Two-Dimensional Gas Chromatography Analysis of Components in Fuel and Fuel Additives Using a Simplified Heart-Cutting GC System

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Abstract

Multidimensional gas chromatography (MGC) using heart cutting is an old idea that can benefit from the performance of modern instruments and capillary columns to provide fast, reliable separation of target analytes from complex sample matrices. A simplified heart-cutting switch is described that uses these improvements to provide very narrow precise heart cuts between columns of different selectivity. This system is used to analyze ppm levels of 4,6-dimethydibenzothiophene in diesel fuel using a standard flame ionization detector instead of a complex sulfur-selective detector. MGC systems also offer the possibility of faster analysis speed by using two short columns of different selectivity instead of very long columns to resolve compounds from complex matrices. The analysis of alcohols in denatured fuel ethanol using the MGC system is performed over six times faster than the standard American Society for Testing and Materials methodology.

Introduction

The analysis of selected components in complex samples has always presented a challenge to the analytical chemist. Although capillary gas chromatography (GC) is a powerful separation technique, samples such as petroleum products, flavor oils, and environmental extracts are so complex that a single GC column cannot often separate compounds of interest from the matrix elements. Approaches to this problem have involved a number of techniques to improve the selectivity of the analytical method such as sample cleanup (solid-phase exctraction, solid-phase microextraction), element selective detectors [sulfur chemiluminescence (SCD), atomic emission detector (AED), inductively coupled plasma (ICP)-mass spectrometer (MS)], and spectral detectors (MS, IR). Multidimensional GC (MGC) adds another tool to the separation scheme that can greatly increase the resolution of one or more specific analytes from other compounds in the sample matrix. A recent review discusses the history, theory, and recent developments in MGC (1,2).

The simplest form of MGC employs two columns of different selectivity coupled together with a device that allows one or more discrete effluent segments from the first column to be transferred to the second column (Figure 1). The sample is injected onto the first column, and a preliminary separation takes place. When a specific analyte of interest exits from this first column, the eluting peak and any interfering peaks are directed via a valve or fluidic switch onto a second column. The second column contains a stationary phase of different selectivity, and the peak of interest is separated from the interfering compounds that coeluted with it on column 1. This approach was first demonstrated by Deans over 30 years ago (1). Although the Deans switch approach was useful, it did not gain widespread use because of problems associated with unreliable column connections, column flow drift, oven temperature imprecision, and column variability. These problems combined to give poor overall retention time precision, thus forcing the analyst to use very wide cut times to ensure transfer of the target analyte from column 1 to column 2. These wider cut times resulted in the transfer of more interference peaks and a loss in overall resolution. Attempts to solve these problems employed multiple GC ovens and cryogenic cooling, adding to the complexity and unreliability of MGC systems, hence the reliance

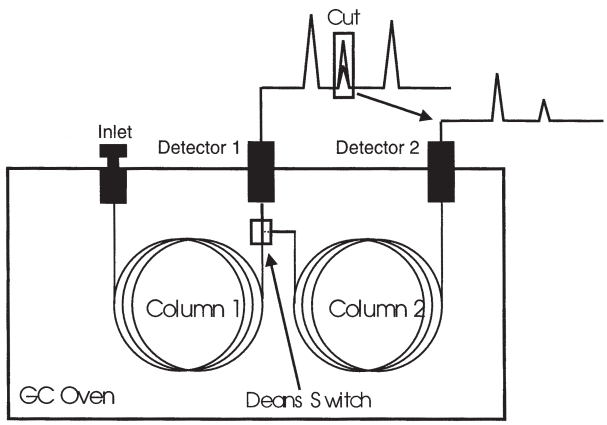

Figure 1. Block diagram showing 2-dimensional GC using two columns of different selectivity coupled with a Deans switch.

on the use of selective detectors with a single GC column to ultimately achieve "apparent" chromatographic separation.

