Group-Type Analysis (PNA) in Jet Fuel by Flow Modulated GCxGC FID

- **Dedicated PNA in Jet Analysis**
- **Novel Flow Modulation**
- **Rugged Solution Easy to Use**

Keywords:
PNA in Jet, Flow Modulation, GCxGC FID, 2D GC

INTRODUCTION

The development of 2D gas chromatography introduced the possibility to provide reliable compositional information on mid-boiling refinery streams like jet fuel. The first GCxGC systems developed mainly relied on cryogenic modulation, which is effective but has a high cost of ownership due to the large consumption of either liquid CO2 or liquid Nitrogen. Moreover, cryogenic modulation is maintenance prone, requires additional lab space and may prove challenging with highly volatile components break through the cryogenic trap.

When properly set up flow modulation provides a much more rugged kind of modulation that requires hardly any maintenance and performs excellent in the modulation of low boiling components.

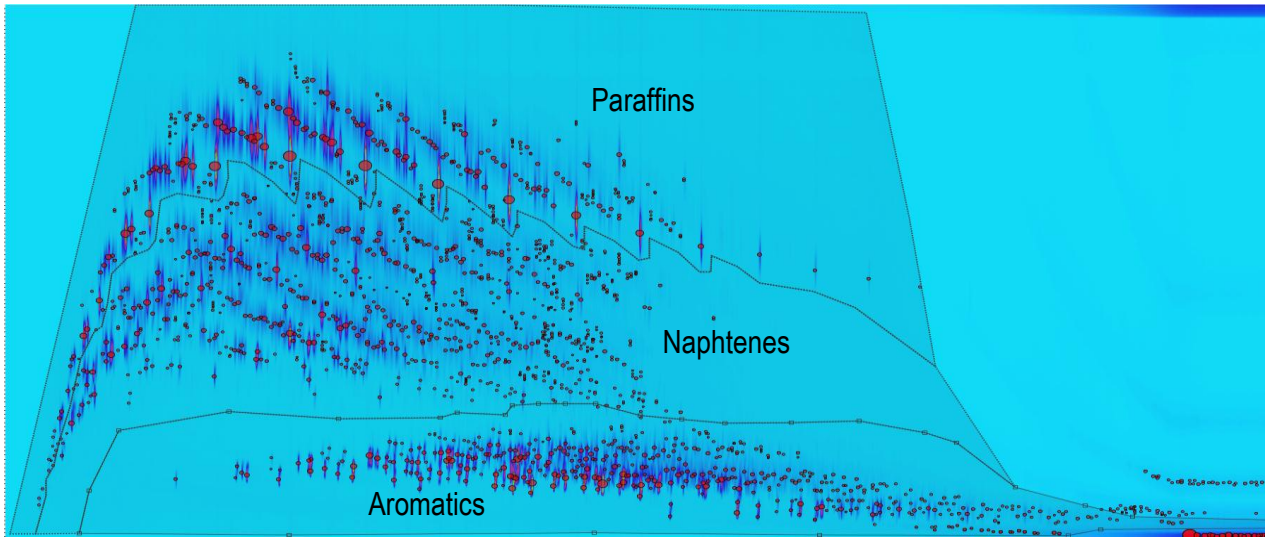

Figure 1. Typical 2D-plot of NIST1616B Jet Fuel

IMPROVED FLOW MODULATION

A novel way of flow modulation was implemented by AC to improve on the more standard way of flow modulation. This yields sharper, better defined peaks and thus better peak resolution as demonstrated in figure 2.

The flow modulation was further optimized for the analysis of Jet Fuels 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.
For the Group Type Analysis (PNA) in Jet Fuel, reversed phase chromatography is prefered to maximize the separations between the different group types.

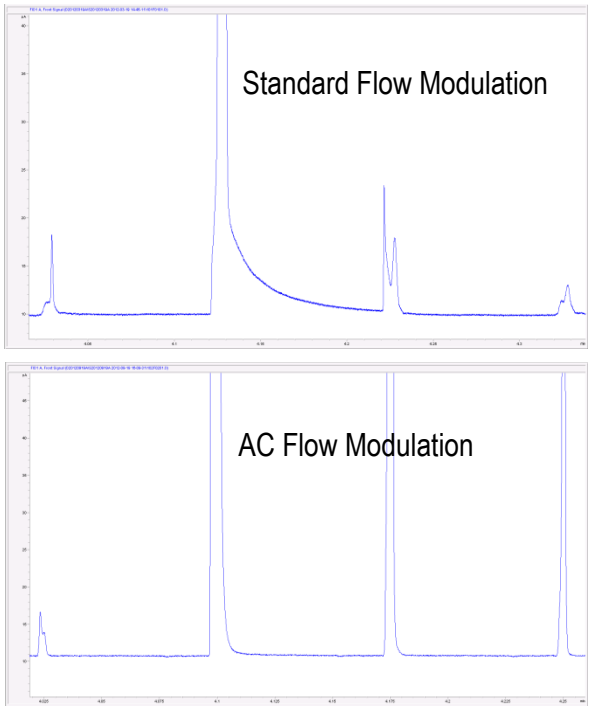

Figure 2. Examples of Standard Flow Modulation (top chromatogram) and AC Flow Modulation (bottom chromatogram) of cyclohexane

