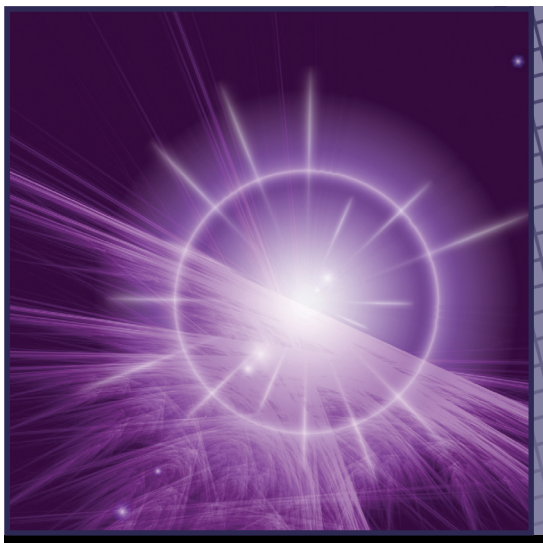

Take Advantage of Better PIONA Analysis

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Changes in quality standards and environmental law over the last decade has meant that engine fuel producers now have to comply with much higher quality specifications and more stringent environmental regulations than ever before. As a result a balance is required between maintaining the fuel performance by adding RON/MON improving components like iso-octanes and (bio-based) oxygenates and reducing environmentally harmful components such as benzene and toluene. Optimisation of this process results in a concerted move toward instrumentation and methodology capable of characterising petroleum fractions, including intermediates and finished products, providing their molecular composition in specific detail.

It is traditional in refineries that gas chromatography (GC) is routinely used to characterise crude oil and its derivatives, each with hundreds or even thousands of compounds. It is essential to extract as much relevant information as possible about the concentrations of these compounds to properly characterise raw materials, intermediates and finished products. This article examines the PIONA methodology, which is the standard test method under the jurisdiction of ASTM International Committee on Petroleum Products and Lubricants.

Analysing Fuel Mixtures

The method of choice for specifying the composition of spark-ignition engine fuels and its precursors has predominantly been O-PIONA group type reporting (Oxygenates, Paraffin, Iso-paraffin, Olefins, Naphthenes and Aromatics) conducted using either single column or multi-dimensional gas chromatography. Due to the complex nature of high olefin samples and the additions of oxygenates, multi-dimensional gas chromatography is the most qualified technique as outlined in ASTM D6839 – 02 'Standard Test Method for Hydrocarbon Types, Oxygenated Compounds and Benzene in Spark-Ignition Engine Fuels by Gas Chromatography'[1].

The methodology, using an O-PIONA analyser or multi-dimensional GC system, allows the single sample injection of a complex mixture of hydrocarbons. These are separated by a combination of highly selective multiple GC columns in series, individual temperature controls provide a specific resolved chromatogram of the components.

The advantages of O-PIONA methods are that they:

- provide a detailed analysis of naphtha fractions and finished products by carbon number, % weight and % volume from C1 to C14 compounds (i.e. olefins, paraffin's and aromatics and optionally oxygenates);
- provide sample properties including RON/MON value, C/H, TBP;

