

**CRC Project AV-09-09**

**Initial Development of an  
Advanced Test Method for Jet Fuel  
Identification and Characterization**

**Phase 1**

**December 2010**



**COORDINATING RESEARCH COUNCIL, INC.**  
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## **CRC Project Final Report – Phase 1 – December 29, 2010**

### **Initial Development of an Advanced Test Method for Jet Fuel Identification and Characterization**

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#### **Executive Summary**

This is a report of progress toward developing an advanced test method for jet fuel identification and characterization using GC  $\times$  GC–TOFMS instrumentation. Sample selection, instrumental methods, and data analysis conducted relevant to the development of a test method are detailed in the report and appendices. Results give some compositional (chemical) characteristics of different fuel types, outline compositional trends (similarities and differences) among fuel types, demonstrate the advantage of GC  $\times$  GC over GC, and give further direction and insight into future investigation for characterization and identification of jet fuel using GC  $\times$  GC–TOFMS and GC  $\times$  GC instrumentation.

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Table 1: A summary of the chemical compositions of 13 different fuels by compound class.

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#### **Background**

This project explores the use of fast two-dimensional gas chromatography ( $GC \times GC$ ) with Time of Flight Mass Spectrometry (TOFMS) detection to elucidate the chemical compositions of current petroleum-based fuels as well as unconventional synthetic and alternative fuels.  $GC \times GC$  analysis provides extensive additional characterization information beyond what is available from one-dimensional gas chromatography (GC). This is accomplished by resolving standard GC chromatographic peaks in a second dimension taking advantage (for example) of polarity differences of multiple compounds that may be incorporated in a single GC peak. In other words, GC alone often results in convoluted peaks where confirmation of their identity with mass spectral (MS) analysis becomes quite difficult. Characterization of the thousands of compounds found in distillate fuels by  $GC \times GC$  greatly elucidates their make up with finer resolution and offers new opportunities for correlating fuel specifications and/or fuel performance as a function of fuel composition.  $GC \times GC$  can also offer finer resolution with increased speed (analysis time) compared to standard GC methods.

The primary goal of Phase 1 was to determine the extent to which the chemical information obtained from  $GC \times GC$ –TOFMS instrumentation can be used to more fully understand the nature and compositional distributions of conventional petroleum jet fuels and jet fuels derived from alternative sources. The intent was to qualitatively compare the data from  $GC \times GC$ –TOFMS instrumentation relative to the data obtained using GC-MS instrumentation. To achieve this goal, the two objectives were (1) to explore the use of  $GC \times GC$ –TOFMS detection to elucidate the chemical compositions of current petroleum-based fuels as well as unconventional synthetic and alternative fuels, ultimately using the instrument in a fast separation run mode, and (2) to establish a comprehensive fuel compositional database and determine the extent to which chemometric modeling of  $GC \times GC$ –TOFMS can be used to rapidly determine fit for purpose. To achieve these objectives, the proposed research was separated into two phases, with Phase 1 focusing on the first objective, and with Phase 2 planned to focus on the second objective.

#### **Experimental Materials**

We began by selecting 99 samples for analysis from among the 966 samples contained in the provided NRL Calibration Fuel sample key spreadsheet. Samples were chosen so that each type of fuel was represented. Further details of the sample selection are included in Appendix A.

#### **Experimental Approach**

To better understand the nature and compositional distributions of these fuels (from conventional petroleum fuels as well as fuels derived from alternative sources), 13 samples were selected, each representing a different fuel type; these were analyzed using a slightly modified in-house standard diesel analysis method on a Leco Pegasus III 4D instrument ( $GC \times GC$ –TOFMS), with the methods used described in the following paragraph:

An autoinjector (Agilent 7683 series) was used with a 10  $\mu$ L syringe, delivering 1  $\mu$ L of sample to the inlet for each replicate. Samples were injected neat (with no liquid solvent dilution) and the syringe rinsed with acetone between runs. The inlet was configured for a 200:1 split, and used a complex pressure program that essentially corrected the second column flow to be constant and approximated a constant flow of 2.0 mL He/min. The capillary GC columns used were: column 1: 20 m, 250  $\mu$ m ID, 0.5  $\mu$ m X-5 film; column 2: 2 m, 180  $\mu$ m ID, 0.2  $\mu$ m X-200 film. The chromatographic temperature profile used was as follows. The temperature program for column 1 began at 50  $^{\circ}$ C for 0.25 min, then ramped at 5  $^{\circ}$ C/min up to 300  $^{\circ}$ C, which was held for 5 min. The temperature program for column 2 was the same except all temperatures were 5  $^{\circ}$ C higher. The inlet was set at 275  $^{\circ}$ C, the modulator block for +20  $^{\circ}$ C, and the transfer line at 305  $^{\circ}$ C. Full mass spectra ( $m/z$  12 to 340) were collected at 100 spectra/s after 6 s into each run. A modulation period of 1.5 s was used, where the modulation period is the separation time on column 2.

We next developed a faster (15 min run time, 25 min cycle time) GC  $\times$  GC–TOFMS instrumental method for analysis of all 99 samples provided by Robert Morris (Naval Research Laboratory). Each of the 99 samples was run on the instrument 4 times (yielding 4 replicates) using this fast method. Details of this method follow. An autoinjector (Agilent 7683 series) was used with a 5  $\mu$ L syringe, delivering 0.5  $\mu$ L of sample to the inlet for each replicate. Samples were injected neat (with no liquid solvent dilution) and the syringe rinsed with acetone between runs. The inlet was configured for a 150:1 split, and was set to constant flow mode at 2.0 mL He/min. The capillary GC columns used were: column 1: 20 m, 250  $\mu$ m ID, 0.5  $\mu$ m X-5 film; column 2: 2 m, 180  $\mu$ m ID, 0.2  $\mu$ m X-200 film. The chromatographic temperature profile used was as follows. The temperature program for column 1 began at 40  $^{\circ}$ C for 1 min, then ramped at 20  $^{\circ}$ C/min up to 290  $^{\circ}$ C, which was held for 1.5 min. The temperature program for column 2 was the same except all temperatures were 10  $^{\circ}$ C higher. The inlet was set at 280  $^{\circ}$ C, the modulator block for +15  $^{\circ}$ C, and the transfer line at 290  $^{\circ}$ C. Full mass spectra ( $m/z$  12 to 502) were collected at 200 spectra/s after 30 s into each run. A modulation period of 0.5 s was used to ensure that there would be at least 3 (more typically 4) modulations across each peak along the first separation dimension.

## Results

Total ion current (TIC) chromatograms of each of the 13 representative samples analyzed are shown in the figures below along with annotations of selected compounds of interest detected in the samples. Also shown are a figure outlining the retention structure of a number of major compound classes in these separations (Figure 1) and a figure highlighting the difference in separation power of these compounds obtained using GC  $\times$  GC vs. GC analysis by means of a peak maximum finding algorithm (Figure 3), with GC chromatograms for this and subsequent figures obtained by summing across the second separation dimension of the GC  $\times$  GC data. Therefore, the GC chromatograms shown here are formed from eliminating the column 2 separation information by reducing each separation in the column 2 dimension down into a single point. In the peak finding comparison between GC  $\times$  GC and GC, we typically located about four times the number of peaks in a given separation time using GC  $\times$  GC as compared with using GC. Each of the different fuel types analyzed generally showed significant visible differences in chemical composition from the other fuel types, so the capabilities of GC  $\times$  GC–TOFMS to characterize fuel composition and to determine the chemical similarity (or differences between) fuels in the training set fuels was established. Example TIC chromatograms from some of the 99 sample replicates run with the fast method are included in Appendix B.

## Conclusions

To summarize the results of the GC  $\times$  GC–TOFMS analysis of the 13 different fuels shown in the figures below (Figures 2, 4–15), we present Table 1, which outlines the compositional distribution by compound class. Structural annotation of the compounds shown in each of Figures 2 & 4–15 was based on both mass spectrum and Kovat's retention indices of the compound for the stationary phases employed, using the NIST database as reference. Compounds may elute at a different time or order than expected in another analysis due to the particular stationary phase used, the fact that retention occurs across two different stationary phases, and different instrumental conditions such as temperature program and carrier gas flow rate. A fuel-by-fuel comparative compositional analysis is included in each of the respective figure captions, compositional trends across the different fuels are given in Table 1, and many specific compounds are annotated in the chromatograms in Figures 2, 4–15. Results in Table 1 are very promising in relation to an ultimate goal of correlating fuel performance data with chemical composition (group type) information provided by the 2D GC  $\times$  GC (Figure 1) information.

## Recommendations for Future Work

For future work, including a comprehensive principal component analysis (PCA) may provide clustering in scores plots and may enable similar fuels to be differentiated, which in turn would lead to chromatographic (and  $m/z$ ) locations (and thus compounds), that can better differentiate the different fuels. In addition, partial least squares (PLS) models of preprocessed data could lead to more discriminating or selective analyses for physical properties (those for which sufficient data was provided) or between the different fuel types, again pointing to compositional differences in different fuel samples or types. Although not a part of the statement of work for the present project, using enough samples, compositional bounds for fuels in terms of commonly measured properties could also be defined through these types of analyses.

(Figures begin on next page.)



