

# Application News

Gas Chromatography

SSI-GC-003

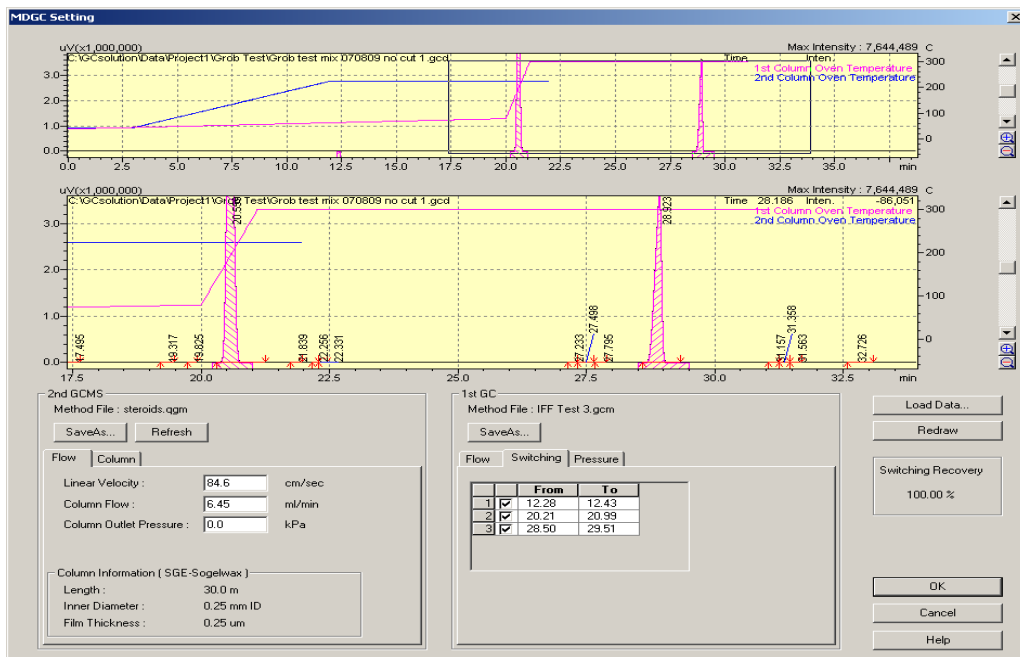
## Trace Oxygenated Hydrocarbons in Liquid Hydrocarbon Streams by Multidimensional GC

### Introduction

It has been widely accepted that oxygenates are related to corrosion and fouling issues in refinery processes. Accurate determination of trace oxygenated hydrocarbons in liquid hydrocarbon streams plays an important role in process design and operation. Method UOP 960 defines testing procedures utilizing a valved gas chromatograph (GC) system. A non-polar column accumulates components of interest, and a polar column is used to separate oxygenates. In fact, the instrumentation is a prototype of multidimensional GC (MDGC) that requires complicated setup and configuration. Determination of valve timing, however, has been proven to be a daunting task. Operators work at optimizing parameters in a trial-and-error process, which is both laborious and time consuming. Furthermore, great difficulties could arise in instrument maintenance and troubleshooting. The goal of this study is to simplify the UOP 960 method and to reduce run time if it is possible. The ultimate goal is to improve overall productivity in refinery processes.

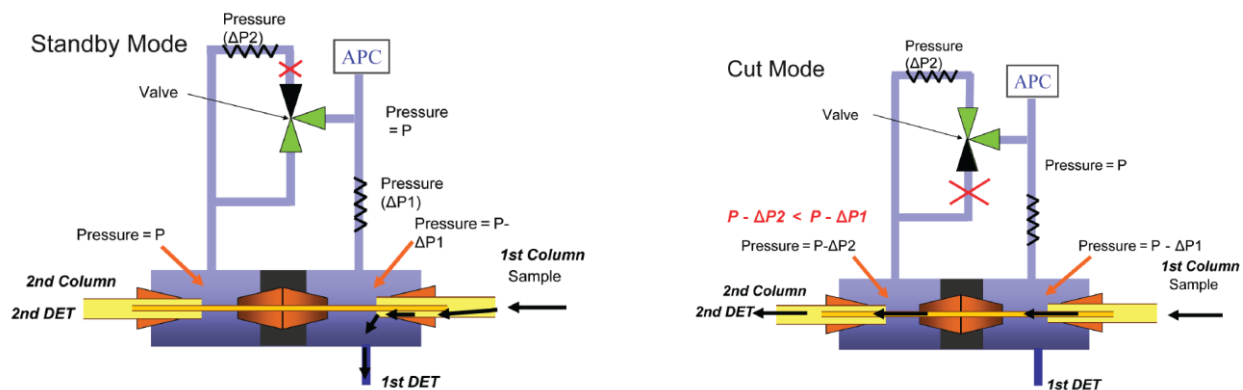
Shimadzu MDGC (Multi-dimensional GC) is a heart-cutting technique, targeted at solving co-elution issues. It takes advantage of combining a non-polar phase capillary column with a polar phase capillary column to achieve separations that would otherwise be impossible. The heart of this system is a low-volume capillary pressure switch (Multi-Deans switch) that directs the eluate from the first column either to the first detector, or on to a second, complementary-phased column along with a second detector. This switch is operated by a software control module (MDGCsolution) that interacts cooperatively with both GCsolution and GCMSsolution software.

MDGCsolution software allows for multiple heart-cuts to be made very simply and reproducibly, as shown in Figure 1.



