# Detailed Hydrocarbon Analysis of Petroleum Naphthas through n-Nonane using ASTM D 5134

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## Introduction

Spark ignition fuels are complex mixtures containing hundreds of components. Detailed information on the composition and concentration of these components is important for quality control, controlling refinery processes and evaluation of raw materials.

This ASTM D 5134 method covers the determination of hydrocarbon components of petroleum naphthas. Components eluting after n-nonane (bp 150.8 °C) are determined as a single group.

The column used in this method is a 50 m x 0.21 mm CP-Sil PONA CB™. Although this is a high resolution GC capillary column, serious co-elutions can occur if olefins are present in the sample. Therefore, the olefin content (v/v) must be lower than 2%.

## Instrumentation

GC: Varian 450-GC Gas Chromatograph
Injector: Split/splitless 1177, full EFC control
Detector: FID, full EFC control
Autosampler: Varian CP-8400 AutoSampler (or Varian CP-8410 AutoInjector)

Software
GC control and data handling: Galaxie™ Software from Varian
DHA calculations: DHA software fully integrated into Galaxie software

## Materials and Reagents

Column: Varian CP-Sil PONA CB, 50 m x 0.21 mm x 0.5 µm, (CP7531)

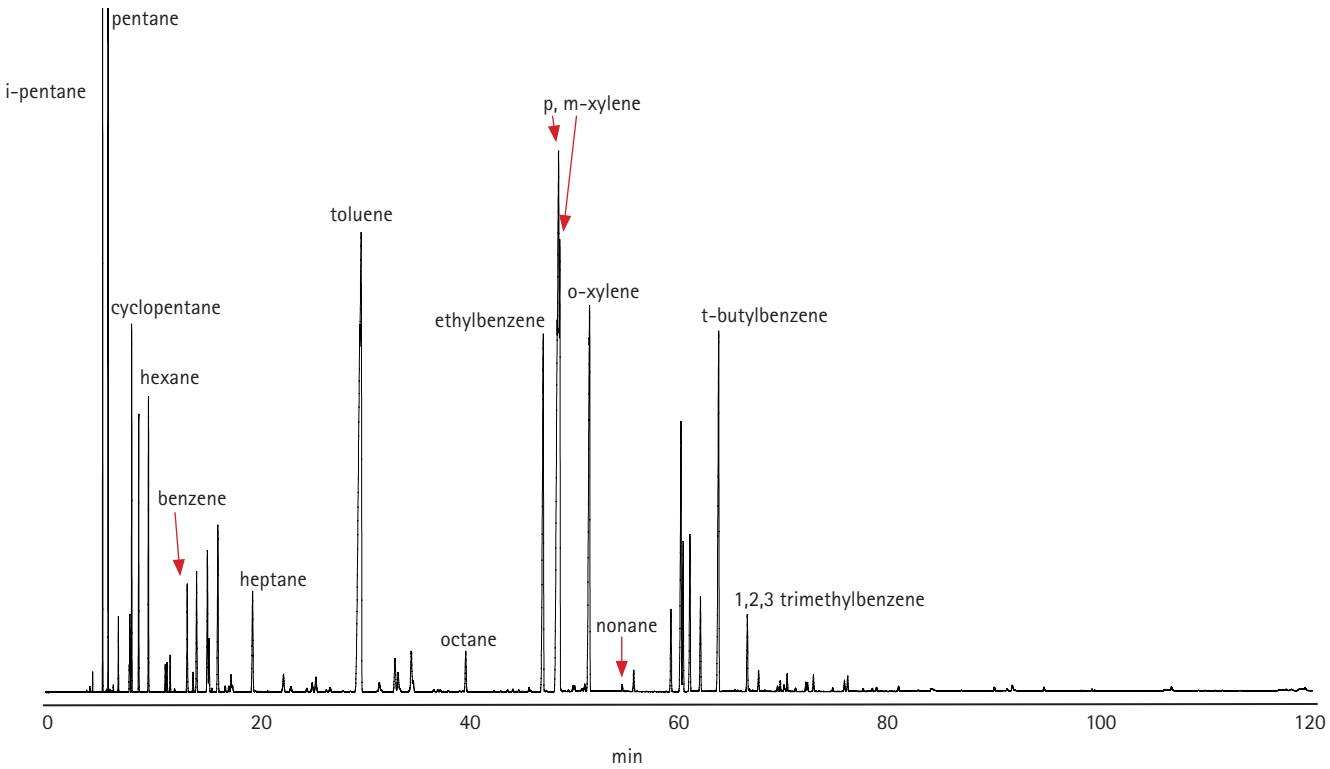


**Figure 1.** Chomatogram of a reformate.

## Conditions

According to the method, carrier gas flow rate is adjusted to that of the retention time of toluene, i.e. 29.9 ± 0.2 min at 35 °C.

Injector: 250 °C, split 200 mL/min
Detector: FID, 250 °C
Oven: 35 °C (30 min) @2 °C/min to 200 °C (10 min)
Sample Size: 0.2 µL
Carrier Gas: Helium (see above)

## Results and Discussion

A calibration mixture containing n-alkanes is used to calculate Kovats Indices of all components in the sample. These indices are compared with known indices in the database and peaks are assigned accordingly (Figure 2).