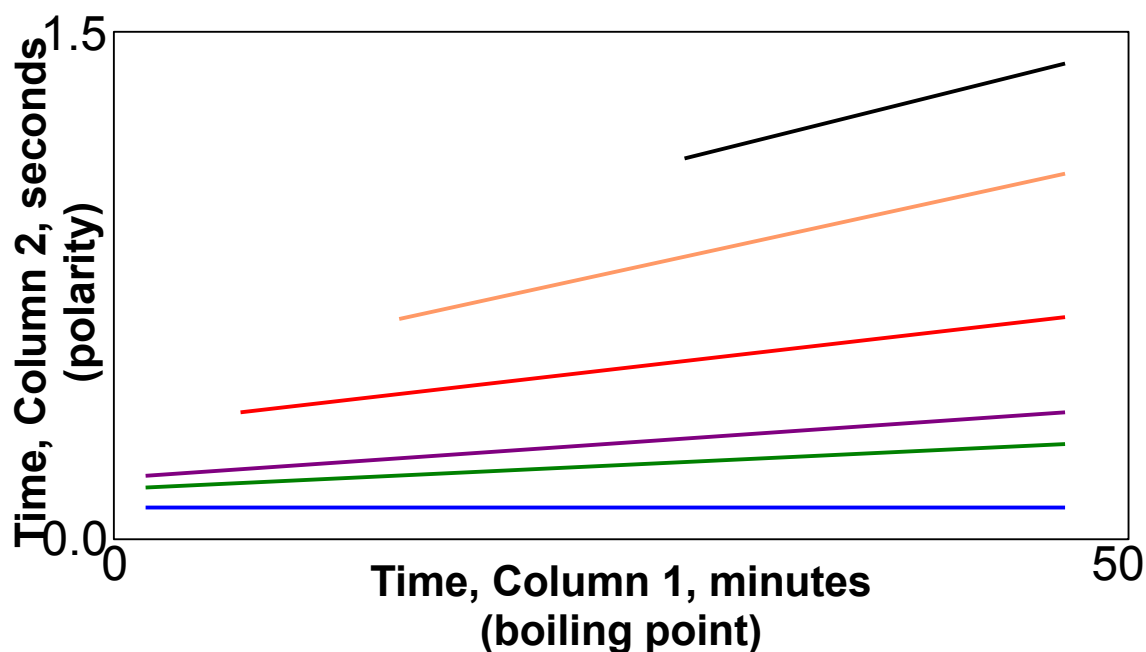


Figure 1: The retention structure of several chemical classes for the separation conditions used is shown above. Classes are (from bottom to top): blue – alkanes, green – branched alkanes, purple – cycloalkanes, red – monoaromatics, orange – diaromatics, black – polyaromatics. The scale on the y-axis is from 0 to 1.5 seconds, and the scale of the x-axis is from 0 to 50 minutes retention time.

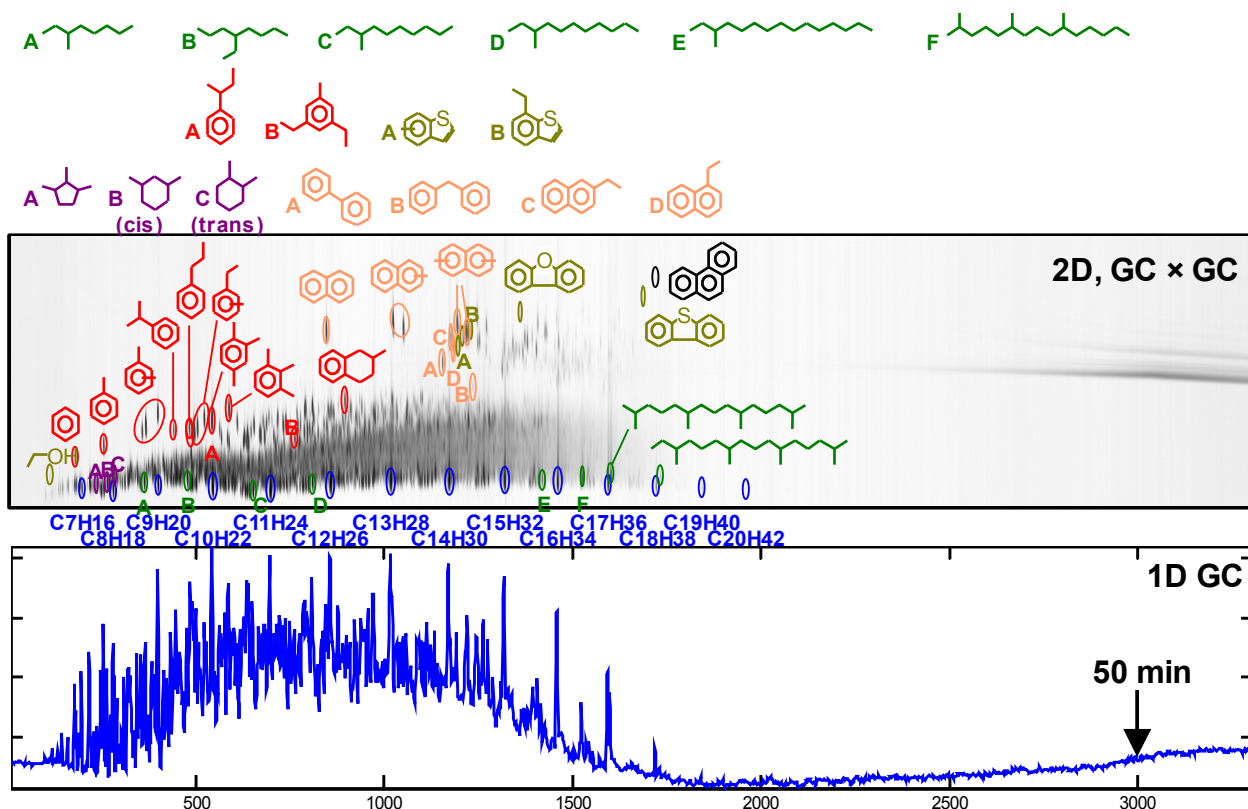


Figure 2: 2D GC×GC and GC chromatograms (TIC) of sample C3 (Jet A) are shown above annotated with some compounds of interest. The column 1 retention times (s) are vertically aligned.

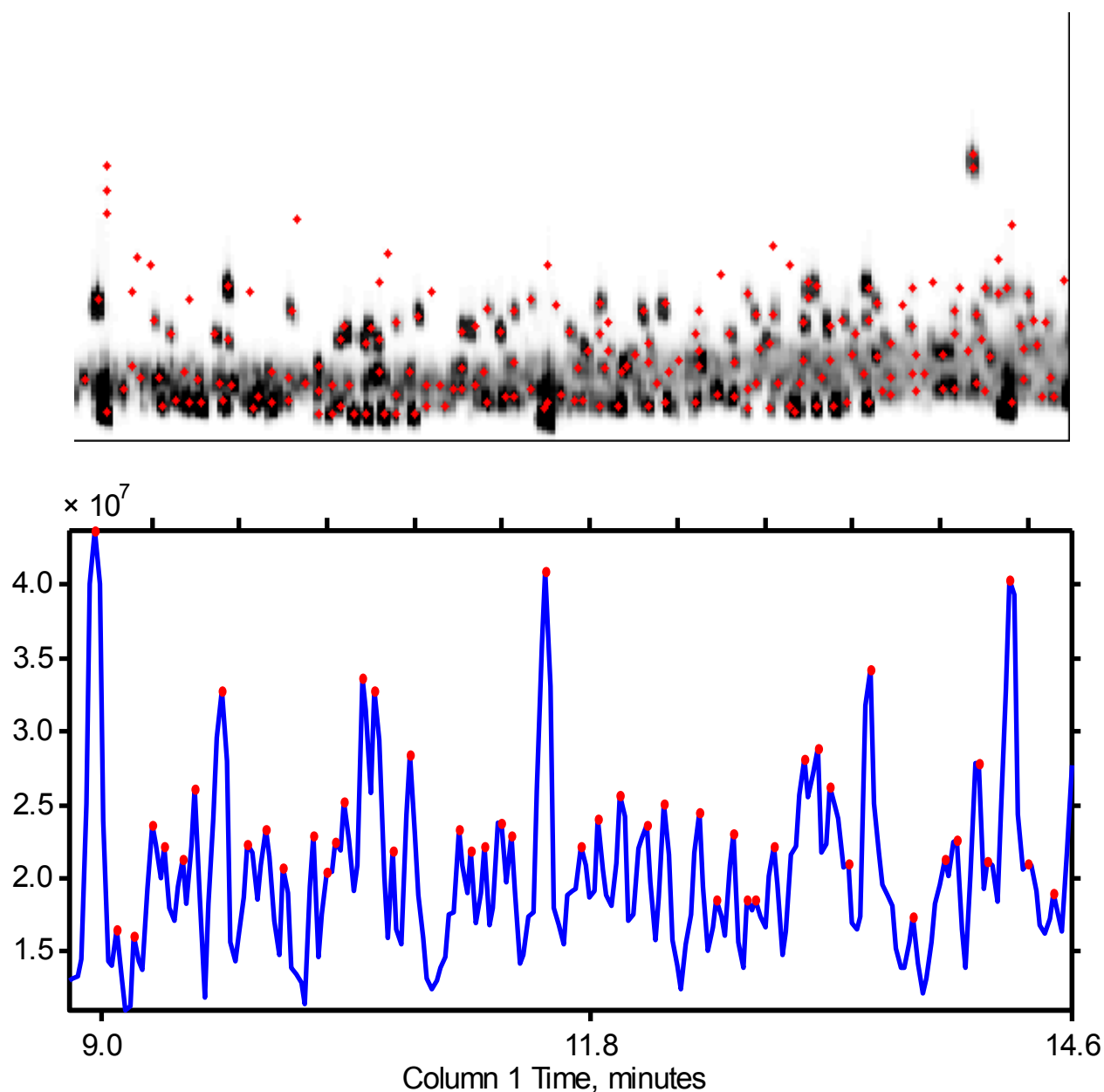


Figure 3: A comparison of the number of peaks detected in a subsection of the GC $\times$ GC and GC chromatograms (shown in the previous figure) using a local maximum-based peak finding algorithm. 201 peaks were found in the GC $\times$ GC subsection, while 49 peaks were found in the same subsection of the GC chromatogram.

