# Pressure-Tunable Dual-Column Ensembles for High-Speed GC and GC/MS

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## Summary

**A series-coupled ensemble of two capillary GC columns of different selectivity with an adjustable pressure at the column junction point is used to obtain tunable selectivity for high-speed GC and GC/TOFMS. An electronic pressure controller with a 0.1-psi step size is used to obtain numerous computer-selected unique selectivities. System configurations for conventional, atmospheric-pressure outlet operation with flame ionization detection and for vacuum-outlet operation with photoionization detection are described for GC-only experiments. Polydimethylsiloxane is used as the non-polar column and polyethylene glycol (atmospheric outlet) or triflouropropylpolysiloxane (vacuum outlet) is used as the polar column. For GC/TOFMS experiments, 5% phenyl polydimethylsiloxane was used as the non-polar column, and polyethylene glycol was used as the polar column. The time-of-flight mass spectrometer can acquire up to 500 complete mass spectra per second. Since spectral continuity is achieved across the entire chromatographic peak profile, severely overlapping peaks can be spectrally deconvoluted for high-speed characterization of completely unknown mixtures. For mixture components with significantly different fragmentation patterns, spectral deconvolution can be achieved for chromatographic peak separations of as little as 6.0 ms. This can result is very large peak capacity for time compressed (not completely resolved) chromatograms. The use of columns with tunable selectivity allows for precise peak-position control, which can result in more efficient utilization of available peak capacity and thus further time compression of chromatograms. The limits of tunability and deconvolution are tested for near co-elutions of different classes of hydrocarbon compounds as well as for more multi-functional mixtures.**

## 1 Introduction

Combinations of two columns having different selectivities have been used in several schemes to obtain enhanced selectivity and increased peak capacity for gas chromatography [1–3]. Parallel packed columns in instruments having two injectors and two detectors have been used often to obtain more detailed analytical information on mixtures that could not be completely separated on either column alone. Often component pairs which elute with excessive overlap on a non-polar phase will be adequately separated on an appropriate polar phase. This takes advantage of differences in the stationary-phase chemistries of the two compounds in the polar phase. This strategy is particularly attractive for packed columns, which generally have relatively low peak capacity. Parallel capillary columns also are used for confirmation analysis, often for regulatory-driven procedures.

The much greater peak capacity available with capillary (open-tubular) columns often obviates the need for parallel separations with columns of different selectivity. However, as needs grow for the separation of more complex mixtures and as recognition increases that conventional GC is just too slow for some important applications, the use of combinations of capillary columns of different selectivities is receiving more attention [4].

While parallel separations on two capillary columns are very useful, strategies to enhance selectivity and increase peak capacity, using series-coupled columns may be more flexible and more powerful. Two columns of different selectivity can be combined in series (tandem) with or without an intermediate trap. When a trap is used, a portion of the effluent from the first column containing one or more target compounds is focussed in the trap and then re-injected onto the second column. This forms the bases for heart-cut methods [2, 3], which result in much larger peak capacity for targeted portions of the mixture. The use of the trap de-couples the chemistries of the two different columns, and provides independent retention data for the target compounds on two different stationary phases. In addition, with the focusing provided by the trap, peak dispersion from the first column does not contribute to the peak dispersion in the chromatogram from the second column.

If sequential heart cuts are made for the entire effluent from the first column, and if the peak widths from the first column are sufficiently large that several cuts are made during the elution from the first column of a single peak, the trap serves to modulate the chemical signal from the first column. The result is comprehensive two-dimensional GC [5–7]. This powerful technique results in very high peak capacity and has been applied to very complex mixtures.

If two capillary column of different selectivity are combined in series without an intermediate trap, the stationary-phase chemistries from the individual columns are combined, and a unique selectivity is obtained [8–10]. While this does not significantly change the peak capacity, it can result in the more efficient utilization of the available peak capacity by providing a more favorable selectivity for a set of target compounds. In many cases, this can dramatically reduce the separation time for multifunctional mixtures [11, 12].

Selectivity tuning for an ensemble of two capillary columns using different stationary phases can be obtained by changing the relative contributions that the individual columns make to the overall separation selectivity. This can be accomplished by changing the column length ratio [13], the column tem-

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peratures [14, 15] or the carrier gas pressure at the junction point between the columns [16–18]. Since the manipulation of the junction-point pressure is very convenient and can obtain a wide range of available selectivities with both columns in a single GC oven, this approach for tuning column selectivity has been most frequently used. By using electronic pressure control at the junction point between the columns, high-precision, computer-controlled selectivity can be obtained [19, 20].

Column ensembles with tunable selectivity are less useful for high-speed separation of complex mixtures containing mostly compounds of similar polarity. For these compounds, the relative changes in elution patterns with changes in column polarity are small. For high-speed GC, relative peak position shifts with changes in polarity on the order of several peak widths are desirable for at least some of the targeted component pairs. The recent development of time-of-flight mass spectrometer (TOFMS) detection [21, 22] for high-speed GC, however, dramatically reduces the separation requirements for characterization and analysis of complex, unknown mixtures.

With time-array ion detection [23], some TOFMS instruments can obtain up to 500 complete mass spectra per second. In addition, TOFMS provides very constant ion abundance ratios over the entire chromatographic peak profile. This allows for the spectral deconvolution and thus characterization of even severely overlapping chromatographic peaks from high-speed separations of unknown mixtures. Since peak separations of only a few ms are required for spectral deconvolution, pressure-tunable column ensembles with TOFMS detection can be very useful for mixtures containing predominately non-polar compounds.

This report describes experiments with computer-controlled tunable column ensembles for high-speed GC and GC/TOFMS. Pneumatic systems are described for conventional GC with atmospheric-pressure flame ionization detection and vacuum-outlet GC with photoionization detection. Applications are presented for multifunctional mixtures of volatile organic compounds. An absolute pressure controller is used so that tunable selectivity can be obtained with sub-ambient as well as super-ambient column junction-point pressures. A pressure-tunable column ensemble also is used with TOFMS detection for enhancing the spectral deconvolution capabilities of this powerful detection method for high-speed GC. Application to the high-speed characterization of hydrocarbon mixtures is emphasized.

