APPLICATION NOTE

Group-Type Analysis (PiPNA) in Diesel and Jet Fuel by Flow Modulated GCxGC FID.

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

Keywords:
PiPNA 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 has developed a dedicated solution for (bio)diesel fuels which is easy to use and provides a complete PiPNA group-type analysis of diesel fuel streams including Fatty Acid Methyl esters. The application also can be applied to Jet fuels. A comparable analysis is described in UOP method 990-11.

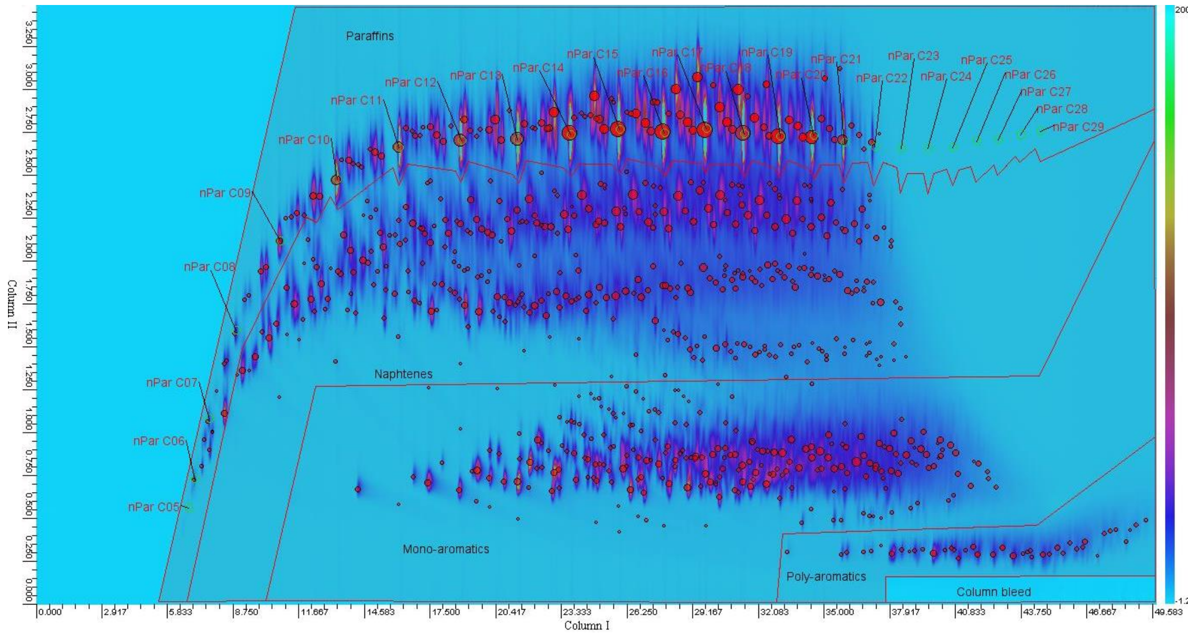

Figure 1. Typical 2D-plot of diesel sample

APPLICATION NOTE

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.

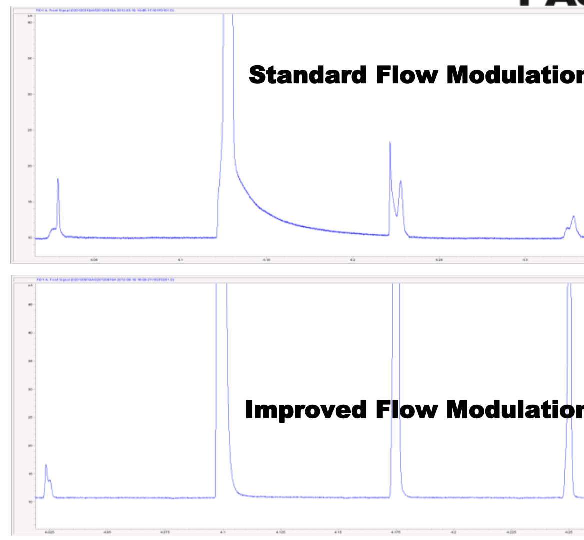

Figure 2a and 2b. Examples of Standard Flow Modulation (top chromatogram) and improved Flow Modulation (bottom chromatogram) of Cyclohexane

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. Fatty acid Methyl Esters can also be included in the same analysis. Quantitative calculation is done by the use of theoretical FID response factors (except for FAME's if present). The calculated results are normalized for optimum accuracy and precision. Fig 3 and Table 1 represent measured concentrations against theoretical values for a gravimetric QC mixture.

