



A Honeywell Company

C₆ and Lower Boiling Hydrocarbons in Olefin Free Naphthas by GC

UOP Method 551-08

Scope

This method is for determining benzene, individual hexanes and lower boiling hydrocarbons in olefin free naphthas having a final boiling point of 260°C or lower. Results may be reported in mass-% or liquid volume (LV-%). The lower limit of detection for any single component is 0.01 mass-%.

C₇ and heavier hydrocarbons are measured for calculation purposes, but are not reported by this method. For analysis of C₇ and heavier hydrocarbons in addition to the C₆ and lighter hydrocarbons, see ASTM Method D6729, "Determination of Individual Components in Spark Ignition Engine Fuels by 100 Metre Capillary High Resolution Gas Chromatography," UOP Method 690, "Octanes and Lower Boiling Hydrocarbons in Olefin Free Gasolines by GC," or UOP Method 880, "Hydrocarbon Types and Distributions in Low Olefin C₁₂ and Lower Endpoint Distillates by GC."

References

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

ASTM Method D4307, "Preparation of Liquid Blends for Use as Analytical Standards," www.astm.org

ASTM Method D6729, "Determination of Individual Components in Spark Ignition Engine Fuels by 100 Metre Capillary High Resolution Gas Chromatography," www.astm.org

Scanlon, J. T. and Willis, D. E., *Journal of Chromatographic Science*, **23**, 333-340 (1985)

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

UOP Method 880, "Hydrocarbon Types and Distributions in Low Olefin C₁₂ and Lower Endpoint Distillates by GC," www.astm.org

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

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).

© COPYRIGHT 1966, 1986, 2008 UOP LLC. All rights reserved.

Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, USA. The UOP 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.

Outline of Method

The sample to be analyzed is injected into a gas chromatograph that is equipped with a fused silica capillary column. The mass-% composition of the sample is obtained by the internal normalization technique of quantitation wherein the peak areas of the entire sample are first corrected for differences in response and then normalized to 100%. An additional calculation converts the results to LV-%.

Apparatus

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

Balance, readability 0.1-mg

Chromatographic column, 50 m of 0.21-mm ID fused silica capillary, internally coated to a film thickness of 0.50 μm with cross-linked methyl silicone, Agilent Technologies, Cat. No. 19091S-001, or equivalent

Data system, electronic, for obtaining peak areas. This device must integrate areas at a sufficiently fast rate so that narrow peaks typically resulting from use of a capillary column can be accurately measured. ChemStation, Agilent Technologies.

Gas chromatograph, temperature programmable, built for capillary column chromatography, utilizing a split injection system having a glass injection port insert and equipped with an FID that will give a minimum peak height response of five times the background noise for 0.01 mass-% *n*-hexane when operated under the recommended conditions, Agilent Technologies, Model 7890

Regulator, air, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-590

Regulator, hydrogen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-350

Regulator, nitrogen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-580

Sample injector, syringe or injector capable of introducing a 0.5- μL volume of sample. An autosampler (or autoinjector) is recommended, Agilent Technologies, Model 7683.

Reagents and Materials

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

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

Benzene, 99.5% minimum purity, VWR, Cat. No. AA39196-K2

Ethylbenzene, 99.0% minimum purity, VWR, Cat. No. AAA14542-AP

Gas purifier, to remove oxygen from the hydrogen carrier gas, VICI Mat/Sen, Cat. No. P-200-1

n-Hexane, 99.5% minimum purity, Aldrich, Cat. No. BJ216-1

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

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

Toluene, 99% minimum purity, VWR, Cat. No. AA22903-K2

m-Xylene, 99.0% minimum purity, VWR, Cat. No. AA16370-A1

o-Xylene, 98.0% minimum purity, VWR, Cat. No. EM-XX0020-5

p-Xylene, 99.0% minimum purity, VWR, Cat. No. AA31813-A1

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of gas chromatography, and the equipment being used.

Chromatographic Technique

1. Install the gas purifier in the supply line between the carrier gas source and the carrier gas inlets on the gas chromatograph.
 - Column life is significantly reduced if the gas purifier is not used.
2. Install the fused silica capillary column in the gas chromatograph, according to the column and gas chromatograph manufacturer's instructions.
 - CAUTION: Hydrogen leakage into the confined volume of the column oven can cause a violent explosion. Therefore, it is mandatory to check for leaks each time a connection is made and periodically thereafter.
3. Establish the recommended operating conditions as given in Table 1.

