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

Christina N. Kelly, Jonathan D. Byer, David E. Alonso, Lorne E. Fell, Joseph E. Binkley | LECO Corporation, St. Joseph, MI

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.
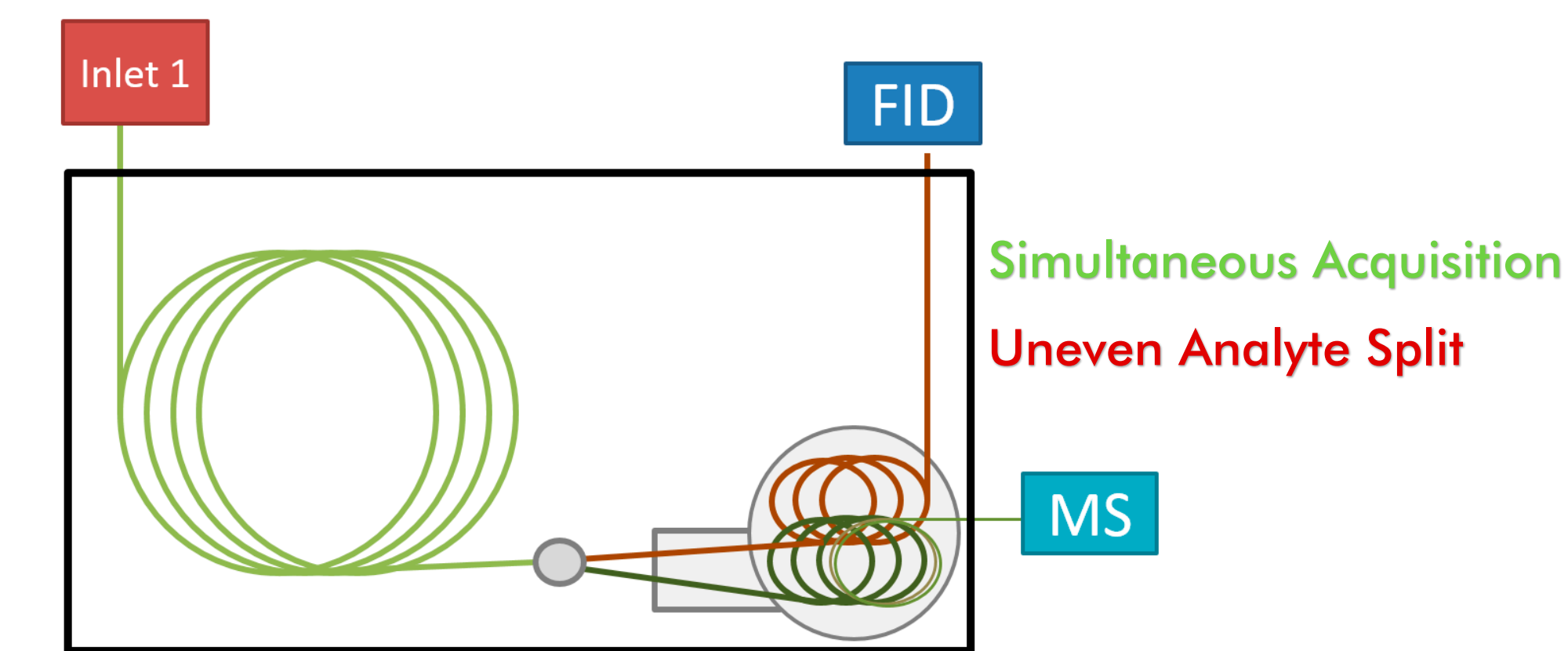
Configurations

