

CARBON NUMBER DISTRIBUTION OF PARAFFINS, NAPHTHENES AND AROMATICS BY GC

UOP Method 870-90

SCOPE

This is an automated method for determining the distribution of paraffins, naphthenes and aromatics by carbon number in hydrocarbon fractions having an endpoint of 200 C or less (C_3 - C_{11}) (see *NOTE*). C_{12} paraffins and naphthenes at concentrations less than 3% can be determined. C_9 + aromatics are reported as a group. Olefins, if present, are hydrogenated and the resultant saturates are included in the paraffin and naphthene distribution. The lower limit of detection for a single carbon number hydrocarbon type is 0.05 mass- or liquid volume (LV)-%.

OUTLINE OF METHOD

The sample is injected into a gas chromatographic system that is equipped with three packed columns and appropriate valving. The first column is polar, typically packed with OV-275 on Chromosorb; the second column is non-polar, typically packed with OV-101 on Chromosorb and the third column is selective, typically packed with specially treated molecular sieves. Initially, the polar and selective columns are connected in series. After the elution of C_{11} saturates from the polar column, the polar column flow is stopped, holding the aromatics until the paraffins and naphthenes have eluted from the selective column. The aromatics are then eluted from the polar column in 3 fractions, each fraction being separated on the non-polar column.

Internal normalization of peak areas after correction for difference in response is used to obtain a mass- or LV-% distribution of the components.

APPARATUS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

This method requires the use of a dedicated gas chromatographic system that is configured for automated hydrocarbon types analysis and is capable, via valve switching, of multi-column operation. The suggested GC is supplied complete with columns, valves and programming specific to this analysis.

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).
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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Balance, readability 0.1-mg

Gas chromatograph, Hewlett-Packard, Model 5890 modified by Analytical Controls as PNA analyzer, available from Analytical Controls

Integrator, electronic for obtaining peak areas. An integrator may be included with the gas chromatograph.

Oxygen remover, Oxy-Trap, Alltech Associates, Cat. No. 4001. An oxygen remover in the carrier gas line ensures optimum column life.

Recorder, 1-mv full scale, 1-sec or less full-scale response. A recorder may be included with the gas chromatograph.

Regulator, air, two-stage, high purity, Matheson, Model 3104-590

Regulator, hydrogen, two-stage, high purity, Matheson, Model 3104-350

Regulator, nitrogen, two-stage, high purity, Matheson, Model 3104-580

Sample injector, any syringe or injector capable of introducing a 0.2- μ L volume of sample, such as a Hamilton 701-NWG syringe, Alltech Associates

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified.

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Air, zero gas, total hydrocarbons less than 2.0 ppm as methane

Benzene, 99.9% minimum purity, Wiley Organics, Cat. No. 0160.84

n-Butylcyclohexane, 99% minimum purity, Wiley Organics, Cat. No. 0419.70 (C₁₀ naphthene)

Cyclohexane, 99.9% minimum purity, Wiley Organics, Cat. No. 0679.02 (C₆ naphthene)

Cyclopentane, 99.9% minimum purity, Wiley Organics, Cat. No. 745.05 (C₅ naphthene)

n-Decane, 99.9% minimum purity, Wiley Organics, Cat. No. 0812.57 (C₁₀ paraffin)

Ethylbenzene, 99.9% minimum purity, Wiley Organics, Cat. No. 2379.03 (C₈ aromatic)

Ethylcyclohexane, 99.9% minimum purity, Wiley Organics, Cat. No. 2442.00 (C₈ naphthene)

n-Heptane, 99.9% minimum purity, Wiley Organics, Cat. No. 3111.00 (C₇ paraffin)

n-Hexane, 99.9% minimum purity, Wiley Organics, Cat. No. 3442.00 (C₆ paraffin)

Hydrogen, zero gas, 99.95% minimum purity, total hydrocarbons less than 0.5 ppm as methane