## 2 Apparatus and Experiment Design

### *2.1 Apparatus for High-Speed GC*

**Figure 1** shows two instrument configurations developed for selectivity tuning with capillary columns. Configuration (a) is used for conventional GC at atmospheric outlet pressure with a flame ionization detector (FID), and (b) is used for vacuum outlet operation with a photoionization detector (PID). Both systems make use of a cryofocusing inlet system (Cryointgator Model L, Chromatofast, Inc, Ann Arbor, MI). The inlet, which concentrates organic vapor samples from a gas stream and then injects them as vapor plugs typically 5–10 ms in width, has been described in detail [24, 25]

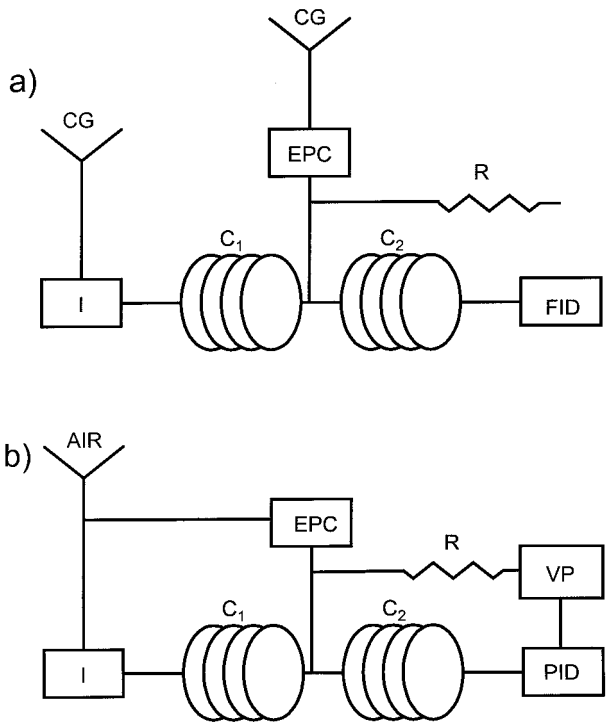


**Figure 1.** Apparatus used for pressure-tunable column selectivity with atmospheric-outlet pressure operation (a) and vacuum-outlet operation (b). $C_1$ and $C_2$, capillary columns; PC, electronic pressure controller; I, cryofocusing inlet system; R, capillary pneumatic restrictors; P, pressure monitors; CG, carrier gas inputs; FID, flame ionization detector; PID, photoionization detector; VP, vacuum pump.

For both systems, the junction point between columns $C_1$ and $C_2$ is connected to electronic pressure controller EPC. The controller (Model 640A, MKS Instruments, Andover, MA) uses an absolute-pressure capacitance manometer to control the pressure in the range 0 to 100 psia in 0.l psi steps. Setpoint reproducibility typically is ±0.01 psi. The controller is also connected to carrier gas supply CG. The controller output is connected to the column junction point by means of a low-restriction capillary tube in order to minimize the pressure drop along the connection.

An uncoated fused silica restrictor R connected by a glass Y splitter is used as a vent between the controller and the column junction point. This serves two functions. If the control pressure is set below the value that would normally exist at the column junction point in the absence of any other connections, the efluent from the first column is split between the second column and the vent line. Without the vent line, this split flow would pass through the controller and thus contam-

inate it. With the vent line, the controller set-point pressure can be anywhere between the inlet pressure of the first column and the outlet pressure of the second column without risk of contamination. The vent line also results in much more rapid equilibration of the junction-point pressure for the case of downward changes in the set-point pressure. The controller output has considerable dead volume. Without the vent line, higher-pressure gas trapped in this volume must bleed off through column $C_2$ before the equilibrium set-point pressure is achieved. A smaller vent-line restriction results in faster equilibration but greater carrier gas consumption.

For configuration (a), a Varian 3500 capillary GC was used as an experimental platform. The Varian FID was used without change. The column ensemble consists of a 6.0-meter length of 0.25-mm i.d. non-polar DB-1 (J & W Scientific, Folsom, CA) followed by a 6.0-meter length of 0.25-mm i.d. polar Stabilwax (Resteck, Bellefonte, PA). Both columns used 0.25-µm stationary phase film thickness. A high-speed electrometer built in house was interfaced to a Pentium, 75-MHz PC by means of a 16-bit A/D board (CIO DAS 1602/16, Computer Boards, Inc, Middleboro, MA).

Configuration (b) was designed for vacuum-outlet operation using atmospheric-pressure air as a carrier gas. A Varian 3700 GC was used as the platform. The PID (Model PI52-02A, HNU Systems, Newton, MA) uses a 10.2 eV lamp. The PID cell volume is less than 100 µL. The PID and the pressure-controller vent line are connected to a vacuum pump (CENCO Model HYVAC 14, Central Scientific, Chicago, IL). All experiments were conducted with a detector cell pressure of 0.3 psia (2.1 kPa). The column ensemble consists of a 4.5-meter length of 0.25-mm i.d. non-polar DB-1 (J & W Scientific, Folsom, CA) followed by a 7.5-meter length of 0.25-mm i.d. polar Rtx-200 (Restek, Bellefonte, PA). An electrometer with a time constant less than 10 ms (Chromatofast, Inc, Ann Arbor, MI) was interfaced to a Pentium II 350 MHz PC by means of a 16-bit A/D board (C10-DAS1602/16, Computer Boards, Inc, Middleboro, MA).

### *2.2 Apparatus for High-Speed GC/TOFMS*

The mass spectrometer used for these studies was a LECO Model Pegasus II time-of-flight instrument (LECO Instruments, St. Joeseph, MI). The instrument uses time-array detection [23] so a complete mass spectrum (5–1000 amu) is obtained every 0.2 ms (5000 spectral transients per second). Ten or more of these spectral transients are summed for every display point in the extracted ion chromatograms. Thus full-spectra acquisition rates up to 500 Hz can be obtained. Instrument software provides for completely automated peak finding on unknown mixtures. Since there is no concentration biasing (constant ion abundance ratios across the entire chromatographic peak profile), spectral deconvolution and thus characterization can be obtained for even severely overlapping and unknown chromatographic peaks. Instrument software provides for completely automated spectral deconvolution.

The TOFMS is interfaced to an HP-6890 GC equipped with an HP 7683 autoinjector. The column ensemble consists of a 10-meter length of 0.18-mm i.d. polar DB-Wax (J & W Scientific, Folsom, CA) followed by a 10-meter length of 0.18-mm i.d. non-polar DB-5 (J & W Scientific, Folsom, CA). Both columns used 0.25-µm stationary phase film thickness. The pressure controller was mounted outside the GC oven, and the connecting line was passed through a hole in the GC which is usually used for detector connection. The instrument was used with a Dell Pentium II, 333 MHz PC.