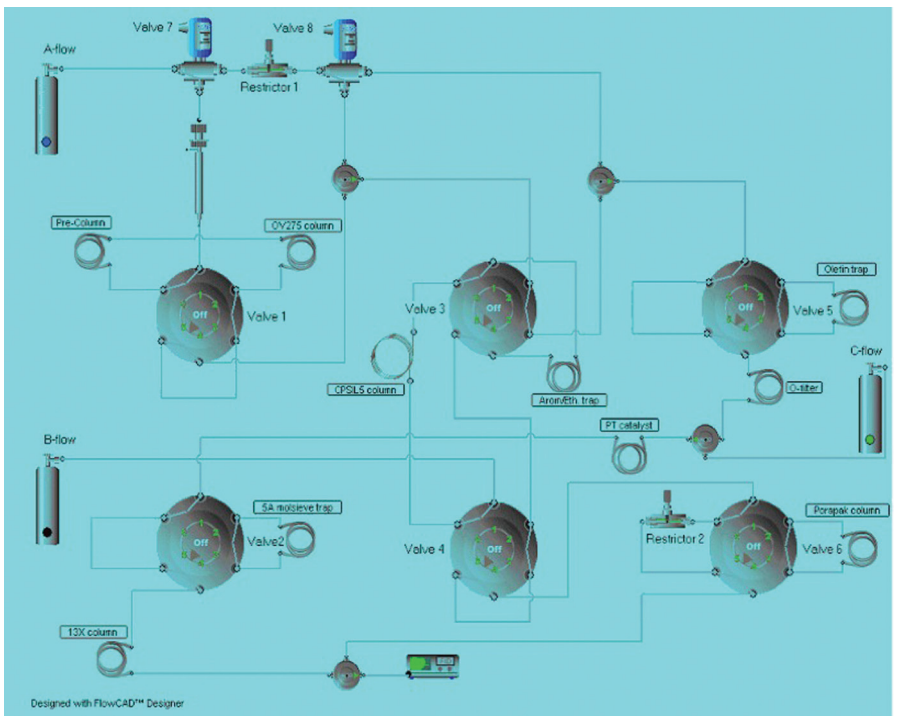

Figure 1: The PIONA+ Analyser is a multi-dimensional GC and trap system providing an accurate compositional analysis (% weight or % volume) of spark-ignition engine fuels and its pre-blending fractions

- use multiple high selective columns and traps to provide an optimal summation of components, especially the olefins within a single group type and a high resolution between the different group types per carbon number;
- provide individual data for specific components, including benzene, toluene, ethanol, MTBE and other oxygenates;
- provide an ASTM recognised method of providing hydrocarbon analysis on complex samples within a short timescale using a single instrument; and
- offer flexibility by including only those columns in the analysis to tailor make the separation per sample stream type, including FCC naphtha, reformate, alkylate and gasoline. This is achieved by selecting the right mode of operation; PIONA, PONA, PNA and oxygenated fuel additives (i.e. O-PIONA, O-PONA).

Fuel Analysis Case Study

The PIONA+ Analyser from Bruker is the perfect solution for characterising the complete hydrocarbon and oxygenates composition of a spark-ignition fuel sample. The five groups of hydrocarbon types (PIONA) and optionally oxygenated additives have different properties and occur in varying proportions in different products. The instrument performs a single injection, total eluting analysis using the universal flame ionisation detection (FID). The sample undergoes separation into its component groups (O-PIONA) according to carbon number, through the use of multiple columns and highly selective traps. The analyser itself is a GC system supplemented with a series of interlinked switching valves, columns, two oxygenated component traps, an olefin trap, two molecular sieve traps and a hydrogenation catalyst, operating at independent controlled temperatures. The system switches the valves at pre-determined times to direct the fractions of the sample by back flushing or forward flow to the appropriate columns and traps. Time based by-passing together with temperature control of a column allows trapping and reinjection of a group at a required time. As the analysis proceeds, the columns separate these sample portions sequentially into their component groups of different hydrocarbon that elute to the FID.

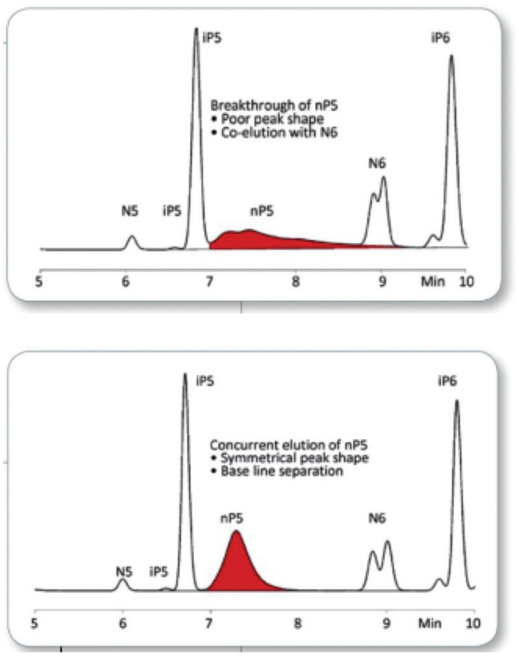

Figure 2a and 2b: The effect of breakthrough of normal paraffins

The universal detection properties of FID for hydrocarbons allows peak area conversion to weight and volume factions. Since a 100% elution occurs, normalisation done by the PIONA+ software results in a matrix report in weight and volume %. Additional sample properties are also calculated from this matrix report.

