Designation: D2712 – 91(Reapproved 2010)

Standard Test Method for Hydrocarbon Traces in Propylene Concentrates by Gas Chromatography[1]

This standard is issued under the fixed designation D2712; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of 5 to 500 ppm each of ethylene, total butylenes, acetylene, methyl acetylene, propadiene, and butadiene in propylene concentrates.

1.2 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

1.3 *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]

E260 Practice for Packed Column Gas Chromatography
F307 Practice for Sampling Pressurized Gas for Gas Analysis

3. Summary of Test Method

3.1 A relatively large volume of sample is charged to a gas partition chromatography apparatus which has a column that will separate the trace hydrocarbon constituents from the major components. Any column or combination of columns may be used provided they have the necessary resolution and the detecting system has sufficient sensitivity. Several columns that have been found satisfactory are given in 5.1.

3.2 Calculation is performed by calculating the concentration of the trace compound from its area relative to the area of a standard compound of known concentration.

4. Significance and Use

4.1 The trace hydrocarbon compounds listed in Table 1 may have an effect in the commercial use of propylene concentrates, and information on their concentration is frequently necessary.

5. Apparatus

5.1 *Columns*—Any column may be used provided it will resolve the trace compound peaks present in concentrations of 20 ppm or more so that the resolution ratio, *A/B*, will not be less than 0.4, where *A* is the depth of the valley on either side of peak *B* and *B* is the height above the baseline of the smaller of any two adjacent peaks (see Fig. 1). For compounds present in concentrations of less than 20 ppm the ratio *A/B* may be less than 0.4. In the case where the small-component peak is adjacent to a large one, it may be necessary to construct the baseline of the small peak tangent to the curve as shown in Fig. 2. Butylenes need not be resolved from each other. Columns found to be acceptable together with operating conditions used are shown in Table 2. Table 3 shows typical retention times.

5.1.1 Columns may be constructed of 3.2 -mm (⅛-in.), 6.4 -mm (¼-in.), or capillary tubing and usually need to be a minimum of 6 m (20 ft) in length. They usually have 20 to 40 g of liquid substrate to 100 g of solid support. If packed columns are used, the liquid may be placed on the solid support by any suitable method, provided the column has the desired resolution and sensitivity.

NOTE 1—Separation of all the desired compounds on a single column has been found by cooperators to be very difficult. Most laboratories have found it necessary to use two or more columns. Typical instructions for preparing such columns may be found in Practice E260.

5.2 *Gas Chromatograph*—Any gas chromatography apparatus may be used provided the system has sufficient sensitivity to detect the trace compounds of interest. For calculation techniques utilizing a recorder, the signal for 20 ppm concentration shall be at least 5 chart divisions above the noise level on a 0 to 100 scale chart. The noise level must be restricted to a maximum of 2 chart divisions. When electronic integration is employed, the signal for 20-ppm concentration must be at least twice the noise level.

NOTE 2—A flame ionization detector is preferred. When using with relatively volatile liquid phases, such as HMPA, an additional 0.31-m

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricantsand is the direct responsibility of Subcommittee D02.D0.03 on Propylene.

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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.

TABLE 1 Molecular Weight and Specific Gravity

Compound	Molecular Weight	Specific Gravity, 60/60
Propylene	42.08	0.5220
Propane	44.09	0.5077

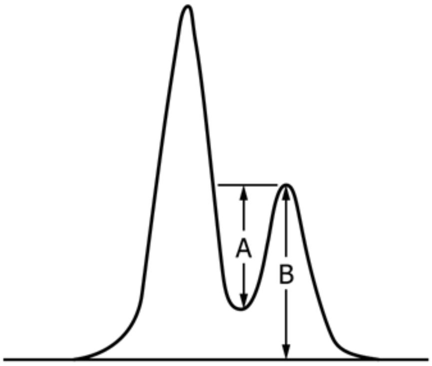

FIG. 1 Illustration of *A/B* Ratio

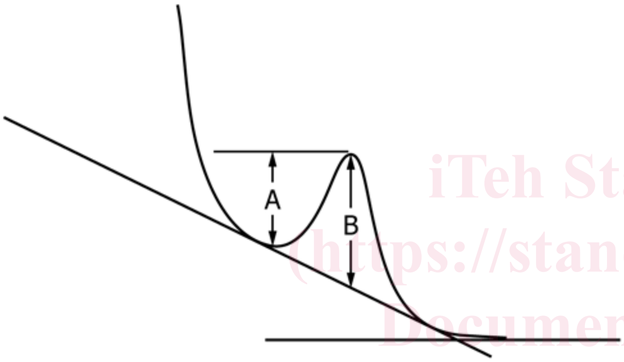

FIG. 2 Illustration of *A/B*Ratio for Small-Component Peak

(1-ft) section of column containing uncoated solid support will aid in reducing noise.

