**White Paper 020**
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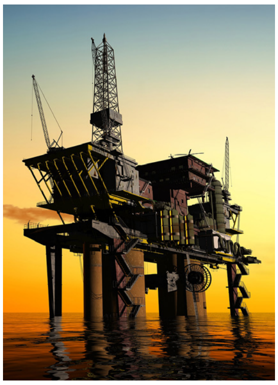
# Determining petrochemical composition by GC×GC–TOF MS/FID: Reliable, automated group-type analysis



Characterising petrochemicals by assigning individual analytes to structurally-related groups in a GC×GC workflow has great potential to improve the speed with which petrochemical compositions can be assessed. This article illustrates how ChromSpace software, in conjunction with dual TOF MS/FID detection and Tandem Ionisation, can streamline the process of achieving robust and reliable analyte speciation and quantitation in an acceptable time frame.

## Introduction

Precise characterisation of petroleum-derived fuels is crucial for quality control, to understand the reactions that take place during refining processes, and also for environmental monitoring. However, individually identifying the thousands of components present in these complex samples can be impractical.[1,2]

Group-type analysis using comprehensive two-dimensional gas chromatography (GC×GC) offers a practical approach to this problem. The vastly expanded separation space of GC×GC (compared to conventional chromatography) reduces the incidence of co-elution, while the 'roof-tiling' effect facilitates the simple division of hydrocarbons into structurally-similar classes. This approach is now widely used for the analysis of petrochemicals, typically in conjunction with flame ionisation detection (FID) for 'gold-standard' quantitation.

However, difficulties can arise when compound classes overlap, and for this reason time-of-flight mass spectrometry (TOF MS) has become important to identify class boundaries accurately, and so generate 'stencils' that can be reliably applied to unknown samples (acquired on either TOF MS or FID).

This article describes how group-type analysis can be applied to the case of petrochemicals, using flow-modulated GC×GC and the data-mining tools available in the ChromSpace® GC×GC software package. We additionally show how analyte speciation can be aided by the generation of soft EI data using Tandem Ionisation® technology.

## Experimental

**Samples:** 1 µL injections of naphtha and a heavy alkylate.

**GC×GC:** INSIGHT™ flow modulator (SepSolve Analytical, Peterborough, UK). For the heavy alkylate, a splitter was used to direct the flow to the TOF MS and FID detectors in the ratio 1:4.5.

**TOF MS:** Instrument: BenchTOF-Select™; Mass range: m/z 35–550; Ionisation: Tandem Ionisation® mode at 70 eV and 14 eV.

**FID:** $H_2$ flow: 40 mL/min; Air flow: 400 mL/min; Temperature: 300°C.

**Software:** Instrument control and GC×GC data processing was carried out using TOF-DS™ with ChromSpace® (SepSolve Analytical).

Full experimental details are available from SepSolve.

## Results and discussion

### 1. Performance of flow-modulated GC×GC

Figure 1 shows the GC×GC–TOF MS separation achieved for the naphtha sample, with the inset highlighting the excellent peak shape and narrow peak widths (<100 ms), visualised here using ChromSpace® software. This is attributable to the reverse fill/flush dynamics used in the INSIGHT™ flow modulator – providing a counter-example to the common belief that flow modulation cannot provide high peak capacity. For details on the operation of INSIGHT and its application to petrochemical analysis, see the companion white paper.

It is also worth noting that flow modulation avoids the inconvenience of liquid nitrogen, and does not suffer from the same volatility restrictions associated with thermal modulation. This expands the range of applications that can be tackled with GC×GC, by enabling volatiles from $C_1$ to be efficiently modulated, as illustrated for the naphtha analysis (Figure 2).

