Capillary Flow Technology with Multi-Dimensional Gas Chromatography for Trace Analysis of Oxygenated Compounds in Complex Hydrocarbon Matrices

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Abstract

By employing multi-dimension gas chromatography with capillary flow technology in combination with highly selective capillary columns and a pressurized liquid injection system, light oxygenated compounds such as methanol, ethanol, *n*-propanol, 2-propanol, and *n*-butanol in the presence of either light hydrocarbon, heavy hydrocarbon, or aromatic matrices can be measured accurately with minimal possibility of a false positive. Using this technique, a detection limit of at least 0.20 ppm (w/w) with a linear correlation coefficient greater than 0.9993 over a range from 0.5 ppm to 600 ppm (w/w) and a relative standard deviation of greater than 2.7% are achieved for the solutes tested. The technique can also be effective for the measurement of other classes of oxygenated compounds such as ethers, aldehydes, and ketones. Another added benefit for the implementation of capillary flow technology is the capability to conduct column back-flushing, where heavier, undesired solutes in a sample can be back-flushed from the chromatographic system to improve system cleanliness and sample throughput.

Introduction

It is a common practice to add methanol into hydrocarbons for pipeline operations in cold climate environment to prevent hydration. But the presence of sub part-per-million levels of oxygenated compounds in hydrocarbon matrices can have a negative impact on the quality of products produced, as well as on the catalysts used for down-stream final products such as polyolefins (1). Some analytical challenges are encountered for said applications. First is the lack of a reliable, low cost selective detector that has a high degree of sensitivity for oxygenated compounds (examples include atomic emission detector, differential mobility detector, oxygen-specific flame ionization detector, or mass selective detector). The second challenge is the complicated and labor-intensive sample pre-concentration techniques, such as solid-phase extraction or water extraction. Third is the intensive valving configuration for the isolation of the solute of interest against matrix interferences. Fourth is that while there are commercially available column technologies that offer unique selectivity towards oxygenated compounds such as polyethylene glycol or tris [2-carboxyethyl] phosphine (TCEP) classes, and even more selectivity with the Varian CP-Lowox or Agilent GS-OxyPLOT, this selectivity is inadequate against hydrocarbons heavier than nC_{10} or aromatic compounds, known to exist in matrices such as gasoline or diesel fuel. The fifth challenge is that although methanol in crude oils can be analyzed by direct injection, multi-dimensional gas chromatography, this method was found to be unsuitable for light hydrocarbon such as ethylene, propylene, propane, butane, and butadiene, and the quantitative limit of 15 ppm (w/w) for methanol attained by this method was found to be too high for the measurement of sub-ppm levels of oxygenated compounds in the aforementioned applications (2). Finally, while stacked injection can be employed to measure ppb levels of oxygenated compounds, it is ineffective in dealing with the heavier hydrocarbon matrices mentioned because the premise of the enrichment and separation processes are based on highly selective column technologies cited earlier (1). The recently introduced capillary flow technology was successfully employed as an enabler for the implementation of multi-dimensional gas chromatography to improve separation resolution, selectivity, and peak capacity for the measurement of compounds of interest in both light hydrocarbon of less than nC_5 and complex hydrocarbon matrices. This paper summarizes the results obtained.

Experimental

Two GCs were used for application development. One was a recently commercialized Agilent 7890A GC (Wilmington, DE, SN# US10705002), equipped with one split/splitless injector, one PTV injector, two flame ionization detectors, and an Agilent G-2855B capillary flow plate (PN# G2855-60500) revision C system. Control of the second pressure source was handled with a pressure control module (PCM). A three-way, 24 V DC, 5 W

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fluid automation system valve (FAS PN#6-311-003-46) was used for flow switching. A Chemstation software version B.03.01 build 317 was used for data collection.

The column sets used for multi-dimension GC in this apparatus included: primary column, Varian VF-5ms, 30 m, 0.25-mm i.d., 1 µm; secondary column, Varian CP-Lowox, 10 m, 0.53-mm i.d., 15 µm.

An Agilent 6890N GC (SN# US10547055) equipped with a Transcendent Enterprise pressurized liquid injection system (Edmonton, Alberta, Canada), two split/splitless injectors, two flame ionization detectors, and an Agilent G-2855B capillary flow plate (PN# G027855-60500), revision B system was also used. Controlling of the second pressure source was handled by using one channel of a three-channel Auxiliary Pressure Pack (Aux Pack). A three-way, 24 V DC, 5 W fluid automation system valve (FAS PN#6-311-003-23) was used for flow switching. A Chemstation software B.01.02 was used for data collection.