**Figure 1:** MDGCsolution software makes heart-cut as simple as double clicks

The advent of the Deans switch<sup>1</sup> allowed simplification of complicated valved GCs and made heart-cut MDGC possible. The development and applications of the heart-cut MDGC technique are, however, still in their infancy. The original Deans switch achieved flow switching by controlling pressures. It had inherent pressure control issues, however, that could lead to shifting retention times for components eluting after the switching time. Pressure was controlled on only one side of the switch, and the column pressure changed each time a component was switched on to the second column. This made it difficult to reproduce results when taking multiple cuts in the same run. To circumvent this problem, Shimadzu invented an improved Deans switch. Adding pressure control to both sides of the Deans switch allows for making multiple cuts with reproducible retention times on both the first and the second columns. The working mechanism is depicted in Figure 2.



**Figure 2:** Mechanism of improved Multi-Deans switch.

## Instrumentation

Two Shimadzu GC-2010 Plus units were used to provide independent column oven temperature control, each equipped with a split/splitless (SPL) injector and a Flame Ionization Detector (FID). An improved MDGC switching device was mounted in the 1<sup>st</sup> GC oven, and a heated transfer line bridged the 1<sup>st</sup> GC and the 2<sup>nd</sup> GC, which also serves as an injection port for the 2<sup>nd</sup> GC. A 15m X 0.32mm X 0.50 $\mu$ m Rtx-1 column was installed in the 1<sup>st</sup> GC oven, and a 10m X 0.53mm X 10 $\mu$ m CP-Lowox column was installed in the 2<sup>nd</sup> GC oven. A piece of 0.5m X 0.32mm fused silica untreated capillary tubing was used as mid-point restrictor of the switching device that was connected to the 1<sup>st</sup> FID detector. An AOC20i autosampler was mounted on the 1<sup>st</sup> GC to perform standard split/splitless injections, and a 4-port liquid valve with 1 $\mu$ L internal sample loop was mounted on the side of the 1<sup>st</sup> GC to perform valve injections, as shown in Figure 3. GCsolution and MDGCsolution software were used throughout the study.

### UOP960 GC-2010 Plus

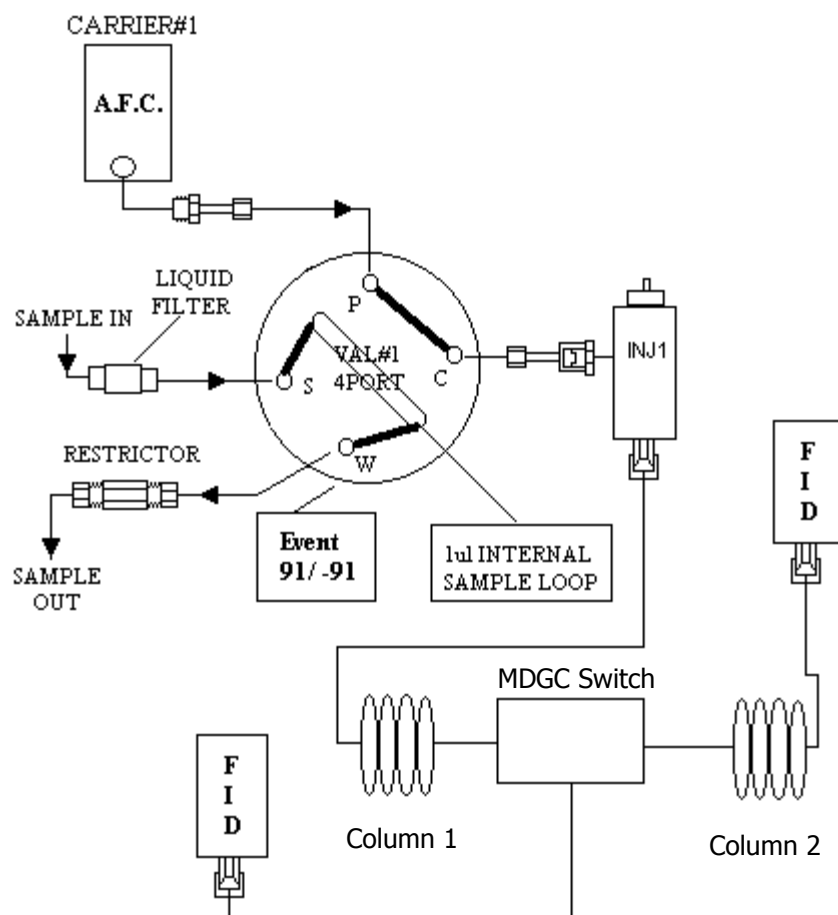


Figure 3: UOP960 GC-2010 Plus drawing of valve sampling

## Analytical Conditions

Columns: Rtx-1, 15m X 0.32mm X 0.50µm  
CP-Lowox, 30 m X 0.53mm X 0.25 µm

### AOC-20i conditions:

Injection volume: 1µL  
# of Solvent Rinses pre-injection: 2  
# of Solvent Rinses post-injection: 2  
Plunger Speed (Suction): high  
Plunger Speed (Injection): high  
Injection Mode: normal  
Inj. Port Dwell Time: 0.3 sec  
Washing Volume: 8 µL  
Viscosity Comp. Time: 0.2 sec  
Syringe Insertion Speed: high  
Pumping Times: 5  
Plunger Washing Speed: high

### 1<sup>st</sup> GC conditions:

INJ Temp: 280°C  
Flow Control Mode: Pressure  
Column Flow: 0.91mL/min  
Split Ratio: 10.0  
Valve Box: 25°C  
Oven1 Temp: 40.0°C, 10°C/min to 250°C, hold 4 min  
DET Temp: 300°C  
Makeup Flow: 0.0mL/min  
Air Flow: 400.0mL/min.  
Carrier Gas: He  
INJ Pressure: 35KPa  
Purge Flow: 1mL/min  
CON1 Temp: 280.0°C  
Makeup Gas: He  
H<sub>2</sub> Flow: 40.0mL/min

