Fast Gasoline Characterisation by Optimising Multi-Dimensional GC (PIONA+)

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For many years the petrochemical industry has been in need of powerful and time-efficient separation capabilities to effectively analyse complex hydrocarbon mixtures of spark-ignition fuels like gasoline. Gas chromatographic-based techniques such as multi-dimensional gas chromatography (MDGC) have been shown to provide the necessary level of capacity to analyse complex hydrocarbon mixtures including oxygenate containing gasoline. However, such methods may take in excess of two hours.

In this article Bruker experts detail the way in which gasoline characterisation can be optimised through smart manipulation of the interaction between individual columns using MDGC as with the PIONA+™ Analyser. Column optimisation through the use of the PIONA+ Analyser can result in a reduction in analysis time of up to 40% without jeopardising the analytical performance.

The Key to Ignition

Cheating in motorsport reached new heights in 2007 when it was suggested that an American stock car racing team had 'doped' their engines with 'rocket fuel' in order to gain an advantage in qualifying. Following analysis it was revealed that the fuel contained an illegal oxygenating additive which, somewhat disappointingly, was not exactly rocket fuel but was enough to result in their disqualification.

With applications ranging from testing for illegal additives in stock cars to tailoring oil refinery processing methods, gas chromatography (GC) has become a widely used technique for spark-ignition fuel analysis throughout the petrochemical industry.

Today by far the most common spark-ignition fuel is gasoline, a highly complicated mixture of hydrocarbons, olefins and oxygenated compound additives. Unsurprisingly, separation of these complex species can be a lengthy process

When Every Drop Counts

The motivation for adding biofuel additives to fossil gasoline is often presented as part of the long-term solution to climate change. The reality, however, is quite different[1]. With petroleum prices continuously rising, the market is starting to deploy every available source of energy in an attempt to reduce the reliance on imported oil[2]. Oxygenated additives like ethanol[3] and MTBE are easily available and produce a positive effect on the gasoline performance, increasing the octane number and reducing engine knocking. However, legislation restricts the maximum amount of oxygenates added to gasoline and for MTBE, the maximum concentration has even lowered due to the environmental pollution that can result from wastage[4].

Petroleum companies, in particular, continually look to optimise efficiency, throughput and revenue without sacrificing the necessary industrial levels of accuracy and compliance. The concentrations of components within gasoline are highly regulated and failure to meet stringent specifications can result in large quantity recalls. A major oil company in the United States recently found themselves in such a costly situation, having to recall two million gallons of gasoline after thousands of motorists across the Midwest of the United States suffered fuel related problems[5]. The financial cost incurred by distributing this contaminated gasoline was estimated to run into several million dollars. More importantly the cost was felt more in terms of professional reputation. The PIONA+ Analyser from Bruker provides a complete solution for analysis of spark-ignition fuels, offering a separation system that can run 35-40% faster than standard techniques, whilst maintaining the high degree of accuracy that is demanded by the industry in compliance with ASTM D6839[6]. The potential for the PIONA+ Analyser to provide significant cost-savings may not be immediately obvious to those unfamiliar with the petrochemical process. The PIONA+ design is suited to analysing the intermediate streams and final products. This makes it ideal for analysis during processing and just prior to transportation. Tankers and barges each charge by the hour and prices can be high. Therefore, more efficient chromatographic analysis serves to quicken the quality control period resulting in a faster time to market. Not only does this result in a direct saving on each batch but allows for a faster turnover presenting the opportunity for increased throughput.

In addition to savings on transport and storage, the fast gasoline methodology allows rapid lab to line alterations, offering increased time-savings of analysis associated with developing the refinery process.

Introducing Faster Analysis

The PIONA+ acronym stands for paraffins, iso-paraffins, olefins, naphthenes, aromatics and the "plus" for oxygenates. One unique advantage of the PIONA+ Analyser is its flexibility as the instrument can be customised to provide highly de-convoluted hydrocarbon analysis. For example,