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.
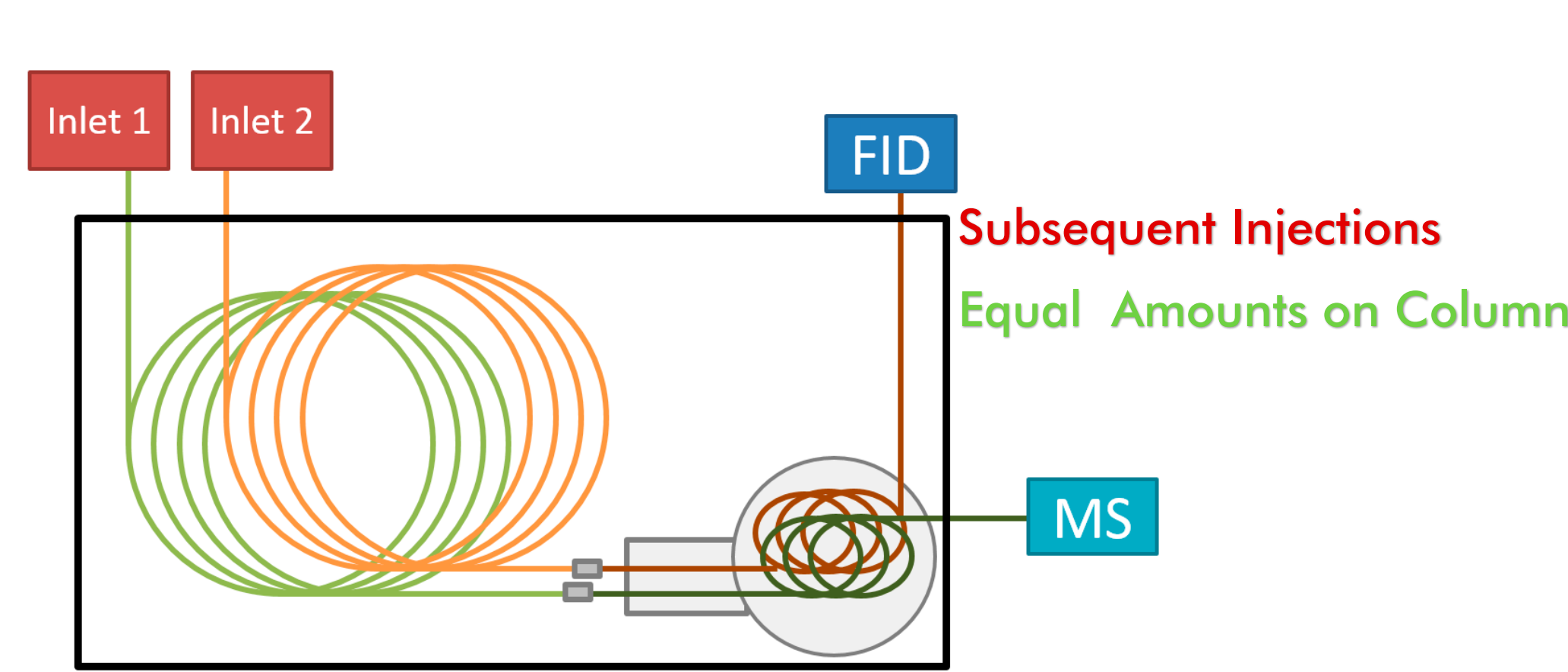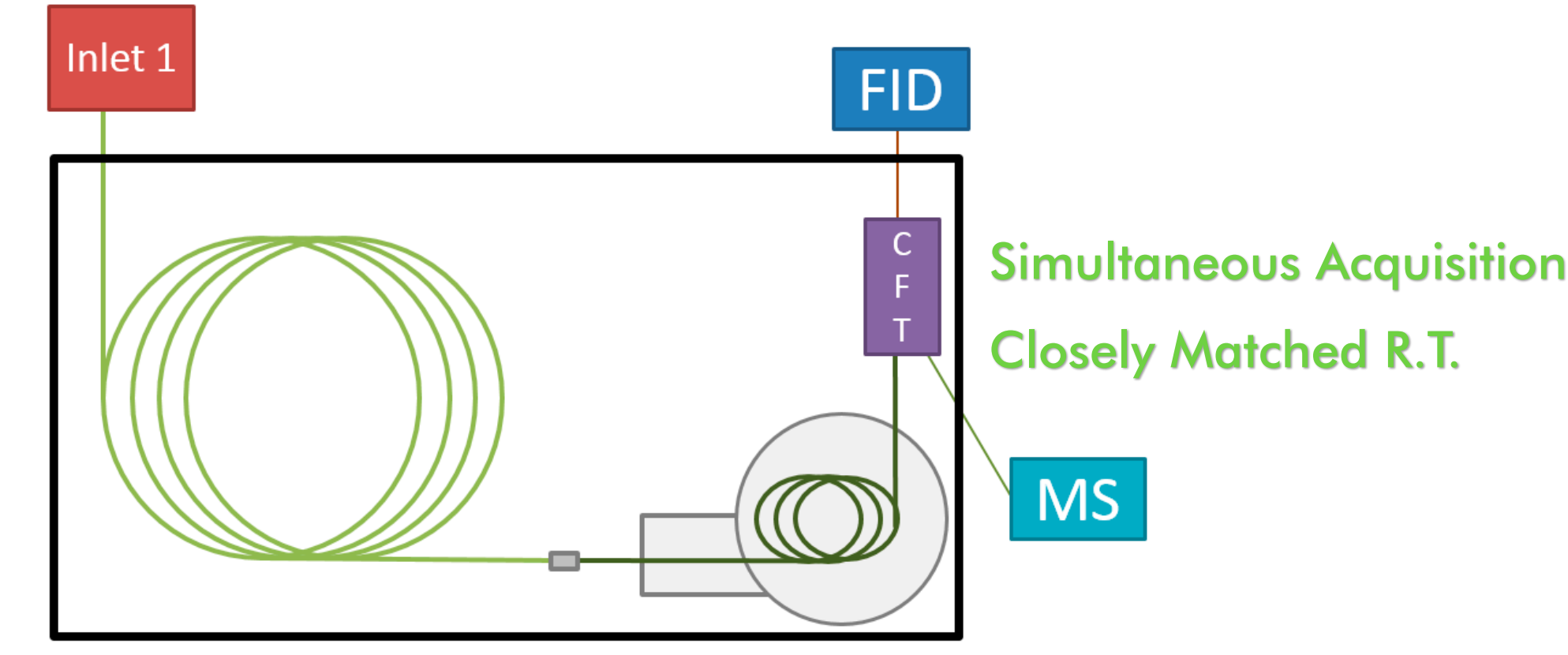