### *2.3 Materials and Procedures*

All experiments with FID or TOFMS detection used $H_2$ as carrier gas after purification with filters for water vapor, oxygen, and hydrocarbons. All experiments with PID detection under vacuum-outlet conditions used tank air as carrier gas after purification with filters for water vapor and hydrocarbons.

All compounds used for preparing test mixtures were reagent grade or better. For GC experiments using the cryointegrating inlet system, gas-bag vapor samples were used. The pure liquid samples were mixed, usually in equal volume ratios, and the mixture was micropipetted into a Saran or Tedlar gas-sampling bag and diluted with nitrogen. Typically about 0.5 mL of the vapor mixture was introduced into the inlet system for each experiment. For GC/TOFMS experiments, mixtures were prepared in 2-mL autoinjector vials, and a 5.0-µL head-space sample injected for each experiment. **Table 1** lists the mixtures used for each set of experiments. Mixture A was used for GC experiments with both FID and TOFMS detection. Mixture B was used for vacuum-outlet experiments with PID detection. Mixture C, which contains only hydrocarbon compounds, was used to demonstrate the use of tunable selectivity for the high-speed GC/TOFMS characterization of mixtures containing more chemically similar components.

Hold-up times for the individual columns, $t_{m1}$ and $t_{m2}$, are needed to calculate the fractional contributions that the individual columns make to the overall selectivity of the tandem column ensembles. For atmospheric outlet pressure operation (configuration (a) of Figure 1), values of $t_{m1}$ and $t_{m2}$ were obtained directly from measured values using a second FID (not shown in the Figure) to monitor a portion of the effluent from column $C_1$. For vacuum-outlet operation (configuration (b) of Figure 1), values of $t_{m1}$ and $t_{m2}$ were calculated for air as carrier gas at 30 °C using standard equations for gas flow in capillary tubes [3].

Instrument operation and data acquisition for all GC experiments were controlled with Labtech Notebook software (Laboratory Technologies, Corp, Wilmington, MA). Chromatographic data were processed with Grams 32 software (Galactic Industries, Salem, NH). All calculations were performed with MS Excel spreadsheets. Data acquisition and instrument control for all GC/TOFMS experiments was provided by the Pegasus II software.

**Table 1.** Compounds used for test mixtures.

| | Mixture A | Mixture B | Mixture C |
|---|---|---|---|
| 1. | Nitrogen | Isopropyl alcohol | 2,3-Dimethylpentane |
| 2. | *n*-Pentane | Acetone | 2,2,4-Trimethylpentane |
| 3. | 2,2-Dimethylbutane | *n*-Heptane | 1-Heptene |
| 4. | Cyclopentane | 2-Butanone | *n*-Heptane |
| 5. | *n*-Hexane | *n*-Octane | Benzene |
| 6. | Methyl alcohol | Ethylbenzene | 2-Heptene |
| 7. | Ethyl alcohol | *p*-Xylene | Methylcyclohexane |
| 8. | 1-Propyl alcohol | Butyl acetate | 2,5-Dimethylhexane |
| 9. | Cyclohexane | | 2,4-Dimethylhexane |
| 10. | 1,1,1-Trichloro-ethane | | 2,3,4-Trimethylpentane |
| 11. | Benzene | | 2-Methylheptane |
| 12. | *n*-Heptane | | Cycloheptene |
| 13. | Toluene | | Cycloheptane |
| 14. | 1,2-Dichloropropane | | *n*-Octane |
| 15. | 1-Butyl alcohol | | Toluene |
| 16 | *n*-Octane | | 2-Octene |
| 17. | *n*-Nonane | | |
| 18. | 1-Pentyl alcohol | | |
| 19. | Ethylbenzene | | |
| 20. | *m*-Xylene | | |
| 21. | *o*-Xylene | | |
| 22. | 2-Hexyl alcohol | | |

## 3 Results and Discussion

Pressure-tunable tandem column ensembles are very useful for obtaining dramatic reductions in separation times for many mixtures containing up to 20–30 components. With electronic pressure control, a large number of unique, computer selectable and very repeatable selectivities can be obtained. For many single-column separations, only 10–20% or less of the available peak capacity is used in the separation. A two-fold increase in this efficiency can be translated into a four-fold reduction in separation time, if extra-column band broadening can be appropriately scaled. The inlet system used in these studies injects vapor plugs which are typically 5–10 ms in width. This does not make a significant contribution to peak variances for the retention time range considered in these studies.

For the total column lengths used in these GC studies, 40,000–50,000 theoretical plates typically are generated, and hold-up times are in the 8–12 s range. For these conditions, isothermal peak capacity values are in the 30 to 50 peak range for separations in the timeframe of 30–60 s. If this available peak capacity can be used with 50% efficiency, then separations of 15–25 components should be possible in this timeframe.

The principle of operation of pressure-tunable tandem column ensembles is described easily by reference to Figure 1. It is assumed that the inlet and detector pressures are fixed and are the highest and lowest pressures in the system, respectively. Any change in the column junction-point pressure results in a differential change in the pressure drops along the two columns. For example, a decrease in the junction-point pressure results in an increase in the pressure drop along the first column and a decrease in pressure drop along the second column. This results in an increase in the carrier gas velocity in the first column with an attendant decrease in the residence times of all components in the first column. The opposite occurs in the second column. The influence of each column in determining the overall selectivity of the tandem column ensemble varies with the component residence times.

The overall retention factor $k_o$ for a compound on the tandem-column ensemble is found from the overall hold-up time $t_m$ and the overall retention time $t_R$.

$$k_o = (t_R - t_m)/t_m \quad (1)$$

The overall retention factor is also equal to the weighted sum of the retention factors $k_1$ and $k_2$ for the individual columns. The weighting factors, which correspond to the fractional contributions of the two columns to the overall selectivity, are equal to the fractional contribution that the hold-up time of each column makes to the overall hold-up time of the column ensemble [12].

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

Thus, plots of $k_o$ *vs.* either of the weighting factors are straight lines. This forms the basis for selectivity optimization for any set of target compounds.