1 iso-butane
2 butane
3 iso-pentane
4 pentane
5 2,2-dimethylbutane
6 cyclopentane
7 2,3-dimethylbutane
8 2-methylpenatne
9 3-methylpentane
10 hexane
11 2,2-dimethylpentane
12 methylcyclopentane
13 2,4-dimethylpentane
14 2,2,3-trimethylbutane
15 benzene
16 3,3-dimethylpentane
17 cyclohexane
18 2-methylhexane
19 2,3-dimethylpentane
20 1,1-dimethylcyclopentane
21 3-methylhexane
22 cis-1,3-dimethylcyclopentane
23 trans-1,3-dimethylcyclopentane
24 3-ethylpentane
25 trans-1,2-dimethylcyclopentane
26 heptane

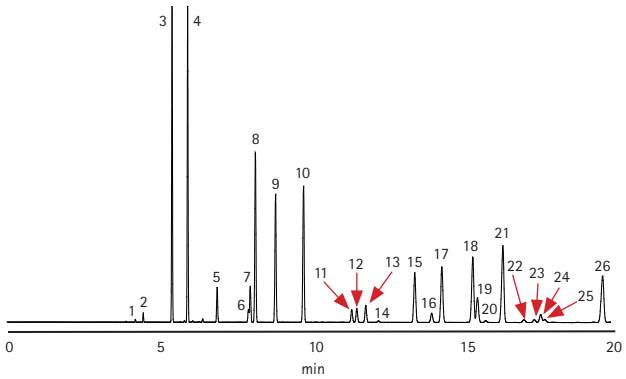


**Figure 2.** Detailed view of the reformate analysis.

Virtually all peaks are identified in this way. Galaxie software calculates the weight percent via normalization. The DHA software combines this with the properties listed in the database and a volume percent profile is calculated. Both reports are combined in a detailed hydrocarbon analysis report as seen in Table 1. In this table all peaks eluting between pentane and heptane are listed.

To ensure accurate results the DHA software calculates peak symmetry. Depending on the peak skewing, a corrected retention time is calculated and subsequently the corresponding Kovats indices. This is also reported in Table 1 in the CRT (corrected retention time) column.

**Table 1.** Detailed hydrocarbon analysis of a reformate

**DHA**

Analysis according to ASTM D5134

| | | | |
|---|---|---|---|
| Sample Info | N.A. | | |
| Sample Type | Sample | | |
| Date Analysed | 20 Dec 2005, 15:06:27 | Date Printed | 17 Feb 2006, 13:51:20 |
| Analyst | Coen Duvekot | Vial | 4 |
| Data File | \DHA Software test\ASTM D5134 COEN\Reformate 43_5.DATA | | |
| Method | \GC-DATA\DHA Software test\ASTM D5134 COEN\ASTM D5134 CD.dha | | |
| Description | Reformate Sample | | |
| Instrument | CP-3800 | | |

