

# Flow-switching device for comprehensive two-dimensional gas chromatography

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## Abstract

A simple flow-switching device has been developed as a differential flow modulator for comprehensive two-dimensional gas chromatography (GC × GC). The device is assembled from tubing, four tee unions, and a solenoid valve. The solenoid valve is located outside the oven of the gas chromatograph and is not in the sample path. The modulation technique has no inherent temperature restrictions and passes 100% of the primary column effluent to the secondary column(s). Secondary peaks are produced with widths at half maximum less than 100 ms when operating in GC × 2GC mode with a 2.0 s modulation period. The efficacy of this approach is demonstrated through the analysis of a standard mixture of volatile organic compounds (VOCs) and diesel fuel.

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## 1. Introduction

Liu and Phillips introduced comprehensive two-dimensional gas chromatography (GC × GC) 12 years ago [1]. Their original design employed a two-stage thermal modulator. This modulator was effective at demonstrating the resolving power of GC × GC separations but not sufficiently robust for routine use. Several new modulators have been introduced over the past decade. Current thermal modulators employ cryogenic sampling [2–5]. These devices are applicable to a broad range of samples and are much more rugged than the original design. The main disadvantages are that liquid cryogen is required and a system capable of delivering liquid cryogen into the oven of the gas chromatograph must be engineered.

A few investigators have developed modulation schemes that do not employ thermal techniques. Current designs use multi-port valves to either divert a portion of the primary column effluent to the head of the secondary column [6] or to collect primary column effluent in a sampling loop and subsequently inject the material into the secondary column [7]. The direct diverting approach reduces the sensitivity of the analysis because only a small amount (<10%) of each component is transferred from the primary column to the

secondary column. The low duty cycle of sampling can also lead to imprecision in component quantitation [8].

A multi-port, two-position valve fitted with a sample loop can provide greater component transfer and reduce quantitative imprecision [7]. A schematic of a typical configuration is shown in Fig. 1. Similar devices have been fabricated with eight-port valves [9]. When the valve is in the “fill” position, primary column effluent flows into the sample loop while an auxiliary flow of carrier gas is directed to the secondary column. When the valve is switched to the “flush” position, primary column effluent is directed to the exhaust while the auxiliary flow flushes the sample loop contents into the secondary column. After the loop is flushed, the valve is returned to the “fill” position to begin collecting more primary column effluent. If the volumetric flow rate of the primary column and the secondary column are equal, then the time required to flush the loop is the same as the time required to fill the loop. However, if the secondary column flow is greater than the primary column flow then the loop will be flushed in less time than it was filled. In practice, a primary to secondary flow ratio of 1:20 is often used [10]. Under such conditions, the entire volume of primary column effluent collected in 1.0 s can be injected into the secondary column as a 50 ms wide pulse. This approach is called differential flow modulation.

There are three drawbacks to the differential flow modulation approach. First, high secondary flows are required to produce high peak capacity. High flows lead to an increase

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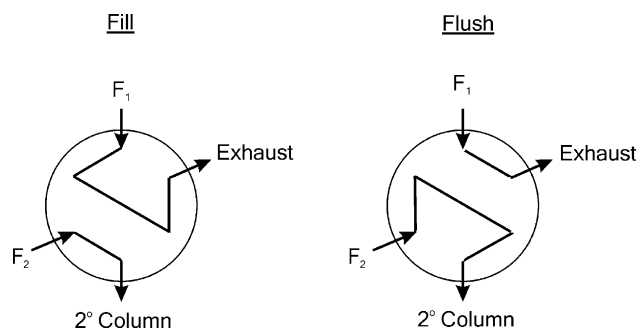


Fig. 1. Schematic of a two-position six-port valve used for differential flow modulation GC  $\times$  GC. When the valve is in the fill position shown on the left, the flow exiting the primary column,  $F_1$ , fills the sample loop (shown as a diagonal line in the center of the valve) while the secondary column flow,  $F_2$ , passes directly to the secondary column. When the valve is in the flush position shown on the right, the flow exiting the primary column passes directly to the exhaust while the secondary column flow flushes the sample loop contents into the secondary column.

in the theoretical plate height of the secondary column, but high flows also allow longer secondary columns to be used. As a result, the total number of accessible theoretical plates is largely independent of flow [11]. However, the requirement of high flow and long columns limits the use of micro-bore secondary columns (i.e., columns with internal diameters less than 0.15 mm) because excessively high head pressures would be required.

