

HYDROCARBON TYPES IN PETROLEUM FRACTIONS BY CHROMATOGRAPHY

UOP Method 777-77

SCOPE

This method describes a procedure for determining paraffin, olefin, naphthene and aromatic hydrocarbon types in stabilized gasolines or fractions therefrom. The endpoint of these stocks (ASTM D 86) should not exceed 196 C (385 F), *see NOTE 1*. Paraffins and naphthenes are determined by carbon number with cyclopentane, methylcyclopentane and cyclohexane determined individually. C₆ minus hydrocarbons can be reported either individually or by carbon number. Aromatics are determined by carbon number through C₈ with the C₉+ determined as a composite. Olefins are reported undistributed.

Determination of C₈ aromatic isomer distribution and/or C₇ and C₈ saturate isomers is optional, and may be determined if desired.

OUTLINE OF METHOD

A stabilized sample is subjected to gas chromatographic analyses to determine the aromatic content and the C₅ minus content of a high olefinic sample, or the C₆ minus content of a low olefinic sample. The sample is analyzed by Fluorescent Indicator Adsorption (FIA) to determine the total olefin content. A breakdown of the saturates to determine the percentages of paraffins and naphthenes by carbon number is accomplished by processing the sample through silica gel to obtain a saturates fraction and analyzing this portion by gas chromatography. Densities of the sample and of the various fractions are determined as necessary for calculations. A more detailed breakdown of the C₈ aromatic isomers and/or the C₇ and C₈ saturate isomers can be obtained by additional gas chromatographic analyses, when required.

APPARATUS

The apparatus required is described in the following methods:

Pentane and Lower Boiling Hydrocarbons in Olefinic Gasoline by Gas Chromatography — UOP Method 725

Individual Saturated Hydrocarbons Through C₈ in Petroleum Distillates by Gas Chromatography — UOP Method 690

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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Aromatics in Hydrocarbons by Gas Chromatography — UOP Method 394

Hydrocarbon Types by Fluorescent Indicator Adsorption (FIA) — UOP Method 311

Isolation of Representative Saturates Fraction from Low-Olefinic Petroleum Naphthas — ASTM D 2002

Isolation of Representative Saturates Fraction from High-Olefinic Petroleum Naphthas — ASTM D 2003

Paraffin and Naphthene Distribution by Carbon Number of Saturated Petroleum Distillates by Gas Chromatography — UOP Method 741

Density and Specific Gravity of Liquids by Lipkin Bicapillary Pycnometer — ASTM D 941

C₈ Aromatic Isomer Distribution by Gas Chromatography — UOP Method 581

REAGENTS AND MATERIALS

These are indicated in each of the methods listed in the preceding section.

PROCEDURE

Low Olefin Samples

Obtain the density of the sample by ASTM D 941.

Determine the C₆ minus saturate composition of the sample by UOP Method 690. This analysis determines the cyclopentane, methylcyclopentane and cyclohexane as well as other low boiling components that may be lost in subsequent handling. Determine the C₆, C₇, C₈ and C₉+ aromatics content by UOP Method 394 (*see NOTE 2*).

Determine the total olefin content by UOP Method 311. Obtain a saturates portion of the sample by ASTM D 2002, Method B. This method states that samples containing more than about 15% aromatics will require, for adequate separation, a high capacity column which is described in ASTM D 936. Alternatively, ASTM D 2003, which also utilizes a high capacity column, can be used for separating this type of sample. Care should be exercised to obtain a good separation and to recover the maximum quantity of olefin- and aromatic-free saturates.

Obtain the density of the saturates portion by ASTM D 941, if results are to be calculated in weight percent. Analyze the saturates by UOP Method 741 to obtain the paraffin-naphthene distribution by carbon number (*see NOTE 3*). Report results in either liquid volume- or weight-percent, as required, *see CALCULATIONS*.

High Olefin Samples

Obtain the density of the sample by ASTM D 941.

Determine the C₅ minus composition of the sample by UOP Method 725. Determine the C₆, C₇, C₈ and C₉+ aromatic content by UOP Method 394.

