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Comprehensive two-dimensional gas chromatography of volatile and semi-volatile components using a diaphragm valve-based instrument

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Abstract

A high-temperature configuration for a diaphragm valve-based gas chromatography (GC×GC) instrument is demonstrated. GC×GC is a powerful instrumental tool often used to analyze complex mixtures. Previously, the temperature limitations of valve-based GC×GC instruments were set by the maximum operating temperature of the valve, typically 175 °C. Thus, valve-based GC×GC was constrained to the analysis of mainly volatile components; however, many complex mixtures contain semi-volatile components as well. A new configuration is described that extends the working temperature range of diaphragm valve-based GC×GC instruments to significantly higher temperatures, so both volatile and semi-volatile compounds can be readily separated. In the current investigation, separations at temperatures up to 250 °C are demonstrated. This new design features both chromatographic columns in the same oven with the valve interfacing the two columns mounted in the side of the oven wall so the valve is both partially inside as well as outside the oven. The diaphragm and the sample ports in the valve are located inside the oven while the temperature-restrictive portion of the valve (containing the O-rings) is outside the oven. Temperature measurements on the surface of the valve indicate that even after a sustained oven temperature of 240 °C, the portions of the valve directly involved with the sampling from the first column to the second column track the oven temperature to within 1.2% while the portions of the valve that are temperature-restrictive remain well below the maximum temperature of 175 °C. A 26-component mixture of alkanes, ketones, and alcohols whose boiling points range from 65 °C (*n*-hexane) to 270 °C (*n*-pentadecane) is used to test the new design. Peak shapes along the first column axis suggest that sample condensation or carry-over in the valve is not a problem. Chemometric data analysis is performed to demonstrate that the resulting data have a bilinear structure. After over 6 months of use and temperature conditions up to 265 °C, no deterioration of the valve or its performance has been observed.

Keywords: Gas chromatography, comprehensive two-dimensional; Instrumentation; Volatile organic compounds; Alkanes; Ketones; Alcohols

1. Introduction

Two-dimensional comprehensive gas chromatog-

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raphy (GC×GC) is a powerful technique that is well suited to analyzing complex chemical mixtures [1–12]. A GC×GC instrument consists of two chromatographic columns interconnected by a sample modulation interface. The sample modulation interface injects portions of the first column effluent onto the second column at rapid intervals. The first column is the longer of the two columns, and often has a non-polar stationary phase, while the second column is shorter, often with a polar stationary phase. Thus, GC×GC separations utilize two columns providing complementary separations [13]. This leads to a greatly enhanced peak capacity [14], making GC×GC more powerful and less time-consuming than traditional one-dimensional GC.

Since its debut in 1991 [15], GC×GC instrumentation has continually evolved. Major differences in instrumentation design stem from differences in the sample modulation interface used to manipulate the first column effluent and re-inject chemical components onto the second column. The most commonly used method is thermal modulation. The initial reliable design consists of a slotted heater that sweeps over a thick-filmed capillary that connects the columns. The chemical components that have been retained are volatilized and then injected onto the second column when the heater sweeps over the capillary [16–18]. The second method, cryogenic modulation, also involves the manipulation of temperature to make injections on the second column. In this design, a jet of cryogenic CO_2 is applied with a moving trap to a small portion of the capillary between the two columns. The trap moves back and forth over a portion of capillary to accumulate and then inject portions of the first column effluent onto the second column [19,20]. Other designs use strategically placed and timed jets of cryogenic gas or a combination of heated and cooled jets to eliminate the moving parts [21,22].

The third instrument design employs a diaphragm valve for the sample modulation interface between the two columns. There have been several different configurations of this modulation method. The first design had both columns and the valve inside the same GC oven [23]. This initial configuration worked for mixtures that could be separated without pushing the temperature beyond 175 °C, the maximum manufacturer-specified operating temperature for the diaphragm valve. More recently a modified design introduced a second independently controlled oven that housed the valve and the second column [5,24]. Independent temperature control results in a more versatile system to optimize separations on both columns. The first column can therefore be subjected to much higher temperatures in this design while maintaining the diaphragm valve at or below 175 °C. Since the effluent from the first column may contain high-boiling components, there is the possible complication of component condensation in the valve or the sample loop. This would be seen as a substantial increase in tailing in the first dimension of late-eluting peaks compared to early eluting peaks. Seeley et al. have constructed a valve-based GC×GC in which the valve is mounted between the GC oven and the detector platform. The valve body is maintained at 125 °C while the ports of the valve are pointed towards the oven and follow the oven temperature closely [25]. Both columns are housed inside the main oven and connected to the valve via short segments of deactivated silica capillary. This configuration allows both columns to be taken to higher temperatures and programmed at the same rate, but the underlying potential for excessive heat accumulation in the valve at high oven temperatures and the possibility of high-boiling point components condensing in the valve both exist.