Temperature limitations are a second drawback of differential flow modulation. Diaphragm valves are currently the only multi-port valves capable of continuous switching at a rate of 1 Hz. Such valves have internal actuating mechanisms that are damaged at temperatures greater than 200 °C. This reduces the range of samples that can be analyzed. For example, diesel fuel contains semi-volatile compounds that would condense inside a valve held at 200 °C. However, special heating configurations can be employed that allow the wetted valve parts to be at temperatures greater than 200 °C while the actuating mechanism is kept at temperatures less than 200 °C [7,12]. This increases the temperature limit of the technique, but the current maximum temperature of a published diaphragm valve separation is 240 °C [12].

Pressure and flow fluctuations produced by valve switching are a third problem associated with diaphragm valve modulation. Fluctuations are produced when the secondary column head pressure is much greater than the pressure of the sample loop. Upon switching the valve from the fill to the flush position, the volumetric flow rate of the gas entering the secondary column temporarily decreases as the sample loop is brought up to the proper secondary column head pressure. Fortunately, the current practice of using long secondary columns (5 m) dampens the flow fluctuations and losses in chromatographic resolution have not been observed [7]. However, it is possible that fluctuations would lead to degraded resolution if short secondary columns were used.

This article describes a new modulation device that allows differential flow GC  $\times$  GC separations to be performed

without diaphragm valves. The device is somewhat similar to previously published flow-switching devices [13,14] in that flow directions are controlled by a three-port solenoid valve located outside of the column oven and not in the sample path. The portion of the modulation device inside the oven contains no moving parts and is constructed with material that can withstand a wide range of temperatures. In addition, the device employs very small pressure differences to produce modulation. Thus, flow disturbances to the primary and secondary columns are minimized. This article is divided into two parts: a theoretical analysis of the flow-switching device and an experimental validation of the device as a GC  $\times$  GC modulator.

## 2. Theoretical analysis

### 2.1. General principle of operation

A schematic of the device is shown in Fig. 2. The flow exiting the primary column,  $F_1$ , enters the device at union A. Union A is connected to two peripheral unions,  $B_L$  and

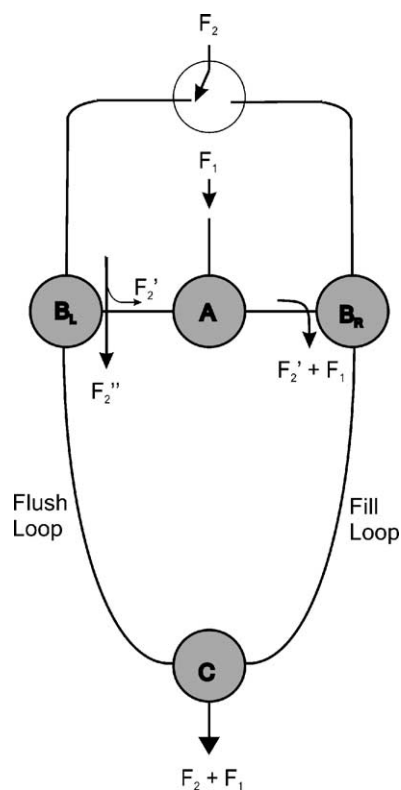


Fig. 2. Schematic of the flow-switching device used for differential flow modulation GC  $\times$  GC. The schematic shows the case when the three-port valve (shown as a circle at the top of the figure) is set such that the primary column flow,  $F_1$ , fills the right sample loop and the auxiliary flow,  $F_2$ , flushes the left sample loop. Switching the three-port valve reverses the position of the fill loop and the flush loop. Pulses of primary column effluent are generated by switching the three-port valve at regular intervals.

$B_R$ , with pieces of tubing having the same dimensions (i.e., the same length and internal diameter). An auxiliary flow of carrier gas,  $F_2$ , enters the common port of a three-port valve. This flow is substantially greater than the primary column flow. The auxiliary flow exits the three-port valve and travels to either union  $B_L$  or union  $B_R$ . The direction of travel is determined by the state of the three-port valve. The pieces of tubing extending from the valve to the unions  $B_L$  and  $B_R$  have the same dimensions. The unions  $B_L$  and  $B_R$  are also connected to union C. The tubing extending from  $B_L$  to C has the same dimensions as the tubing from  $B_R$  to C. These two pieces of tubing serve as collection loops for primary column effluent. The flow  $F_1$  and  $F_2$  exit the device through union C to enter the secondary column.

