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Comprehensive analysis of automotive diesel using flow-modulated GC×GC technology coupled with GC-MS

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Goal

To demonstrate the use of flow-modulated comprehensive GC×GC with the Thermo Scientific™ TRACE™ 1310 GC, Thermo Scientific™ ISQ™ 7000 MS, and Thermo Scientific™ Orbitrap™ Exploris™ GC-MS for the analysis of automotive diesel.

Introduction

Analyzing complex samples by traditional one-dimensional GC methods can often result in hundreds of peaks, which on occasion can only be partially resolved from each other. There is also the potential for even more peaks to be present that are true coelutions and are therefore difficult to detect by one-dimensional chromatography.

To fully characterize the samples, detection techniques such as high-resolution accurate mass (HRAM) mass spectrometry with spectral deconvolution can be used to help identify these additional compounds, although this approach is challenging for compounds with significantly different responses. Another alternative approach is utilizing sample preparation processes to fractionate the sample before analyzing the individual fractions, which adds additional time and costs to the process, while still not guaranteeing that any co-elutions will be resolved. The alternative described in this technical note is the use of comprehensive two-dimensional gas chromatography (GC×GC).

GC×GC is a technique that allows for separation of a sample by two different column phases, increasing the potential chromatographic resolving power by an order of magnitude.[1] A key part of any GC×GC system is the modulator. To retain the separation achieved in the first column, the analytes must be introduced in narrow bands to the 2nd dimension column where they are further separated. The two main types of modulator involve either thermal or flow modulation.

As the name suggests, thermal modulation works based on temperature. Analytes eluting from the first column are trapped using cold jets before hot jets then desorb the analytes on to the 2nd dimension column for further separation. This process happens alternately throughout the entire analytical run. In flow modulation, carrier and auxiliary gas flow are precisely controlled so that the eluate from the 1st dimension column fills a sampling loop which is then flushed onto the 2nd dimension column for further separation. The benefits of flow modulation include the cost benefit of not requiring a liquid cryogen or additional gases for the jets as well as high reproducibility and the ability to efficiently modulate compounds as volatile as C_1.

This increased chromatographic resolving power allows for a reduction in the sample preparation steps that may be required prior to analysis by traditional one dimensional GC,[2] and allows for screening of the entire sample, simultaneously analyzing several different classes of organic contaminants.[3]

For the work presented here, reverse fill/flush flow modulation GC×GC was performed utilizing the SepSolve Analytical INSIGHT® flow modulator, within the TRACE 1310 GC, coupled to a range of detectors, including the ISQ 7000 single quadrupole mass spectrometer, Orbitrap Exploris GC mass spectrometer, and the Thermo Scientific™ Instant Connect Flame ionization detector (FID).

Experimental

Instrument and method setup

To perform comprehensive GC×GC analysis, the SepSolve Analytical INSIGHT flow modulator was connected to a Thermo Scientific TRACE 1310 GC fitted with an auxiliary pressure control module. Separation was performed using a Thermo Scientific™ TraceGOLD™ TG-17SilMS, 20 m × 0.18 mm × 0.18 µm, column (P/N 26072-5780) in the 1st dimension and an Rxi®-5Sil MS, 5 m × 0.25 mm × 0.1 µm (cut from a 15 m column), column in the 2nd dimension. The flow was then split to two detectors using a three port SGE SilFlow™ splitter and deactivated transfer line. Two different detector configurations were used. The FID was used in both cases and the MS system was changed from the ISQ 7000 GC-MS in the one experiment and the Orbitrap Exploris GC in the other.

Full method details can be found in Tables 1–4.

Table 1. TRACE 1310 GC parameters

TRACE 1310 parameters	
Inlet module and mode	SSL, Split
Split ratio	1,000:1
Liner	4 mm i.d. single taper quartz wool liner (P/N 453A1925-UI)
Inlet temperature	320 °C
Injection volume	1 µL
1D column	TraceGOLD TG-17SilMS, 20 m × 0.18 mm × 0.18 µm (P/N 26072-5780)
2D column	Rxi-5Sil MS, 5 m × 0.25 mm × 0.1 µm (Cut from 15 m column)
Bleed line	5 m × 0.1 mm Deactivated fused silica
Transfer line to MS	1.2 m × 0.18 mm Deactivated fused silica
Transfer line to FID	1.0 m × 0.32 mm Deactivated fused silica
Carrier gas	Helium
1D column flow	0.5 mL/min
2D column flow	20 mL/min
Oven ramp	40 °C (no hold), 2.5 °C/min to 300 °C, hold for 5 min
Run time	109 min
FID temperature	320 °C
FID hydrogen flow	35 mL/min
FID air flow	350 mL/min
FID makeup gas and flow	N_2, 40 mL/min
FID acquisition rate	100 Hz
GC peak width	Fast (<1 s)

