DESIGNING HIGH RESOLUTION SEPARATIONS FOR ENHANCED CHARACTERISATION OF PETROCHEMICAL SAMPLES

Advanced separation science – why petrochemical analysis?

The history of petrochemical analysis by using gas chromatography (GC) closely reflects the milestone developments in the technology that has defined improvements in GC separation, use of detection methods for improved characterisation, and exploitation of multidimensional separation approaches. The obvious reason for this is that petrochemical samples are exceedingly complex, comprising multiple chemical classes, along with heteroatomic species, requiring speciation in order to understand a range of chemical parameters. These range from processing conditions, to molecular markers, and overall characterisation. This essentially means that petroleum analysts are generally early adopters of technical advances in GC and mass spectrometry (MS).

As an example, the analytical team at Shell (Amsterdam) [1] were quick to recognise the new capabilities offered by comprehensive two-dimensional gas chromatography (GC×GC), soon after its introduction by Liu and Phillips, [2] and worked with early modulator devices to investigate operational effects and define the applications scope of GC×GC. The US Centres for Disease Control and Prevention likewise had challenging analyses (e.g. dioxins) that demanded superior GC separations. [3] Along with the Free University of Amsterdam, [4] one could justifiably believe that the epicentre of this new technique had a firm home in The Netherlands. The first GC×GC symposium was held at Volendam, The Netherlands, organised by key Dutch researchers and the Free University of Amsterdam academics, who were instrumental in promoting GC×GC.

Comprehensive analysis of a sample implies analysis of all components in the sample. For a GC method, this will focus on the volatile / semi-volatile compounds. Whilst GC-FID accomplishes this task, complex (multi-component) samples will suffer indeterminate overlap that prevents adequate reporting of the components – along with limited identification. GC-MS also has the same resolution limitations, however identification can be provided in those cases where the MS allows searchable unique spectra. To some extent, deconvolution may permit overlapping components to be reported. However, the total sample composition will still largely be uncertain. The two-column separation method, GC×GC, addresses this problem by significantly increasing 'peak capacity' (i.e. total separable peaks) with potential to theoretically resolve up to ca. 10,000 components. Here, we expand on separation methods that describe instrumental approaches designed for high resolution separations.

Instrumental Schematics, Advantages and Attributes of GC×GC

An instrument schematic is shown in Fig 1, [5] with stages A-B-C-B defining a sequential arrangement of up to 4 columns, in which between each stage is a device for heart-cutting or modulation. For example, a 'simple' multidimensional GC separation will involve stages A-B, with a heart-cutting 'switch' (e.g. a microfluidic Dean's switch. [6] In this case, the Dean's switch cuts one or more segments from the first column (^{1}D; A) to the second column (^{2}D; B), and the detector (FID here) provides a monitor signal for the total first column elution. The ^{2}D column and detector completes the analysis.

The simplest conventional GC×GC system will be described by A1-B1 with a sampling modulator device. The choice of columns largely depends on the nature of the stationary phases chosen for best separation of compounds on the ^{2}D column, and then the column dimensions. The usual phase selection will be to combine a non-polar (NP) phase with a high polarity (P) or medium polarity (MP) phase, in either order. For instance, for petrochemicals, a 95% methyl/5% phenyl polysiloxane (NP), with a 50% methyl/50% phenyl polysiloxane (P) column is commonly used. This normally meets the requirements for modulation ratio considerations [7] ($M_R = {}^1w_b/P_M$); if $M_R = 3$, the ^{1}D peak is sampled (modulated) to produce about 3 modulated peaks; the length of the ^{2}D column will be determined by the need to complete each ^{2}D chromatogram within the P_M time – e.g. 2-4 s. General characteristics of GC×GC are listed in Table 1, and the new nomenclature required of GC×GC has been outlined. [8]

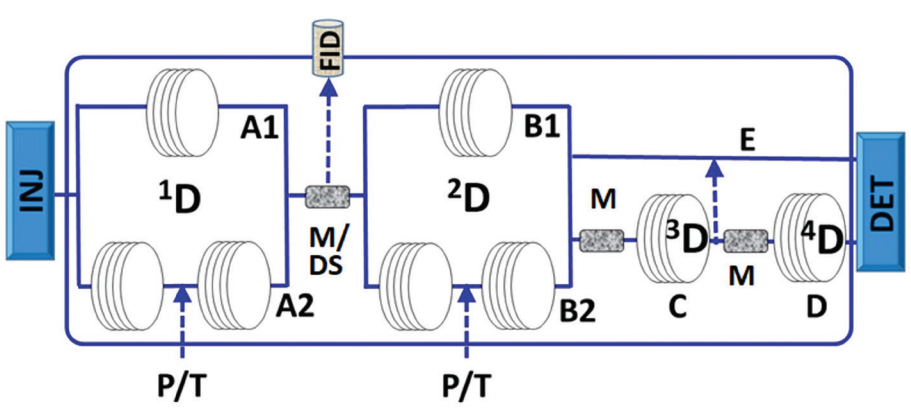

Figure 1: Schematic diagram summarising various hyphenated multiple column systems in a GC oven. Separation dimensions are shown as ^{1}D – ^{4}D; pressure tuning between two columns is indicated as P/T; M is a modulator, and DS is a Deans switch option. INJ and DET are injector and detector; FID is a monitor detector for use with a DS in an MDGC arrangement. Reprinted from Trends in Analytical Chemistry vol 106, Nolvachai et al., Multi-column trajectory to advanced methods in comprehensive two-dimensional gas chromatography. p 11-20, (2018) with permission from Elsevier.

Various advanced approaches are summarised in Fig 1. For instance, a comprehensive GC×GC×GC arrangement comprises 3 columns (A-B-C), usually of progressively shorter length, with modulation devices between ^{1}D and ^{2}D, and ^{2}D and ^{3}D respectively. [9] This necessitates data presentation in 3D space, with 3 independent axes for ${}^1t_R$, ${}^2t_R$ and ${}^3t_R$ respectively. Investigations in this area are still largely exploratory, so rationalising column phase choice, and applications are awaited. The A2 and B2 options in Fig 1 describe a pressure-tuning (P/T) approach, [10] for either the ^{1}D or ^{2}D separation. In this method, two columns replace either ^{1}D or ^{2}D, and effectively provide a variable apparent 'polarity' as a composite column. Thus if the two columns for the A2 coupling comprise NP and P phases, the resulting P/T ^{1}D separation can range from a non-polar- to a polar-type separation. When coupled with the ^{2}D column, the 2D separation space can be tuned by the effect of pressure between the two A2 ^{1}D columns.

A third option uses a 'hybrid' arrangement which combines both MDGC and GC×GC. [11] Briefly, this allows an operation such as selection of heart-cut region(s) from a ^{1}D column, followed by GC×GC analysis on ^{2}D and ^{3}D columns. The alternative – GC×GC followed by MDGC – permits a special operation; the modulation process can use a slow P_M setting, then using a flow switching device (Dean's switch) an individual compound, or zone or class of compounds, can be cut to a ^{3}D column.

A further comprehensive mode may be contrived, which maximises separation on the ^{2}D column. Clearly, the short ^{2}D column has limited 'capacity' so cannot separate many compounds. Using a long ^{2}D column is incompatible with a fast P_M setting. There are two possible scenarios for operation with a longer ^{2}D column. (1) Use a slow P_M setting, and a longer ^{2}D column, whilst ensuring that wraparound does not occur (i.e. each modulation is completed on ^{2}D before the next sampling). Thus a P_M of 1 min and ^{2}D narrow bore column of 7 m length might be suggested. (2) Perform multiple injections, and take a narrow heart-cut for each injection. Cryofocus the heart-cut, cool the oven and elute the heart-cut as a second analysis on a long, high efficiency column. Repeat the process but shift the heart-cut to take the next fraction, to eventually analyse the total sample. This has been recently demonstrated. [12] Re-constructing all the ^{2}D data presents a 2D separation space. This can be called comprehensive, since the total sample is subjected to analysis, but now with multiple injections, and much greater ^{2}D separation.

Table 1: Summary of comprehensive two-dimensional gas chromatography attributes, for GC×GC employing cryogenic modulation

Two-column technique; first column (^{1}D) of standard length, e.g. 30 m; second column (^{2}D) short length e.g. 1 m. The retention on the two columns is 'decoupled' i.e. independent
A modulator is located between the columns, the function of which is to provide independent elution on the ^{2}D column.
The modulator samples – collects – narrow fractions (usually shorter than the ^{1}D column peak width at baseline) and passes them as a focussed band to the ^{2}D column.
The ^{2}D column provides additional separation for the narrow sampled zone
Increased response (peak compression) is obtained according to the sampling process, which is approximately the (modulation period / ${}^2w_b$). This improves detection.
A 2D separation space is obtained with axes of total retention on the first column, and the short retention on the second column.
The much greater resolution achieved means that resolved peaks have considerably less interference from matrix, and the effect of phase bleed is also reduced. This translates to improved mass spectrometry data for each component – a pure mass spectrum will improve MS quality.
The 2D separation space is a unique display of the exquisite chemical property of the molecule, reflected in its position on the two different columns.

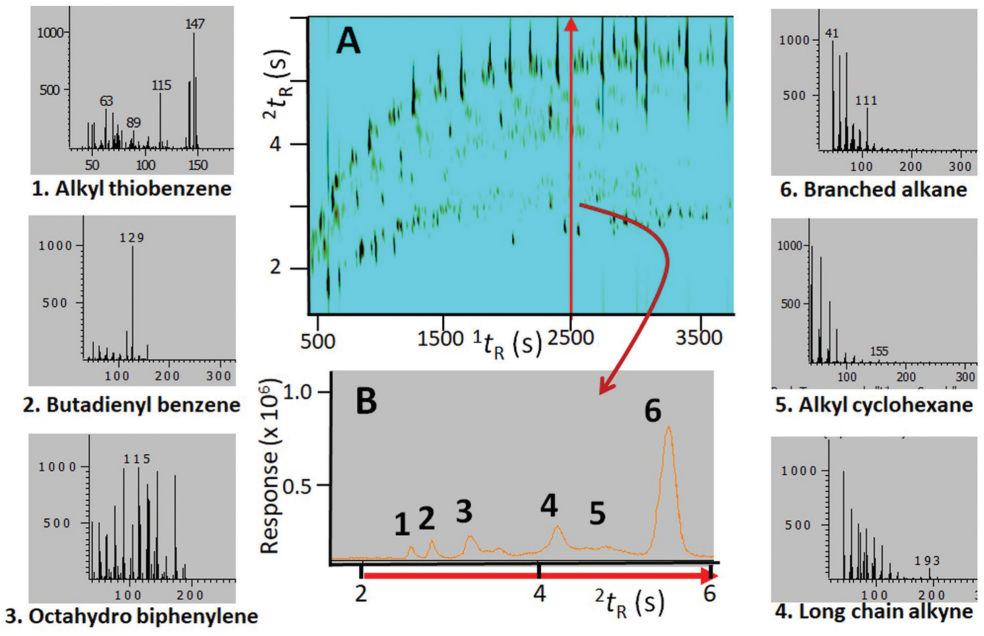

Figure 2: A. GC×GC analysis of a Late Cretaceous crude oil sample, using a modulation period of 6 s, and a ^{1}D polar / ^{2}D non-polar column arrangement. B. A single 6 s modulation event at about 2500 s is shown with molecular speciation of polar to non-polar compounds illustrated as compounds 1. – 6. The chemical classes are indicated as their library matched spectra.

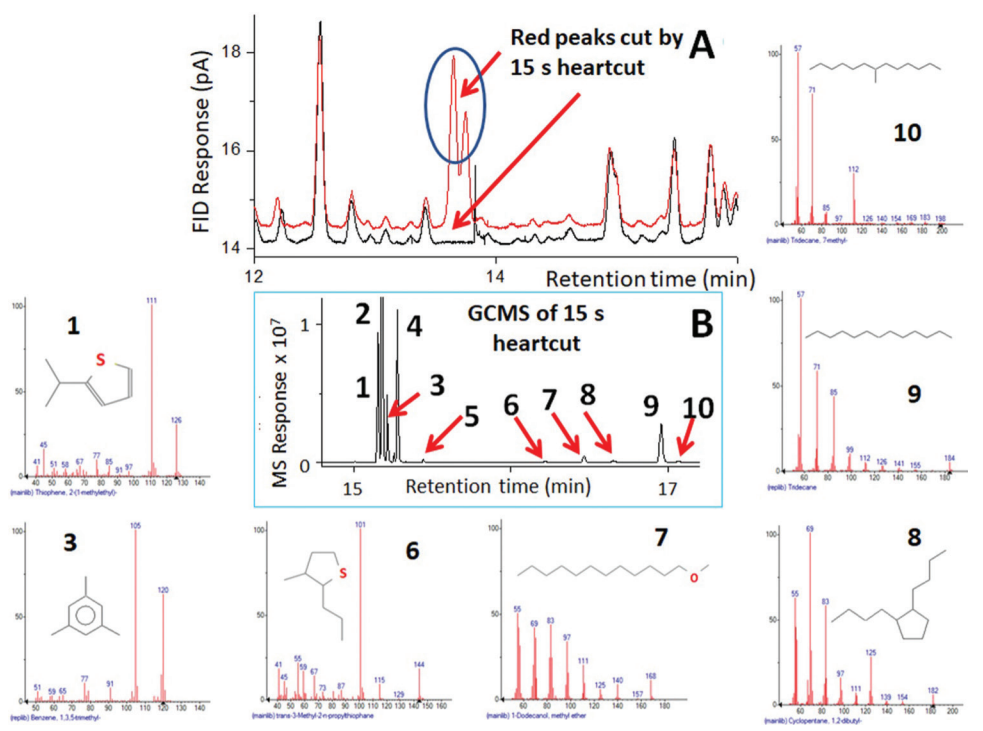

Figure 3: A. A partial GC separation of a high-sulfur shale oil sample over a 12-16 min region is shown before (red trace) and after (black trace) a 15 s heart-cut zone comprising two major peaks as shown. B. The 15 s heart-cut transferred to a ^{2}D column is eluted over a 2 min period, showing at least 10 components, ranging from major to trace abundance. This ^{2}D column is capable of a peak capacity of about 40, between the most polar and least polar compounds. Reprinted from Talanta, vol 120, Amer et al., Multidimensional and comprehensive two-dimensional gas chromatography of dichloromethane soluble products from a high sulfur Jordanian oil shale, p 55-63, (2014) with permission from Elsevier.

Example applications for petrochemical samples Classical GC×GC analysis

Fig 2A is a presentation of a crude oil sample, Late Cretaceous, classified as low-level biodegraded material. A column set of a P ^{1}D (50% phenyl) phase and NP ^{2}D (5% phenyl) shows that nonpolar compounds are more retained (i.e. elute at greater ^2t_R) than polar compounds. Choices for NP/P and P/NP phases for GC×GC have been discussed. [13] Fig 2A is a reconstruction of multiple individual modulations, one of which is shown in Fig 2B. Since this arises for a brief 6 s sampling of the ^{1}D elution, all the compounds displayed in Fig 2B essentially overlap, before the ^{2}D column provides additional separation. This is the rationale and justification for the GC×GC technique. Unresolved compounds can now be effectively separated on the ^{2}D column, here in order of decreasing polarity, allowing facile quantification. Importantly, mass spectrometry will now give a relatively 'pure' mass spectrum of the separated compounds, as well as the total number of compounds at any given ^{1}D position.

Each modulation may be interrogated for molecular information for the resolved compounds. The spectra of separated compounds 1. -6 are presented in Fig 2, and a few points can be made. First the individual spectra may be matched with their proposed identities using a MS database, subject to specificity. The spectra are of sufficient quality, without suffering matrix interference that arises on the ^{1}D column. For instance, spectra for peaks 1 and 2 are very well resolved and not cross-contaminated. The suggested component identities are indicative of the various classes, but in the absence of authentic standards, absolute structures have not been confirmed.

Multidimensional GC and new approaches to MDGC

Fig 3 shows results for a representative 15 s heart-cut of a sulfur-rich oil shale sample; both the original chromatogram in red (see column A1, Fig 1) and the 15 s heart-cut in black are illustrated in Fig 3A.[14] Only the 15 s heart-cut analytes are transferred to the ^{2}D column (e.g. column B1 Fig 1), and all other analytes are recorded at a mid-point detector (FID Fig 1). Classically, a microfluidic Deans switch is used for the transfer process. At least 10 components are reported in the 15 s heart-cut, as shown in Fig 3B. However many more could be fitted into the ^{2}D column 'space' ('peak capacity') between the first (most polar) component, to 10 (the least polar), maybe more than 40. A few points are relevant here. First, the minor components shown on the ^{2}D column are very well resolved, have well defined mass spectra, and the chemical class can be reasonably well classified. Second, the minor components are as little as 0.1% abundance of the major components here, and in all likelihood, without this additional separation, would be unlikely to be detected or identified in a ^{1}D separation. S-, O- and aromatic compounds constitute the first 7 compounds here.

Third, the operation of the heart-cut/modulation/^{2}D column process needs explanation. The process here functions as follows: the 15 s heart-cut is transferred to a cryogenic trap device, which focusses the heart-cut to a narrow band, so dispersion on the ^{1}D column is essentially negated. The cryotrap rapidly (instantaneously) remobilises the heart-cut band to the ^{2}D column, hence maximising its efficiency. The ^{2}D column is operated according to the prevailing oven temperature program, so is 'on-the-fly' as it were. This suggests a range of possible method variations. For example, cooling the oven prior to releasing the heart-cut will increase the ^{2}D peak capacity, which is the classical MDGC approach. Using a shorter ^{2}D column will elute the heart-cut components much faster, with some loss of peak capacity. It is possible to adjust the heart-cut time and the ^{2}D column length so that a true 'comprehensive' ^{2}D analysis is possible, taking contiguous heart-cuts e.g. every 1 min, and eluting each on the ^{2}D column before the next is sampled into the ^{2}D column.

Future perspectives

The higher dimensional separations afforded by GC×GC and MDGC offer much improved separations along with additional advantages such as structured separations that group compounds into predictable retention positions; all these allow significantly better sample characterisation. These techniques are reliable, reproducible, and combined with mass spectrometry provide information-rich data on identity – as well as searchable archived data for future reference. As protocols are established across a broader suite of applications, a reference base that will further validate these approaches for petrochemical-related samples will ensue.

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