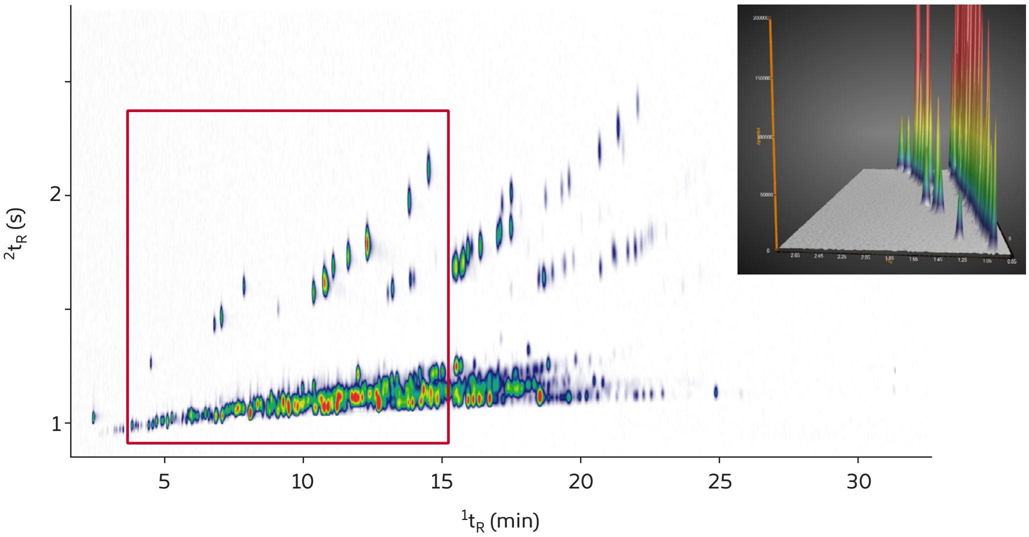


**Figure 1**

GC×GC–TOF MS colour plot for naphtha. The surface plot in the inset, visualised in ChromSpace, shows the sharp, symmetrical peaks in this example (basal widths <100 ms).

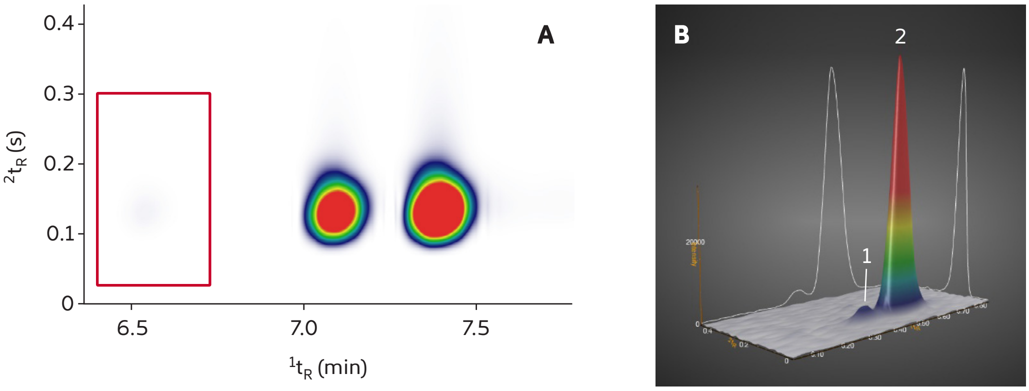


**Figure 2**

(**A**) GC×GC–TOF MS colour plot showing efficient modulation of $C_4$ and $C_5$ volatiles for naphtha.
(**B**) Surface plot showing the excellent peak shape for isobutane (1) and n-butane (2), visualised in ChromSpace.

## 2. Simple templating for FID

Templating works by defining chromatographic regions ('stencils') for particular sample types, and then applying these to new samples for rapid group-type speciation of the components, as well as reporting of summed peak integrals. Using ChromSpace, stencil regions are easily drawn around the target class, can be altered to the desired shape, and can even be connected in contiguous meshes to ensure no areas of the chromatograms are overlooked (illustrated in Figure 3 for the naphtha sample).

Integration is carried out by summing the areas of peaks that have apexes within each region (even if they have tails that extend outside that region). This information is translated into an area percent table (Figure 4) that allows fast overview of sample composition. In this case, >99.9% of the total sample composition is classified using the stencil regions.