### *3.1 Atmospheric-Pressure Outlet Operation*

**Figure 2(a)** shows plots of overall retention factor *vs.* the fractional contribution (phase fraction) of column $C_1$ for most of the components of mixture A in Table 1. The numbers identifying the plots are the same as the numbers in Table 1. The oven temperature was 50 °C. The later-eluting components in the mixture are not included so that most of the components can be shown on an expanded vertical scale. The straight lines connecting the points are from linear regression analysis. Correlation Coefficients typically are in the 0.90–0.99 range. Note that a phase fraction of 0 corresponds to the separation being done using only column $C_2$, and a phase fraction of 1.0 corresponds to using only column $C_1$. These data were collected over a junction-point pressure range from 18.0 to 29.0 psia. Since the pressure controller step size is 0.1 psi, a total of 110 unique set-point pressures are available, each one resulting in a somewhat different retention pattern.

Plots with positive slopes correspond to mixture components which show greater retention on column $C_1$. Plots with negative slopes are from components with greater retention on $C_2$.

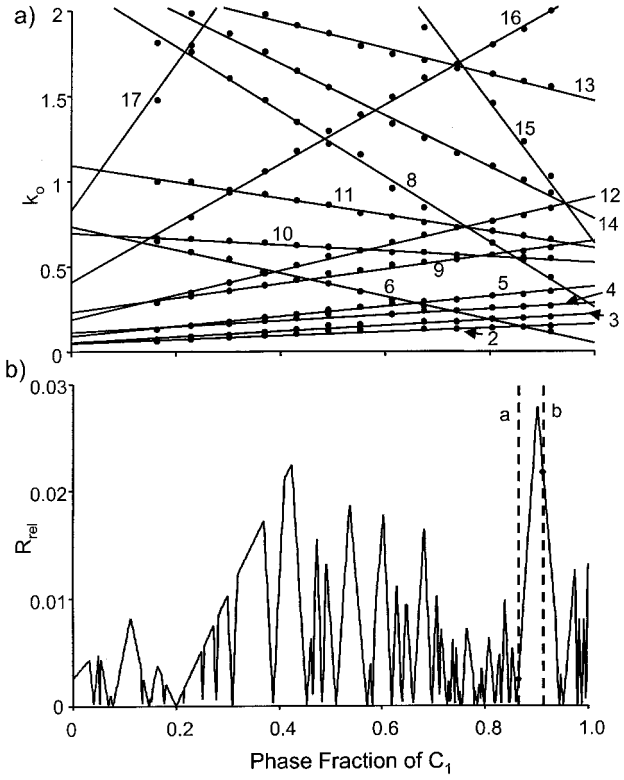


**Figure 2.** Plots of overall retention factor $k_o$ *vs.* phase fraction of column $C_1$ (a) and corresponding window diagram (b) for mixture A of Table 1 using the atmospheric-outlet pressure configuration shown in Figure 1(a). Numbers next to plots correspond to the compound numbers in Table 1.

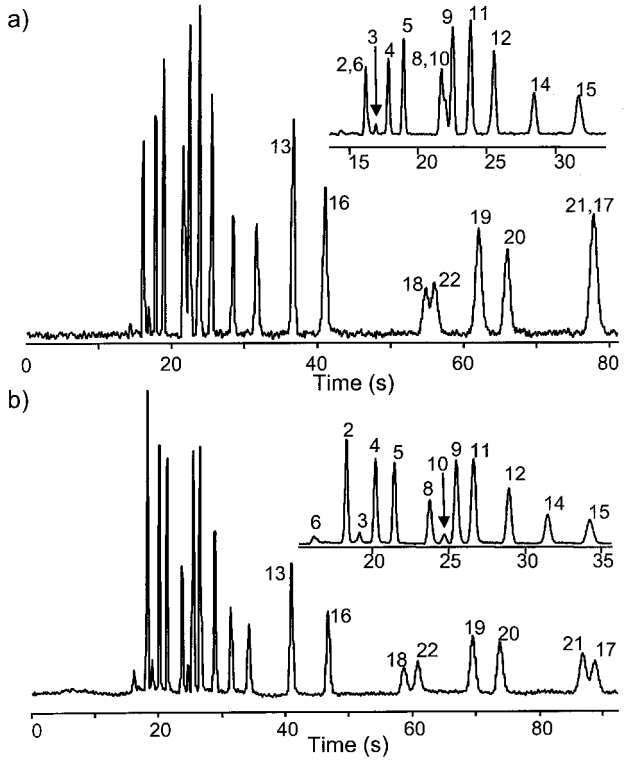


**Figure 3.** Chromatograms of mixture A from Table 1 using the atmospheric-outlet pressure configuration shown in Figure 1(a). Numbers next to peaks correspond to the compound numbers in Table 1. The phase fraction values used for the chromatograms correspond to the vertical broken lines in Figure 2(b).

The slopes indicate the relative polarity of the mixture components for the particular columns used in the ensemble. Wherever a pair of plots cross, that pair of components will co-elute at the corresponding phase fraction, and a complete separation of the mixture cannot be achieved. Note that for this multifunctional mixture, many co-elutions occur over the range of phase fractions.

**Figure 2(b)** shows a window diagram [26, 27] for the complete mixture. For this plot, the relative resolution $R_{rel}$ [28], described by equation 3, is computed for all possible component pairs and the smallest value (poorest resolution) for every phase-fraction value is plotted *vs.* the phase fraction of either column.

$$R_{rel} = \Delta k_o/(k_{oave} + 1) \quad (3)$$

where $\Delta k_o$ is the difference in overall retention factors for the two components, and $k_{oave}$ is their average value. Every zero point in the plot corresponds to the co-elution of a particular component pair. Between each pair of zero points, a window occurs with finite resolution of the worst-case pair.

The goal of the optimization is the determination of the phase fraction giving the greatest relative resolution for the worst-case component pair. This corresponds to the tallest window in the diagram. The idea is that if the worst-case pair (critical pair) is adequately separated, then all mixture components will be adequately separated. For this multifunctional mixture, many co-elutions occur and thus the window diagram is quite complex.

**Figure 3** shows chromatograms obtained with conditions corresponding to vertical lines labeled **a** and **b** in the window diagram. The insets show the early portions of the corresponding chromatograms on an expanded time scale. Chromatogram (a) was obtained with a phase fraction for $C_1$ of 0.865 at a junction-point pressure of 27.5 psia. This corresponds to a valley in the window diagram, and corresponds to the co-elution of components 2 (*n*-pentane) and 6 (methanol). Note that for this phase fraction, component pairs 17/21 and 8/10 nearly coelute.