Improvements in GC hardware over the past several years now allow the construction of MGC systems that are much simpler and easier to use. Column connections are now available that have low dead volume and are inert and reliable. Setting up the precise flows and pressures required to operate the system is greatly simplified with flow calculation software and electronic pneumatic control (EPC). Modern GC ovens have extremely precise temperature control, and bonded-phase fused-silica columns are robust and reliable. All of these developments in modern GC provide retention times that are highly reproducible from run to run. Because peaks eluting from column 1 can now have very repeatable retention times, much narrower cut windows can be used. These narrower cut windows result in better peak shapes and less interference observed on column 2. The degree of improvement in performance is such that multiple ovens and cryogenic focusing devices can be avoided.

Figure 2 shows a block diagram of the simplified heart-cutting switch hardware when there is no heart cutting being performed. The length and diameter of the restrictor connected to flame ionization detector (FID) 1 is chosen to have the same flow versus pressure characteristics as column 2. With the fluidic switch in the "off" position, the pneumatics control module (PCM) delivers gas flow through the lower flow path. This supplies carrier gas to column 2 and switching flow to the outlet of column 1. This switching flow will divert any peaks eluting from column 1 to the restrictor and FID 1. Figure 3 shows the flow path when performing a heart cut with the fluidic switch. Just before the peaks of interest elute from the column 1, the fluidic switch is set to the "on" position. Gas from the PCM is now directed through the upper flow path so that the switching flow will now divert peaks eluting from column 1 to column 2. After the peaks are loaded onto column 2, the fluidic switch is reset to the off position, and the flow paths return to those shown in Figure 2.

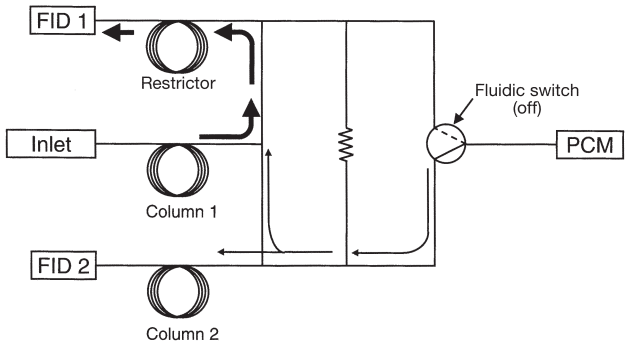

Figure 2. With the fluidic switch in the "off" position, no heart cutting is done with the Deans switch.

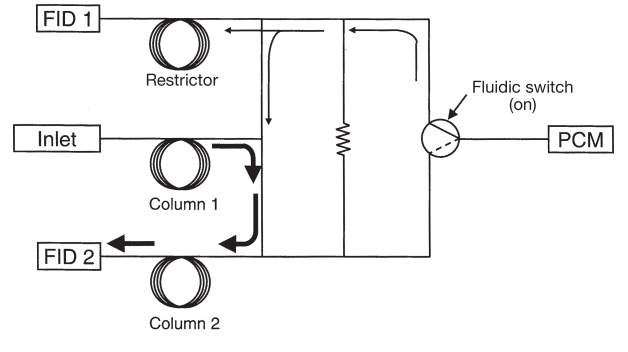

Figure 3. With the fluidic switch in the "on" position, a heart cut is made from column 1 to column 2, where the compound of interest is completely separated from any matrix interference.

The analysis of contaminants and additives in fuels can be easily and quickly performed with an MGC system using a simplified heart-cutting switch. This system has already been used for the analysis of oxygenated additives and aromatic hydrocarbons in reformulated gasoline (3). This work reports the capabilities of this MGC system to analyze trace levels (ppm) of 4,6-dimethyldibenzothiophene (4,6-DMDBT) in diesel fuel with FID. Many sulfur compounds such as 4,6-DMDBT are naturally present in diesel fuel and must be reduced to ppm levels to meet new emission regulations. Because 4,6-DMDBT is one of the most difficult sulfur compounds to remove, refiners can monitor the effectiveness of desulfurization by measuring its concentration. GC analysis of 4,6-DMDBT required the use of nonquenching sulfur-selective detectors such as SCD or AED because there is no single column that can separate it from the hydrocarbon matrix. However, MGC can be used to completely separate 4,6-DMDBT and uses simpler, more robust FIDs.