Table 2. INSIGHT module parameters

INSIGHT module parameters	
Loop volume	50 µL
Modulation time	4.5 s
Flush time	115 ms

Table 3. ISQ 7000 parameters

ISQ 7000 MS parameters	
Transfer line temperature	320 °C
Ion source temperature	350 °C
Ionization mode	EI, 70 eV
Scan range	45–400 *m/z*
Dwell time	0.02731 s

Table 4. Orbitrap Exploris GC-MS parameters

Orbitrap Exploris GC parameters	
Transfer line temperature	320 °C
Ion source temperature	350 °C
Ionization mode	EI, 70 eV
Scan range	45–400 *m/z*
Resolution	7,500 @ *m/z* 200

Sample preparation

A sample of diesel fuel was sourced from a local filling station and aliquoted into a 2 mL vial for analysis. No manipulation of the sample was performed.

Data acquisition, processing, and reporting

Data were acquired using Thermo Scientific™ Xcalibur™ software and then processed using SepSolve Analytical ChromSpace® software.

Results and discussion

Chromatography

The major benefit of comprehensive GC×GC chromatography is the increased chromatographic resolving power of the second dimension. For complicated samples, such as diesel, many compounds may not be resolved by traditional one-dimensional chromatography. Figure 1 shows an example color plot of the chromatography produced for the Orbitrap Exploris GC-MS where the more intense colors represent more intense peaks.

