

PENTENES AND LOWER BOILING HYDROCARBONS IN OLEFINIC GASOLINES BY GC

UOP Method 725-86

SCOPE

This method is for determining C₅ and lighter paraffins and monoolefins in olefinic gasolines having a final boiling point of 260 C or lower. The lower limit of detection for any single component is 0.05 mass-%.

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 are first corrected for differences in response and then normalized to 100%.

APPARATUS

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, Hewlett Packard Analytical Supplies, Cat. No. 19091S-001, or equivalent

Gas chromatograph, multi-ramp temperature programmable and capable of isothermal operation at 32 C, built for capillary column chromatography, utilizing a split injection system, and equipped with a flame ionization detector that will give a minimum peak height response of 30 μV for 0.1 mass-% *n*-pentane when operated at the stated conditions. Background noise at these conditions is not to exceed 3 μV .

Integrator, electronic or equivalent, for obtaining peak areas. This device must integrate areas at a sufficiently fast rate so that narrow peaks typically resulting from a capillary column can be accurately measured.

Recorder, 1-mV full scale, 1-sec or less full-scale response

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.

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

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

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

Sample injector, any syringe or injector capable of injecting a 0.5- μ L volume of sample, such as a Hamilton 701-NWG syringe, Alltech Associates, or equivalent

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 water mean deionized or distilled water.

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

Benzene, 99.9% minimum purity, Aldrich Chemical, Cat. No. 27, 070-0, or equivalent

Ethylbenzene, 99% minimum purity, Aldrich Chemical, Cat. No. El, 250-8, or equivalent

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)

n-Pentane, 99% minimum purity, Aldrich Chemical, Cat. No. 27,041-5, or equivalent

Toluene, 99% minimum purity, Aldrich Chemical, Cat. No. 24,451-1, or equivalent

m-Xylene, 99% minimum purity, Aldrich Chemical, Cat. No. 18,556-6, or equivalent

o-Xylene, 97% minimum purity, Aldrich Chemical, Cat. No. X104-0, or equivalent

p-Xylene, 99% minimum purity, Aldrich Chemical, Cat. No. 13,444-9, or equivalent

PROCEDURE

Operating Conditions

The operating conditions for this analysis are given in Table 1.

Table 1

Carrier gas	hydrogen
Carrier gas velocity	58 cm/sec (1.1 mL/min flow rate)
Detector	flame ionization
Detector temperature	250 C
Injection port temperature	225 C
Hydrogen flow rate*	30 mL/min
Air flow rate*	400 mL/min
Makeup gas	nitrogen
Makeup flow rate*	30 mL/min

Split ratio	200:1
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	230 C
Final time	9 min
Chart speed	1 cm/min
Sample size	0.5 μL

***Consult the manufacture's instrument manual for suggested flow rates.**

Chromatographic Technique

Install the fused silica capillary column in the gas chromatograph and establish the specified operating conditions. **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. Recheck the carrier gas flow and then program the column oven to 230 C. Maintain this temperature until a stable baseline has been obtained at the required sensitivity. Cool the column oven to 32 C. Inject 0.5 μ L of sample and immediately start the recorder, integrator and column temperature programming sequence.

Identify the components from the resultant chromatogram. A typical chromatogram is shown in the attached Figures. If necessary, confirm the sites of the aromatic components by comparison with the calibration blend (see *Calibration*).

Calibration

This analysis uses internal normalization of the entire sample to quantitate the C₅ components. In order to accurately measure the entire sample, certain components beyond the C₅ 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.

Prepare a calibration blend as described in ASTM Method D 4307 to contain approximately equal quantities of *n*-pentane, ethylbenzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene. Weigh the appropriate quantities of each component to the nearest 0.1 mg. Chromatograph the blend as described under *Chromatographic Technique*. *m*-Xylene and *p*-xylene may co-elute under these conditions. Based on 3 replicate runs, determine the average relative response factor for each component using *n*-pentane as the reference using the following formula:

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

where:

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

Determine relative response factors as directed above for each instrument used. The factors shown in Table 2 are examples and will not be valid for all instruments.