Also reported is the use of this MGC system to provide faster analysis for target compounds in complex samples. Many GC methods use very long, narrow capillary columns (60–150 m) in a "brute force" attempt to achieve adequate resolution. Although this approach is often successful, the analysis times can be very long and require subambient oven temperatures. One example of this is American Society for Testing and Materials (ASTM) D5501, "Standard Test Method for Determination of Ethanol Content of Denatured Fuel Ethanol by Gas Chromatography" (4). Distillation of fermented biomass is used to produce a fuel ethanol that contains 85–98% ethanol and natural impurities such as water and methanol. Before it can be used as a gasoline additive, the fuel ethanol is denatured with approximately 2–5 vol% of natural gasoline to make it unsuitable for beverage use. GC is used to determine the purity of denatured fuel ethanol and the methanol content. However, the natural gasoline complicates this measurement because it is difficult to separate the alcohols from the C_4 and C_5 hydrocarbons. D5501 uses a 150-m methyl silicone capillary column and subambient oven temperatures for this analysis, with run times in excess of 40 min. However, by carefully selecting two short columns of different selectivity, MGC systems can separate the polar alcohol peaks from the nonpolar hydrocarbons in much less time.

Experimental

Instrument

An Agilent 6890N GC (Agilent Technologies, Wilmington, DE) was equipped with a split/splitless inlet, a PCM, two FIDs, an Agilent 7683 automated liquid sampler, and a Deans switch kit. This kit consists of microvolume Hastelloy C tees with special

fused-silica column adapters (VICI, Houston, TX), inert Silcosteel tubing (Restek, Bellfonte, PA), and other hardware and software (Agilent Technologies). Helium was used as the carrier gas, and nitrogen was used as the FID makeup gas. All gas flows and pressures were controlled by EPC.

Materials

For the 4,6-DMDBT in diesel fuel, a 15-m × 0.25-mm, 0.25-µm film HP-5MS (Agilent Technologies) was used for column 1, and a 30-m × 0.25-mm i.d., 0.25-µm film Innowax (Agilent Technologies) was used for column 2. For the ethanol analysis, a 15-m × 0.25-mm, 0.25-µm film HP-1 was used for column 1, and a 30-m × 0.25-mm i.d., 0.25-µm film Innowax was used for column 2. Both applications used a fixed restrictor made from uncoated deactivated fused-silica tubing, 0.77-m long × 0.1-mm i.d. All pure chemicals were ACS-reagent grade (Aldrich, St. Louis, MO), and all instrument gases were chromatographic grade according to manufacturer's specifications. Diesel fuel and gasoline samples were obtained from refiners and commercial fuel stations.

GC conditions for 2,6-DMDBT in diesel fuel

The split/splitless inlet pressure was 35 psig, giving a column 1 flow of 1.3 mL/min. The split ratio was set to 25:1. The PCM pressure was set to 28.6 psig to give a flow of 1.9 mL/min to column 2. The initial GC oven temperature was set to 180ºC for 0 min, programmed to 260ºC at 5ºC/min, and held for 4 min. The inlet temperature was 280ºC, and both FID temperatures were 280ºC. A 10-µL syringe was used to introduce a 2-µL sample to the system. Heart cut times were determined by preparing a 700-ng/µL standard of 4,6-DMDBT in iso-octane. This standard was run with the fluidic switch in the off position for the entire run. After the cut time was determined, the standard was run again using this cut time so that the 4,6-DMDBT retention time on column 2 could be measured.

GC conditions fast denatured fuel ethanol

The split/splitless inlet pressure was 44.99 psig, giving a column 1 flow of 2 mL/min. The split ratio was set to 200:1. The PCM pressure was set to 41.18 psig to give a flow of 5 mL/min to column 2. The initial GC oven temperature was set to 70ºC for 3 min, programmed to 200ºC at 30ºC/min, and held for 0 min. The inlet temperature was 225ºC, and both FID temperatures were 250ºC. A 10-µL syringe was used to introduce a 0.2-µL sample to the system. A standard containing 0.6 vol% methanol and 7 vol% natural gasoline in absolute ethanol was prepared. This standard was run on the system with the fluidic valve in the off position to determine the heart cut time. This standard was run again using this cut time to measure the retention times of all compounds on column 2.