The device uses the auxiliary flow  $F_2$  to guide the primary column effluent into one of the collection tubes while simultaneously flushing out the other collection tube. For instance, when the three-port valve is in the position shown in Fig. 2, a small portion of  $F_2$  (shown as  $F'_2$ ) directs the primary column effluent to the right sample loop (i.e., the tube between  $B_R$  and C) while the remainder of  $F_2$  (shown as  $F''_2$ ) flushes out the left sample loop (i.e., the tube between  $B_L$  and C). When the valve is switched to the opposite position (not shown in the figure),  $F'_2$  emerges from union  $B_R$  and pushes the primary column effluent to the left sample loop while the remainder of  $F_2$  flushes out the right sample loop. Switching the three-port valve at regular intervals results in a series of pulses of primary column effluent exiting the device through union C. Optimal modulation is predicted when  $F'_2$  is just large enough to direct the primary column effluent into the sample loop. Higher values of  $F'_2$  would be counter-productive as they would dilute the primary column effluent and broaden the resulting pulses.

## 2.2. Estimate of required flow resistances

Creating conditions where  $F'_2$  is smaller than  $F_1$  (but still greater than zero) requires proper proportioning of the flow resistances within the device. It is useful to derive an equation that predicts how  $F'_2$  is related to the flows  $F_2$  and  $F_1$  and the resistances within the device. The following derivation assumes that the change in pressure between the center of any two unions,  $\Delta P$ , follows an Ohm's law form; i.e.,  $\Delta P = FR$  where  $F$  is the volumetric flow rate and  $R$  is the resistance to flow. This equation is a good approximation when the pressure change is substantially smaller than the average pressure [15].

The device is represented in the form of a resistor diagram in Fig. 3. The flow resistance from union  $B_L$  to union A is assumed to be the same as the resistance from union  $B_R$  to union A. These resistances are denoted as  $R_{BA}$ . The resistance from union  $B_L$  to union C is assumed to be the same as the resistance from union  $B_R$  to union C. These resistances are denoted as  $R_{BC}$ .

The derivation starts with the assertion that the pressure drop from the center of union  $B_L$  to the center of union C

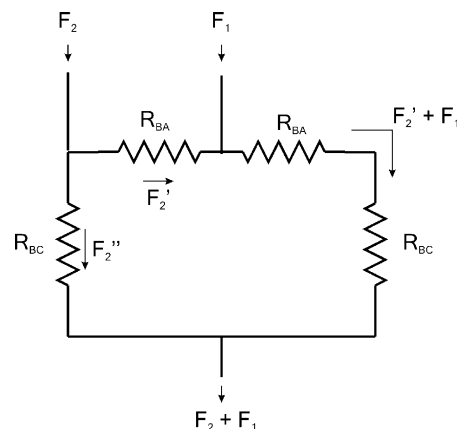


Fig. 3. Resistor diagram for the flow-switching device. The diagram is drawn for the case of injecting the auxiliary flow,  $F_2$ , into the left peripheral union (i.e., union  $B_L$  in Fig. 2).

along the tube directly connecting  $B_L$  to C is the same as the pressure drop along the path of union  $B_L$  to union A to union  $B_R$  to union C. Thus, equating the pressure drops along these two paths produces:

$$F''_2 R_{BC} = F'_2 R_{BA} + (F'_2 + F_1)(R_{BA} + R_{BC})$$

Using  $F''_2 = F_2 - F'_2$ , this equation can be rewritten as

$$F_1(R_{BA} + R_{BC}) + 2F'_2(R_{BA} + R_{BC}) - F_2 R_{BC} = 0$$

Upon further rearrangement, this equation gives:

$$\frac{F'_2}{F_2} = \frac{1}{2} \left[ \frac{R_{BC}}{R_{BA} + R_{BC}} - \frac{F_1}{F_2} \right] \quad (1)$$

Optimal differential flow modulation will be produced when  $F'_2$  is greater than zero but substantially smaller than both  $F_1$  and  $F_2$ . Such a condition is produced when the right side of Eq. (1) is positive but close to zero. This is achieved when  $R_{BC}/(R_{BA} + R_{BC})$  is just slightly greater than  $F_1/F_2$ . Equivalently, this corresponds to the case when  $R_{BA}/R_{BC}$  is slightly less than  $(F_2/F_1) - 1$ .