Table 2

Relative Response Factors

<i>n</i>-Pentane	1.000
Benzene	0.917
Toluene	0.960
Ethylbenzene	0.973
<i>o</i>-Xylene	0.990
<i>m, p</i>-Xylene	0.973

All paraffins and monoolefins have the same relative response factor as *n*-pentane.

CALCULATIONS

Obtain peak areas for each individual component or group of components and calculate the concentration of each C₅ and lighter component in the sample to the nearest 0.1 mass-% using the following formula:

$$\text{Component, mass-\%} = 100 \frac{\text{PF}}{\text{T}}$$

where:

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

PRECISION

Based on 6 replicate determinations, the estimated standard deviation (esd) for components at their given concentrations are listed in Table 3. Duplicate results by the same operator should not differ by more than the allowable difference indicated (95% probability).

Table 3
Precision Data

Component	Concentration, mass-%	esd, mass-%	Allowable Difference, mass-%
Isobutane	1.0	0.063	0.23
<i>n</i>-Butane	0.5	0.024	0.09
Isopentane	12.8	0.206	0.75
<i>n</i>-Pentane	5.0	0.079	0.29
2-Methyl-2-butene	1.9	0.030	0.11

TIME FOR ANALYSIS

The elapsed time for one analysis is 0.75 hour. The labor requirement is 0.38 hour.