Isopropylcyclohexane, 99.7% minimum purity, Wiley Organics, Cat. No. 8260.52 (C₉ naphthene)

Methylcyclohexane, 99.9% minimum purity, Wiley Organics, Cat. No. 4082.00 (C₇ naphthene)

Nitrogen, zero gas, 99.99% minimum purity, total hydrocarbons less than 0.5 ppm as methane

n-Nonane, 99.5% minimum purity, Wiley Organics, Cat. No. 6782.00 (C₉ paraffin)

n-Octane, 99.9% minimum purity, Wiley Organics, Cat. No. 7056.50 (C₈ paraffin)

n-Pentane, 99.9% minimum purity, Wiley Organics, Cat. No. 7372.40 (C₅ paraffin)

Toluene (methylbenzene), 99.0% minimum purity, Wiley Organics, Cat. No. 3829.90

1,2,4-Trimethylbenzene, 99.6% minimum purity, Wiley Organics, Cat. No. 8779.00 (C₉ aromatic)

o-Xylene (1,2-dimethylbenzene), 99.8% minimum purity, Wiley Organics, Cat. No. 1240.02 (C₈ aromatic)

PROCEDURE

Install the oxygen remover in the supply line between the carrier gas source and the carrier gas inlet on the gas chromatograph.

The operating conditions for the analysis are provided in the Instruction Manual received with the instrument.

Chromatographic Technique

Installation, set-up and training are provided by the instrument supplier or its representatives. Follow the chromatographic technique outlined in the manufacturer's Instruction Manual received with the instrument. **CAUTION: Hydrogen carrier gas leakage into the confined volume of the column oven can cause a violent explosion. It is, therefore, mandatory to test for leaks each time a connection is made and periodically thereafter.** An example of the type of chromatogram to expect is shown in the Figure. Identify each hydrocarbon type by comparison with the calibration blend, see *Calibration*. Separate incompletely resolved hydrocarbon types with a vertical line as shown. Due to column switching, a component, such as benzene, or group of components, such as C₈ aromatics, can elute at multiple retention times and hence the separate peaks or groups of peaks must be summed to obtain a total area for each component or group.

Calibration

Response factors are required to relate instrument response of the various components to mass-or LV-%. Prepare a blend as described in ASTM Method D 4307 containing the paraffin, naphthene and aromatic components at approximately the concentrations expected in the samples. Analyze the blend in duplicate using the chromatographic technique described in the manual and determine the average area for each component peak. Calculate the mass response factor for each component relative to *n*-heptane as follows:

$$F = \frac{AB}{CD}$$

where:

A = component in blend, mass-%

B = peak area of *n*-heptane

- C** = *n*-heptane in blend, mass-%
D = peak area of the blend component
F = relative response factor for component

Determine relative response factors as directed above for each instrument used. The factors shown in Table 1 are examples and will not be valid for all instruments. Use the response factor of C₆ paraffins for C₃ and C₄ paraffins. Use the response factor of C₁₀ paraffins for C₁₁ and C₁₂ paraffins and C₁₀ naphthenes for C₁₁ and C₁₂ naphthenes.

Table 1

Typical Mass Response Factors

C₅ Naphthene	1.02
C₅ Paraffin	1.02
C₆ Naphthene	1.00
C₆ Paraffin	1.03
C₇ Naphthene	0.98
C₇ Paraffin	1.00
C₈ Naphthene	0.99
C₈ Paraffin	0.98
C₉ Naphthene	0.98
C₉ Paraffin	0.99
C₁₀ Naphthene	0.98
C₁₀ Paraffin	0.99
Benzene	0.95
Toluene	0.95
C₈ Aromatics	0.96
C₉+ Aromatics	0.95

CALCULATIONS

Calculate the concentration of each paraffin, naphthene and aromatic by carbon number to the nearest 0.1 mass-%, using the following equation:

$$\text{Component, mass-\%} = \frac{100 \text{ EF}}{\text{S}}$$

where:

