Application Note CA703979

Fast Gasoline Characterization by Optimizing Multi-dimensional GC (PIONA+)

Introduction

Within the petrochemical industry the need for powerful separation capabilities and capacity has been found with high resolution gas chromatography (HRGC) and multi-dimensional gas chromatography (MDGC) for many years. The complex nature of hydrocarbon mixtures, and especially finished products like spark-ignition fuels (such as gasoline), include a mixture of different hydrocarbons including high olefins and additives such as oxygenated compounds. The result is analytical times as long as two hours or more to separate the samples into its individual components. To improve the analysis time in HRGC, a limited number of options are available; the most common methods of reduced column inner diameter or faster column temperature programming, affect the separation performance of the system. Reducing the analysis time is most feasible with MDGC since the architecture of the system allows the elution sequence and elution time of the different columns and traps to be optimized. This application note describes the analysis time reduction for gasoline analysis in the O-PONA mode (Oxygenated compounds, Paraffins (normal and iso-combined), Olefins (normal and iso-combined), Naphthenes and Aromatics) according to ASTM D6839 using the PIONA+™ Analyzer from 115 minutes down to 70 minutes [1, 2].

Experimental

Instrumentation

Bruker PIONA+ Analyzer running in the O-PONA mode.

Software

CompassCDS chromatography software from Bruker with PIONA+ software plug-in.

Samples

1) Tuning sample: Proposed O-PONA System Validation Mixture ASTM-P-0080 (AccuStandard).
2) Test sample: Gasoline.

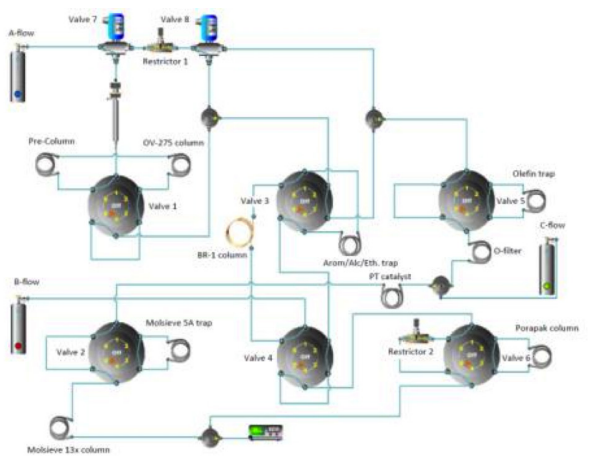
The timetable for the fast O-PONA mode has been optimized with respect to heating rate of the molecular sieve separation column, as well as specific valve actions to reduce voids. An overview between the Standard and the Fast O-PONA mode is listed in Table 1. Figure 1 illustrates the analytical flow scheme of PIONA+ Analyzer.

Step	Time (mins)		Components*
	Standard	Fast	
1	0.0 - 25.0	0.0– 17.0	C1 – C10 N + P
2	25.0 - 30.0	17.0 – 20.0	>185 ˚C Paraffins
3	30.0 - 40.0	20.0- 25.0	Ethers
4.1	40.0 - 45.0	25.0 – 29.0	C6 – C8A and pN (fast) C8A + pN (standard)
5	45.0 - 50.0	30.0 – 34.0	>185°C Paraffins
4.2	50.0 - 60.0	-	See step 4.1 (fast) C6A + C7A (standard)
6	60.0 - 90.0	34.0- 50.0	C1 – C11 cO + O
7	90.0 - 96.5	50.0 – 56.0	C8 – C10 A
8	96.5 - 105.0	56.0 – 65.0	>185°C Aromatics
9	105.0 - 115.0	65.0 - 70.0	Alcohols

Table 1. PONA+ elution scheme of the O-PONA mode (standard vs fast).