A change in phase fraction for $C_1$ to a value of 0.912 results in chromatogram (b). The corresponding junction-point pressure change was +0.7 psi. Note in the window diagram that this corresponds to a much greater resolution of the worst-case component pair. Note also that the worst-case pair has changed to 17/21. Component pairs 2/6 and 8/10 are now completely separated. This clearly shows the utility of a pres-

sure-tunable column ensemble for improving the quality (completeness) of the separation.

### *3.2 Vacuum-Outlet Operation*

General features of vacuum-outlet GC have been discussed in detail [29–31]. Important advantages include enhanced column performance at high average linear carrier gas velocities and reduced detector dead time. The vacuum-outlet system (configuration (b) in Figure 1) is being developed for a highly portable instrument, which requires no compressed gas tanks. To this end, atmospheric-pressure air is used as the carrier gas. For the outlet pressure used here (2.1 kPa), the inlet-to-outlet pressure ratio is large, and for a single-column instrument, the average linear carrier gas velocity is determined by the inlet pressure (1.0 atmosphere), the column length, the column diameter and the viscosity of the carrier gas at the column operating temperature. The value for a 12-meter long, 0.25-mm i.d. column in air at 30 °C is about 50 cm/s.

Adapting a pressure-tunable column ensemble to this instrument requires connecting the pressure controller vent line to the vacuum pump so that sub-ambient pressure air can be delivered to the column junction point. In addition, the polar column was changed to trifluoropropylpolysiloxane, since this phase is much more resistant to oxygen degradation than the polyethylene glycol phase. The accessible range of column junction-point pressures is determined by the pressure drops in the various pneumatic restrictions in the system. This includes contributions from the controller itself. For this system, the junction-point pressure could be controlled in the range from 7.5 to 14.0 psia. For a pressure step size of 0.1 psi, this pressure range results in 65 computer-selectable selectivities.

**Figure 4(a)** shows plots of overall retention factor *vs.* the phase fraction of $C_1$ (dimethylpolysiloxane) for the eight components in mixture B of Table 1. The column ensemble temperature was 30 °C. The plots are all very linear with linear-regression correlation coefficients in the range 0.980–0.999. Extrapolations to phase fraction values of 0 and 1.0 show the retention patterns and retention factors for the individual columns.

**Figure 4(b)** shows the corresponding window diagram. Since the mixture was simpler than for Figure 2, the window diagram is simpler and shows only four co-elutions over the entire phase fraction range. The vertical lines in Figure 4(b) correspond to the conditions used for the chromatograms shown in **Figure 5**. Chromatogram (a) was obtained at a phase fraction $C_1$ of 0.405. This is a valley point in the window diagram corresponding to the co-elution of component pair 7/8. Note that this co-elution is observed in the chromatogram. Chromatogram (b) was obtained with a phase fraction of 0.546. This corresponds to another valley in the window diagram for the co-elution of component pair 6/8. The predicted co-elution is seen in the chromatogram. Chromatogram (c) was obtained with a phase fraction of 0.752. This corresponds to a very favorable window, and a complete separation of these components is observed in the chromatogram. However, some overlap of component 8 with an impurity is observed is chromatogram (c)

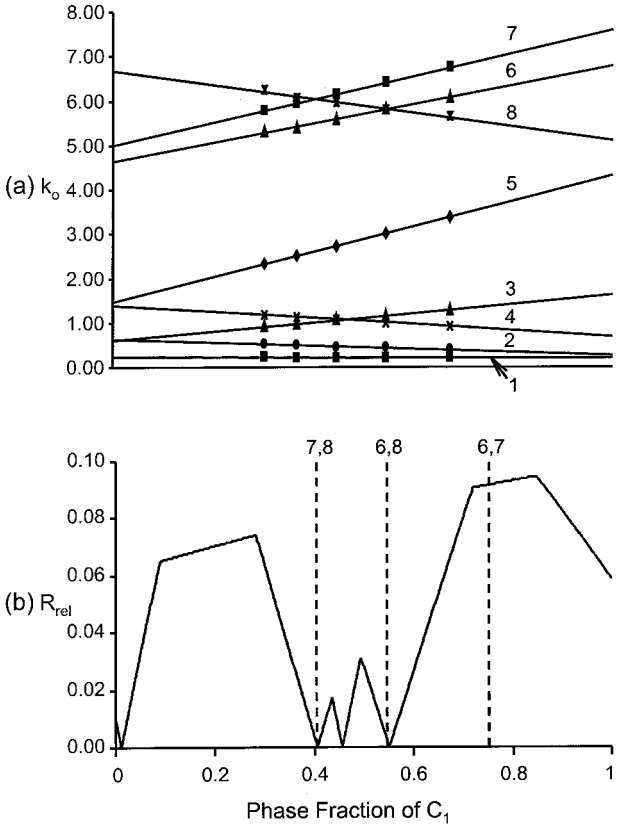


**Figure 4.** Plots of overall retention factor $k_o$ *vs.* phase fraction of column $C_1$ (a) and corresponding window diagram (b) for mixture B of Table 1 using the vacuum-outlet configuration shown in Figure 1(b). Numbers next to plots correspond to the compound numbers in Table 1.

While the trifluoropropylpolysiloxane phase is less polar than polyethylene glycol, it is still very useful in pressure-tunable ensembles using dimethylpolysiloxane as the non-polar phase. Its greater thermal stability and much greater resistance to oxygen are attractive features for this application. Current studies with this vacuum-outlet instrument involve the use of mixtures of interest in indoor air monitoring and industrial hygiene studies.

