Paraffins, Naphthenes and Aromatics (PNA) in Hydrocarbon Streams with the Varian PIONA+™ Analyzer

Coen Duvekot
Varian, Inc.

Introduction

This application note describes the quantitative determination of paraffins, naphthenes and aromatics (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 and offers the ability to characterize and quantify the components in a variety of spark ignition fuels according to an array of industry standard method protocols. The system is very flexible and can be operated in 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 PNA content of spark ignition fuel.

Instrumentation

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

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

Conditions

The analysis/separation is achieved through the use of carefully chosen columns and traps. All analysis parameters are set by Varian at the factory to achieve optimal separation for the specified analysis mode, in this case, PNA. The analysis scheme used to determine the sample's PNA composition is detailed in Table 1.

Table 1. Elution scheme for PNA

From	To (min)	Components	Column route
0	30.0	C1 to C12 N + P	1st OV-275 fraction 13x
30.0	35.0	C6 to C8 A and PN	2nd OV-275 fraction via arom/eth to CP-Sil 5CB
35.0	40.0	>200 °C fraction	Back flush CP-Sil 5CB of 2nd OV-275 fraction
40.0	46.5	C8 to C10 A	3rd back flush OV-275 fraction via aom/eth to CP-Sil 5CB
46.5	55.0	>200 °C fraction	Back flush CP-Sil 5CB of 3rd OV-275 fraction

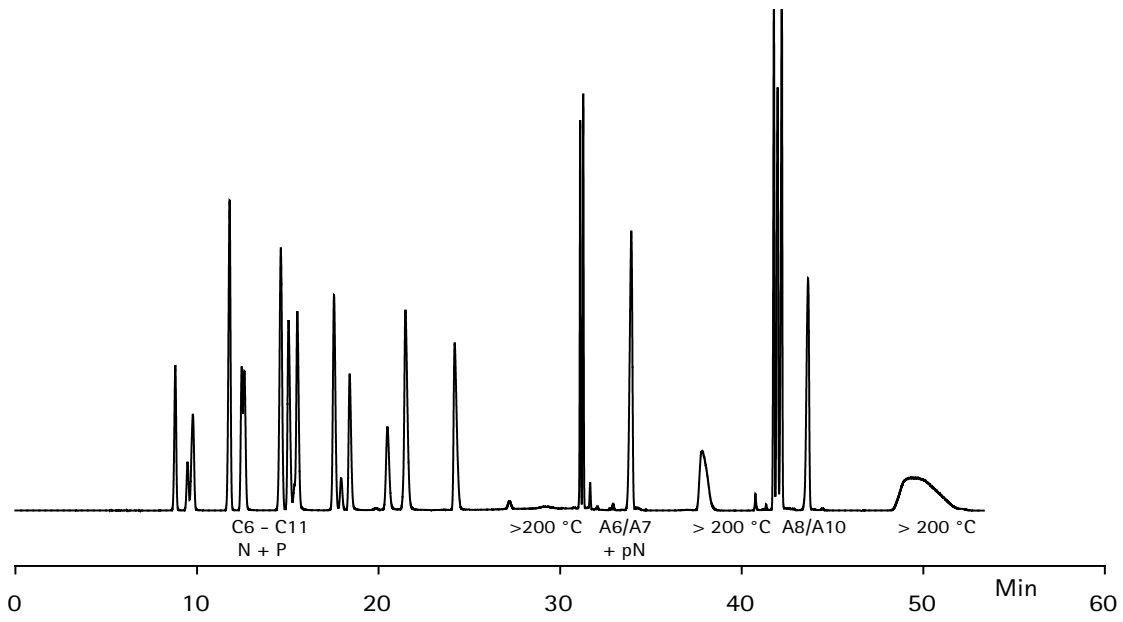

Figure 1. Chromatogram of a calibration sample CP299107.

Results and Discussion

A calibration sample (pn: CP299107) was chosen and subjected to analysis on the PIONA+ Analyzer in PNA mode. A representative chromatogram is shown in Figure 1.

The Varian PIONA+ Analyzer includes a number of report/type options. For this application, the summary by weight% and summary by volume% options were selected and examples are shown in Tables 2 and 3. The results are well within the requirements of methods, such as DIN 5148, ASTM D 5443, UOP 870 and IP 382.

Table 2. Mass% results of the calibration sample.

Normalized Weight Percent Profile				
Carbon	**Naphthenes**	**Paraffins**	**Aromatics**	**Total**
2				
3	0.00	0.00	0.00	**0.00**
4	0.00	0.00	0.00	**0.00**
5	0.00	0.00	0.00	**0.00**
6	2.40	3.15	2.88	**8.43**
7	5.69	5.11	2.86	**13.65**
8	5.80	8.71	10.38	**24.88**
9	4.65	3.62	6.70	**14.97**
10	2.30	5.51	5.09	**12.95**
11	0.00	4.30	0.00	**4.30**
Total	**20.89**	**30.39**	**27.91**	**79.18**

Fraction >200 °C	14.19
Polynaphthenes	6.63

Table 3. Volume% results of the calibration sample.

