Using a New Gas Phase Micro-Fluidic Deans Switch for the 2-D GC Analysis of Trace Methanol in Crude Oil by ASTM Method D7059

Application

Petrochemical

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Abstract

A new ASTM method was developed for the analysis of trace methanol in crude oil samples. This method relies on the use of two-dimensional heart-cutting gas chromatography to separate methanol from the complex matrix. A new microfluidic Deans switch was developed for the Agilent 6890N GC system that improves the performance of heart-cutting two-dimensional gas chromatography. This system was used to perform the analysis of methanol in crude oil with results that exceed the performance requirements of the ASTM method.

Introduction

The chemical characterization of crude oils present a real challenge to analytical chemists due to the varied and complex nature of the sample matrix. This is especially true when trying to separate and quantify trace amounts of low boiling contaminants or additives that cannot be separated using conventional capillary gas chromatography (GC). For such analyses, two-dimensional (2-D) GC offers a relatively simple yet powerful solution. Recently, ASTM Committee D2 has developed a heart-cutting 2-D GC method for the analysis of methanol in crude between 15 ppm (m/m) and 900 ppm (m/m) [1]. Methanol is added to crude oil to prevent the formation of gas hydrates, but it must be removed since the oxygen can cause problems with further refining processes.

Heart-cutting 2-D GC using a Deans switch has recently experienced a revival due to the advanced technology of modern columns and instruments [2]. The latest GC instruments make heart-cutting GC much easier to set-up, more reliable, and precise. However, the actual hardware used to perform heart-cutting has not kept pace with the advances offered by today's instruments. A typical 2-D manifold still consists of a collection of individual plumbing pieces such as tees, stainless tubing, and graphite/vespel ferrules that are assembled by hand. While this plumbing works well for some applications, especially those with packed columns, it is not optimized for modern capillary chromatography.

The large thermal mass of the device can be difficult to heat uniformly, introducing cold spots in the plumbing resulting in reduced chromatographic performance for higher boiling compounds. While the fittings are machined to reduce dead volume and minimize flow paths, there are still significant plumbing problems that contribute to peak broadening within the device. Capillary columns are also difficult to connect to these fittings and must rely on a graphite/vespel ferrule and sleeve combination to make a tight seal. This connection is difficult to make and can leak with repeated oven temperature cycling from <80 °C to >250 °C. Additionally, the graphite/vespel ferrules

can adsorb solvents and analytical components, resulting in reduced sensitivity, increased peak tailing, and elevated baselines.

To overcome these difficulties, a new micro-fluidic Deans switch was designed that combines the individual switch components into a smaller, single device (Figure 1).

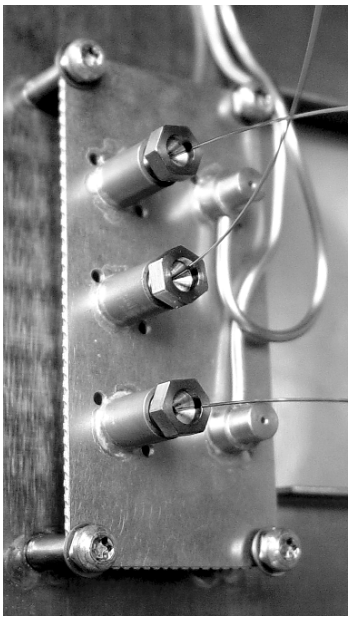

Figure 1. A close-up view of the new micro-fluidic Deans switch in the 6890N GC.

The switch's flow paths and connections are laid out and etched onto a small, thin, stainless steel plate using photolithography and chem-milling technologies. The plate is diffusion bonded, mounted with column connectors, and surface deactivated, resulting in an integrated, micro-fluidic switch that has a number of advantages for heart-cutting 2-D GC. The 4-times smaller thermal mass does not act as a heat sink; therefore, the device works optimally with modern GC ovens, especially for faster applications. The micro-fluidic switch also has far fewer connections, greatly reducing leak potential. Metal ferrules are used to interface capillary columns to the device that are also leak-free in high-temperature cycling applications. These metal ferrules will also not adsorb solvents or sample matrix, improving sensitivity for trace analysis applications. This application note describes the use of the micro-fluidic Deans switch in the analysis of trace methanol in crude oil with ASTM method D7059.

Experimental

An Agilent 6890N gas chromatograph was equipped with a split/splitless injector, a pneumatics control module (PCM), two flame ionization detectors (FIDs), and an automatic liquid sampler (ALS). A DB-1 (polydimethylsiloxane) column was used as the primary column and a CP-Lowox (Chrompack International BV) was used as the secondary column. The two columns were linked using a micro-fluidic Deans switch. Table 1 lists the details of the hardware configuration. The instrument operating conditions for this analysis are outlined in Table 2.