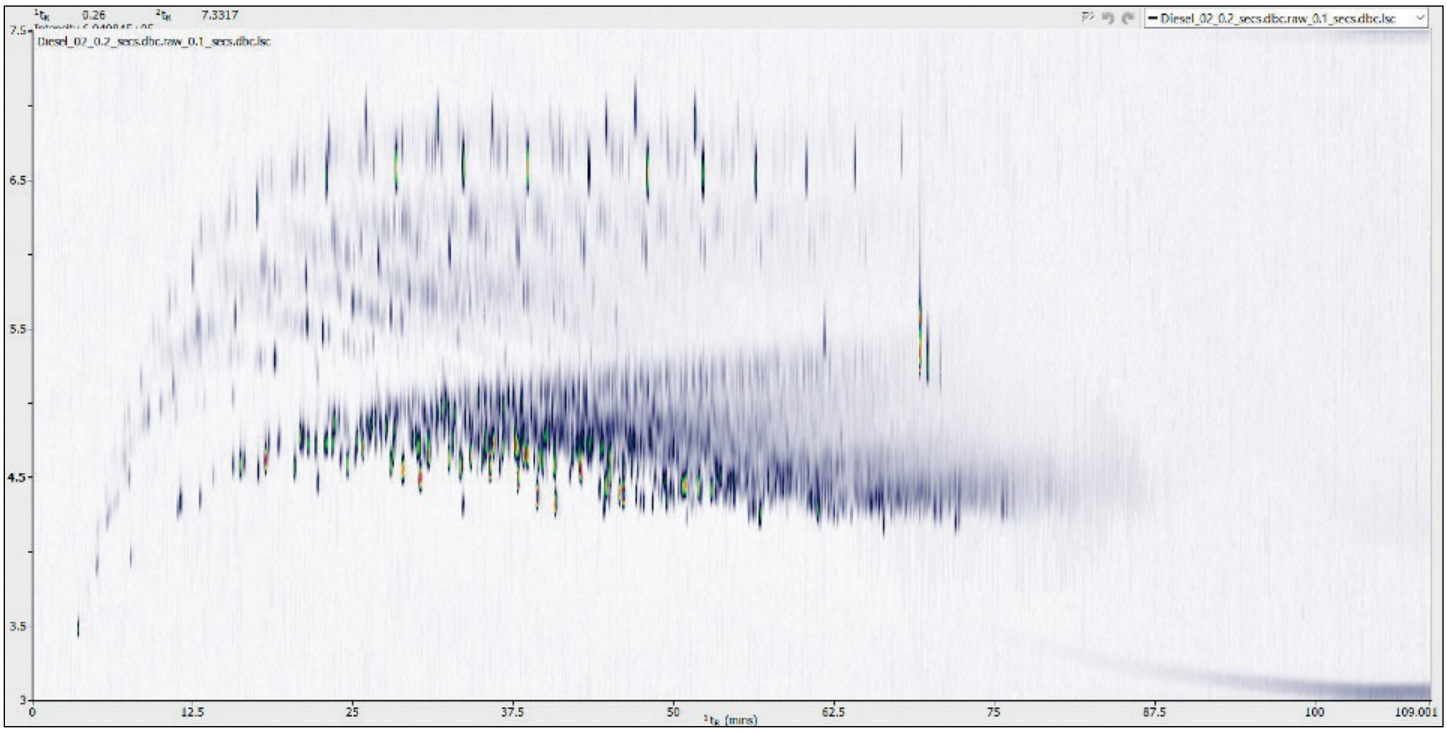

Figure 1. Color plot of the chromatogram produced by a diesel sample run using the Orbitrap Exploris GC

It can be hard to visualize the color plots as peaks when first starting out with GC×GC. Within the ChromSpace software it is also possible to view a 3D image of the chromatography (Figure 2).