5.3 *Sample Introduction*—Means shall be provided for introducing a measured quantity of sample into the apparatus. Pressure sampling devices may be used to inject a small amount of the liquid directly into the carrier gas. Introduction may be by means of a gas valve to charge the vaporized liquid.

6. Reagents and Materials

6.1 *Hydrocarbons,* for peak identification, including propylene, ethylene, ethane, acetylene, methyl acetylene, propadiene, propane, 1,3-butadiene, isobutylene, 1-butene, *cis* and *trans* 2-butene, iso- and normal butane, and cyclopropane. (**Warning**—Liquefied petroleum gas under pressure and flammable.) Mixtures of these hydrocarbons may be used for calibration provided there is no uncertainty as to the identity of the desired compound.

6.2 *Propane or Propylene,* for synthetic base stock containing less than 2 ppm by weight of acetylene or 1,3-butadiene. (**Warning**—Liquefied petroleum gas under pressure and flammable.)

6.3 *Calibration Compounds*—Acetylene and 1,3-butadiene 99 % minimum purity. (**Warning**—Liquefied petroleum gas under pressure and flammable.)

6.4 *Carrier Gases—Helium or Nitrogen.* (**Warning**—Compressed gas under pressure.)

6.5 *Hydrogen.* (**Warning**—Compressed gas under pressure and flammable.)

6.6 *Liquid Phase for Column*—See Table 2. (**Warning**—Hexamethylphosphoramide is a potential carcinogen.)

6.7 *Solid Support*—C_{22} firebrick or diatomaceous earth, usually 40 to 60 or 60 to 80 mesh.

6.8 *Stainless Steel Sample Cylinder,* 300 to 500-cm^3 capacity, capable of withstanding a minimum of 1723 kPa gage (250 psig).

6.9 *Silicone Rubber Septum,* with suitable fittings for attachment to sample cylinder.

6.10 *Gas Syringe,* 10-cm^3.

6.11 *Vacuum Pump,* capable of evacuating sample cylinder to less than 2 mm Hg absolute pressure.

6.12 *Aluminum or Stainless Steel Tubing,* 0.61 m (2 ft), 3.2 mm (⅛ in.), or 1.6 mm (1⁄16 in.), outside diameter with fittings on one end to connect to butadiene cylinder and the other end modified so as to have an opening with an inside diameter of about 0.5 mm larger than the outside diameter of the gas syringe needle.

7. Sampling

7.1 This section is to be followed on all samples including unknown samples and the synthetic standards.

7.2 Samples should be supplied to the laboratory in high-pressure sample cylinders, obtained using the procedures described in Practice F307 or similar methods.

7.3 Place the cylinder in a horizontal position in a safe location such as a hood. Check to see that the container is at least one-half full by slightly opening the valve. If liquid is emitted (a white cloud of vapors) the container is at least one-half full. Do not analyze any samples or use any synthetic standard if the liquid in the container is less than this amount.

7.4 Place the cylinder in a vertical position and repressurize to 1723 kPa gage (250 psig) with the chromatographic carrier gas through the valve at the top of the cylinder, ensuring that no air enters during the operation.

7.5 Use either of the following two procedures for obtaining a sample from the container:

7.5.1 *Using a Liquid Valve*—Connect the cylinder to the liquid valve on the chromatograph using a minimum length of connecting tubing, so that sample is withdrawn from the bottom of the cylinder and a liquid sample is obtained. The liquid valve on the chromatograph must be designed in such a manner that full sample pressure can be maintained through the valve without leaking and that means are provided for trapping a liquid sample in the chromatograph valve under static conditions of flow. With the exit of the chromatograph valve closed open the valve on the cylinder. Slowly open the exit from the chromatograph valve so that liquid flows through the connecting line and valve. Close the exits so that the liquid