### 2<sup>nd</sup> GC Conditions:

Oven2 Temp: 50°C, 10°C/min to 250°C, hold 4 min  
Sample Inlet Unit: GC  
Makeup Gas: He  
H<sub>2</sub> Flow: 40.0mL/min  
Switch Pressure: 20.0KPa  
Switch Window: 0.25min to 5.68min out of the 1<sup>st</sup> GC chromatogram  
DET Temp: 300°C  
Makeup Flow: 20.0mL/min  
Air Flow: 400.0mL/min

## Standards

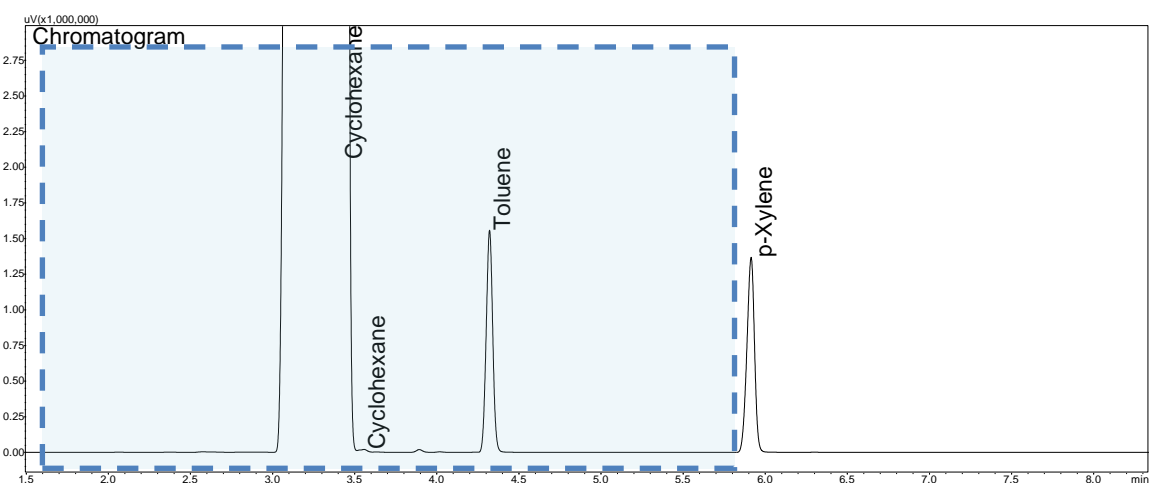
Scott™ LPG standard were purchased from Air Liquide America Specialty Gases LLC. It contains 51.1ppm 2-butanone, 1.02ppm 2-methyl-2-propanol, balanced with isobutane.

Qualitative mixture of oxygenate standards were prepared according to method ASTM D4307. A 500mL Glass bottle was wrapped with aluminum foil, and all GC sample vials were amber glass vials. cyclohexane, benzene, toluene, *p*-xylene, dimethyl ether, acetaldehyde, methyl formate, *tert*-butyl ethyl ether, *tert*-butyl methyl ether, propylene oxide, *sec*-butyl methyl ether, propionaldehyde, butyl methyl ether, *tert*-amyl methyl ether, butyl ethyl ether, isobutyraldehyde, tetrahydrofuran, ethyl ether, acetone, 2-butanone, ethyl alcohol, 1,4-dioxane, 2-propanol, 2-butanol, 1-butanol were obtained from Sigma-Aldrich. Methyl alcohol and 1-pentanol were obtained from Fisher Scientific. 450mL of cyclohexane was spiked with 1mL toluene and 1mL *p*-xylene. Another 450mL of cyclohexane was spiked with 5µL of other

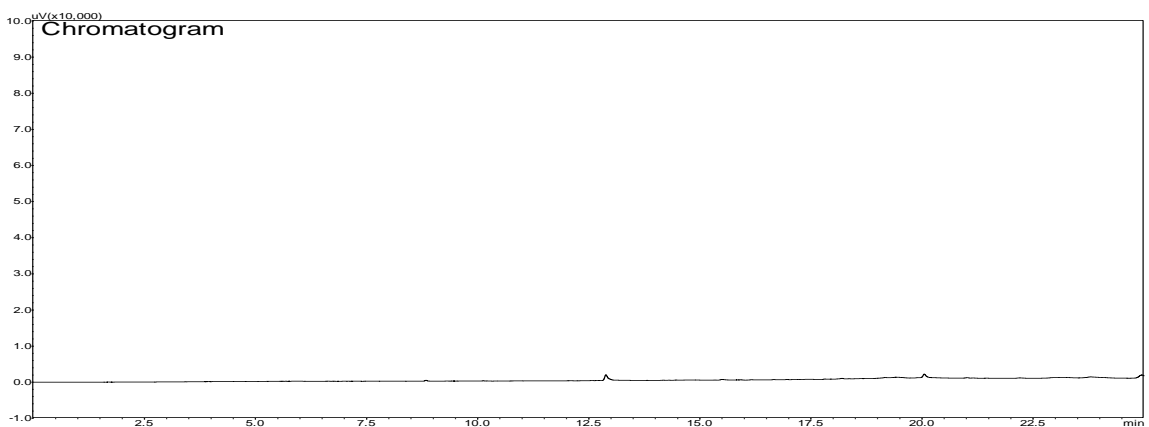
standards listed above (qualitative standard). Since dimethyl ether is a gas at STP, it was bubbled into the solution for 3 to 4 seconds via a piece of 1/8 inch tubing.

