Improving Workflow in Group-Type GC×GC Analysis of Petrochemicals

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Group-type GC×GC analysis has great potential to improve the speed with which chemical compositions of petrochemicals can be assessed. This article illustrates how software tools can streamline the process of achieving robust and reliable quantitation in an acceptable time frame.

Precise characterisation of petroleum-derived fuels is important for both the oil industry and for environmental monitoring, for fuel classification and liability claims respectively, but individually identifying the thousands of components present in these complex samples is so impractical as to be impossible [1,2]. Group-type analysis using comprehensive two-dimensional gas chromatography (GC×GC) offers a practical approach to such samples, with its vastly expanded separation space compared to conventional chromatography, and the added benefit of highly structured groupings of compounds for simple classification of hydrocarbons.

This article briefly describes how data-mining tools available in modern GC×GC software packages can streamline this process for the case of two petrochemical samples. The examples shown were carried out using GC×GC–TOF MS/FID with flow modulation for affordable, consumable-free GC×GC.

Experimental

Samples: 1 µL injections of naphtha (in DCM) and a heavy alkylate (in hexene) with a split ratio of 200:1.

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; Airflow: 400 mL/min; Temperature: 300°C.

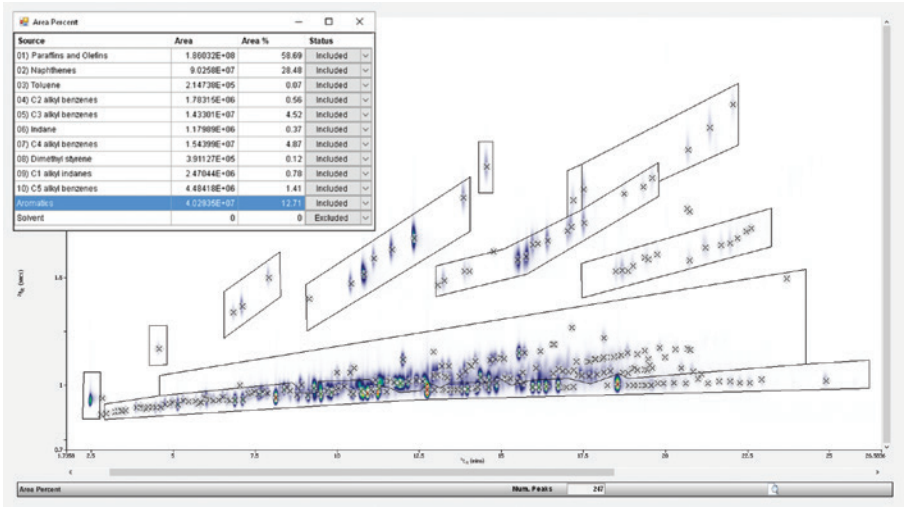

Figure 1. GC×GC–FID colour plot of naphtha, showing the pre-defined stencil regions and integrated peaks (denoted by 'x' symbols). This information is translated into an area percent table (inset) that provides a fast overview of sample composition – in this case, >99.9% of the total sample composition is classified using the stencil regions.

Software: ChromSpace® GC×GC software (Markes International, Llantrisant, UK) for full instrument control and data processing.

Full experimental details are available from SepSolve.

Simple Templating for FID

In relatively simple samples, stencils can be created in the software for particular sample types, and then applied to new samples for rapid group-type speciation of the components, as well as reporting of summed peak integrals. The stencil regions are easily drawn around the target class and altered to the desired shape. Stencil regions can even be connected in contiguous meshes to ensure no areas of the chromatograms are overlooked. This is illustrated in Figure 1 for the case of a sample of naphtha, with integration carried out by summing the areas of peaks that fall within each region (even if they have tails that extend outside that region).

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 quantitation using 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

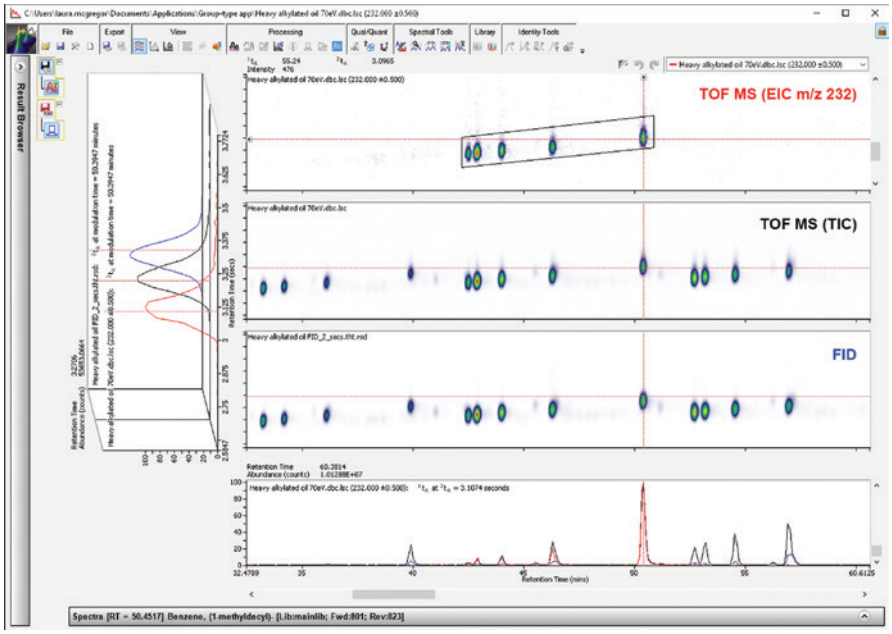

Figure 2. Classification of C_{11}-alkylbenzenes in a heavy alkylate using GC×GC with dual FID/TOF MS detection. The excellent retention-time correlation (highlighted in the left-hand panel for the selected peak) allows stencils to be transferred easily from TOF MS to FID.