The column sets used for multi-dimension GC in this apparatus included: primary column, Agilent DB-5ms, 30 m, 0.25-mm i.d., 1 µm; secondary column, Varian CP-Lowox, 10 m, 0.53-mm i.d., 15 µm. And: primary column, Agilent DB-5ms, 30 m, 0.25-mm i.d., 1 µm; secondary column, Varian CP-Sil 52CB, 25 m, 0.25-mm i.d., 1.2 µm.

The VF-5ms and the DB-5ms are 5% phenyl arylene columns with separation characteristics equivalent to that of 5% phenyl methyl polysiloxane. The DB-5ms is a 5% phenyl arylene column with separation characteristics equivalent to that of 5% phenyl methyl polysiloxane. In terms of polarity, the DB-5ms is similar to that of the VF-5ms. The Varian CP-Sil 52B is a polar column with polyethylene glycol as stationary phase. The Varian CP-Lowox is an ultra-polar porous layer open tubular column with ionic adsorbent as the stationary phase.

Two Valco Mini Helium Purifiers (PN# HPM) were used. The purifiers were installed with one at each entrance of the capillary flow plate to remove chromatographic system artifacts and to attain ultra-trace detection of oxygenated compounds. The use of the Valco Mini Helium Purifiers will be discussed later in the report.

Chemical standard solutions and hydrocarbon products were obtained from the local hydrocarbon plant laboratory. Alcohol mixtures of methanol, ethanol, iso-propanol, *n*-propanol, and *n*-butanol were prepared in *n*-pentane at the concentration of 1000 ppm (w/w) each, and the lower concentration standards diluted from this stock solution.

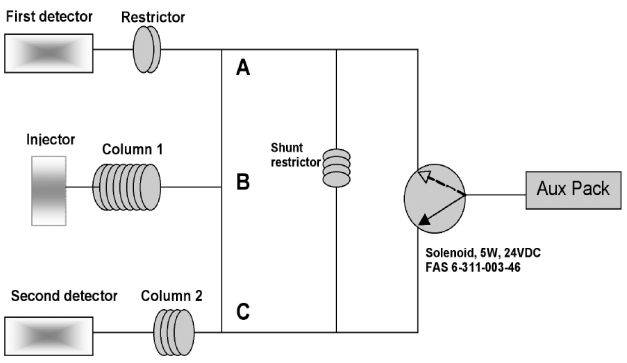

Figure 1. Principles of operation of capillary flow technology: Deans Switch.

GC conditions were as follows: Varian VF-5ms or Agilent DB-5ms with Varian CP-Lowox; carrier gas, helium, 20.7 psig, 41 cm/s, (2.0 mL/min) for the first dimension; carrier gas, helium, 4.9 psig, 69 cm/s (5 mL/min) for the second dimension; injector, 250°C, split ratio 5:1, injection volume, 2 µL; column temperature, 50°C held for 3.5 min increased at 25°C/min to 150°C and held for 2 min; detector, FID 250°C, H_2, 40 mL/min, Air, 450 mL/min, Make-up N_2, 45 mL/min; restrictor parameters, 0.25 mm i.d., 0.50 m fused silica column. Varian VF-5ms or Agilent DB-5ms with Varian CP-Sil 52CB: carrier gas, helium, 35.1 psig, 30 cm/s, (2.0 mL/min) for the first dimension; carrier gas, helium, 24.5 psig, 69 cm/s (3 mL/min) for the second dimension; injector, 250°C, split ratio 5:1, injection volume, 2 µL; column temperature, 50°C held for 3.5 min increased at 20°C/min to 150°C and held for 2 min; detector, FID 250°C, H_2, 40 mL/min, air, 450 mL/min, make-up N_2, 45 mL/min; restrictor parameters, 0.10 mm i.d., 0.64 m fused silica column.

Discussion

Multi-dimensional GC and capillary flow technology

Despite the availability of a multitude of column stationary phases for chromatographic separations, the analysis of target compounds in complex sample matrices has always been a challenge, especially for one-dimensional GC. Due to the limitation of peak capacity and column selectivity, it is difficult to separate all the components of interest by using a single column, especially when the analytes cover a wide range of boiling points or polarity. Multi-dimensional GC, or more specifically, two-dimensional GC which couples two columns with different separation mechanisms, is an alternative which improves the separation resolution, selectivity, and peak capacity (3,4,5). There are two analytical approaches in two-dimensional (2-D) GC: comprehensive 2-D and heart-cutting 2-D. In comprehensive 2-D analysis, the effluent from the first dimension is continuously refocused and transferred into the second dimension at certain intervals (transfer frequency) with a modulator (4,5,6,7). The peak capacity of the 2-D system can be improved as the product of peak capacities of each dimension, which means that the number of resolved peaks will be greatly increased. The chromatograms of comprehensive 2-D separation, however, can be more complicated to interpret. In general, higher analytical skill is required to realize the power of comprehensive 2-D.