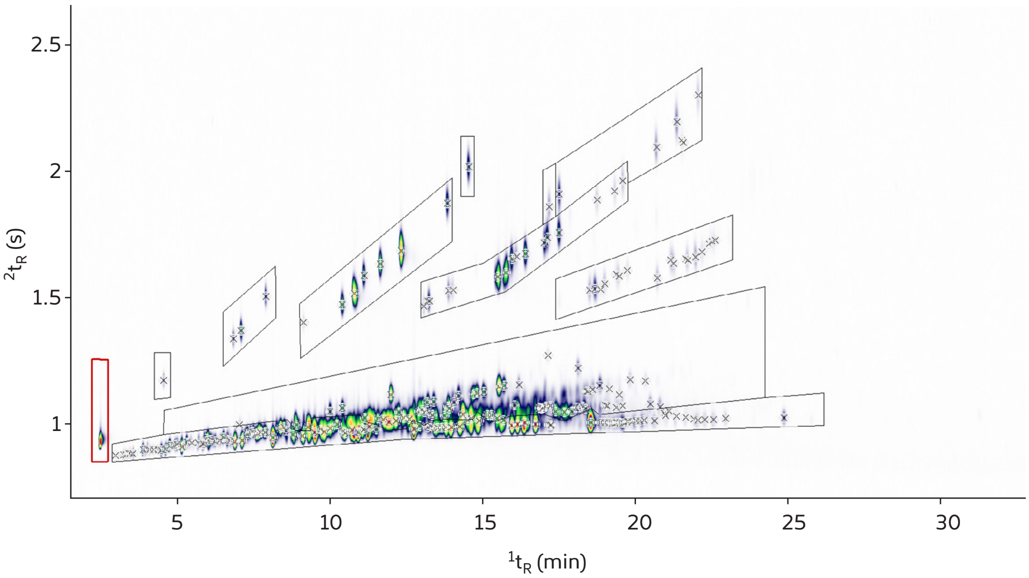
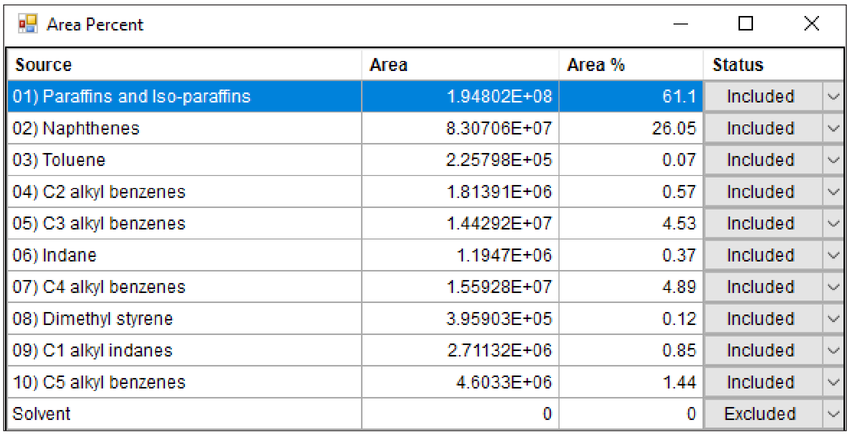


**Figure 3**

GC×GC–FID colour plot of naphtha, showing integrated peaks (⊗) and optimised stencil regions, with the excluded solvent peak shown in red.



| Source | Area | Area % | Status |
|---|---|---|---|
| 01) Paraffins and Iso-paraffins | 1.94802E+08 | 61.1 | Included |
| 02) Naphthenes | 8.30706E+07 | 26.05 | Included |
| 03) Toluene | 2.25798E+05 | 0.07 | Included |
| 04) C2 alkyl benzenes | 1.81391E+06 | 0.57 | Included |
| 05) C3 alkyl benzenes | 1.44292E+07 | 4.53 | Included |
| 06) Indane | 1.1947E+06 | 0.37 | Included |
| 07) C4 alkyl benzenes | 1.55928E+07 | 4.89 | Included |
| 08) Dimethyl styrene | 3.95903E+05 | 0.12 | Included |
| 09) C1 alkyl indanes | 2.71132E+06 | 0.85 | Included |
| 10) C5 alkyl benzenes | 4.6033E+06 | 1.44 | Included |
| Solvent | 0 | 0 | Excluded |

