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Application Note SI-01352

Analysis of Oxygenates, Paraffins, Olefins, Naphthenes and Aromatics (O-PONA) of Hydrocarbon Streams

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Introduction

This application note describes the quantitative determination of oxygenates, paraffins, naphthenes and aromatics (O-PONA) in spark ignition fuels by the multi-dimensional gas chromatography separation approach utilized in the Varian PIONA+™ GC analysis system. The Varian PIONA+ Analyzer is a comprehensive GC system that offers the ability to characterize and quantify components in a variety of spark ignition fuels according to an array of industry standard method protocols. The system can be operated in one of multiple method "modes" depending on the analysis requirement of a given stream type. For this particular application, the system was set up to characterize the O-PONA content of spark ignition fuels.

Instrumentation

Varian PIONA+ Analyzer
Varian 450-GC Gas Chromatograph
PIONA+ multi column module

Software

Galaxie™ Software from Varian with PIONA+™ Software plug-in

Table 1. Elution scheme for O-PONA.

From	To (min)	Components	Column route
0	25.0	C1 to C10 N + P	1st OV-275 fraction via arom/eth and olefin trap to 13x
25.0	30.0	>185 °C fraction	Back flush CP-Sil™ 5CB of 2nd OV-275 fraction
30.0	40.0	ethers	1st OV-275 fraction via arom/eth and CP-Sil 5CB to porous polymer column
40.0	45.0	C8 A and pN	2nd OV-275 fraction via arom/eth and CP-Sil 5CB
45.0	50.0	>185 °C fraction	Back flush CP-Sil 5CB of 2nd OV-275 fraction
50.0	60.0	C6 A + C7 A	2nd OV-275 fraction via arom/eth and CP-Sil 5CB to porous polymer column
60.0	90.0	C3 to C10 cO + O	Olefin trap in flow to 13x
90.0	96.5	C8 to C10 A	3rd back flush OV-275 and precolumn back flush fraction via arom/eth to CP-Sil 5CB
96.5	105.0	>185 °C fraction	Back flush CP-Sil 5CB of 3rd OV-275 and pre back flush fraction
105.0	115.0	alcohols	3rd OV-275 and precolumn back flush fraction via arom/eth and CP-Sil 5CB to porous polymer column

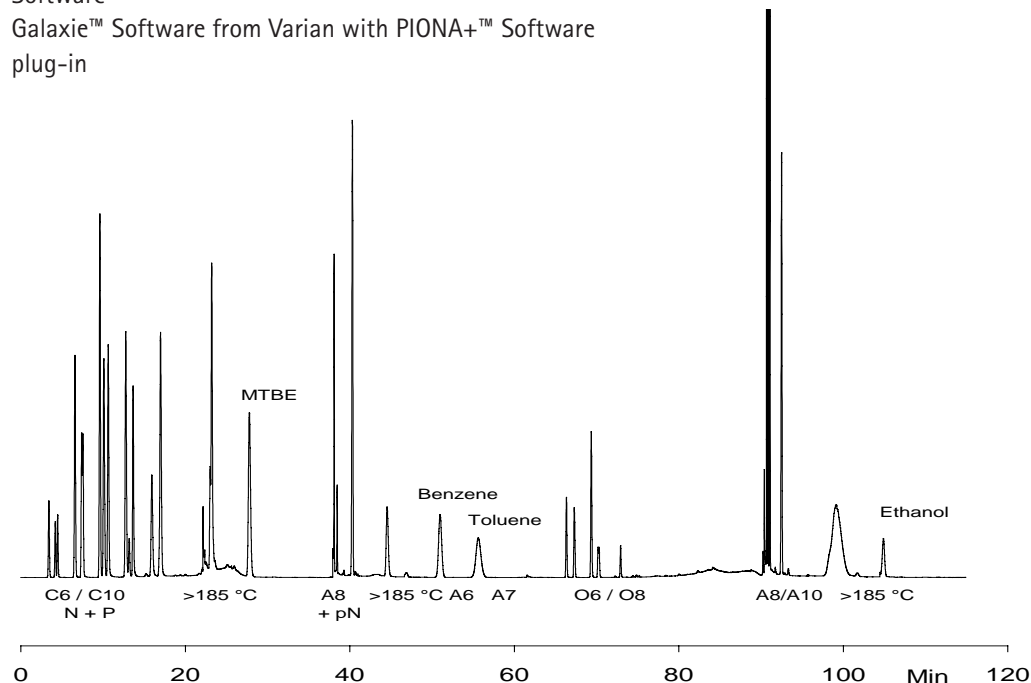


Figure 1. Chromatogram of a calibration sample.

