Group-Type Analysis in Jet Fuel and Diesel by Flow Modulated GCxGC-FID

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Introduction

The development of two-dimensional gas chromatography introduced the possibility to provide reliable compositional information on middle distillate refinery streams such as jet fuel and diesel. The original GCxGC systems mainly relied on cryogenic modulation, which is effective but has some analytical challenges and downsides for routine laboratory use. The most common are:

- High cost of ownership due to the large consumption of liquid CO2 or liquid Nitrogen.
- Requires a lot of lab space.
- Cryogenic modulation is maintenance intensive.
- Low boiling point components are hard to trap and may break through the cryogenic trap.

The challenge that flow modulation presents method developers is in optimising application parameters such as column length, column phase, column flows and GC oven programming to achieve the desired separations. However, once the right parameters have been determined, flow modulation rewards the operator with a lower cost, lower maintenance, and easier to use GC x GC application which also eliminates low boiler breakthrough issues common to the cryogenic trap.

AC Analytical Controls BV (AC) (Netherlands) has solved this analytical challenge and has developed a ready to use flow modulated GC x GC application that provides a complete group-type analysis of jet fuel and diesel fuel streams, including biodiesels blends such as B5, B7 and B10. In addition to the commonly required paraffin (P), naphthene (N) and aromatic (A) species and group results, additional information about the speciated and total Fatty Acid Methyl Esters (FAME) content is reported for biodiesel blends.

This article describes the basic configuration for this AC GC x GC application, and provides information regarding group-type separation and the used quantification method. In addition, we describe how the quantitation results of the application are validated for jet fuel and diesel samples by comparing the values found using the GC x GC method with existing CEN methods for the determination of Total Aromatics and Total FAME content in the applicable products.

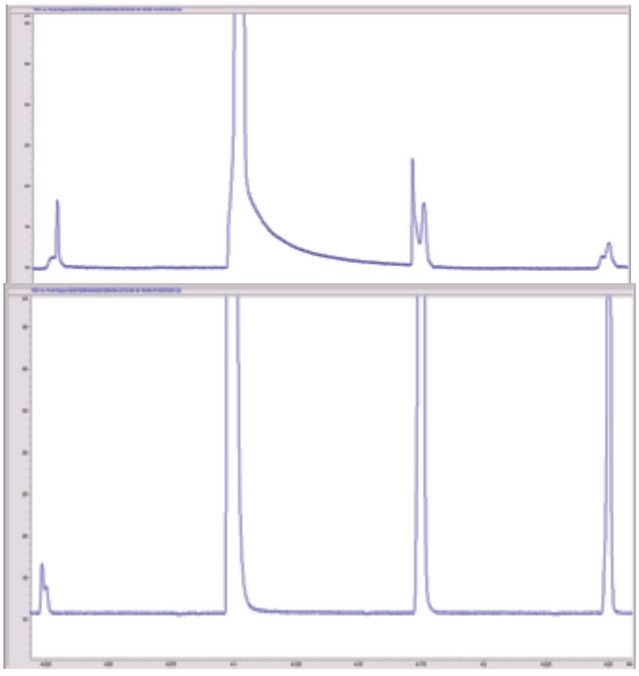

Figure 1. Examples of Standard Flow Modulation (top chromatogram) and AC Flow Modulation (bottom chromatogram of Cyclohexane

Experimental

Instrument configuration

The flow modulated AC group-type in jet fuel and diesel GCxGC application uses reversed phase chromatography, a polar column as the 1st dimension column and a non-polar column as the 2nd dimension column. This modulation method and column setup yields sharper, better defined peaks and thus better peak resolution, as demonstrated in Figure 1.

The flow modulation setup (Figure 2) was further optimised for the application by tuning column lengths, column phase, column coating, column flows and GC oven programming. These system parameters are all critical in obtaining proper modulation, and since the modulator is the heart of every GCxGC system they are vital for getting proper results.

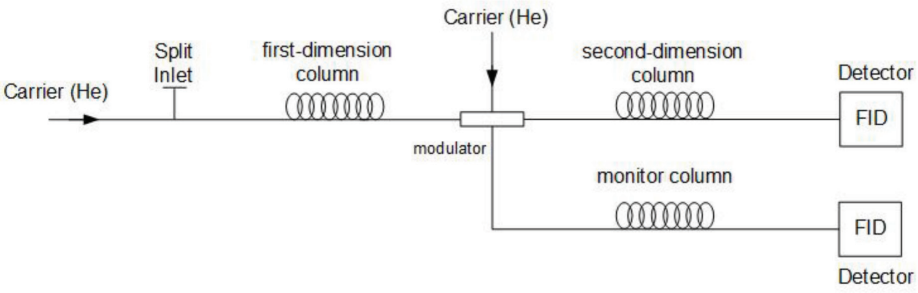

Figure 2. Diagram of the flow modulation setup.