In the current investigation we report herein a new valve-based GC×GC configuration that manipulates the valve placement to circumvent the temperature-specified limitations of the diaphragm valve. The most commonly used diaphragm valve has a temperature limit of 175 °C due to three O-rings in the interior of the valve [26]. Operating the valve beyond the manufacturer's specifications can result in unsatisfactory valve performance over time. We note that, fortunately, the O-rings are located at the opposite end of the valve relative to the position of the valve diaphragm, valve ports and sample loop. Thus, by maintaining the portion of the valve that is in contact with sample components at the same temperature as the columns, while keeping the portion of the valve containing the O-rings below 175 °C, the temperature limitations of the valve can be overcome. In this new instrument configuration, we have mounted the valve such that the valve diaphragm, valve ports and sample loop are inside

the GC oven and the rest of the valve is outside the oven, freely exposed to room air. This new configuration allows a much larger workable temperature range for valve-based GC×GC instruments than previous configurations. A separation of a test mixture containing volatile and semi-volatile components is demonstrated, with boiling points ranging from 65 to 270 °C. Data quality was evaluated, such as retention time precision and achievement of a bilinear data structure, both important criteria for chemometric data analysis. Temperature studies were conducted in order to ascertain that the sample loop, valve ports and valve diaphragm were held at or sufficiently near the oven temperature while the valve O-rings were kept well below the maximum specified temperature of 175 °C.

2. Experimental

In the valve-based comprehensive GC×GC configuration modified for high temperature operation (Fig. 1), both columns were housed inside the same oven. Sample traveled through the first column and into a 1.3-μl sample loop on a high-speed six-port micro diaphragm valve (VICI, Valco, Houston, TX, USA). The effluent in the sample loop from the first column (i.e. column 1) was injected periodically onto the second column (i.e. column 2) and then detected with flame ionization detection (FID). The first column effluent was vented during each injection onto the second column. The valve was mounted partially inside the oven so that the sample loop and the diaphragm were inside the oven and the temperature-sensitive O-rings were outside the oven (Fig. 2). A Varian 3600 CX gas chromatograph (Varian, Palo Alto, CA, USA) was equipped with a HP 7673A automatic sampler (Hewlett-Packard, San Fernando, CA, USA) and modified by cutting a 1 3/8 in. (1 in.=2.54 cm) hole in the top of the oven to allow for the new valve placement. A tight fit between the valve and oven wall was achieved so the oven performance was not compromised. An in-house LabVIEW 6i (National Instruments, Austin, TX, USA) program and a data acquisition board (model AT-MIO-16XE-50, National Instruments) were used to control the valve actuation and to collect the data at a rate of 20,000 points per second

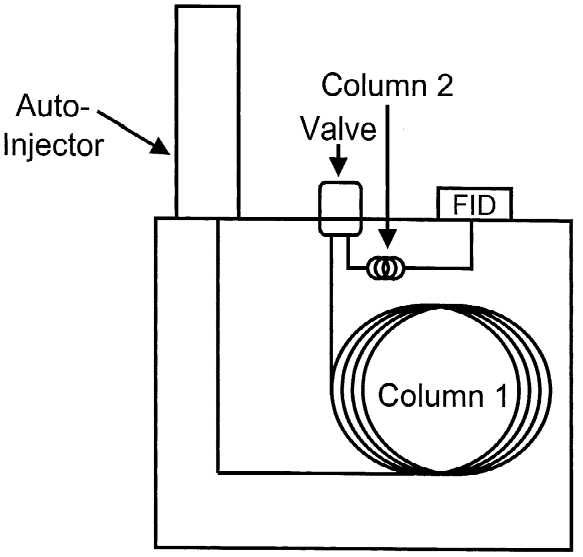

Fig. 1. GC×GC configuration with dual-column temperature program capabilities. Sample is injected with an auto-injector onto column 1 (AT-1; 12 m×200 μm, 0.33 μm film thickness). Portions of the sample are injected onto column 2 (CP Wax-52; 0.5 m×100 μm, 0.2 μm film thickness) from a sample loop on a six-port mini-diaphragm valve. Effluent from column 2 is detected with FID. A LabVIEW program, written in-house, is used to control the valve and collect data.

boxcar averaged to 250 points per second. All data processing was accomplished with Matlab 6.0 R12 (The Mathworks, Natick, MA, USA).