Table 1
Recommended Operating Conditions

Carrier gas	hydrogen
Mode	constant pressure
Head Pressure	140 kPa (20 psig)
Linear Velocity @ 32°C	31 cm/sec
Equivalent flow @ 32°C	1.1 mL/min
Split Flow	220 mL/min
Injection port temperature	225°C
Column temperature program	
Initial temperature	32°C
Initial time	6 min
Programming rate 1	5°C/min
Intermediate temperature	52°C
Intermediate time	14 min
Programming rate 2	20°C/min
Final temperature	250°C
Final time	9 minutes
Detector	flame ionization
Detector temperature	260°C
Hydrogen flow rate*	30 mL/min
Air flow rate*	400 mL/min
Makeup gas	nitrogen
Makeup flow rate*	30 mL/min
Sample size	0.5 µL

- Consult the manufacturer's instrument manual for suggested flow rates.

- Different conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatograms (Figures 1 and 2).
4. Program the column oven to 260°C and maintain this temperature until a stable baseline has been obtained at the required sensitivity.
 5. Cool the column oven to a stabilized 32°C.
 6. Inject nominally 0.5 µL of sample into the gas chromatograph and start the integrator and the column oven programming sequence.
 - When using an autosampler or autoinjector, the injection sequence of a GC is typically automated, performing the injection, and starting the data system and column temperature program simultaneously.
 7. Identify the components in the resultant chromatogram and determine the areas of the peaks.
 - A typical chromatogram is shown in Figures 1 and 2. The C₃-C₆ Region shown in Figure 1 and expanded in Figure 2 may contain low boiling C₇ components.
 - *m*-Xylene and *p*-xylene may elute together under these conditions.
 8. If the results are to be reported in LV-%, determine the relative density of the sample at 15.6°C by ASTM Method D 4052 or other suitable technique.

Calibration

This analysis uses internal normalization (total corrected area normalization) of the entire sample to quantitate the C₆ minus components. In order to accurately measure the entire sample, certain components beyond the C₆ range must be identified and calibrated. This is necessary because C₆ through C₈ aromatic components that may be present in the sample do not have the same detector response as the non-aromatic components. The non-aromatic components all have essentially the same detector response.

1. Prepare a calibration blend as described in ASTM Method D 4307 to contain approximately equal quantities of *n*-hexane, benzene, toluene, ethylbenzene, *m*-xylene, and *o*-xylene. Weigh the appropriate quantities of each component to the nearest 0.1 mg.
2. Analyze the blend as described under *Chromatographic Technique*.

Based on 3 replicate runs of the blend, determine the average relative response factor for each component using *n*-hexane as reference and the following formula:

$$F = \frac{AB}{CD} \quad (1)$$

where:

- A** = component of interest, mass-%
- B** = area of *n*-hexane peak
- C** = *n*-hexane, mass-%
- D** = area of component of interest
- F** = relative response factor

Determine relative response factors as directed above for each instrument used. Calculated relative response factors should be similar to the theoretical relative response factors shown in Table 2. The theoretical relative response factors were calculated using the effective carbon number (ECN) concept as described by Scanlon and Willis. If the determined relative response factors differ by more than 10% from those shown in Table 2, check the apparatus, operating conditions, and blend preparation procedures.

Table 2
Theoretical Relative Response Factors, mass-%

<i>n</i> -Hexane	1.000
Benzene	0.906
Toluene	0.917
Ethylbenzene, <i>m</i> -, <i>p</i> -, <i>o</i> -Xylene	0.924

For all components in the sample, other than the aromatic components listed in Table 2, use the relative response factor for *n*-hexane.

Calculations

Obtain peak areas for each individual component or group of components and calculate the concentration of each C6 and lighter component in the sample to the nearest 0.01 mass-% using the following formula:

$$\text{Component, mass-\%} = 100 \frac{PF}{T} \quad (2)$$

where:

- F** = relative response factor, previously defined
- P** = area of individual component
- T** = sum of the products, PF, of all recorded peaks
- 100** = factor to convert to mass-%

For LV-% results, convert the mass-% results previously obtained using the following formula:

$$\text{Component, LV-\%} = \frac{MS}{R} \quad (3)$$

where:

- M** = mass-% of component of interest
- S** = relative density of sample at 15.6°C
- R** = relative density of component of interest, see Table 3

Table 3
Relative Density at 15.6°C

Propane	0.5077
Isobutane	0.5631
<i>n</i> -Butane	0.5844
Isopentane	0.6248
<i>n</i> -Pentane	0.6312
2,2-Dimethylbutane	0.6540
Cyclopentane	0.7505
2,3-Dimethylbutane	0.6664
2-Methylpentane	0.6579
3-Methylpentane	0.6690
<i>n</i> -Hexane	0.6641
Methylcyclopentane	0.7535
Benzene	0.8846
Cyclohexane	0.7834

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods," from precision data obtained using an autosampler.

