



Designation: ~~D2427 – 06 (Reapproved 2011)~~ D2427 – 06 (Reapproved 2015)

Standard Test Method for Determination of C₂ through C₅ Hydrocarbons in Gasolines by Gas Chromatography¹

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1. Scope

1.1 This test method covers the determination of the two (C₂) through five (C₅-) carbon paraffins and mono-olefins in gasolines. The concentrations by volume or mass (weight) of the following components are generally reported:

- 1.1.1 Ethylene plus ethane
- 1.1.2 Propane
- 1.1.3 Propylene
- 1.1.4 Isobutane
- 1.1.5 *n*-Butane
- 1.1.6 Butene-1 plus isobutylene
- 1.1.7 *trans*-Butene-2
- 1.1.8 *cis*-Butene-2
- 1.1.9 Isopentane
- 1.1.10 3-Methylbutene-1
- 1.1.11 *n*-Pentane
- 1.1.12 Pentene-1
- 1.1.13 2-Methylbutene-1
- 1.1.14 *trans*-Pentene-2
- 1.1.15 *cis*-Pentene-2
- 1.1.16 2-Methylbutene-2

1.2 This test method does not cover the determination of cyclic olefins, diolefins, or acetylenes. These are usually minor components in finished gasolines.

1.3 Samples to be analyzed should not contain significant amounts of material boiling lower than ethylene.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4.1 *Exception*—Alternative units, in common usage, are also provided to improve the clarity and aid the user of this test method.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards*:²

[D2001 Test Method for Depentanization of Gasoline and Naphthas](#)

3. Summary of Test Method

3.1 The sample is injected into a gas-liquid partition column. The components are separated as they pass through the column with an inert carrier gas and their presence in the effluent is detected and recorded as a chromatogram. Materials containing

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

components having more than five carbon atoms can either be backflushed from the system without measurement, or recorded as a broad peak by reversing the direction of the carrier gas through the column at such time as to regroup the higher-boiling portion (C_6 and heavier) of the sample. If backflushing is used, the concentration of C_2 through C_5 hydrocarbons may be related to the whole sample by adding a known quantity of low-boiling internal standard to the sample prior to analysis. Alternatively, a known amount of sample can be charged and compared to a standard sample run under the same conditions. Sample composition is determined from the chromatogram by comparing peak areas with those obtained using known amounts of calibration standards or a synthetic blend.

4. Significance and Use

4.1 In hydrocarbon type analyses of gasolines, highly volatile fuels can need to be stabilized by depentanization (Test Method **D2001**) prior to analysis. A knowledge of the composition of light hydrocarbons in the overhead from the depentanization process is useful in converting analyses of the depentanized fraction to a total sample basis.

5. Apparatus

5.1 *Chromatograph*—Any chromatograph having a thermostated oven and a detection system of adequate sensitivity may be used. The detection system must have sufficient sensitivity to produce a recorder deflection of at least ~~5 mm~~ 5 mm for 0.1 liquid volume percent of pentene-1 in the sample or synthetic blend being analyzed.

NOTE 1—If the sensitivity of a given system is inadequate, it can be increased by using a more sensitive recorder or detector, or by using more sample if the resolution is substantially unaffected.

5.2 *Recorder*—A ~~± 1 mV~~ to ~~10 mV~~ 10 mV recorder with a full-scale response time of 2 s or less and a noise level no greater than ± 0.3 % of full scale.

5.3 Columns:

5.3.1 A description of columns and valving arrangements that meet the requirements of this method are described in **Annex A1**. Persons using other column materials must establish that the column gives results that meet the precision requirements of Section **10**.

5.3.2 *Analyzer Column*—The column system used must be capable of resolving the individual C_2 to C_5 paraffins and olefins well enough so that the individual hydrocarbons listed in Section **1** may be reported. The resolution should be such that at the operating conditions selected, the distance from the base line in the valley between two peaks representing compounds reported is not greater than 50 % of the height of the smaller peak. If an internal standard is used, it must be completely resolved from the other components.

5.3.3 *Precut Column*—This column must be capable of separating the C_5 and lighter olefins and paraffins from the C_6 and heavier olefins and paraffins. The resolution should be such that at the operating conditions selected, the distance from the base line to the valley between 2-methylbutene-2 and 2,2-dimethylbutane is not greater than ~~50%~~ 50 % of the height of the smaller peak. If an internal standard is used, it must be eluted with the C_5 and lighter materials.

6. Reagents and Materials

6.1 Compounds for calibration shall be of a purity of not less than 99 mole %. Calibrants should include compounds **1.1.5 – 1.1.16** as listed in Section **1**. The concentration of ethylene, ethane, propylene, and propane is generally so low in most samples that calibration with these materials is unnecessary (**Warning**—Extremely flammable gas under pressure. Extremely flammable liquids.) Commercially available certified blends of light hydrocarbons may be used to establish calibration data where their compositions are applicable. If an internal standard is used to relate the concentration of light hydrocarbons to the whole sample it must be included as a calibrant.

