PAC Application Note

Group-Type Analysis (PiPNA) in middle distillate range (D2887 scope) by Flow Modulated GCxGC FID.

- Group-Type PiPNA in extended range (D2887 scope)
- PAH analysis
- Flow Modulated GC*GC
- Ease of Use / No Cryogenics Required

Keywords:
PiPNA in extended range, Lube oil, Flow Modulation, GCxGC FID, 2D GC

INTRODUCTION

A detailed chemical composition analysis in the middle distillate product range has been accomplished by Flow modulated GC*GC. The major advantage of this set-up is the ability to obtain detailed compositional information of ASTM D2887 sample types.

Sample compatibility <540 °C	PiPNA Group type
Light Cyclo Oil	Paraffins
Lube Oils	i-Paraffins
Gas Oil	Naphthenes
Diesel	1R – 5R Aromatics

The high resolution information provides a powerful tool for product optimization / blending processes. Blending of middle distillate products provides opportunity to dramatically improve product margins. Better distribution of different middle distillate streams allows manufactures to maximize the production of higher value products.

AC developed a GCxGC application which is easy to use and provides a complete group-type analysis of middle distillate streams like lube oil, fuel oil or light cycle oil. The Analytical Controls application doesn't need cryogenic modulation, which makes the system much less complex.

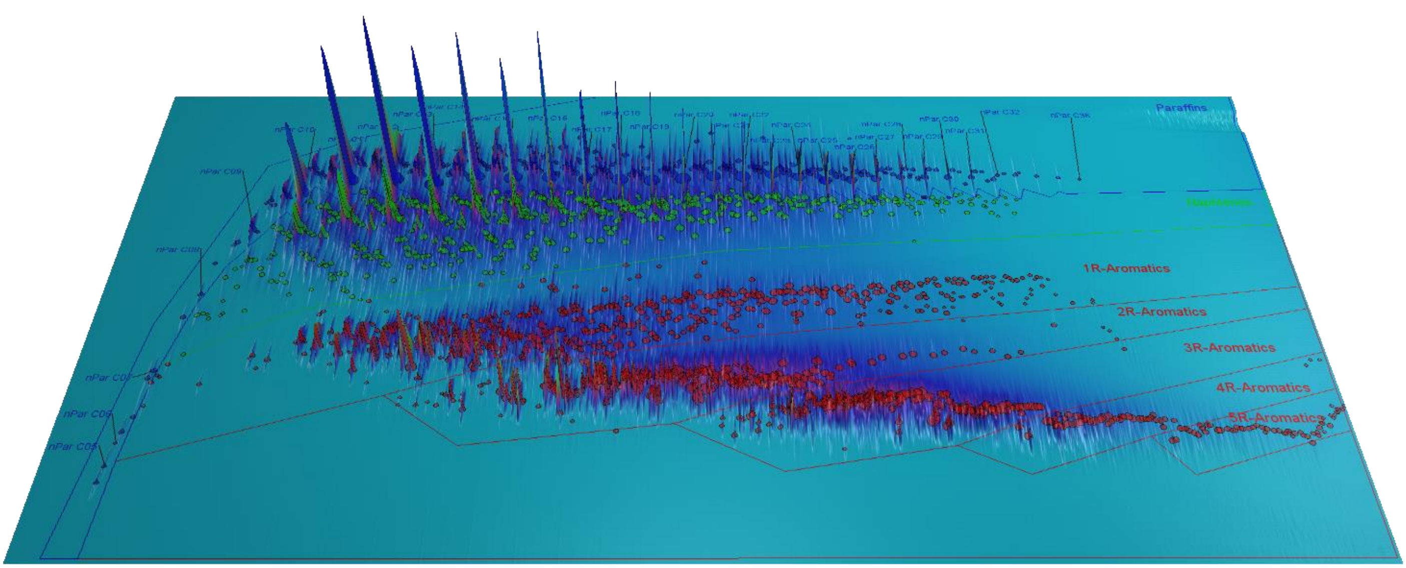

Figure 1. Typical 3D-plot of light cycle oil sample

SAMPLE DISCRIMINATION

Sample discrimination leads to a non-representative sample entering the analytical column. Verification of discrimination will be especially important for heavier samples like described in this application note.