Heart-cutting 2-D, either with valves or Deans switching, is a relatively simple but efficient method for target analysis (8,9). In heart-cutting methods, only effluents of interest, typically coeluting pairs from the first dimension are transferred into the second dimension. When compared to comprehensive 2-D, although offering substantially less in resolving power, heart-cutting 2-D with Deans switching affords simplified chromatograms, more robust performance through the elimination of the need for a mechanical modulator, and depending on the modulator design, the elimination of the need for cryogens (6,7), as well as the need for advanced software to perform de-convolu-

tion, especially for quantitative analysis. These aforementioned attributes make heart-cutting 2D with Deans switching a versatile chromatographic technique, suitable for implementation in both research and remote production facilities. One of the key challenges of implementing heart-cutting 2-D GC lies on the interface, which requires low-dead-volume, a high degree of inertness, and efficient sample transfer. Previous versions of Deans switches employ multi-port valves or connectors to realize flow transfer. It is not convenient to install such a device in a GC oven due to the larger thermal mass, the difference in thermal expansion coefficients between metal and column ferrules which can result in leaks, and more importantly, the large void volume which negatively impacts chromatographic fidelity. For this application to perform well, a precise flow control system is required. Until recently, the lack of reliable electronic pressure/flow control devices made practicing heart-cutting 2-D GC unpopular, and the technique is employed only when it is absolutely necessary.

The advent of highly accurate commercially available electronic pressure control systems, with precision of up to third decimal point, such as those offered by the Agilent 7890A GC, combined with innovations like capillary flow technology, have aided in eliminating many deficiencies encountered with heart-cutting 2-D GC and made practicing heart-cutting 2-D GC simple and reliable. Capillary flow technology plate, employed as a microfluidic Deans switch, is a new generation of improved flow switching devices: the device's flow paths and connections are laid out and etched onto a small, thin stainless steel plate of a mere 3 × 6.2 × 0.1 cm, using photolithography and chem-milling technologies. Then the manifold is diffusion bonded, with column connectors projection welded, and the surface deactivated. By manipulating the pressure and the valve on/off time, the critical pairs from the first dimension can be effectively and reliably transferred into the second dimension for further separation (10,11).

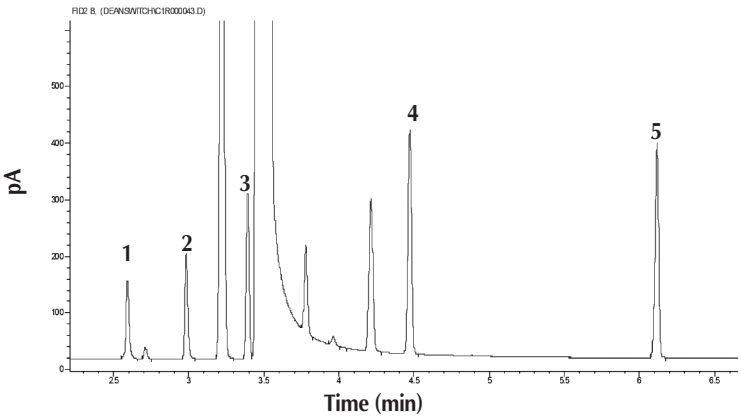

Figure 2. Five alcohols in Pentane, non switched, ca. 1000 ppm (w/w) in Pentane. Peak numbers are: methanol, 1; ethanol, 2; 2-propanol, 3; 1-propanol, 4; 1-butanol, 5.

Oxygenated compounds in complex hydrocarbon matrices

The analysis of oxygenated compounds in hydrocarbons is important in the petrochemical and chemical industries. To prevent hydration in pipeline operations under cold climate environment, methanol is purposely added to hydrocarbon products such as liquefied natural gas. The presence of low-level oxygenated compounds in hydrocarbon matrices, however, does have a negative impact on products produced or a detrimental effect on catalysts used for the production of downstream products (1,11).

One common approach used for the measurement of said compounds involves the use of conventional polar columns such as polyethylene glycol or Tris[2-carboxyethyl] phosphine (TCEP) class columns. But these columns do not have sufficient resolving power for the compounds of interest. Also, the maximum operating temperature of said columns is rather low, typically less than 250°C for polyethylene glycol or worse yet, 130°C for TCEP. This is an undesirable feature, especially when backflushing is not employed because a high temperature is required to remove contaminants or heavier matrices such as gasoline or diesel, once the elution of the compounds of interest is completed. There are other ionic sorbent columns that helped in addressing these limitations, such as the Varian CP-Lowox or Agilent GS-OxyPLOT (1,12). Unfortunately, these columns also exhibit significant retention for hydrocarbons with molecular weight greater than nC_{10} and for aromatics, even though the maximum operating temperature is much improved, up to 350°C. Thus, using a single column for the measurement of oxygenated compounds in the presence of high molecular weight hydrocarbons and/or aromatics, as in the case of gasoline or diesel, is not a viable analytical solution. From an analytical perspective, the lack of a low-cost, highly reliable selective detector for oxygenated compounds further exacerbates the issue.