## Results and Discussion

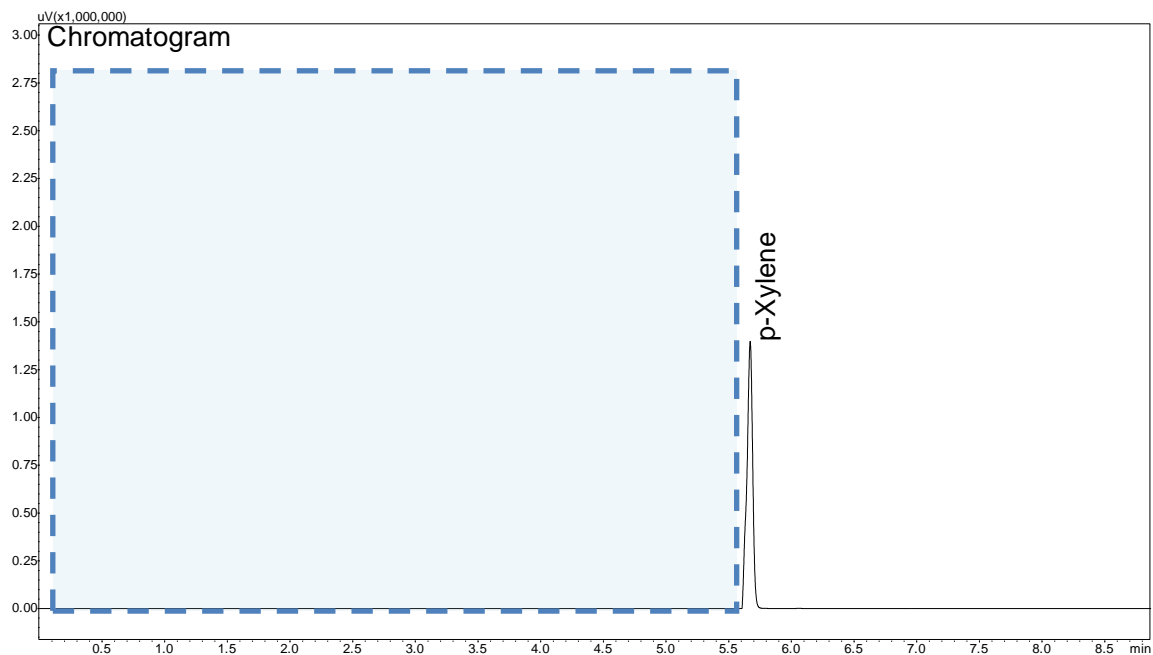
Toluene and *p*-xylene mixed standard was injected with an AOC20i autosampler without heart-cutting. Two sets of chromatograms were obtained from the same single injection, as illustrated in Figures 4.1 and 4.2, from the 1<sup>st</sup> GC and the 2<sup>nd</sup> GC, respectively. One heart-cut window (the timing of valve switch) was then selected from 0.25min to 5.68 min by MDGC software. It is worth to note that operators no longer need to work blindly any more – a switching window was selected simply by making double clicks with a mouse. The resulting chromatograms are illustrated in Figures 5.1 and 5.2. Scrupulous chromatograms indicated excellent heart-cutting efficiency, and baseline fluctuation was negligible.



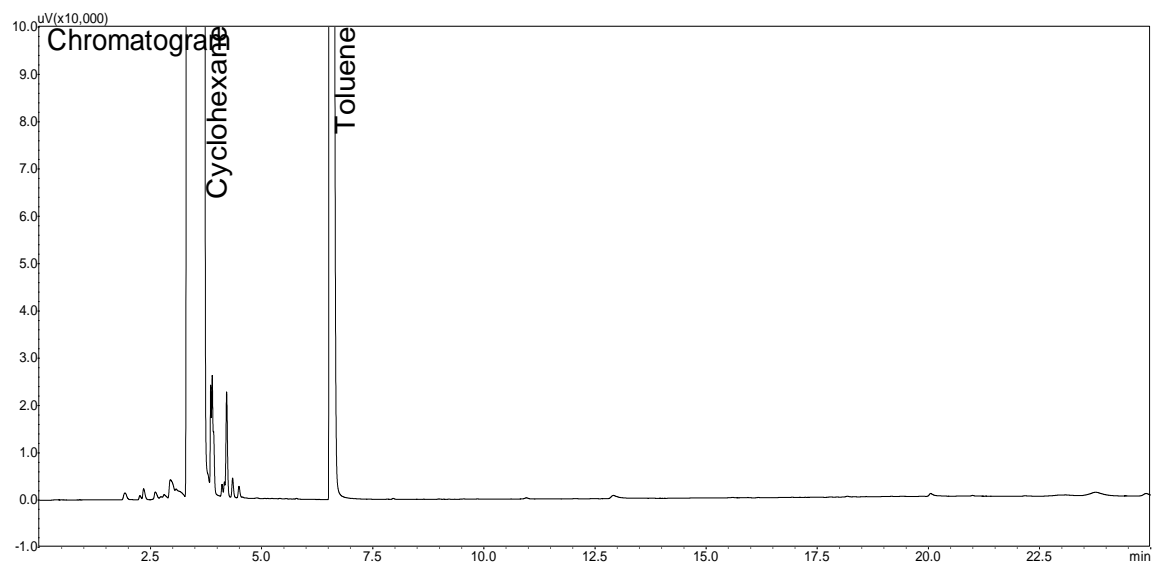
**Figure 4.1:** Chromatogram of toluene and *p*-xylene from the 1<sup>st</sup> GC without heart-cutting. Shaded area represents the cut-off region.