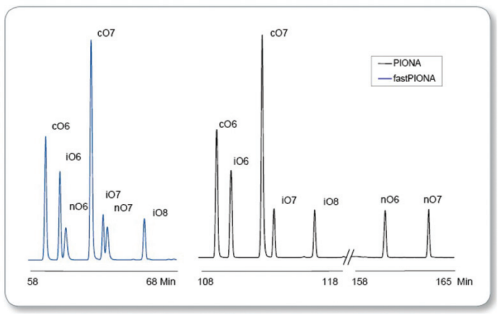

Figure 3a and 3b: Concurrent heating of the molecular sieves combines the elution profiles of paraffins (iso and normal) and naphthenes, reducing the analysis time compared to the former method

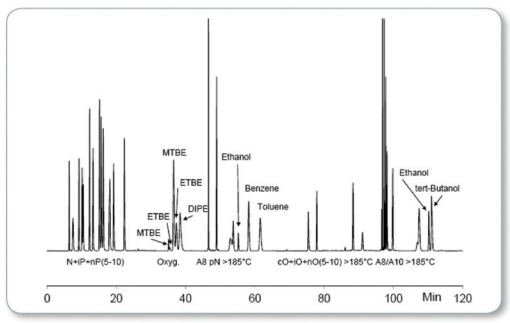

Figure 4. Chromatogram of a commercial standard in fast

Analyser Advantages

The independent trap temperature control design, the trap capacity and trap selectivity allows the analyser to optimise the analysis performance. In the case of broad samples ranging from C4 up to C12, a high selectivity demand is required to separate the different groups. By using smart concurrent heating of both molecular sieves, the eluting profile of the paraffins (normal and iso) and the naphthenes is well defined without the overlap of especially light normal paraffins in the iso-paraffin and naphthenes elution area, Figure 2a and 2b illustrate the effect of breakthrough of normal paraffin. This improves analyses interpretation and quantitation [2].

Applying concurrent heating also reduces the analysis time significantly since the separate elution profiles of iso-paraffins and naphthenes and the normal paraffins can be combined (Figure 3a and 3b). This solution is also applicable to the olefins reducing the analysis time by 33% for an O-PIONA analysis as illustrated in Figure 4 [3].

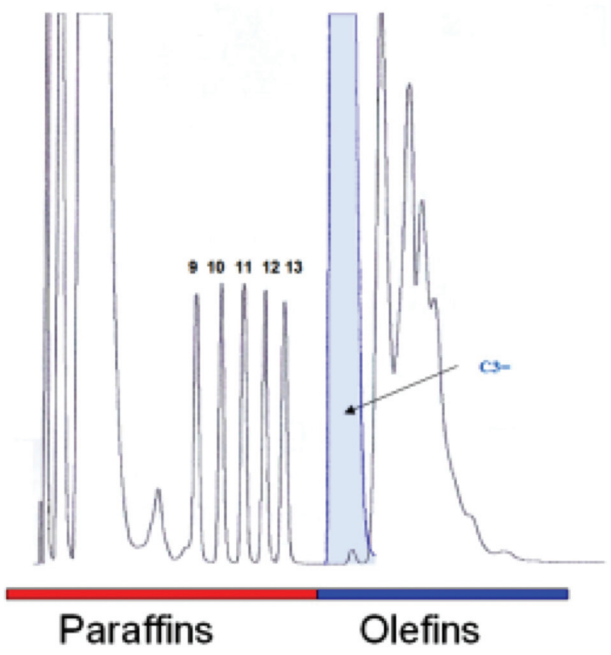

Figure 5:Elution profile of the olefin trap. The high selectivity and capacity ensures a good separation between paraffins and olefins even for broad samples ranging from C3 to C13

Preventing component breakthrough of a trap is also evident to the olefin trap preventing co-elution with its saturated equivalents. Especially high resolution single column detailed hydrocarbon ASTM methods, including ASTM D5134, ASTM D 6729, ASTM D6730 and D6733, refer to a multi-dimensional PONA-type of instrument in case the olefin content exceeds an amount of more than <2%, 25% and 25%, 20% respectively. Utilising an olefin trap with high capacity and selectivity ensures a good separation between the paraffins and olefins (Figure 5).

Conditions: 0.1 µL injection liquid 40°C (3') 15°C/min 220°C.

	Saturates			Unsaturates					
Carbon	Cyclic	Iso	Normal	Cyclic	Iso	Normal	Aromatics	Oxyg	Total
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.06	0.00	0.03	0.54	0.00	0.00	0.64
5	0.31	11.33	2.98	0.87	9.91	7.57	0.00	0.03	32.99
6	3.17	9.95	1.40	2.40	8.58	4.40	1.72	0.04	31.67
7	4.31	6.77	0.00	2.14	4.76	1.91	7.46	0.00	27.35
8	1.42	3.12	0.00	0.39	2.06	0.00	0.07	0.00	7.05
9	0.01	0.00	0.00	0.04	0.02	0.00	0.03	0.00	0.10
10	0.01	0.00	0.00	0.09	0.00	0.03	0.01	0.00	0.13
11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	**9.23**	**31.17**	**4.43**	**5.93**	**25.36**	**14.46**	**9.29**	**0.07**	**99.93**

Figure 6: Weight % report of high olefinic sample of 46 % (highlighted in red)

The high capacity of the olefin trap also allows hydrocarbon fractions such as FCC naphtha with a considerable amount of olefins to be analysed in the standard mode as shown in Figure 6 [4].