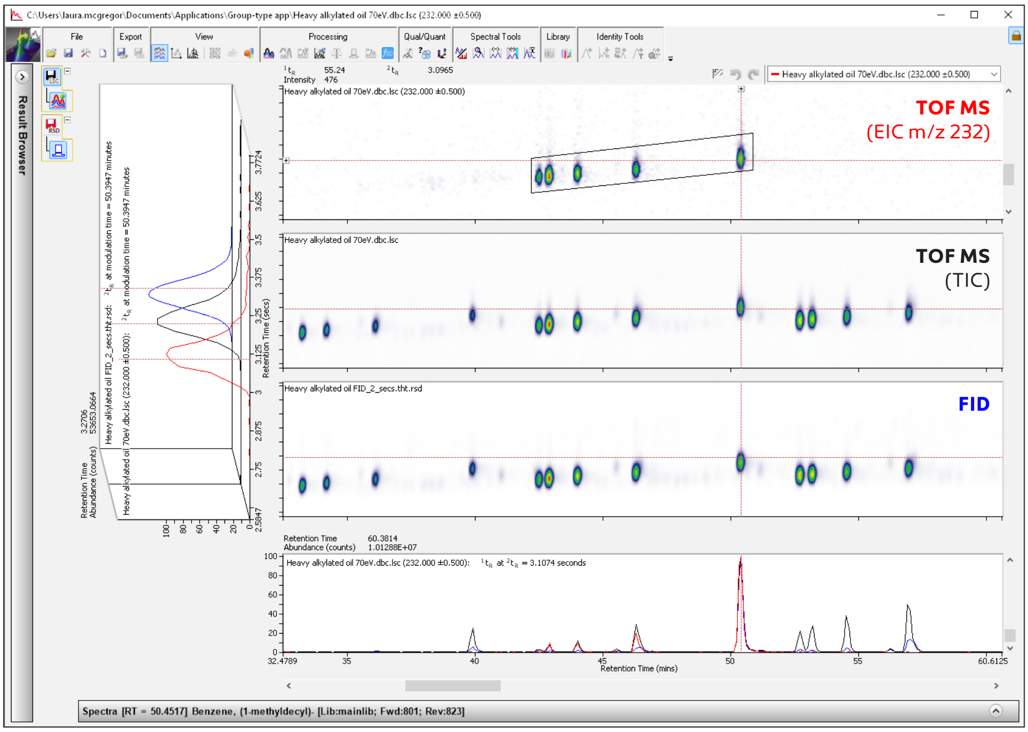
**Figure 4**

Area percent table in ChromSpace, resulting from the analysis shown in Figure 3.

## 3. Parallel detection by TOF MS/FID

For more complex samples, parallel detection with TOF MS/FID provides improved confidence in results, because the TOF MS data can be used to precisely define the stencil boundaries, prior to quantitative analysis by FID. For example, heavy alkylates may contain extensive overlap between chemical classes, making it impossible to accurately define regions based solely on FID data.

This can be resolved by using extracted ion chromatograms (EICs) on the MS data to enable accurate, close-fitting class boundaries to be defined. As shown in Figure 5, these stencils can then be applied to the FID data for quantitative analysis, assisted by the excellent retention-time correspondence for parallel detection that is possible by using the INSIGHT flow modulator. Additionally, the ability of ChromSpace to open multiple data files in a single window (and indeed, multiple data file formats) makes creation and translation of the stencils even easier.