### *3.3 Pressure Tunable Columns for High-Speed GC/TOFMS*

The TOFMS technology used in this study is extremely powerful for the high-speed characterization and analysis of organic compounds. The maximum spectral acquisition rate of 500 Hz is adequate to track chromatographic peaks with widths of only a few tens of milliseconds. In addition, spectral deconvolution of even severely overlapping unknown peaks obviates the need for complete chromatographic

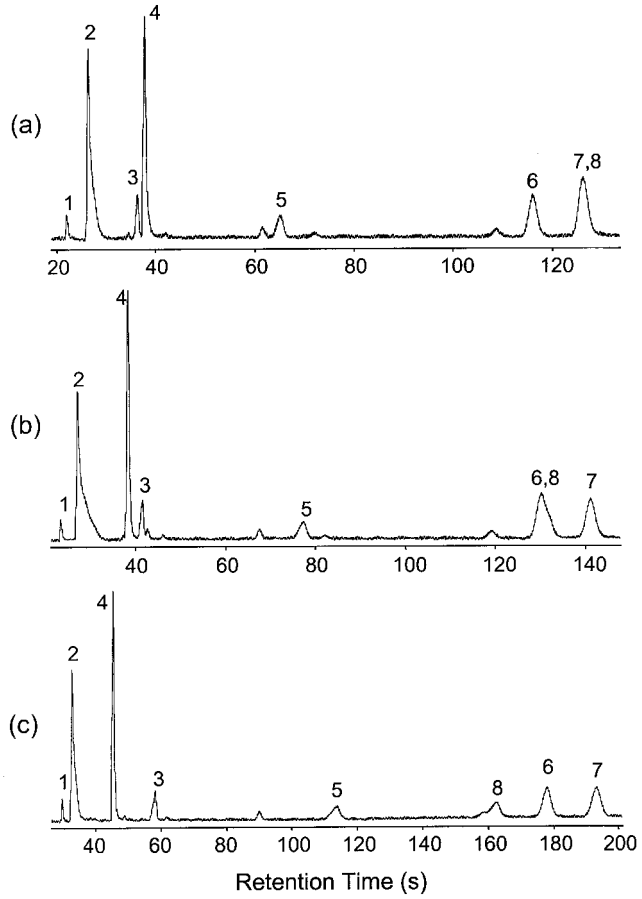


**Figure 5.** Chromatograms of mixture B from Table 1 using the vacuum-outlet configuration shown in Figure 1(b). Numbers next to peaks correspond to the compound numbers in Table 1. The phase fraction values used for the chromatograms correspond to the vertical broken lines in Figure 4(b).

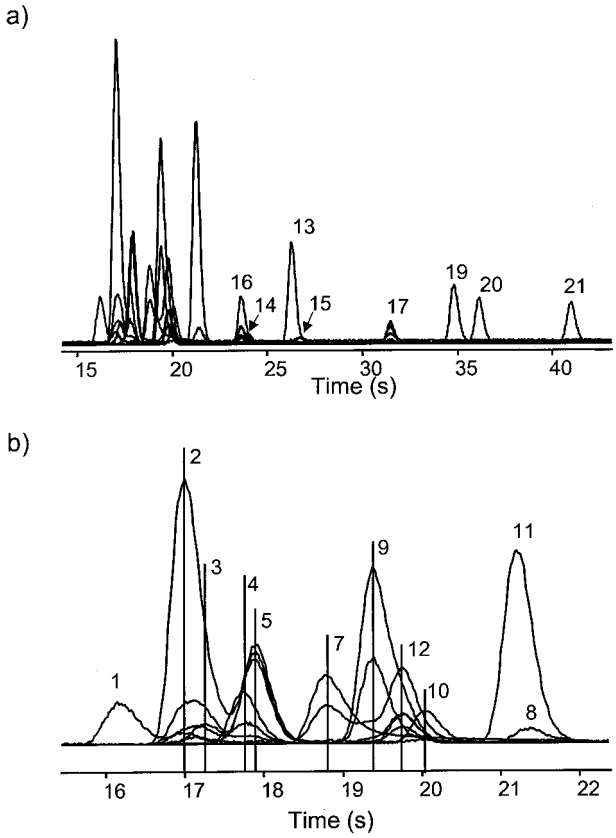


**Figure 6.** Time-compressed extracted-ion chromatograms for mixture A in Table 1 from the GC/TOFMS system. Peak numbers correspond to compound numbers in Table 1. The GC oven temperature was 80 °C and the spectral acquisition rate was 200 Hz. Extracted ion chromatograms are shown for masses 43, 45, 57, 58, 59, 70, 71, 78, 91, and 97.

separation. This greatly increases peak capacity and thus allows for dramatic time compression of chromatograms. For mixture components with significantly different fragmentation patterns, automated deconvolution is achieved if two or more spectra can be obtained between the peak apexes. With a 500 Hz spectral acquisition rate, the corresponding minimum temporal separation of the peak apexes is only 6.0 ms. This gives a maximum peak capacity of about 167 peaks per second. If this available peak capacity can be used with only 5% efficiency, an 80-component mixture could be completely characterized in a 10-s time window.

Pressure-tunable column ensembles for high-speed GC are less useful for mixtures containing more chemically similar compounds such as hydrocarbon mixtures. Usually critical component pairs show similar behavior on both columns and thus large changes in elution patterns cannot be obtained. Relative peak shifts of less than one peak width over the entire tuning pressure range are common for hydrocarbon mixtures. However, for GC/TOFMS, much smaller peak separations are acceptable. In many cases, an unknown component pair, which completely co-elutes at a certain column tuning pressure, can be characterized if a separation of only 6 ms can be obtained at a different tuning pressure.

**Figure 6** shows an example of a time compressed extracted-ion chromatogram for 18 components of the multifunctional mixture A in Table 1. Methanol, *n*-pentanol, and 2-hexanol were not present in the sample. Extracted-ion masses of 43, 45, 57, 58, 59, 70, 71, 78, 91, and 97 are displayed so that all mixture components could be observed. The spectral acquisition rate was 200 Hz. This requires a minimum peak separation of 15 ms in order to obtain spectral deconvolution.

The pressure tunable column ensemble used 10-meter lengths of 5% phenyl dimethylpolysiloxane and polyethylene glycol. In order to increase the speed of the separation, a column temperature of 80 °C was used. This was the highest temperature for which baseline separation of ethylbenzene (component 19) and *m*-xylene (component 20) could be obtained. The fragmentation patterns of these compounds are too similar for spectral deconvolution.