Table 1. Hardware Configuration

6890N GC Hardware	
G1540N	Agilent 6890N Series GC
Option 112	Capillary split/splitless inlet with EPC control
Option 210 (2 of each)	FID with EPC control
Option 309	Pneumatics control module with EPC control
G2855B	Micro-fluidic Deans switch kit
G2613A	Agilent 7683 Autoinjector
Columns	
Primary column	DB-1 column, 5.00-µm film, 10 m x 0.53-mm id (Agilent part no. 125-10H5)
Secondary column	CP-Lowox column, 10 m x 0.53-mm id (Chrompack International BV)
Fixed restrictor	Deactivated fused silica tubing, 0.5 m x 0.25-mm id (Agilent part no. 160-2255-10)
Data System	
G2070A	Agilent Multitechnique ChemStation
Other Consumables	
Agilent part no. 5181-1267	10-µL fixed tapered needle autoinjector syringe
Agilent part no. 5183-4647	Inlet liner optimized for splitless operation
Agilent part no. 5183-4759	Advanced green septa

Table 2. Instrument Conditions

Injection port	Split mode, 7:1 ratio
Temperature	325 °C
EPC pressure	3.51 psi helium, constant pressure mode
Injection size	1 µL
DB-1 column flow	3 mL/min
Pneumatics control module (PCM)	5.07 psi helium, constant pressure mode
CP-Lowox column flow	5 mL/min
FID temperatures	350 °C
Oven temperature program	
Initial temp	150 °C for 3 min
Ramp #1	20 °C to 300 °C for 5 min

Electronic pneumatics control (EPC) pressures, flow rates, and the fixed restrictor dimensions were determined using a Deans switch calculator software program that was designed for this system. This calculator program is included with the Deans switch hardware option for the Agilent 6890N GC.

Crude oil samples spiked with methanol were obtained from Spectrum Quality Standards (Houston, TX, USA). Each sample was prepared according to ASTM Method D7059 by mixing 5.0 g of crude oil sample with 5 mL of ACS grade toluene containing 1000 µg/g of 1-propanol. The 1-propanol was used as an internal standard (ISTD). If the samples were not analyzed immediately, they were stored in glass vials with TFE-fluorocarbon lined caps below 5 °C. During storage there was little or no headspace in the vials to reduce the partition of methanol into the headspace. Seven calibration standards were prepared containing 5 to 1000 ppm (m/m) of methanol in toluene, and each containing 500 ppm (m/m) of 1-propanol. The calibration standards should be used immediately after preparation since the methanol concentration is not stable in toluene. The standards can be stored for several days below 5 °C in glass vials with little or no headspace.

Results and Discussion

Heart-cut times were determined by injecting the 1000-ppm methanol standard onto the primary DB-1 column with no cutting to the Lowox column. The retention time for methanol was 1.82 min and 2.11 min for 1-propanol. Using this data, the cut-time for all standards and samples was 1.70 to 2.35 min. The 1000-ppm standard was then analyzed using this cut time to evaluate the separation of the alcohols on the Lowox column after cutting. The methanol and 1-propanol were easily separated on the Lowox column with retention times of 4.72 and 6.38 min, respectively (Figure 2).

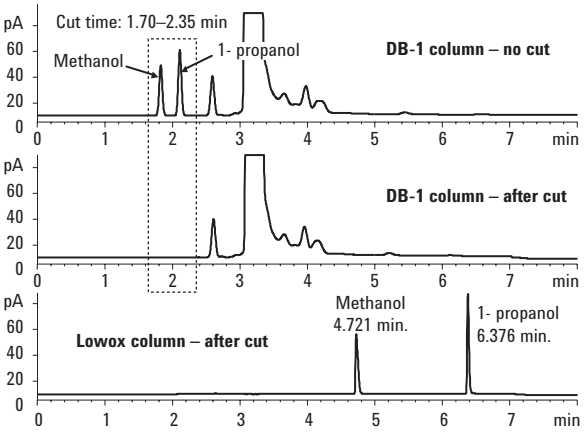

Figure 2. Setting the heart-cut times for the 2-D GC analysis of methanol in crude oil.

Calibration of the systems was performed using seven standards of methanol in toluene at concentrations of 5, 25, 75, 125, 250, 500, and 1000 ppm with 500 ppm of 1-propanol as the ISTD. The ChemStation was used to develop a calibration curve (Figure 3). This calibration exceeded the correlation coefficient of 0.99 required by the ASTM method. The detectability of the system was also checked using a 1-ppm standard of methanol in toluene, with no ISTD. This sample was analyzed and the signal-to-noise of the methanol peak on the second column (Lowox) was found to be 5:1, which exceeded the method requirement of a 5:1 signal to noise for a 2-ppm standard.