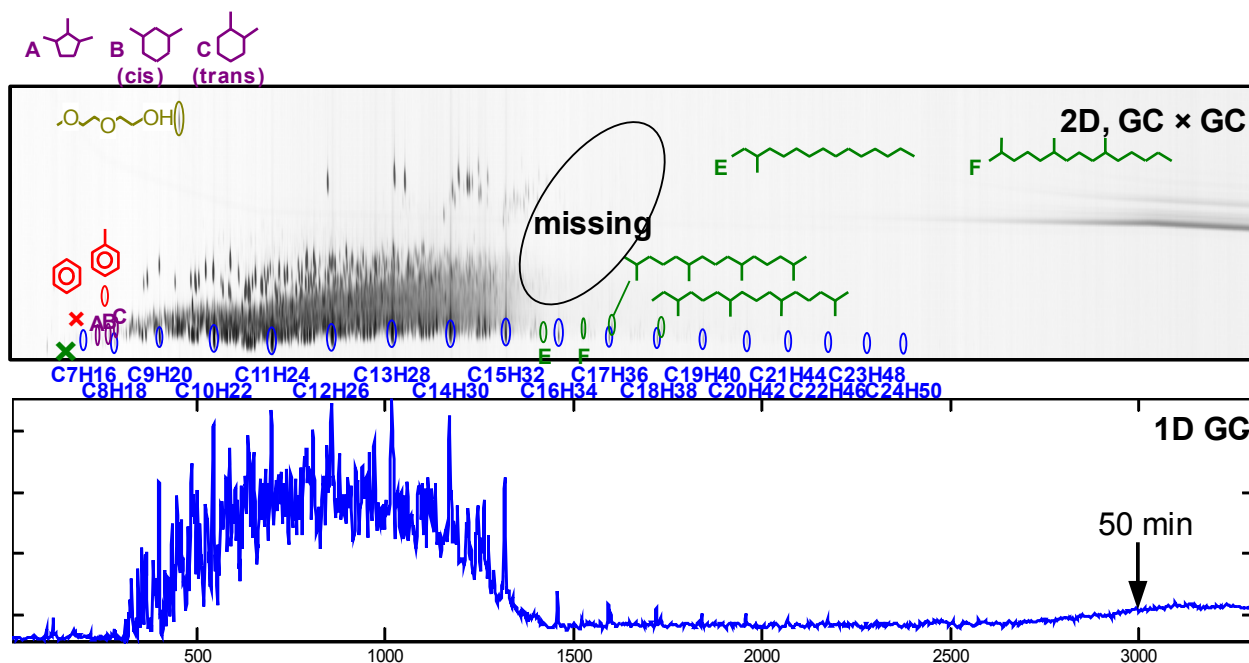


Figure 4: 2D GCxGC and GC chromatograms (TIC) of sample C146 (downgraded jet fuel) are shown above annotated with some compounds of interest. The column 1 retention times (s) are vertically aligned. X markers indicate compounds not seen in this sample that are seen in sample C3. For this sample, some of the more volatile compounds seen in C3 are missing, as well as many of the heavier aromatics.

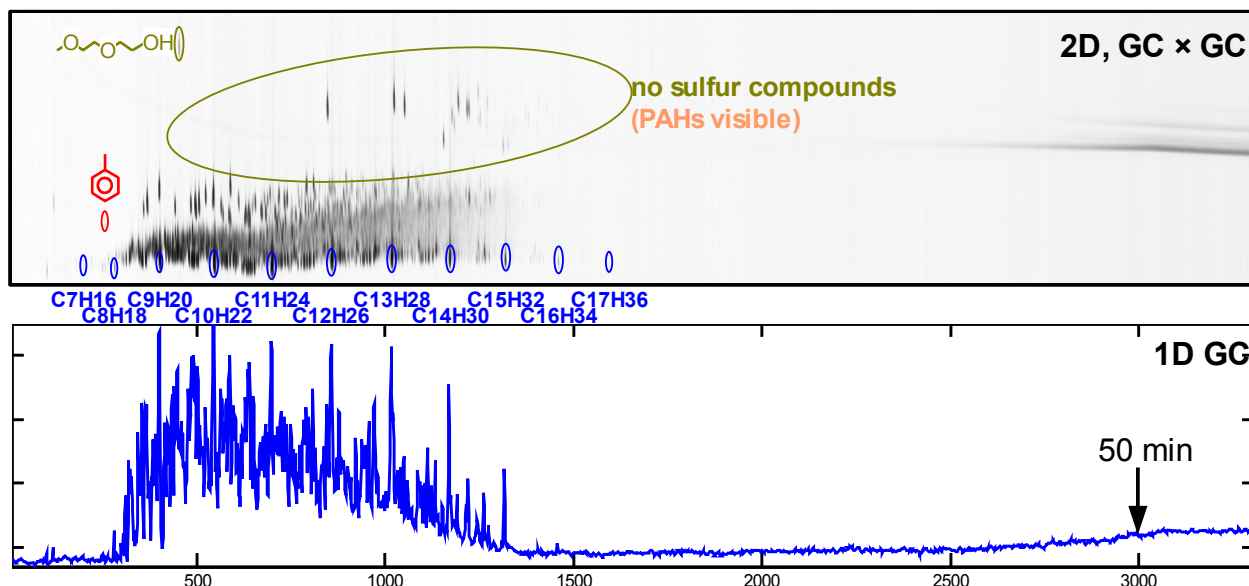


Figure 5: 2D GC×GC and GC chromatograms (TIC) of sample C378 (JPTS) are shown above annotated with some compounds of interest. The column 1 retention times (s) are vertically aligned. Sulfur containing compounds present in C3 are not visible in the 2D GC×GC chromatogram. There is also a slightly narrower boiling point distribution with more compounds with lower boiling points compared with C3.



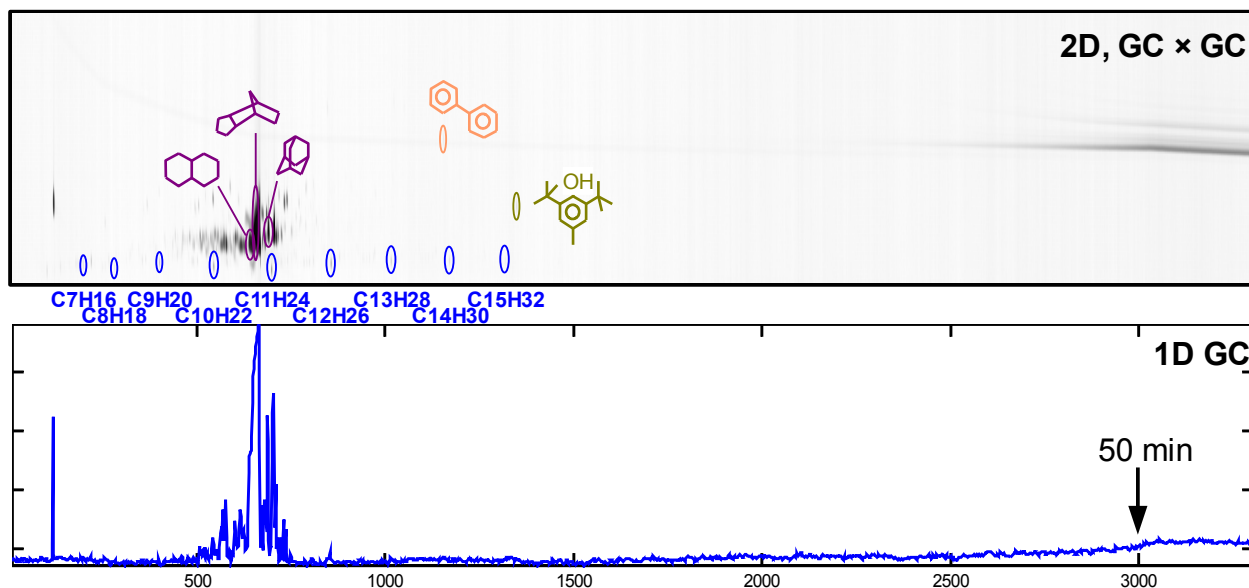


Figure 7: 2D GC×GC and GC chromatograms (TIC) of sample C247 (JP10) are shown above annotated with some compounds of interest. The column 1 retention times (s) are vertically aligned. This sample consists primarily of cyclic alkanes, with some alkane, branched alkane, and aromatic compounds also present. Butylated hydroxytoluene is also present, likely added as an antioxidant, but no other oxygenated compounds are readily visible.