Temperature studies on the valve were performed using four type-K thermocouples (chromel–alumel). The precision and accuracy of the thermocouples

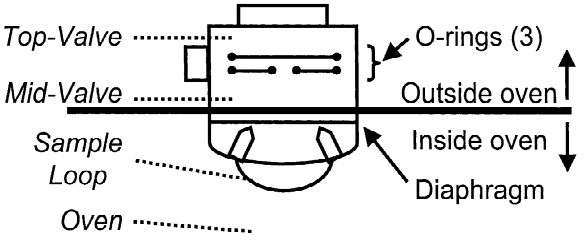

Fig. 2. Cross-sectional view of the six-port mini-diaphragm valve (VICI, Valco instruments). The valve is mounted with the sample loop and diaphragm inside the oven and the temperature-sensitive O-rings outside the oven. Placement of type-K thermocouple sensors at three locations (top-valve, mid-valve and sample loop), attached to the surface of the valve using high temperature polyimide tape. Another thermocouple sensor (oven) is located in the middle, front of the GC oven.

was determined by recording the temperature of boiling water for 5 min. The thermocouples agreed to the standard (100 °C) and to each other to within less than 0.4%. Three of the thermocouples were attached to the valve using high-temperature Kapton polyimide tape (ESD Systems.com, Marlboro, MA, USA) (Fig. 2). The top-valve thermocouple was mounted on the outside of the valve nearest the location of the O-rings; the mid-valve thermocouple was mounted on the surface of the valve just above the top of the oven; and, the sample loop thermocouple was mounted on the sample loop inside the oven. The fourth thermocouple (''oven'') was used to record the oven temperature and was located approximately halfway down near the door of the oven. Temperature data were recorded using a LabVIEW program that uses an eighth-order polynomial and the built-in cold-finger compensator on the National Instruments DAQ board to convert the voltage measurement of the thermocouple to a temperature in degrees Celsius.

A test solution of 26 components of homologous series of *n*-alkanes (C_6–C_{15}), 2-ketones (C_4–C_9), and *n*-alcohols (C_3–C_{11}) was mixed from Poly-Standard Kits (AccuStandard, New Haven, CT, USA). An equal volume of each component was added to the solution resulting in an ~3.8% (v/v) concentration for each test compound. Boiling points for all components are listed in Table 1 and range from 65 to 270 °C.

A GC×GC separation was performed on the 26-component test mixture to demonstrate the separation characteristics of the new configuration. The first column of the GC×GC was a 12 m×200 μm I.D. capillary column with a 0.33-μm poly(dimethylsiloxane) film (SPB-1; Supelco, Bellefonte, PA, USA). The second column was a 0.5 m×100 μm I.D. capillary column with a 0.2-μm poly(ethylene glycol) film (CP-Wax 52 CB; Chrompack, Varian). The valve was actuated with 1-s cycle times with a 20-ms injection pulse width. Helium was used as the carrier gas. Both columns were operated under constant head pressure. Column 1 had a head pressure of 4 p.s.i. providing an initial flow of 0.3 ml/min and column 2 had a head pressure of 20 p.s.i. resulting in an initial flow of 3.55 ml/min (1 p.s.i.=6894.76 Pa). The oven was held at 40 °C for 1 min and then programmed to ramp to 250 °C at 15 °C/min. A 1-μl injection of the 26-component mixture was split 100:1.

Table 1
Composition and individual boiling points of a 26-component test mixture of alkanes, ketones, and alcohols. Each component is ~3.8% (v/v) of the mixture

Label	Component	Boiling point, °C
A1	Ethanol	78
A2	1-Propanol	97
A3	1-Butanol	118
A4	1-Pentanol	137
A5	1-Hexanol	157
A6	1-Heptanol	176
A7	1-Octanol	196
A8	1-Nonanol	215
A9	1-Decanol	231
A10	1-Undecanol	249[a]
B1	2-Butanone	76
B2	2-Pentanone	98
B3	2-Hexanone	124
B4	2-Heptanone	147
B5	2-Octanone	173
B6	2-Nonanone	192
C1	*n*-Hexane	65
C2	*n*-Heptane	98
C3	*n*-Octane	126
C4	*n*-Nonane	151
C5	*n*-Decane	174
C6	*n*-Undecane	192
C7	*n*-Dodecane	216
C8	*n*-Tridecane	232
C9	*n*-Tetradecane	253
C10	*n*-Pentadecane	270

[a] Boiling point of 1-undecanol calculated from linear fit of the boiling points of alcohol homologous series. Lit. value=146 °C at 30 mmHg (1 mmHg=133.322 Pa).