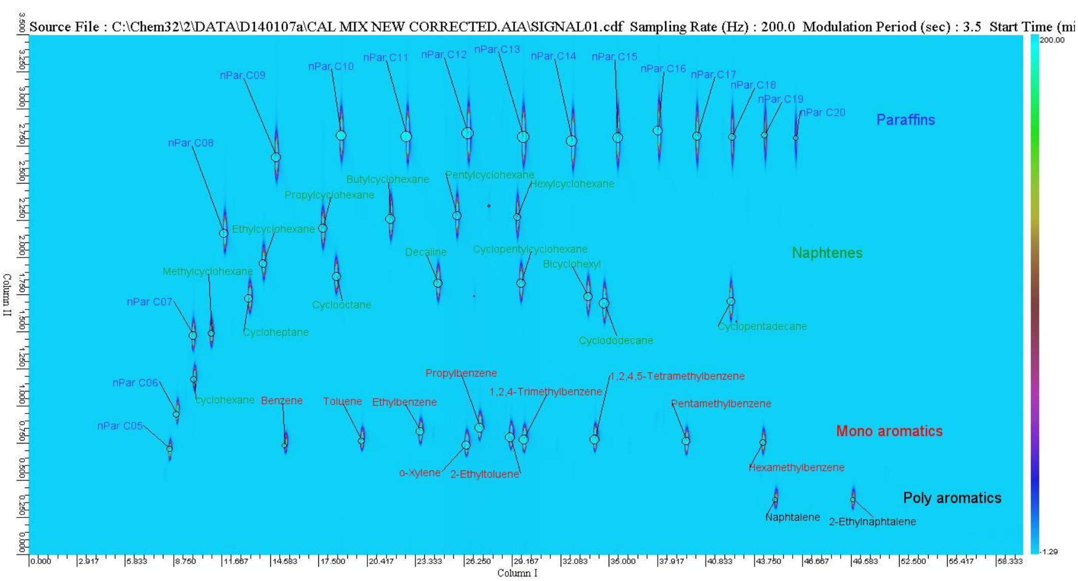

Figure 3 . Gravimetric Standard.