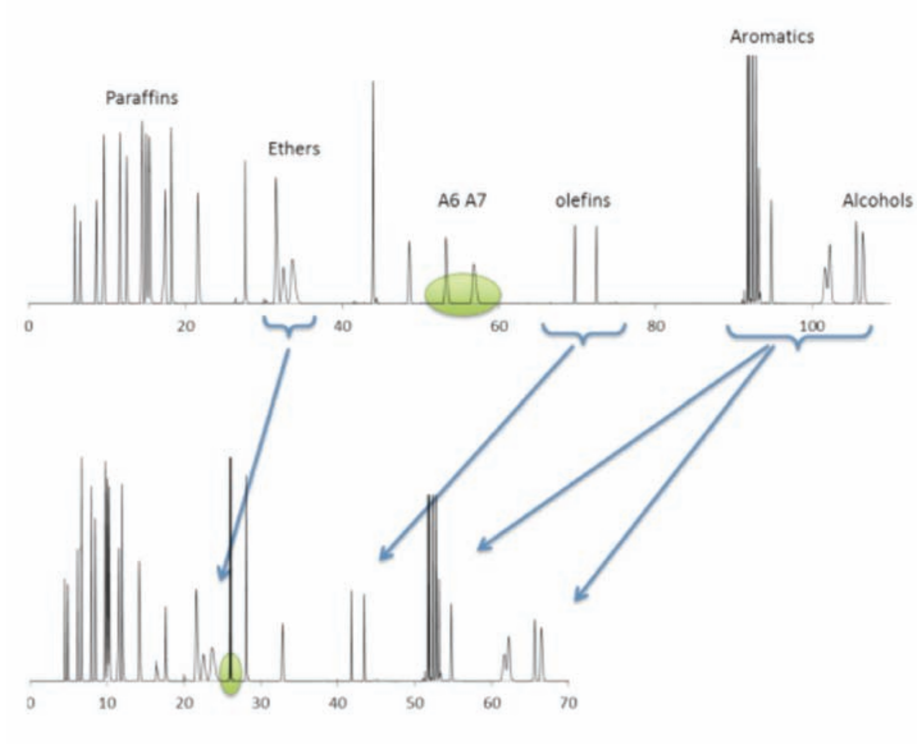

Figure 1: Tuning sample analysed in the Standard Mode (top) and in the Fast Mode.

in case the analysis does not require olefin reporting, the olefin trap of the PIONA+ Analyser is excluded and the separation of all paraffinic hydrocarbons (olefins and paraffins) are merged per carbon number, resulting in a more optimised and faster analysis.

The PIONA+ Analyser operates based on MDGC and uses independent controlled traps and columns in order to optimise temperature settings of the various traps, to apply faster column temperature program rate of the molsieve 13x column and to enable parallel, independent column/trap heating. With a merged analysis of molsieve 13x column and molsieve 5A trap only a single cycle is required for paraffin separation instead of two. This allows the PIONA+ Analyser to reduce the sample analysis time by nearly 45% while enhancing the applicability for wide range samples (C4-C11)[7]. The time spent on each GC run can lead to a massive systematic loss in efficiency. These simple, yet crucial adaptations from standard GC allow the instrument to optimise efficiency during analysis.

PIONA+ Analyser Case Study - Satisfying Gasoline Producers' Need for Speed

A case study presented by Bruker illustrates the savings that can be made using the optimised PIONA+ Analyser to analyse gasoline[8]. The PIONA+ Analyser used in this example is set to the PONA+ configuration, with the necessary set-up to measure the constituents of gasoline.

Figure 1 visualises the PIONA+ analysis with a test sample of gasoline, shown in both the Standard and the Fast mode. The shift in time between the various components of the different groups clearly shows the potential time-saving gained by optimising the PIONA+ Analyser. An overlay of the paraffin section following GC in Standard and Fast mode is illustrated in Figure 2.

Both plots overlap precisely and the only variation between the two is the time taken. In Standard mode elution time was 25 minutes compared to 15 for Fast mode. The elution integrity of the component groups remains intact with no negative influence on either group. When performed on

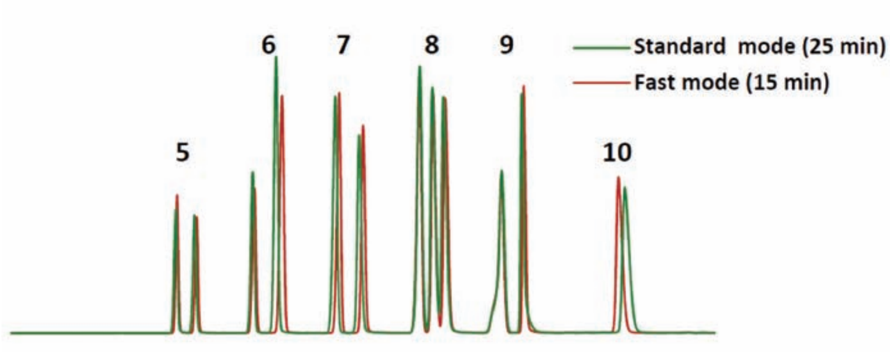

Figure 2: Overlay of the paraffin section of the Standard and Fast mode.

