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

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 the 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:*
E 260 Practice for Packed Column Gas Chromatography[2]
F 307 Practice for Sampling Pressurized Gas for Gas Analysis[3]

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 (1/8-in.), 6.4-mm (1/4-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 E 260.

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

TABLE 1 Molecular Weight and Specific Gravity

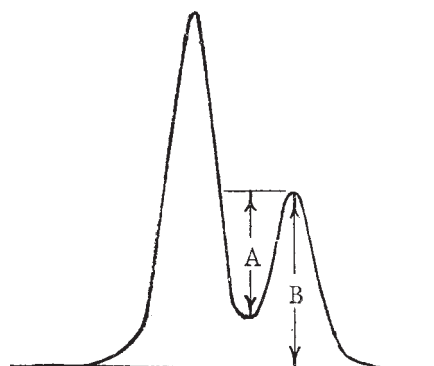| Compound	Molecular Weight	Specific Gravity, 60/60
Propylene	42.08	0.5220
Propane	44.09	0.5077

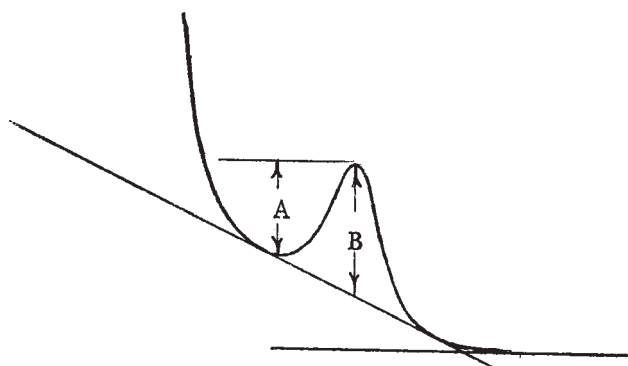**FIG. 1 Illustration of *A/B* Ratio**

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

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 (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 F 307 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

TABLE 2 Typical Column Conditions

Column	1		2			3	4	5	6	7	8	9	10	11	
Column:	Series[A]		Series					Mixed 20 TCEP				Mixed 80 MEEE		Series	
Liquid	DMS	Squa	DMS	ODPN	UCON	DMS	None	80 % SE-30	ODPN	n C$_{16}$	HMPA	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.

connecting line and valve. Close the exits so that the liquid 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
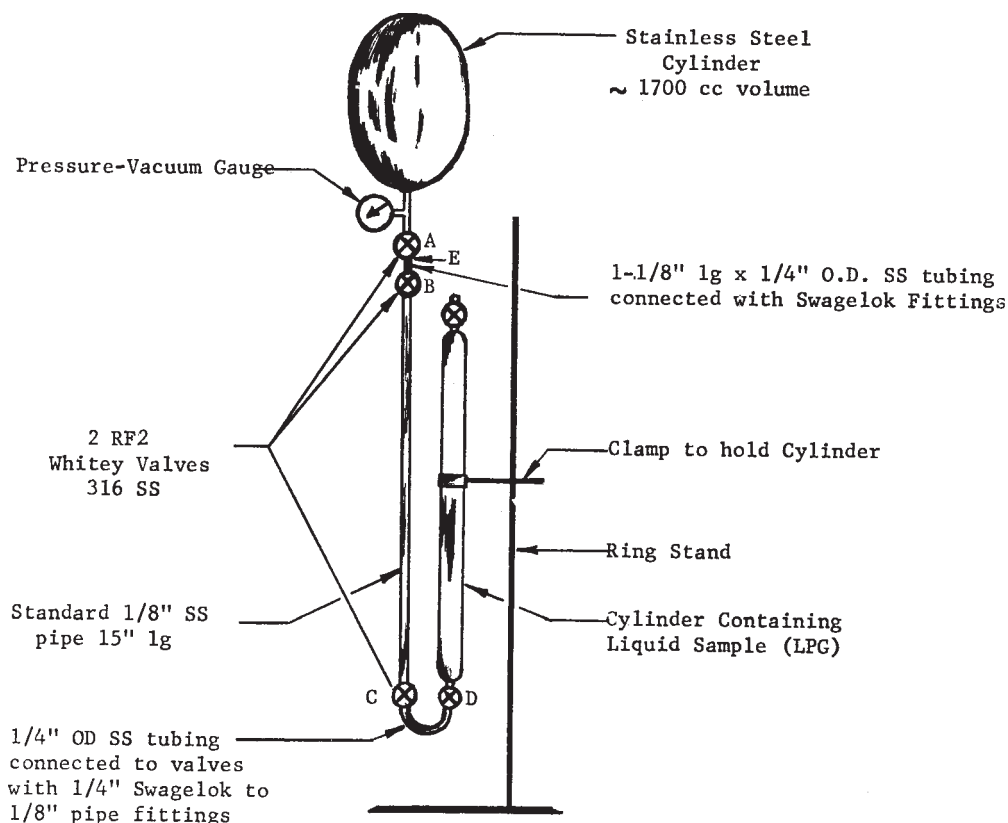
Stainless Steel Cylinder ∼ 1700 cc volume