At 80 °C, numerous co-elutions occur in the early portions of the chromatogram, which is shown on an expanded time

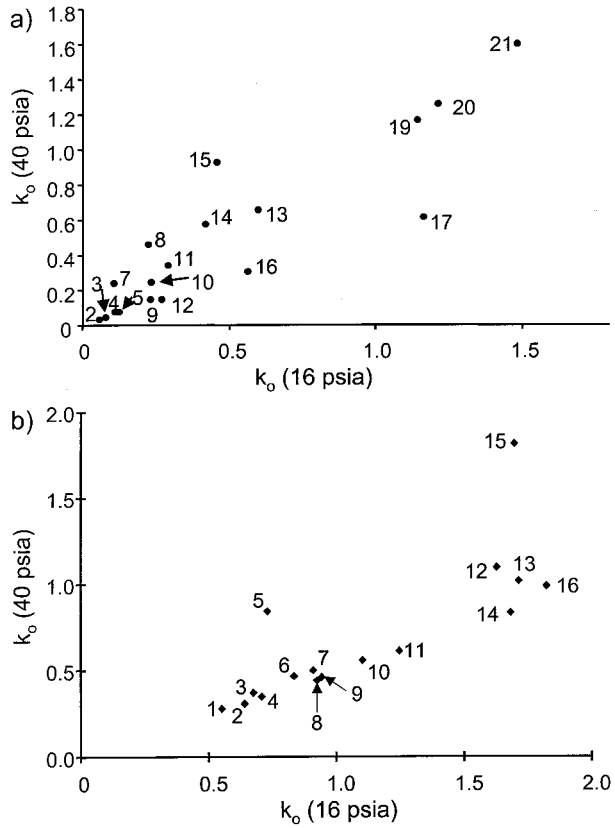


**Figure 7.** Plots of overall retention factors for the components of mixture A (a) and mixture C (b) in Table 1 for a column junction pressure of 40 psia *vs.* values for a junction pressure of 16 psia. Data are from GC/TOFMS measurements with an 80 °C GC oven temperature for plot (a) and a 50 °C oven temperature for plot (b). The spectral acquisition rate was 200 Hz. The numbers by the points correspond to the compound numbers in Table 1.

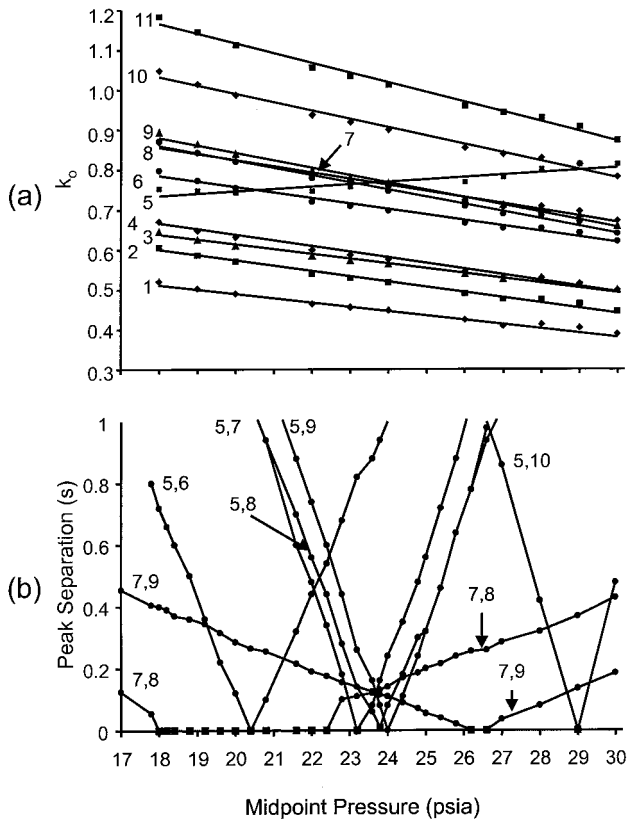


**Figure 8.** Plots of overall retention factor *vs.* column junction-point pressure (a) and peak separation *vs.* junction-point pressure for co-eluting peak pairs (b) for the first 11 eluting components of mixture A from Table 1. Data are from GC/TOFMS measurements with a 50 °C GC oven temperature. The spectral acquisition rate was 200 Hz. Numbers by the plots correspond to the compound numbers in Table 1.

scale in part (b) of Figure 6. Experiments were conducted at several column junctions-point pressures. For Figure 6, the junction-point pressure was 25.4 psia, and the automated peak find and deconvolution algorithms in the instrument software successfully characterized the complete mixture. Note that 11 components were characterized in a time window extending only from 16 to 22 s.

The combination of a pressure-tunable column ensembles and TOFMS is clearly very powerful for high-speed characterization and analysis of multifunctional mixtures. A greater challenge for this combination of technologies involves the high-speed characterization of hydrocarbon mixtures, which exhibit a much smaller range of polarities. The polarities of the components in mixtures A (multifunctional) and C (hydrocarbons only) from Table 1 for the column ensemble used in these GC/TOFMS studies are shown in **Figure 7**. These plots show overall retention factors $k_o$ obtained from GC/TOFMS experiments at a column junction-point pressure of 40 psia *vs.* values at a pressure of 16 psia. This is about the useful pressure range for the system. The low pressure end is limited by the atmospheric-pressure vent used with the pressure controller, and the high pressure end is limited by the GC inlet pressure. The numbers by the points correspond to the compound numbers of the respective mixtures in Table 1. Note that data for the multifunctional mixture were obtained at 80 °C, and the data for the hydrocarbon mixture were obtained at 50 °C.

If the overall polarities of the tandem-column ensemble were the same at the two different junction-point pressures, then the points representing the various mixture components would lie along a straight line, and no overall selectivity control could be obtained. The scatter in the plots represents the degree of orthogonality in the selectivities obtained at the different junction point pressures. The points representing the hydrocarbon compounds in Figure 7(b) show significantly greater correlation at the two junction-point pressure values than is the case for the multifunctional mixture. Components 5 and 15, which are for aromatic compounds, and 12 and 13, which are for cyclic compounds, are important exceptions.

