Analysis of Oxygenates, Paraffins, Naphthenes and Aromatics (O-PNA) in Hydrocarbon Streams

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Introduction

This application note describes the quantitative determination of oxygenates, paraffins, naphthenes and aromatics (O-PNA) 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 in O-PNA mode and used to characterize the oxygenate, paraffin, naphthene and aromatic 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+ plug-in software

Conditions

All conditions for the different columns and traps were set in order to obtain the elution scheme represented in Table 1.

Table 1. Elution scheme for O-PNA

From	To (min)	Components	Column route
0	25.0	C1 to C10 N + P	1st OV-275 fraction via arom/eth 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	66.5	Ca to C10 A	3rd back flush OV-275 and precolumn back flush fraction via arom/eth to CP-Sil 5CB
66.5	75.0	>185 °C fraction	Back flush CP-Sil 5CB of 3rd OV-275 and pre back flush fraction
75.0	85.0	alcohols	3rd OV-275 and precolumn back flush fraction via arom/eth and CP-Sil 5CB to porous polymer column

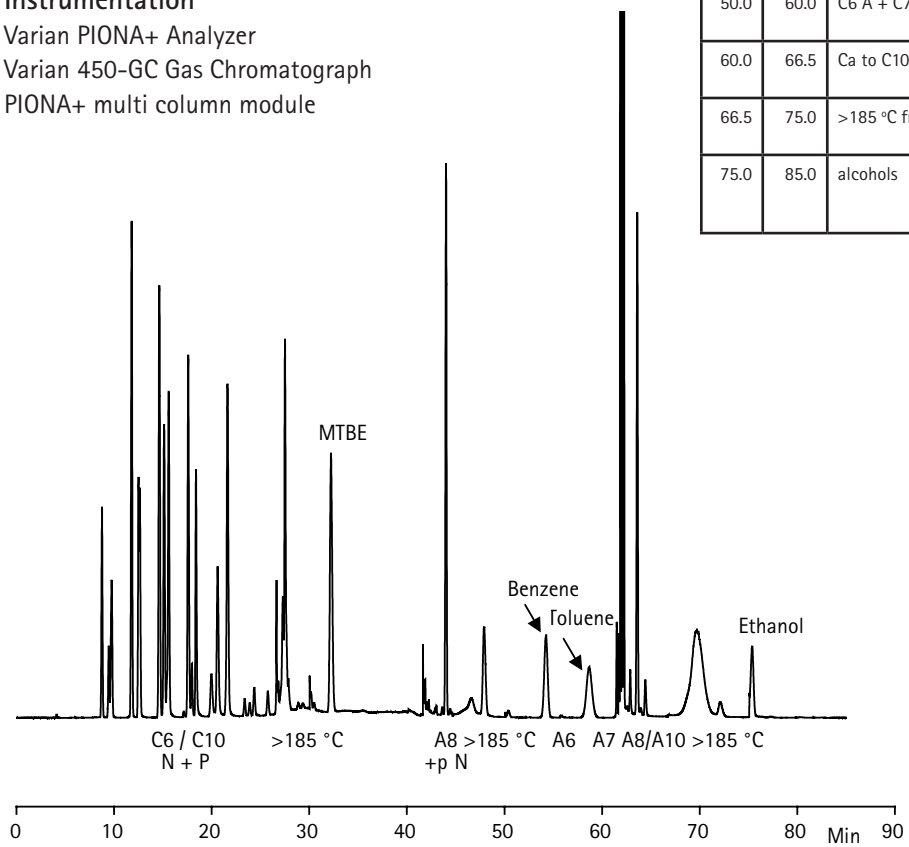

Figure 1. Chromatogram of a calibration sample CP299107 spiked with oxygenates.

Results and Discussion

When all columns and traps are set in the O-PNA mode required settings, a chromatogram according to the elution scheme in Table 1 is obtained. In this case, a chromatogram of a calibration mix CP299107 spiked with oxygenates is shown. The Varian PIONA+ Analyzer is preset with a number of reports, as shown in Tables 2 and 3.

Table 2. Mass% results of a calibration sample.

Normalized Weight Percent Profile

Carbon	Naphthenes	Paraffins	Aromatics	Oxygenates	**Total**
2	0.00	0.00	0.00	3.92	**3.92**
3	0.00	0.02	0.00	0.00	**0.00**
4	0.00	0.00	0.00	0.00	**0.00**
5	0.00	0.00	0.00	8.18	**8.18**
6	1.87	2.45	2.18	0.00	**6.51**
7	4.65	4.12	2.09	0.00	**10.86**
8	4.89	70.19	9.42	0.00	**21.50**
9	4.07	2.97	6.21	0.00	**13.25**
10	2.27	4.59	5.18	0.00	**12.04**
11	0.00	0.00	0.00	0.00	**0.00**
Total	**17.76**	**21.34**	**25.09**	**12.11**	**76.29**

Fraction >200 °C	18.31
Polynaphthenes	5.40

MTBE	8.18
Ethanol	3.92

Table 3. Volume% profile of a calibration sample.