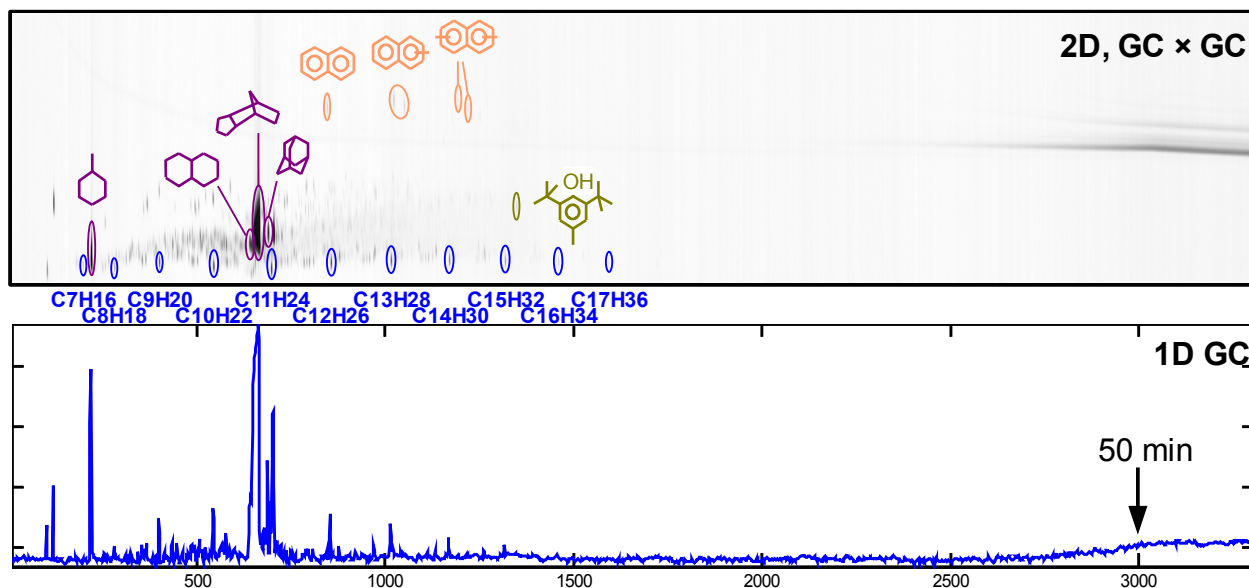


Figure 8: 2D GC×GC and GC chromatograms (TIC) of sample C268 (priming fluid) are shown above annotated with some compounds of interest. The column 1 retention times (s) are vertically aligned. This sample could be a mixture of JP10 and jet fuel. However, it contains a significant amount of methylcyclohexane not seen in sample C247.

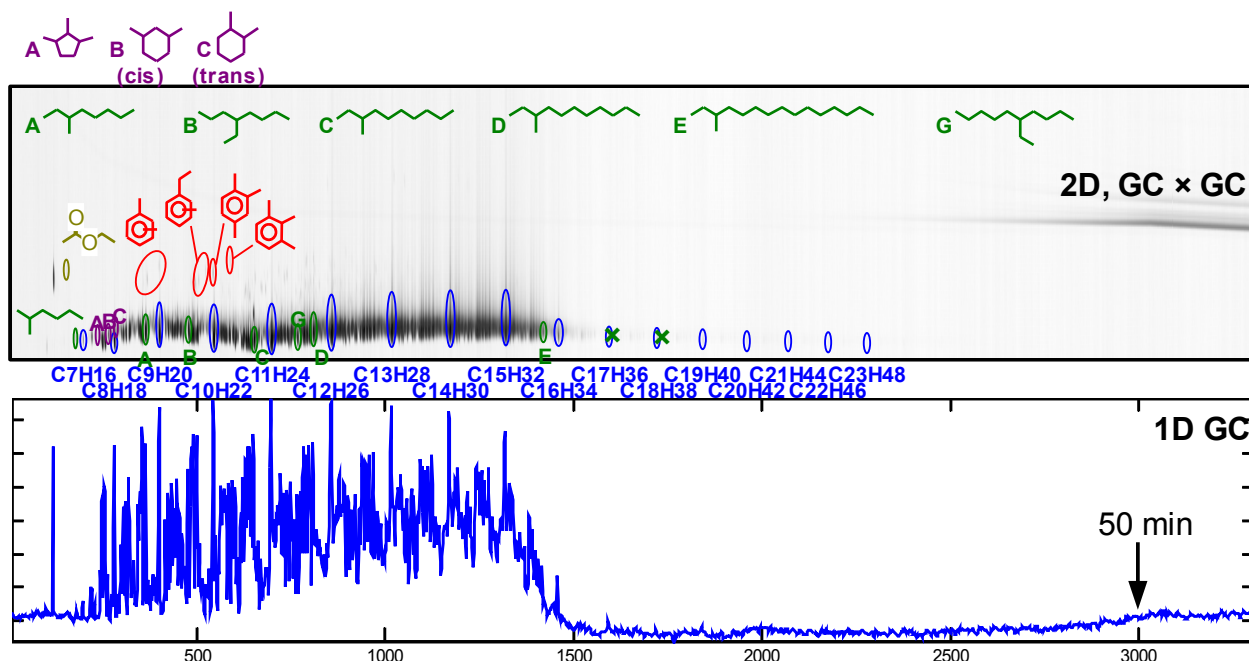
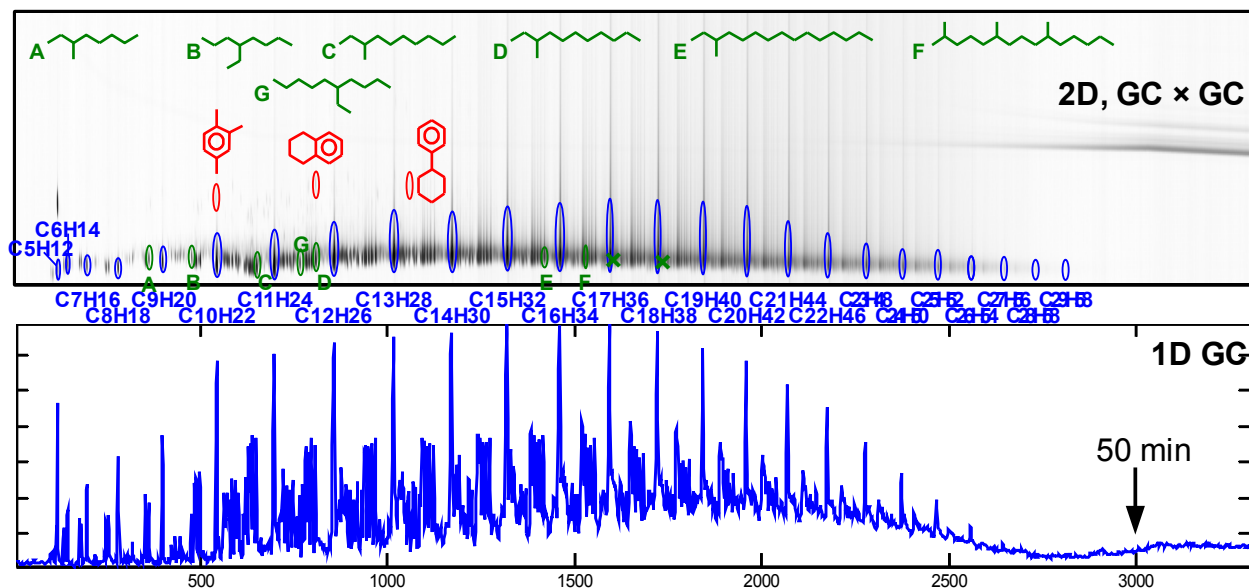


Figure 9: 2D GCxGC and GC chromatograms (TIC) of sample C435 (Fischer-Tropsch jet fuel) are shown above annotated with some compounds of interest. The column 1 retention times (s) are vertically aligned. This sample consists primarily of branched and normal alkanes, with much fewer aromatic compounds visible than for a petroleum-derived fuel. As expected, the pristane and phytane peaks present for petroleum-derived fuels (containing the sufficiently high boiling point compounds) are not visible (green X's).





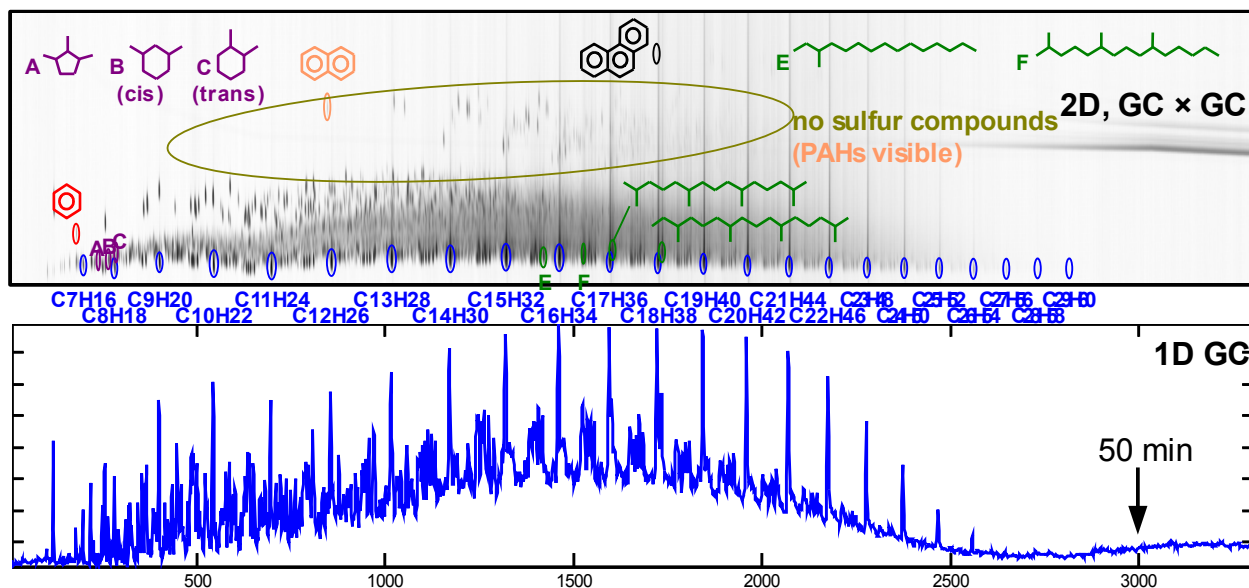


Figure 11: 2D GCxGC and GC chromatograms (TIC) of sample C840 (ultra-low sulfur diesel fuel) are shown above annotated with some compounds of interest. The column 1 retention times (s) are vertically aligned. This sample is somewhat similar to C3, but contains higher boiling point compounds and much fewer heteroatom containing compounds. As such, it resembles a typical ULSD.