For higher boiling (less volatile) analytes, the residence time of the syringe needle is too short. The analyte will condense on the cold inner and outer surfaces of the needle – prior to it being withdrawn from the inlet. Some less volatile analytes may never properly volatilize and the sample passes the split point (head of the capillary column) as a mixture of sample vapor and non-uniform liquid droplets.

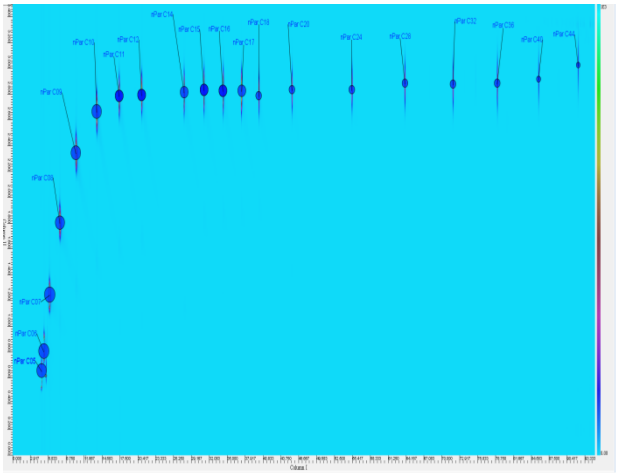

Figure 2. 2D-view of n-paraffin calibration mixture.

The GCxGC system is effectively optimized to reduce the effect of sample discrimination by using optimized liner geometry and packing material to promote sample mixing and volatilization. The instrument design (EPC control) is developed to reduce fluctuation in split flow. Finally, the injection parameters (solvent cycle, injection speed etc.) are set to reduce sample discrimination.

