

Appendix

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This section of the manual includes the various Procedure sections of the ASTM test methods discussed. This is intended for a quick reference on the details of performing the measurement test procedures to yield the distillation and/or vapor pressure data. This part of the manual is divided into Distillation test methods, Vapor Pressure and V/L Ratio test methods, and Simulated Distillation Test Methods. The test methods are given in numerical order.

DISTILLATION TEST METHODS

D86 - 04b Procedure Section



Designation: D86–04b

Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure¹

10. Procedure

10.1 Record the prevailing barometric pressure.

10.2 *Groups 0, 1, and 2*—Fit a low range thermometer provided with a snug-fitting cork or stopper of silicone rubber, or equivalent polymeric material, tightly into the neck of the sample container and bring the temperature of the sample to the temperature indicated in Table 3.

10.3 *Groups 0, 1, 2, 3, and 4*—Check that the temperature of the sample is as shown in Table 3. Pour the specimen precisely to the 100-mL mark of the receiving cylinder, and transfer the contents of the receiving cylinder as completely as practical into the distillation flask, ensuring that none of the liquid flows into the vapor tube.

NOTE 14—It is important that the difference between the temperature of the specimen and the temperature of the bath around the receiving cylinder is as small as practically possible. A difference of 5°C can make a difference of 0.7 mL.

10.3.1 *Groups 3 and 4*—If the sample is not fluid at ambient temperature, it is to be heated to a temperature between 9 and 21°C above its pour point (Test Method D97, D5949, D5950, or D5985) prior to analysis. If the sample has partially or completely solidified in the intervening period, it shall be vigorously shaken after melting, and prior to sampling, to ensure homogeneity.

10.3.1.1 If the sample is not fluid at ambient temperatures, disregard the temperature range shown in Table 1 for the receiving cylinder and sample. Prior to analysis, heat the receiving cylinder to approximately the same temperature as the sample. Pour the heated specimen precisely to the 100-mL mark of the receiving cylinder, and transfer the contents of the receiving cylinder as completely as practical into the distillation flask, ensuring that none of the liquid flows into the vapor tube.

NOTE 15—Any material that evaporates during the transfer will contribute to the loss; any material that remains in the receiving cylinder will contribute to the observed recovery volume at the time of the IBP.

10.4 If the sample can be expected to demonstrate irregular boiling behavior, that is, bumping, add a few boiling chips to the specimen. The addition of a few boiling chips is acceptable for any distillation.

10.5 Fit the temperature sensor through a snug-fitting device, as described in 6.4, to mechanically center the sensor in the neck of the flask. In the case of a thermometer, the bulb is centered in the neck and the lower end of the capillary is level with

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the highest point on the bottom of the inner wall of the vapor tube (see Fig. 5). In the case of a thermocouple or resistance thermometer, follow the manufacturer's instructions as to placement.

NOTE 16—If vacuum grease is used on the mating surface of the centering device, use the minimum amount of grease that is practical.

10.6 Fit the flask vapor tube, provided with a snug-fitting cork or rubber stopper of silicone, or equivalent polymeric material, tightly into the condenser tube. Adjust the flask in a vertical position so that the vapor tube extends into the condenser tube for a distance from 25 to 50 mm. Raise and adjust the flask support board to fit it snugly against the bottom of the flask.

10.7 Place the receiving cylinder that was used to measure the specimen, without drying the inside of the cylinder, into its temperature-controlled bath under the lower end of the condenser tube. The end of the condenser tube shall be centered in the receiving cylinder and shall extend therein for a distance of at least 25 mm, but not below the 100-mL mark.

10.8 *Initial Boiling Point:*

10.8.1 *Manual Method*—To reduce evaporation loss of the distillate, cover the receiving cylinder with a piece of blotting paper, or similar material, that has been cut to fit the condenser tube snugly. If a receiver deflector is being used, start the distillation with the tip of the deflector just touching the wall of the receiving cylinder. If a receiver deflector is not used, keep the drip tip of the condenser away from the wall of the receiving cylinder. Note the start time. Observe and record the IBP to the nearest 0.5°C (1.0°F). If a receiver deflector is not being used, immediately move the receiving cylinder so that the tip of the condenser touches its inner wall.