- E** = peak area of the sample component
F = relative response factor, previously defined
S = sum of the products EF of all the paraffin, naphthene and aromatic peaks
100 = factor to convert to mass-%

To calculate LV-%, the relative mass response factor is adjusted for difference in relative density for each hydrocarbon group as follows:

$$L = \frac{F}{M}$$

where:

L = liquid volume response factor for component

F = relative mass response factor for component, previously defined

M = average relative density for hydrocarbon group (see Table 2)

Table 2

<u>Hydrocarbon Group</u>	<u>Average Relative Density</u>
C₄ Paraffins	0.568
C₅ Naphthenes	0.745
C₅ Paraffins	0.625
C₆ Naphthenes	0.776
C₆ Paraffins	0.660
C₇ Naphthenes	0.763
C₇ Paraffins	0.684
C₈ Naphthenes	0.775
C₈ Paraffins	0.705
C₉ Naphthenes	0.775
C₉ Paraffins	0.715
C₁₀ Naphthenes	0.775
C₁₀ Paraffins	0.732
C₁₁ Naphthenes	0.790
C₁₁ Paraffins	0.740
C₆ Aromatics	0.879
C₇ Aromatics	0.867
C₈ Aromatics	0.868
C₉+ Aromatics	0.864

Calculate the LV-% concentration of each paraffin, naphthene and aromatic group by carbon number to the nearest 0.1 LV-% as follows:

$$\text{Component, LV-\%} = \frac{100 \text{ EL}}{P}$$

where:

E = peak area of the sample component

L = relative liquid volume response factor, previously defined

P = sum of the products EL of all peaks

100 = factor to convert to LV-%

NOTE

C₃ and C₄ Paraffins can be calculated but the determined concentrations may be in error due to the instability of these compounds in the sample. If samples are known to contain C₃ and C₄ paraffins and a reliable value is required, precautions must be taken in the handling of the sample to maintain its integrity.

PRECISION

Precision data were obtained using the Analytical Controls instrument equipped with an autosampler.

Repeatability

Based on two tests performed by each of two analysts on each of two different days (8 tests), the within-laboratory estimated standard deviations (esd) were calculated for components at specific concentrations and are listed in Table 3. Two tests performed in one laboratory by different analysts on different days should not differ by more than the allowable differences in Table 3 at the concentrations listed (95% probability).

Reproducibility

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

Table 3

Component	Concentration, mass-%	Repeatability	
		Within-Lab esd, mass-%	Allowable Difference, mass-%
C ₅ Paraffin	0.3	0.01	0.1
C ₆ Paraffin	11.4	0.03	0.1
C ₇ Naphthene	10.2	0.01	0.1
C ₇ Paraffin	5.9	0.01	0.1
C ₈ Naphthene	8.6	0.01	0.1
C ₈ Paraffin	9.4	0.01	0.1
C ₉ Naphthene	6.8	0.01	0.1
C ₉ Paraffin	7.5	0.01	0.1
C ₁₀ Paraffin	6.2	0.01	0.1
Benzene	1.8	0.01	0.1
Benzene	12.3	0.02	0.1
Toluene	23.7	0.05	0.2
C ₈ Aromatics	25.2	0.04	0.2
C ₉ Aromatics	19.7	0.04	0.2

TIME FOR ANALYSIS

The elapsed time for one analysis is 2.2 hours. The labor requirement is 0.6 hour.

REFERENCES

ASTM Method D 4307, www.astm.org
Instruction Manual, Analytical Controls

SUGGESTED SUPPLIERS

Alltech Associates, Inc., 2051 Waukegan Rd., Deerfield, IL 60015
Analytical Controls, Inc., 3448 Progress Dr., Bensalem, PA 19020
Hewlett-Packard, 1200 E. Diehl Road, Naperville, IL 60540
Matheson, P.O. Box 96, Joliet, IL 60434
Wiley Organics, 1245 S. Sixth St., Coshocton, OH 43812

