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## Application Note SI-01314

### Paraffins, Olefins, iso-Paraffins, iso-Olefins, Naphthenes and Aromatics (PIONA) in Hydrocarbon Streams

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#### Introduction

This application note describes the quantitative analysis of n- and iso-saturates, n- and iso-olefins, and aromatics in spark-ignition engine fuels by multi-dimensional gas chromatography using the Varian PIONA+™ Analyzer. Through the use of this system, hydrocarbon types (paraffins, iso-paraffins, olefins, iso-olefins, naphthenes and aromatics) are analyzed and reported, based on carbon number or as a total.

#### 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 (temperatures, valve/switch timings) for the different columns and traps are set and tuned at the Varian factory per method/mode to obtain an optimized chromatographic separation.

In this application, the PIONA mode for the analyzer has been selected. In the PIONA mode of operation, the MolSieve 5A trap is not only used to separate the n-paraffins from the iso-paraffins but also the n-olefins from the iso-olefins as well. An example is shown in Figure 1.

#### Results and Discussion

An example of a PIONA analysis is shown in the chromatogram below. A calibration sample (pn: CP299107), is used to calibrate the PIONA+ analyzer as shown in Figure 1. Clearly visible is the group type separation per carbon number. The high resolution allows for easy identification and thus accurate and precise quantification.

Table 1. Elution scheme for PIONA.

From	To (min)	Components	Column Route
0	30.0	C1 to C12 N + iP	1st OV-275 fraction via 5A and olefin trap to 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
50.0	80.0	C3 to C12 nP	5A in flow to 13x
80.0	86.5	C8 to C10 A	3rd back flush OV-275 fraction via aom/eth to CP-Sil 5CB
86.5	95.0	>200 °C fraction	Back flush CP-Sil 5CB of 3rd OV-275 fraction
100.0	130.0	C3 to C12 c0+i0	Olefin trap in flow via 5A trap to 13x
130.0	150.0	None	Cooling 13x column
150.0	180.0	C3 to C12 n0	5A in flow to 13x

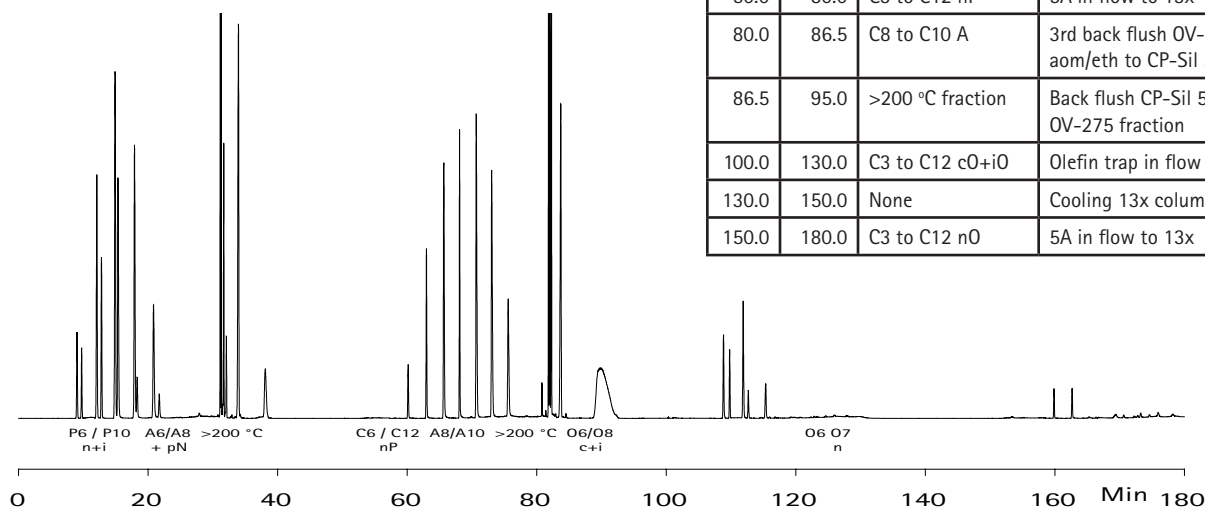


Figure 1. Chromatogram of a calibration sample CP299107.

Galaxie™ software, together with the PIONA+ plug-in, generate weight% and volume% profile reports as shown in Tables 2 and 3. In one view, the amounts of the different groups as well as the totals per group and per carbon number can be seen.

Table 2. Weight% report of calibration sample CP229107.