Configuration 1: Two inlets are each equipped with a primary column (30 m x 0.25 mm x 0.25 µm Rxi-5MS) connected to a secondary column (2 m x 0.25 mm x 0.25 µm). One column set routes to the FID, while the other column set routes to the MS.
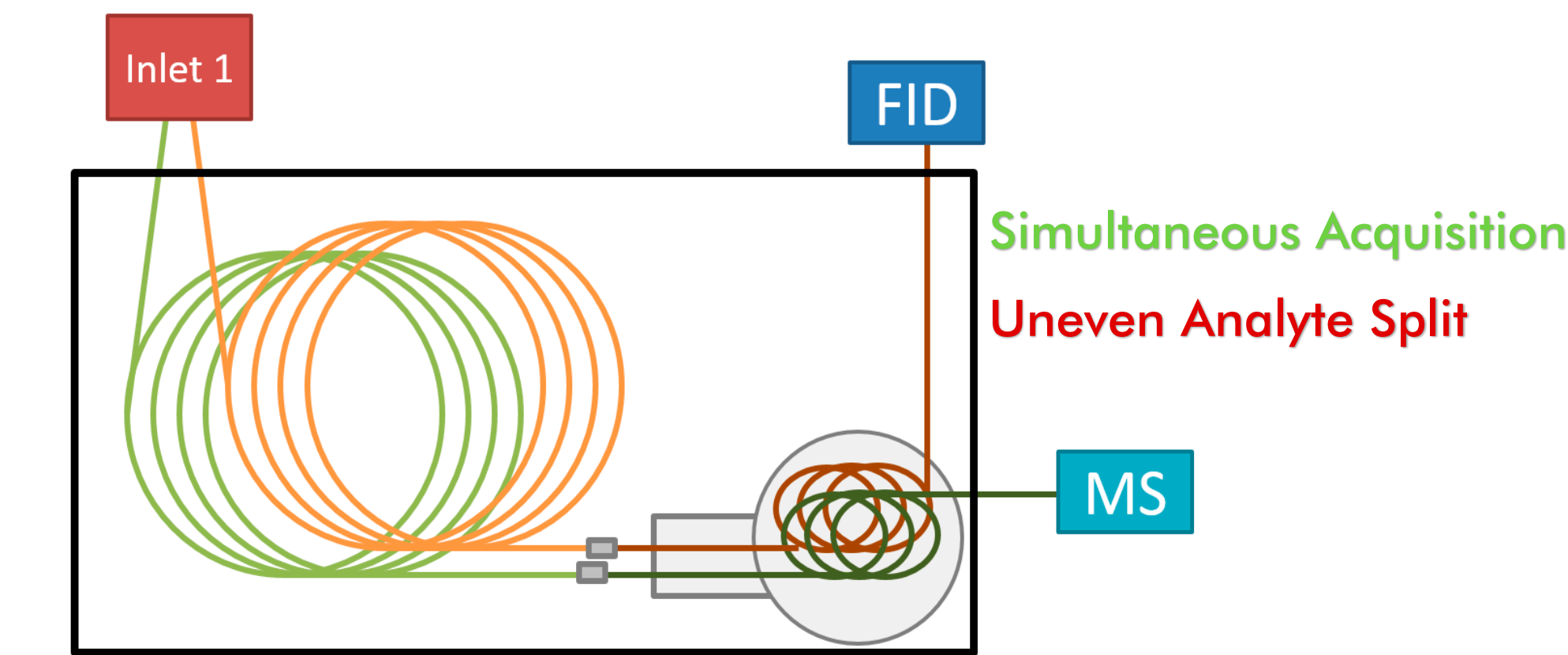
Configuration 2: Two independent column sets as described in Configuration 1 (left) were attached to a single inlet via a dual-holed ferrule. One column set routes to the FID, while the other column set routes to the MS.

