Analysis of Petroleum Products Using Comprehensive Two-Dimensional Gas Chromatography (GC×GC) with Both Time-of-Flight MS and Flame Ionization Detectors

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Introduction

Comprehensive two-dimensional gas chromatography (GC×GC) has proven to be an extremely valuable analytical technique for the petroleum industry due to its ability to substantially increase the chromatographic peak capacity beyond that of traditional single-dimension gas chromatography. Pairing GC×GC with Time-of-Flight Mass Spectrometry (TOFMS) provides unsurpassed characterization capabilities due to the separation power of GC×GC and the ability of TOFMS to provide rich data to deconvolution algorithms, which help unravel the complexity of difficult petroleum matrices. Petrochemical labs also often utilize flame ionization detectors (FID) for GC×GC to provide quantitative results via area percent calculations.
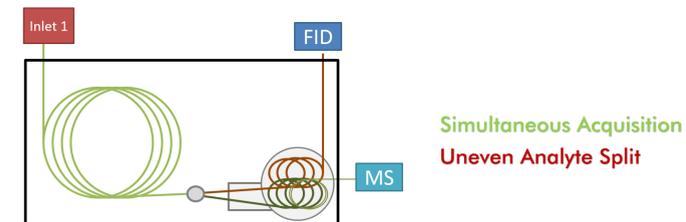
Configurations

Several possible configurations have been tested to develop a workflow which would allow either subsequent or simultaneous acquisitions of GC×GC TOFMS and FID data on the same GC×GC instrument.

Subsequent Injections
Equal Amounts on Column
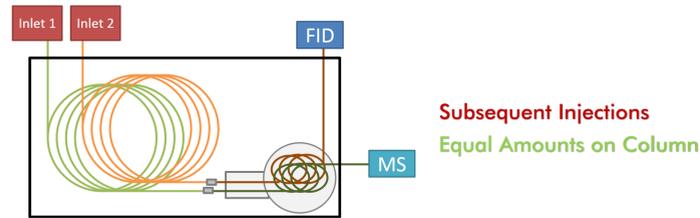
Configuration 1: Two inlets are each equipped with a primary column (30 m x 0.25 mm x 0.25 μm Rxi-5MS) connected to a secondary column (2 m x 0.25 mm x 0.25 μm). One column set routes to the FID, while the other column set routes to the MS.


Simultaneous Acquisition
Uneven Analyte Split
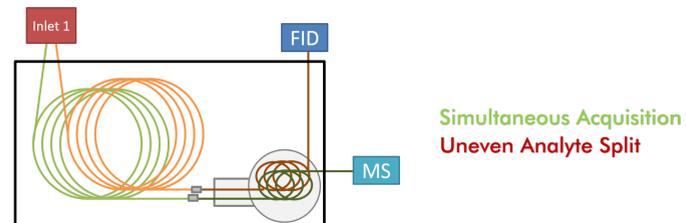
Configuration 2: Two independent column sets as described in Configuration 1 above were attached to a single inlet via a dual-holed ferrule. One column set routes to the FID, while the other column set routes to the MS.
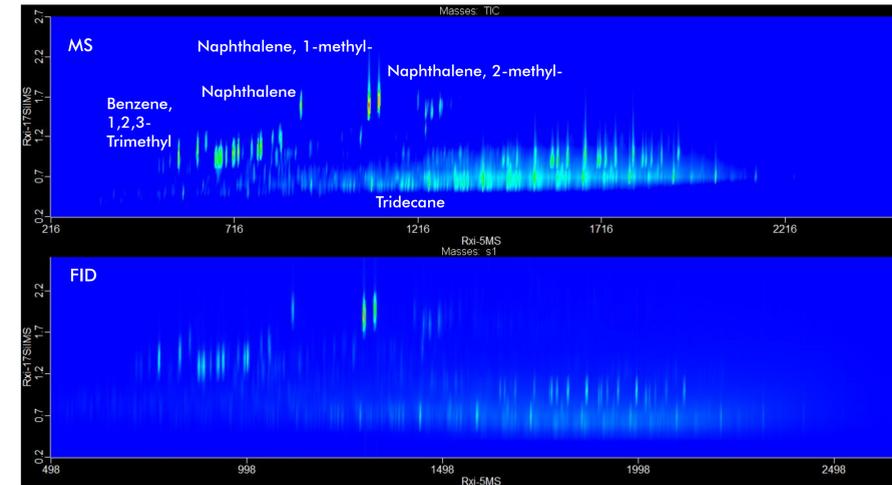