## 2.3. Estimate of device dimensions

In addition to resistance restrictions, proper operation of the device can only be achieved if the volumes of the tubes that connect the union A to the unions  $B_L$  and  $B_R$  are minimized, while the volumes of the sample loops (i.e., the pieces of tubing that connecting  $B_R$  to C and  $B_L$  to C) are large enough to hold the primary column effluent during the desired sampling period. This requirement can be satisfied by using short tubes with small internal diameters to connect union A to the peripheral unions and long tubes with larger diameters as sample loops.

We now estimate the dimensions of tubing that would produce optimal modulation for the case of  $F_1 = 1 \text{ cm}^3 \text{ min}^{-1}$ ,  $F_2 = 20 \text{ cm}^3 \text{ min}^{-1}$ , and a switching frequency is 0.5 Hz. If tubing with an internal diameter of 0.53 mm is used as

the sample loops, the volume of each of these tubes needs to be at least the volume delivered by  $F_1$  in the 2 s collection period. For a flow of  $1 \text{ cm}^3 \text{ min}^{-1}$  this corresponds to  $0.0333 \text{ cm}^3$ . Approximately 15 cm of 0.53 mm i.d. tubing is necessary to hold this volume. With the dimensions of the sample loops determined, we now estimate the dimensions of tubing between the A and B unions that would properly balance the resistance of the sample loops. In this particular case,  $F_2/F_1$  is 20 so optimal modulation performance is predicted when  $R_{BA}/R_{BC}$  is slightly less than 19. The Poiseuille equation for laminar flow predicts that the flow resistance of tubing is inversely proportional to the fourth power of the internal diameter [15]. Thus, 0.15 mm i.d. tubing is 156 times more flow resistant than the 0.53 mm tubing per unit length. Therefore a  $R_{BA}/R_{BC}$  ratio of 19 can be generated using 1.8 cm pieces of 0.15 mm i.d. tubing to connect union A to  $B_R$  and  $B_L$ . This result shows that adequate resistance can be generated without creating a large volume between the A and B unions: The internal volumes of the pieces of tubing that connecting union A to the peripheral unions are less than 2% of the volume of the sample loops.

The previous analysis assumes that the flow resistances are determined completely by the pieces of tubing within the device. In practice we have found that the unions make a significant contribution (approximately 30%) to the sample loop resistance. Thus, slightly longer tubes between the union A to the peripheral unions are needed to properly balance the device. The key result of these calculations is that they demonstrate that a flow-switching device can be constructed with readily available materials (i.e., unions and tubing of standard dimensions) and that the size of the resulting device will easily fit inside a gas chromatograph.

### 3. Technique validation

#### 3.1. Experimental

##### 3.1.1. General setup

A schematic of the  $\text{GC} \times 2\text{GC}$  system is shown in Fig. 4. A Perkin-Elmer (Norwalk, CT, USA) Autosystem XL gas chromatograph with electronic pneumatics and dual flame-ionization detection (FID) systems was used as the experimental platform. Ultra-high purity hydrogen was used as the carrier gas in the primary and secondary columns. Neat mixtures were injected into the primary column through a split inlet (30:1 split ratio,  $250^\circ\text{C}$ ). The primary column flow was passed into the flow-switching device for modulation. The flow exiting the switching device was divided between two secondary columns with a tee union. Effluent from each secondary column was passed through a FID system at  $250^\circ\text{C}$ . The 100 nF filtering capacitor on each FID system electrometer was replaced by an 8 nF capacitor. The signals from the detectors were monitored at 200 Hz by a personal computer equipped with a data acquisition board. Custom software was used to convert the one-dimensional

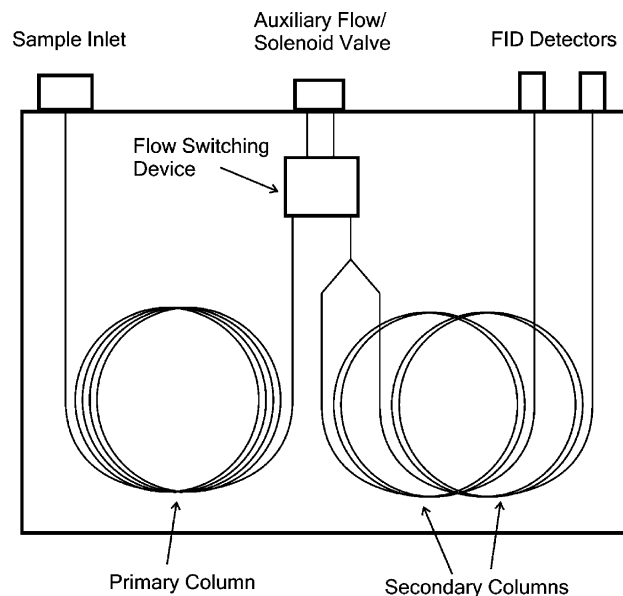


Fig. 4. Schematic of the  $\text{GC} \times 2\text{GC}$  instrument.

signal arrays into two-dimensional chromatograms. The capillary columns used in these studies can be purchased from Agilent Technologies (Folsom, CA, USA).