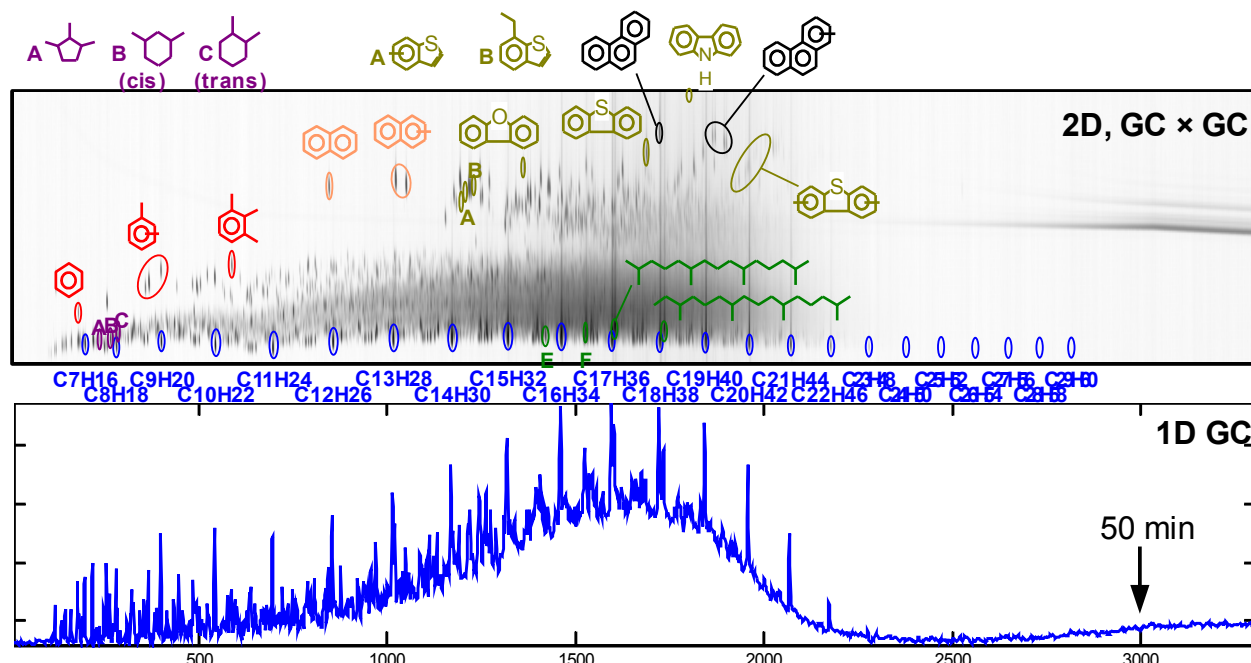


Figure 12: 2D GC×GC and GC chromatograms (TIC) of sample C56 (F76) are shown above annotated with some compounds of interest. The column 1 retention times (s) are vertically aligned. This sample appears similar to diesel fuel, but contains more aromatic and heteroatom containing compounds (particularly for the higher boiling point compounds).

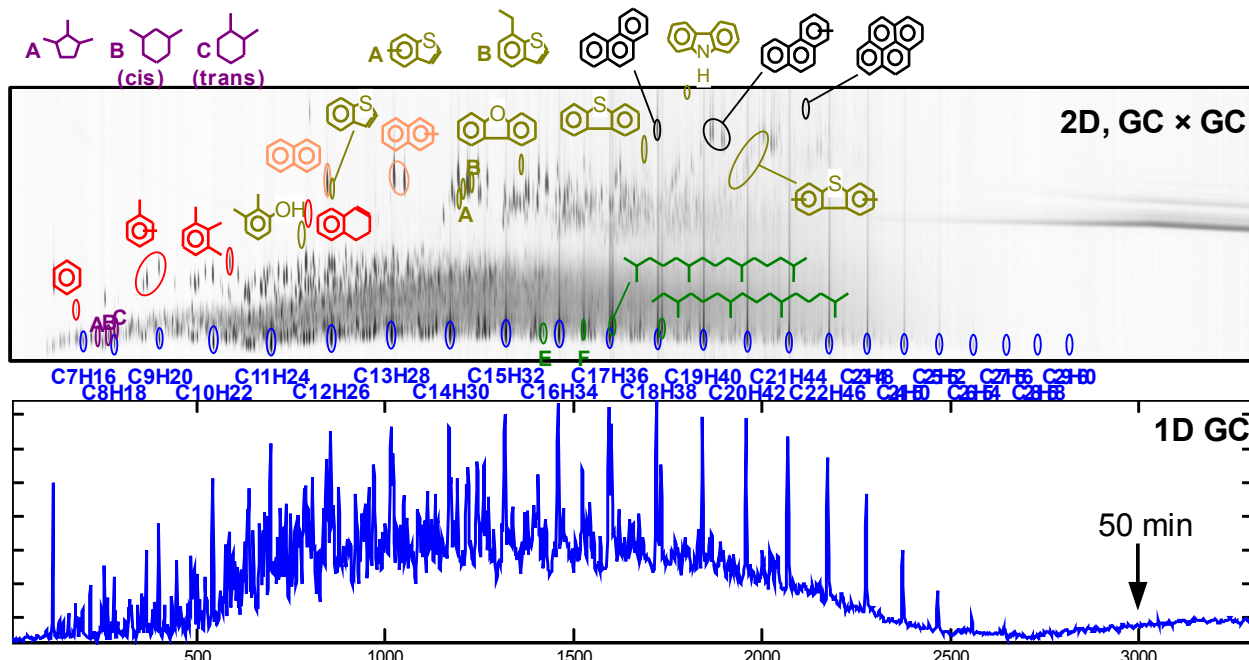


Figure 13: 2D GC×GC and GC chromatograms (TIC) of sample C783 (marine gas oil) are shown above annotated with some compounds of interest. The column 1 retention times (s) are vertically aligned. This sample appears similar to F76, but contains even more aromatic and heteroatom containing compounds (particularly for the higher boiling point compounds). However, the boiling point distribution of this sample is more similar to diesel.

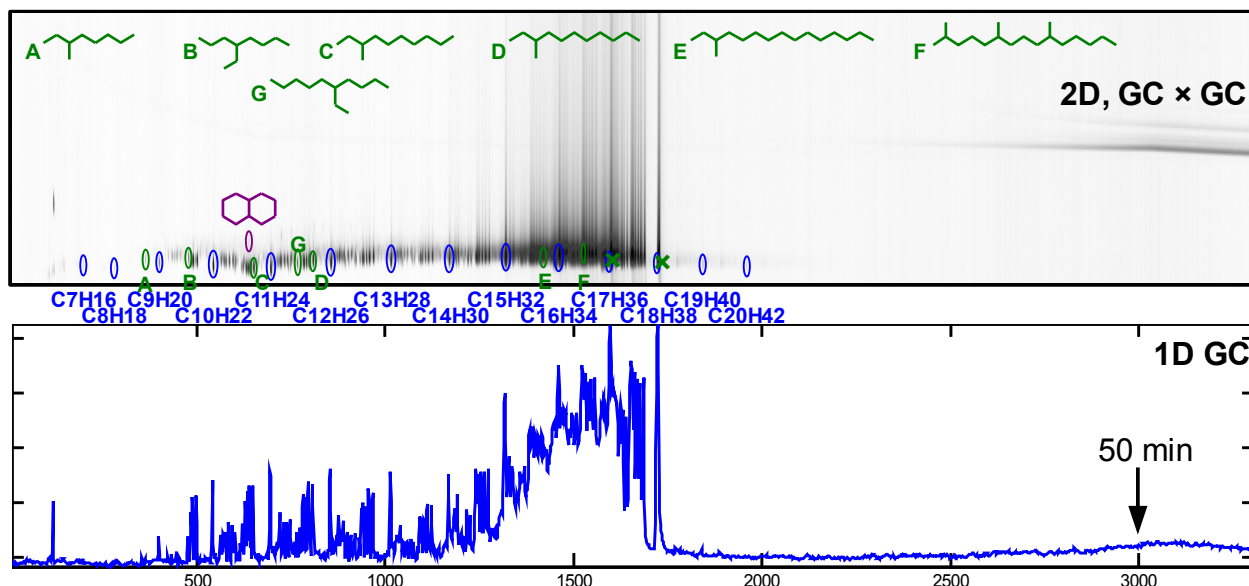


Figure 14: 2D GC×GC and GC chromatograms (TIC) of sample C992 (hydrotreated fatty-acid methylesters) are shown above annotated with some compounds of interest. The column 1 retention times (s) are vertically aligned. This sample appears similar to a Fischer-Tropsch jet fuel (primarily containing branched and normal alkanes), although the distribution of some of the branched compounds appears to be different. Again, no pristane or phytane peaks are visible (green X's).

