



A Honeywell Company

Hydrocarbon Types and Distributions in Low Olefin C₁₂ and Lower Endpoint Distillates by GC

UOP Method 880-08

Scope

This method is a procedure for calculating paraffin, olefin, naphthene and aromatic hydrocarbon types in hydrocarbon fractions, such as reformer feeds and reformates, having endpoints of 200°C or less (C₃ through C₁₁). C₁₂ paraffins and naphthenes at concentrations totaling less than 3% can be determined. Olefins must be less than 2%. C₈ minus paraffins and naphthenes are reported individually. C₉ through C₁₂ paraffins and naphthenes are determined by carbon number. Aromatics through C₁₀ are determined individually with C₁₁+ aromatics determined as a composite. Olefins are reported undistributed. If analysis by carbon number only for all hydrocarbon types over all carbon number ranges is sufficient, use ASTM Method D6839, "Hydrocarbon Types, Oxygenated Compounds, and Benzene in Spark Ignition Engine Fuels by Gas Chromatography." Results are reported to the nearest 0.01 mass-%. Conversion to liquid volume-percent (LV-%) is described in the *Appendix*.

References

ASTM Method D4052, "Density and Relative Density of Liquids by Digital Density Meter," www.astm.org

ASTM Method D6839, "Hydrocarbon Types, Oxygenated Compounds, and Benzene in Spark Ignition Engine Fuels by Gas Chromatography," www.astm.org

UOP Method 690, "Octanes and Lower Boiling Hydrocarbons in Olefin Free Gasolines by GC," www.astm.org

UOP Method 744, "Aromatics in Hydrocarbons by GC," www.astm.org

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

The sample is analyzed by three gas chromatographic methods: UOP Methods 690, "Octanes and Lower Boiling Hydrocarbons in Olefin Free Gasolines by GC," 744, "Aromatics in Hydrocarbons by GC," and ASTM Method D6839, "Hydrocarbon Types, Oxygenated Compounds, and Benzene in Spark Ignition Engine Fuels by Gas Chromatography." The sample is analyzed by ASTM Method D6839 to determine total paraffins, naphthenes and aromatics by carbon number. The sample is analyzed by UOP

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Method 690 to determine the individual C₈ minus paraffin and naphthene distribution. Total C₈ minus olefins are also determined by UOP Method 690. The sample is analyzed by UOP Method 744 to determine the individual C₆ through C₁₀ aromatics and the C₁₁+ aromatic composite. Data are combined from each analysis to report the total composition of the sample.

Apparatus, Reagents, and Materials

The apparatus, reagents, and materials required for this analysis are described in the three GC methods listed in *References*. A spreadsheet or computer program may be developed to automate the calculations.

Procedure

1. Determine the total paraffins, naphthenes and aromatics, by carbon number, of the sample using the equipment for ASTM Method D6839, but run in the PNA mode. The analyzer specified in D6839 reports results in both mass-% and LV-%. Use the mass-% values.
 - Olefins, if present, are hydrogenated and determined as paraffins or naphthenes in this analysis when run in the PNA mode.
2. Determine the C₈ minus paraffin and naphthene distribution as well as the total C₈ minus olefin composition of the sample by UOP Method 690. Perform both analysis A and B and the additional calculations required by analysis B as described in the method.
 - This analysis is normally performed on olefin-free samples. However, for the purpose of this determination, any unidentified components eluting before methylcyclohexane are considered to be olefins and totaled. Olefins eluting after methylcyclohexane cannot be determined.
 - If the olefin content is above 2%, interferences will make the paraffin and naphthene results invalid. The sample may still be analyzed for hydrocarbon types by carbon number using ASTM D6839 run in the PIONA mode.
3. Determine the C₆ through C₁₀ aromatics individually and the total C₁₁+ aromatic composite by UOP Method 744.

Calculations

The composition of the sample is calculated and reported to the nearest 0.01 mass-%. See Table 1 for a listing of the components and composites typically reported.