Detailed Hydrocarbon Analysis

| ID | RT | CRT | Index | Name | Area | Area Percent | Weight Percent | Volume Percent |
|---|---|---|---|---|---|---|---|---|
| 8 | 5.97 | 5.97 | 500.04 | pentane | 6393.3 | 3.14 | 3.80 | 4.8 |
| 9 | 6.14 | 6.14 | 505.75 | 2-methyl-1,3-butadiene | 21.6 | 0.01 | 0.02 | 0.0 |
| 10 | 6.34 | 6.32 | 511.57 | t-2-pentene | 14.5 | 0.01 | 0.01 | 0.0 |
| 11 | 6.47 | 6.47 | 516.25 | c-2-pentene | 60.1 | 0.03 | 0.04 | 0.0 |
| 12 | 6.95 | 6.95 | 530.65 | 3-methyl-1,2-butadiene | 787.4 | 0.39 | 0.58 | 0.6 |
| 13 | 7.99 | 7.96 | 558.02 | 4-methyl-1-pentene | 254.3 | 0.13 | 0.14 | 0.1 |
| 14 | 8.05 | 8.05 | 560.19 | 3-methyl-1-pentene | 944.0 | 0.46 | 0.51 | 0.6 |
| 15 | 8.22 | 8.22 | 564.45 | cyclopentane | 4584.4 | 2.25 | 2.72 | 2.9 |
| 16 | 8.88 | 8.88 | 580.19 | 3-methylpentane | 3533.1 | 1.73 | 2.01 | 2.4 |
| 17 | 9.81 | 9.81 | 600.19 | hexane | 4038.6 | 1.98 | 2.10 | 2.5 |
| 18 | 11.41 | 11.41 | 621.84 | c-2-hexene | 396.0 | 0.19 | 0.22 | 0.2 |
| 19 | 11.58 | 11.58 | 623.92 | 2,2-dimethylpentane | 444.2 | 0.22 | 0.24 | 0.2 |
| 20 | 11.88 | 11.88 | 627.59 | methylcyclopentane | 552.9 | 0.27 | 0.30 | 0.3 |
| 21 | 12.30 | 12.30 | 632.57 | 2,4-dimethylpentane | 48.7 | 0.02 | 0.03 | 0.0 |
| 22 | 13.50 | 13.50 | 645.91 | benzene | 2110.0 | 1.04 | 0.94 | 0.8 |
| 23 | 14.06 | 14.06 | 651.77 | 1-methylcyclopentene | 366.7 | 0.18 | 0.22 | 0.2 |
| 24 | 14.40 | 14.40 | 655.15 | 3,3-dimethylpentane | 2541.3 | 1.25 | 1.38 | 1.6 |
| 25 | 15.43 | 15.43 | 665.06 | 4-methyl-1-hexene | 3127.7 | 1.54 | 1.55 | 1.7 |
| 26 | 15.58 | 15.58 | 666.49 | 2-methylhexane | 1157.6 | 0.57 | 0.63 | 0.7 |
| 27 | 15.85 | 15.85 | 668.98 | 2,3-dimethylpentane | 69.9 | 0.03 | 0.04 | 0.0 |
| 28 | 16.42 | 16.38 | 673.63 | 1,1-dimethylcyclopentane | 3890.0 | 1.91 | 2.02 | 2.1 |
| 29 | 17.12 | 17.12 | 680.01 | 3-methylhexane | 134.9 | 0.07 | 0.07 | 0.0 |
| 30 | 17.46 | 17.46 | 682.86 | t-1,3-dimethylcyclopentane | 132.8 | 0.07 | 0.07 | 0.0 |
| 31 | 17.67 | 17.67 | 684.58 | c-1,3-dimethylcyclopentane | 385.1 | 0.19 | 0.20 | 0.2 |
| 32 | 17.81 | 17.81 | 685.65 | 3-ethylpentane | 150.7 | 0.07 | 0.08 | 0.0 |
| 33 | 19.42 | 19.38 | 697.77 | 2,4-dimethyl-1-pentene | 11.3 | 0.01 | 0.01 | 0.0 |
| 34 | 19.72 | 19.67 | 699.93 | heptane | 2779.0 | 1.36 | 1.38 | 1.6 |

The DHA software is capable of grouping the different sample components into their chemical groups. This grouping is visualized in the weight percent profile report in Table 2. A volume percent profile report can also be generated.