10.8.2 *Automated Method*—To reduce evaporation loss of the distillate, use the device provided by the instrument manufacturer for this purpose. Apply heat to the distillation flask and contents with the tip of the receiver deflector just touching the wall of the receiving cylinder. Note the start time. Record the IBP to the nearest 0.1°C (0.2°F).

10.9 Regulate the heating so that the time interval between the first application of heat and the IBP is as specified in Table 5.

10.10 Regulate the heating so that the time from IBP to 5 or 10 % recovered is as indicated in Table 5.

10.11 Continue to regulate the heating so that the uniform average rate of condensation from 5 or 10 % recovered to 5 mL residue in the flask is 4 to 5 mL per min. (**Warning**—Due to the configuration of the boiling flask and the conditions of the test, the vapor and liquid around the temperature sensor are not in thermodynamic equilibrium. The distillation rate will consequently have an effect on the measured vapor temperature. The distillation rate shall, therefore, be kept as constant as possible throughout the test.)

NOTE 17—When testing gasoline samples, it is not uncommon to see the condensate suddenly form non-miscible liquid phases and bead up on the temperature measuring device and in the neck of the boiling flask at a vapor temperature of around 160°C. This may be accompanied by a sharp (about 3°C) dip in the vapor temperature and a drop in the recovery rate. The phenomenon, which may be due to the presence of trace water in the sample, may last for 10 to 30 s before the temperature recovers and the condensate starts flowing smoothly again. This point is sometimes colloquially referred to as the Hesitation Point.

10.12 Repeat any distillation that did not meet the requirements described in 10.9, 10.10, and 10.11.

10.13 If a decomposition point, as described in 3.1.3, is observed, discontinue the heating and proceed as directed in 10.17.

10.14 In the interval between the IBP and the end of the distillation, observe and record data necessary for the calculation and reporting of the results of the test as required by the specification involved, or as previously established for the sample under test. These observed data can include temperature readings at prescribed percentages recovered or percentages recovered at prescribed temperature readings, or both.

10.14.1 *Manual Method*—Record all volumes in the graduated cylinder to the nearest 0.5 mL, and all temperature readings to the nearest 0.5°C (1.0°F).

10.14.2 *Automated Method*—Record all volumes in the receiving cylinder to the nearest 0.1 mL, and all temperature readings to the nearest 0.1°C (0.2°F).

10.14.3 *Group 0*—In cases in which no specific data requirements have been indicated, record the IBP, the EP (FBP), and temperature readings at each 10 % multiple of volume recovered from 10 to 90, inclusive.

10.14.4 *Group 1, 2, 3, and 4*—In cases in which no specific data requirements have been indicated, record the IBP and the EP (FBP) or the dry point, or both, and temperature readings at 5, 15, 85, and 95 % recovered, and at each 10 % multiple of volume recovered from 10 to 90, inclusive.

10.14.4.1 *Group 4*—When a high range thermometer is used in testing aviation turbine fuels and similar products, pertinent thermometer readings can be obscured by the centering device. If these readings are required, perform a second distillation in accordance with Group 3. In such cases, reading from a low range thermometer can be reported in place of the obscured high range thermometer readings, and the test report shall so indicate. If, by agreement, the obscured readings are waived, the test report shall so indicate.

10.14.5 When it is required to report the temperature reading at a prescribed percent evaporated or recovered for a sample that has a rapidly changing slope of the distillation curve in the region of the prescribed percent evaporated or recovered

reading, record temperature readings at every 1 % recovered. The slope is considered rapidly changing if the change in slope (C) of the data points described in 10.14.2 in that particular area is greater than 0.6 (change of slope (F) is greater than 1.0) as calculated by Eq. 1 (Eq. 2).

$$\text{Change of Slope } (C) = (C_2 - C_1)/(V_2 - V_1) - (C_3 - C_2)/(V_3 - V_2) \quad (1)$$

$$\text{Change of Slope } (F) = (F_2 - F_1)/(V_2 - V_1) - (F_3 - F_2)/(V_3 - V_2) \quad (2)$$

where:

C_1	=	temperature at the volume % recorded one reading prior to the volume % in question, °C,
C_2	=	temperature at the volume % recorded in question, °C,
C_3	=	temperature at the volume % recorded following the volume % in question, °C,
F_1	=	temperature at the volume % recorded one reading prior to the volume % in question, °F,
F_2	=	temperature at the volume % recorded in question, °F,
F_3	=	temperature at the volume % recorded following the volume % in question, °F,
V_1	=	volume % recorded one reading prior to the volume % in question,
V_2	=	volume % recorded at the volume % in question, and
V_3	=	volume % recorded following the volume % in question.

10.15 When the residual liquid in the flask is approximately 5 mL, make a final adjustment of the heat. The time from the 5 mL of liquid residue in the flask to the EP (FBP) shall be within the limits prescribed in Table 5. If this condition is not satisfied, repeat the test with appropriate modification of the final heat adjustment.

NOTE 18—Since it is difficult to determine when there is 5 mL of boiling liquid left in the flask, this time is determined by observing the amount of liquid recovered in the receiving cylinder. The dynamic holdup has been determined to be approximately 1.5 mL at this point. If there are no front end losses, the amount of 5 mL in the flask can be assumed to correspond with an amount of 93.5 mL in the receiving cylinder. This amount has to be adjusted for the estimated amount of front end loss.

10.15.1 If the actual front end loss differs more than 2 mL from the estimated value, the test shall be rerun.

10.16 Observe and record the EP (FBP) or the dry point, or both, as required, and discontinue the heating.

10.17 Allow the distillate to drain into the receiving cylinder, after heating has been discontinued.

10.17.1 *Manual Method*—While the condenser tube continues to drain into the graduated cylinder, observe and note the volume of condensate to the nearest 0.5 mL at 2 min intervals until two successive observations agree. Measure the volume in the receiving cylinder accurately, and record it to the nearest 0.5 mL.

10.17.2 *Automated Method*—The apparatus shall continually monitor the recovered volume until this volume changes by no more than 0.1 mL in 2 min. Record the volume in the receiving cylinder accurately to the nearest 0.1 mL.

10.18 Record the volume in the receiving cylinder as percent recovery. If the distillation was previously discontinued under the conditions of a decomposition point, deduct the percent recovered from 100, report this difference as the sum of percent residue and percent loss, and omit the procedure given in 10.19.

10.19 After the flask has cooled and no more vapor is observed, disconnect the flask from the condenser, pour its contents into a 5-mL graduated cylinder, and with the flask suspended over the cylinder, allow the flask to drain until no appreciable increase in the volume of liquid in the cylinder is observed. Measure the volume in the graduated cylinder to the nearest 0.1 mL, and record as percent residue.

10.19.1 If the 5-mL graduated cylinder does not have graduations below 1 mL and the volume of liquid is less than 1 mL, prefill the cylinder with 1 mL of a heavy oil to allow a better estimate of the volume of the material recovered.

10.19.1.1 If a residue greater than expected is obtained, and the distillation was not purposely terminated before the EP, check whether adequate heat was applied towards the end of the distillation and whether conditions during the test conformed to those specified in Table 5. If not, repeat test.

NOTE 19—Test Method D86 distillation residues for gasoline, kerosine, and distillate diesel are *typically* 0.9–1.3, 0.9–1.3, and 1.0–1.4 volume %, respectively.

NOTE 20—The test method is not designed for the analysis of distillate fuels containing appreciable quantities of residual material (see 1.2 [1.2 The test method is designed for the analysis of distillate fuels; it is not applicable to products containing appreciable quantities of residual material.]).

10.19.2 *Group 0*—Cool the 5-mL graduated cylinder to below 5°C. Record the volume in the graduated cylinder, to the nearest 0.1 mL, as percent residue.

10.19.3 *Groups 1, 2, 3, and 4*—Record the volume in the 5-mL graduated cylinder, to the nearest 0.1 mL, as percent residue.