1. Olefins, mass-%, are totaled and reported directly from UOP 690.
2. Correct the C₈ minus saturated from ASTM D6839 for hydrogenated olefins using Equation 1:

$$\text{Corrected C}_8 \text{ minus saturates, mass-\%} = \text{C-D} \quad (1)$$

where:

C = sum of the C₈ minus paraffins and naphthenes by ASTM D6839, mass-%

D = total C₈ minus olefins by UOP 690, mass-%

3. Normalize the C₈ minus paraffins and naphthenes from ASTM D6839 to the percentage determined in Step 2. Report the C₉ through C₁₂ paraffins and naphthenes from the original ASTM D6839, as well as any heavy material, called Poly Naphthenes or >C₁₂ P+N by the method.
4. Normalize each individual C₈ minus component from UOP 690 to the corresponding carbon number and type total percentage determined in Step 3. Report the C₈ minus components individually.
5. Report the C₉ through C₁₂ paraffins and naphthenes from the original ASTM D6839, as well as any heavy material, called Poly Naphthenes or >C₁₂ P+N by the method.

6. Report benzene and toluene directly from ASTM D6839 results.
7. Normalize and report individual C₈ aromatic components from UOP 744 to the total C₈ aromatic percentage from ASTM D6839.
8. Normalize and report the C₉+ aromatics from UOP 744 to the total C₉+ aromatic percentage from ASTM D6839. Report as individual C₉ and C₁₀ aromatic components and total C₁₁+ aromatics.
9. Sum all the reported components. Rounding each of the components to the nearest 0.01% may cause the grand total to differ slightly from 100.00. If this occurs, adjust the value of the highest concentration component such that the grand total is exactly 100.00.

Table 1
Typical Components Reported

The numbers in parentheses behind the paraffin and naphthene components are not reported, but may be used as an aid in distributing paraffins (P) and naphthenes (N) from the UOP 690 analysis to the group totals from ASTM D6839.

<u>Component</u>	<u>Component</u>	<u>Component</u>
Total Olefins	Propane (P3)	1,1,2-Trimethylcyclopentane (N8)
	Isobutane (P4)	2-Methyl-3-ethylpentane (P8)
Benzene	n-Butane (P4)	2-Methylheptane (P8)
Toluene	Isopentane (P5)	4-Methylheptane (P8)
Ethylbenzene	n-Pentane (P5)	3,4-Dimethylhexane
p-Xylene	Cyclopentane (N5)	+ 3-Methyl-3-ethylpentane (P8)
m-Xylene	2,2-Dimethylbutane (P6)	1-cis-2-trans-4-Trimethylcyclopentane
o-Xylene	2,3-Dimethylbutane (P6)	+ 1-cis-2-cis-4-Trimethylcyclopentane (N8)
Cumene	2-Methylpentane (P6)	3-Methylheptane (P8)
n-Propylbenzene	3-Methylpentane (P6)	1-cis-3-Dimethylcyclohexane
1-Methyl-4-ethylbenzene	n-Hexane (P6)	+ 1-cis-2-trans-3-Trimethylcyclopentane (N8)
1-Methyl-3-ethylbenzene	2,2-Dimethylpentane (P7)	1-trans-4-Dimethylcyclohexane (N8)
tert-Butylbenzene	Methylcyclopentane (N6)	1,1-Dimethylcyclohexane (N8)
iso-Butylbenzene	2,4-Dimethylpentane (P7)	1-Methyl-trans-3-ethylcyclopentane (N8)
1,3,5-Trimethylbenzene	2,2,3-Trimethylbutane (P7)	1-Methyl-cis-3-ethylcyclopentane (N8)
sec-Butylbenzene	3,3-Dimethylpentane (P7)	1-Methyl-trans-2-ethylcyclopentane (N8)
Styrene	Cyclohexane (N6)	1-Methyl-1-ethylcyclopentane (N8)
1-Methyl-2-ethylbenzene	2-Methylhexane (P7)	1-trans-2-Dimethylcyclohexane (N8)
1-Methyl-3-isopropylbenzene	2,3-Dimethylpentane (P7)	1-cis-2-cis-3-Trimethylcyclopentane (N8)
1-Methyl-4-isopropylbenzene	1,1-Dimethylcyclopentane (N7)	n-Octane (P8)
1,2,4-Trimethylbenzene	3-Methylhexane (P7)	1-cis-4-Dimethylcyclohexane (N8)
1-Methyl-2-isopropylbenzene	1-cis-3-Dimethylcyclopentane (N7)	1-trans-3-Dimethylcyclohexane (N8)
+ 1,3-Diethylbenzene	1-trans-3-Dimethylcyclopentane (N7)	Isopropylcyclopentane (N8)
1-Methyl-3-n-propylbenzene	3-Ethylpentane (P7)	1-Methyl-cis-2-ethylcyclopentane (N8)
1-Methyl-4-n-propylbenzene	1-trans-2-Dimethylcyclopentane (N7)	1-cis-2-Dimethylcyclohexane (N8)
1,4-Diethylbenzene	2,2,4-Trimethylpentane (P8)	Ethylcyclohexane (N8)
n-Butylbenzene	n-Heptane (P7)	n-Propylcyclopentane (N8)
1,3-Dimethyl-5-ethylbenzene	Methylcyclohexane (N7)	
1,2-Diethylbenzene	1-cis-2-Dimethylcyclopentane (N7)	C9 Naphthenes
1-Methyl-2-n-propylbenzene	1,1,3-Trimethylcyclopentane (N8)	C9 Paraffins
1,2,3-Trimethylbenzene	2,2-Dimethylhexane (P8)	C10 Naphthenes
1,4-Dimethyl-2-ethylbenzene	Ethylcyclopentane (N7)	C10 Paraffins
1,3-Dimethyl-4-ethylbenzene	2,5-Dimethylhexane (P8)	C11 Naphthenes
1,2-Dimethyl-4-ethylbenzene	2,4-Dimethylhexane	C11 Paraffins
Indane	+ 2,2,3-Trimethylpentane (P8)	C12 Naphthenes
1,3-Dimethyl-2-ethylbenzene	1-trans-2-cis-4-Trimethylcyclopentane (N8)	C12 Paraffins
1,2-Dimethyl-3-ethylbenzene	3,3-Dimethylhexane (P8)	
1,2,4,5-Tetramethylbenzene	1-trans-2-cis-3-Trimethylcyclopentane	Poly Naphthenes
1,2,3,5-Tetramethylbenzene	2,3,4-Trimethylpentane (P8)	> 200 P + N
1,2,3,4-Tetramethylbenzene	2,3,3-Trimethylpentane (P8)	
C11+ Aromatics	2,3-Dimethylhexane (P8)	

