Using flow-modulated GC × GC technology coupled with GC-Orbitrap mass spectrometry for the profiling of automotive diesel

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ABSTRACT

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

Methods: 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 Orbitrap Exploris GC mass spectrometer, and the Thermo Scientific™ Instant Connect Flame ionization detector (FID).

Results: 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. To visualize the two dimensions of chromatographic data a color plot of the chromatography produced for the Orbitrap Exploris GC-MS where the more intense colors represent more intense peaks was used. It is important that the retention times and relative responses of the peaks obtained remain the same. The reproducibility of %area for the four groups and 1D and 2D retention times for selected compounds was assessed. %RSDs ranged from 0.9-3.2% over the three days.

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 poster 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.

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 Orbitrap Exploris GC mass spectrometer, and the Thermo Scientific™ Instant Connect Flame ionization detector (FID)

MATERIALS AND METHODS

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.

Test Method

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 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. Full details shown in tables 1-3.

Table 1. GC and injector conditions.

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 – Flow modulator parameters .

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

Table 3 - 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

RESULTS

Chromatography with GCxGC

The major benefit of comprehensive GC × GC chromatography is the increased chromatographic resolving power of the second dimension. For complex 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. 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 1. Color plot of the chromatogram produced by a diesel sample run using the Orbitrap Exploris GC shown in ChromSpace® software

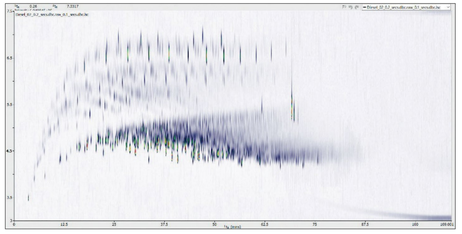
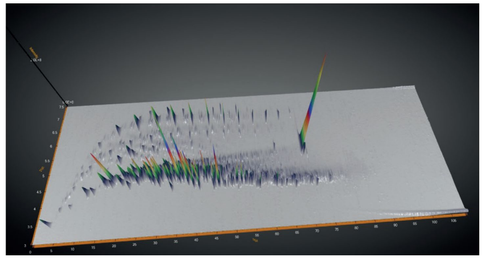
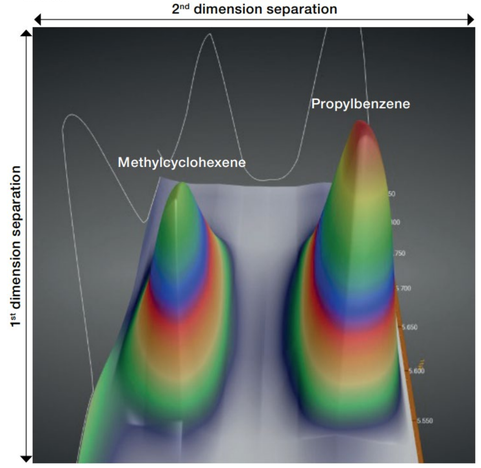


Figure 2. . 3D surface plot of the chromatogram produced by a diesel sample run using the Orbitrap Exploris GC.



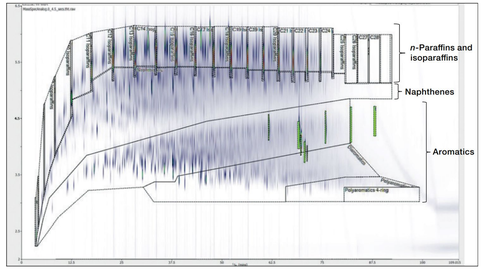
An example of the additional resolving power of GC × GC is shown in Figure 3 where propylbenzene and methylcyclohexene are perfectly coeluting in the 1st dimension but are well resolved in the 2nd dimension, making identification of these compounds more straightforward.

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



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

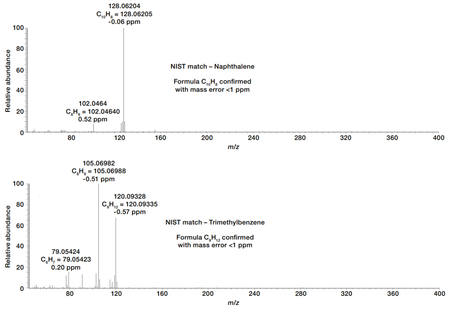


PINA Analysis

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 4. 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 4.

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 ions within the spectrum to support known identification and elemental formula proposal for unknowns. Either traditional EI at70 eV can be used for chemical ionisation to support identification of molecular ion, which is critical in the case of unknown peaks Examples for naphthalene and trimethylbenzene are shown in Figure 5 utilizing the Thermo Scientific™ XCalibur™ Qual Browser.

Figure 5. . 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 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.
- 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 < 1ppm mass accuracy.

REFERENCES

1. Phillips, J.B. and Beens, J. Comprehensive two-dimensional gas chromatography: A hyphenated method with strong coupling between the two dimensions, Journal of Chromatography A, 1999, 856, 331–347.
2. SepSolve Analytical White Paper 007: Technical note: Comprehensive two-dimensional gas chromatography, https://www.sepsolve.com/overview-of-gcgc/
3. Technical Note 000050. Comprehensive analysis of automotive diesel using flow-modulated GC × GC technology coupled with GC-MS. Thermo Fisher Scientific, 2021.

TRADEMARKS/LICENSING

PO66134-EN0422S