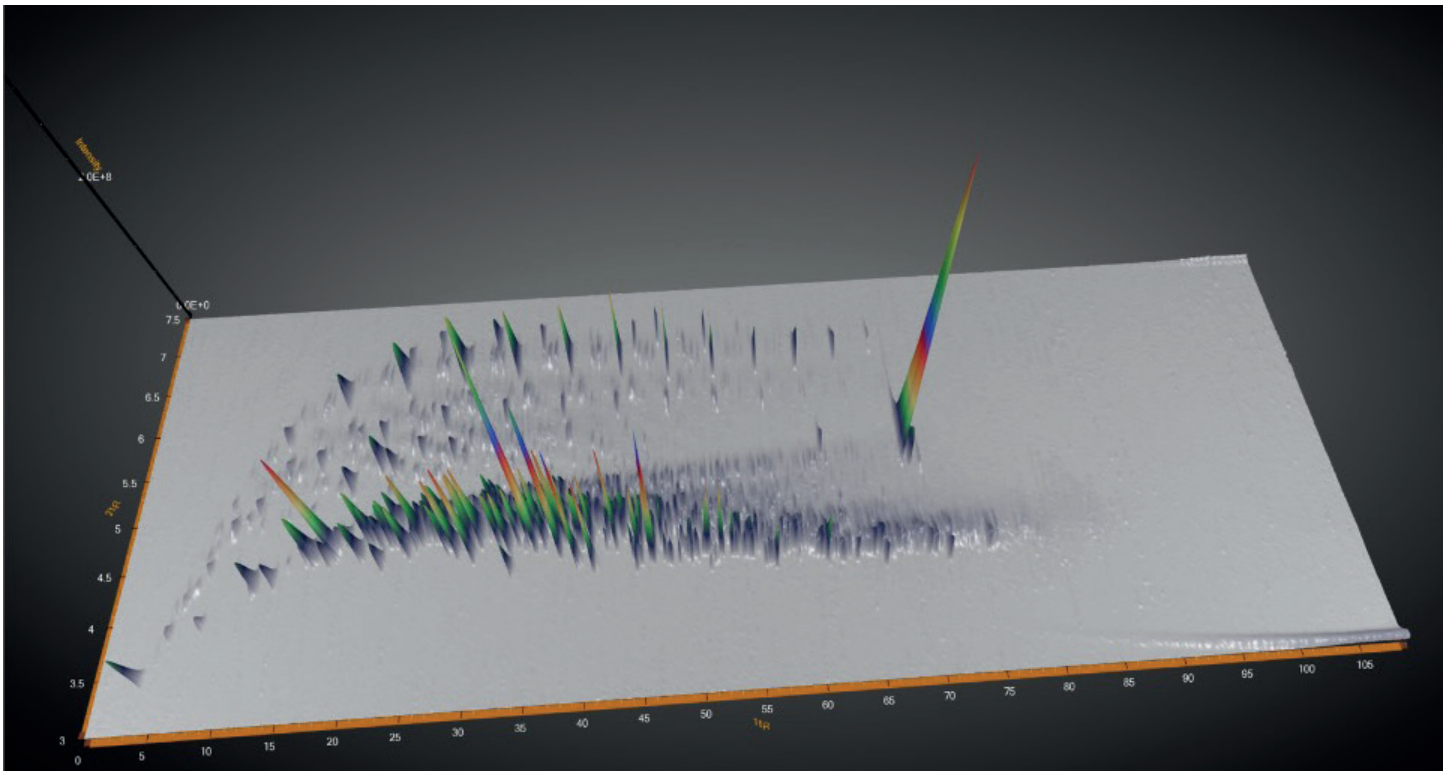

Figure 2. 3D surface plot of the chromatogram produced by a diesel sample run using the Orbitrap Exploris GC

An example of the additional resolving power of GC×GC is shown in Figure 3 where propylbenzene and methylcyclohexene are perfectly coeluting in the 1st dimension but are well resolved in the 2nd dimension, making identification of these compounds more straightforward.

For the analysis of this type of sample it can be useful to use MS data for identification of peaks and determination of group windows and to use FID data for quantitation. This setup allows for simultaneous acquisition of both MS and FID data with the same separation efficiency. When the correct dimensions of transfer line are used, the MS and FID data can also be aligned the same so that a peak that is identified from the MS data can then be easily matched by its retention times in the FID data. An example of the simultaneously acquired, aligned chromatograms is shown in Figure 4.

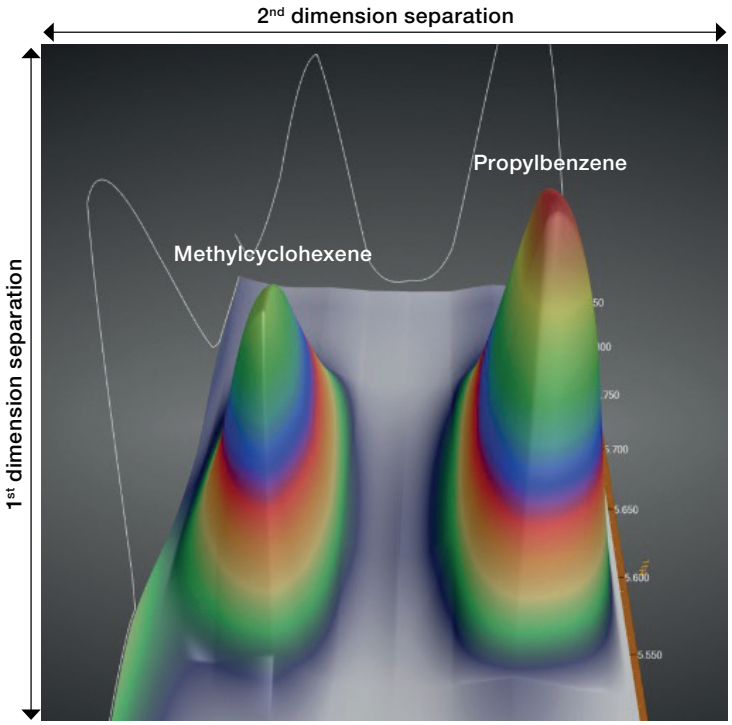

Figure 3. 3D image of a diesel sample zoomed in to show the co-elution in the 1st dimension of propylbenzene and methylcycohexene and the separation of these compounds achieved by the 2nd dimension