Precision

Precision statements were determined using UOP Method 999 from precision data obtained using an autosampler.

Repeatability and Site Precision

A nested design was carried out for determining components in two samples with two analysts in one laboratory. Each analyst carried out tests on two separate days, performing two tests each day. The total number of tests for each component in each sample was 8. The precision data are summarized in Table 2.

Two tests performed by the same analyst on the same day should not differ by more than the repeatable allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable difference with 95% confidence.

Table 2

Repeatability and Site Precision, Reformer Feed, mass-%

<u>Component</u>	<u>Mean Conc.</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within- Day esd</u>	<u>Allowable Difference</u>	<u>Within- Lab esd</u>	<u>Allowable Difference</u>
Benzene	1.16	0.006	0.02	0.011	0.04
Toluene	2.83	0.005	0.02	0.005	0.02
C ₁₁ + Aromatics	0.19	0.004	0.01	0.004	0.01
Cyclopentane	0.03	0.004	0.02	0.005	0.02
2-Methylpentane	0.69	0.000	0.00	0.010	0.04
n-Heptane	6.75	0.013	0.05	0.016	0.06
1,1,3-Trimethylcyclopentane	0.17	0.004	0.01	0.004	0.01
n-Octane	7.86	0.009	0.03	0.011	0.04
Ethylcyclohexane	1.12	0.010	0.04	0.010	0.04
C ₉ Paraffins	12.56	0.013	0.05	0.014	0.05
C ₁₁ Naphthenes	1.05	0.004	0.01	0.004	0.01

Repeatability and Site Precision, Reformate, mass-%

<u>Component</u>	<u>Mean Conc.</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within- Day esd</u>	<u>Allowable Difference</u>	<u>Within- Lab esd</u>	<u>Allowable Difference</u>
Benzene	11.13	0.052	0.20	0.067	0.26
Toluene	24.23	0.031	0.12	0.044	0.17
C ₁₁ + Aromatics	1.63	0.004	0.01	0.007	0.03
Cyclopentane	0.17	0.004	0.01	0.005	0.02
2-Methylpentane	2.75	0.032	0.12	0.033	0.13
n-Heptane	1.21	0.004	0.02	0.005	0.02
C ₉ Paraffins	0.07	0.004	0.01	0.005	0.02
C ₁₁ Naphthenes	0.02	0.006	0.02	0.008	0.05

The data in Table 2 are a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Reproducibility

There is insufficient data to calculate reproducibility of the test at this time.

