APPLICATION NOTE

FAME analysis in Diesel by Flow Modulated GCxGC FID.

- **Dedicated PiPNA + FAME**
- **For (Bio-)Diesel and Jet Fuels**
- **Robust System, Easy to use**
- **No Cryogenic coolant Required**

Keywords:
FAME in Diesel, Flow Modulation, GCxGC FID, 2D GC

INTRODUCTION

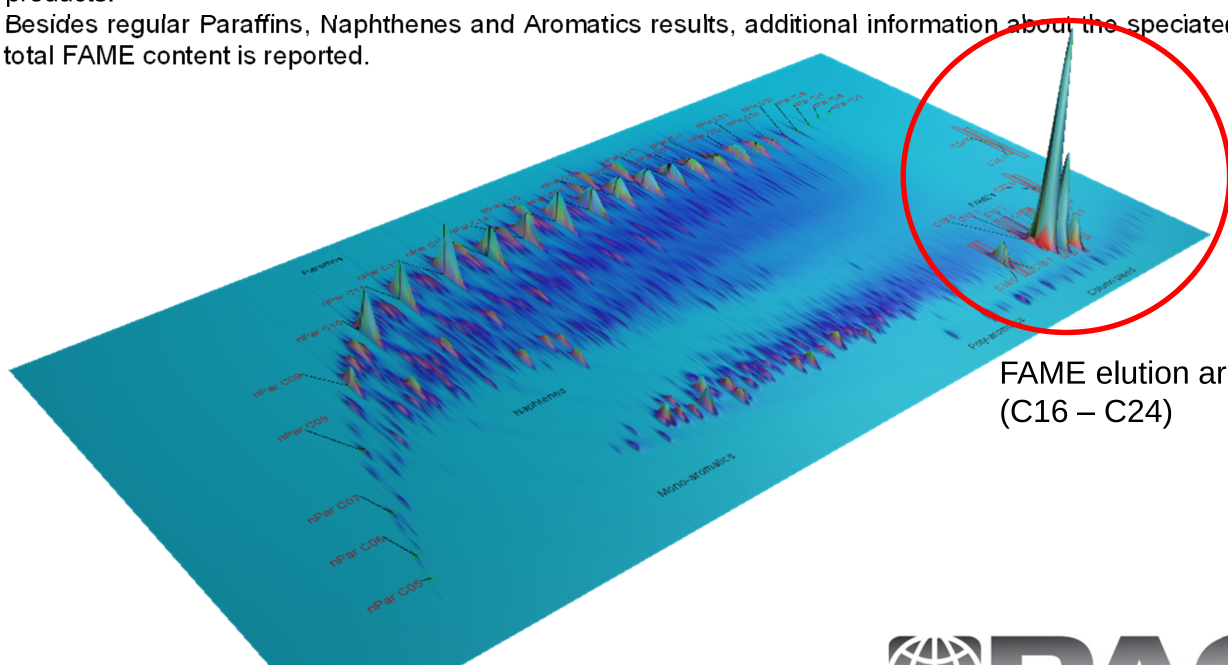
Recent developments in comprehensive (GCxGC) gas chromatography now allow for obtaining highly detailed compositional information on complex mid-boiling refinery streams such as biodiesels and Jet fuels for routine analysis.

The first GCxGC systems developed mainly relied on the rather cumbersome cryogenic modulation, which is effective but has a high cost of ownership due to the large consumption of either liquid CO2 or liquid Nitrogen. This cryogenic modulation is maintenance prone, requires additional lab space and can be problematic for relatively volatile components, which are often seen to break through the cryogenic trapping system.

Flow modulation comprehensive GC provides a more robust kind of modulation that hardly requires maintenance and experiences no problems in the modulation of low boiling components.

AC developed a dedicated GCxGC solution which is easy to use and provides a complete group-type analysis of diesel fuel streams with Final Boling Point up to 450°C, including biodiesels like B5, B7 and B10 products.

Besides regular Paraffins, Naphthenes and Aromatics results, additional information about the speciated and total FAME content is reported.



FAME elution area
(C16 – C24)

Figure 1. Typical 3D-plot of B7 diesel sample

IMPROVED FLOW MODULATION

A novel way of flow modulation was developed with the scope of improving peak width and resolution. Compare Figure 2a vs 2b, with the lower picture representing the improved modulation set-up.

The flow modulation was further optimized for the analysis of diesel 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 accurate results.

For the Group-Type Analysis (PiPNA) in Diesel, reversed phase chromatography was preferred to maximize separation between the different chemical groups, so a polar column was used as a first dimension colu, and a non-polar in the second.