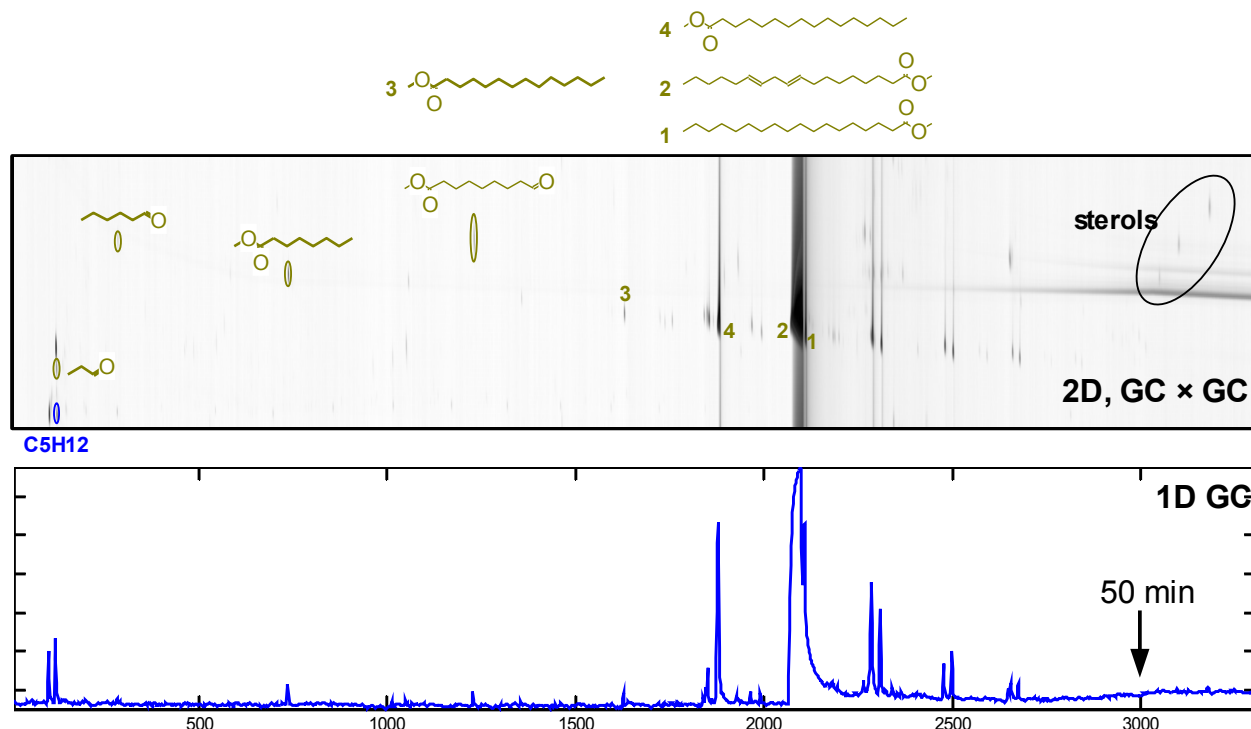


Figure 15: 2D GC×GC and GC chromatograms (TIC) of sample C822 (B100) are shown above annotated with some compounds of interest. The column 1 retention times (s) are vertically aligned. This sample mostly consists of a few fatty-acid methylesters (some saturated, others not, and primarily of about five different chain lengths). As opposed to the other samples where there are obvious benefits in resolving compounds of different classes when using GC×GC, this sample is simple enough that GC-MS analysis alone would suffice (although some benefit from the GC×GC retention structure does remain).

Figure #	Sample	Type	alkanes	branched alkanes	cyclic alkanes	mono-aromatics	di-aromatics	poly-aromatics	heteroatomics
2	C3	Jet A	yes; high concentrations, C6-C20	yes; many	yes	yes; many	yes; many	yes; only phenanthrene visible	yes; sulfur containing cyclics, dibenzofuran, some alcohol
4	C146	dg-jet	yes; high concentrations, C6-C24	yes; many	yes	yes; many	yes; many, but fewer more substituted	no	yes; sulfur containing cyclics, some alcohols
5	C378	JPTS	yes; high concentrations, C6-C17	yes; many	yes	yes; many	yes; many, but fewer more substituted	no	only 2-(2-methoxyethoxy)-ethanol
6	C17	st-solvent	yes; high concentrations, C7-C15	yes; many	yes	yes; many	yes; few	no	yes; various oxygenated compounds
7	C247	JP10	yes; lower concentrations, C7-C15	yes; few	yes; very concentrated	yes; some	yes; very little	no	BHT
8	C247	priming	yes; lower concentrations, C6-C17	yes; many	yes; very concentrated	yes; some	yes	no	BHT
9	C435	FTJ	yes; lower concentrations, C7-C23	yes; many	yes	yes; some	no	no	ethyl acetate
10	C432	FTD	yes; lower concentrations, C5-C29	yes; many	yes; few	yes; some	no	no	no
11	C840	ULSD	yes; high concentrations, C6-C29	yes; many	yes	yes; many	yes; many	yes; only phenanthrene visible	no
12	C56	F76	yes; high concentrations, C6-C29	yes; many	yes	yes; many	yes; many	yes	yes; thiophenes, furans, carbazole
13	C783	MGO	yes; high concentrations, C6-C29	yes; many	yes	yes; many	yes; many	yes	yes; various oxygenated compounds, thiophenes, furans, carbazole
14	C992	HT-FAME	yes; high concentrations, C7-C20	yes; many	yes; few	no	no	no	no
15	C822	B100	no	no	no	no	no	no	yes; FAMEs with chain lengths ~8-22, aldehydes, some other oxygenated

Table 1: A summary of the chemical compositions of 13 different fuels by compound class, as provided by locations in the 2D separation space. For more details on the specific compounds, see Figures 2, 4–15.

## **Appendix A.**

### **Sample Selection Details.**

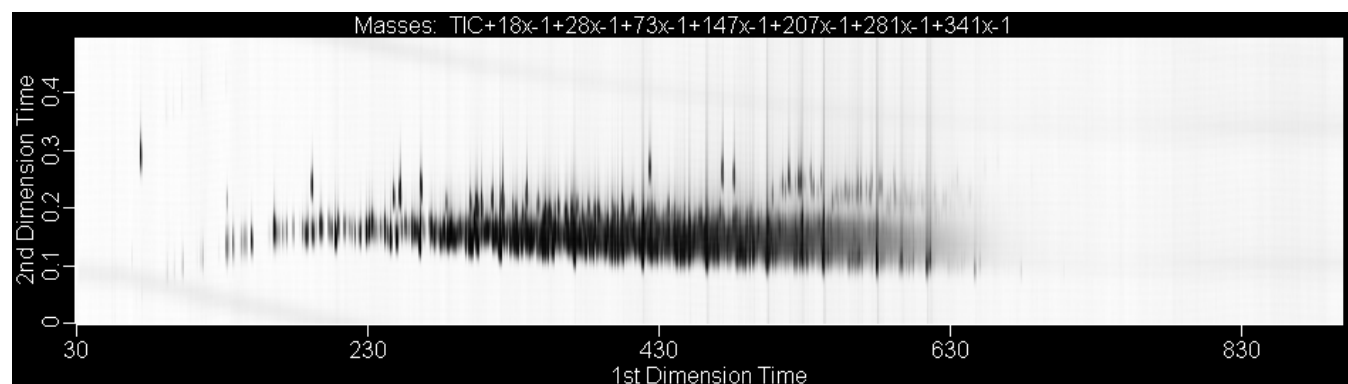
1. Samples were separated by category (i.e. jet fuel, MGO, nonfuel, etc.) so as to include samples from each category.
2. Samples labeled as outliers (not including downgraded fuels) were removed.
3. For those categories with more than 14 samples (except the synthetic blends i.e. FT fuels), a design of experiments using Kennard-Stone Uniform mapping of the optimal design space. [Ref: Technometrics Vol. 11 Number 1, 1969] to reduce the number of samples down to 14. The key variables used for this were: Flash point, Freeze point, IBP, 90% BP, and FBP.
4. Samples having few measured property values (especially for the key properties) were removed from the list.
5. Duplicate samples in origin, date, and property values were removed from the list. This was done such that the replicates chosen to be removed were picked at random. From subsequent instrumental analysis, none of the samples chosen by the Kennard-Stone method appeared to be duplicates.