Multi-dimensional GC with capillary flow technology was employed to resolve this analytical challenge by providing an analytical approach capable of measuring sub-part-per-million levels of oxygenated compounds in both light and heavy hydrocarbon matrices. In this application, the column set used

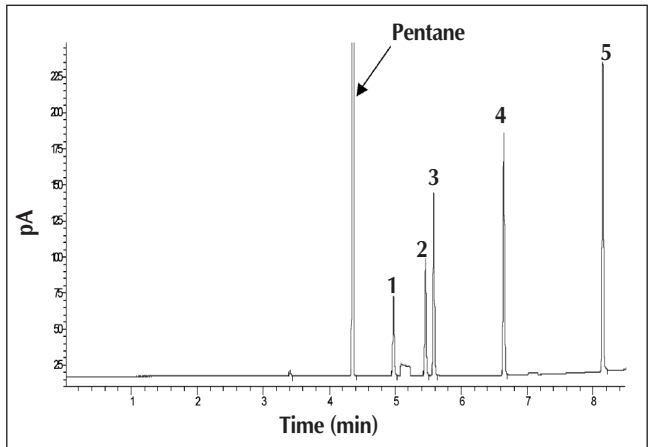

Figure 3. Five alcohols in Pentane, switched, ca. 1000 ppm (w/w) in Pentane. Peak numbers are: methanol, 1; ethanol, 2; 2-propanol, 3; 1-propanol, 4; 1-Butanol, 5.

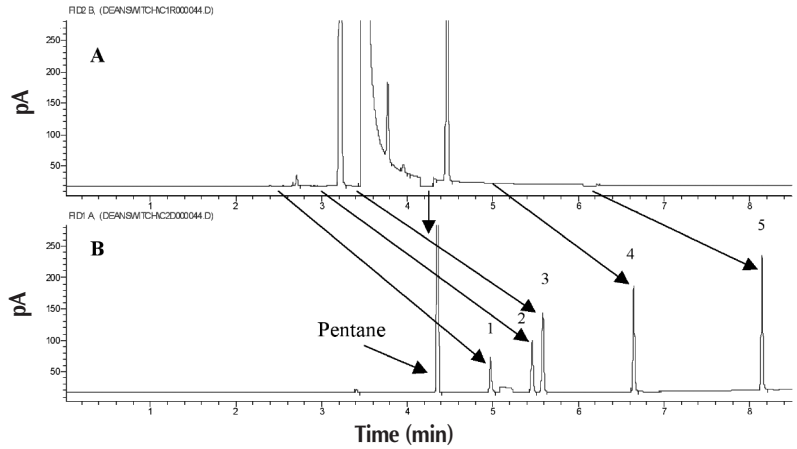

Figure 4. An overlay comparing retention times of some oxygenated compounds in a heart-cutting 2-D system employing a 30 m, 0.25-mm i.d., 1-µm VF-5ms in the first dimension and a 25 m, 0.25-mm i.d., 1.2-µm CP-Sil 52CB in the second dimension. Peak numbers are: methanol, 1; ethanol, 2; 2-propanol, 3; 1-propanol, 4; 1-butanol, 5. Chromatogram of first dimension, A; Chromatogram of second dimension, B.

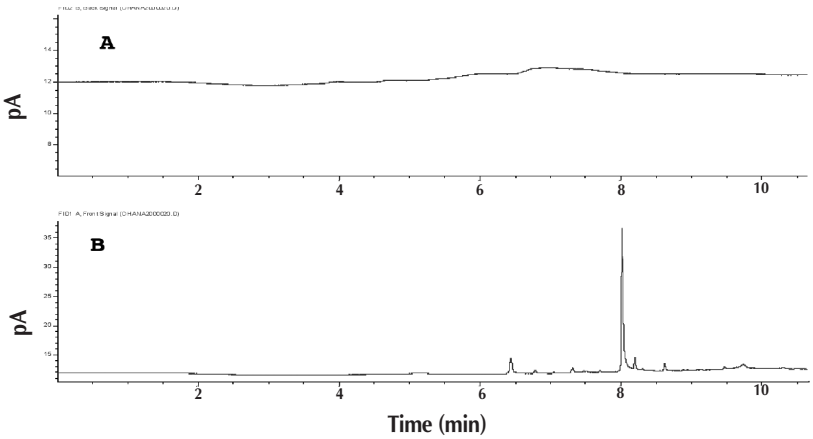

Figure 5. Chromatographic artifacts (ghost peaks) encountered when CP-Lowox was used in the second dimension. Note that one of these ghost peaks has the same retention time as methanol. Chromatogram of the first dimension (A) and chromatogram of the second dimension (B).