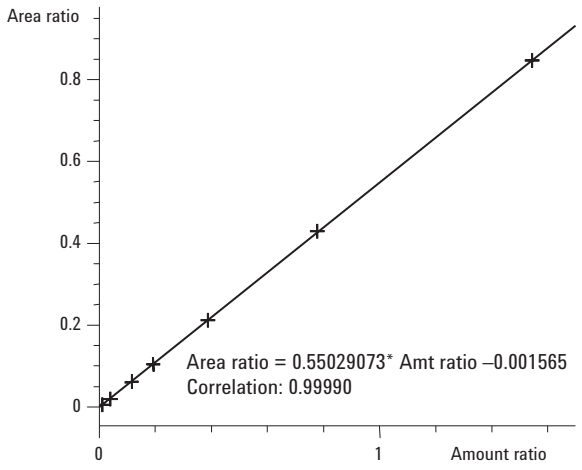

Figure 3. Calibration of methanol from 5 ppm (m/m) to 1000 ppm (m/m) using 2-D heart-cutting GC.

A quality control check of the system was also made using two crude oil samples; one contained 15-ppm methanol, and the other 670 ppm. For the 15-ppm sample, the reported result must be within ±5 ppm and for the 670-ppm sample, within ± 35 ppm. Figure 4 shows the data obtained from the analysis of the crude oil sample containing 15 ppm of methanol in crude oil. Two replicates of the 15-ppm sample yielded results of 10 ppm and 17 ppm. For the 670-ppm samples, the replicates yielded results of 670 ppm and 667 ppm.

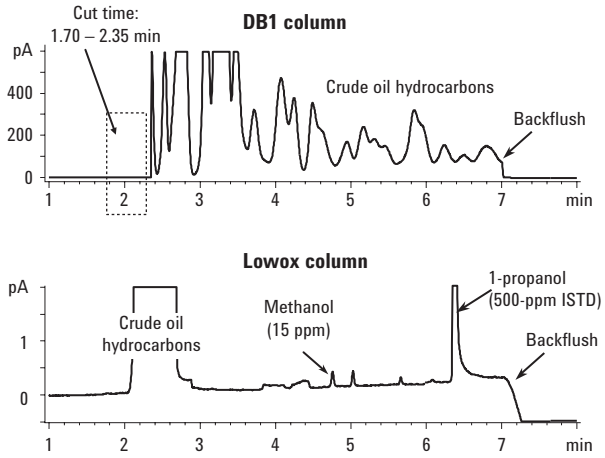

Figure 4. The 2-D GC analysis of 15 ppm (m/m) of methanol in crude oil using a micro-fluidic Deans switch.

The analysis time of the method was reduced by backflushing the primary column to quickly remove the higher boiling crude oil components from the DB-1 column. Backflushing was done after the elution of the 1-propanol peak from the Lowox column. At 7 min, the split/splitless inlet pressure was reduced to 0.5 psi while the PCM pressure was increased to 35 psi. This reversed the flow in the primary DB-1 column so that any remaining compounds at the head of the column were eluted through the split vent (Figure 5).

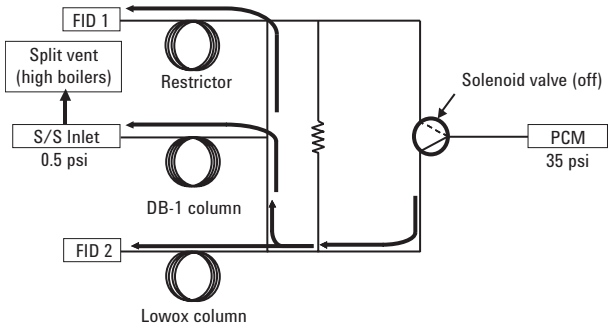

Figure 5. Backflushing the DB-1 column can be done to reduce the analysis time using the EPC on the 6890N Deans system.

Crude oil analysis also requires more maintenance than with more volatile samples. Since crude contains a wide range of compounds, from low boiling to nonvolatile, the inlet liner will need more frequent replacement. It is recommended that the liner be changed after 50 injections. Additionally, one should also inspect the top of the split/splitless inlet body to evaluate any contamination of crude oil tars that can accumulate at the top of the inlet and at the outlet of the split vent line. Depending on the samples, the inlet body may need to be cleaned after 100 injections.

Conclusions

The analysis of any components in crude oil presents a number of challenges due to the difficult nature of the sample matrix. The recently developed ASTM method D7059 uses heart-cutting 2-D GC to separate and quantify trace levels of methanol in crude oil samples. A new micro-fluidic Deans switch designed for the 6890N was shown to be ideally suited to this difficult application. It has 4-times less thermal mass so that it is effectively and uniformly heated, avoiding cold spots where high-boiling crude oil components could be condensed. The shorter flow paths, inert surfaces, and capillary optimized fittings ensure that active compounds like methanol can be separated and detected at trace levels in crude oil.

References

1. Annual Book of ASTM Standards, Vol. 05.04 "Petroleum Products and Lubricants (IV)", ASTM, 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA.
2. McCurry, J.D. and Quimby, B.D., "Two-dimensional Gas Chromatographic Analysis of Components in Fuel and Fuel Additives Using a Simplified Heart-Cutting GC System," (2002) *J. Chromatogr. Sci.*, **41**(10): 524-527.

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