Normalized Weight Percent Profile								
Carbon	Saturates			Unsaturates			Aromatics	Total
	Cyclic	Iso	Normal	Cyclic	Iso	Normal		
3	0.00	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	0.00
5	0.00	0.00	0.00	0.00	0.78	0.00	0.00	0.00
6	1.20	0.87	0.74	1.16	0.85	0.35	2.83	8.00
7	3.56	2.14	2.13	1.80	0.40	0.41	2.90	13.35
8	5.76	4.19	4.04	0.00	0.63	0.00	10.71	25.33
9	4.65	0.70	3.02	0.00	0.20	0.00	6.22	14.59
10	2.45	0.45	5.20	0.00	0.00	0.00	5.30	13.40
11	0.00	0.00	4.32	0.00	0.00	0.00	0.00	4.32
<b>Total</b>	<b>17.62</b>	<b>8.35</b>	<b>19.45</b>	<b>2.97</b>	<b>1.89</b>	<b>0.77</b>	<b>27.95</b>	<b>78.98</b>
Fraction >200 °C 14.22								
Polynaphthenes 6.80								

Table 3. Volume% report of calibration sample CP299107.

Normalized Volume Percent Profile								
Carbon	Saturates			Unsaturates			Aromatics	Total
	Cyclic	Iso	Normal	Cyclic	Iso	Normal		
3	0.00	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	0.00
5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	1.22	1.02	0.87	1.15	0.96	0.40	2.49	8.13
7	3.64	2.42	2.41	1.77	0.45	0.46	2.59	13.73
8	5.74	4.61	4.44	0.00	0.68	0.00	9.56	25.03
9	4.57	0.75	3.23	0.00	0.00	0.00	5.51	14.06
10	2.35	0.47	5.51	0.00	0.00	0.00	4.62	12.95
11	0.00	0.00	4.00	0.00	0.00	0.00	0.00	4.00
<b>Total</b>	<b>17.52</b>	<b>9.26</b>	<b>20.46</b>	<b>2.93</b>	<b>2.09</b>	<b>0.86</b>	<b>24.77</b>	<b>77.90</b>
Fraction >200 °C 14.95								
Polynaphthenes 7.15								

Another example is shown in Figure 2. A calibration mix (pn: CP299103), containing additional components, was analyzed using the PIONA+ system. It is noteworthy that in spite of the fact that additional components are present (compared to the example shown in Figure 1), excellent peak resolution and group separation are still produced. This enables the analyst to achieve precise identification and subsequent quantification, as shown in Table 4 (weight% report) and Table 5 (volume% report).