Determine the total olefin content by UOP Method 311. Obtain a saturates portion by ASTM D 2003. If results are to be calculated in weight percent, also obtain the olefin portion and determine a density on it by ASTM D 941.

Obtain the density of the saturates portion by ASTM D 941, and analyze the saturates for C₆ minus content by UOP Method 690 to determine the cyclopentane, methylcyclopentane, cyclohexane and C₆ paraffins. Analyze the saturates portion by UOP Method 741 to obtain the paraffin-naphthene distribution by carbon number.

CALCULATIONS

Low Olefin Samples

Compositions can be calculated in either liquid volume- or weight-percent.

Liquid Volume-Percent [LV-%]

Convert the C₆ minus saturate compounds from weight to LV-% as follows:

$$\text{Component, LV - \%} = \frac{AB}{C}$$

where:

A = component (from UOP Method 690), wt-%

B = density of sample

C = density of component

Report the cyclic compounds individually and the paraffins either individually or by carbon number as desired.

The aromatics from UOP Method 394 and the total olefins from UOP Method 311 are determined in LV-% and, therefore, require no conversion. The paraffin-naphthene distribution by carbon number, obtained on the saturate portion (UOP Method 741) should be reported in LV-%. Obtain the LV-% of the C₇+ saturates in the original sample as follows:

$$C_7 + \text{ saturates, LV - \%} = 100 - (S + E + O)$$

where:

S = sum of C₆ minus saturates (from UOP Method 690), LV-%

E = sum of aromatics (from UOP Method 394), LV-%

O = total olefins (from UOP Method 311), LV-%

Normalize the distributed C₇+ paraffins and naphthenes to this percentage.

Weight-Percent [wt-%]

The C₆ minus saturate compounds are determined in wt-% and require no conversion.

Convert the aromatics obtained by UOP Method 394 from LV- to wt-% as follows:

$$\text{Aromatics, wt - \%} = \frac{DH}{I}$$

where:

D = component, LV-%
H = density of component
I = density of sample

Convert the total olefins obtained by UOP Method 311 from LV- to wt-% as follows:

$$\text{Olefins, wt - \%} = \frac{FG}{J}$$

where:

F = olefins, LV-%
G = density of saturates
J = density of the sample

The density of the olefins is difficult to obtain because the olefins are present in low concentrations and, therefore, are too low to readily separate. In this calculation, the density of the saturates is used. Small differences in density between the saturates and olefins will not make a significant difference in the conversion.

The paraffin-naphthene distribution by carbon number, obtained on the saturate portion (UOP Method 741), should be reported in wt-%. Obtain the wt-% C₇+ saturates in the original sample as follows:

$$\text{C}_7 + \text{saturates, wt - \%} = 100 - (J + K + L)$$

where:

J = sum of C₆ minus saturates (from UOP Method 690), wt-%
K = sum of aromatics (from UOP Method 394), wt-%
L = total olefins (from UOP Method 311), wt-%

Normalize the distributed C₇+ paraffins and naphthenes to this percentage.

High Olefin Samples

Liquid Volume-Percent

Convert the C₅ minus paraffin compounds from wt- to LV-% as follows:

$$\text{Component, LV - \%} = \frac{AB}{C}$$

where:

A = component (from UOP Method 725), wt-%

B = density of sample

C = density of component

Olefins (although determined) are not reported individually and require no conversion since total olefins are reported from UOP Method 311. Cyclopentane is not determined by UOP Method 725, but is later determined on the saturates portion by UOP Method 690.

The aromatics from UOP Method 394 and the total olefins from UOP Method 311 are determined in LV-% and, therefore, require no conversion.