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) using a low dead-volume Y-connector. An additional restrictive guard column (0.1 mm) routed to the mass spectrometer accounts for the difference between atmospheric and vacuum outlet detectors.

Configuration 4: One 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) is routed to a controlled flow splitter (CFT), which uses different lengths and diameters of restrictive tubing to evenly split analyte between the two detectors.

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 Parameters		
Transferline Temp (°C)	300	
Source Temp (°C)	200	
FID Parameters		
Data Collection Rate (Hz)	200	
Temperature (°C)	300	

MS Parameters		
Acquisition Rate (s/s)	200
Mass Range	35-500
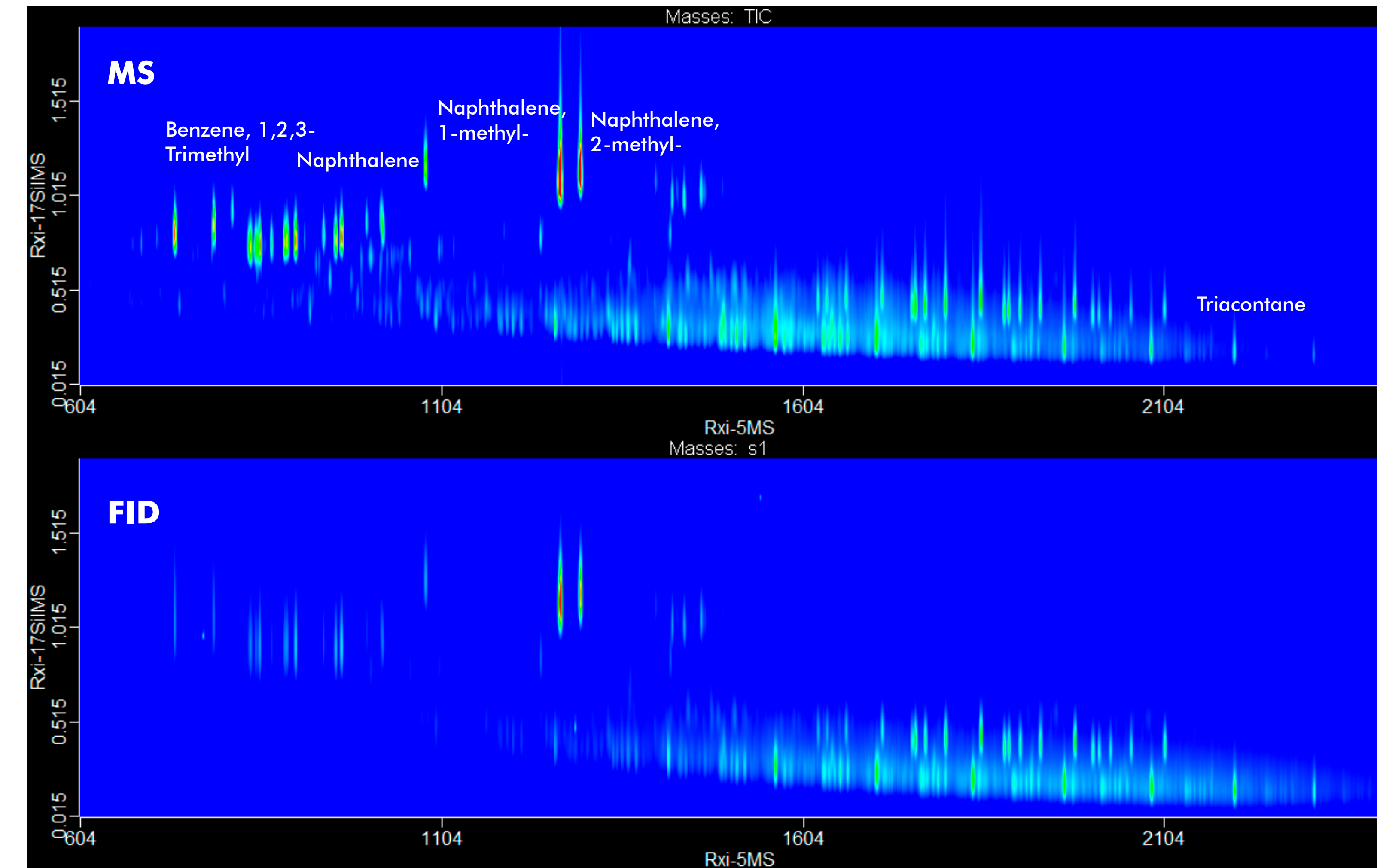
Diesel Sample