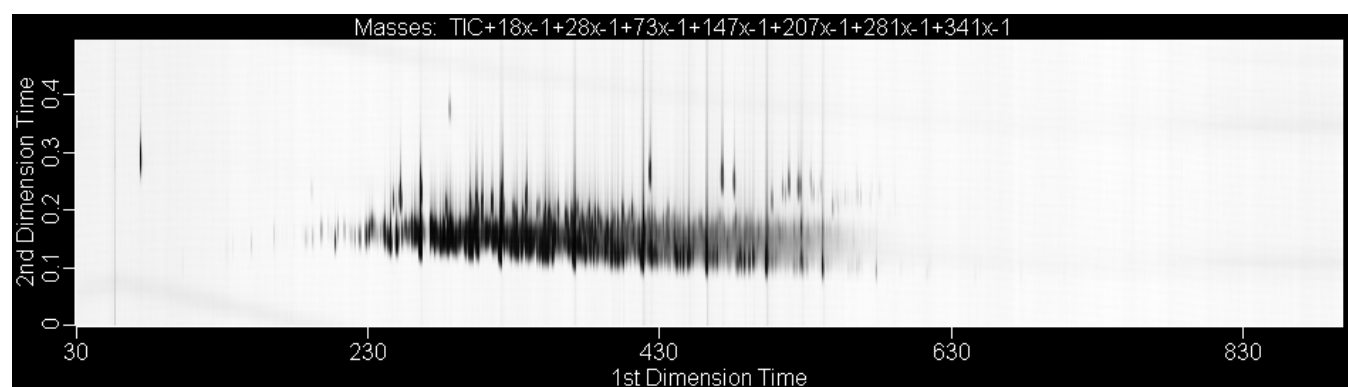
## Appendix B.

Example TIC Chromatograms From the Set of 99 Fuels Run using the Fast Method.

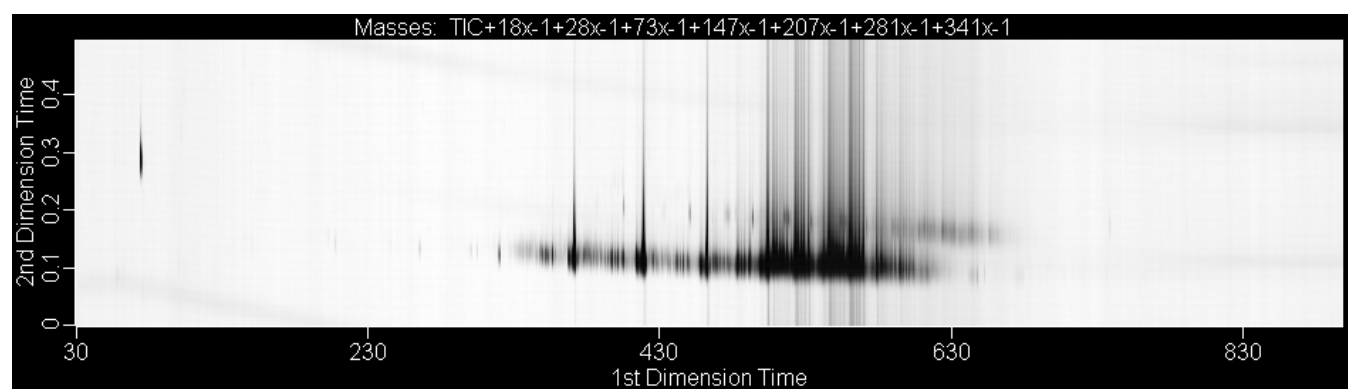
Sample name, fuel type, and replicate number are given for each of the shown TIC chromatograms.



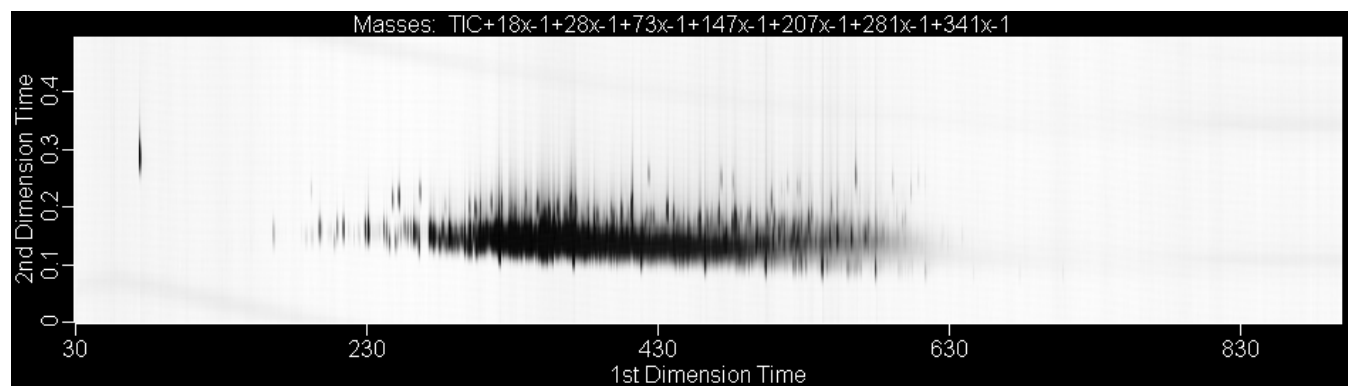
C3 Jet A (rep.3)



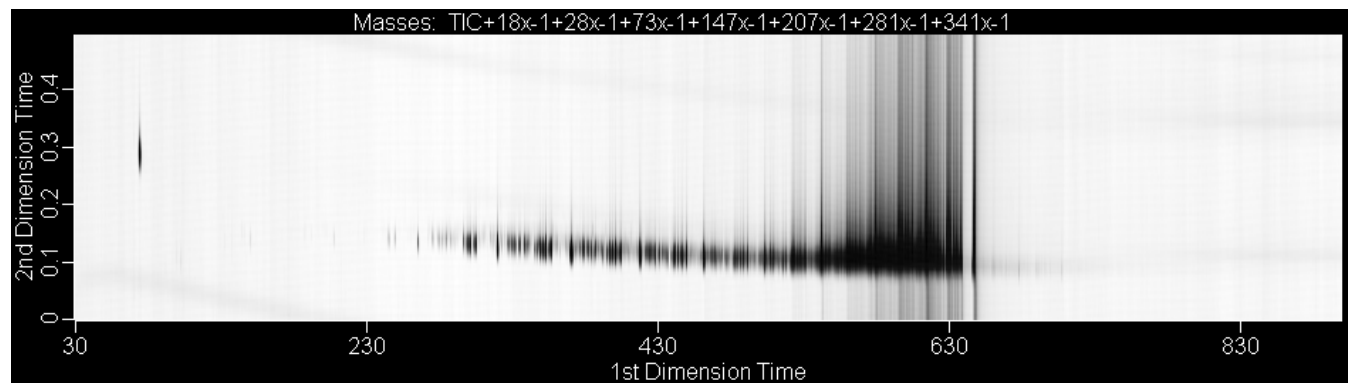
C290 JPTS (rep.1)



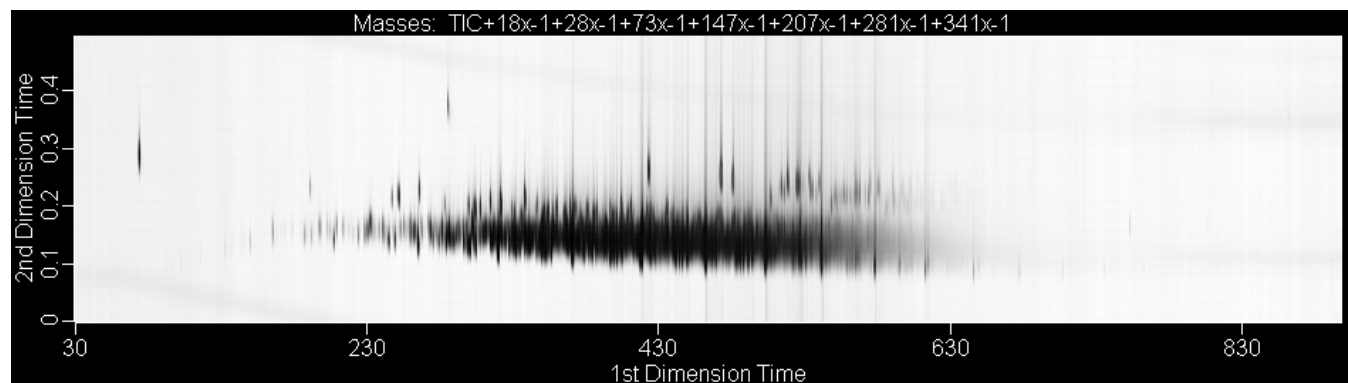
C433 FTD (rep.4)



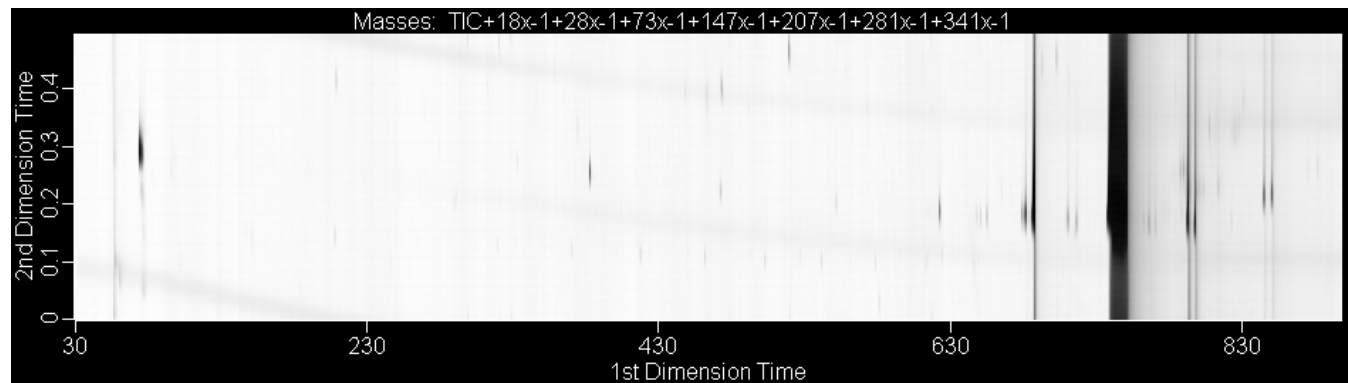
C436 FTJ (rep.2)