**Figure 8(a)** shows plots of overall retention factor *vs.* junction-point pressure for the first 11 components in the hydro-

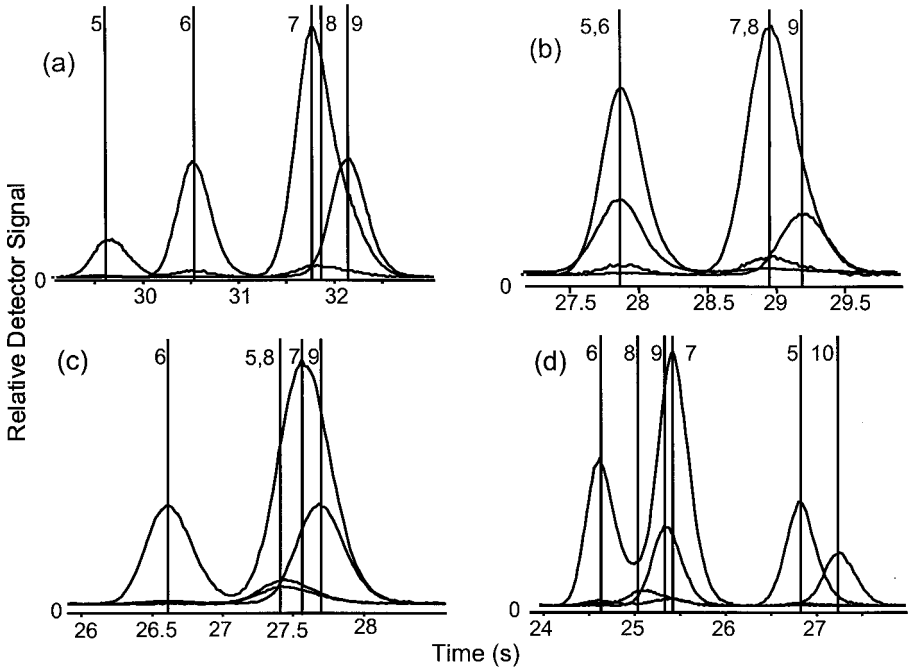


**Figure 9.** Extracted ion chromatograms for components 5–10 from mixture C in Table 1 using column junction-point pressure values of 17.6 psia (a), 20.4 psia (b), 23.2 psia (c) and 28.0 psia (d). The GC oven temperature was 50 °C, and the spectral acquisition rate was 200 Hz. Peak numbers correspond to compound numbers in Table 1. Vertical lines correspond to peak locations from the automated peak-find TOFMS software. Chromatograms are displayed for masses 55, 63, 85, and 99.

carbon mixture. The plots are not shown for the remaining components so that the first 11 could be presented on an expanded vertical scale. Numbers by the plots correspond to the numbers for mixture C in Table 1. Hold-up time for retention-factor calculations was measured as the retention time of the $N_2^+$ ion from the headspace samples. Correlation coefficients for the linear-regression lines are in the range 0.981–0.991. For this study, hold-up times for the individual columns were not computed, and junction-point pressure was used directly as the independent variable for the plots in Figure 8(a). Previous work has shown that the fractional contribution of the first column in the ensemble varies nearly linearly with junction-point pressure [20].

All of these plots have negative slopes except for except for plot 5 (benzene). Toluene (not shown in the Figure) also has a positive slope. Negative slopes are expected for these relatively non-polar compounds since the fractional contribution of the first (polar) column increases with increasing junction-point pressure. Note that the plots for components 3 (1-heptene) and 6 (2-heptene) have significantly smaller slopes than the plots for the saturated hydrocarbon compounds.

**Figure 8(b)** shows plots of peak-pair separation for all component pairs from Figure 8(a) which co-elute for some junction-point pressure value. These peak separation values were found directly from the automated peak find algorithm available with the TOFMS software. Zero values of peak separation indicate that only one peak was indicated. The corresponding junction-point pressure values do not provide for complete characterization of the mixture. Note that for component pair 7 (methylcyclohexane) and 8 (2,5-dimethylhexane), deconvolution failed over a considerable range of junction-point pressure values. This is because of the low sensitivity with respect to junction-point pressure for the peak separation of this component pair. Plots of the type shown in Figure 8(b) can be used for the selection of junction-point pressure values which will obtain complete characterization of a target mixture.

**Figure 9** shows portions of extracted ion chromatograms for four values of junction-point pressure. For case (a), the pressure was 17.6 psia, and from the plots in Figure 8(b), all components should be adequately separated for complete characterization of the mixture. While peaks 7 and 8 show severe overlap, both peaks were found, and deconvolution was successful. For case (b), the junction-point pressure was increased to 20.4 psia. For this case, only a single peak should be found for peak pair 7/8 and also for peak pair 5/6. This is confirmed in the extracted-ion chromatograms. When the pressure is increased to 23.2 psia for case (c), component pair 5/8 shows nearly complete overlap, and deconvolution was not successful. Finally, for case (d) the pressure was increased to 28.0 psia, and all components are adequately separated for complete characterization of the mixture. This is predicted from the plots in Figure 8(b).

## 4 Conclusions

Pressure-tunable column ensembles using electronic pressure control are very useful for high-speed GC and GC/TOFMS. With electronic pressure control, very precise peak position control can be achieved, and window-diagram procedures can be used to reliably predict the junction-point pressure values needed for the most complete separation that can be obtained for a specified set of target compounds using a particular pair of stationary phases. All of the studies reported here involved isothermal column operation. While pressure-tunable column ensembles can be used with temperature programming, the prediction of peak elution times is more difficult and was not attempted in this work.

By the use of a vent line between the pressure controller and the column junction point, a very wide tuning range can be achieved without risk of contaminating the controller. However, for the extreme ends of the tuning range the pressure drop along one of the columns becomes very small, and the average carrier gas velocity in that column becomes so low that column efficiency and separation time both are seriously degraded. In addition, when the controller set-point pressure is below the value that would normally exist at the junction point in the absence of external connections, some of the sample is lost through the vent. The implications of this for accurate quantitation are under investigation.

The development of a pressure-tunable system for vacuum-outlet operation is significant and may impact on the design of small, portable instrumentation using atmospheric-pressure air as carrier gas. Column stability studies have indicated that both dimethylpolysiloxane and trifluoropropylpolysiloxane columns show good stability in air at temperatures up to at least 150 °C. The use of vacuum-outlet operation also significantly increases column performance at higher flow rates and reduces the dead time of closed-cell detectors.

The recent introduction of TOFMS for GC detection provides powerful technology for high-speed mixture characterization. The combination of TOFMS and pressure-tunable column ensembles should allow for very rapid and complete characterization of complex mixtures. The results reported here are very encouraging and show that even for hydrocarbon mixtures, the combination of dimethylpolysiloxane and polyethylene glycol columns can achieve considerable control of elution patterns. This control coupled with the ability of TOFMS to automatically find and deconvolute severely overlapping chromatographic peaks should be very useful for the high-speed characterization of complex hydrocarbon mixtures of interest to the petroleum industry.

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