Simultaneous Acquisition
Uneven Analyte Split

Configuration 3: A single primary column (30 m x 0.25 mm x 0.25 μm Rxi-5MS) is connected to two identical secondary columns (2 m x 0.25 mm x 0.25 μm) through a Y-connector. An additional restrictive guard column (0.1 μm) is attached to the column routed to the mass spectrometer to account for the difference between atmospheric and vacuum outlet detectors.
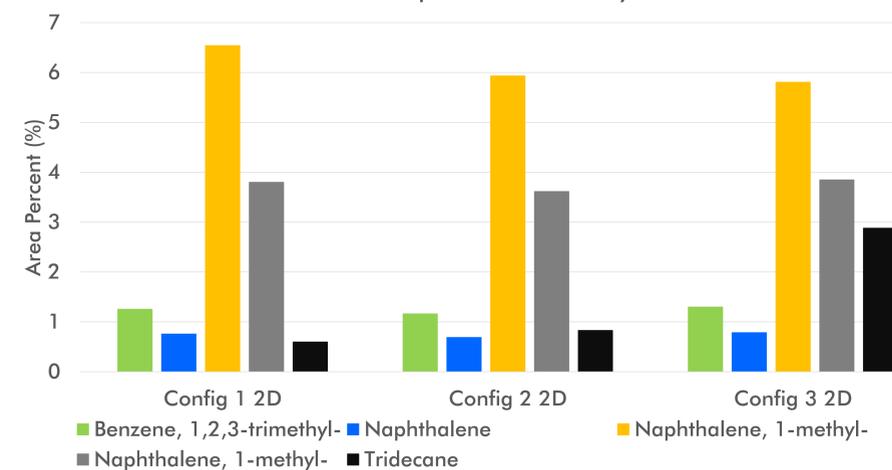
Standard Grob
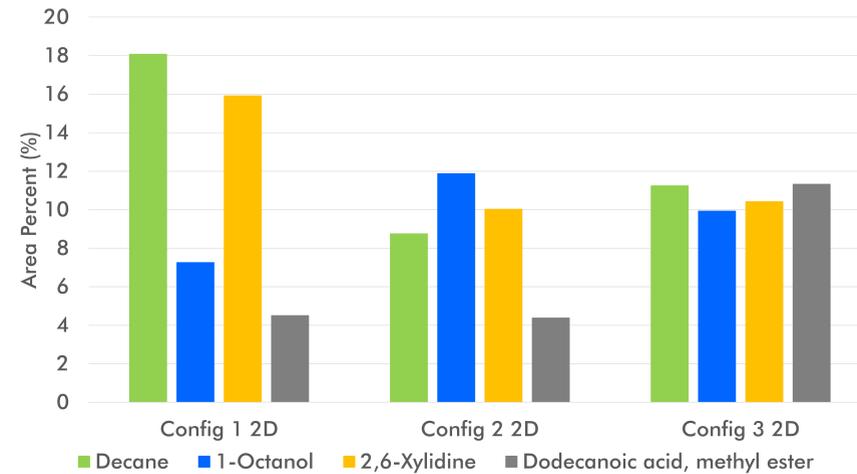
Standard Grob Analyte Tables: The bar graph above shows the Area Percent values for Decane, 1-Octanol, 2,6-Xylidine, and Dodecanoic Acid, Methyl Ester for the GC×GC (2D) runs in all three configurations.

Standard Grob Contour Plot: The contour plots above show data acquired in Configuration 1. Standard Grob mix analytes are identified by GCxGC-MS, with the corresponding FID peaks shown below. Although retention times are not identical, the general pattern in the 2-dimensional space allows for correlation of peaks.
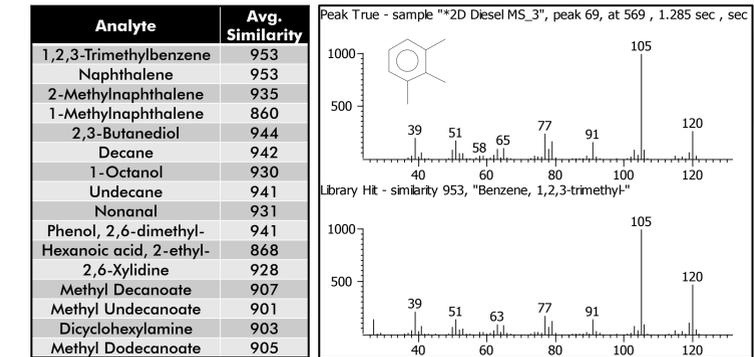
Diesel Sample