Results and Discussion

4,6-DMDBT in diesel fuel

Without heart cutting, the 700 ng/µL of 4,6-DMDBT in iso-octane was found to have a retention time of 6.34 min on column 1 (HP-5MS). Using the peak start and end times from column 1, a cut time of 6.29–6.57 min was used to transfer the 4,6-DMDBT peak from column 1 to column 2 (Innowax). The retention time of the 4,6-DMDBT on column 2 was 14.19 min. This is shown in Figure 4. However, when a diesel fuel sample was run, the elution of the 4,6-DMDBT from column 1 was shifted to slightly longer retention times. The actual retention time was determined by spiking several hundred ppm of 4,6-DMDBT in diesel fuel then adjusting the cut window start and stop times so that a maximum amount of 4,6-DMDBT was transferred to column 2. Using this technique, a cut time of 6.40–6.65 min was set for all diesel fuel samples.

On the nonpolar column 1 (HP-5MS), the diesel components eluted in boiling-point order, and the 4,6-DMDBT peak coeluted with a large number of hydrocarbon peaks. After heart cutting to the polar Innowax column, the 4,6-DMDBT was easily separated from the less polar hydrocarbons (Figure 5). The 4,6-DMDBT in this sample was measured to be 165 ng/µL with the 2-D system versus 162 ng/µL measured using a GC–AED system. The MDL for this analysis by MGC was estimated to be 2 ng/µL.

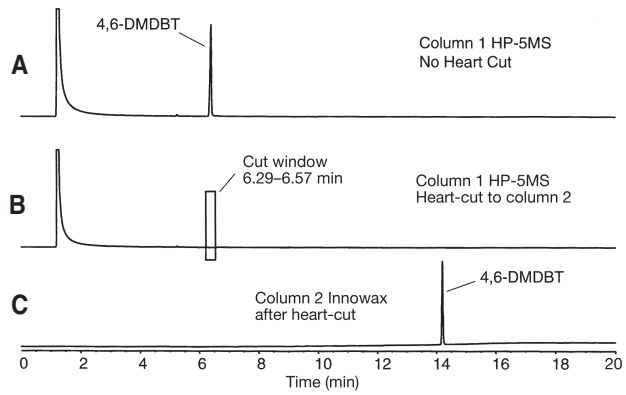

Figure 4. (A) 700 ng/µL 4,6-DMDBT in iso-octane with no heart cut. (B) With a cut time of 6.29–6.57 min, the 4,6-DMDBT is transferred to column 2. (C) After heart cutting, the 4,6-DMDBT is chromatographed on column 2.

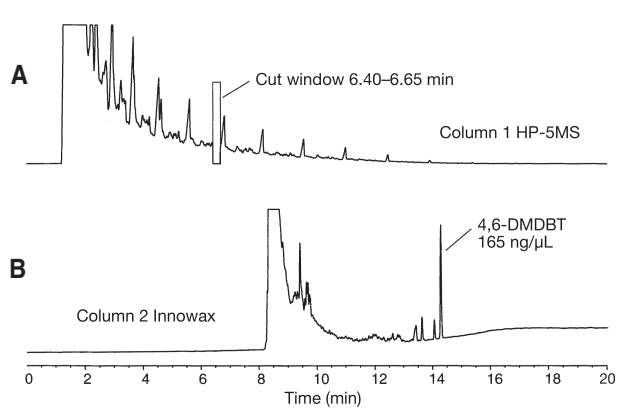

Figure 5. (A) Because 4,6-DMDBT in diesel fuel has a slightly longer retention time on column 1, the cut time was changed to 6.40–6.65 min. (B) The 4,6-DMDBT peak is completely separated on column 2 from any interfering hydrocarbons. After calibration, 165 ng/µL of 4,6-DMDBT was measured in this diesel sample.

Fast analysis of fuel ethanol

On the short nonpolar column 1 (HP-1), the methanol and ethanol coeluted with C_4 and C_5 hydrocarbons from the gasoline denaturant. The two alcohol peaks eluted from this column between 0.91 and 1.1 min. Using these times for the heart cut, the peaks were transferred to the polar Innowax column, where the nonpolar hydrocarbons were quickly eluted and the polar alcohols were easily separated (Figure 6). Any remaining hydrocarbons on column 1 were eluted, and the overall run time for this analysis was less than 7 min.