TABLE 2 Typical Column Conditions

Column	1		2			3	4	5	6	7	8	9	10	11	
Column:	Series[A]		Series					Mixed				Mixed		Series	
Liquid	DMS	Squa	DMS	ODPN	UCON	DMS	None	20 TCEP 80 % SE-30	ODPN	$n\,C_{16}$	HMPA	80 MEEE 8 DIDP	None	DMS	Squa
Weight, %	33	22	U	15	15	15		25	25	20	30	20		33	20
Solid	Chrom	Chrom	Chrom	Chrom	Chrom	Chrom	SiGel	Chrom	Chrom	Chrom	Chrom	Chrom	SiGel	Chrom	Chrom
Mesh	60 to 80	60 to 80	100	80 to 100	U	60 to 80	U	30 to 60	30 to 60	60 to 80	60 to 80	60 to 80	40 to 60	60 to 80	60 to 80
Treatment	none	none	U	U	U	U	U	AW	AW	AW	AW	none	FeCl	none	none
Length, ft	4	30	22	20	8	16	3.5	50	50	20	20	25	15	8	35
Inside diameter, in.	0.19	0.13	0.085	0.085	0.085	0.085	0.18	0.19	0.19	0.085	0.085	0.085	0.19	0.085	0.085
Temperature:															
Inlet, °C	RT		RT			RT	RT	160	70	RT	RT	RT	RT	RT	
Detector, °C	150		RT			50	50	175	70	RT	RT	RT	RT	RT	
Column, °C	RT		RT			50	50	30	70	RT	RT	RT	RT	RT	
Sample:															
Injection	GV		GV			GV	GV	Syr	Syr	GV	GV	GV	GV	GV	
Gas, cm^3	0.5		0.2			1	0.7	3.0	1	0.5	5	0.4	0.4	1	
Split											40:1				
Carrier:															
Gas	He		He			He	He	He	He	H_2	He	He	He	He	
cm^3/min	50		22			24	42	40	40	17	60	30	30	52	
Detector:															
Type	FI		TC			FI	TC	FI	TC	FI	FI	FI	FI	FI	
Voltage			8				12		70						
Recorder:															
Range, mV	1		1			5	1	1	1	5	5	1	1	1	
in./h	30		60			30	30	30	30	30	30	60	60	30	
Measurement	Tri		Plan			Plan	Plan	PH	PH	PH	PW/2	Tri	Tri	Tri	

Abbreviations:

AW	Acid washed	ODPN	β,β'-oxydipropionitrile
Chrom	"Chromosorb" P (trademark of Johns-Manville Products Corp.)	PH	Peak height
DIDP	Diisodecyl phthalate	Plan	Planimeter
DMS	2,4-dimethyl sulfolane	PW/2	Peak height × width at ⅓ height
FeCl	Ferric chloride, modified	RT	Room temperature
FI	Flame ionization	SE-30	SE-30 gum rubber
GV	Gas valve	SiGel	Silica gel
He	Helium	Squa	Squalane
H_2	Hydrogen	Syr	Syringe
HMPA	Hexamethyl phosphoramide	TC	Thermal conductivity
MEEE	Bis-2(methoxy ethoxy ethyl) ether	TCEP	1,3-tris(2-cyano ethoxy)propane
$n\,C_{16}$	Normal hexadecane	Tri	Triangulation
		U	Unknown

[A] Detector bypassed during major peaks.

TABLE 3 Typical Retention Time, Min

Column	1	2	3	4	5	6	7	8	9	10	11
Acetylene	10.1	...	...	...	...	6.5	2.2	22.3	...	...	8.0
1,3-Butadiene	39.4	24.9	...	...	15.3	...	...	20.8	17.4	...	35.1
Isobutene	33.3	...	8.7	...	...	15.7	...	11.0	10.9	...	29.7
1-Butene	33.3	...	9.5	...	...	15.7	...	11.4	10.9	...	29.7
trans-2-Butene	42.1	...	11.8	...	...	18.1	...	13.1	12.9	...	38.0[A]
cis-2-Butene	46.9	...	14.2	...	...	20.5	...	15.1	14.8	...	42.8
Cyclopropane	22.8	...	...	...	...	12.0	7.2	8.3	...	...	...
Ethylene	8.1	...	...	5.1	...	5.8	2.3	...	...	3.6	5.7
Methyl acetylene	24.2	26.1	...	...	18.3	...	...	28.0	16.4	...	21.1
Neopentane	34.3[B]	...	...	...	...	...	15.4	8.8	...	...	...
Propadiene	20.6	...	10.2	...	...	11.3	...	...	10.0	...	17.6

[A] DMS portion only.
[B] Squalane portion only.

sample is trapped in the valve. Perform the necessary operations to introduce the liquid sample into the chromatograph column.

7.5.2 *Vaporized Sample*—Assemble the apparatus similar to that illustrated in Fig. 3. Disconnect the 1700-cm^3 cylinder at *E* and evacuate. Close valve *B* and open valves *C* and *D*, allowing the liquid sample to flow into the small cylinder. Slowly open valve *B* and allow the sample to flow through until a steady slow stream of liquid emerges from *B*. Close valves *B*, *C*, and *D* in that order, trapping a portion of the liquid sample in the pipe cylinder (Note 4). Attach the evacuated cylinder (1700-cm^3 volume) at *E*. Open valve *A* and then valve *B*. The