Pressure-Vacuum Gauge

1-1/8" lg x 1/4" O.D. SS tubing connected with Swagelok Fittings

2 RF2 Whitey Valves 316 SS

Clamp to hold Cylinder

Ring Stand

Standard 1/8" SS pipe 15" lg

Cylinder Containing Liquid Sample (LPG)

1/4" OD SS tubing connected to valves with 1/4" Swagelok to 1/8" pipe fittings

FIG. 3 Sampling and Expansion Cylinder Arrangement

(1700-cm^3 volume) at *E*. Open valve *A* and then valve *B*. The liquid will expand, filling the larger cylinder and give a gage pressure of approximately 55 kPa (8 psi) for propylene concentrates. Close valve *A* and disconnect at *E*.

NOTE 3—To avoid possible rupture of the liquid-filled pipe cylinder, the sample cylinder and its contents should be at room temperature prior to sampling and the liquid should be allowed to remain in the pipe cylinder for only a minimum amount of time.

7.5.2.1 Connect the cylinder containing the vaporized sample to the chromatograph gas valve. Evacuate the sample loop and the lines up to the sample cylinder. Close the valve to the vacuum source and allow the sample loop to fill with sample up to atmospheric pressure. Repeat the evacuation and filling of the sample loop with vaporized sample. Turn the valve so that the vaporized sample is displaced with carrier gas into the chromatograph.

8. Calibration

8.1 Select the conditions of column temperature and carrier gas flow that will give the prescribed separation.

8.2 Determine the retention time for each compound by injecting small amounts of the compound either separately or in a mixture using the same method of charging as is used for the sample.

9. Synthetic Standard

9.1 Connect the silicone septum to a valve of the stainless steel sample cylinder in such a manner that the volume between the septum and the valve is less than 1 % of the total

volume of the cylinder. By means of suitable fittings connect the other valve of the cylinder to a vacuum pump and evacuate the cylinder and space between the cylinder valve and septum. Close the valves, disconnect the cylinder from the vacuum pump, and weigh the empty cylinder on a suitable platform balance to the nearest 1 g.

9.2 Connect the tubing to the 1,3-butadiene cylinder and crack the valve on this cylinder so that there is a constant flow of vapors from the end of the tubing which must be at room temperature. Insert the syringe into the end of the tubing and slowly withdraw 5 cm^3 of the butadiene vapors. Flush the syringe three times with vapors and inject exactly 5 cm^3 of the vapor through the septum into the evacuated cylinder. Close the valve between the cylinder and the septum. Inject 5 cm^3 of acetylene to the evacuated cylinder in the same manner.

9.3 Fill another cylinder of the same size with propane or propylene base stock. Establish outage in the base stock cylinder by removing 25 % of the liquid contents. Place the cylinder containing the blend stock in a vertical position so that the bottom valve is above the top of the cylinder containing the butadiene. If the cylinder containing the base stock is equipped with a dip pipe be sure that this valve is at the top. Connect the bottom valve of the base stock cylinder to the other cylinder by means of suitable tubing capable of withstanding 1723 kPa (250 psi) pressure. Flush the connecting line with base stock before tightening connections to the evacuated cylinder. Cool the evacuated cylinder to a temperature of 11 to 17°C (20 to 30°F) below that of the base stock. Open the valves between the two cylinders and allow the base stock to flow into the

cylinder containing the butadiene. Close the valves, disconnect, and allow the cylinder to warm to room temperature. Reweigh on the platform balance and determine the total weight of base stock containing the butadiene and acetylene.