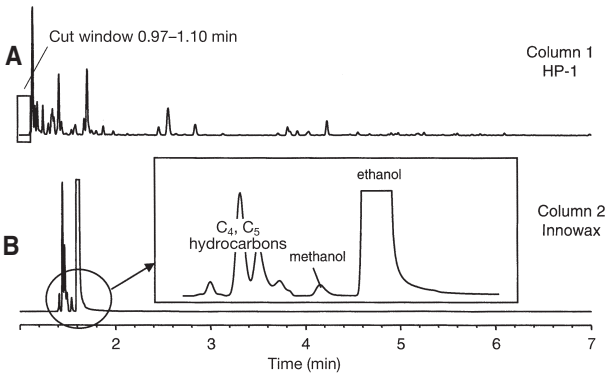

Figure 6. (A) A denatured fuel ethanol sample is run on a short nonpolar column, and the alcohol peaks are cut to a polar column. (B) Methanol and ethanol are separated from the interfering hydrocarbons by the polar column. The total run time is less than 7 min.

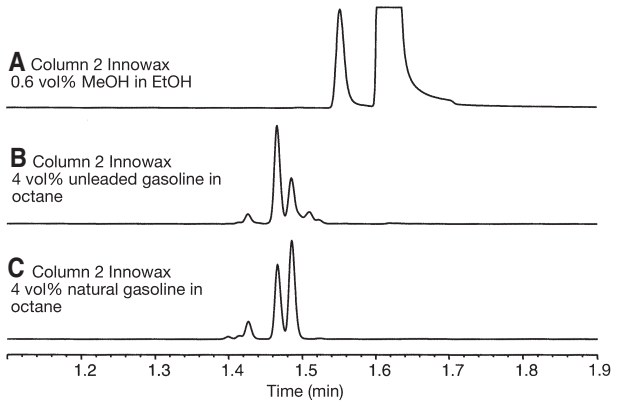

Figure 7. (A) After heart cutting to column 2, methanol elutes at 1.552 min and ethanol at 1.622 min. (B and C) Unleaded gasoline and natural gasoline hydrocarbons cut to column 2 show no interference with the alcohol peaks.

Table I. Qualitative and Quantitative Precision for Fuel Analysis by MGC

	Methanol		
	t_R (min)	Area counts (pA)	Vol%
Average	1.552	47.92	0.3
SD	0.0004	0.35	0.002
%RSD	0.025	0.74	0.7
	Ethanol		
	t_R (min)	Area counts (pA)	Vol%
Average	1.622	20410.55	95.4
SD	0.0004	118.93	0.6
%RSD	0.023	0.58	0.6

* Abbreviations: t_R = retention time, SD = standard deviation, and RSD = relative standard deviation.

To assure that there was no hydrocarbon interference with the alcohols on column 2, two samples of 4 vol% gasoline in octane were prepared and run on the MGC system using the same operating conditions used for the fuel ethanol. No interfering hydrocarbon peaks were observed on column 2 that elute during the methanol and ethanol retention times (Figure 7). After calibration, the qualitative and quantitative precision of this method was measured by running a fuel ethanol sample 30 times over a 5-day period. Table I shows the retention time, detector response, and quantitative precision for this system.

Conclusion

An easy-to-use and reliable MGC system with a simplified heart-cutting switch was used to analyze a trace sulfur compound in diesel fuel and the alcohol content in denatured fuel ethanol. The system was used to measure ppm levels of 4,6-DMDBT in diesel using two columns of different selectivity coupled together with the Deans switch. Because the 4,6-DMDBT was completely separated from the large hydrocarbons, complex sulfur-selective detectors were not needed, and the peak was easily detected with an FID.

MGC methods can also improve analysis speed by using two short columns of different selectivity instead of relying on very long single column methods. This was demonstrated by the analysis of alcohols in denatured fuel ethanol. The standard ASTM methodology using a very long column takes 40–60 min to complete this analysis. The MGC method completed this analysis in less than 7 min. The system was also shown to provide high qualitative and quantitative precision for these measurements. MGC using a simplified heart-cutting switch can also be combined with other techniques, such as selective detectors and modern sample cleanup, to provide a powerful tool for the most difficult separations.

References

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