**Figure 4.2:** Chromatogram of toluene and *p*-xylene from the 2<sup>nd</sup> GC without heart-cutting

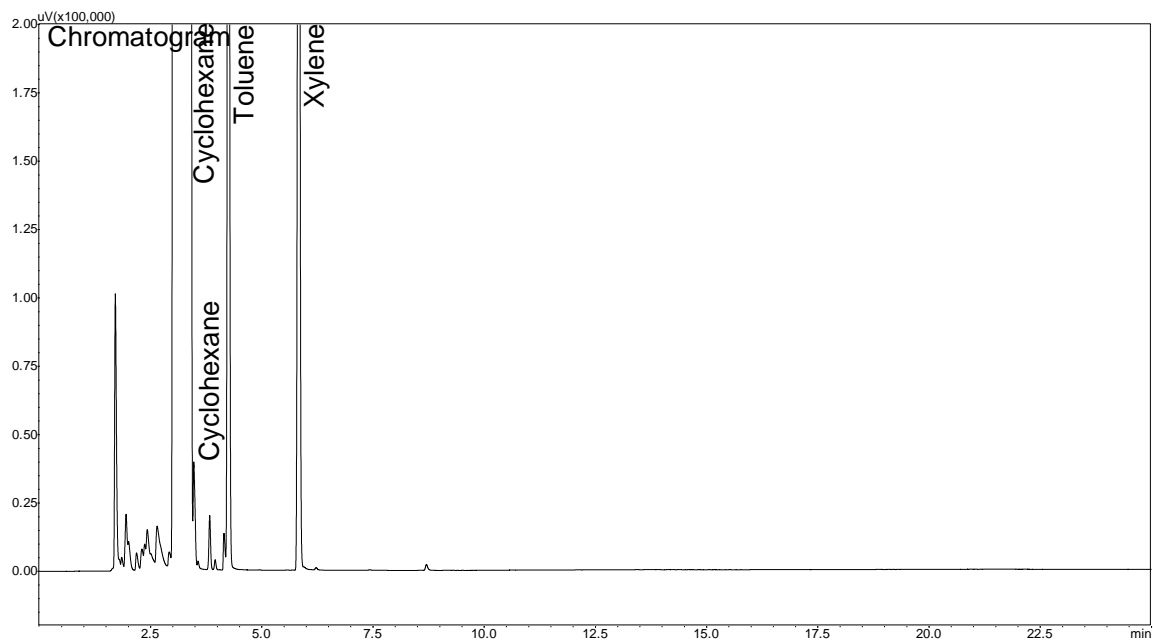


**Figure 5.1:** *p*-Xylene was left behind on the 1<sup>st</sup> GC after cutting the cyclohexane and toluene peaks

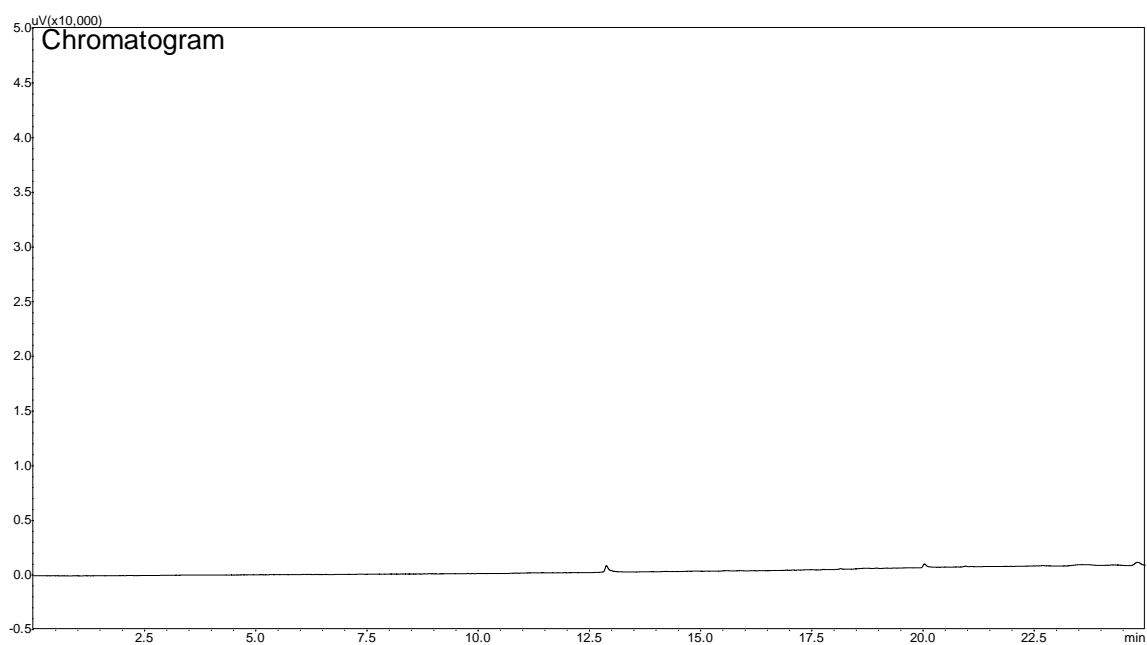


**Figure 5.2:** Chromatogram of cyclohexane and toluene from the 2<sup>nd</sup> GC after cut. No *p*-xylene peak was observed.

Chromatograms of qualitative standard without heart-cutting were then obtained, as shown in Figures 6.1 and 6.2, respectively.



**Figure 6.1:** 1<sup>st</sup> GC Chromatogram of the qualitative standard before cut



**Figure 6.2:** 2<sup>nd</sup> GC chromatogram of the qualitative standard before cut

Correspondingly, the 2<sup>nd</sup> GC chromatogram after cut is illustrated in Figure 7.1, and the peak table is listed in Figure 7.2. Ethyl ether was co-eluted with toluene; butyl ethyl ether and isobutyraldehyde were not baseline separated.