Obtain the LV-% of the total C₅+ naphthenes and C₆+ paraffins in the original sample as follows:

$$\text{Saturates, LV - \%} = 100 - (\text{R} + \text{E} + \text{O})$$

where:

R = sum of C₅ minus paraffins (from UOP Method 725), LV-%

E = sum of aromatics (from UOP Method 394), LV-%

O = total olefins (from UOP Method 311), LV-%

Convert the cyclopentane and C₆ components determined from the C₆ minus analysis (UOP Method 690) of the saturates portion to LV-% of the original sample as follows:

$$\text{Component, LV - \%} = \frac{\text{MNP}}{\text{C } 100}$$

where:

M = component, wt-%

N = density of the saturates portion

P = total C₅+ naphthenes and C₆+ paraffins as calculated above, LV-%

C = density of component

The C₅-C₆ cyclic compounds are reported individually and the C₆ paraffins may be reported individually or as a total.

The paraffin-naphthene distribution by carbon number (UOP Method 741) should be reported in LV-%. Calculate the LV-% of C₇+ saturates in the sample as follows:

$$\text{C}_7 + \text{saturates, LV - \%} = \text{P} - \text{Q}$$

where:

P = is as previously defined

Q = sum of cyclopentane and C₆ saturates, LV-%

Normalize the distributed C₇+ paraffins and naphthenes to this percentage.

Weight-Percent

The C₅ minus paraffin compounds are determined by UOP Method 725 in wt-% and no conversion is required.

Convert the aromatics obtained by UOP Method 394 from LV-% to wt-% as follows:

$$\text{Aromatics, wt - \%} = \frac{TU}{B}$$

where:

T = compound, LV-%
U = density of component
B = density of sample

Convert the total olefins obtained by UOP Method 311 from LV-% to wt-% as follows:

$$\text{Olefins, wt - \%} = \frac{VW}{B}$$

where:

V = olefins, LV-%
W = density of olefins
B = density of the sample

Obtain the wt-% C₅+ naphthenes and C₆+ paraffins in the original sample as follows:

$$\text{Saturates, wt - \%} = 100 - (R + K + L)$$

where:

R = sum of C₅ minus paraffins (from UOP Method 725), wt-%
K = sum of aromatics (from UOP Method 394), wt-%
L = total olefins (from UOP Method 311), wt-%

Cyclopentane and the C₆ components are determined in wt-% from the C₆ minus analysis (UOP Method 690) of the saturate portion. Calculate the wt-% of these components in the original sample as follows:

$$\text{Component, wt - \%} = \frac{XY}{100}$$

where:

X = component, wt-% in saturates portion
Y = total C₅+ naphthenes and C₆+ paraffins as calculated above, wt-%

The paraffin-naphthene distribution by carbon number (UOP Method 741) should be reported in wt-%. Calculate the wt-% of C₇+ saturates in the sample as follows:

$$C_7 + \text{saturates, wt - \%} = Y - Z$$

where:

Y = is as previously defined

Z = sum of cyclopentane C_6 and saturates, wt-%

Normalize the distributed C_7+ paraffins and naphthenes to this percentage.

NOTES

1. The method can be extended to stocks with endpoints of 216 C (421 F) but the ratio of C_{12} paraffins to naphthenes may be difficult to obtain.
2. A distribution of the C_8 aromatic isomers can be obtained through the use of UOP Method 581. The concentrations of the isomers are normalized to the C_8 aromatic percentage determined by UOP Method 394.
3. A distribution of the C_7 and C_8 saturate isomers can be obtained on the saturate portion of the sample through the use of UOP Method 690. The concentrations of the isomers are normalized to the total of the C_7 and C_8 saturate percentages as determined by UOP Method 741.

PRECISION

Based on seven replicate determinations of a high and low naphthene sample, the estimated standard deviations (esd) in the following table were calculated for the components listed.

Duplicate results should not differ by more than the allowable differences indicated (95% probability).