6.2 *Carrier Gas*—A carrier gas appropriate to the type of detector used should be employed. Helium or hydrogen can be used with thermal conductivity detector (**Warning**—Compressed gas under high pressure.) (**Warning**—Hydrogen is extremely flammable under pressure.) Nitrogen or argon can be used with ionization or gas density detectors (**Warning**—Compressed gas under high pressure).

6.3 *Liquid Phase*—See **Annex A1**.

6.4 *Solid Support*, for use in packed column; usually crushed firebrick or diatomaceous earth. Mesh size should be appropriate to the system selected from the supplement.

7. Preparation of Apparatus

7.1 *Column Preparation*—The method used to prepare the column is not critical as long as the finished column produces the desired separation. Preparation of the packing is not difficult once the support, partitioning liquid, and loading level have been determined. Some stationary phases are susceptible to oxidation and must be protected from excessive exposure to air during the evaporation and drying steps. The following general directions have been found to produce columns of acceptable characteristics:

7.1.1 Weigh out the desired quantity of support, usually twice that required to fill the column.

7.1.2 Calculate and weigh out the required quantity of partitioning agent. Dissolve the partitioning agent in a volume of chemically inert, low-boiling solvent equal to approximately twice the volume of support.

7.1.3 Gradually add the support material to the solution with gentle stirring.

7.1.4 Slowly evaporate the solvent while gently agitating the mixture until the packing is nearly dry and no free liquid is apparent.

7.1.5 Spread the packing in thin layers on a nonabsorbent surface and air or oven dry as required to remove all traces of solvent.

7.1.6 Resieve the packing to remove fines and agglomerates produced in the impregnation step.

7.1.7 Fill the column tubing with packing by plugging one end with a wad of glass wool and pouring the packing into the other end through a small funnel. Vibrate the tubing continuously over its entire length while filling. When the packing ceases to flow, tap the column gently on the floor or bench top while vibrating is continued. Add packing as necessary until no further settling occurs during a $2\text{--}2\text{ min}$ period. Remove a small amount of packing from the open end, plug with a wad of glass wool, and shape the column to fit the chromatograph.

7.1.8 If multiple columns are joined by tubing unions, the dead volume in the union should be filled with column packing.

7.2 *Chromatograph*—Mount the column in the chromatograph and establish the operating conditions required to give the desired separation (see [Annex A1](#)). Allow sufficient time for the instrument to reach equilibrium as indicated by a stable recorder base line. Control the oven temperature so that it is constant to within 0.5°C without thermostat cycling which causes an uneven base line. Set the carrier gas flow rate, measured with a soap film meter, so that it is constant to within 1 mL/min of the selected value.

8. Procedure

8.1 *Calibration*—Determine the relative area response of the compounds to be reported by injecting known quantities of the pure compounds or by using synthetic blends of known composition. For those compounds that are normally gases at room temperature it is advantageous to use commercially available certified light hydrocarbon blends. Sample light hydrocarbon blends contained in pressure containers from the liquid phase (**Warning**—Extremely flammable gas under pressure.) Blends of those hydrocarbons that are normally liquid at room temperature are easily prepared by volume with sufficient accuracy to establish relative response factors (**Warning**—Extremely flammable liquids.) If measurement of the C_6 and heavier material by reverse flow through the detector is intended, an average calibration factor for these heavy materials must be determined. Gasolines that have been depentanized by laboratory distillation may be used as calibrants for this purpose (**Warning**—Extremely flammable.) If use of an internal standard is contemplated, the internal standard selected should be included in the calibration program.

8.2 Analysis:

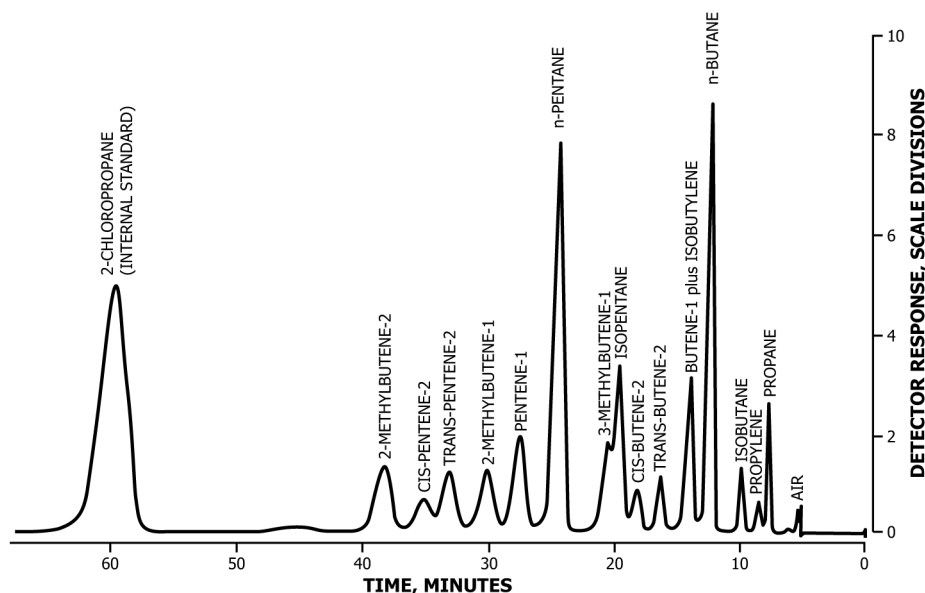
8.2.1 *Backflush Method*—When the backflush technique is used, add a known quantity of internal standard equal to about 5 % to the sample. The internal standard can be added on either a weight or volume basis depending upon the method of reporting. One method of adding the internal standard that has been found convenient is given in [Annex A1](#). Alternatively, quantitative results can be obtained by injecting repeatable quantities of the sample and of a known blend, and comparing the peak areas obtained for the sample with those obtained for the known concentration of components in the blend.