Normalized Volume Percent Profile				
Carbon	**Naphthenes**	**Paraffins**	**Aromatics**	**Total**
2				
3	0.00	0.00	0.00	**0.00**
4	0.00	0.00	0.00	**0.00**
5	0.00	0.00	0.00	**0.00**
6	2.45	3.70	2.53	**8.68**
7	5.80	5.76	2.55	**14.11**
8	5.77	9.54	9.24	**24.55**
9	4.55	3.86	5.93	**14.34**
10	2.25	5.83	4.42	**12.50**
11	0.00	3.97	0.00	**3.97**
Total	**20.82**	**32.66**	**24.67**	**78.15**

Fraction >200 °C	14.89
Polynaphthenes	6.96

In the next example, a naphtha sample was analyzed in PNA mode. A representative chromatogram is shown in Figure 2. It is apparent that, as with the first example, there is very clear group separation making identification and quantification straightforward. The weight% and volume% results by carbon number and total reports are shown in Tables 4 and 5.

Table 4. Weight% results of the naphtha sample.

Normalized Weight Percent Profile				
Carbon	**Naphthenes**	**Paraffins**	**Aromatics**	**Total**
3	0.00	0.01	0.00	**0.01**
4	0.00	2.24	0.00	**2.24**
5	1.28	17.51	0.00	**18.79**
6	12.41	22.66	0.83	**35.91**
7	15.62	20.52	1.89	**38.03**
8	2.18	2.06	0.20	**4.44**
9	0.10	0.15	0.10	**0.35**
10	0.03	0.03	0.02	**0.08**
11	0.00	0.02	0.00	**0.02**
Total	**31.63**	**65.21**	**3.05**	**99.87**

Fraction >200 °C	0.11
Polynaphthenes	0.02

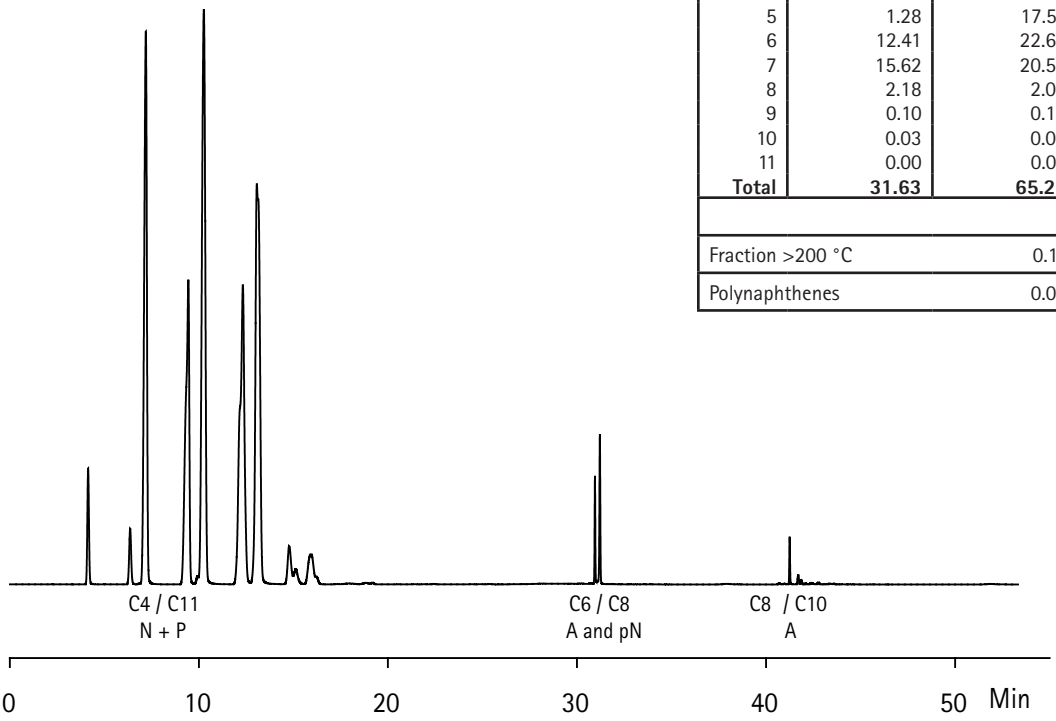

Figure 2. Chromatogram of a naphtha sample.

Table 5. Volume% results of the naphtha sample.

Normalized Volume Percent Profile				
Carbon	Naphthenes	Paraffins	Aromatics	Total
3	0.00	0.02	0.00	**0.02**
4	0.00	2.69	0.00	**2.69**
5	1.18	19.38	0.00	**20.56**
6	11.32	23.74	0.65	**35.71**
7	14.22	20.67	1.50	**36.39**
8	1.94	2.01	0.16	**4.11**
9	0.09	0.15	0.08	**0.31**
10	0.02	0.03	0.02	**0.07**
11	0.00	0.02	0.00	**0.02**
Total	**28.76**	**68.70**	**2.42**	**99.88**

Fraction >200 °C	0.10
Polynaphthenes	0.02

Weight and volume% profile reports were generated as before. In these reports, grouping of naphthenes, paraffins and aromatics is shown per carbon number as well as the totals of the different groups and the totals per carbon number.

Conclusion

The Varian PIONA+ Analyzer provides the required mass% and volume% reports fully in accordance with DIN 5148-1, ASTM D 5443, UOP 870 and IP 382.

References

ASTM D 5443-04, "Paraffin, Naphthene and Aromatic Hydrocarbon Type Analysis in Petroleum Distillates Through 200°C by Multi Dimensional Gas Chromatography," ASTM International, West Conshohocken, PA, www.astm.org.

These data represent typical results.
For further information, contact your local Varian Sales Office.

Varian, Inc.
www.varianinc.com
North America: 800.926.3000 – 925.939.2400
Europe: *The Netherlands*: 31.118.67.1000
Asia Pacific: *Australia*: 613.9560.7133
Latin America: *Brazil*: 55.11.3238.0400