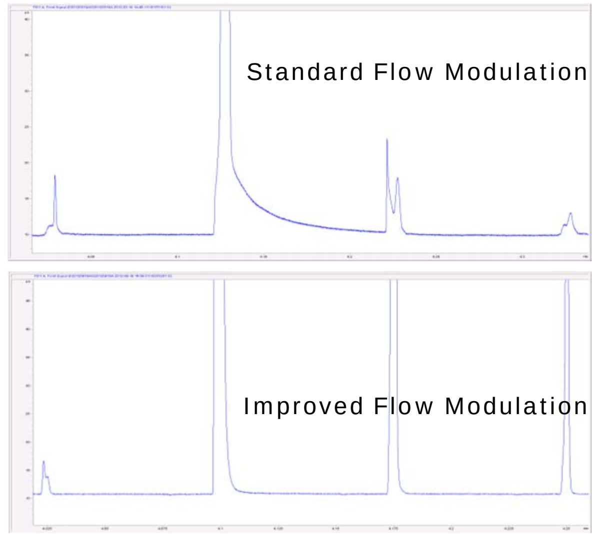


Figure 2a and 2b. Examples of Standard Flow Modulation (top chromatogram) and improved Flow Modulation (bottom chromatogram) of Cyclohexane

RESULTS

The analysis of diesel on the AC optimized flow modulated GCxGC, as presented in this application note, yields total Paraffins, n-Paraffins, iso-Paraffins, total Naphthenes, mono-Aromatics, poly-Aromatics and total Aromatics (PiPNA) results plus the analysis of speciated and total FAME.

Quantitative calculation is done by the use of theoretical response factors, except for FAME's. FAME response factors are calibrated externally (see figure 3). Consecutively the calculated results are normalized for optimum accuracy and precision.

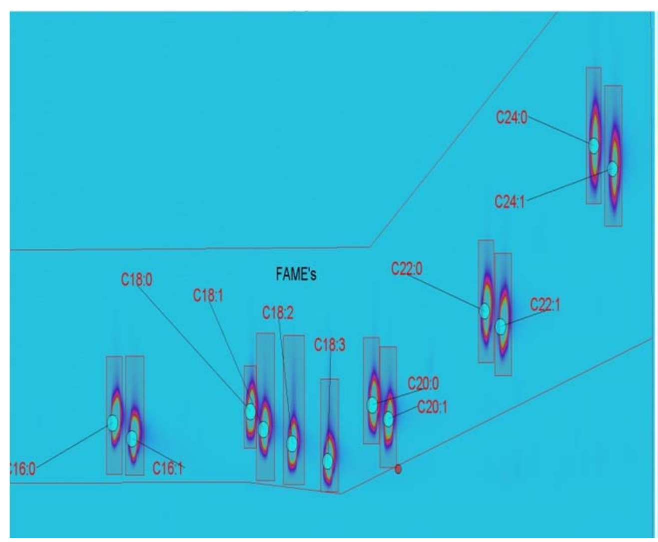


Figure 3: FAME calibration sample to determine individual FID response factors and 1st and 2nd dimension retention times

The developed method was compared against EN 14078 (Determination of fatty methyl ester (FAME) content in middle distillates - Infrared spectrometry method) for bias using two well characterized samples from a FAM Round Robin.

Determined values for Total FAMES Content using the GCxGC method were quite similar to the IR methods, and well within the reproducibility of the EN12916 method reference (Figure 4). Absolute Value calculated (6.78% v/v) is well within expectation for a B7 sample.

A repeatability test was run using the #764 FAM B7 diesel round robin sample for determining short term repeatability. Table 2 summarizes run by run data for individual and total FAME content. It proves stability and ruggedness for the method

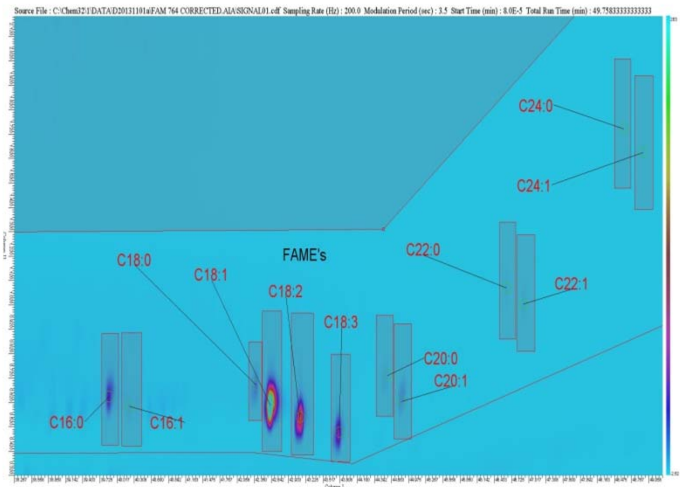


Figure 4: FAME pattern in B7 diesel sample.