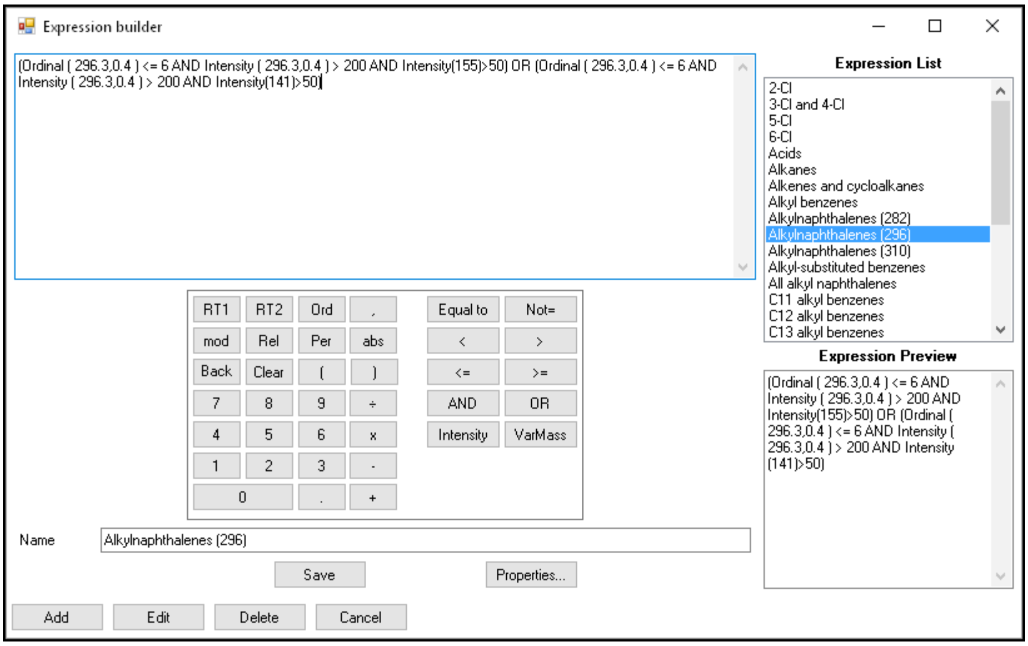
Spectra [RT = 50.4517] Benzene, (1-methyldecyl)- [Lib:mainlib; Fwd:801; Rev:823]

**Figure 5**

Classification of the $C_{11}$-alkylbenzenes in a heavy alkylate, using EICs to generate class boundaries. The excellent retention-time correlation (highlighted in the left-hand panel for the selected peak) allows stencils to be transferred easily from TOF MS to FID, while the bar at the bottom of the window instantly returns library hit information for easier data navigation.

## 4. Advanced applications: Use of filtering scripts and soft EI detection

Filtering scripts are simple expressions (based on mass spectral or chromatographic properties) used to extract target compounds or classes from the acquired data. They can be selected from a default list of popular chemical classes in ChromSpace software, or created easily by the analyst using preconfigured buttons in the expression builder (Figure 6). Filtering scripts