In contrast to high resolution single column and GC X GC analysis, the modular design of a

	PNA	PINA	PONA	O-PONA	PIONA	O-PIONA
Alkylate	X	X				
Gasoline			X	X		X
Blended Gasoline				X		
Naphtha straight	X	X				
Naphtha FCC			X		X	
Isomerate	X	X				
Reformate		X	X			

Or equivalent fast-modes.

Figure 7: Depending on the sample stream, a specific mode of analysis is applicable [5]

PIONA+ Analyser allows customisation of the analysis optimising the separation requirements. By excluding selective traps, i.e. the olefin trap and the Molsieve 5A trap, the analysis is reduced to a PNA (paraffins, naphthenes and aromatics) analysis in the case that iso- and normal paraffins and their olefinic equivalents are grouped per carbon number [5]. This is useful for sample streams that do not need a complete O-PIONA analysis as groups of components are lacking in the sample or are of no interest to be specified separately (Figure 7). By simplifying the analysis method, the analysis time is reduced while the sample interpretation is improved.

The flexibility to in- and exclude traps allows using different modes from PNA up to O-PIONA analysis using one instrument. This is useful when the samples are analysed according to official methods (Figure 8) [4].

Bruker PIONA+ Benefits

Bruker has specifically designed the PIONA+ Analyser to create multi-modal hydrocarbon analysis that is less complicated for the petrochemical analyst. There are many advantages to the instrument, including that it is designed to operate within the parameters set for official methods such as ASTM D-6839, EN 14517, ASTM D 6293, and DIN 5148-1. It is able to operate in multiple-modes to analyse specific groups of compounds including PIONA, PIANO, PINA, PONA, PNA, O-PONA and O-PIONA; and the olefin traps are high capacity (i.e. allow broad range of samples), have high selectivity and a long operating life time. Concurrent heating allows fast analysis with a broader range of samples, for example from C2 to C14. Reporting is undertaken according to standard methods and includes; grouping per hydrocarbon type/per carbon number, weight %, volume %, mol %, TBP, density, Reid Vapor Correlation, RON/MON Correlation, H/C Ratio and Heating Values.

	PNA	PONA	PIONA	O-PONA	O-PIONA
EN 14517					X
EN-ISO-22854					X
ASTM D6839				X	x
DIN 51448-2			X	x	x
ASTM D1319 (FIA)		X	x	x	x
DIN 51448-1	X	x	x	x	x
ASTM D5443	X	x	x	x	x
UOP 870	X	x	x	x	x
IP 382	X	x	x	x	x

= Compliant with Method = Reports Available

Figure 8: The PIONA+ Analyser is highly flexible and can be configured to run a wide variety of methods in the single instrument

Conclusion

PIONA analysis is a work-horse methodology and the preferred technique to characterise petroleum streams by hydrocarbon group type by utilising a multi-dimensional GC approach for the refinery laboratory. The PIONA+ Analyser from Bruker has been designed to permit routine PIONA analyses in all refinery laboratories, with a high degree of flexibility in the GC analysis platform to obtain comprehensive characterisation and quantitative information, including hydrocarbon group type, oxygenates and carbon distribution for spark-emission fuels.

References

[1] D6839 – 02 (Reapproved 2007) Standard Test Method for Hydrocarbon Types, Oxygenated Compounds and Benzene in Spark Ignition Engine Fuels by Gas Chromatography. ASTM 2007.

[2] Bruker Application Note # CA-270383. Fast Analysis of Paraffins, iso-Paraffins, Naphthenes and Aromatics in Hydrocarbon Streams.

[3] Bruker Application Note # CA-270384. Fast Analysis of Paraffins, iso-Paraffins, Olefins, iso-Olefins, Naphthenes and Aromatics in Hydrocarbon Streams.

[4] Bruker PIONA+ Brochure.

[5] Bruker Application Note # CA-270378. Paraffins, Naphthenes and Aromatics (PNA) in Hydrocarbon Streams with the Bruker PIONA+™ Analyser.