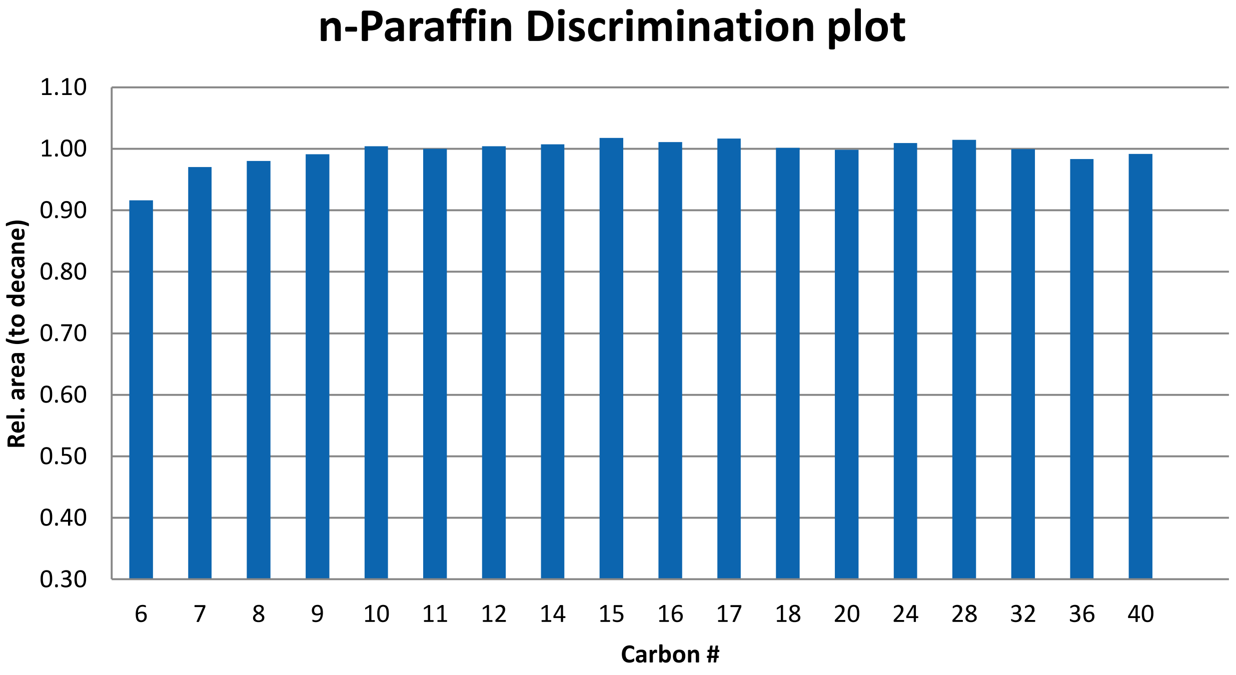

Figure 3: Normalized (to decane) detector response to an injection of n-alkanes . Response of whole range is within 10 %.

POLYCYCLIC AROMATIC HYDROCARBONS
Polycyclic aromatic hydrocarbons (PAHs) are composed of multiple aromatic rings. Formally, the class is further defined as lacking further branching substituents off of these ring structures. Though poly- in these cases literally means "many", there is precedence in nomenclature for beginning this class and subclass with the two ring cases, where napthalene would therefore be considered a simple example; beginning at three rings, examples include anthracene and phenanthrene. PAHs are found in fossil fuels (oil and coal) and in tar deposits.

A reference sample containing 16 different PAH's is analyzed by GCxGC. All 16 components are clearly separated as displayed in selected image (figure 4).