Component name	Type	Th. Concentration (Wt%)	Measured Value	Recovery
n-Pentane	C5 nP	0.74	0.75	102%
n-Hexane	C6 nP	1.06	1.00	94%
n-Heptane	C7 nP	1.87	1.84	98%
n-Octane	C8 nP	2.45	2.42	99%
n-Nonane	C9 nP	3.19	3.16	99%
n-Decane	C10 nP	3.84	3.84	100%
n-Undecane	C11 nP	4.58	4.58	100%
n-Dodecane	C12 nP	5.30	5.38	101%
n-Tridecane	C13 nP	5.27	5.29	100%
n-Tetradecane	C14 nP	4.61	4.55	99%
n-Pentadecane	C15 nP	3.84	3.77	98%
n-Hexadecane	C16 nP	3.18	3.06	96%
n-Heptadecane	C17 nP	2.50	2.38	95%
n-Octadecane	C18 nP	1.75	1.64	94%
n-Nonadecane	C19 nP	1.25	1.16	93%
n-Eicosane	C20 nP	0.51	0.48	93%
Benzene	C6 A	0.61	0.60	99%
Toluene	C7 A	1.14	1.13	99%
Ethylbenzene	C8 A	1.84	1.83	100%
o-Xylene	C8 A	2.43	2.46	101%
2-ethyltoluene	C9A	3.19	3.22	101%
n-Propylbenzene	C9 A	3.23	3.29	102%
1,2,4-Trimethylbenzene	C9 A	3.20	3.21	100%
1,2,4,5-Tetramethylbenzene	C10 A	2.82	2.84	101%
Pentamethylbenzene	C11 A	1.92	1.89	98%
Hexamethylbenzene	C12 A	1.09	1.10	101%
Naphtalene	C10 2-ring A	0.52	0.54	102%
2-Ethylnaphtalene	C12 2-ring A	0.57	0.56	98%
Methylcyclohexane	C7N	1.07	1.09	102%
Ethylcyclohexane	C8 N	1.79	1.81	101%
Propylcyclohexane	C9 N	2.43	2.45	101%
Butylcyclohexane	C10 N	3.12	3.17	102%
Pentylcyclohexane	C11 N	2.33	2.37	102%
Hexylcyclohexane	C12 N	1.74	1.79	103%
Cyclohexane	C6N	1.05	1.05	101%
Cycloheptane	C7 N	1.90	1.92	101%
Cyclooctane	C8 N	2.42	2.45	101%
Cyclododecane	C12 N	3.97	4.04	102%
Cyclopentadecane	C15 N	2.26	2.28	101%
trans-Decahydronaphtalene	C10 2-ring N	2.53	2.56	101%
Cyclopentylcyclohexane	C11 2-ring N	2.43	2.48	102%
Bicyclohexyl	C12N 2-ring N	2.45	2.48	101%
Total Paraffines		45.95	45.31	99%
Total Naphtenes		31.49	31.93	101%
Total Aromatics		22.56	22.66	100%
Totals		100.000	99.907	100%

Table 1: Quantitative Reference Sample – theoretical values versus measured values for selected components

The developed method was compared against EN 12916 (Determination of aromatic hydrocarbon types in middle distillates - High performance liquid chromatography method with refractive index detection) for bias using two well characterized samples from a FAM Round Robin.

Determined values for Total Aromatic Content were slightly lower for the GCxGC method, but within the reproducibility of the EN12916 method reference (Figure 4)

A repeatability test was run using the #764 FAM B7 diesel round robin sample for determining short term repeatability. Table 2 summarizes results by chemical group including FAMEs. It proves stability and ruggedness for the method

Multiple commercially obtained Diesel fuels were analyzed was analyzed. The power of comprehensive GC is evident from Figure 5, as not only the FAMEs are clearly visible in the chromatogram, but also the resolution in the C20-C24 paraffins region is sufficient to separate what appears to be a typical cluster of components for this type of diesel fuel.

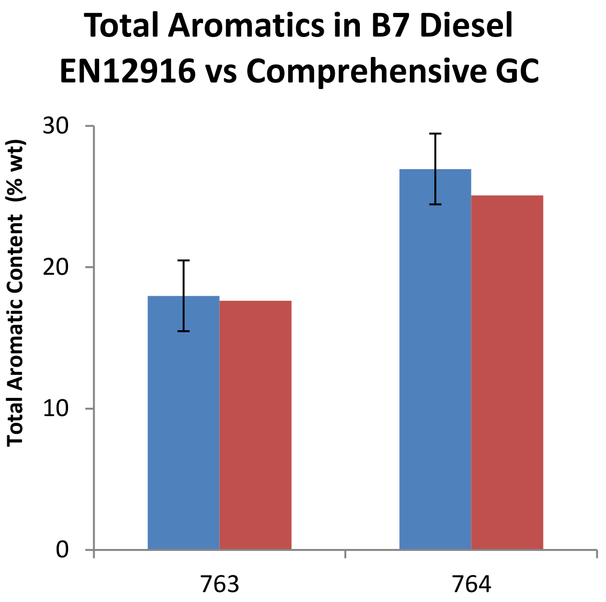

Figure 4: Determined value of total aromatic content by GCxGC (red) versus FAM Round Robin results (blue) according EN12916
(for FAM Round Robin : n=26, uncertainty bars are from EN 12916)