3. Results and discussion

The temperature effects on the valve during a typical chromatographic run were studied by recording a temperature reading every second from the four type-K thermocouples attached to the valve (Fig. 2). Representative data are reported herein. The oven was programmed to ramp four times from 50 to 250 °C at a rate of 15 °C/min and the results of the fourth ramp are shown in Fig. 3A. The other temperature program runs were essentially identical but not shown for brevity. The data indicate that the temperature of the sample loop sensor position

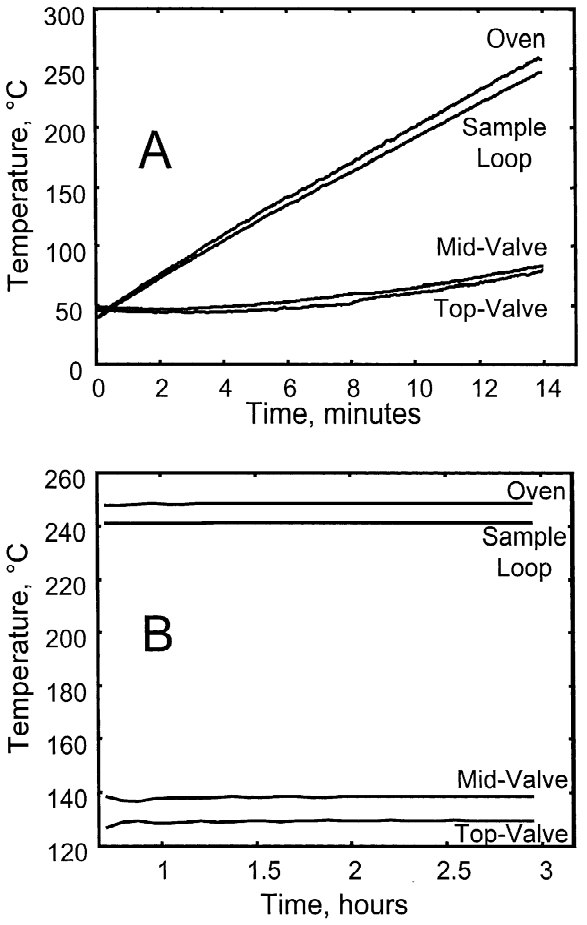

Fig. 3. (A) Temperature profiles for the four type-K thermocouple sensors: top-valve, mid-valve, sample loop and oven as indicated in Fig. 2. The GC oven was programmed to ramp from 50 to 250 °C at 15 °C/min. Data were collected at 1 Hz. (B) Temperature profile for the same four thermocouples when the GC oven is programmed to hold for 3 h at 240 °C. Data were collected at 1 Hz and boxcar averaged every 5 min.

closely follows the temperature of the oven sensor position while the portions of the valve outside the oven, as monitored at the top-valve and mid-valve sensor positions, are significantly lower in temperature throughout the entire temperature program. The sample loop reached 247 °C at the end of the temperature program, deviating from the oven set point of 250 °C by only 1.2%. The O-rings, situated inside the valve and between top-valve and mid-valve, reached a temperature between 79.5 °C (top-valve) and 82.7 °C (mid-valve) by the end of the temperature program. The temperature of the O-rings were well below the maximum operating temperature of 175 °C provided the temperature on the surface of the valve is not substantially different to the internal temperature of the valve near the O-rings. Since the position of the mid-valve temperature sensor is substantially closer to the oven than any of the O-rings, and the mid-valve temperature reading was close to the top-valve temperature reading, it is reasonable to presume the O-rings are indeed in an environment well below 175 °C. While it is difficult to fully prove this condition, one must rely upon the performance of the system over extended time of testing, as was done in this work.