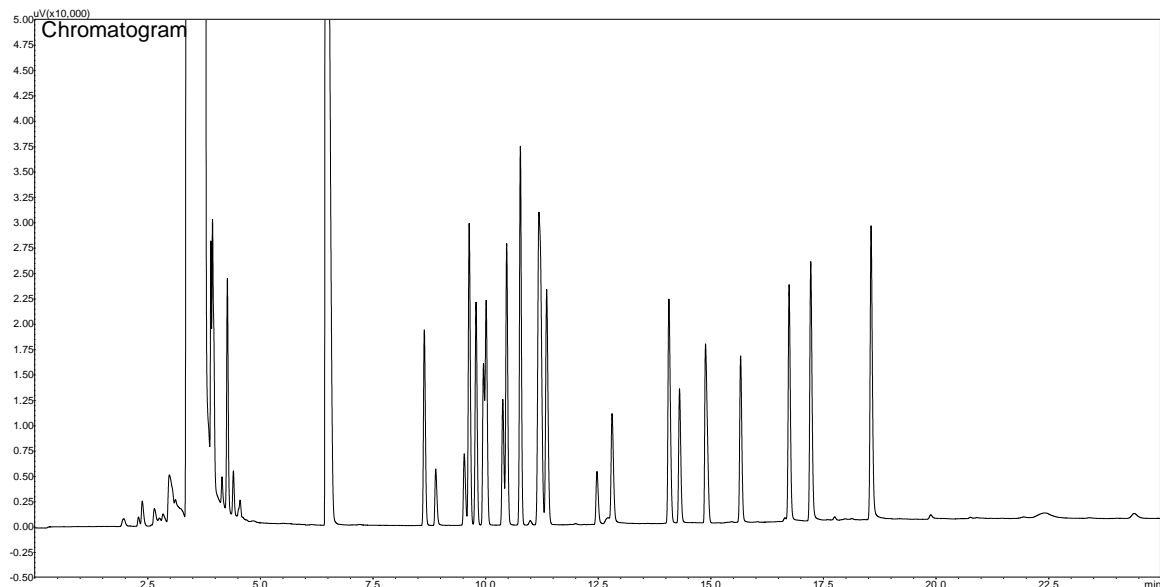


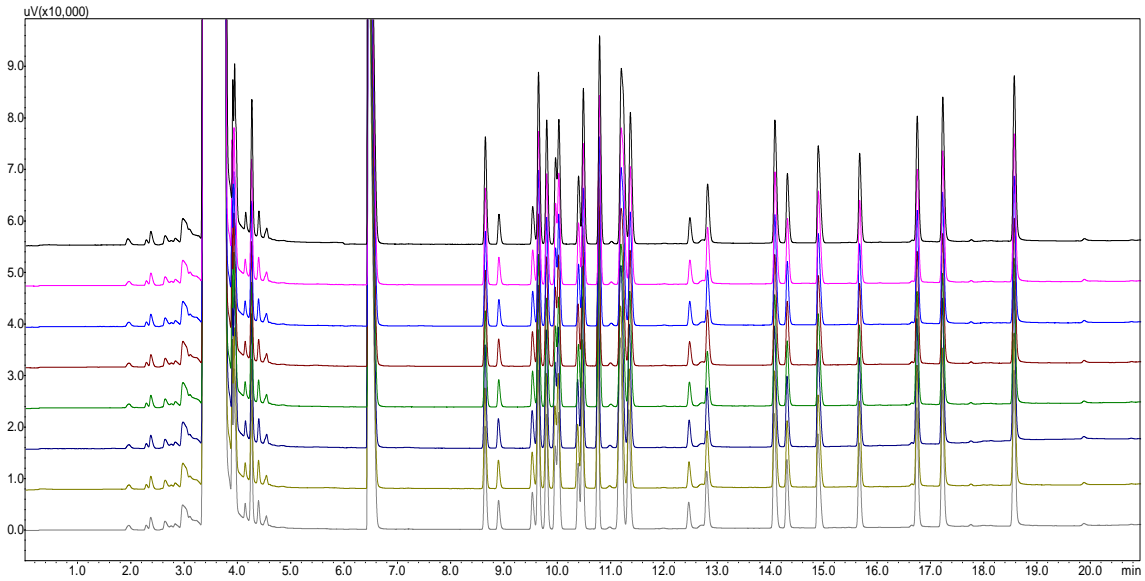
Figure 7.1: 2<sup>nd</sup> GC chromatogram of the qualitative standard

Method - Compound Table								
Integration	Quantitative	Compound	Group	Performance				
ID#	Name	Type	Ret. Time	Band	Conc. 1	Curve	Zero	Weight
1	Cyclohexane	Target	3.691	Default	1	Default	Default	Default
2	Methyl ether	Target	6.593	Default	1	Default	Default	Default
3	Ethyl ether	Target	8.682	Default	1	Default	Default	Default
4	Acetaldehyde	Target	8.939	Default	1	Default	Default	Default
5	Methyl formate	Target	9.570	Default	1	Default	Default	Default
6	tert-Butyl ethyl ether	Target	9.673	Default	1	Default	Default	Default
7	tert-Butyl methyl ether	Target	9.822	Default	1	Default	Default	Default
8	Propylene oxide	Target	10.040	Default	1	Default	Default	Default
9	sec-Butyl methyl ether	Target	10.409	Default	1	Default	Default	Default
10	Propionaldehyde	Target	10.505	Default	1	Default	Default	Default
11	Butyl methyl ether	Target	10.774	Default	1	Default	Default	Default
12	tert-Amyl methyl ether	Target	10.993	Default	1	Default	Default	Default
13	Butyl ethyl ether/Isobutylaldehy	Target	11.232	Default	1	Default	Default	Default
14	Tetrahydrofuran	Target	11.422	Default	1	Default	Default	Default
15	Methyl alcohol	Target	12.501	Default	1	Default	Default	Default
16	Acetone	Target	12.878	Default	1	Default	Default	Default
17	2-Butanone	Target	14.162	Default	1	Default	Default	Default
18	Ethyl alcohol	Target	14.355	Default	1	Default	Default	Default
19	1,4-Dioxane	Target	14.947	Default	1	Default	Default	Default
20	2-Propanol	Target	15.720	Default	1	Default	Default	Default
21	2-Butanol	Target	16.803	Default	1	Default	Default	Default
22	1-Butanol	Target	17.283	Default	1	Default	Default	Default
23	1-pentanol	Target	18.628	Default	1	Default	Default	Default