<u>Component</u>	<u>Concentration, wt-%</u>	<u>esd, wt-%</u>	<u>Allowable Diff., wt-%</u>
Low Naphthene Sample			
Benzene	2.5	0.02	0.06
Toluene	9.5	0.03	0.09
C_8 Aromatics	18.3	0.07	0.23
C_9+ Aromatics	37.0	0.18	0.64
Olefins	0.3	(a)	(a)
C_4 Paraffins	0.9	0.03	0.09
C_5 Paraffins	2.9	0.04	0.13
C_6 Paraffins	7.0	0.09	0.32
C_7 Paraffins	9.6	0.10	0.33
C_8 Paraffins	7.0	0.07	0.26
C_9 Paraffins	3.0	0.06	0.19
C_{10} Paraffins	0.9	0.05	0.18
C_{11} Paraffins	0.2	0.02	0.08
Total Paraffins	31.5	0.28	0.97
Cyclopentane	0.1	0.004	0.01
Methylcyclopentane	0.2	0.02	0.07

Component	Concentration, wt-%	esd, wt-%	Allowable Diff., wt-%
Cyclohexane	<0.05	(a)	(a)
C₇ Naphthenes	0.1	(a)	(a)
C₈ Naphthenes	0.2	(a)	(a)
C₉ Naphthenes	0.1	(a)	(a)
C₁₀ Naphthenes	0.1	(a)	(a)
C₁₁ Naphthenes	<0.05	(a)	(a)
Total Naphthenes	0.9	0.02	0.06

(a) Concentration is too low to reliably calculate esd or allowable difference.

High Naphthene Sample			
Benzene	0.3	0.01	0.03
Toluene	1.7	0.01	0.02
C₈ Aromatics	5.0	0.02	0.06
C₉+ Aromatics	12.1	0.06	0.22
Olefins	---		
C₅ Paraffins	0.1	0.01	0.04
C₆ Paraffins	4.4	0.04	0.14
C₇ Paraffins	9.4	0.07	0.25
C₈ Paraffins	12.5	0.11	0.36
C₉ Paraffins	14.6	0.09	0.31
C₁₀ Paraffins	13.8	0.12	0.42
C₁₁ Paraffins	8.4	0.06	0.21
Total Paraffins	63.2	0.14	0.50
Cyclopentane	0.1	0.004	0.01
Methylcyclopentane	0.6	0.01	0.02
Cyclohexane	0.7	0.01	0.04
C₇ Naphthenes	3.2	0.05	0.17
C₈ Naphthenes	3.8	0.05	0.15
C₉ Naphthenes	3.8	0.06	0.21
C₁₀ Naphthenes	3.6	0.14	0.49
C₁₁ Naphthenes	1.9	0.07	0.25
Total Naphthenes	17.7	0.11	0.39

TIME FOR ANALYSIS**Low Olefin Sample**

	Elapsed Time	Man- Hours
Density of sample (ASTM D 941)	0.50	0.30
C ₆ minus saturates analyses (UOP Method 690)	0.75	0.50
Aromatics analysis (UOP Method 394)	0.50	0.50
FIA Analysis (UOP Method 311)	2.00	0.80
Saturates separation		
a) Low aromatics (ASTM D 2002)	2.50	1.00
b) High aromatics (ASTM D 2002)	3.00	1.00
Density of saturates (ASTM D 941)	0.50	0.30
Saturates distribution by carbon number (UOP Method 741)	1.15	0.50
Calculations	0.25	0.25

High Olefin Samples

Density of sample (ASTM D 941)	0.50	0.30
C ₅ minus saturates analysis (UOP Method 725)	0.70	0.70
Aromatic analysis (UOP Method 394)	0.50	0.50
FIA analysis (UOP Method 311)	2.00	0.80
Saturates separation (ASTM D 2003)	4.00	2.00
Density of saturates (ASTM D 941)	0.50	0.30
Density of olefins (ASTM D 941)	0.50	0.30
C ₆ minus saturates analysis (UOP Method 690)	0.75	0.50
Saturate distribution by carbon number (UOP Method 741)	1.15	0.50
Calculations	0.25	0.25

Additional Optional Analyses As Shown in *NOTES*

C ₈ aromatic isomer distribution (UOP Method 581)	0.66	0.66
C ₇ and C ₈ saturate isomer distribution (UOP Method 690)	2.60	0.90