The potential of heat accumulation in the valve was studied by holding the GC oven at 240 °C for a period of 3 h, recording temperature data every second and then boxcar averaging every 5 min. Fig. 3B contains the temperature profiles for the four thermocouples after a steady-state temperature in the top-valve and mid-valve positions was reached. For over 2 h the temperatures on the valve recorded inside and outside the oven were relatively constant. The area containing the O-rings had an average temperature between 129.2±0.6 °C (top-valve) and 138.3±0.5 °C (mid-valve). This was well below the limit of 175 °C although higher than the maximum temperatures recorded during the temperature program study. This suggests that there is a potential for heat to build up in the valve over time, but not enough to exceed acceptable operating temperatures under normal conditions. Inside the oven, the sample loop reached a steady-state temperature of 241.0±0.1 °C (sample loop) while the oven had a steady-state temperature of 248.1±0.1 °C (oven). The sample loop temperature only differs from the set point of 240 °C by 0.5% while the measured oven temperature 248.3 °C differs by 3.5% from the oven set point. This discrepancy is due to the vertical temperature variations within the GC oven itself. The built-in thermocouple used to regulate oven temperature is located in the upper-rear right corner at a similar vertical position as the thermocouple on the sample loop, while the ''oven'' thermocouple was located in the vertical middle near the front of the GC oven.

After 6 months of use, the valve in this new configuration has not suffered any noticeable deterio-

ration in performance. The system has also been temperature programmed to 265 °C, a 90 °C increase from the previous maximum operating temperature of 175 °C. At these high temperatures the stability of many stationary phases (e.g. polar) is an issue. Most commonly used polar phases (phenyl, cyano, and poly(ethylene glycol)) have maximum temperature limits of around 250 °C. Thus, the temperature limits of the polar stationary phases may be the most prominent limitation to further increasing the maximum temperature of valve-based GC×GC instruments.

A 26-component test mixture of alkanes, ketones, and alcohols was utilized to investigate the characteristics of the new system configuration. Table 1 lists the individual components of the mixture and their boiling points. Fig. 4A depicts a three-dimensional (3D) surface plot of the separation for this mixture. The more highly retained large alcohols such as 1-decanol (A9) and 1-undecanol (A10) are the least prominent peaks in relation to other components in the mixture. This is caused by peak broadening due to a combination of decreasing flow-rate on the second column with increasing temperature and a relatively thick stationary phase that highly retains alcohols. Peak widths at 10% of the peak height for representative analytes range from 6.58 to 9.69 s on column 1 and 0.101 to 0.211 s on column 2 (Table 2). Fig. 4B depicts a contour plot of the same separation of this mixture with alcohols labeled A1–A10, ketones labeled B1–B6, and alkanes labeled C1–C10. By temperature programming both columns, it is possible to produce a well-tuned separation [27]. In this type of separation, the homologous series elutes in different near-horizontal bands across the two-dimensional separation space dependent upon their retention on the second column. In this way, the separation space is used more uniformly. Note that an excellent separation is achieved for the test mixture containing components ranging from volatile species (65 °C lowest boiling point) to semi-volatile species (270 °C being the highest boiling point).

The retention time reproducibility of the new configuration was studied. Representative data are reported, herein, by comparing four replicate sets of data. Table 3 summarizes the mean retention time and standard deviation for four test compounds