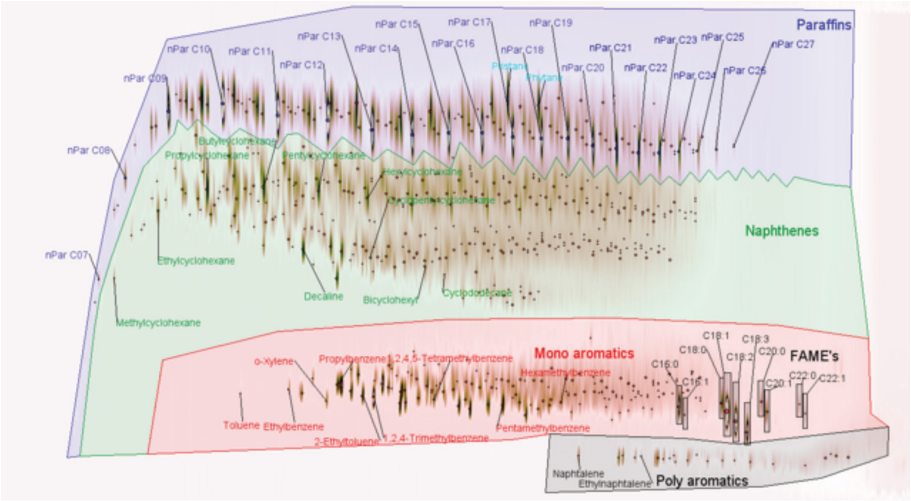

Figure 3. Typical 2D - plot of a Diesel B7

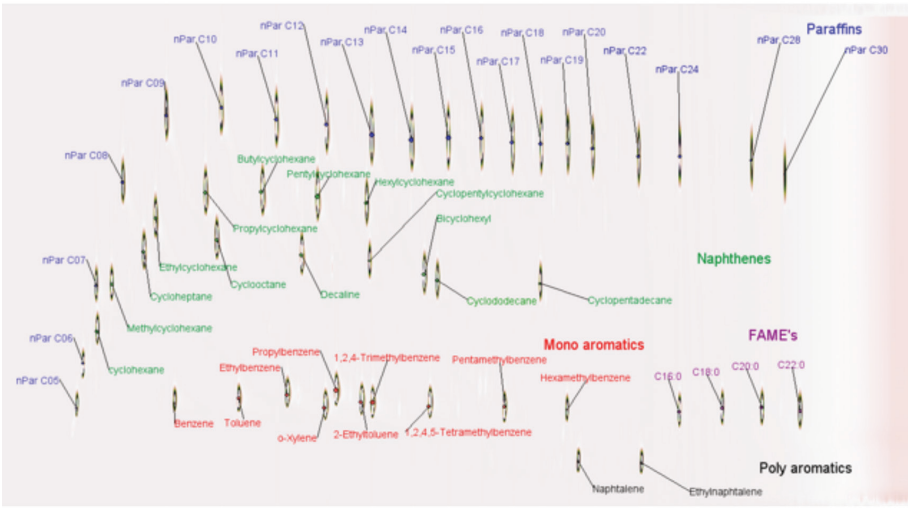

Figure 4. 2D-plot of a gravimetric blend reference sample

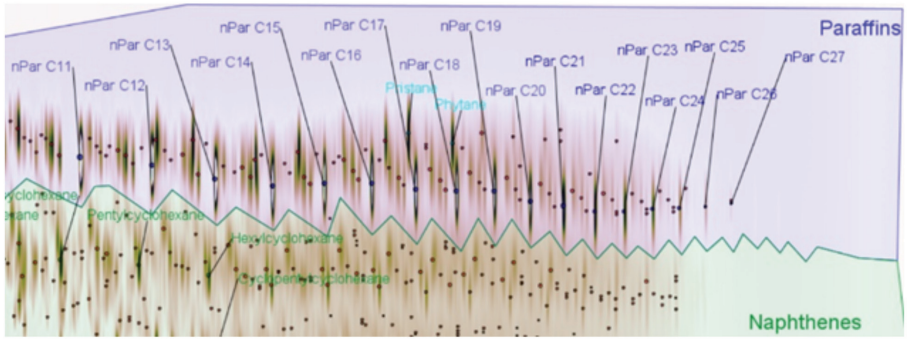

Figure 5. Chromatographic area plot Naphthenes and Paraffins

Separation range

The AC GC x GC application focusses on middle distillates up to 450°C, separating and quantifying paraffins, Iso-paraffins, naphthenes, aromatics and fatty acid methyl esters chemical classes, and reports group totals as well as selected individual compounds. This allows for detailed reporting of various types of fuel such as jet fuels (including synthetic Paraffinic Kerosene (SPK) and sustainable aviation fuel (SAF), diesel and biodiesel blends. A typical chromatogram for diesel fuel is presented in Figure 3.

Quantification and Validation

Quantitative calculation is performed using theoretical response factors. The calculated results are normalised for optimum accuracy and precision. The system performance and response factors are validated by analysing two separate gravimetric blends dedicated for jet fuel and diesel by comparing the found concentrations for each component versus the target concentrations in the sample certificate. See Figure 4 for a 2D plot of a gravimetric blend reference sample.

The blend consists of normal paraffins from Pentane (C5) up to Triacontane(C30) (blue in Figure 3), naphthenes from Cyclohexane up to Cyclopentadecane (green in Figure 3), monoaromatics from benzene up to hexamethylbenzene (red in Figure 3) and the poly aromatics naphthalene and Ethylnaphthalene (black in Figure 3). The blend also contains FAME C16 up to C22 (purple in Figure 3)

Other reference samples are analysed to determine and set the chromatographic area in the GCxGC 2D plot for each group-type (Paraffins, Naphthene's, Aromatics, FAME's).

In Figure 5 the dividing line between the chromatographic area for naphthenes (green) and Paraffins (blue) is shown.

Repeatability and Performance