Time for Analysis

The elapsed time and labor requirement for the calculations described in this method are identical. A fully manual calculation could require up to one hour. If programming for automated data transfer and calculation is developed, the calculation time could be reduced to a few minutes.

Suggested Suppliers

Refer to the individual methods referenced.

Appendix

Calculation of Results in Liquid Volume Percent

Scope

The Appendix describes the calculation of the results in liquid volume-% (LV-%) instead of the usual mass-%. It also describes the conversion of existing mass-% results to LV-%.

References

ASTM Method D4052, "Density and Relative Density of Liquids by Digital Density Meter,"
www.astm.org

ASTM Publication DS 4B, "Physical Constants of Hydrocarbon and Non-Hydrocarbon Compounds," www.astm.org

Outline of Method

The sample is analyzed by three GC methods as in the body of the method. The LV-% results of ASTM D6839 are used along with the results of the other methods to calculate results in LV-%. Alternatively, existing mass-% results are converted to LV-% using a formula incorporating published density values for individual components.

Apparatus, Reagents, and Materials

The apparatus, reagents, and materials required for this analysis are described in the method listed in *References*. A spreadsheet or computer program may be developed to automate the calculations.

Procedure

Procedure A, Calculation from the Individual GC Analyses

Procedure A takes advantage of the fact that the ASTM D6839 analysis is programmed to report both mass- and LV-%. For purposes of this analysis, the densities of all the components of a specific carbon number and hydrocarbon type group (e.g., C₈ naphthenes) are taken to be the same.

1. Determine the total paraffins, naphthenes and aromatics, by carbon number, of the sample by ASTM Method D6839 run in the PNA mode. The analyzer specified in D6839 reports results in both mass-% and LV-%. Use the LV-% values.
 - Olefins, if present, are hydrogenated and determined as paraffins or naphthenes in this analysis.
2. Determine the paraffin, naphthene, and aromatic distributions as described in Steps 2 and 3 under *Procedure* in the body of the method.
3. Obtain the density of the sample by ASTM D4052, "Density and Relative Density of Liquids by Digital Density Meter."
4. Proceed with the calculation under *Calculations for Procedure A*, below.

Procedure B, Calculation from a Completed Mass-% Report

Procedure B uses a completed mass-% report along with known densities of individual components and averaged group densities to obtain an LV-% report.

1. Obtain the density of each individually reported component from ASTM Publication DS 4B, "Physical Constants of Hydrocarbon and Non-Hydrocarbon Compounds," or other reference. For grouped components, use an average of the individual listed components.
2. Proceed with the calculation under *Calculations for Procedure B*, below.

Calculations

The composition of the sample is calculated and reported to the nearest 0.01 LV-%.

Calculations for Procedure A

1. Convert the total C₈ minus olefins obtained by UOP 690 from mass-% to LV-% using Equation A1:

$$\text{Olefins, LV-\%} = \frac{AB}{0.70} \quad (\text{A1})$$

where:

A = density of the sample from ASTM D4052, g/mL

B = total olefins from UOP 690, mass-%

0.70 = average density of C₈ minus olefins, g/mL

2. Correct the C₈ minus saturated from ASTM D6839 for hydrogenated olefins using Equation A2:

$$\text{Corrected C}_8 \text{ minus saturates, LV-\%} = \text{E-F} \quad (\text{A2})$$

where:

E = sum of the C₈ minus paraffins and naphthenes by ASTM D6839, LV-%

F = total C₈ minus olefins, from Equation A1

3. Perform Steps 3 through 9 under Calculations in the body of the method, substituting LV-% wherever mass-% is listed.

Calculations for Procedure B

1. Calculate the LV-% concentration for each component or group of components using Equation A3:

$$\text{Component or component group, LV-\%} = 100 \frac{M/S}{T} \quad (\text{A3})$$

where:

M = concentration of component or group of components, mass-%

S = density of component or group of components

T = sum of the quotients, **M/S**, of all the components and groups of components in

the sample; also expressed as $\sum_{i=1}^n \frac{M_i}{S_i}$

100 = factor to convert to percent

2. Sum all the reported components. Rounding each of the components to the nearest 0.01% may cause the grand total to differ slightly from 100.00. If this occurs, adjust the value of the highest concentration component such that the grand total is exactly 100.00.