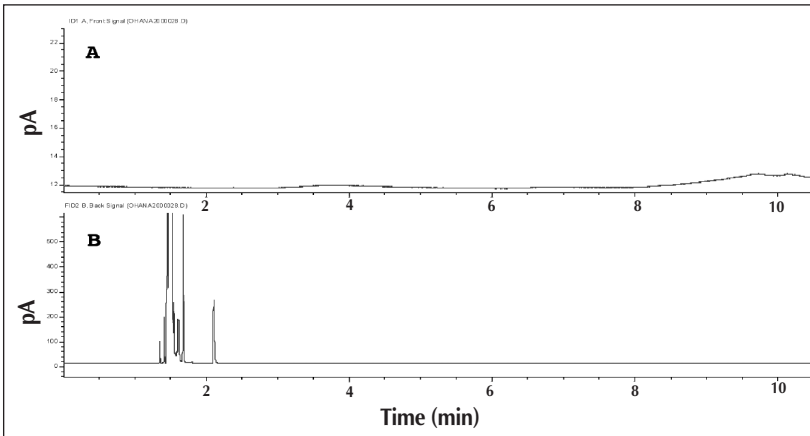

Figure 6. An injection of Hexanes with no switch, showing ghost peak free in the second dimension, after installation of Valco Helium Mini purifier. Chromatogram of the first dimension (A) and chromatogram of the second dimension (B).

involves a non-polar column in the first dimension and a polar column in the second dimension. The principles of the system operation are shown in Figure 1. A sample is injected onto the non-polar column where rough separation between alcohols and hydrocarbons takes place. The solenoid valve is not energized as denoted by the solid line, and the gas pressure from the secondary pressure source provided either by the pressure control module or the auxiliary pressure pack will force the gas to flow from point C to point A, resulting in the effluent from the non-polar column to flow towards the first detector via a deactivated, but uncoated capillary tube. The capillary tube provides similar flow resistance to that of the secondary column.

When the solenoid is actuated and switched to the other side of the assembly (dotted line state), gas pressure provided by the secondary pressure source induces a flow from point A to point C, which makes the effluent of the non-polar column flow towards the secondary column and subsequently to the second detector. The secondary column is purposely chosen because it has dissimilar selectivity to the non-polar column used in the first dimension for reasons stated earlier. As such, components which are not well resolved with the first column, such as light oxygenated and light hydrocarbons, are now separated with the column used in the second dimension, and the heavier hydrocarbons/aromatics which can cause chromatographic interferences for the measurements of alcohols are retained on the first dimensional, non-polar column. The time duration for the valve switching can be chosen with reference to the retention time of target components or critical pairs in the first dimension. By cycling the valve position, any component of interest can be transferred, or "cut", from the first column onto the second column.

Analytical performance

The original column set selected for this application involved the use of a 30 m, 0.25-mm i.d., 1 µm VF-5ms column in the first dimension, and a 25 m, 0.25-mm i.d., 1.2 µm CP-Sil 52CB (PEG column) in the second dimension. Although this column set worked adequately for the separation of oxygenated compounds such as alcohols in light hydrocarbons of up to C_5 as shown in Figures 2, 3, and 4, chromatographic interferences were encountered for the measurement of said compounds in heavier hydrocarbon matrices ranging up to C_{24}, if all the targeted compounds were to be measured in one analysis. Clearly, a more selective and polar column is needed in the second dimension to increase overall separation

between the oxygenated compounds of interest and the matrices encountered. As a result, the CP-Sil 52CB was replaced with a 10 m, 0.53-mm i.d., 15-µm CP-Lowox column.

The deployment of the CP-Lowox revealed another analytical challenge. Upon start-up of this application on both chromatographic systems, close examination of the chromatograms obtained showed that chromatographic artifacts exist within the analytical systems used. One of these artifacts, identified by mass spectrometry to be para-dichlorobenzene (CAS# 106-46-7), coelutes perfectly with methanol (an important analyte on the CP-Lowox column as shown in Figure 5) regardless of temperature and flow conditions used. It was found that the artifacts were introduced into the chromatographic system via the solenoid valve used for flow switching. While an artifact-free solenoid supplier is being sought, a simple analytical solution was found by installing a Valco Helium Mini Purifier at each inlet of the switch plate for the removal of chromatographic impurities coming from upstream of the plate. Figure 6 shows a chromatogram of the baseline with the purifiers installed. Note the excellent baseline obtained from 50°C to 275°C and the absence of chromatographic artifacts. A clean, artifact-free baseline is essential to achieve sub-ppm level detection limit. This also helps minimize the possibility of misidentifying compounds, especially at the trace level, with a flame ionization detector. Care also must be taken in handling the porous layer open tubular column such as the CP-Lowox. Particles released from the column, if not carefully handled, can clog the capillary plate, resulting in partial pluggage or flow imbalance.