9.4 Calculate the ppm by weight of acetylene and butadiene in the standards as follows:

$$\text{Weight, ppm} = \frac{\text{cm}^3 \text{ compound} \times 273}{273 + T}$$
$$\times \frac{Z}{22\,410} \times \frac{\text{mol wt}}{\text{total wt}} \times 10^6 \quad (1)$$

where:
T = room temperature, °C,
Z = 1.026 correction factor for butadiene, ideal volume/absolute volume, and
    1.0 correction factor for acetylene, ideal volume/absolute volume, and
mol wt = 54.1 for butadiene, and
    26.0 for acetylene.

10. Procedure

10.1 Using the same conditions as were used for identification of peaks, record the peaks of all compounds of interest at a maximum sensitivity in a manner to allow measurement of the area of each hydrocarbon trace component.

10.2 Charge the synthetic standard in the same manner as the sample and under the same conditions. Make duplicate runs of the standard.

11. Calculation

11.1 Measure the area of each hydrocarbon trace peak and the area of the butadiene peak in the standard. Use acetylene in the standard as comparison for ethylene and acetylene in the sample. Use butadiene in the standard as comparison for the other trace compounds in the sample.

11.2 *Flame Ionization Detector*—Assume that the area is proportional to the weight concentration of each compound.

$$\text{Trace compound, ppm} = (A_s/A_0) \times S \quad (2)$$

where:
A_s = area due to the trace compound,
A_0 = average area of acetylene or butadiene in the standard, and

TABLE 4 Relative Response Factors

Compound	Response Factor, g/relative area
Acetylene	62
Butadiene	68
Isobutylene	69
Ethylene	59
Methyl acetylene	57
Propadiene	62
Cyclopropane	63

S = concentration of acetylene or butadiene, ppm, in the standard.

Note 4—If the standard is prepared in a base stock different from the sample, an additional correction must be made to compensate for the fact that identical weights are not charged when charging at constant gas volume or constant liquid volume. When charging at *constant gas volume*, multiply the results in 10.2 or 10.3 by the factor:

mol wt standard/mol wt sample

When charging at *constant liquid volume*, multiply by:

(sp gr 60/60 standard)/(sp gr 60/60 sample) (3)

11.3 *Thermal Conductivity Detector*—Using the relative response factors in Table 4, correct the areas for difference in response.

$$\text{Trace compounds, ppm} = [(A_s \times RF)/(A_0 \times 68)] \times S \quad (4)$$

where:
A_s = area due to the trace compound,
A_0 = area of acetylene or butadiene in the standard,
RF = response factor of acetylene or butadiene, and
S = concentration of acetylene or butadiene, ppm, in the standard.
(See Note 4.)

12. Precision and Bias

12.1 The criteria shown in Table 5 should be used for judging the acceptability of results (95 % probability). The precision statements are based on the results from seven laboratories analyzing two samples and should be considered tentative pending further study and evaluation.

12.1.1 *Repeatability*—Duplicate results by the same operator should be considered suspect if they differ by more than the

TABLE 5 Precision of Test Method^A

Compound	Concentration, ppm	Amount Present, %	
		Repeatability	Reproducibility
Acetylene^B	15 to 30	11	53
	101	6	26
Butadiene^A	29	22	53
	75	7	39
Butenes, total^C	346	5	30
Ethylene^B	37	11	64
	82 to 220	4.3	64
Methyl acetylene^D	21	14	42
	60	14	23
Propadiene^D	44 to 53	8	52

^{A} Subject to revision as further cooperative work is completed.
^{B} Based on results from six laboratories on three samples.
^{C} Based on results from eight laboratories on one sample.
^{D} Based on results from eight laboratories on two samples.

amounts shown in Table 5 for repeatability as percent of the average amount present.

12.1.2 *Reproducibility*—The results submitted by two laboratories should be considered suspect if they differ by more than the amount shown in Table 5 for reproducibility as percent of the average amount present.

12.1.3 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in Test Method D 2712 for measuring hydrocarbon traces, no statement on bias is being made.

13. Keywords

13.1 gas chromatography; hydrocarbon impurities; propylene