Repeatability and Site Precision

One sample was analyzed on 20 separate days, performing three analyses each day for a total of 60 analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table 4. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 4 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 4 with 95% confidence.

Table 4
Repeatability and Site Precision, mass-%

<u>Component</u>	<u>Mean</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>
Cyclopentane	0.39	0.009	0.03	0.010	0.03
n-Hexane	5.99	0.027	0.08	0.045	0.13

The data in Table 4 represent short-term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

Reproducibility

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

Time for Analysis

The elapsed time for one analysis is 1.0 hour. The labor requirement is 0.4 hour.

Suggested Suppliers

Agilent Technologies, 2850 Centerville Rd., Wilmington, DE 19808-1610 (302-633-8000)
www.agilent.com

Aldrich, 1000 West Saint Paul Avenue, Milwaukee, WI 53233 (414-273-3850) www.sigma-aldrich.com

Matheson Gas Products Inc., 166 Keystone Drive, Montgomeryville, PA 18936 (215-641-2700)
www.mathesontrigas.com

Supelco, 595 North Harrison Road, Bellefonte, PA 16823 (814-359-3441) www.sigma-aldrich.com

VICI Mat/Sen, 7806 Bobbitt, Houston, TX 77055 (713-688-9345) www.vicimatsen.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380 (610-431-1700) www.vwr.com