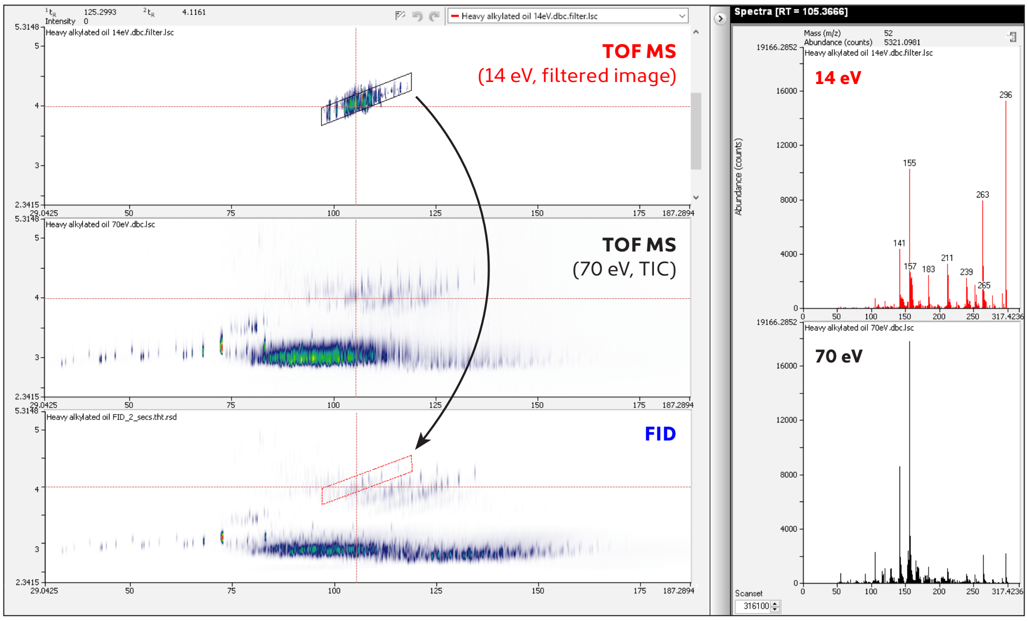


```
(Ordinal ( 296.3,0.4 ) <= 6 AND Intensity ( 296.3,0.4 ) > 200 AND Intensity(155)>50) OR (Ordinal ( 296.3,0.4 ) <= 6 AND
Intensity ( 296.3,0.4 ) > 200 AND Intensity(141)>50)
```

Name: Alkylnaphthalenes (296)

**Figure 6**

ChromSpace expression builder used to create the stencil for the $C_{12}$-alkylnaphthalenes employed in Figure 7. The expression used here returns only GC×GC peaks with m/z 296 as one of the most intense ions and with m/z 155 or 141 as significant fragments, when analysed using 14 eV soft EI.



## Figure 7

Classification of the $C_{12}$-alkylnaphthalenes in a heavy alkylate, using the expression in Figure 6 to filter the 14 eV TOF MS data, and generate an accurate stencil boundary that can be applied to the FID data. The spectral comparisons on the right-hand panel show the enhancement in structurally-significant ions using soft EI, for one of the targeted components.

provide increased selectivity compared to EICs, because they only show peaks that pass the qualifier expression, meaning a clean baseline – in contrast, EICs will show all peaks with that ion in common.

Scripts are valuable time-saving tools even in simple analyses, but they offer particular benefits for highly complex samples investigated using the TOF MS instrument in Tandem Ionisation mode, which simultaneously generates electron ionisation spectra at both high (70 eV) and low (10–16 eV) ionisation energies. These low-energy 'soft ionisation' spectra typically display reduced fragmentation and enhanced structurally-significant ions, which greatly enhance the use of filtering scripts. An example of this approach is shown in Figure 7, which uses the expression defined in Figure 6 to identify $C_{12}$-alkylnaphthalenes in the heavy alkylate sample.

## Conclusions

This article has demonstrated the creation of precisely-defined stencils in ChromSpace® software using TOF MS data, and their use for the automated group-type GC×GC analysis of complex petrochemicals. In the examples shown, peak separation across a wide volatility range is enabled by the use of consumable-free INSIGHT™ flow modulation, and the development of scripts for automated identification of challenging analyte groups is assisted by the complementary soft EI data acquired with Tandem Ionisation®. Finally, the addition of FID via a dual-detection setup allows reliable quantitation in accordance with best-practice in the petrochemical industry.

For more information on this application, or any of the techniques or products used, please contact SepSolve.

## References

[1] R.C. Striebich, L.M. Shafer, R.K. Adams, Z.J. West, M.J. DeWitt and S. Zabarnick, Hydrocarbon group-type analysis of petroleum-derived and synthetic fuels using two-dimensional gas chromatography, *Energy & Fuels*, 2014, 28: 5696–5706, http://dx.doi.org/10.1021/ef500813x.

[2] F. Adam, F. Bertoncini, D. Thiébaut, S. Esnault, D. Espinat and M.C. Hennion, Towards comprehensive hydrocarbons analysis of middle distillates by LC-GCxGC, *Journal of Chromatographic Science*, 2007, 45: 643–649, http://dx.doi.org/10.1093/chromsci/45.10.643.