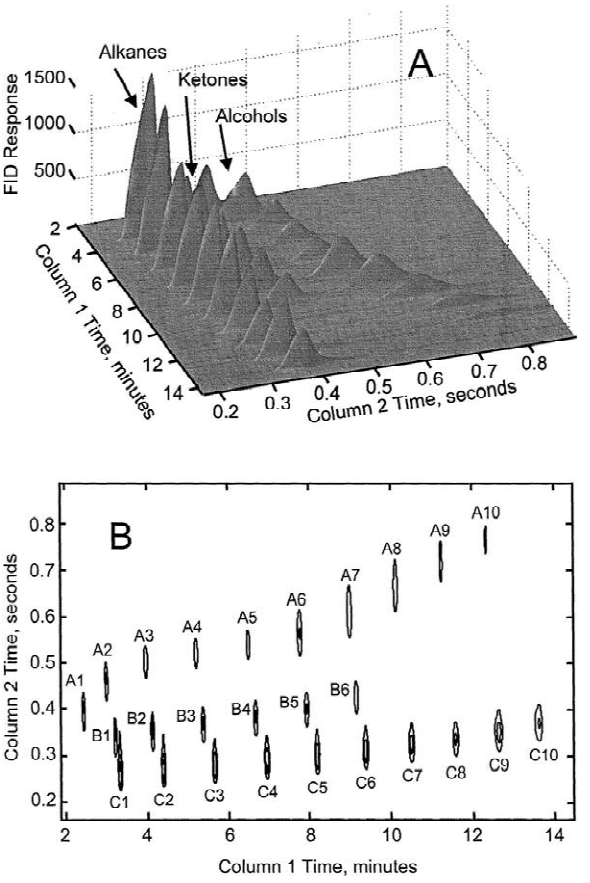

Fig. 4. (A) Three-dimensional plot of the GC×GC separation of a 26-component test mixture of a homologous series of *n*-alkanes, 2-ketones and *n*-alcohols injected at equal volume percent listed in Table 1. Instrumental parameters: column 1 head pressure, 4 p.s.i.; column 2 head pressure, 20 p.s.i.; oven program, held at 40 °C for 1 min and then programmed to ramp to 250 °C at 15 °C/min. (B) Contour plot of the GC×GC separation of the 26-component mixture. A1–A10, ethanol through *n*-undecanol; B1–B6, 2-butanone through 2-nonanone; C1–C10, *n*-hexane through *n*-pentadecane. Boiling points range from 65 °C (*n*-hexane) to 270 °C (*n*-pentadecane).

selected to represent and span the two-dimensional separation space: 1-butanol (A3), 2-heptanone (B4), 1-nonanol (A8), and *n*-tridecane (C8). The sub-matrix signal of 1-nonanol, A8, is shown in Fig. 5A. The sub-matrix is organized such that each second column profile is a column of data in the matrix. The run-to-run retention time variability for each compound on both the column 1 time axis and the column 2 time axis was determined. For each run of

Table 2
Column 1 and column 2 mean peak widths at 10% peak height and mean empirical asymmetry factors (B/A) and standard deviations for 1-butanol (A3), 2-heptanone (B4), 1-nonanol (A8) and *n*-tridecane (C8) determined following the method in Ref. [30]

Test compound	Column 1 mean widths at 10% peak height and standard deviation (s)	Column 1 mean empirical asymmetry factor (B/A) and standard deviation	Column 2 mean widths at 10% peak height and standard deviation (s)	Column 2 mean empirical asymmetry factor (B/A) and standard deviation
1-Butanol (A3)	7.44±0.27	1.2±0.2	0.111±0.003	1.18±0.04
2-Heptanone (B4)	6.58±0.04	1.1±0.2	0.101±0.002	1.14±0.04
1-Nonanol (A8)	9.69±0.20	1.2±0.2	0.211±0.007	1.81±0.09
n-Tridecane (C8)	9.54±0.04	1.09±0.08	0.101±0.001	1.2±0.1

Experimental conditions: column 1: 12 m×200 μm I.D. capillary column with a 0.33-μm poly(dimethylsiloxane) film with 4 p.s.i. head pressure; column 2: 0.5 m×100 μm I.D. capillary column with a 0.2-μm poly(ethylene glycol) film with 20 p.s.i. head pressure; valve actuation, 1-s cycles, 20 ms injection widths; oven program, held at 40 °C for 1 min then programmed to reach 250 °C at 15 °C/min; carrier gas, helium; injection, 1 μl split 100:1.

the test mixture, the column 1 peak profile for each test compound was obtained by summing all of the data from each column 2 run onto the column 1 time axis using the sub-matrix for each isolated signal. The first moment of the resulting peak profile was determined, providing the retention time. The mean retention time and standard deviation for each test compound was determined using the four replicate runs. The run-to-run retention time variability for each test compound on the column 2 time axis was similarly determined. The run-to-run retention time variability on column 1 was less than 0.1% for each of the four test compounds of interest. The run-to-run retention time variability on column 2 was greatest for highly retained compounds, 0.7% for 1-nonanol (A8), and lower for less retained compounds, 0.1% for 2-heptanone (B4). The within-run retention time variability on column 2 was analyzed by calculating the first moment of each column of data in each test compound sub-matrix. The mean and standard deviations of the retention times for each data column comprising the peak were calculated for each of the four replicate runs. The average of these four means and standard deviations is reported as the within-run variability of column 2 retention times. The within-run standard deviations are greater than run-to-run variations; however, the largest of the variations is still only 1.4% indicating that, in general, the retention time reproducibility is quite good.