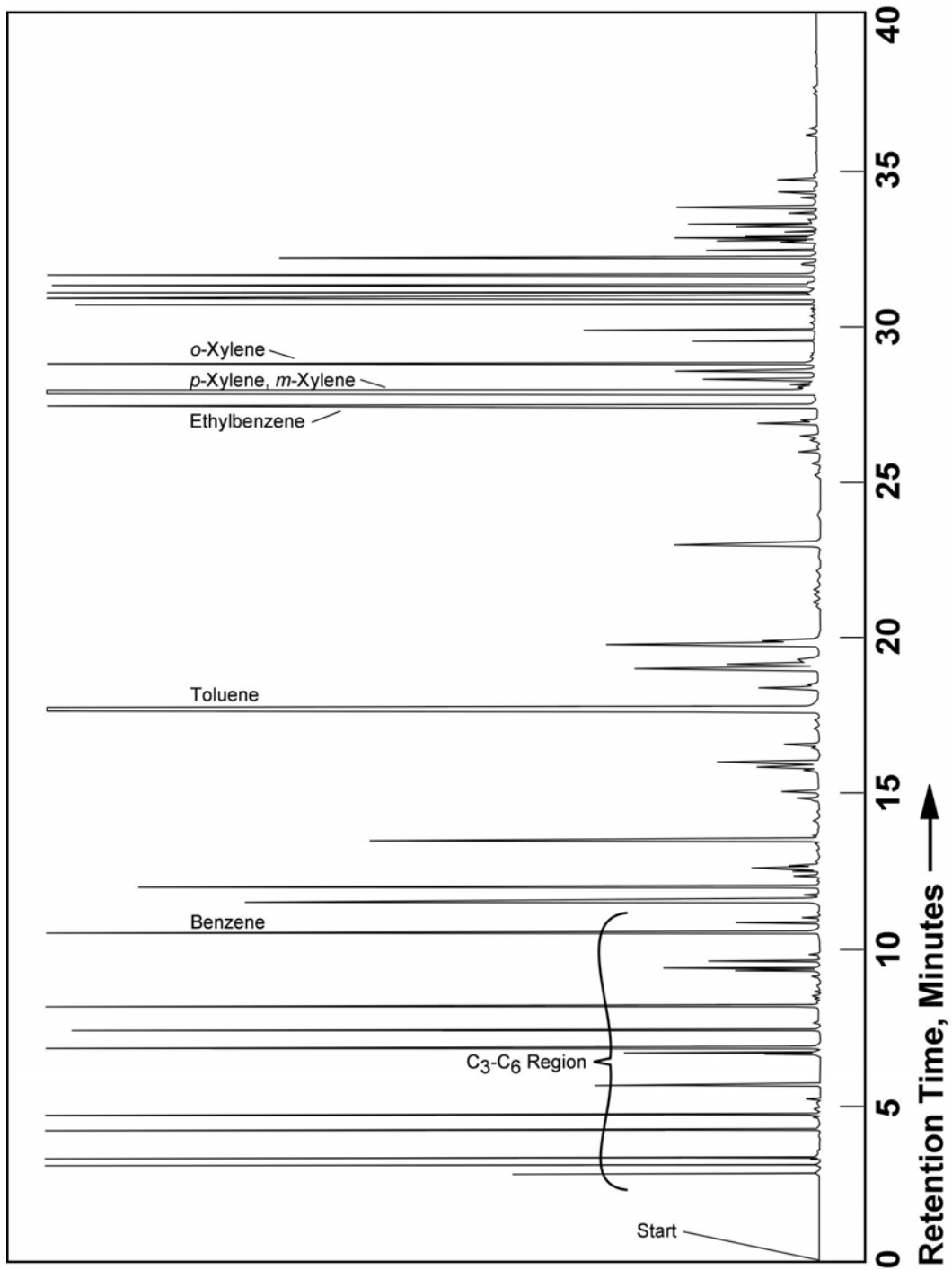


Figure 1
Typical Chromatogram

UOP Method 551

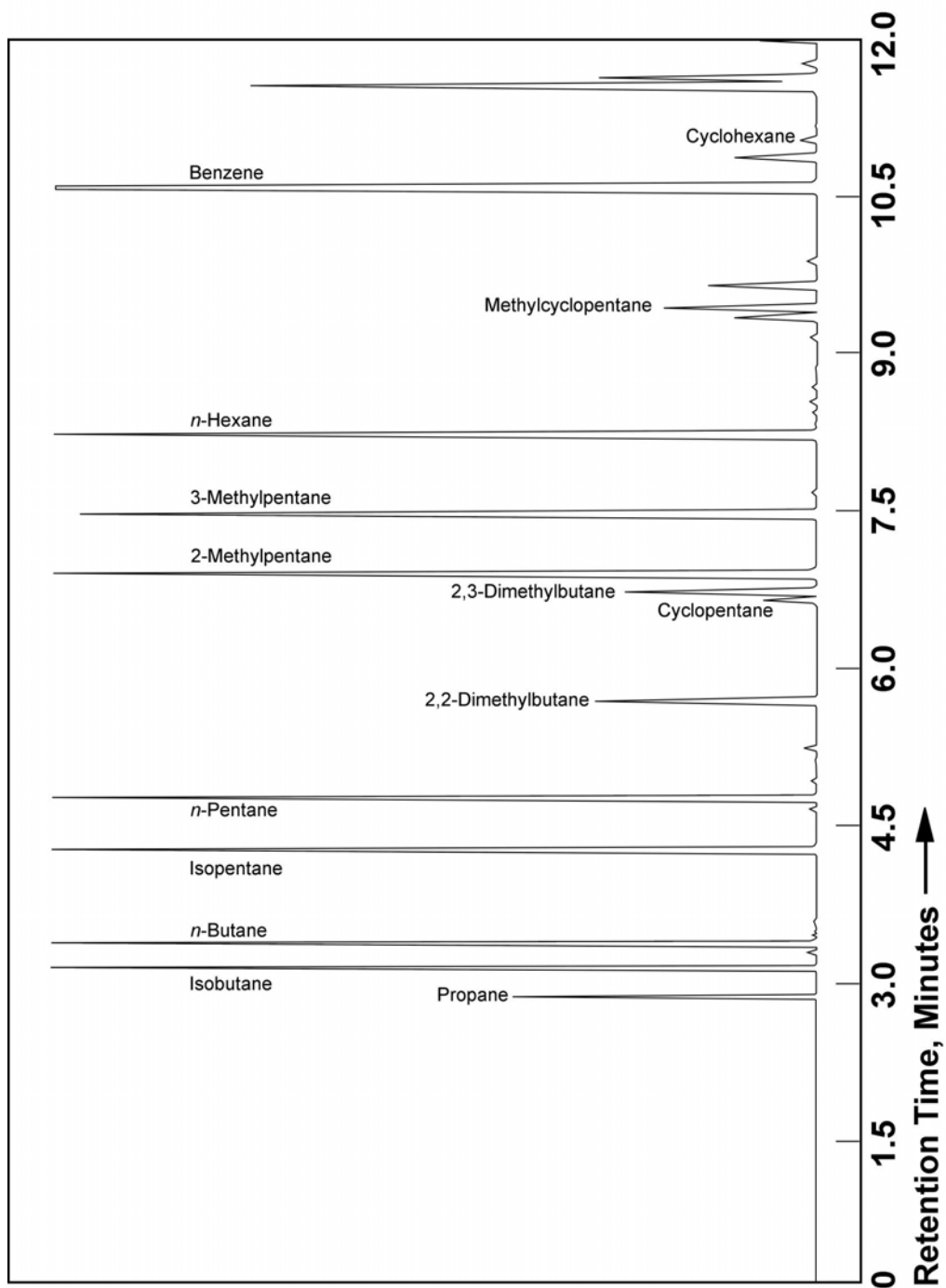


Figure 2
Typical Chromatogram
Expansion of C₃ - C₆ Region (See Fig. 1)

UOP Method 551