Figure 7 shows a chromatogram of 200 ppm (w/w) of methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol in pentane with the non-polar column (first dimension). Note the partial separation of 2-propanol and pentane. Figure 8 shows a chromatogram of the entire sample transferred over to the CP-Lowox column. 1-Propanol and 2-Propanol partially coelute on the CP-Lowox; however, by choosing the appropriate "cut" time, these solutes can be individually quantitated. In terms of reproducibility of retention time, an RSD of less than 0.02% was established at three levels: 25 ppm (w/w), 125 ppm (w/w), and 600 ppm (w/w) for methanol, ethanol, 1-Propanol, 2-Propanol, and 1-Butanol, highlighting the high degree of reproducibility of the technique involved, as shown in Table I. As can be seen from the data collected, capillary flow technology, with modern electronic pressure control, offers a high degree of repeatability when compared to conventional valve switching techniques. Table I also tabulates the area counts obtained for the solutes cited. An RSD of less than 2.7% for all solutes was achieved.

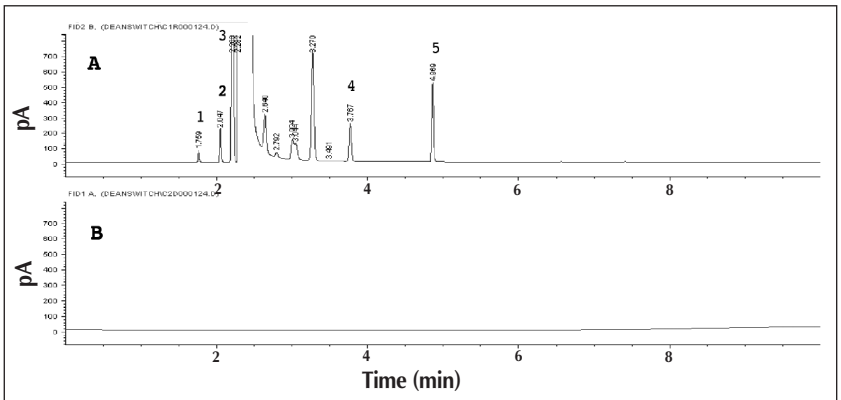

Figure 7. An injection of alcohols in pentane on first dimension (VF-5ms). Peak numbers are: methanol, 1; ethanol, 2; 2-propanol, 3; 1-propanol, 4; 1-butanol, 5. Chromatogram of the first dimension (A) and chromatogram of the second dimension (B).

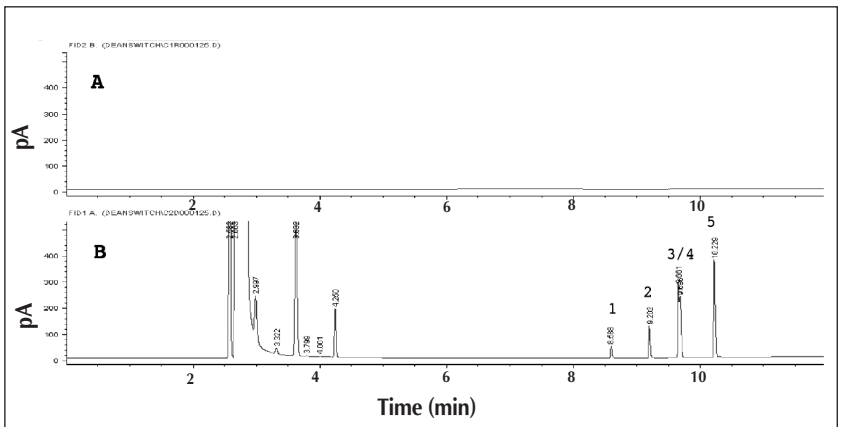

Figure 8. An injection of alcohols in pentane switched on to second dimension (CP-Lowox). Peak numbers are: methanol, 1; ethanol, 2; 2-Propanol, 3; 1-Propanol, 4; 1-Butanol, 5. Chromatogram of the first dimension (A) and chromatogram of the second dimension (B).

Using the technique described, detection limit of 0.2 ppm (w/w) or better was achieved for compounds tested, with a linear correlation coefficient of greater than 0.9993 for all solutes over a range from 0.5 ppm to 600 ppm (w/w). Figure 9 plots a linear curve of some oxygenated compounds over the range described.

With the heart-cutting technique, because chromatographic fidelity of the first dimension is not that critical (i.e., the first dimension is employed mainly as a coarse separation), deliberate overloading of the first dimension can be conducted when a lower detection limit is required. Also, by choosing the appropriate "cut" time, the same technique can be employed for the measurements of other classes of compounds such as ethers, aldehydes, and ketones.