##### 3.1.2. The switching device

A schematic of the flow-switching device is shown in Fig. 5. The device was constructed with deactivated fused silica tubing, stainless steel tubing, four “T” unions (stainless steel, 0.25 mm i.d. orifices, VICI, Houston, TX, USA, part number MT.5CS6), and a three-port solenoid valve (Parker-General Valve, Fairfield, NJ, USA, part number 009-0284-900). An auxiliary flow of carrier gas was connected to the common port of the three-port solenoid valve. The solenoid valve was positioned on the top of the chromatograph outside of the oven. The remainder of flow-switching device was mounted on a thin piece of stainless steel sheet and housed inside the column oven. The output ports of the solenoid valve were connected to the peripheral unions of the switching device with two pieces of stainless steel tubing (20 cm length, 0.5 mm i.d.). The exit of the primary column was connected to the center union. The center union was connected to the peripheral unions with two pieces of deactivated fused silica capillary tubing (2.7 cm long, 0.15 mm i.d. for the volatile organic compound (VOC) studies; 4.0 cm long, 0.15 mm i.d. for the diesel fuel studies). The peripheral unions were connected to the lower union with two pieces of wide-bore deactivated fused silica capillary tubing (15 cm long, 0.53 mm i.d.). The primary column flow and auxiliary flow exited the device through the lower union. During operation, the solenoid valve was switched every 2 s by a computer controlled circuit. Switching the solenoid valve did not produce observable pressure or flow fluctuations at the head of the primary column, in the auxiliary flow controller, or at the exit of the secondary columns.