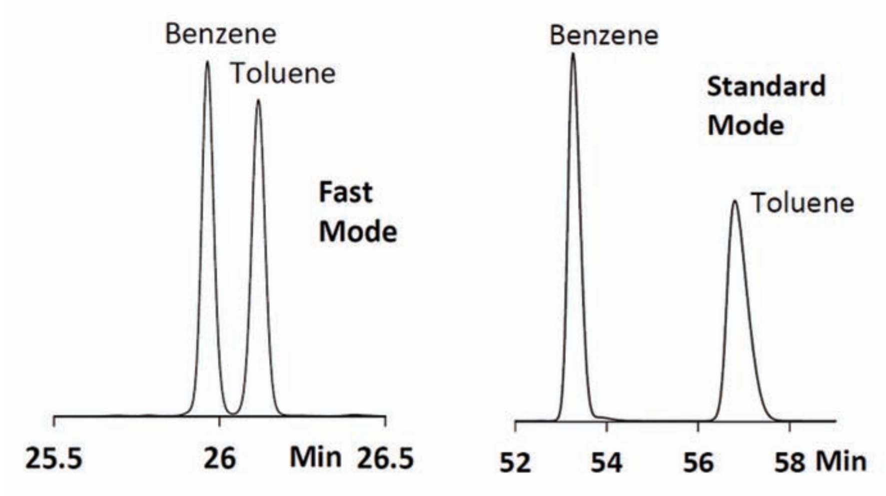

Figure 3a and 3b: Benzene and Toluene separation in the Fast mode (3a) and the Standard mode (3b).

an industrial scale this presents the potential for significant levels of time-saving. The reduction of analysis time is achieved by applying a faster column temperature program rate of the molsieve 13x column. In the separation of saturates and olefins analysis time is reduced by 10 minutes for both groups. By using an overlay of the paraffin elution area for the standard technique and stretching the Fast mode to overlap, it is obvious that an identical separation performance of the peaks is achieved.

A second reduction in analysis time is the elution and analysis of benzene and toluene. In Standard O-PONA mode a further technique is required to separate these similar compounds. However, in Fast mode this becomes unnecessary as the BR-1 column has sufficient resolution to separate benzene and toluene, whilst ensuring a good quantification of benzene as shown in Figure 3.

The results of the Fast O-PONA analysis of gasoline are shown in Figure 4 and Table 1. The high concentration of light olefins and high concentration of toluene can be analysed within the dynamic range of the system. Perfect separation of all the components of interest and accurate quantifiable separation of toluene and benzene is achieved.

The advantage of MDGC being used by the PIONA+ Analyser proves to be the capability to optimise the analysis speed per group-type without interference to other groups and the ability to optimise the analysis sequence for all groups. The benefit of optimising gasoline analysis is clear, fast GC methods, such as the PIONA+ Analyser, save time and as the old adage goes, time is money.