An added benefit of implementing capillary flow technology for heart-cutting 2-D chromatography is that the system configuration facilitates column back-flushing. When analyzing samples with a broad boiling point range, more often than not, only parts of the sample are of interest. Longer analytical times and high temperature programs are only necessary to ensure that all the components elute from the column, to prevent contamination of the analytical system or carry-over for the next analysis. It is not only time-consuming but inevitably results in unwanted column bleeding. In back-flushing, after the last component of interest elutes, the carrier gas flow in the analytical column is reversed and later-eluting components will be flushed back towards the column inlet and vented via the split vent line. This approach

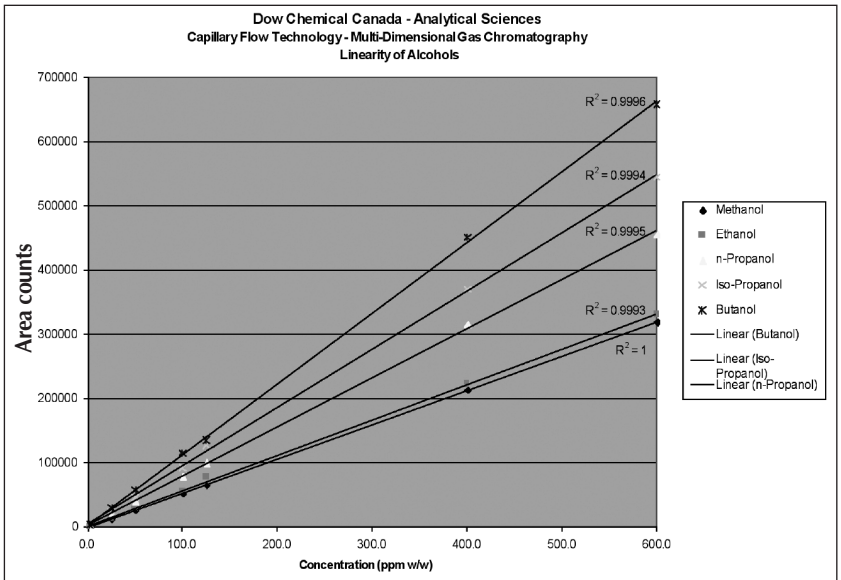

Figure 9. Linearity curves of some oxygenated compounds.

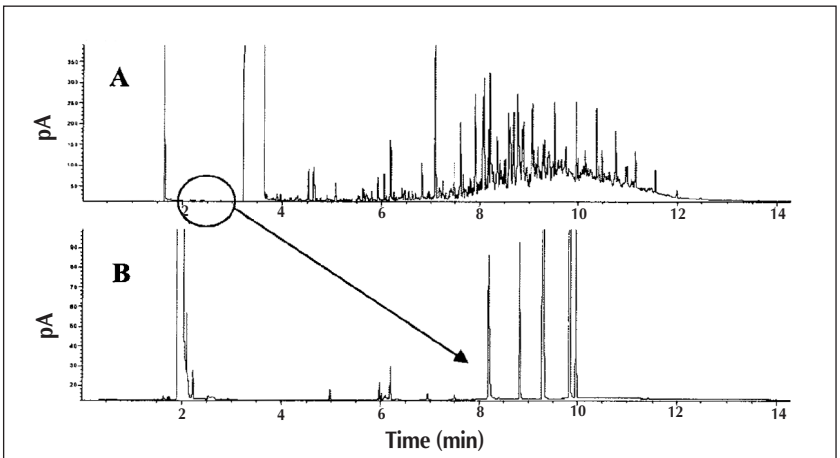

Figure 10. Alcohols in crude diesel fuel "cut" to second dimension. Chromatogram of the first dimension (A) and chromatogram of the second dimension (B).