Conditions

In the O-PONA mode, an olefin trap is used to separate the olefins from paraffins (Table 1).

Results and Discussion

The chromatogram shown in Figure 1 is an example of an O-PONA analysis. In this case, a calibration sample is run. Clearly made visible here is the group separation making identification and quantification very easy. The oxygenates elute without co-elution of other sample components allowing accurate and precise quantification. All conditions for the different columns and traps are set in order to obtain the elution scheme represented in Table 1. Galaxie Software from Varian, together with the PIONA+ Software plug-in, generate a weight% and a volume% profile report.

A summary of these reports is shown in Tables 2 and 3. The amount of the different groups per carbon number is shown as well as the totals per group and per carbon number. Oxygenates are reported as a group per carbon number but also per component.

In Figure 2, a chromatogram of a gasoline is shown. Again, a clear view of the group type separated by carbon number and the oxygenates is obtained, in this case only MTBE.

From this chromatogram, volume and weight percent profile reports are generated. The reports are divided into several columns showing saturated and unsaturated component groups. Furthermore, a clear overview per carbon number is shown as well as the totals per group and per carbon number.

Table 2. Mass% results of a calibration sample.

Normalized Weight Percent Profile							
Carbon	Saturates		Unsaturates			Oxygenates	Total
	Cyclic	Normal + Iso	Cyclic	Normal + Iso	Aromatics		
2	0.00	0.00	0.00	0.00	0.00	2.72	2.72
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00	7.14	7.14
6	1.04	1.45	1.06	1.09	2.40	0.00	7.05
7	3.16	3.74	1.98	0.74	2.90	0.00	15.52
8	5.12	7.33	0.00	0.38	9.43	0.00	22.27
9	4.12	3.17	0.00	0.00	6.16	0.00	13.46
10	2.12	4.74	0.00	0.00	4.70	0.00	11.56
11	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	15.57	20.44	3.04	2.21	25.59	9.85	76.70
Fraction >200 °C		17.36		MTBE		7.14	
Polynaphthenes		5.94		Ethanol		2.72	

Table 3. Volume% profile of a calibration sample.

Normalized Volume Percent Profile							
Carbon	Saturates		Unsaturates			Oxygenates	Total
	Cyclic	Normal + Iso	Cyclic	Normal + Iso	Aromatics		
2	0.00	0.00	0.00	0.00	0.00	2.73	2.73
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00	7.65	7.65
6	1.09	1.75	1.08	1.27	2.17	0.00	7.37
7	3.32	4.34	2.00	0.84	2.65	0.00	15.15
8	5.24	8.27	0.00	0.42	8.65	0.00	22.58
9	4.16	3.48	0.00	0.00	5.61	0.00	13.25
10	2.09	5.16	0.00	0.00	4.21	0.00	11.45
11	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	15.90	23.01	3.08	2.53	23.28	10.38	78.18
Fraction >200 °C		15.41		MTBE		7.65	
Polynaphthenes		6.41		Ethanol		2.73	