Diesel Sample Contour Plot: The contour plots above show data acquired in Configuration 2. Diesel Sample analytes are identified by GC×GC-MS, with the corresponding FID peaks shown below. Although retention times are not identical, the general pattern in the 2-dimensional space allows for correlation of peaks.

Standard Grob Analyte Tables: The bar graphs above show the Area Percent values for Benzene,1,2,3-Trimethyl, Naphthalene, 2-Methylnaphthalene, 1-Methylnaphthalene, and Tridecane for GC×GC (2D) runs in all three configurations.

MS Identification

Analyte	Avg. Similarity
1,2,3-Trimethylbenzene	953
Naphthalene	953
2-Methylnaphthalene	935
1-Methylnaphthalene	860
2,3-Butanediol	944
Decane	942
1-Octanol	930
Undecane	941
Nonanal	931
Phenol, 2,6-dimethyl-	941
Hexanoic acid, 2-ethyl-	868
2,6-Xylidine	928
Methyl Decanoate	907
Methyl Undecanoate	901
Dicyclohexylamine	903
Methyl Dodecanoate	905

Spectral Similarity: The table above shows the excellent average similarity scores of analytes of interest across all configurations, which allow for confident identification of MS peaks.

Methods

Pegasus® GC-HT/4D			
Column Configuration			
Primary Column	RXI-5MS 30 m x 0.25 mm x 0.25 μm		
Secondary Column	Rxi-17Sil MS 2 m x 0.25 mm x 0.25 μm		
Temperature Program— Grob	1.00 min at 40°C, ramp 10°C/min to 150°C, ramp 30°C/min to 230°C and hold 5.00 min		
Temperature Program— Diesel	1.00 min at 40°C, ramp 5°C/min to 280°C and hold 5.00 min		
MS Source Parameters			
Transferline Temp (°C)	300	Acquisition Rate (s/s)	200
Source Temp (°C)	200	Mass Range	35-500
FID Parameters			
Data Collection Rate (Hz)	200		
Temperature (°C)	300		

Discussion

In every configuration, one of the chief difficulties was trying to match the flows between analyte streams. With the difference between the atmospheric pressure of the FID and vacuum pressure from the MS, it was impossible to force retention times to line up in either the first or second dimension of separation. With the temperature ramp throughout the run, this also resulted in uneven splitting of analytes in Configurations 2 and 3. Especially in Configuration 3, a restrictor column was needed on the MS side so analytes could reach the FID and not completely be pulled into the MS.

One consequence of using the restrictor was the need for a longer modulation period in Configuration 3, which led to a loss in efficiency in the 1D separation. This can be seen in the much higher area percent for tridecane in the Diesel sample in Configuration 3 compared to the other configurations, because of coelutions in the FID trace.

While it was simple enough to correlate the MS to FID peaks for a Grob standard, GC×GC allowed for enough chromatographic resolution of certain peaks so that pattern recognition could be used to correlate the MS and FID peaks in the more complex Diesel sample. Area percent was automatically calculated for each peak using the S1 signal for FID data and the Deconvoluted Total Ion Chromatogram (DTIC) signal for the MS data.

Conclusions

Of the configurations presented here, Configuration 2 would be an appealing option for analysis of petroleum products. While there was some loss of sensitivity due to the additional column split and some uneven distribution of analyte between columns, the ability to acquire FID and MS data simultaneously greatly reduced acquisition time. There was also less difficulty in setting up Configuration 2 as compared to Configuration 3, which required a restrictor that led to significant retention time shifts in the second-dimension data. However, potential solutions to the problem of mismatched retention times and column flows could be explored by using a gas-flow controlled splitter in Configuration 3, which would allow for greater control of flow rates near the detectors. Future experiments will include the evaluation of an Agilent two-way splitter as an additional scenario for dual detector configurations.