**Table 2.** Weight percent profile report of a reformate

**DHA**

Analysis according to ASTM D5134

| | | | |
|---|---|---|---|
| Sample Info | N.A. | | |
| Sample Type | Sample | | |
| Date Analysed | 20 Dec 2005, 15:06:27 | Date Printed | 17 Feb 2006, 13:51:20 |
| Analyst | Coen Duvekot | Vial | 4 |
| Data File | \DHA Software test\ASTM D5134 COEN\Reformate 43_5.DATA | | |
| Method | \GC-DATA\DHA Software test\ASTM D5134 COEN\ASTM D5134 CD.dha | | |
| Description | Reformate Sample | | |
| Instrument | CP-3800 | | |

Weight Percent Profile

| | Saturates | | | Unsaturates | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Carbon | Cyclic | Iso | Normal | Cyclic | N+ Iso | Aromatics | Oxyg | Unknown | Total |
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | 0.01 | | | | | | **0.01** |
| 4 | | 0.02 | 0.07 | | | | | | **0.10** |
| 5 | 2.73 | 3.57 | 3.80 | | 0.66 | | | | **10.76** |
| 6 | 0.30 | 2.01 | 2.10 | | 1.09 | 0.94 | | | **6.43** |
| 7 | 2.58 | 2.47 | 1.37 | | 1.59 | 17.20 | | 0.18 | **25.40** |
| 8 | 1.58 | 0.84 | | | 0.53 | 34.98 | | 0.02 | **37.96** |
| 9 | 2.23 | 0.33 | 0.07 | | | 6.78 | | 0.01 | **9.41** |
| 9+ | 0.22 | 2.30 | 0.29 | | | 6.41 | | 0.71 | **9.93** |
| **Total** | **9.65** | **11.54** | **7.71** | | **3.86** | **66.31** | | **0.93** | **100.00** |

In the database all physical properties of the different sample components are listed. The DHA software uses these properties and combines them with the weight%. These combined calculations lead to the properties of the sample reported in the physical properties report (Table 3).

**Table 3.** Physical properties report of a reformate

**DHA**

Analysis according to ASTM D5134

VARIAN

| | | | |
|---|---|---|---|
| Sample Info | N.A. | | |
| Sample Type | Sample | | |
| Date Analysed | 20 Dec 2005, 15:06:27 | Date Printed | 17 Feb 2006, 13:51:20 |
| Analyst | Coen Duvekot | Vial | 4 |
| Data File | \DHA Software test\ASTM D5134 COEN\Reformate 43_5.DATA | | |
| Method | \GC-DATA\DHA Software test\ASTM D5134 COEN\ASTM D5134 CD.dha | | |
| Description | Reformate Sample | | |
| Instrument | CP-3800 | | |

Physical Properties Report

| %OFF | TBP °C | D86 °C | Property | | |
|---|---|---|---|---|---|
| IBP | 27.8 | 58.1 | MON Value | 100.8 | |
| 5% | 36.1 | 55.1 | RON Value | 111.6 | |
| 10% | 40.8 | 70.8 | | | |
| 20% | 79.2 | 94.6 | Reid Vapor P. | 4.0 | mm Hg |
| 30% | 105.9 | 111.0 | | | |
| 40% | 110.6 | | Net Heat | 41.9 | kJ/g |
| 50% | 136.1 | 135.1 | Gross Heat | 44.3 | kJ/g |
| 60% | 138.4 | | | | |
| 70% | 138.4 | 131.6 | Density | 0.8166 | g/ml |
| 80% | 144.4 | 136.3 | | | |
| 90% | 162.0 | 151.2 | | | |
| 95% | 169.1 | | | | |
| FBP | 205.0 | 179.6 | | | |

To determine the repeatability of the system the reformate sample was analyzed several times. The results are shown in Table 4.