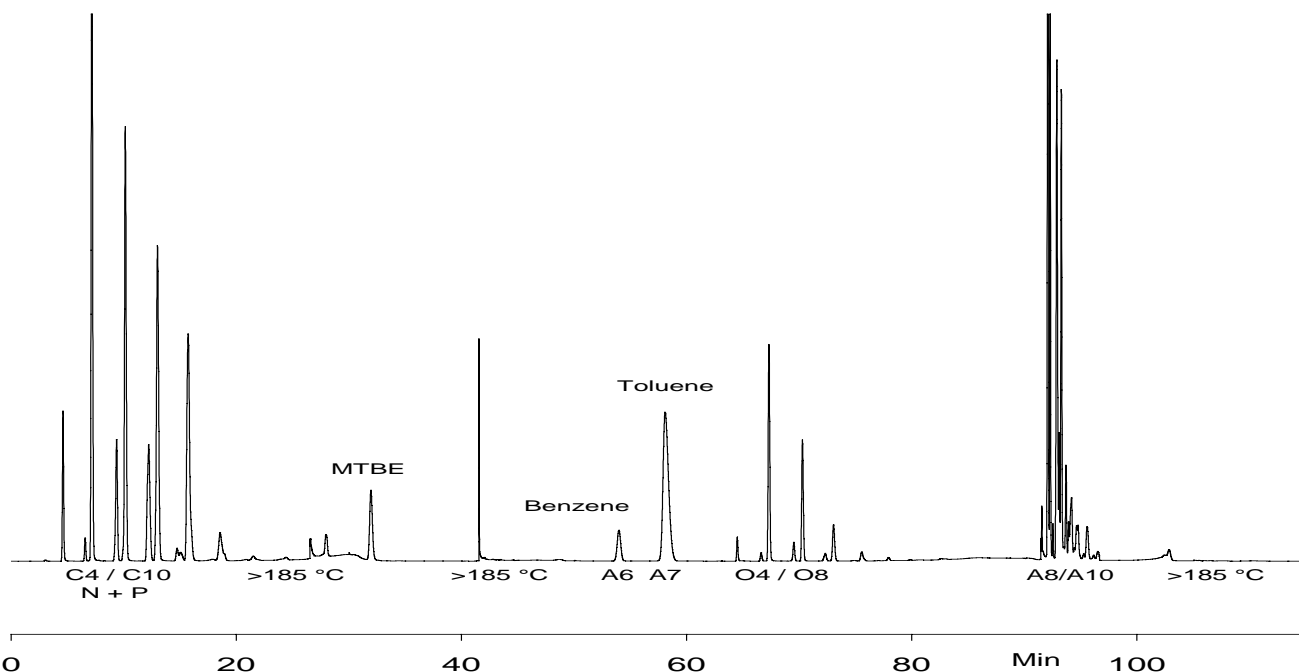


Figure 2. Chromatogram of a gasoline sample.

Finally, the oxygenates are reported per carbon number and as individual components (Tables 4 and 5).

Table 4. Volume% profile of a gasoline.

Normalized Volume Percent Profile							
Carbon	Saturates		Unsaturation				Total
	Cyclic	Normal + Iso	Cyclic	Normal + Iso	Aromatics	Oxygenates	
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	2.52	0.00	0.39	0.00	0.00	2.90
5	0.31	13.07	0.14	4.17	0.00	3.10	20.78
6	2.28	8.95	0.33	2.36	2.00	0.00	15.91
7	3.27	8.07	0.18	0.87	7.19	0.00	19.57
8	0.53	7.44	0.02	0.26	15.82	0.00	24.07
9	3.00	1.14	0.01	0.07	14.44	0.00	15.66
10	0.00	0.12	0.00	0.00	0.99	0.00	1.11
11	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	6.39	41.31	0.67	8.11	40.44	3.10	100.0
Fraction >200 °C	0.00	MTBE		3.10			
Polynaphthenes	0.00						

Table 5. Weight% results of a gasoline.

Normalized Weight Percent Profile							
Carbon	Saturates		Unsaturation				Total
	Cyclic	Normal + Iso	Cyclic	Normal + Iso	Aromatics	Oxygenates	
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	1.92	0.00	0.31	0.00	0.00	2.23
5	0.31	10.80	0.14	3.61	0.00	3.04	17.90
6	2.29	7.82	0.34	2.12	2.33	0.00	14.90
7	3.28	7.33	0.19	0.81	8.26	0.00	19.86
8	0.54	6.95	0.02	0.25	18.18	0.00	25.95
9	3.00	1.09	0.01	0.07	16.72	0.00	17.89
10	0.00	0.12	0.00	0.00	1.16	0.00	1.28
11	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	6.42	36.02	0.69	7.17	46.65	3.04	100.00
Fraction >200 °C	0.00	MTBE		3.04			
Polynaphthenes	0.00						

Conclusion

This application note describes the determination of oxygenates, paraffins, olefins, naphthenes and aromatics with the Varian PIONA+ Analyzer. This analyzer provides the required mass% and volume% reports and functions fully according the ASTM methods D 6839 and D 6293.

References

ASTM D 6293-98, (2003)e1, "Standard Test Method for Oxygenates and Paraffin, Olefin, Naphthene, Aromatic (O-PONA) Hydrocarbon Types in Low-Olefin Spark Ignition Engine Fuels by Gas Chromatography", ASTM International, West Conshohocken,PA, www.astm.org.

Other methods

ASTM D 6839, DIN 5148 (1 and 2), ASTM D 1319 (FIA), ASTM D 5443, UOP 870, IP 382, ASTM D 3710 (TBP), ASTM D 4815, ASTM D 6296, DIN 51413-2, DIN 51413-9, ASTM D 5580 and ASTM D 3606

These data represent typical results.

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