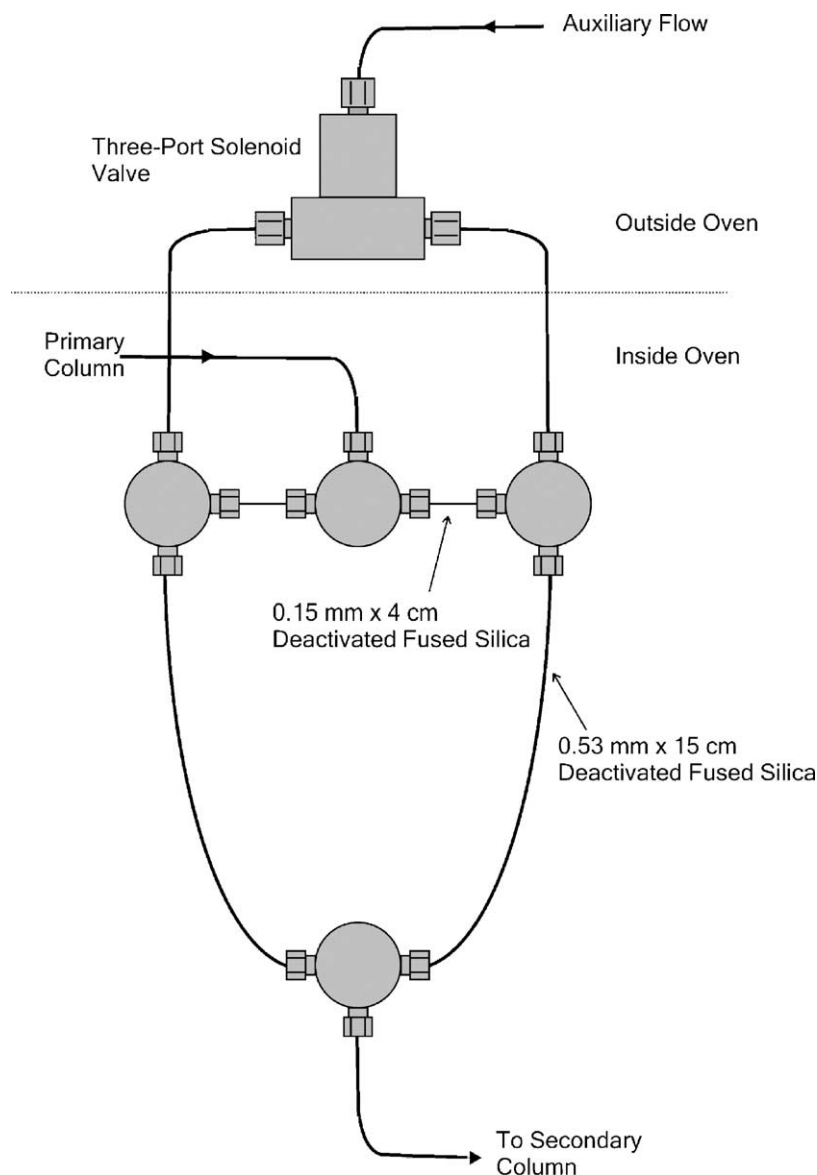


Fig. 5. Schematic of flow-switching device used for the diesel fuel studies. The GC  $\times$  2GC separations of volatile organic compounds were performed with an identical device except the 0.15 mm  $\times$  4 cm fused silica tubes were replaced by 0.15 mm  $\times$  2.7 cm fused silica tubes.

### 3.1.3. Volatile organic compound studies

Neat mixtures of VOCs were injected in 0.05  $\mu$ l quantities. The primary column flow was 0.80 ml min<sup>-1</sup> and the auxiliary flow was 20.0 ml min<sup>-1</sup>. The oven temperature was ramped according to the following program: 40 °C for 1.0 min, ramp to 75 °C at 14.0 K min<sup>-1</sup>, ramp to 120 °C at 10.0 K min<sup>-1</sup>, ramp to 160 °C at 6.5 K min<sup>-1</sup>, hold for 1.0 min. A 5.0 m  $\times$  250  $\mu$ m DB-624 capillary column (6% cyanopropylphenyl, 94% dimethylpolysiloxane, 1.4  $\mu$ m film thickness) was used as the primary column. A 5.2 m  $\times$  250  $\mu$ m DB-Wax column (polyethylene glycol, 0.10  $\mu$ m film thickness) and a 5.2 m  $\times$  250  $\mu$ m DB-210 column (trifluoropropylmethyl-polysiloxane, 0.25  $\mu$ m film thickness) were used as the secondary columns. Measurements of the flow exiting from each secondary column

indicated that the secondary flow was evenly split to within 2%.

### 3.1.4. Diesel fuel studies

A sample of diesel fuel was obtained from a local service station and injected in 0.5  $\mu$ l quantities. The primary column flow was 0.90 ml min<sup>-1</sup> and the auxiliary flow was 26.4 ml min<sup>-1</sup>. The oven temperature was ramped according to the following program: 50 °C for 1.5 min, ramp to 240 °C at 12.5 K min<sup>-1</sup>, hold for 6.0 min. A 27.0 m  $\times$  250  $\mu$ m HP-5 capillary column (5% diphenyl-95% dimethylpolysiloxane, 0.25  $\mu$ m film thickness) was used as the primary column. A 5.7 m  $\times$  250  $\mu$ m DB-Wax column (polyethylene glycol, 0.10  $\mu$ m film thickness) and a 1.4 m  $\times$  250  $\mu$ m deactivated fused silica column were used as the secondary columns.