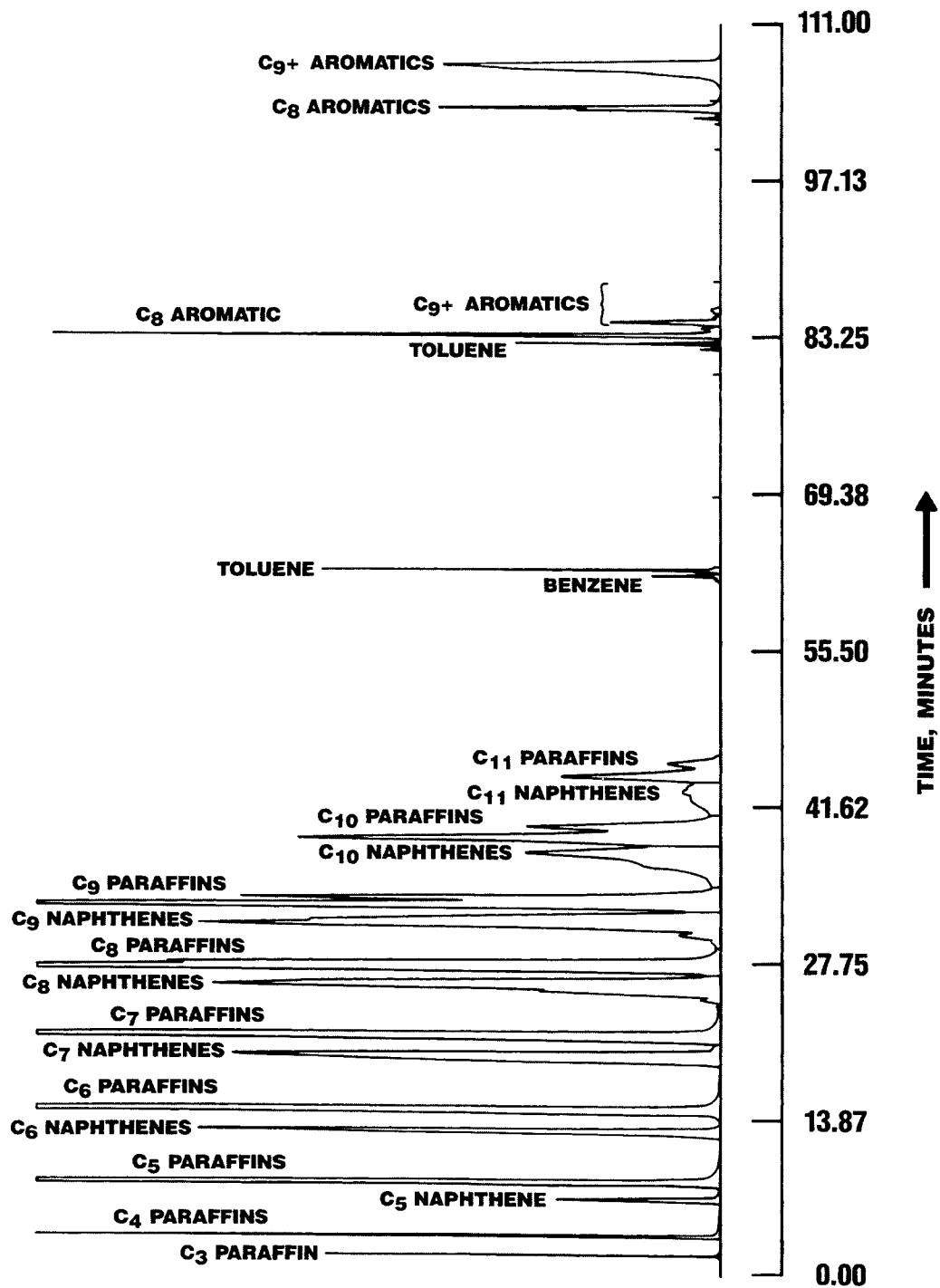


Figure
Typical Chromatogram