One test to determine whether the within-run retention time variation has detrimental effects on the data structure is to employ a multivariate data analysis technique that requires bilinear data. The generalized rank annihilation method (GRAM) has been shown to quantify and deconvolute bilinear data

Table 3
Column 1 mean retention times and column 2 mean retention times with run-to-run standard deviations, and column 2 mean retention times with mean within-run standard deviations for 1-butanol (A3), 2-heptanone (B4), 1-nonanol (A8) and *n*-tridecane (C8)

Test compound	Column 1 mean retention time and run-to-run standard deviation (min)	Column 2 mean retention time and run-to-run standard deviation (s)	Column 2 mean retention time and mean within-run standard deviation (s)
1-Butanol (A3)	3.994±0.005	0.517±0.003	0.518±0.007
2-Heptanone (B4)	6.678±0.004	0.3887±0.0004	0.389±0.005
1-Nonanol (A8)	10.117±0.004	0.688±0.005	0.69±0.01
n-Tridecane (C8)	11.570±0.003	0.350±0.002	0.351±0.002

Experimental conditions: same as for Table 2.

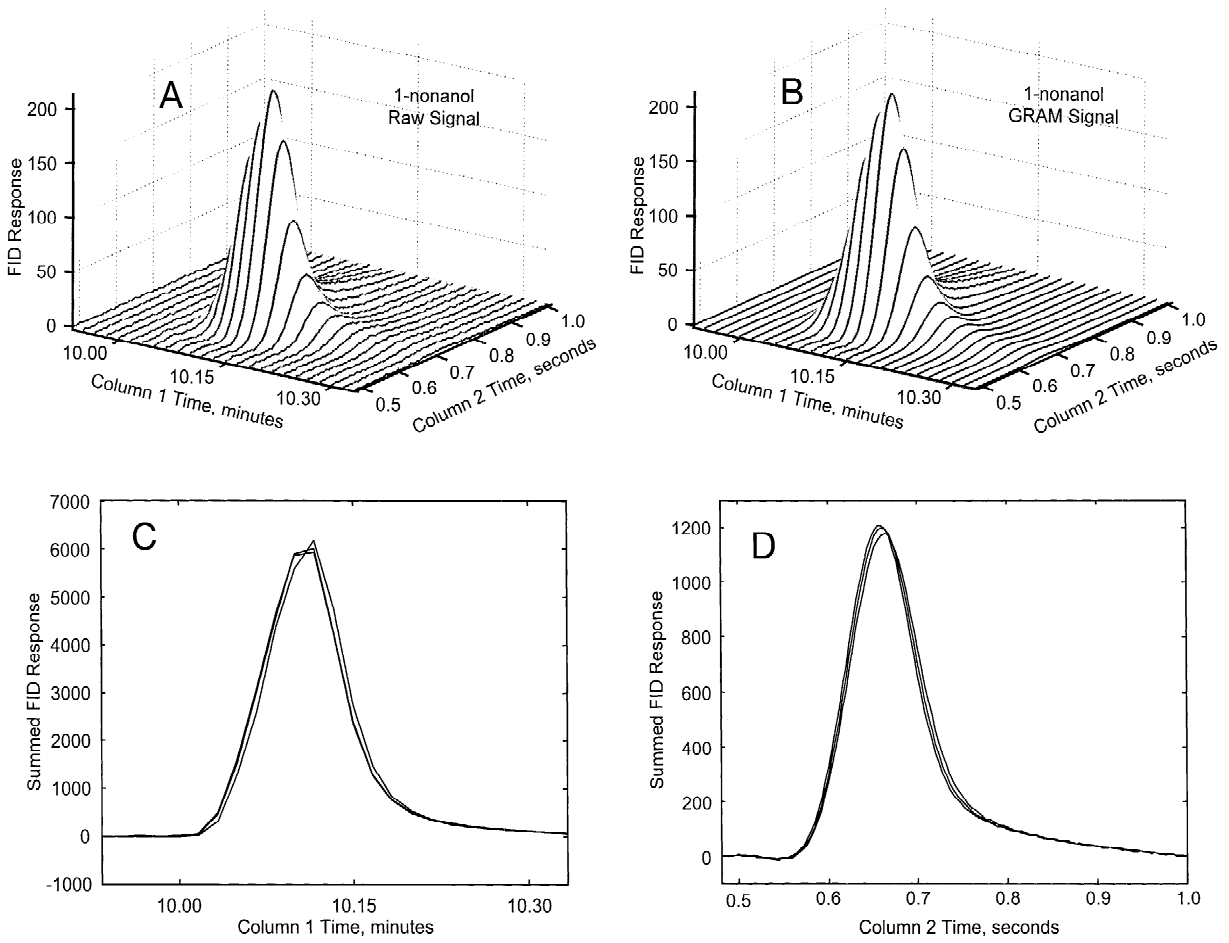

Fig. 5. (A) Three-dimensional (3D) sub-matrix of 1-nonanol (A8) from 26-component mixture. (B) Representative 3D sub-matrix of 1-nonanol reconstructed from GRAM analysis. (C) Summed column 1 signal profiles for reconstructed sub-matrices of three replicate sample runs following application of GRAM. (D) Summed column 2 signal profiles for reconstructed sub-matrices of three replicate sample runs following application of GRAM.

using a calibration data set containing the chemical species of interest [23,28,29]. GRAM was applied to the data for the test compound with the worst within-run retention time variation in Table 3, i.e. 1-nonanol (A8), to determine whether or not data from this high-temperature configuration is well suited for multivariate data analysis. A sub-matrix of the 1-nonanol data was isolated from each of the four replicate data sets (Fig. 5A). Typically GRAM requires the calibration data set and the sample data sets to have differing concentrations; however, with the unique case of having only one component in the matrix, using one of the replicate runs as the standard data set and the other three replicate runs as samples is feasible. For example, using the standard and one of the samples, application of GRAM resulted in the reconstructed peak shown in Fig. 5B. The GRAM result in Fig. 5B is essentially identical to the raw data depicted in Fig. 5A. The three trials gave reproducibly good results as shown in the summed peak profiles for each dimension (Fig. 5C and D). Therefore, the data from the high-temperature valve-based GC×GC configuration is appropriate for multivariate data analysis.

The shape of the column 1 peak profile of 1-nonanol is also significant because there is no