* N = Naphthenes, P = iso- and normal- paraffins, A = aromatics, pN= polynaphthenes, cO = cyclic Olefins, O = Olefins (non-cyclic)

Figure 1

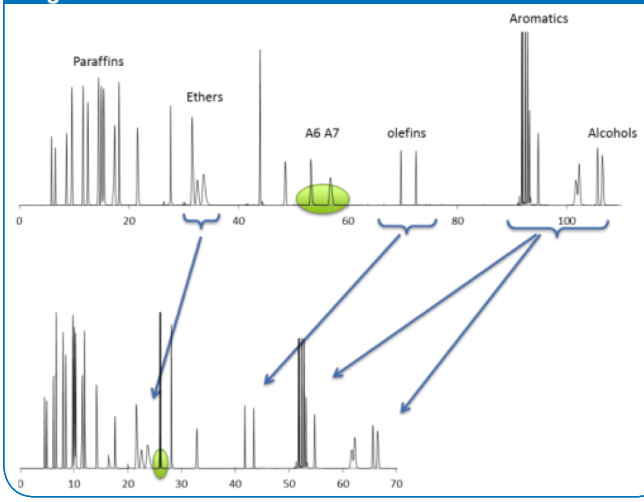


Analytical flow scheme of the PIONA+ Analyzer.

Results

The increase in the column temperature heating rates and the rearrangement of the analysis sequence has resulted in a shorter analysis time of the O-PONA mode. In Figure 2 a test sample is shown in both the Standard and the Fast mode highlighting the shifts of the different groups between the two analyses.

Figure 2

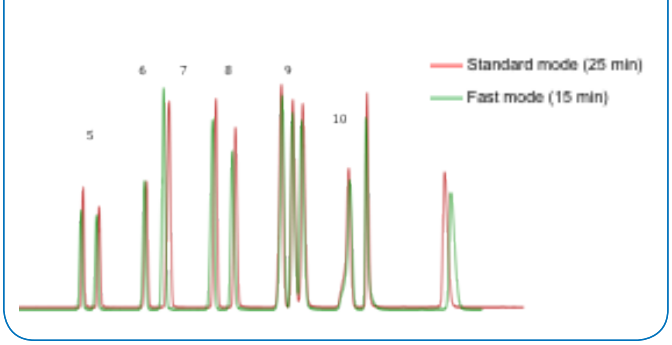


Tuning sample analyzed in the Standard mode (top) and in the Fast mode (bottom).

Analysis Time Optimization

The reduction of analysis time is achieved by applying a faster column temperature program rate of the molsieve 13x column. An acceleration of the analysis of two times 10 minutes is achieved for the separation of saturates and olefins. Visual performance validation, using an overlay of the paraffin elution area and by stretching the Fast mode to match the Standard mode shows identical separation performance of the peaks. In addition to faster column heating is the maximum carbon number required to separate using the Molsieve 13x column. The PIONA+ Analyzer is designed for separation up to C11 and to report C12 and higher as >200°C. In the gasoline mode separation up to C10 is required and C11 and higher is reported as >185°C.

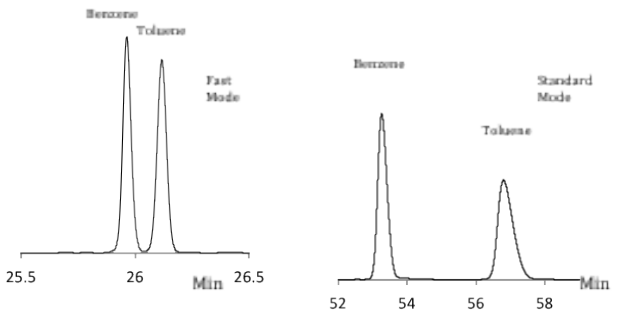
Figure 3



Overlay of the paraffin section of the Standard and Fast mode.

A second reduction of analysis time is the elution of benzene and toluene. The BR-1 column has sufficient resolution to separate benzene and toluene and ensures good quantification of benzene. Further separation on the Porapak® column as done in the Standard O-PONA mode is unnecessary .