The standard deviation of the application was validated by 10 repeat runs of a B7 diesel sample. The results suggest that the application has excellent stability for the PNA + FAME groups (Paraffins, Naphthenes, Aromatics, Fatty Acid Methyl Ester). See Table 1.

The accuracy of the application was validated by comparing different jet fuels and diesels and reference material with known aromatics content established by EN12916 [1] (CEN - Technical Bodies) analysis (Petroleum

Table 1

Run	FAME Concentration in % m/m	Paraffins Concentration in % m/m	n-Paraffins Concentration in % m/m	Naphthenes Concentration in % m/m	1R aromatics Concentration in % m/m	2R aromatics Concentration in % m/m
1	7.27	32.53	15.30	35.18	23.73	1.29
2	7.27	32.49	15.34	35.14	23.78	1.32
3	7.29	32.49	15.34	35.12	23.77	1.33
4	7.31	32.47	15.28	35.19	23.74	1.29
5	7.3	32.45	15.27	35.18	23.76	1.31
6	7.24	32.47	15.26	35.19	23.79	1.31
7	7.29	32.43	15.27	35.15	23.79	1.34
8	7.31	32.43	15.36	35.16	23.78	1.32
9	7.3	32.43	15.26	35.18	23.77	1.32
10	7.32	32.42	15.25	35.22	23.75	1.29
Average	7.29	32.46	15.29	35.17	23.77	1.31
Min	7.24	32.42	15.25	35.12	23.73	1.29
Max	7.32	32.53	15.36	35.22	23.79	1.34
stdev	0.023	0.037	0.040	0.029	0.021	0.016
RSD	0.31%	0.12%	0.26%	0.08%	0.09%	1.23%

Table 2

Compound	1	2	3	4	5	6	7	8	9	10	Average	stdev	RSD
C16:0	0.481	0.481	0.48	0.484	0.483	0.48	0.48	0.481	0.483	0.483	0.48	0.0015	0.32%
C16:1	0.115	0.115	0.116	0.116	0.115	0.115	0.115	0.115	0.115	0.116	0.11	0.0004	0.34%
C18:0	0.15	0.15	0.152	0.153	0.152	0.151	0.151	0.152	0.151	0.153	0.15	0.0012	0.79%
C18:1	4.259	4.259	4.258	4.273	4.264	4.229	4.25	4.259	4.255	4.274	4.25	0.0127	0.30%
C18:2	1.31	1.31	1.316	1.32	1.317	1.307	1.313	1.316	1.316	1.32	1.31	0.0043	0.33%
C18:3	0.535	0.535	0.54	0.543	0.542	0.537	0.541	0.544	0.541	0.544	0.54	0.0033	0.61%
C20:0	0.08	0.08	0.081	0.081	0.081	0.081	0.082	0.083	0.081	0.081	0.08	0.001	1.28%
C20:1	0.116	0.116	0.118	0.118	0.118	0.117	0.119	0.128	0.118	0.119	0.11	0.0035	2.92%
C22:0	0.032	0.032	0.033	0.032	0.033	0.033	0.033	0.033	0.033	0.033	0.03	0.0006	1.76%
C22:1	0.03	0.03	0.032	0.03	0.031	0.031	0.032	0.034	0.032	0.031	0.03	0.0012	3.95%
Total FAME	7.109	7.109	7.125	7.15	7.138	7.081	7.115	7.145	7.126	7.154	7.13	0.0225	0.32%