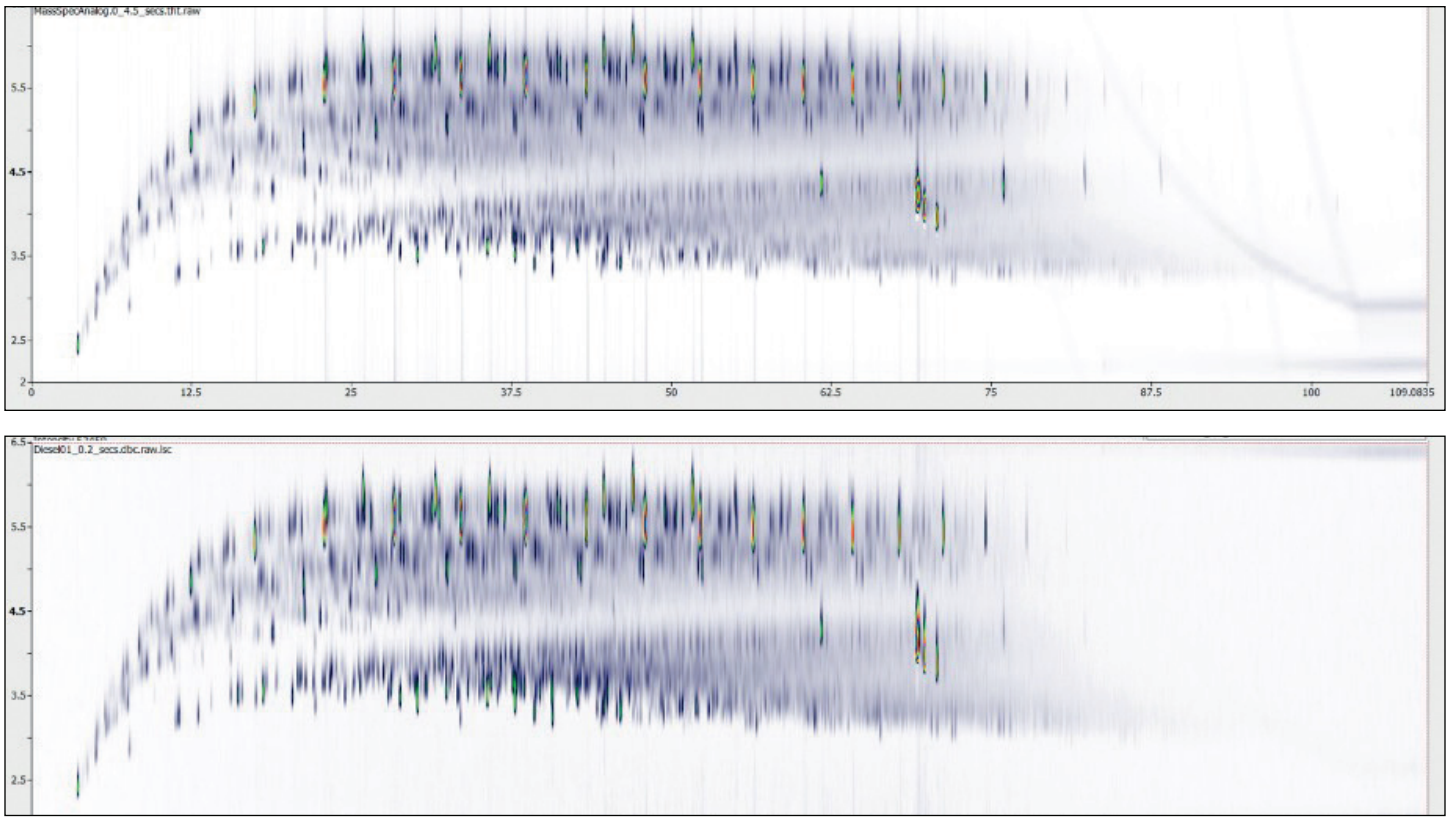

Figure 4. Stacked chromatograms showing simultaneously acquired FID (top) and ISQ (bottom) data in the form of color plots

A common method for the analysis of diesel samples is PINA analysis. This splits the sample into four main groups: *n*-paraffins, isoparaffins, naphthenes, and aromatics (PINA). ChromSpace software makes analysis of these groups straightforward by enabling the user to build stencils so that every peak within a stencil area can be grouped together. Multiple stencil areas across the chromatogram can also be grouped together so that the %area of PINA groups can be quickly determined. An example of a stencil is shown in Figure 5. Compounds such as fatty acid methyl esters (FAMEs) that do not fall into any of these four groups can also be excluded from the calculations by drawing a separate stencil around them, for example the bright green sections in Figure 5.