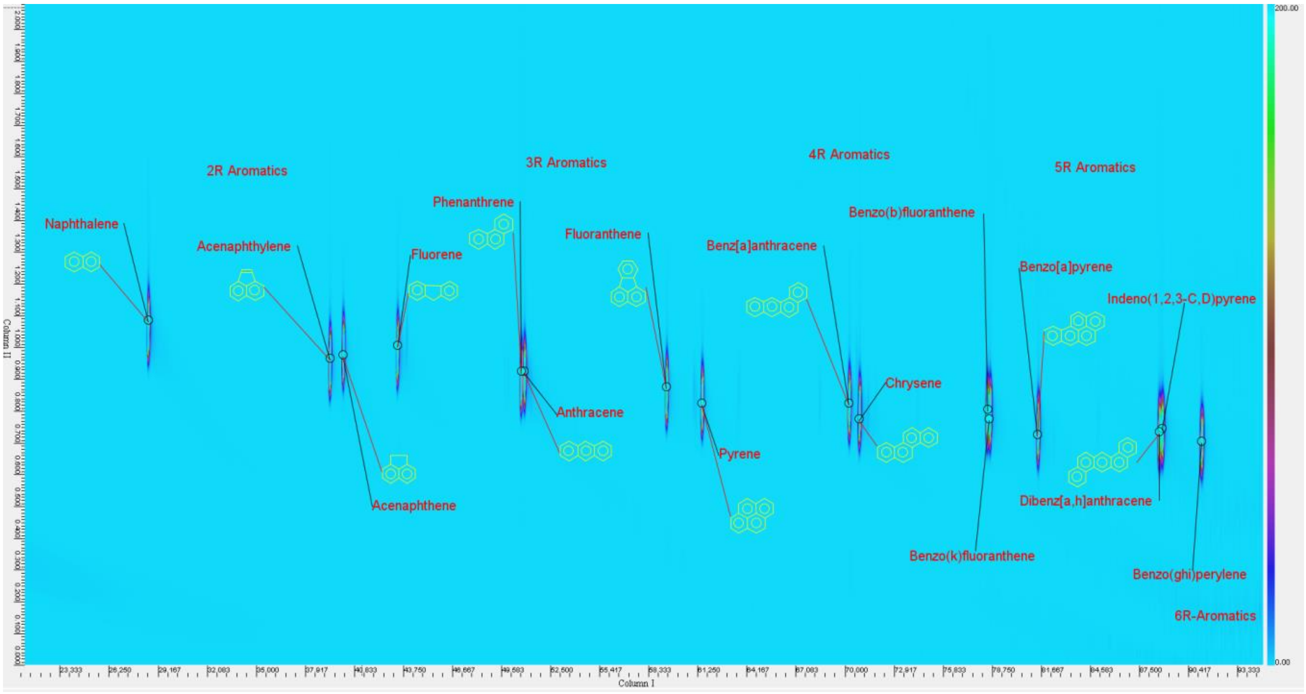

Figure 4: 2D-image view of 16 different PAH's mixture

REPEATABILITY
The analysis of middle distillate streams like lube oil, fuel oil or light cycle oil on the AC optimized flow modulated GCxGC, as presented in this application note, yields total Paraffins, n-Paraffins, iso-Paraffins, total Naphthenes, mono-Aromatics, di-Aromatics, 3R-Aromatics, 4R-Aromatics and 5R-Aromatics (PiPNA) results.

Quantitative calculation is done by the use of theoretical response factors. The calculated results are normalized for optimum accuracy and precision.
A repeatability test on a LCO (Light Cycle oil) sample proved excellent stability and ruggedness results (see table 1).

Run	1R aromatics (% m/m)	2R aromatics (% m/m)	3R aromatics (% m/m)	4R aromatics (% m/m)	Naphthenes (% m/m)	n-Paraffins (% m/m)	Paraffins (% m/m)
1	14.89	26.03	22.59	0.80	10.18	7.44	25.51
2	14.80	26.05	22.65	0.81	9.98	7.56	25.72
3	14.88	25.89	22.70	0.83	9.83	7.40	25.87
4	14.86	25.81	22.78	0.84	9.97	7.40	25.74
5	14.84	25.99	22.73	0.71	9.87	7.43	25.86
6	14.84	25.64	22.59	0.74	9.86	7.35	26.17
7	14.92	25.74	22.72	0.79	10.11	7.39	25.72
8	14.87	25.99	22.55	0.75	9.63	7.42	26.19
9	14.77	25.92	22.73	0.74	9.86	7.45	25.99
10	14.69	26.12	22.67	0.76	9.74	7.43	26.02
MIN	14.69	25.64	22.55	0.71	9.63	7.35	25.51
MAX	14.92	26.12	22.78	0.84	10.18	7.56	26.19
Average	14.84	25.92	22.67	0.77	9.90	7.43	25.88
stdev	0.0677	0.1498	0.0744	0.0439	0.1631	0.0554	0.2184
RSD	0.46%	0.58%	0.33%	5.67%	1.65%	0.75%	0.84%

Table 1: Repeatability data for reported PiPNA group results from Light Cycle Oil sample

CONCLUSION

Analytical controls developed a robust GCxGC application for PiPNA analysis in extended range (D2887 scope) like lube oils, light cycle oils etc. Polycyclic Aromatics Hydrocarbons (PAH's) can be measured up to 5 rings aromatics. 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.

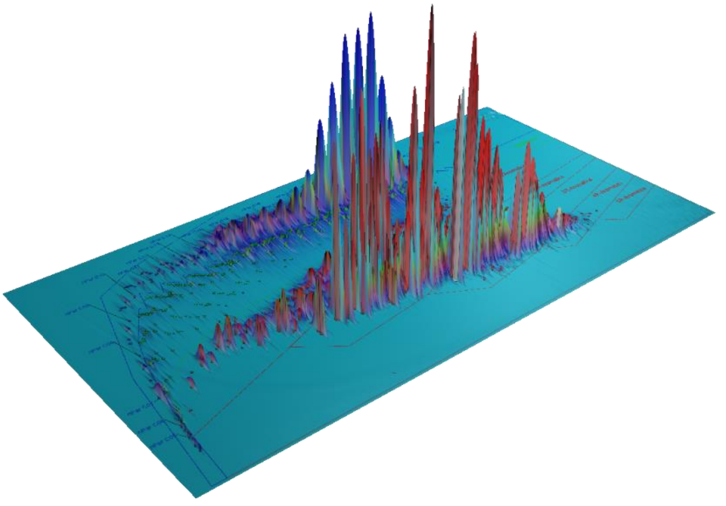

Figure 4: 3D plot of a light cycle oil sample