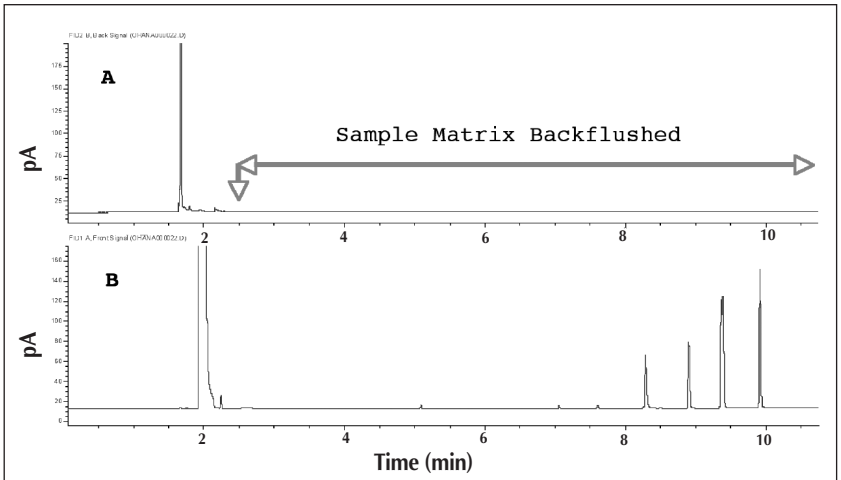

Figure 11. Alcohols in crude diesel fuel "cut" to second dimension with first dimension back-flushed after 2.5 min: Note the exceptionally clean baseline obtained after back-flush was initiated. Chromatogram of the first dimension (A) and chromatogram of the second dimension (B).

shortens the analytical time, plus column exposure time to high temperatures can be greatly reduced (12,13). This concept was demonstrated by the determination of alcohols in hydrocarbons.

Figure 10 shows an overlay of chromatograms of a crude diesel fuel sample containing hydrocarbons ranging from nC_5 to nC_{24}, aromatics, and light alcohols of up to *n*-butanol, where the oxygenated compounds have been transferred over to the CP-Lowox column, while the heavier hydrocarbons were retained on the first dimension column and removed from the system by temperature programming. The broad distribution of heavy hydrocarbons would interfere with the measurements of oxygenated compounds should this sample be injected directly on the CP-Lowox column. Figure 11 shows an overlay of chromatograms, where, after the transfer of the oxygenated compounds, the heavier hydrocarbons were back-flushed by increasing the auxiliary pressure to 6.4 psig while inlet pressure decreased to 1 psig. Note the excellent baseline obtained. The back-flushing technique aids in improving overall sample throughput and system cleanliness. The utilization of the PLIS valve as a sample delivery means enables the injection of both highly volatile liquid hydrocarbons such as liquid ethylene or less volatile matrices such as gasoline or diesel fuels (14).

There are some potential constraints encountered with the capillary flow technology device for heart-cutting 2-D chromatography. Firstly, the installation of the device needs some practice and care. Connecting the columns and restrictor to the manifold plate, and the handling of Siltite ferrules also require skillful practice. Because the volume of flow path inside the plates is very minute, foreign particles from tubings, fused silica, and ferrules can cause blockage. The employment of porous layer open tubular column, which has a tendency of shedding, particularly in the first dimension must be carefully considered. Secondly, the best chromatographic performance occurs when critical pairs in the first dimension elute early in the temperature programming process. This helps in maximizing the separation power of the second dimension. If the critical pairs elute very late in the first dimension, the separation power of the second dimension is reduced or compromised. Therefore, the selection of column set for a typical application should be carefully considered for these reasons. Another solution to resolve this issue involves the use of a separate oven module for each dimension, such as the RVM Scientific low thermal mass module. Finally, while this is not a limitation, in selecting a column set for use with

Table I. Percent Relative Standard Deviation of Retention Times and Area Counts for Oxygenated Compounds Tested

n = 7 Concentration (ppm w/w)	Percent relative standard deviation of retention time				
	Methanol	Ethanol	*n*-Propanol	2-Propanol	*n*-Butanol
600	0.01	0.01	0.01	0.01	0.01
125	0.02	0.01	0.01	0.02	0.02
25	0.02	0.01	0.01	0.02	0.02
n = 7 Concentration (ppm w/w)	Percent relative standard deviation of area counts				
	Methanol	Ethanol	*n*-Propanol	2-Propanol	*n*-Butanol
600	2.0	1.9	1.6	1.7	1.3
125	2.3	2.4	1.5	1.7	2.3
25	2.3	1.4	2.7	2.2	2.3

heart-cutting 2D-GC, one must also be cognizant of the fact that the selectivity exhibited by the column in the second dimension is influenced or modified by the selectivity of the column in the first dimension. For example, methanol has a retention index of 1430 on the CP-Lowox column alone, yet when methanol is cut from the first dimensional column of a polydimethyl siloxane to the second dimensional column of the same CP-Lowox column, the retention index of methanol decreases substantially to only 980.

Conclusions

By employing multi-dimension GC with capillary flow technology in combination with highly selective capillary columns, excellent chromatographic performance was obtained for the analysis of trace levels of oxygenated compounds in complex hydrocarbon or aromatic matrices. Using the technique described, light alcohols in the presence of light or heavy hydrocarbons and aromatics can be measured accurately to a sub part-per-million level with a substantially reduced possibility of a false positive. Another benefit for the implementation of capillary flow technology is the capability to conduct column back-flushing, where heavier, undesired solutes in a sample can be back-flushed from the chromatographic system to improve system cleanliness and sample throughput. The technique was found to be practical, easy to operate once installed, and with a high degree of reliability.

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