram for this mixture at 100 °C. The very low maximum value of R_{rel} relative to those in Figure 4 suggests that a poor separation will be achieved. This is confirmed in Figure 6b. This isothermal chromatogram was obtained with a junction-point pressure value of 10.9 psia, which gives a t_{m1}/t_{mo} value of 0.438. This corresponds to a local maximum in the window diagram indicated by the point labeled b. Of particular concern is the peak cluster between 30 and 35 s (components 24, 27, 29, 30, 32, and 37). It is unlikely that a SAW sensor array of any size will have sufficient selectivity for the analysis of this group of unresolved components (*14*, *15*).

Figure 6c shows a chromatogram of the higher boiling point range mixture obtained using fast temperature programming from an initial temperature of 60 to 120 °C with

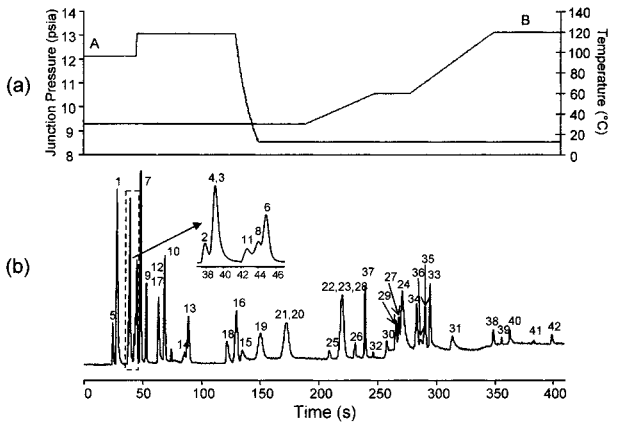

FIGURE 7. (a) Junction-point pressure program A and temperature program B for the analysis of the complete 42-component mixture; (b) chromatogram for the complete 42-component mixture. The inset in the chromatogram shows components 2, 3, 4, 6, 8, and 11 on an expanded time scale.

a programming rate of 50 °C/min. The temperature program was initiated at the time of injection, and after completion of the program, the column was operated isothermally at 120 °C until the last component eluted in about 195 s. The junction-point pressure was 8.8 psia, which corresponds to the local maximum labeled point c in the isothermal window diagram of Figure 6a and corresponds to a t_{m1}/t_{mo} value of 0.291.

Relatively little work has been reported on the optimization of junction-point pressure for a tunable column ensemble operated under temperature-programmed conditions. Here, a relatively good separation was achieved, and all peak apexes were easily identified. The feature observed just after peak 25 is either an artifact or an impurity but does not represent an added component. Note that the combination of pressure tuning and fast temperature programming results in a separation in under 200 s, which is satisfactory for the intended application.

Analysis of the Complete Mixture. It is clear from Figure 6 that adequate separation of the complete 42-component mixture in less than 400 s cannot be achieved under isothermal conditions. For the separation of the first 21 components in the complete mixture, the conditions used were the same as those for the chromatogram of Figure 5b: 30 °C (isothermal) with an initial junction-point pressure value of 12.1 psia and a change to 13.1 psia 45 s after injection. After 130 s, the junction-point pressure was reduced to 8.5 psia for the remainder of the analysis. The pressure profile is shown as plot A in Figure 7a.

Note that the inlet pressure (head pressure for the first column) changes slightly as programmed changes occur in the junction-point pressure. For this reason, a junction-point pressure of 8.5 psia was chosen rather than 8.8 psia as used for Figure 6c. For the pressure-programming conditions, the 8.5 psia value gives the same holdup time fraction (0.291) as used for the chromatogram in Figure 6c. The final pressure of 8.5 psia resulted in the best separation of the last 21 components in the mixture.

The temperature program used for the complete 42-component mixture was based on the results obtained separately for the two 21-component mixture subsets and on a series of empirical trials aimed at reconciling the conditions for both subsets. Temperature programming begins at 195 s with a 30 °C/min ramp to 60 °C. Following an isothermal interval from 240 to 280 s, a 50 °C/min ramp is used to reach a final temperature of 120 °C. The temperature profile is shown as plot B in Figure 7a.

Figure 7b shows the chromatogram for the 42-component mixture. The component concentrations used for the chromatogram in Figure 7b were different from those in the previous chromatograms, and thus peak heights and areas are not comparable. The analysis is complete in about 400 s. The inset shows the congested region of the chromatogram, from 38 to 46 s, on an expanded time scale. The elution pattern for the first 21 components is very similar to that in Figure 5b. Retention times for the last six components in this group are somewhat longer in Figure 7b because the final pressure change to 8.5 psia occurs before elution of these components. The chromatogram for the last 21 components in Figure 7b is very similar to that in Figure 6c except that the resolution of components 22, 23, and 28 (*o*-xylene, styrene, and α-pinene) is poorer and the individual peak apexes are no longer resolved. It is expected that with proper design a SAW sensor array would be capable of discriminating among these three components (*14*−*16*, *36*, *37*).

This study has demonstrated the high-speed separation of a complex mixture of VOCs and SVOCs by vacuum-outlet GC with atmospheric pressure air as carrier gas. Fast temperature programming combined with preset or on-the-fly pressure modulation of the dual-column ensemble permits adjustment of retention and facilitates the separation of mixture components. These capabilities represent a significant advancement toward the realization of field-portable GC instrumentation without onboard gas supplies that is suitable for on-site monitoring of IAQ.

The column ensemble consisting of a dimethyl polysiloxane column and a trifluoropropylmethyl polysiloxane column provides a wide retention tuning range and shows surprisingly good thermal stability after prolonged use with air as carrier gas. While the detailed analyses reported here limited the column temperatures to ≤120 °C, stable operation of these columns up to 210 °C in air was demonstrated for nonpolar solutes. Thus, separation of SVOCs with boiling points well above 250 °C (the limit explored in this study) appears feasible, but further long-term stability studies are needed using more polar solutes. The use of at-column heating (*31*−*35*) is currently being explored as a means of reducing power demands and increasing thermal cycling rates for field applications.

The ultimate goal of this work is to combine this type of separation system with a partially selective dual-stage adsorbent preconcentrator and a detector comprising SAW sensor array. Since the response patterns from the sensor array can be used to recognize and discriminate among compounds coeluting from the column ensemble, the demands on the separation stage are relaxed somewhat and more rapid analyses are possible. The window diagrams presented in this study were used to guide the selection of junction-point pressures, but they were not designed for a system where coelutions are tolerable. Thus, new algorithms are needed for constructing window diagrams to take this feature into account in developing pressure and temperature programs for optimal separations.

The dual-bed, sorption-based preconcentrator under development will introduce significantly wider vapor plugs to the column ensemble than those obtained with the cryofocusing inlet used here. This will result in some loss of chromatographic resolution, particularly for the early-eluting components, and may limit the complexity of mixtures that can be analyzed quantitatively to less than the 42 compounds tested in this study.

Although, the relatively large cell volume of the PID demanded a rather low outlet pressure (0.02 atm) in the current study, preliminary results with a SAW sensor array detector having a cell volume of just a few microliters indicate that vacuum-outlet operation at 0.5 atm is possible with no significant detector band broadening (*38*). Such modest

vacuums can be achieved with a small suction pump that is compatible with field operation.

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