REFERENCE

ASTM Method D 4307, www.astm.org

SUGGESTED SUPPLIERS

Aldrich Chemical Co., 940 W. Saint Paul Ave., Milwaukee, WI 53233

Alltech Associates, 2051 Waukegan Rd., Deerfield, IL 60015

Hewlett-Packard Analytical Supplies, 333 Logue Ave., Mountain View, CA 94043

Matheson, P.O. Box 96, Joliet, IL 60434

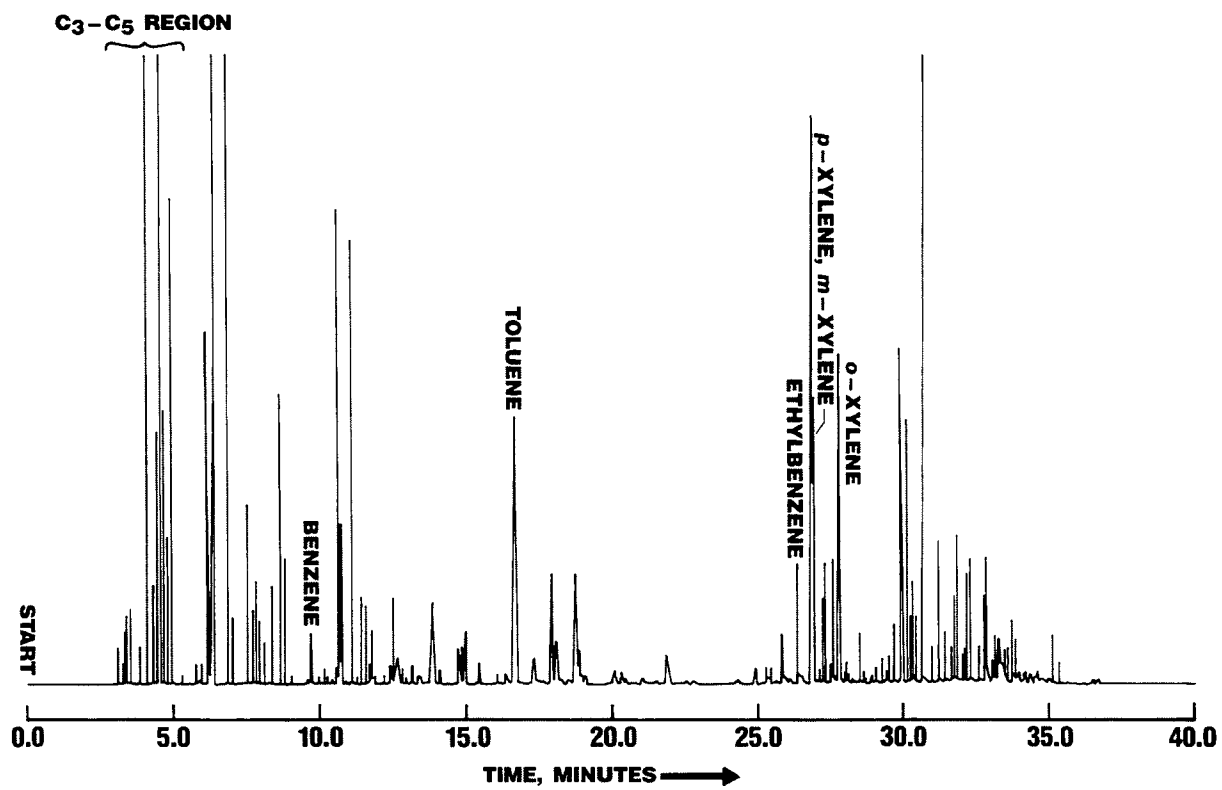


Figure 1

Typical Chromatogram

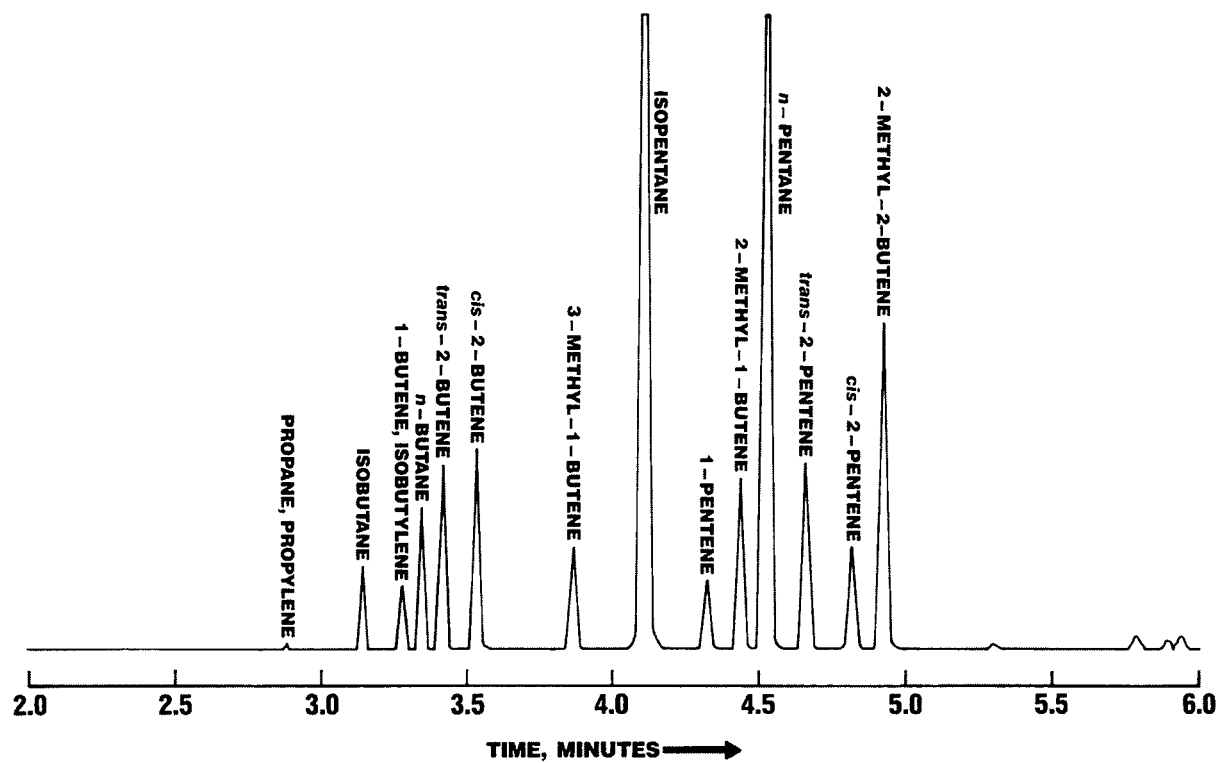


Figure 2
Typical Chromatogram
Expansion of C₃ - C₅ Region (See Fig. 1)