LINEARITY

The linearity of the application is checked using gravimetric additions of FAME compounds to a FAME-free diesel fuel. The standards are prepared between 0 – 10 % (w/w) total FAME. The linear correlation (R^2) exceeds > 0.999 for all single FAME compounds and total FAME content.

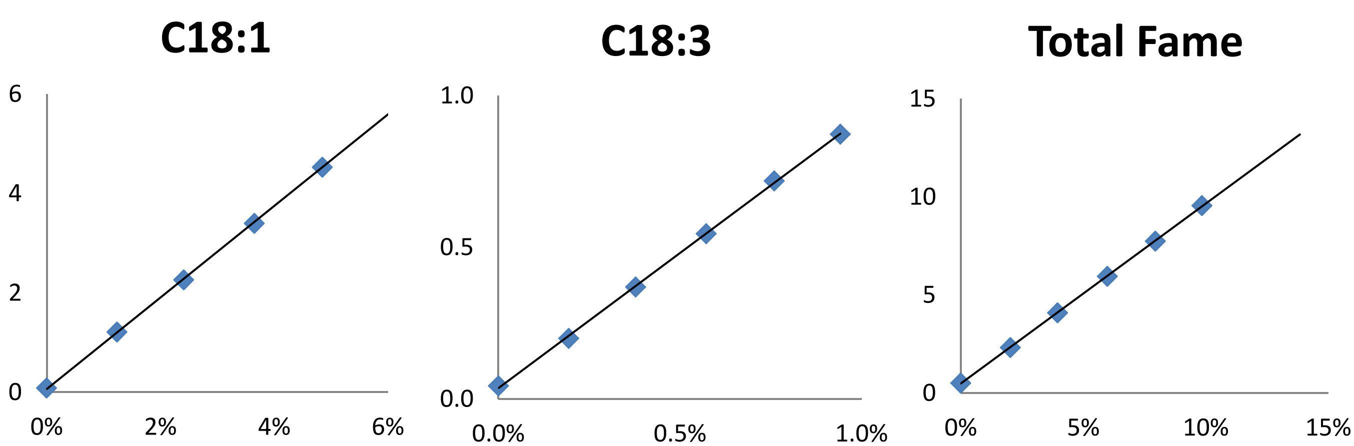


Figure 3: Linearity plots of individual and total FAME content. All Plots are % measured vs % weighed in mass

Sample	FAME Content (% v/v)	Reference Value FAM (% v/v)	repeatability (EN14078)	Reproducibility (EN14078)
FAME B7 #764	6.78*	6.91	0.0950	0.5100

Table 1: Determined total FAME value of B7 diesel #764 compared with target values from FAM round robin. Values are converted from % m/m to % v/v using Round Robin sample density determined @15°C 831.4 g/L and FAME density= 874 g/L

Amount percentage (m/m)													
Compound	1	2	3	4	5	6	7	8	9	10	Average	stdev	RSD
C16:0	0.481	0.481	0.480	0.484	0.483	0.480	0.480	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	0.150	0.150	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	4.250	4.259	4.255	4.274	4.25	0.0127	0.30%
C18:2	1.310	1.310	1.316	1.320	1.317	1.307	1.313	1.316	1.316	1.320	1.31	0.0043	0.33%
C18:3	0.535	0.535	0.540	0.543	0.542	0.537	0.541	0.544	0.541	0.544	0.54	0.0033	0.61%
C20:0	0.080	0.080	0.081	0.081	0.081	0.081	0.082	0.083	0.081	0.081	0.08	0.0010	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	0.030	0.030	0.032	0.030	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	7.150	7.138	7.081	7.115	7.145	7.126	7.154	7.13	0.0225	0.32%

Table 2: Repeatability data for reported FAME results from FAM #764 B7 Diesel. Results in m/m

CONCLUSION

Analytical controls developed a robust GCxGC application for speciated and total FAME analysis of biodiesel fuel products. The measured values for FAME content are within the reproducibility values of the compared method. Because the mechanical complexity of the modulator has been significantly reduced these results can be obtained in less experienced routine lab environments. By using pre-defined automated software actions, the interaction with the software is reduced to a minimum. This makes routinely analyzing samples by GCxGC possible.

AC Analytical Controls® has been the recognized leader in chromatography analyzers for gas, naphtha and gasoline streams in crude oil refining since 1981. AC also provides technology for residuals analysis for the hydrocarbon processing industry. Applications cover the entire spectrum of petroleum, petrochemical and refinery, gas and natural gas analysis; ACs Turn-Key Application solutions include the AC Reformulyzer® , DHA, SimDis, NGA, Hi-Speed RGA and Customized instruments.