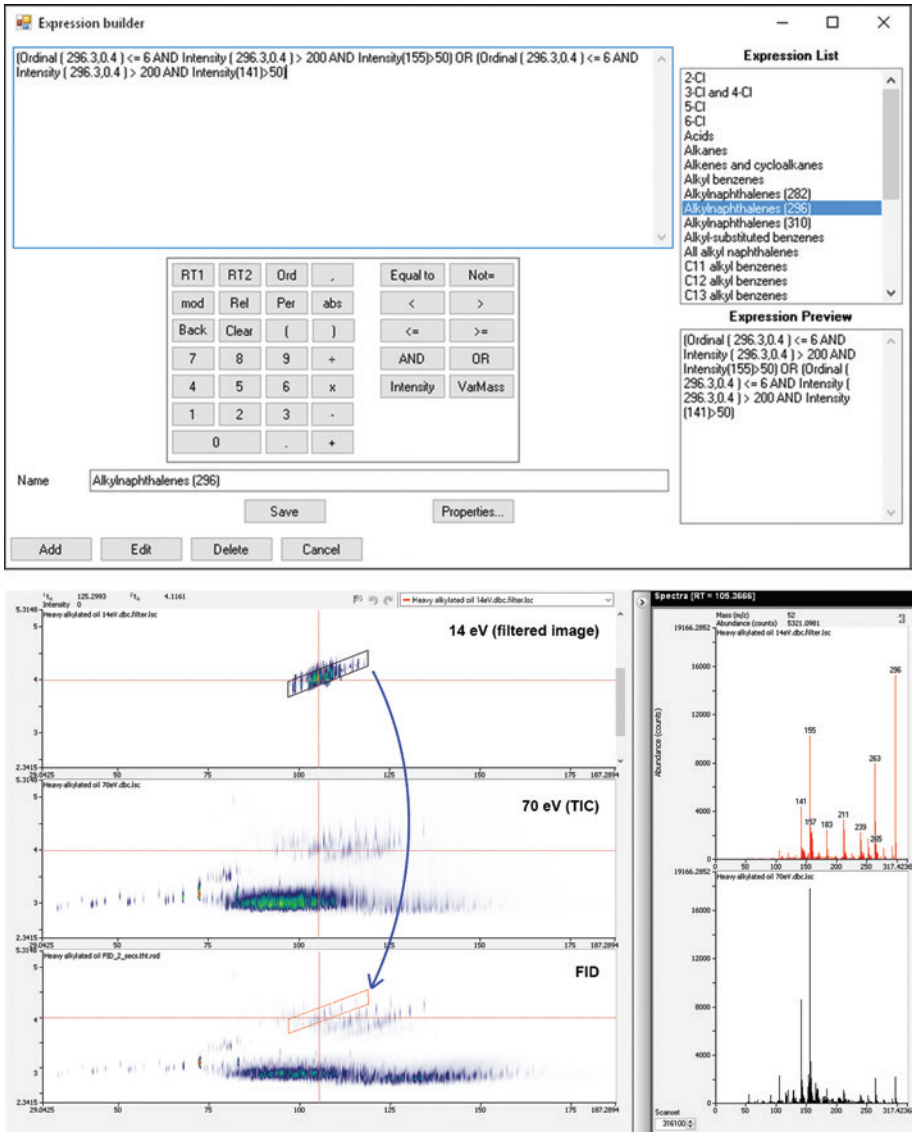

Figure 3. Top: Scripting expression used to classify the C_{12}-alkylnaphthalenes. Bottom: Use of this expression to filter the 14 eV TOF MS data from the analysis of the heavy alkylate, and generate a stencil for this compound group that can be applied to the FID data.

enable accurate, close-fitting class boundaries to be defined. As shown in Figure 2, 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 now possible with flow modulators for GC×GC. 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.

Advanced Applications – Scripting 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 the software, or created easily by the analyst using preconfigured buttons in the expression builder. 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 3, which shows an expression builder in the software interface that has been set up to search for spectral characteristics of C_{12}-alkylnaphthalenes, and application of this script to the heavy alkylate sample. Filtering scripts provide increased selectivity compared to EICs, because they only show peaks that pass the qualifier expression, meaning a clean baseline. This is in contrast to EICs, which will show all peaks with that ion in common.

References

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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, J. Chromatogr. Sci. 45 (2007), 643–649.