New Applications of Heart-Cut Multidimensional GC

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Introduction

Accurate identification and quantification of target compounds from complex matrices continues to be a challenge for analytical chemists. The most demanding issue is co-elution – two or more peaks of interest that elute at the same retention time. Co-elution frequently makes identification and quantification almost impossible. The advent of Heart-Cut multidimensional GC (MDGC) has circumvented the problem by employing a multi-Deans switch that links two capillary columns with different compound selectivity together to create a very powerful separation tool. Compounds that co-elute on one column are usually separated on a dissimilar column. The improved multi-Deans switch allows for performing multiple first dimension cuts without changing the retention times of the remaining peaks eluting in the first dimension.

A new application, improved method UOP960 – trace oxygenated hydrocarbons in liquid hydrocarbon streams by MDGC, has demonstrated the power of two-dimensional separation.

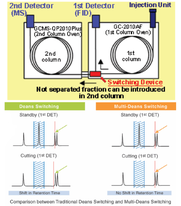
Outside View of MDGC/GCMS System

GC/GCMS System

Multidimensional GC

New improvement

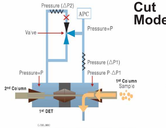
- Outstanding **retention time stability** – allows for performing multiple cuts without causing retention time shift
- Fully integrated **software control** – heart-cut selection can be set simply with mouse operations while viewing the 1st chromatogram



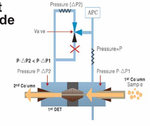
Comparison between Traditional Deans Switching and Multi-Deans Switching

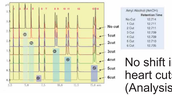
Mechanisms and Advantages

Standby Mode



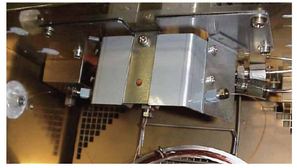
Cut Mode





No shift in retention time with multiple heart cuts
(Analysis of an oxygenated compound)

Multi Dimensional Switch

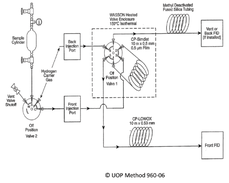


New hardware design – high switching efficiency and ease of maintenance

MDGCsolution

Method UOP 960

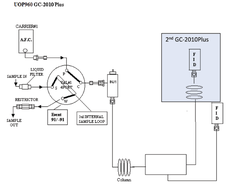
- Determine trace levels of oxygenated hydrocarbons, B.P. < 138 °C in C4 liquefied petroleum gas (LPG)
- Requires two independent runs for
  - Di-methyl ether
  - Other oxygenates



© UOP Method 960-06

Improved MDGC UOP960

- Columns:
  - Rtx-1, 15m X 0.32mm X 0.50µm
  - CP-Lowox, 10m X 0.53mm X 10µm
  - Midpoint restrictor: 0.5m X 0.32mm
- Injection Volume: 1 µL
- Switch Pressure: 20.0KPa
- Switch Window: 0.25min to 5.68min



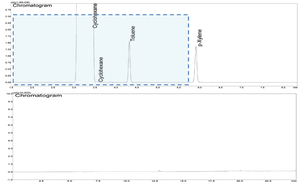
© Shimadzu MDGC design for UOP Method 960-06

GC Conditions

- 1st GC conditions:
  - INJ Temp: 280°C, Carrier Gas: He, Flow Control Mode: Pressure, INJ Pressure: 35KPa, Column Flow: 0.91mL/min, Purge Flow: 1mL/min, Split Ratio: 10.0
  - CON1 Temp: 280.0°C, Valve Box: 25°C
  - Oven1 Temp: 40.0°C, 10°C/min to 250°C, hold 4 min
  - DET Temp: 300°C, Makeup Gas: He, Makeup Flow: 0.0mL/min, H2 Flow: 40.0mL/min, Air Flow: 400.0mL/min.

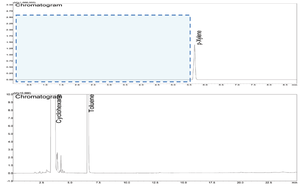
- 2nd GC conditions:
  - Oven2 Temp: 50°C, hold 1 min, 10°C/min to 250°C, hold 4 min
  - Sample Inlet Unit: GC, DET Temp: 300°C
  - Makeup Gas: He, Makeup Flow: 20.0mL/min
  - H2 Flow: 40.0mL/min, Air Flow: 400.0mL/min

Determine Heart-Cutting Window



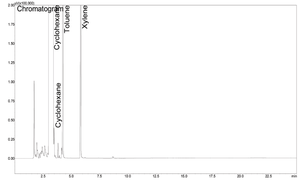
No peaks shown on 2nd chromatogram

1st and 2nd Chromatograms After Cut

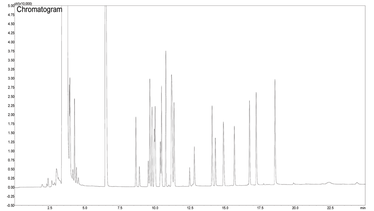


No peaks shown on 1st chromatogram

1st GC Chromatogram Before Cut

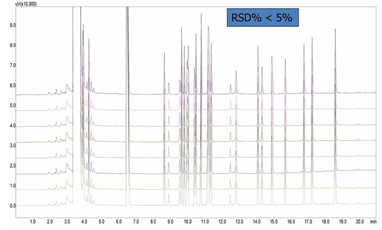


2nd GC Chromatogram After Cut

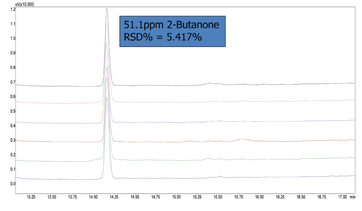


Chromatogram of qualitative standard mix

Reproducibility of 2nd Separations

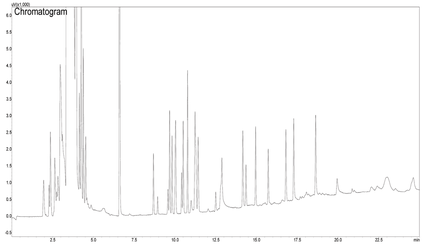


Calibration Standard



Chromatogram of quantitative standard mix

2nd Chromatogram of Unknown



Quantitation

Name	Retention Time	Response factor	Peak Area	Rf Peak Area	Concentration (ppm)
Methyl ether	6.593	1.278	81651	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
Tert-Butyl ethyl ether	9.673	0.945	9342	0.484	23.373
tert-Butyl methyl ether	9.822	0.978	6996	0.362	18.115
Propylene oxide	10.04	1.074	11309	0.581	31.872
sec-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
Tert-Amyl methyl ether	10.993	0.945	2085	0.108	5.216
Butyl ethyl ether/Isobutylaldehyde	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	14.182	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	15.589
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
Total					613.150

Conclusions

- A 0.53mm PLOT column was used for MDGC applications, which offers good separation of oxygenates
- Easy to select heart-cut time
- Integrated two running cycles into one; the simplified method increases productivity
- Excellent qualitative and quantitative results
- The two full GC oven MDGC system is priced at 20% less than the conventional valve GC system