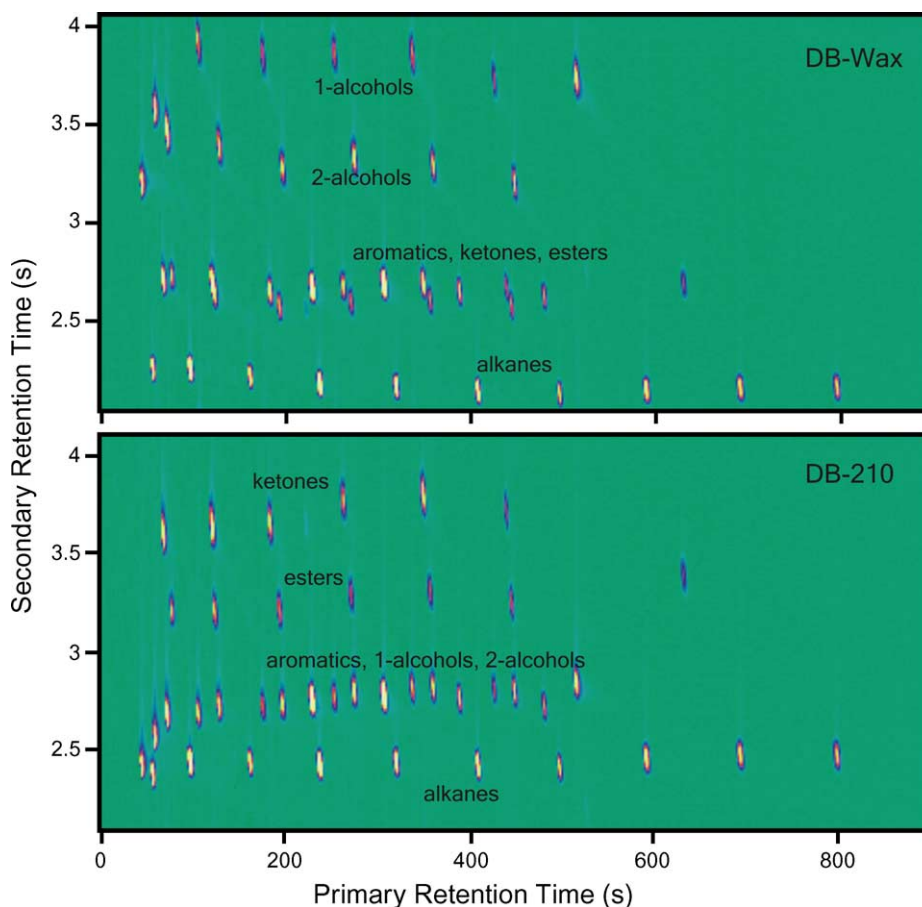


Fig. 6. GC  $\times$  2GC chromatogram of the volatile organic compound mixture.

Measurements of the flow exiting from the secondary columns indicated that the secondary flow was split in a 1:4 ratio between the DB-Wax secondary column and the deactivated fused silica column.

### 3.2. Results and discussion

#### 3.2.1. Volatile organic compound studies

The experimental configuration used for the VOC studies is similar to the setup of previous GC  $\times$  2GC separations performed with a six-port diaphragm valve [10]. A 41-component mixture was used as a test sample. This mixture contained the following VOCs: C<sub>5</sub>–C<sub>14</sub> *n*-alkanes, C<sub>1</sub>–C<sub>8</sub> 1-alcohols, C<sub>3</sub>–C<sub>8</sub> 2-alcohols, C<sub>3</sub>–C<sub>8</sub> and C<sub>10</sub> acetates, C<sub>3</sub>–C<sub>8</sub> 2-ketones, and C<sub>7</sub>–C<sub>10</sub> alkyl aromatics. Compounds within each functional class differed only by the length of their straight-chain alkyl group. The two-dimensional chromatograms for this mixture are shown in Fig. 6. In general, the chromatograms produced by the flow-switching device are similar to those obtained with diaphragm valve modulation. Fig. 7 contains a portion of the signal array recorded from the detector connected to the DB-Wax secondary column. The dodecane peaks are displayed. The width at half maximum of the peaks are 90 ms. Similar widths were observed for all compounds

that were poorly retained on the secondary columns. Highly retained peaks, such as the primary alcohols in the DB-Wax chromatogram, had peak widths at half maximum of approximately 110 ms.

Perfect differential flow modulation with the 0.8–20 flow ratio and a 2 s modulation period would be expected to inject components into the secondary columns as 80 ms wide pulses. The observed peak widths are very close to this value indicating that the flow-switching device produces near optimal modulation. However, we also found that the modulated peaks displayed tailing near the baseline. The degree of tailing was very small (see Fig. 7) but consistently present and not connected with compound polarity (e.g. injections of methane produced the same amount of tailing as primary alcohols). It is possible that this tailing is caused by dead volume within the switching device. Due to the small size of the tailing, we do not believe that it significantly degrades the chromatographic resolution.

#### 3.2.2. Diesel fuel studies

We analyzed diesel fuel to test the performance of the flow-switching device at higher temperatures. The 240 °C maximum temperature of the analysis was set by the temperature limit of the DB-Wax secondary column. A primary to secondary flow ratio of 0.90–26.4 was used. Slightly