Figure 7.2: Peak table of the qualitative standard, associated with the chromatogram of Figure 7.1

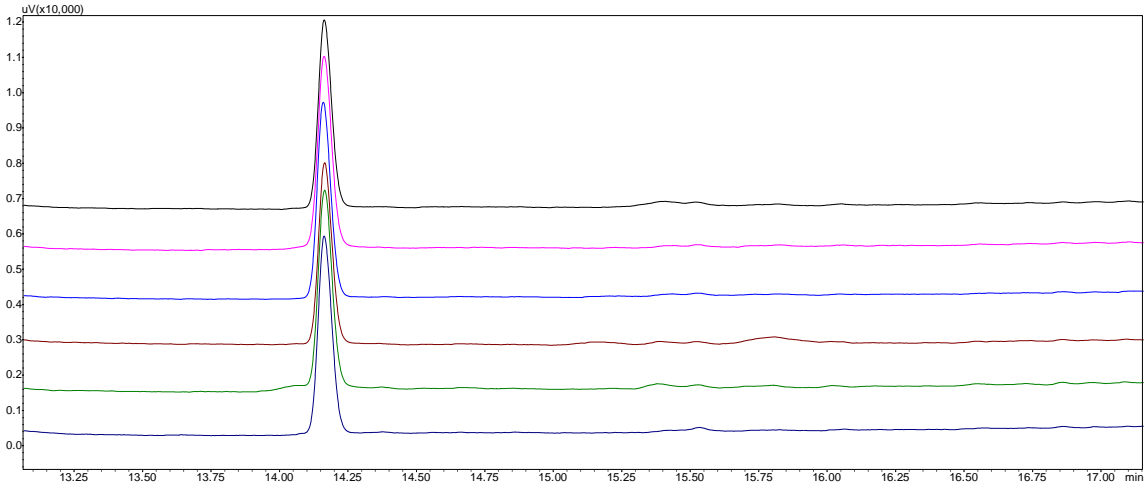
Repeatability study was conducted by making eight independent injections of the qualitative mixed standard, as shown in Figure 8, which yielded approximately 0.1% RSD for retention times and 5% RSD for peak areas.





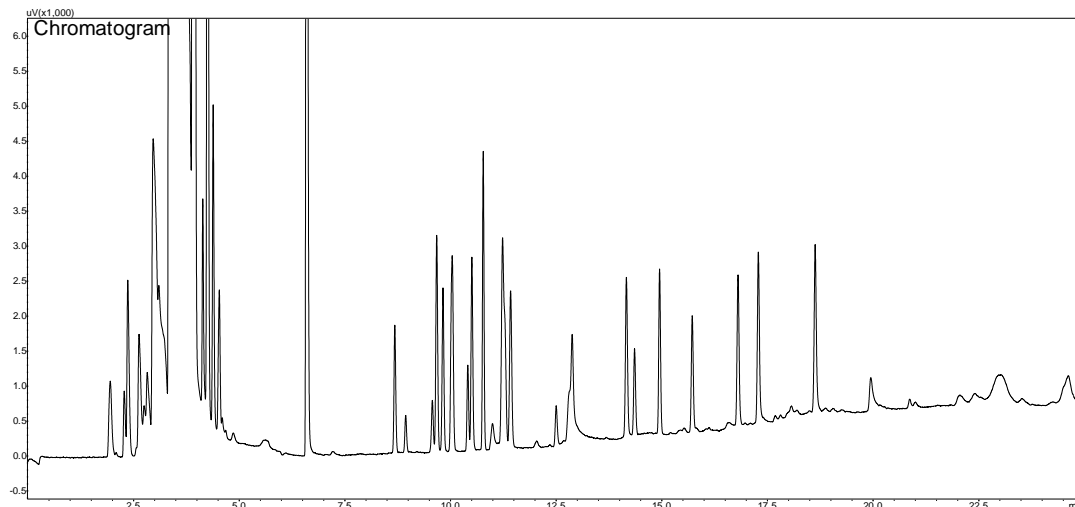
**Figure 8:** 2<sup>nd</sup> GC Chromatograms from eight independent injections of the qualitative standard

To perform quantitative analysis, one point calibration was established by making six parallel valve injections of commercial Scott<sup>TM</sup> liquid 2-butanone standard, illustrated in Figure 9. The average 2-butanone peak area was 19301, with a RSD% of 5.417%. No retention time shift was observed between syringe injections and valve injections.



**Figure 9:** 2<sup>nd</sup> GC chromatograms of six parallel valve injections of 2-butanone standard

An unknown sample was made by mixing qualitative standards, and it was used to demonstrate quantitative capabilities. The 2<sup>nd</sup> GC chromatogram is shown in Figure 10, and the calculation spread sheet is illustrated in Table 1.