**Table 4.** Repeatability figures

| | | | | Mass% | | | |
|---|---|---|---|---|---|---|---|
| File | Mon | Ron | Density | Heptane | Benzene | Toluene | Total Aromatics |
| 1 | 100.8 | 111.5 | 0.8171 | 1.39 | 0.95 | 17.28 | 66.58 |
| 2 | 100.8 | 111.5 | 0.8167 | 1.37 | 0.94 | 17.22 | 66.35 |
| 3 | 100.6 | 111.4 | 0.8166 | 1.37 | 0.94 | 17.20 | 66.31 |
| 4 | 100.7 | 111.5 | 0.8168 | 1.38 | 0.94 | 17.19 | 66.39 |
| 5 | 100.9 | 111.7 | 0.8173 | 1.37 | 0.94 | 17.19 | 66.59 |
| 6 | 100.9 | 111.6 | 0.8167 | 1.38 | 0.95 | 17.22 | 66.36 |
| 7 | 100.8 | 111.6 | 0.8168 | 1.38 | 0.94 | 17.20 | 66.42 |
| 8 | 100.8 | 111.6 | 0.8168 | 1.37 | 0.94 | 17.19 | 66.42 |
| 9 | 100.7 | 111.5 | 0.8168 | 1.37 | 0.94 | 17.21 | 66.40 |
| 10 | 103.0 | 114.1 | 0.8177 | 1.37 | 0.94 | 17.26 | 66.53 |
| 11 | 100.8 | 111.6 | 0.8168 | 1.38 | 0.94 | 17.21 | 66.43 |
| 12 | 100.8 | 111.5 | 0.8166 | 1.37 | 0.94 | 17.20 | 66.34 |
| 13 | 100.8 | 111.6 | 0.8166 | 1.38 | 0.94 | 17.20 | 66.31 |
| Average | 101.0 | 111.7 | 0.8169 | 1.38 | 0.94 | 17.21 | 66.42 |
| St. dv. | 0.6 | 0.7 | 0.0003 | 0.01 | 0.004 | 0.03 | 0.1 |
| St. dev (%) | 0.6 | 0.6 | 0.04 | 0.5 | 0.4 | 0.2 | 0.1 |

The results for two of the components are shown in Figure 3, containing the reproducibility and reproducibility limits. The method demands that for two consecutive runs the results may exceed these limits only once every 20 runs.

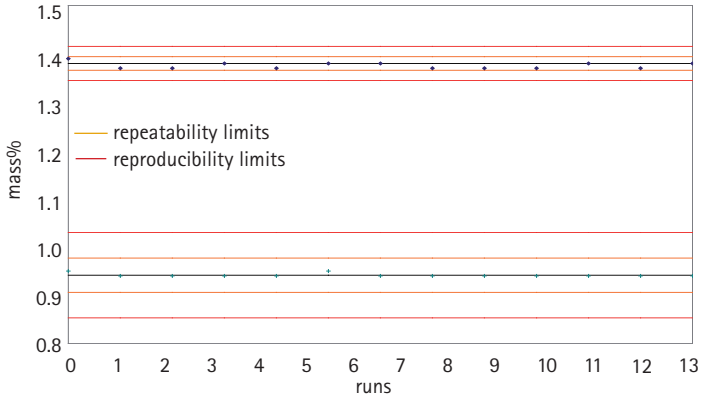


**Figure 3.** Repeatability and reproducibility figures for heptane (above) and benzene (below).

The data clearly show that the repeatability of the system is excellent.

## Conclusion

The Varian 450-GC Gas Chromatograph based Detailed Hydrocarbon Analyzer, together with the Galaxie software and DHA software, give excellent results in DHA analysis according to the ASTM D 5134 method. As well as the required reports per sample component in weight%, volume%, grouping per hydrocarbon type and sample properties can be reported.

Repeatability data are excellent and indicate that the analyzer is well suited for the DHA analysis and performs fully according to the ASTM D 5134 method.

## Reference

ASTM D 5134-98 (2003), "Detailed Analysis of Petroleum Naphthas through n-Nonane by Capillary Gas Chromatography," ASTM International, West Conshohocken, PA, www.astm.org.

*These data represent typical results.*
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