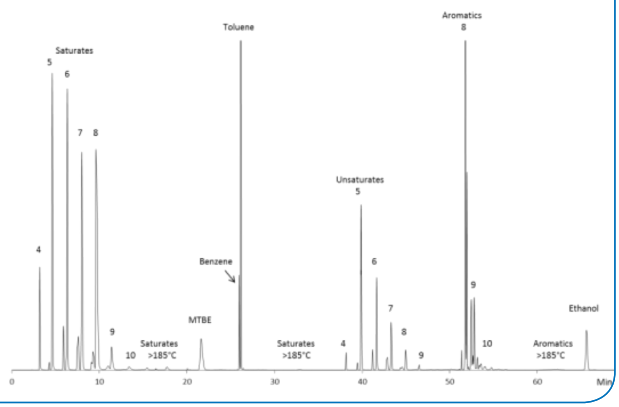
Figure 4a & 4b



Benzene and Toluene separation in the Fast mode (4a) and the Standard mode (4b).

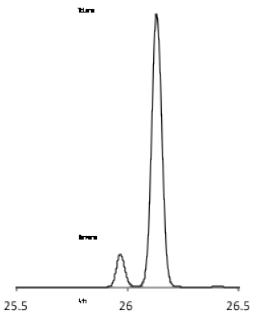
The analytical results of the Fast O-PONA analysis of a gasoline are shown in Figure 5 and Table 2. The analysis shows a perfect separation of all the components of interest. The high concentration of (light) olefins and the high concentration of toluene are analyzed within the dynamic range of the system, with a perfect quantifiable separation of the toluene and benzene as shown in Figure 6.

Figure 5



Gasoline analysis.

Figure 6



Separation of Benzene and Toluene of the Gasoline analysis.

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 2a. Gasoline results in weight percent.

Normalized Weight Percent Profile							
Carbon	Saturates		Unsaturates		Aromatics	Oxygenates	Total
	Cyclic	Paraffin	Cyclic	Paraffin			
2		0.00		0.00		4.89	4.89
3	0.00	0.01	0.00	0.00		0.00	0.01
4	0.00	2.91	0.00	0.47		0.00	3.38
5	0.17	8.89	0.16	4.96		4.14	18.32
6	1.16	8.33	0.51	2.83	0.95	0.00	13.78
7	1.72	8.58	0.59	1.62	9.50	0.00	22.01
8	1.17	15.01	0.20	0.80	12.87	0.00	30.05
9	0.36	1.39	0.05	0.16	4.16	0.00	6.11
10	0.09	0.33	0.04	0.03	0.30	0.00	0.79
Total	**4.67**	**45.43**	**1.55**	**10.88**	**27.78**	**9.03**	**99.34**

Total Saturates	50.10	MTBE	4.14	
Total Unsaturates	12.43	Ethanol	4.89	
Total Aromatics	27.78			
Fraction >185°C	0.65			
Aromatic Fr >185°C	0.25			
Poly Naphthenes	0.01			

Table 2b. Gasoline results in volume percent.

Conclusion

The advantage of MDGC being used by the PIONA+ Analyzer proves to be the capability to optimize the analysis speed per group-type without interference to other groups and the ability to optimize the analysis sequence for all groups. As a result the analysis time for gasoline analysis in the O-PONA mode has been reduced down to 70 minutes, while the separation and quantification performance and component range are maintained identically compared to the Standard O-PONA mode.

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References:

[1] ASTM D6839 - 02(2007) "Standard Test Method for Hydrocarbon Types, Oxygenated Compounds and Benzene in Spark Ignition Engine Fuels by Gas Chromatography". ASTM International, West Conshohocken, PA, www.astm.org

[2] Bruker Application Note # CA-270381, Analysis of Oxygenates, Paraffins, Olefins,Naphthenes and Aromatics (O-PONA) of Hydrocarbon Streams.

Keywords
O-PONA
Gasoline
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ASTM D6839
Spark ignition engine fuel

Instrumentation & Software
PIONA+ Analyzer
CompassCDS Chromatography Software
PIONA+ plug in software

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