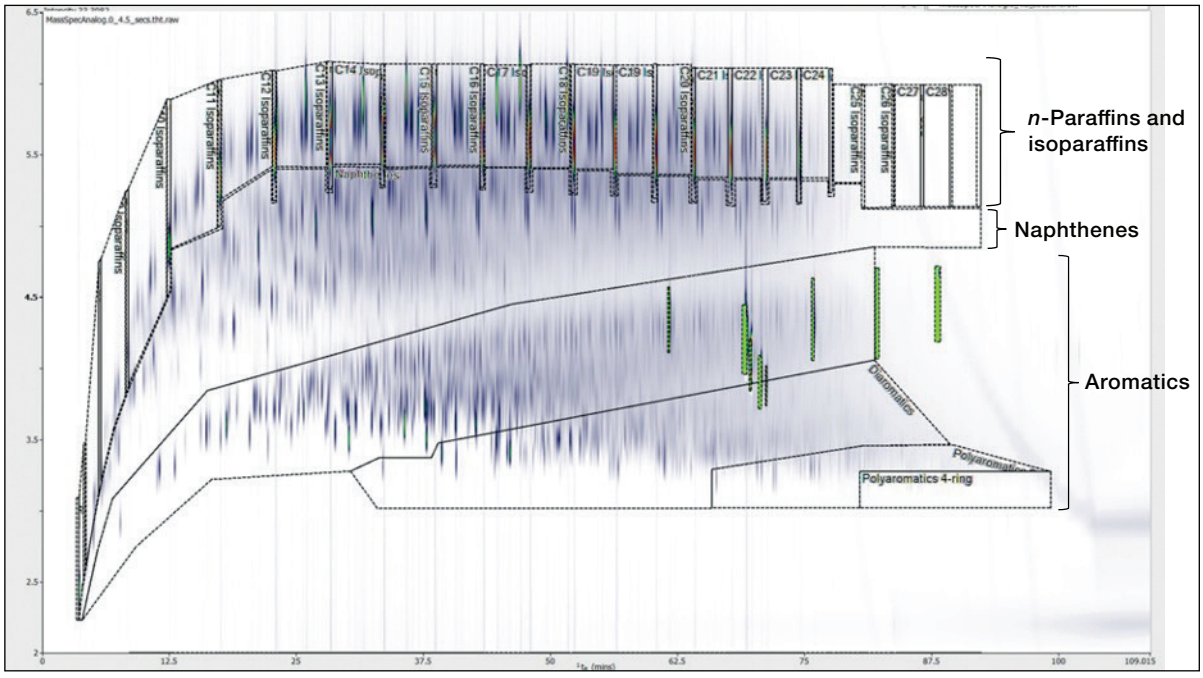

Figure 5. An example of a stencil drawn over the FID color plot with the PINA bands indicated. Detected FAMEs are highlighted in the green boxes.

Reproducibility

Within any sort of chromatography, it is important that the retention times and relative responses of the peaks obtained remain the same to be confident in the identification and quantification of compounds. To test the reproducibility of the method, the same diesel sample was analyzed in triplicate on each of three separate days, using the ISQ/FID configuration, with no instrument maintenance performed. The reproducibility of %area for the four groups and 1D and 2D retention times for selected compounds was then assessed. Representations of these results are shown in Figure 6 and Table 5. %RSDs <4 were achieved for the group %areas and <1.2 were achieved for retention time, showing the stability of the system.

Benefits of accurate mass

GC×GC can also be used in combination with the Orbitrap Exploris GC-MS to gain accurate mass information for all the detected peaks. This information can provide the user with more certainty about the molecular formula and therefore more certainty about the identification of peaks detected. This technology will obtain <1 ppm mass accuracy for some compounds. Examples for naphthalene and trimethylbenzene are shown in Figure 7 utilizing the Thermo Scientific XCalibur Qual Browser.