8.2.1.1 *Precut Column*—If a precut column is used, adjust the valving so that carrier gas is flowing in the normal direction through both the precut and analysis columns. Using a chilled syringe, charge sufficient sample to ensure a minimum of 10 % recorder deflection for a 0.1 % sample concentration of 2-methylbutene-2 at the most sensitive setting of the instrument. When all of the C_5 and lighter hydrocarbons plus internal standard, if used, have entered the analyzer column, position the valves so that backflushing of the precut column is initiated. The time at which backflushing is commenced is critical and may have to be determined by trial and error. If properly done, it results in the elimination of any interference from low-boiling six-carbon paraffins and produces a chromatogram that exhibits peaks for C_2 through C_5 paraffins and olefins only ([Fig. 1](#)). When the last compound has been eluted, remove the chromatogram and proceed as described in [9.1.1](#).

8.2.1.2 *Single Column*—If a single column is used, it may be backflushed if an appropriate valving system has been installed. The operations described above are performed except that backflushing is commenced only when all the C_5 and lighter hydrocarbons and internal standard have been eluted. The purpose of backflushing in this case is not to improve the separation, but merely to shorten the total analysis time and avoid passage of higher boiling hydrocarbons through the detector.

8.2.2 *Reverse Flow Method*—If reverse flow of the C_6 and heavier portion through the detector is employed, the addition of an internal standard is unnecessary if adequate calibration has been performed and the composition of the C_6 and heavier portion does not differ significantly from that of the depentanized gasolines used as calibrants. An internal standard can be used periodically to assure that analytical accuracy is maintained ([Note 2](#)). Adjust the valving so that carrier gas is flowing through the instrument in the normal direction. Charge sufficient sample to ensure a minimum of 10 % recorder deflection for a 0.1 percent sample concentration of 2-methylbutene-2 at the highest sensitivity. As soon as the last pentene peak (2-methylbutene-2) has been eluted, position the valving so that the carrier gas flow is reversed. After the flow has stabilized, adjust the base line. Attenuate for the C_6 + portion as necessary. The run is complete when the recorder returns to the base line after elution of the C_6 portion. This part of the sample will generally emerge as one broad peak with only slight indications of any separation. Proceed as described in [9.1.2](#).

NOTE 2—All reverse flow determinations, including the C_6 and heavier calibration runs should be made in the same carrier gas flow direction. All single-peak determinations and corresponding calibrations will then be made in the opposite carrier gas flow direction. The column should be kept free



Column:
 Precut: SF96-50 silicone fluid
 Analyzer: tricresylphosphate plus DC 550 silicone fluid 4.5/1 by wt followed by ethylene glycol in series.

FIG. 1 Typical Chromatogram of Light Components in a Catalytic Gasoline

of high-boiling residues by periodically sweeping with carrier gas for several hours in the reverse direction. A level base line will quickly be attained in either flow direction when the column is clean and the system is free of leaks.

9. Calculation

9.1 Calculate the percentage of the individual components using the following procedure that applies and report to the nearest 0.1 %.

9.1.1 *Backflush Method*—Measure the areas of all of the peaks representing compounds to be reported and that of the internal standard. Adjust each component peak area by use of the proper calibration factor for differences in response between the component and the internal standard. Calibration factors relative to volume or weight percentages can be used. Calculate the percentage of each component as follows:

$$\text{Component, percent} = \frac{S \times A \times 100}{B \times (100 - S)} \quad (1)$$

where:

- S = percentage of standard,
- A = peak area of the component, and
- B = peak area of the internal standard.

If a constant volume, rather than internal standard method was used, calculate the percentage of each component by comparing its area to that produced by a known concentration of the component when the same constant volume of a standard sample is charged. A linear concentration—area relationship may be assumed and the percentage of each hydrocarbon calculated using the relation

$$C_1 = C_2(A_1/A_2) \quad (2)$$

where:

- C₁ = percentage of component in unknown,
- A₁ = peak area of component in unknown,
- C₂ = known percentage of component in standard sample, and
- A₂ = peak area of component in standard sample.

9.1.2 *Reverse Flow Method*—Measure the areas of all of the peaks, including the area of the broad peak representing the C₆ and heavier portion. Apply the appropriate calibration factors to the areas to correct for the differences in response of the components. Calibration factors relative to volume or weight percentages may be used. Calculate the percentage of each component as follows: