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Quantification of n-/iso-paraffins in petrochemical samples by GC×GC-FID

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Introduction

GC×GC with thermal modulation provides very high resolving power and peak capacity, features that make it a powerful tool for detailed separation of complex samples. Thermal modulation grants elevated flexibility and great second dimension resolution. Nowadays, this technique has reached significant technical robustness and can be successfully applied to quantitative analysis.
Hereby we show the use of GC×GC-FID applied to the quantification of linear (n) and branched (iso) paraffins and carbon number breakdown in petrochemical samples of different origin. The FID detector with its stable response provides robust and accurate quantification of hydrocarbons. Moreover, thanks to its very high acquisition speed it's ideal for the sharp modulated peaks.

Instrumentation and software

Agilent 7890B GC equipped with a Zoex ZX1 cryogenic thermal modulator and a FID detector. All 2D data were displayed and analyzed using the GC Image software.

Results

We used both a "standard" (non-polar × mid-polar) and a "reversed" (mid-polar × non-polar) column set configuration.

To insure proper identification of the n-paraffins, a standard mixture of n-paraffins is analyzed (Fig. 1).

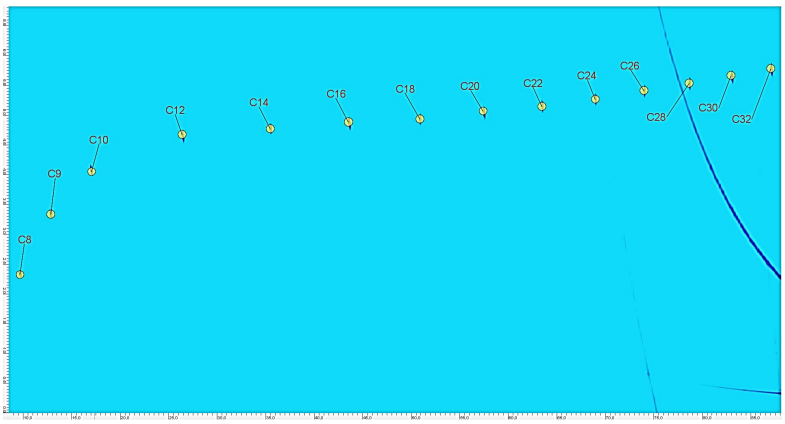

Fig. 1 – Reversed column-set chromatogram of an n-alkanes standard.

Fig. 2 shows the chromatograms obtained for GTL and BTL samples. The quantification results can be automated in GC Image by building templates targeted on the desired compounds or groups, e.g. n-/iso-paraffins. Here the n-paraffins are colorized in yellow while iso-paraffins are shown as red blobs. The n-paraffins are separated from the iso-paraffins and the naphthenes.

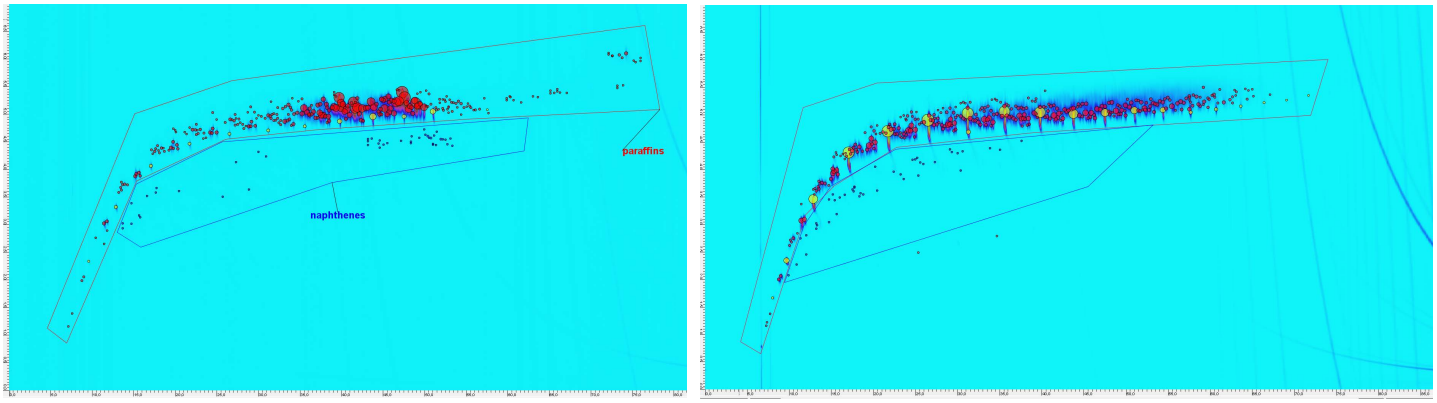

Fig. 2 – Reversed column-set chromatograms of BTL (left) and GTL (right).

Table 1 summarizes all results expressed as %n response, i.e. assuming an equal FID response for all compounds. The different composition in the two matrices are clearly highlighted. As can be clearly seen also from the 2D plots, the two samples have a similar paraffinic content but a very different distribution profile. GTL has much higher content in n-paraffins, especially in the lighter range (C10-C15). BTL is composed mostly by iso-paraffins and higher boiling compounds (C15-C18).

As expected, the different column sets give consistent quantification. The group content results have a maximum deviation of 1.9% for the n-paraffins content in GTL caused by the fact that these are overloaded and therefore separation and integration are somewhat less precise. On the other hand for BTL the results are very consistent.

Table 1 – GC×GC-FID quantification results.

	GTL		BTL	
	Column set			
	Standard	Reversed	Standard	Reversed
Total paraffins (%)	99.8	99.4	99.7	99.8
n-paraffins (%)	45.9	46.8	3.7	3.6
iso-paraffins (%)	54.0	52.6	96.0	96.2
n/iso ratio	0.85	0.89	0.04	0.04

Fig. 3 shows a template built to calculate the carbon number breakdown of BTL. The paraffin group is devied into sub-groups based on the carbon number. The n-paraffins are still labled indipendetly to allow calculation of the n/iso ratios.

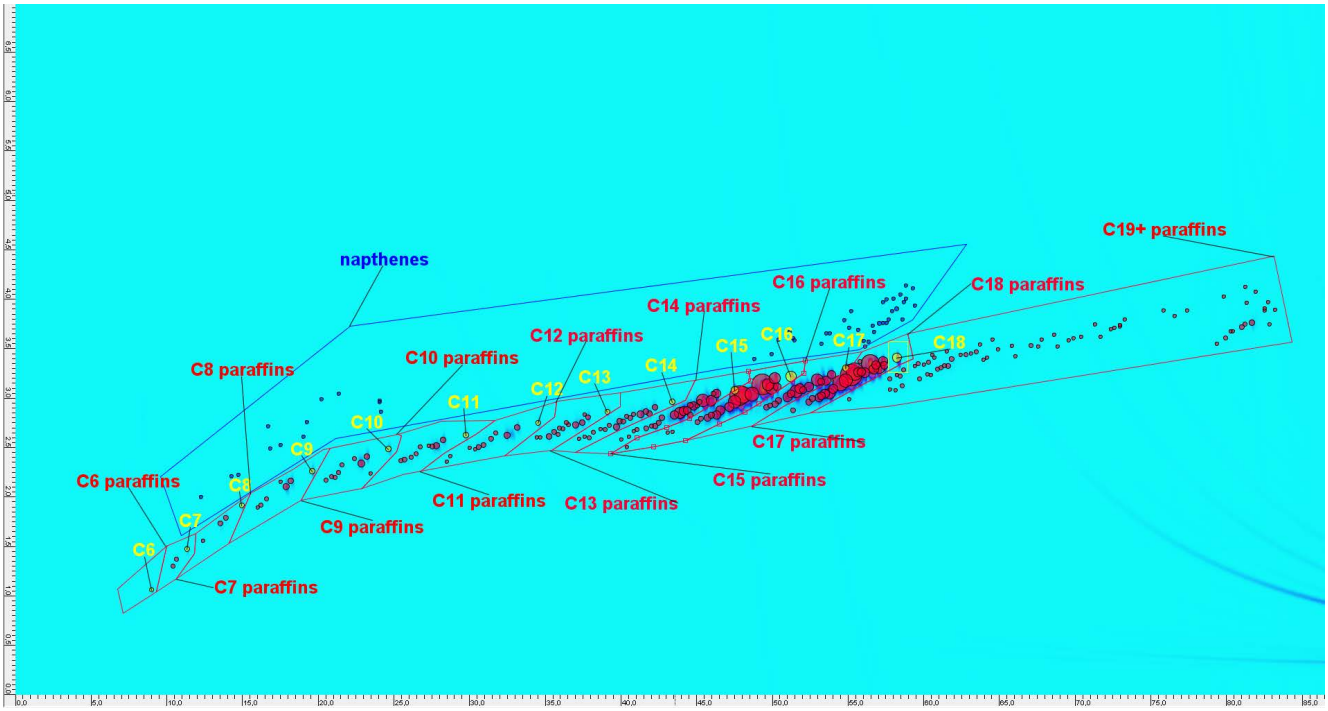

Fig. 3 – Standard column-set chromatogram of BTL with template for carbon number breakdown.

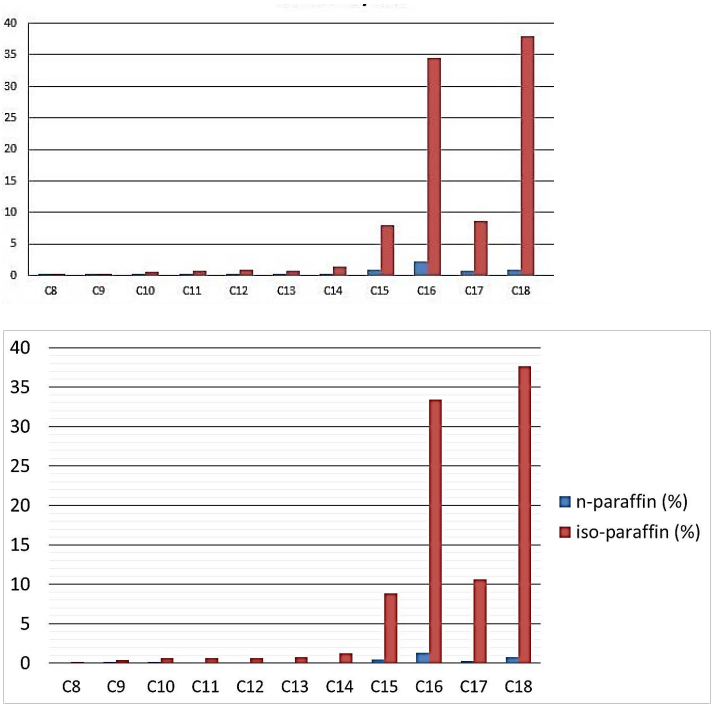

Fig. 4 – BTL carbon breakdown. Expected content (top) and results obtained (bottom).

Fig. 4 shows the comparison of the carbon number breakdown results obtained with the expected composition. The profiles are very consistent, confirming that the method provides good accucracy.

The method can be applied also to much more complex samples. Fig. 5 shows the example for the quantification of n-paraffins in a diesel oil. The results shows very good repeatability (Table 2).

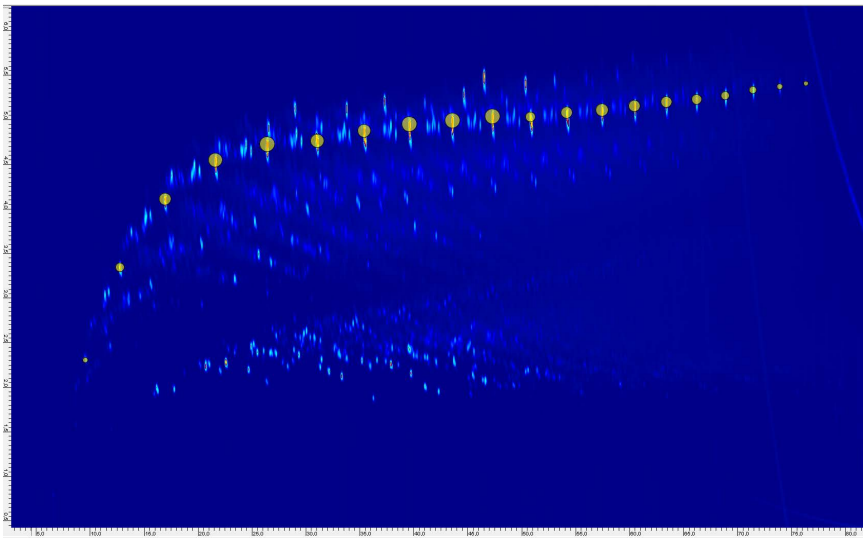

Fig. 5 – Reversed column-set chromatograms of a diesel oil.

Table 2 – Quantification in a diesel oil.

	n-paraffins (%)
Run 1	16.9
Run 2	16.4
Run 3	16.8
Run 4	16.8
Run 5	16.8
Average	16.6
RSD (%)	1.6

Conclusions

- GC×GC with thermal modulation provides very high resolution and allows accurate separation of complex petrochemical samples.
- n-/iso-Paraffins and carbon number groups can be efficiently separated, providing a powerful tool for carbon breakdown profiling and detailed characterization.
- The FID detector provides accurate and reliable results for the quantification of hydrocarbons.
- Quantification of target compounds and can be automated through the GC Image software. Specific templates can be prepared and used to extract rapidly the target quantification results.

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