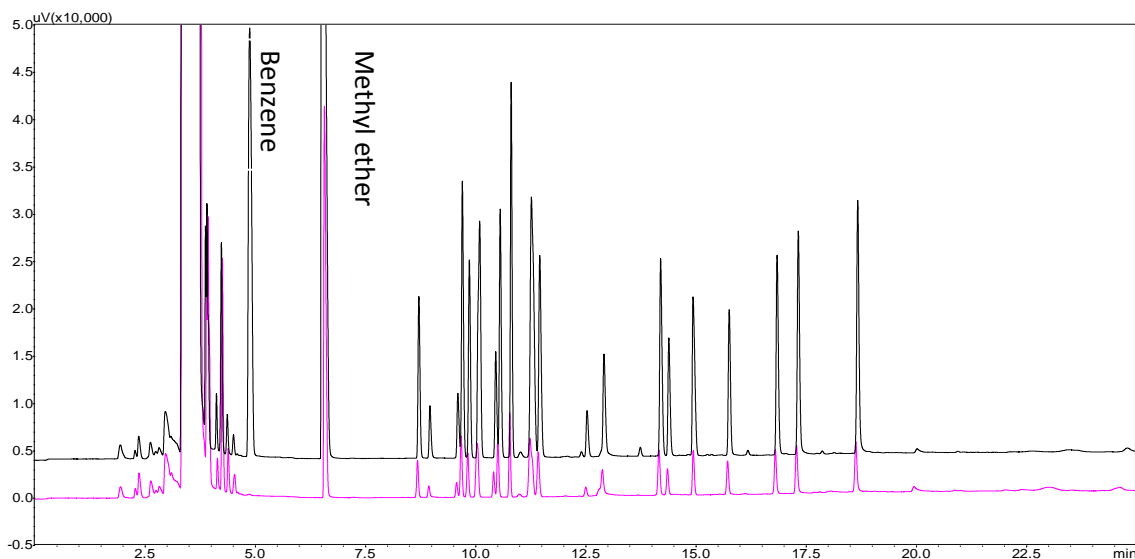


**Figure 10:** 2<sup>nd</sup> GC chromatogram of an unknown sample via valve injection

Name	Retention Time	Response factor	Peak Area	RF Peak Area	Concentration (ppm)
Methyl ether	6.593	1.278	61651	3.194	208.599
Ethyl ether	8.682	1.028	5264	0.273	14.327
Acetaldehyde	8.939	1.222	1546	0.080	5.002
Methyl formate	9.57	1.666	2308	0.120	10.180
<i>tert</i> -Butyl ethyl ether	9.673	0.945	9342	0.484	23.373
<i>tert</i> -Butyl methyl ether	9.822	0.978	6996	0.362	18.115
Propylene oxide	10.04	1.074	11209	0.581	31.872
<i>sec</i> -Butyl methyl ether	10.409	0.978	3512	0.182	9.094
Propionaldehyde	10.505	1.074	8127	0.421	23.109
Butyl methyl ether	10.774	0.978	10805	0.560	27.977
<i>tert</i> -Amyl methyl ether	10.993	0.945	2085	0.108	5.216
Butyl ethyl ether/Isobutyraldehyde	11.232	0.945	17153	0.889	42.915
Tetrahydrofuran	11.422	0.999	8201	0.425	21.691
Methyl alcohol	12.501	1.778	1896	0.098	8.925
Acetone	12.878	1.074	9684	0.502	27.536
2-Butanone	14.162	1	7797	0.404	20.643
Ethyl alcohol	14.355	1.278	3927	0.203	13.287
1,4-Dioxane	14.947	1.222	6955	0.360	22.501
2-Propanol	15.72	1.111	5157	0.267	15.169
2-Butanol	16.803	1.028	7181	0.372	19.544
1-Butanol	17.283	1.028	8063	0.418	21.945
1-pentanol	18.628	0.978	8547	0.443	22.131
<b>Total</b>					<b>613.150</b>

**Table 1:** Calculation spreadsheet

UOP 960, as written, requires determination of dimethyl ether and other oxygenates in two separate runs. However, it seems clear that the MDGC method is capable of integrating the two-step procedures into one. Two 2<sup>nd</sup> GC chromatograms were compared between qualitative mixed standard and benzene spiked qualitative mixed standard, without toluene and p-xylene present. The results are shown in Figure 11, which suggests it is possible to determine both dimethyl ether and other oxygenates in a single run. However, optimized parameters may need to be further investigated when toluene is in present.



**Figure 11:** 2<sup>nd</sup> GC chromatograms of the qualitative mixed standard, with and without spiked benzene

## Conclusion

MDGC has demonstrated that it is possible to perform the separations of UOP 960 in a single run without an increase in cycle time, thus achieving a net reduction in total analysis time for laboratories engaged in determination of oxygenates. Qualitative and quantitative analysis have been successfully and easily achieved without compromising accuracy or precision. Moreover, Shimadzu MDGC simplified instrumental setup and configuration: heart-cut timings can be selected by double clicks with a mouse. Maintenance and troubleshooting are greatly simplified because of the presence of the inter-column detector which can be used to create or adjust a heart-cut region visually. Control data can be obtained automatically.

In addition to the time savings afforded by combining two procedures into one, as shown in this study, the fast oven cooling ability of Shimadzu GC-2010 Plus further reduced MDGC cycle time to less than 30 minutes per run. Finally, this study has demonstrated the feasibility of employing wide bore capillary columns into heart-cut MDGC applications. The demonstrated ruggedness, effectiveness, and greatly improved analytical economy of the method proposed here has opened the door to new MDGC applications, and has demonstrated great potential to improve productivity and shortened analysis time in refinery processes.

1) Deans, D. R. (1968) A new technique for heart cutting in gas chromatography. *Chromatographia* 1: 18-22