substantial tailing in the column 1 time dimension (Fig. 5C). If the valve and sample loop were not accurately tracking the oven temperature, a compound with a high boiling point such as 1-nonanol would encounter a ''cold spot'' in the sample loop upon leaving the first column. The resulting condensation would retard the elution of some of the compound during each injection onto the second column. This condition would manifest itself as tailing on the peaks in the column 1 time dimension. One method for assessing peak tailing, i.e. peak asymmetry, is to graphically measure empirical asymmetry factors (B/A) [30]. To obtain the B/A ratio for a given peak, one must measure the peak width (A) at 10% peak height for the leading portion of the peak, and divide that into the peak width (B) at 10% peak height for the trailing portion of the peak. Both A and B are measured from the time at the peak maximum such that A+B is equal to the total peak width at 10% peak height. The asymmetry factors (B/A) for representative analytes are listed in Table 2. A value of exactly 1 for B/A indicates a perfectly symmetric (Gaussian) peak where a value greater than 1 indicates peak tailing. Column 1 peak profiles have B/A values ranging from 1.09 ± 0.08 to 1.2 ± 0.2 indicating nearly Gaussian peaks within the error of the measurement. Thus, the lack of significant peak tailing in the column 1 time dimension for high-boiling point compounds is an indication that the sample loop and portions of the valve that interact with the sample are closely following the oven temperature, and condensation in the valve is not a significant effect. Column 2 peak profiles have B/A values ranging from 1.14 ± 0.04 to 1.81 ± 0.09 indicating some moderate asymmetry. The asymmetry factor is highest for 1-nonanol, a high-boiling polar compound that is highly retained on column 2. This is likely due to a combination of decreasing flow-rate on the second column with increasing temperature and a thick stationary phase that highly retains alcohols.

4. Conclusions

A novel configuration for high-temperature diaphragm valve-based GC×GC has been proposed and tested. Mounting the valve only partially inside the oven has circumvented the valve temperature limit of 175 °C. Even at high oven temperatures (~250 °C), the surface temperature of the thermally sensitive portion of the valve is well below 175 °C. The detected peak signal profiles for high-boiling compounds such as 1-nonanol (b.p.=215 °C) indicate that condensation in the valve is not observed. The resulting data obtained with this system conforms to requirements necessary to utilize chemometric data analysis techniques such as GRAM. The workable temperature range has been extended to at least 250 °C and is now applicable to semi-volatile sample components. The new valve configuration shows promise for analyzing complex mixtures with a wider range of boiling points than was previously possible with diaphragm valve-based GC×GC.

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