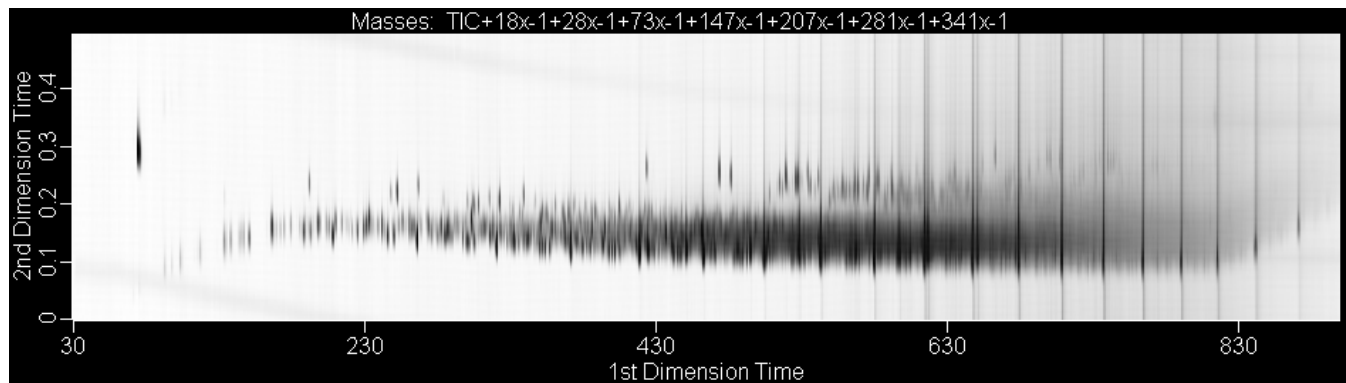
C992 HTFAME (rep.1)



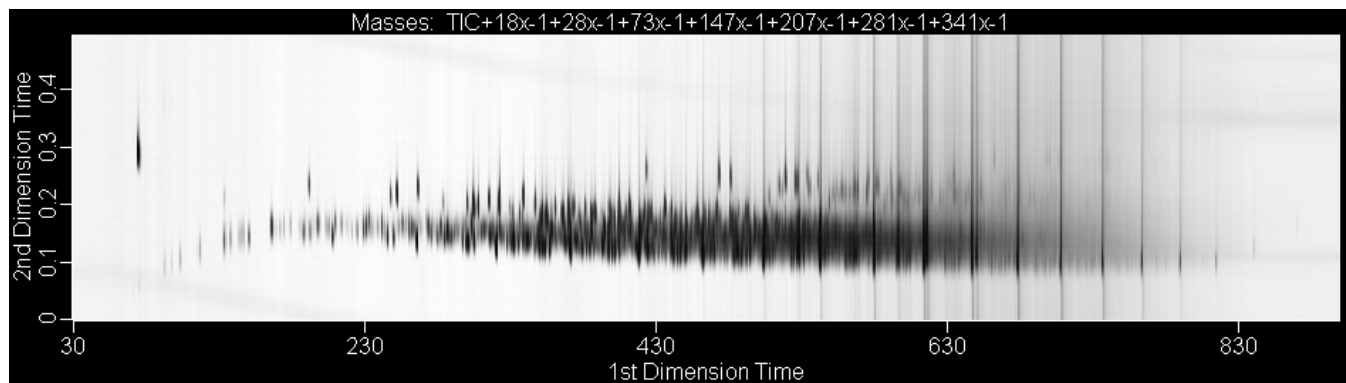
C73 dg-jet (rep.3)



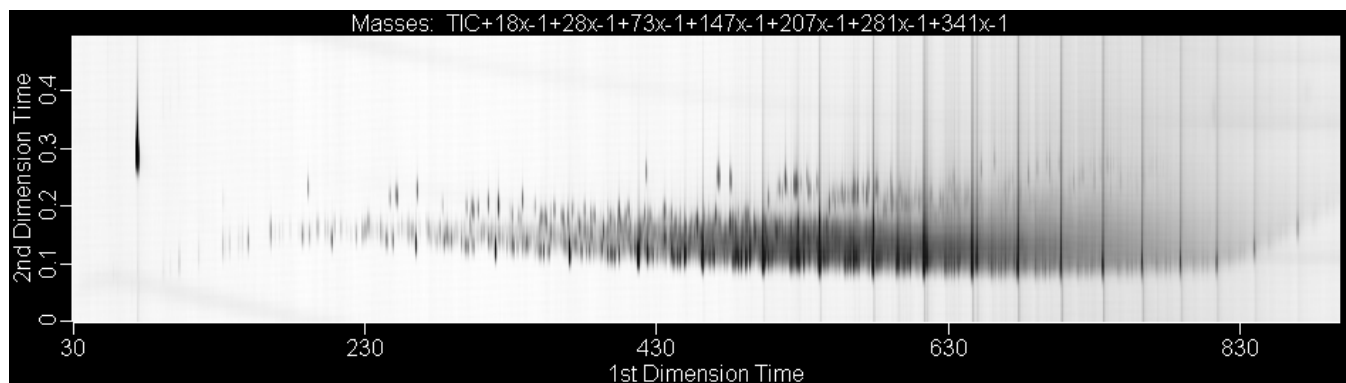
C822 B100 (rep.4)



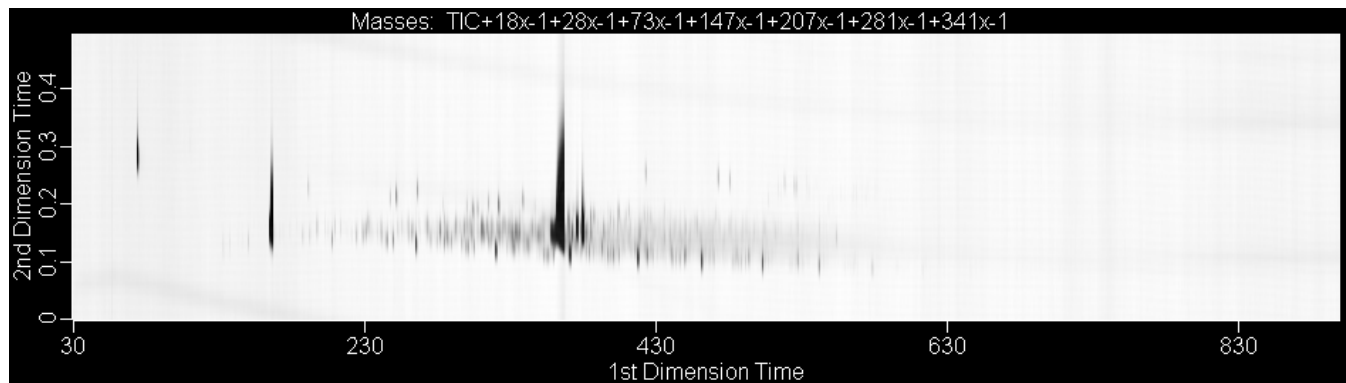
C920 MGO (rep.2)



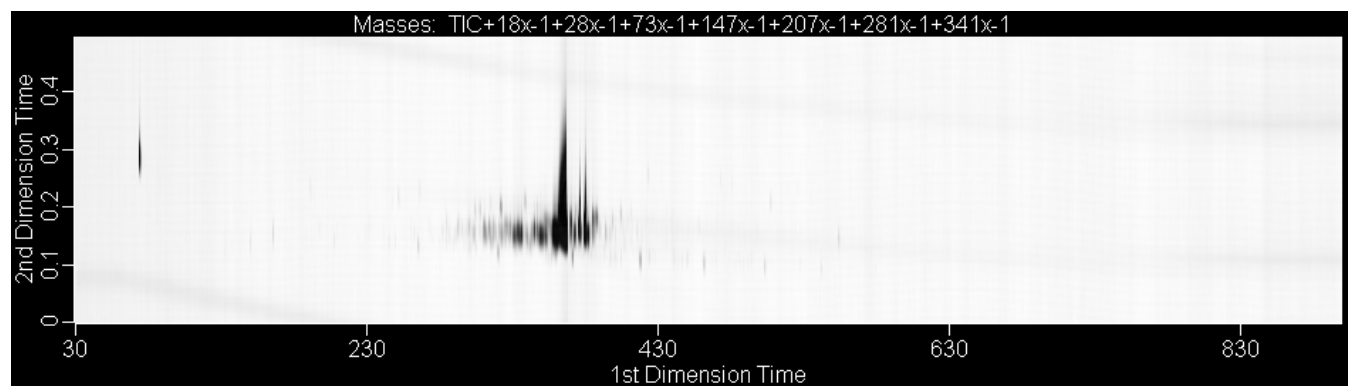
C837 ULSD (rep.2)



C100 F76 (rep.3)



C268 Priming Fluid (rep.4)



C247 JP-10 (rep.1)