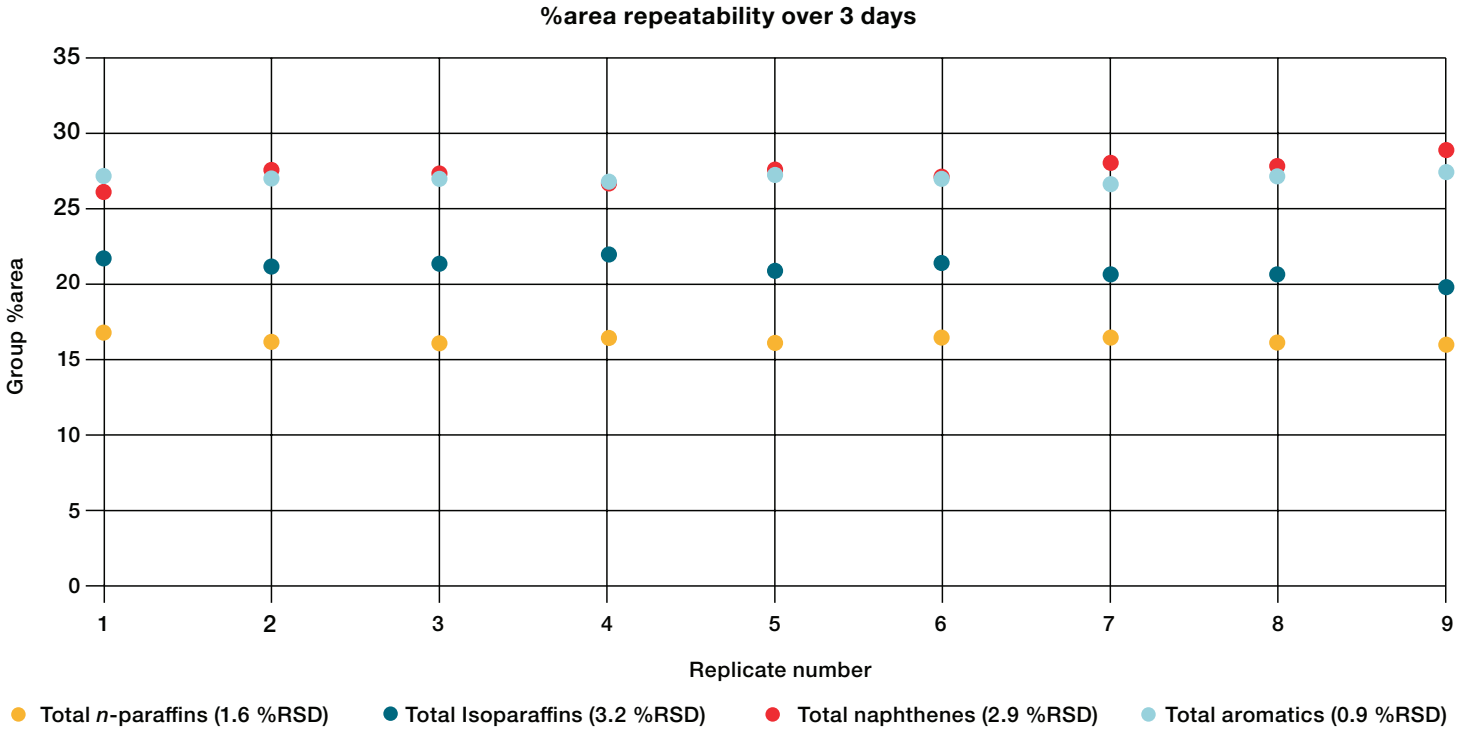

Figure 6. Plot showing the group %areas obtained for *n*-paraffins, isoparaffins, naphthenes, and aromatics from n=9 replicate injections of a diesel sample run over three days

Table 5. Average retention time and retention time %RSD, for n=9 injections performed over three days, for the 1st dimension (x-axis) and 2nd dimension (y-axis) of five selected compounds across the chromatogram range

	Ethyl cyclohexane		Toluene		Dodecane		Napthalene		Tetracosane	
	x-axis (min)	y-axis (s)	x-axis (min)	y-axis (s)	x-axis (min)	y-axis (s)	x-axis (min)	y-axis (s)	x-axis (min)	y-axis (s)
Mean (n=9, over 3 days)	7.54	3.44	7.64	2.85	22.90	5.44	33.54	3.31	74.53	5.42
%RSD (n=9, over 3 days)	0.8%	1.0%	0.6%	1.2%	0.3%	0.9%	0.2%	0.9%	0.0%	0.6%