Table 3

Name	Amount Percent (% v/v)	Target values (% v/v)	repeatability (EN14078)	Reproducibility (EN14078)
FAME	6.78*	6.91	0.095	0.510

**Converted from % m/m to % v/v, using sample density = 831.4 g/L and FAME density = 874 g/L*

products- Determination of aromatic hydrocarbon types in middle distillates- High performance liquid chromatography method with refractive index detection).

The differences between measurements done using the AC GCxGC application and measurements done using the HPLC-RI method EN12916, stayed well within EN12916 reproducibility limits for all samples and standards. The results and accepted reproducibility limitation are displayed in Figure 6.

The total FAME content and the FAME speciation have been validated by comparing the results with known diesel B7 values measured by EN14078 [2] (CEN - Technical Bodies) analysis (Determination of FAME content in middle distillates by Infrared spectrometry). The determined values of total FAME % (m/m) (Table 2) converted to % (v/v) show that the found values measured by the GCxGC application are within the reproducibility of the EN14078 method (Table 3).

Conclusion

The AC GCxGC group-types in diesel and jet fuel application provides detailed insight into the composition of jet fuels & diesels using a rugged, low-maintenance hardware setup. Individual component and group type results are highly repeatable and accurate. The regulatory important result for total aromatics corresponds well to the existing method EN12916. Additionally, the application is also an excellent tool for determining speciated and total FAME content of biodiesel fuel products. The measured values for FAME content are within the reproducibility values of the compared method. Besides offering detailed group-type breakdown, the GCxGC application allows the user to expand its applicability to quantify selected individual components such as benzene, toluene, ethylbenzene and xylene (BTEX) content.

Because the mechanical complexity of the modulator has been significantly reduced,

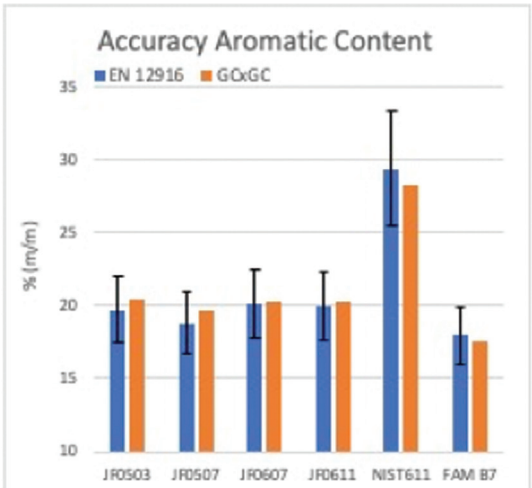

Figure 6. GCxGC aromatic content versus EN 12916:2016 (confidence levels based on Reproducibility calculation EN 12916:2016

these results can be obtained in less experienced routine lab environments, without requiring large volumes of liquid nitrogen or carbon dioxide to operate. By using pre-defined automated software actions, the interaction with the GCxGC software is reduced to a minimum. Additionally, instrument performance is easily validated with dedicated gravimetric reference samples. This makes routine analysis of middle distillate samples by GCxGC not only possible but practical.

The GCxGC application presented in this article provides petroleum refineries with an easy to use analytical tool, which was previously only available to research institutions.

Detailed compositional information of middle distillate streams is a key parameter in modelling refinery processes or predicting final product properties. Having the option to quantify the composition of these streams in far greater detail can enable improved operational efficiency and help to ensure final products meet the highest quality standards.

References

1. EN12916 https://standards.cen.eu/dyn/www/f?p=204:110:0::::FSP_PROJECT:63144&cs=124498A54C8C5BE30FEB873BCFC30A7EC

2. N14078 https://standards.cen.eu/dyn/www/f?p=204:110:0::::FSP_PROJECT:38244&cs=1CB0E2913B07669AF00EEB2A68E9424D3