Normalized Volume Percent Profile

Carbon	Naphthenes	Paraffins	Aromatics	Oxygenates	**Total**
2	0.00	0.00	0.00	3.95	**3.95**
3	0.00	0.04	0.00	0.00	**0.04**
4	0.00	0.00	0.00	0.00	**0.00**
5	0.00	0.00	0.00	8.78	**8.78**
6	1.97	2.96	1.97	0.00	**6.90**
7	4.88	4.78	1.92	0.00	**11.58**
8	5.01	8.12	8.64	0.00	**21.76**
9	4.11	3.26	5.65	0.00	**13.02**
10	2.23	5.00	4.64	0.00	**11.87**
11	0.00	0.00	0.00	0.00	**0.00**
Total	**18.20**	**24.15**	**22.83**	**12.73**	**77.90**

Fraction >200 °C	16.27
Polynaphthenes	5.83

MTBE	8.78
Ethanol	3.95

In Figure 2, a chromatogram of a gasoline is shown. Again, a clear overview of the group type separation per carbon number and the oxygenates is revealed, in this case only MTBE. From this chromatogram volume and weight percent profile reports are generated.

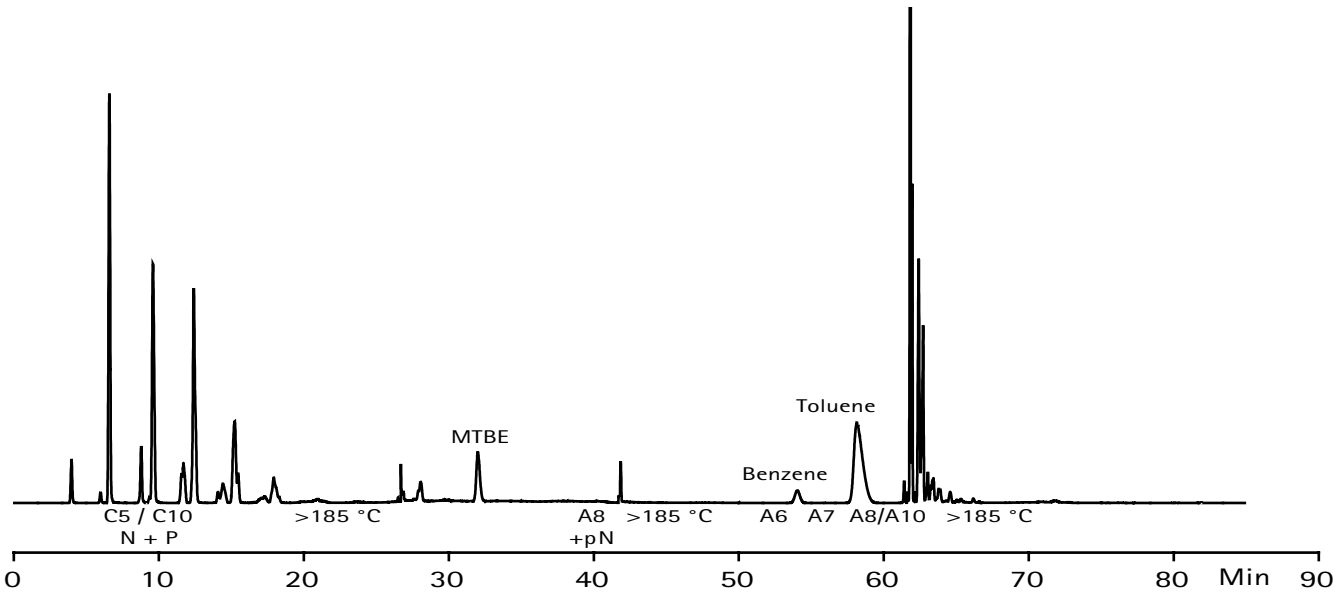

Figure 2. Chromatogram of a gasoline type sample.

The reports are divided into several columns with saturated and unsaturated component groups. Furthermore, a clear overview per carbon number is produced as well as the totals per group and per carbon number. Finally, the oxygenates are reported per carbon number and as individual components (Tables 4 and 5).

Table 4. Weight% profile of a gasoline

Normalized Weight Percent Profile

Carbon	Naphthenes	Paraffins	Aromatics	Oxygenates	**Total**
2	0.00	0.00	0.00	0.00	**0.00**
3	0.00	0.00	0.00	0.00	**0.00**
4	0.00	1.15	0.00	0.00	**1.15**
5	0.30	11.99	0.00	4.66	**16.95**
6	1.64	9.43	1.04	0.00	**12.11**
7	2.41	8.97	11.49	0.00	**22.87**
8	1.63	5.39	20.15	0.00	**27.17**
9	0.70	1.96	11.59	0.00	**14.25**
10	0.18	0.47	3.07	0.00	**3.72**
11	0.00	0.00	0.00	0.00	**0.00**
Total	**6.85**	**39.36**	**47.33**	**4.66**	**98.21**

Fraction >200 °C	1.75	MTBE	4.66
Polynaphthenes	0.04		

Table 5. Volume% profile of a gasoline

Normalized Volume Percent Profile

Carbon	Naphthenes	Paraffins	Aromatics	Oxygenates	**Total**
2	0.00	0.00	0.00	0.00	**0.00**
3	0.00	0.00	0.00	0.00	**0.00**
4	0.00	1.52	0.00	0.00	**1.52**
5	0.30	14.65	0.00	4.79	**19.74**
6	1.65	10.91	0.90	0.00	**13.46**
7	2.42	9.98	10.09	0.00	**22.49**
8	1.60	5.83	17.70	0.00	**25.12**
9	0.68	2.06	10.11	0.00	**12.85**
10	0.17	0.49	2.63	0.00	**3.29**
11	0.00	0.00	0.00	0.00	**0.00**
Total	**6.81**	**45.43**	**41.43**	**4.79**	**98.47**

Fraction >200 °C	1.49	MTBE	4.79
Polynaphthenes	0.04		

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, (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 51448 (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 55

These data represent typical results.
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