Run	FAME (% m/m)	1R aromatics (% m/m)	2R aromatics (% m/m)	Parafins (% m/m)	n-Parafins (% m/m)	Naphtenes (% m/m)
Average	7.29	23.77	1.31	32.46	15.29	35.17
MIN	7.24	23.73	1.29	32.42	15.25	35.12
MAX	7.32	23.79	1.34	32.53	15.36	35.22
stdev	0.023	0.021	0.016	0.037	0.040	0.029
RSD	0.31%	0.09%	1.23%	0.12%	0.26%	0.08%

Table 2: Repeatability data for #764 FAM B7 Sample (PiPNA group results, n =10)

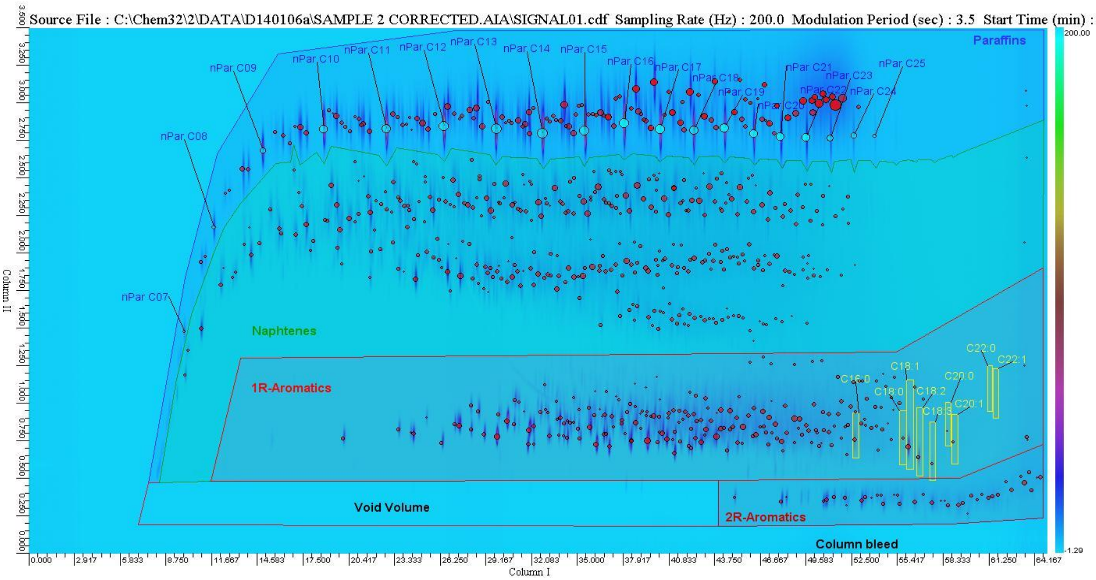

Figure 5 . Commercial Diesel Sample (V-Power Diesel).

Name	Amount Percent (wt %)
FAME	5.8
Paraffins	36.0
n-Paraffins	16.7
1R-Aromatics	20.2
2R-Aromatics	1.6
Naphtenes	36.5

Fame Name	Amount Percent (wt %)
C16:0	0.53
C18:0	0.19
C18:1	3.19
C18:2	1.15
C18:3	0.50
C20:0	0.05
C20:1	0.09
C22:0	0.03
C22:1	0.03

Table 3: Results for a commercial Diesel Sample, PiPNA and FAME by group

CONCLUSION

AC Analytical Controls has developed the first dedicated analyzer for routine group type analysis of (bio)diesel fuel products and Jet fuels, based on comprehensive GCxGC. The analyzer delivers reliable quantitative data on iso- and normal Paraffins, Naphtenes and Aromatics, as well as FAMEs.

Significant improvements to the flow modulator technology deliver high resolution separations sufficient for research goals, but also allows for accurate analysis and a much more robust analyzer that can even be run in routine environments.