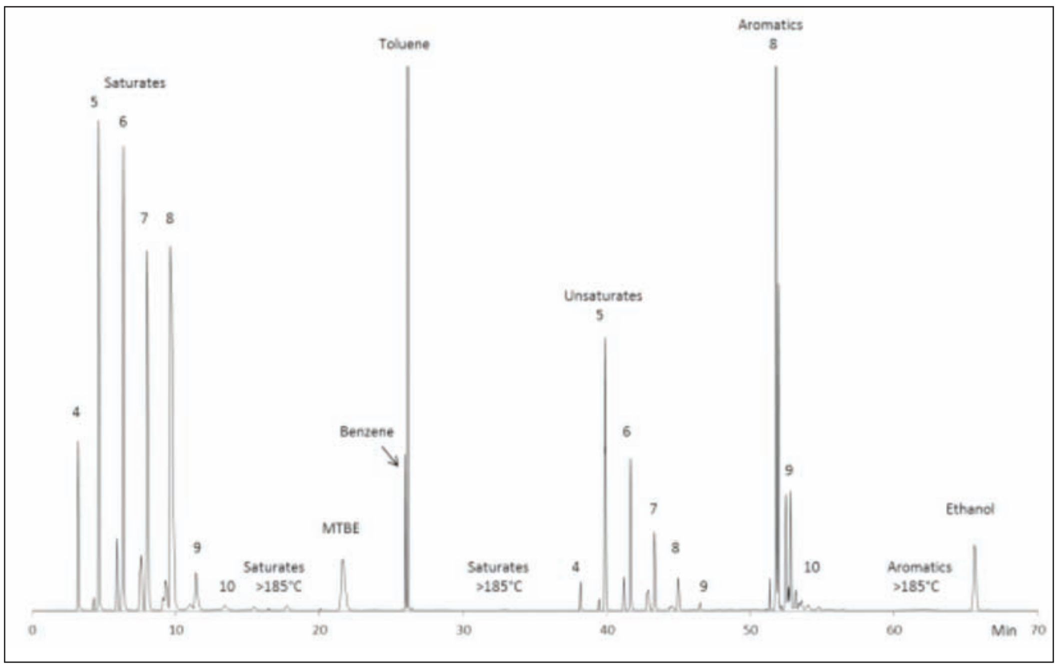

Figure 4: Gasoline analysis with the fast O-PONA set-up.

Refining the Process

The price of gasoline is a contentious issue, one that affects suppliers and consumers alike and one that stimulates wide-spread discussion. From the front pages of the broadsheets to the dinner tables to the presidential debates, the issue of gasoline prices reached new levels in 2012. With these perennially fluctuating costs and increases in quality standards and environmental legislation the petrochemical industry is in need of new methods to increase throughput. The PIONA+ Analyser has been shown to significantly minimise the analysis time of spark-ignition fuels, specifically gasoline, whilst maintaining high levels of accurate chromatographic analysis and operational ease of use.

Normalized Weight Percent Profile

Carbon	Saturates		Unsaturates		Aromatics	Oxygenates	Total
	Cyclic	Paraffin	Cyclic	Paraffin			
2		0.00		0.00		5.21	5.21
3	0.00	0.01	0.00	0.00		0.00	0.01
4	0.00	2.28	0.00	0.38		0.00	2.66
5	0.17	7.52	0.17	4.30		4.14	16.30
6	1.19	7.41	0.54	2.60	1.12	0.00	12.87
7	1.75	7.92	0.63	1.53	11.14	0.00	22.97
8	1.22	14.23	0.22	0.77	15.05	0.00	31.50
9	0.38	1.35	0.05	0.16	4.90	0.00	6.84
10	0.10	0.32	0.04	0.03	0.36	0.00	0.85
Total	**4.81**	**41.04**	**1.64**	**9.78**	**32.58**	**9.35**	**99.20**

Total Saturates	45.86		MTBE	4.14
Total Unsaturates	11.42		Ethanol	5.21
Total Aromatics	32.58		Oxygen %	2.56
Fraction >185°C	0.79			
Aromatic Fr >185°C	0.30			
Poly Naphthenes	0.01			

Table 1: Gasoline results in weight percentage.

[1] http://www.guardian.co.uk/world/2009/may/06/obama-ethanol-green-biofuel

[2] http://www.usda.gov/wps/portal/usda/usdahome?contentid=2012/07/0217.xml

[3] http://www.epa.gov/otaq/regs/fuels/additive/e15/index.htm

[4] http://epa.gov/mtbe/faq.htm#concerns

[5] http://www.telegraph.co.uk/finance/newsbysector/energy/oilandgas/9501851/BP-recalls-two-million-gallons-of-petrol-after-thousands-complain-of-problems.html

[6] ASTM D6839 Standard Test Method for Hydrocarbon Types, Oxygenated Compounds and Benzene in Spark Ignition Engine Fuels by Gas Chromatography

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

[8] Bruker CAM, Application Note CA703919. 2012. Fast Gasoline Characterization by Optimizing Multi-dimensional GC (PIONA+)

all sources accessed 18/01/2013