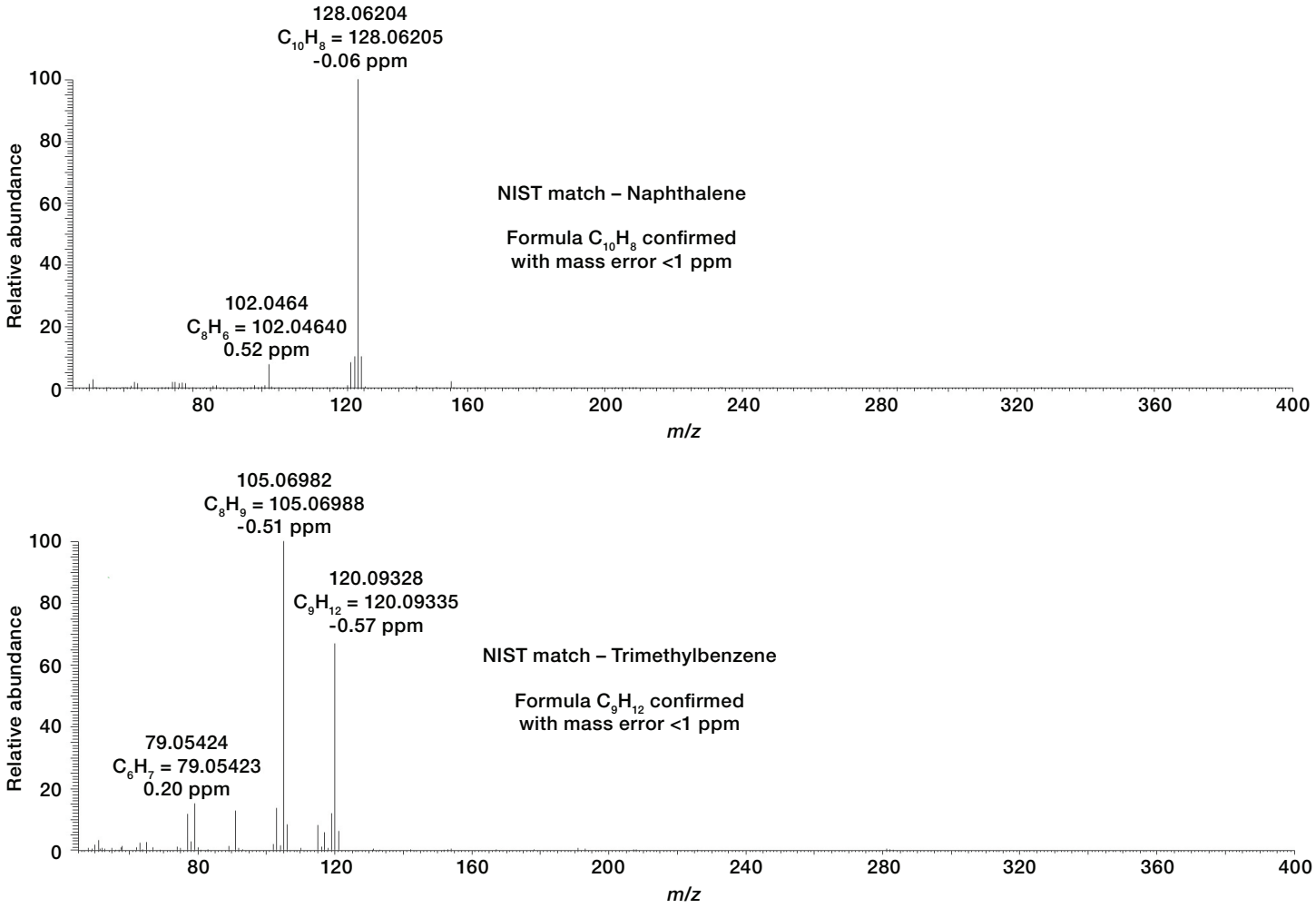

Figure 7. Mass spectra of naphthalene and trimethylbenzene annotated with the confirmed molecular formula and the mass accuracy (in ppm) for the given formula

Conclusions

The combination of flow-modulated GC×GC and single quadrupole GC-MS or high-resolution GC Orbitrap MS will offer the following analytical advantages to laboratories analyzing petrochemical products, such as regular diesel:

- Separation of constituent compounds of diesel with simultaneous detection by FID and MS detectors.
- Analysis of different classes of compounds using stencils in the ChromSpace software.
- Reproducible retention times and %area values for consecutive analysis of diesel samples.
- HRAM data that can be used to further interrogate the data and add confidence in the compound identification by confirming the molecular ions of individual compounds with <1 ppm mass accuracy.

References

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