

Application Note # CA-270382

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

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 Bruker PIONA+™ GC analysis system. The Bruker 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:
Bruker PIONA+ Analyzer

Software:
CompassCDS Chromatography Software from Bruker with PIONA+ plug-in software

Table 1: Elution scheme for O-PNA.

From	To (min)	Components	Column route
0	25.0	C1 to C10 N + P	1 st OV-275 fraction via arom/eth to 13x
25.0	30.0	>185 °C fraction	Back flush non-polar column of 2 nd OV-275 fraction
30.0	40.0	ethers	1 st OV-275 fraction via arom/eth and non-polar to porous polymer column
40.0	45.0	C8 A and pN	2 nd OV-275 fraction via arom/eth and non-polar column
45.0	50.0	>185 °C fraction	Back flush non-polar column of 2 nd OV-275 fraction
50.0	60.0	C6 A + C7 A	2 nd OV-275 fraction via arom/eth and non-polar to porous polymer column
60.0	66.5	Ca to C10 A	3 rd back flush OV-275 and precolumn back flush fraction via arom/eth to non-polar column
66.5	75.0	>185 °C fraction	Back flush non-polar column of 3 rd OV-275 and pre back flush fraction
75.0	85.0	alcohols	3 rd OV-275 and precolumn back flush fraction via arom/eth and non-polar to porous polymer column

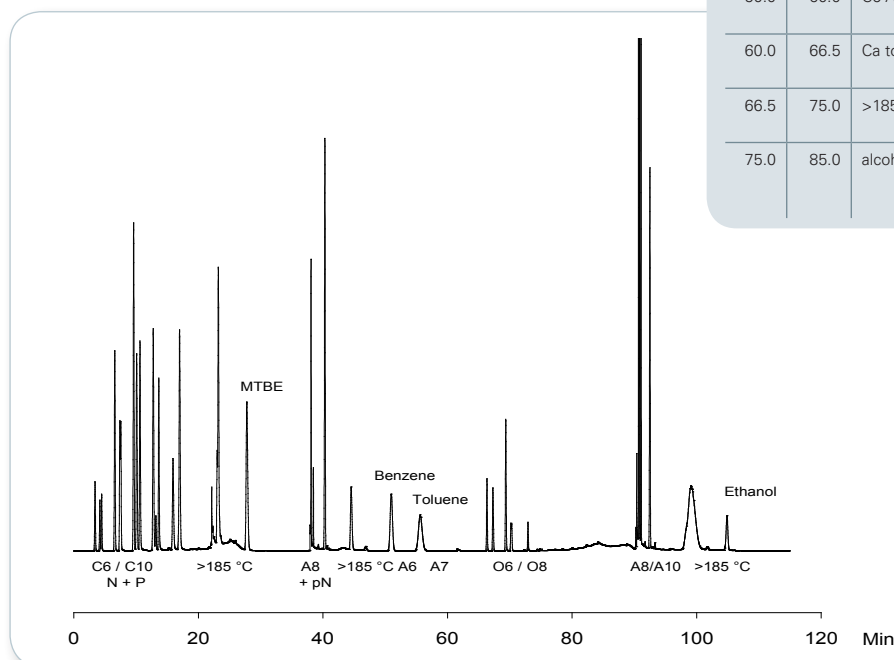


Figure 1:
Chromatogram of test sample 1 spiked with oxygenates.

Conditions

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

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 test sample 1 spiked with oxygenates is shown. The Bruker PIONA+ Analyzer is preset with a number of reports, as shown in Tables 2 and 3.

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.

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).

Conclusion

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

Table 2: Mass% results of test sample 1.

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		MTBE	8.18
Polynaphthenes		5.40		Ethanol	3.92

Table 3: Volume% profile of test sample 1.

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		MTBE	8.78
Polynaphthenes		5.83		Ethanol	3.95

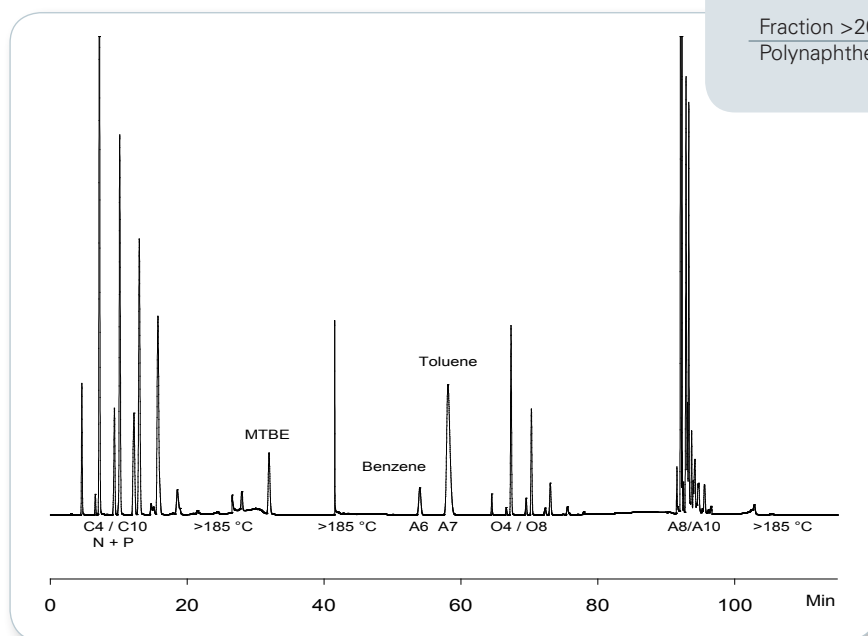


Figure 2: Chromatogram of a gasoline type sample.

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
Polynaphthenes	0.04

MTBE	4.66
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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
Polynaphthenes	0.04

MTBE	4.79
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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

Keywords

ASTM D 6839
ASTM D 6293
Spark ignition fuels
O-PNA

Instrumentation & Software

Bruker PIONA+ Analyzer
CompassCDS Chromatography Software
PIONA plug-in software

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