Diesel Sample Contour Plot: The contour plots above show data acquired in Configuration 4. Diesel Sample analytes are identified by GCxGC-MS, with the corresponding FID peaks shown below. Retention times are closely matched, facilitating MS-to-FID correlation of peaks
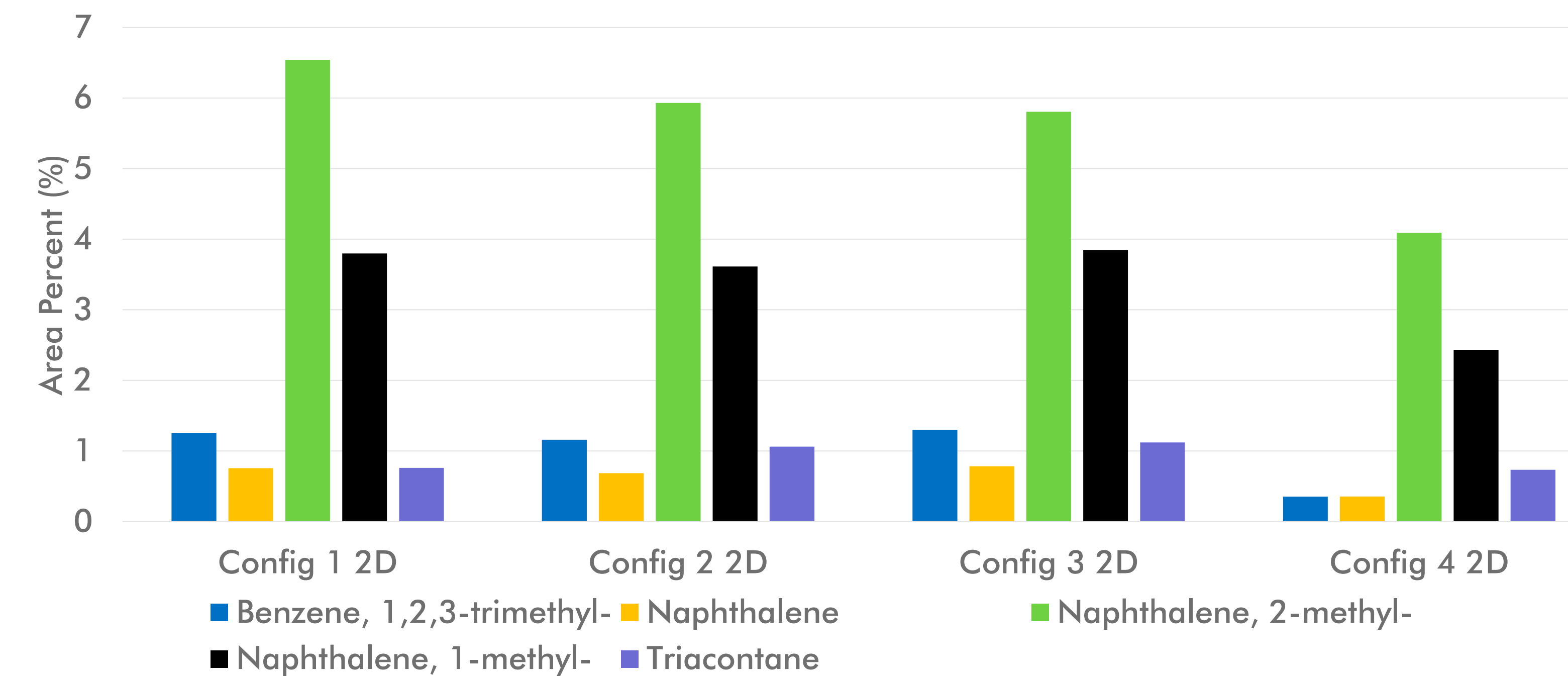

Diesel Sample Analyte Tables: The bar graphs above show the FID Area Percent values for Benzene,1,2,3-Trimethyl, Naphthalene, 2-Methylnaphthalene, 1-Methylnaphthalene, and Triacontane for GCXGC (2D) runs in all four configurations.

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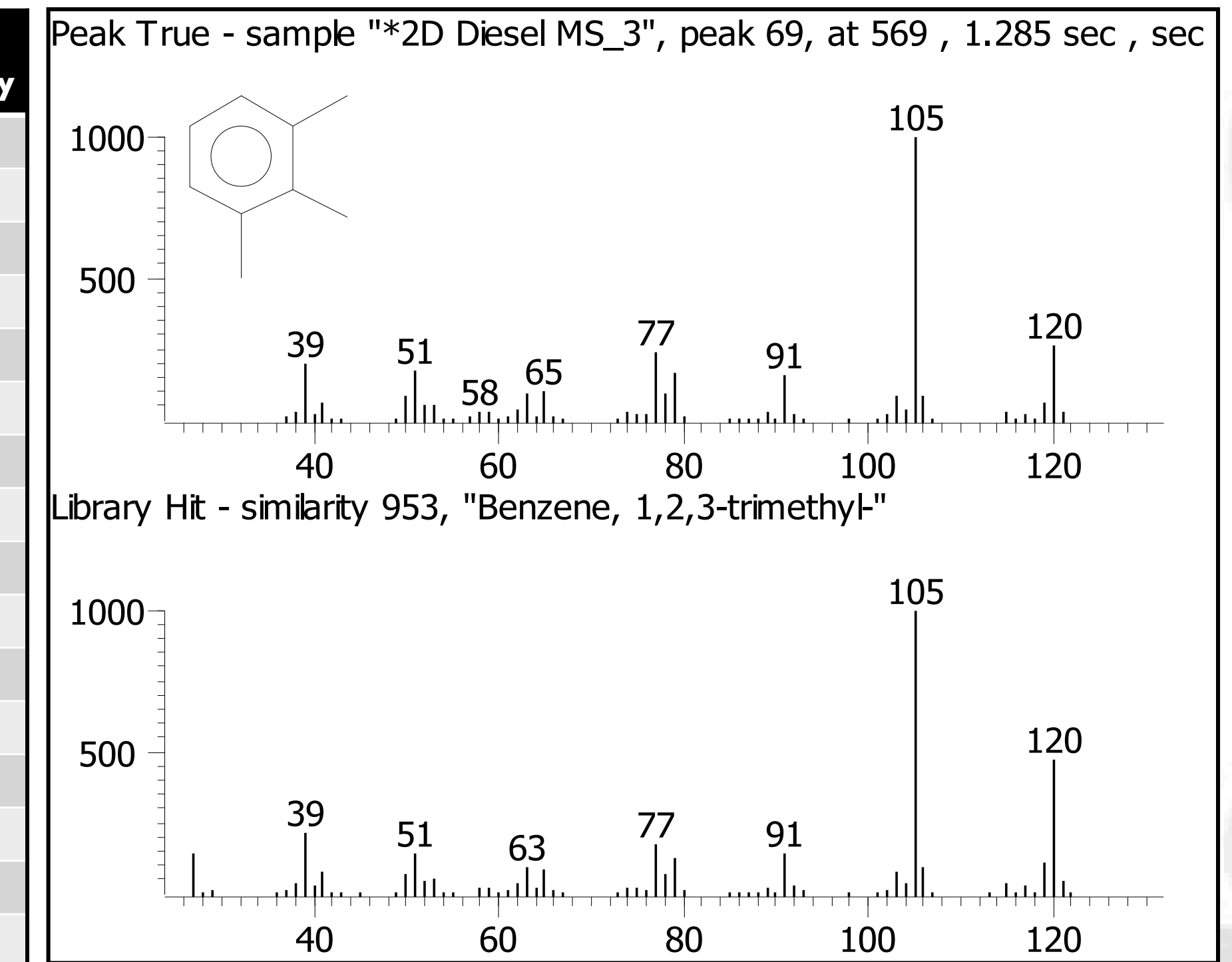
Spectral Similarity: The table above shows the excellent average similarity scores of analytes of interest across all configurations, which allow for confident identification of MS peaks.

Discussion

In every configuration with simultaneous acquisition, one of the chief difficulties was trying to match the flows between analyte streams, because of the difference between the atmospheric pressure of the FID and vacuum pressure from the MS. With the temperature ramp throughout the run, this also resulted in uneven splitting of analytes in Configurations 2 and 3. However, use of a controlled flow splitter (CFT) in Configuration 4 with properly calculated restrictor lengths and diameters going to each detector allowed for retention times to match within one modulation period.

GCXGC 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 4 would be the preferred method for analysis of petroleum products. Configuration 4 allowed for close alignment of peak retention times, greatly facilitating data interpretation. In addition, the integrity of the chromatographic resolution was maintained throughout the run, with the analyte flow only split when very close to each detector, allowing each individual peak from the FID trace to be properly integrated so that more accurate area percent values could be calculated, which led to slightly lower values than in Configurations 1-3. While there was some loss of sensitivity due to the additional analyte flow split, the ability to acquire FID and MS data simultaneously greatly reduced acquisition time, making analysis with two detectors both simpler and more efficient.

Delivering the Right Results