RESULTS

The analysis of Jet Fuel on the AC optimized flow modulated GCxGC, as presented in this application note, yields total Paraffins, total Naphtenes and total Aromatics (PNA) results.

Calibration is performed by external standard method, containing typical components present in Jet Fuels. The external standard results are normalized for optimum accuracy and precision.

Because the mechanical complexity of the modulator has been significanty reduced these results can be obtained in less experienced routine lab environments.

Normalized External Standard Results				
Sample	Paraffins (Wt%)	Naphtenes (Wt%)	Aromatics (Wt%)	Totals (Wt%)
NIST 1616B	38.81	32.85	28.34	100.00
	38.72	32.96	28.32	100.00
	38.76	32.93	28.31	100.00
	38.75	32.98	28.27	100.00
	38.76	32.95	28.29	100.00
	38.69	32.96	28.34	100.00
	38.76	32.99	28.25	100.00
	38.71	32.98	28.31	100.00
	38.74	32.97	28.30	100.00
	38.70	32.93	28.37	100.00
	38.71	32.99	28.30	100.00
Average	38.74	32.95	28.31	
SD	0.03	0.04	0.03	
RSD	0.09	0.12	0.12	

Table 1. Repeatability data on NIST 1616B Reference Jet fuel.

ACCURACY AND PRECISION

Precision (repeatability) of the application was determined by making repeated runs of NIST1616B standard (n=11). Repeatability for the 3 groups paraffins, naphtenes & aromatics was found to be around 0.1% RSD as shown in table 1 on the previous page.

Accuracy of the system was validated by comparing various different Jet Fuels and reference standards with known aromatics content (established by EN12916:2006 analysis (aromatic hydrocarbon types in middle distillates by HPLC-RID)). Results are displayed in figure 3.
Results using the Analytical Controls GCxGC method compare well with EN12916:2006 with respect to EN12916:2006 reproducibility limits for all samples and standards.

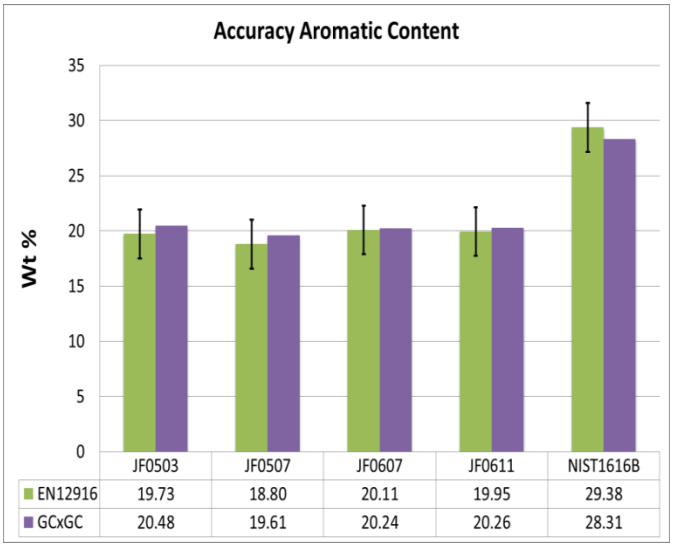

Figure 3. GCxGC Aromatic Content versus EN12916 :2006 (confidence levels based on 2 times standard deviation EN12916:2006)

CONCLUSION

Making use of the novel GCxGC technique provides insight into the group- composition of Jet Fuels without using complex hardware and large volumes of liquid nitrogen or carbon dioxide. It is the combination of a rugged/low-maintenance flow-modulator and the well-established FID detector which makes Jet Fuel group-type information not only feasible, but also rugged enough to run continuously without operator interference when using the in this note discussed application.

Reported Group-Types	Paraffins, Naphtenes, Aromatics
Matrix	Jet Fuel
Repeatability	Better than 0.5 % RSD
Analysis Time	115 minutes
LOQ (Component)	0.1 Wt%

Table 2. Analysis Specifications

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® , SimDis, Hi-Speed RGA and Customized instruments.