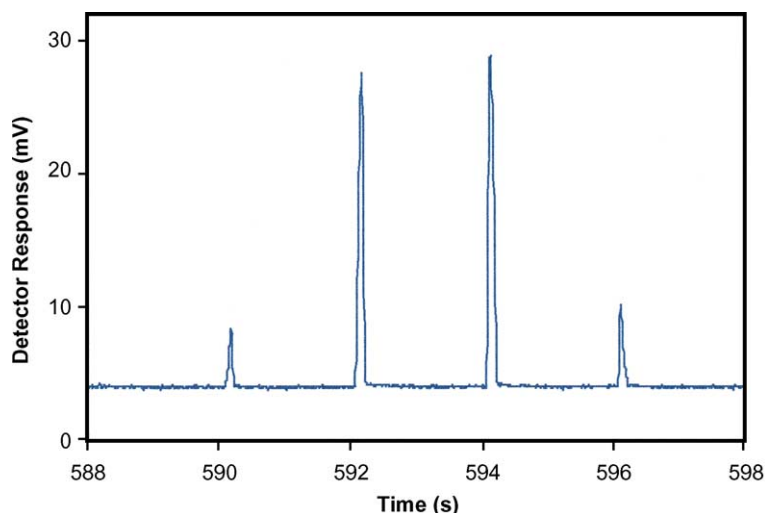


Fig. 7. One-dimensional signal from the DB-Wax detector. The peaks shown are due to dodecane and have widths at half maximum of 90 ms.

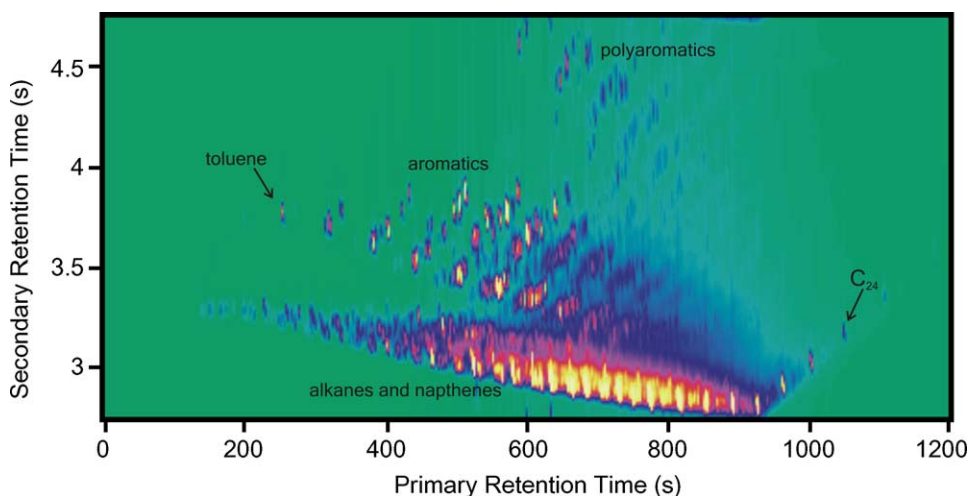


Fig. 8. Two-dimensional gas chromatograph of diesel fuel using a DB-5 primary column and a DB-Wax secondary column. The peaks due to toluene and tetracosane (shown as  $C_{24}$ ) are highlighted. These peaks have the same secondary widths, demonstrating that the performance of the modulator remains constant throughout the entire analysis.

longer capillaries between the central union and the peripheral unions were used to accommodate a higher secondary flow. Fig. 8 contains a typical  $GC \times GC$  chromatogram. The results are similar to diesel fuel separations obtained with thermal modulation and a secondary column containing polyethylene glycol [16]. All of the resolved peaks are very sharp along the secondary dimension, with widths at half maximum of approximately 70 ms. Once again, these widths are close to the theoretical limit imposed by a 0.90–26.4 flow ratio. The one to four splitting of the secondary flow after modulation was used to demonstrate how differential flow with post-modulation splitting can be used to sharpen peaks while still comprehensively sampling the peaks emerging from the primary column.

The flow-switching device performed well at high temperature. For example, the tetracosane (a straight-chain alkane with 24 carbons) peak that eluted at a primary retention time

of 1058 s and an oven temperature of  $240^\circ\text{C}$  had the same width in the secondary dimension (70 ms) as the toluene peak that eluted at a primary retention time of 252 s and a temperature of  $73^\circ\text{C}$ .

#### 4. Conclusions

This study demonstrates that a flow-switching device assembled from a few simple, commercially available components can generate high resolution  $GC \times GC$  separations of volatile and semi-volatile compounds. The device has several advantages over diaphragm valve modulation. The most obvious is an extended upper temperature limit. With the flow-switching device, the upper temperature limit is dictated by the limitations of the capillary columns not the limitations of the modulator. In addition, the flow-switching

device produces much smaller flow disturbances than diaphragm modulation, and the device samples all of the primary column effluent.

### Acknowledgements

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