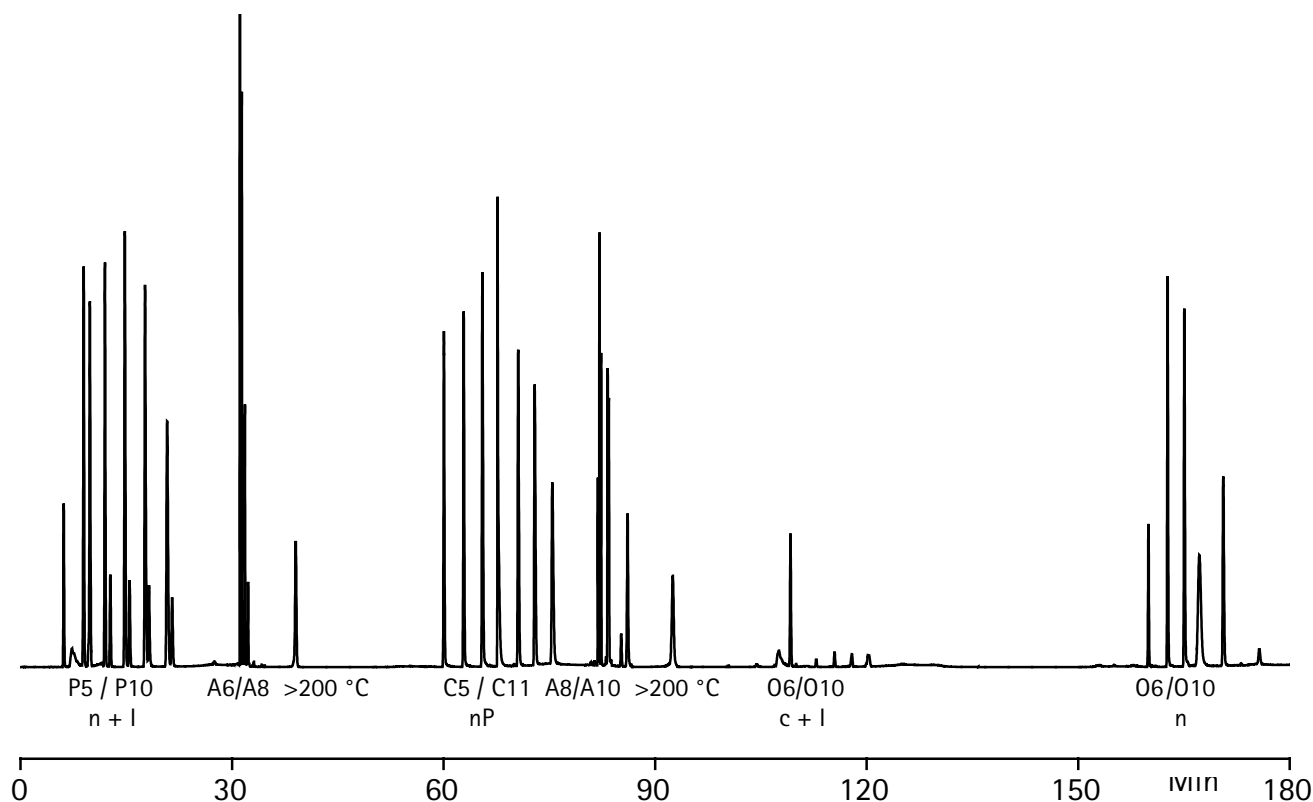


Figure 2. Chromatogram of calibration sample CP299103.

Table 4. Weight% report of calibration sample CP220103.

Normalized Weight Percent Profile								
Carbon	Saturates			Unsaturates			Aromatics	Total
	Cyclic	Iso	Normal	Cyclic	Iso	Normal		
3	0.00	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	0.00
5	1.42	0.00	0.95	0.00	0.78	0.00	0.00	3.15
6	4.05	4.49	3.49	1.47	0.00	1.36	9.15	14.01
7	4.07	1.02	3.88	0.00	0.09	3.81	2.02	14.90
8	5.12	1.08	4.81	0.00	0.18	4.08	4.47	19.74
9	5.05	1.08	4.99	0.00	0.20	3.92	5.19	20.43
10	4.10	1.04	4.05	0.00	0.00	2.68	2.20	14.07
11	0.00	3.70	0.00	0.00	0.00	0.00	0.00	3.70
<b>Total</b>	<b>23.81</b>	<b>12.40</b>	<b>22.17</b>	<b>1.47</b>	<b>1.26</b>	<b>15.85</b>	<b>23.03</b>	<b>100.00</b>
Fraction >200 °C		0.00						
Polynaphthenes		0.00						

Table 5. Volume% report of calibration sample CP229103.

Normalized Volume Percent Profile								
Carbon	Saturates			Unsaturates			Aromatics	Total
	Cyclic	Iso	Normal	Cyclic	Iso	Normal		
3	0.00	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	0.00
5	1.45	0.00	1.16	0.00	0.90	0.00	0.00	3.51
6	4.07	5.17	4.02	1.43	0.00	1.52	7.89	24.10
7	4.07	1.13	4.30	0.00	0.10	4.13	1.77	15.51
8	5.00	1.17	5.18	0.00	0.19	4.33	3.91	19.78
9	4.86	1.13	5.23	0.00	0.21	4.05	4.51	20.00
10	3.85	1.08	4.21	0.00	0.00	2.73	1.88	13.75
11	0.00	3.36	0.00	0.00	0.00	0.00	0.00	3.36
<b>Total</b>	<b>23.30</b>	<b>13.04</b>	<b>24.10</b>	<b>1.43</b>	<b>1.41</b>	<b>16.76</b>	<b>19.97</b>	<b>100.00</b>
Fraction >200 °C		0.00						
Polynaphthenes		0.00						

Thus, in one overview, the saturated and unsaturated groups are reported as a total and per carbon number. In addition, the totals per carbon number are revealed.

## Conclusion

The data and results clearly demonstrate that the Varian PIONA+ Analyzer is capable of providing both mass% and volume% in accordance with the DIN 51448-2 standard method.

## Reference

DIN (Deutsches Institut für Normung e. V) 51448-2, "Testing of liquid petroleum hydrocarbons - Determination of hydrocarbon types - Part 1: Gas chromatographic analysis by column switching procedure", Berlin, Germany. [www2.din.de](http://www2.din.de).

*These data represent typical results.*

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