10.20 If the intent of the distillation is to determine the percent evaporated or percent recovered at a predetermined corrected temperature reading, modify the procedure to conform to the instructions described in Annex A4.

10.21 Examine the condenser tube and the side arm of the flask for waxy or solid deposits. If found, repeat the test after making adjustments described in Footnote A of Table 5.

TABLE 1 Preparation of Apparatus

	Group 0	Group 1	Group 2	Group 3	Group 4
Flask, mL	100	125	125	125	125
ASTM distillation thermometer	7C (7F)	7C (7F)	7C (7F)	7C (7F)	8C (8F)
IP distillation thermometer range	low	low	low	low	high
Flask support board	A	B	B	C	C
diameter of hole, mm	32	38	38	50	50
Temperature at start of test					
Flask °C	0–5	13–18	13–18	13–18	not above
°F	32–40	55–65	55–65	55–65	ambient
Flask support and shield	not above	not above	not above	not above	
	ambient	ambient	ambient	ambient	
Receiving cylinder and 100 mL charge					
°C	0–5	13–18	13–18	13–18 ^A	13–ambient ^A
°F	32–40	55–65	55–65	55–65 ^A	55–ambient ^A

^A See 10.3.1.1 for exceptions.

TABLE 3 Sampling, Storage, and Sample Conditioning

TABLE 5 Sampling, Storage, and Sample Conditioning						
		Group 0	Group 1	Group 2	Group 3	Group 4
Temperature of sample bottle	°C	<5	<10			
	°F	<40	<50			
Temperature of stored sample	°C	<5	<10 ^A	<10	ambient	ambient
	°F	<40	<50 ^A	<50	ambient	ambient
Temperature of sample after conditioning prior to analysis	°C	<5	<10	<10	ambient or 9 to 21°C above pour point ^B	ambient or
	°F	<40	<50	<50	ambient or 48 to 70°F above pour point ^B	ambient or
If sample is wet		resample	resample	resample	dry in accordance with 7.5.3	
If resample is still wet ^C		dry in accordance with 7.5.2				

^A Under certain circumstances, samples can also be stored at temperatures below 20°C (68°F). See also 7.3.3 and 7.3.4.

^B If sample is (semi)-solid at ambient temperature, see also 10.3.1.1.

^C If sample is known to be wet, resampling may be omitted. Dry sample in accordance with 7.5.2 and 7.5.3.

TABLE 5 Conditions During Test Procedure

		Group 0	Group 1	Group 2	Group 3	Group 4
Temperature of cooling bath ^A	°C	0–1	0–1	0–5	0–5	0–60
	°F	32–34	32–34	32–40	32–40	32–140
Temperature of bath around receiving cylinder	°C	0–4	13–18	13–18	13–18	±3
	°F	32–40	55–65	55–65	55–65	±5 of charge temperature
Time from first application of heat to initial boiling point, min		2–5	5–10	5–10	5–10	5–15
Time from initial boiling point to 5 % recovered, s			60–100	60–100		
Time from initial boiling point to 10 % recovered, min		3–4				
Uniform average rate of condensation from 5 % recovered to 5 mL in flask, mL/min		4–5	4–5	4–5	4–5	4–5
Time recorded from 5 mL residue to end point, min		5 max	5 max	5 max	5 max	5 max

^A the proper condenser bath temperature will depend upon the wax content of the sample and of its distillation fractions. The test is generally performed using one single condenser temperature. Wax formation in the condenser can be deduced from (a) the presence of wax particles in the distillate coming off the drip tip, (b) a higher distillation loss than what would be expected based on the initial boiling point of the specimen, (c) an erratic recovery rate and (d) the presence of wax particles during the removal of residual liquid by swabbing with a lint-free cloth (see 8.3). The minimum temperature that permits satisfactory operation shall be used. In general, a bath temperature in the 0 to 4°C range is suitable for kerosine, Grade No. 1 fuel oil and Grade No. 1-D diesel fuel oil. In some cases involving Grade No. 2 fuel oil, Grade No. 2-D diesel fuel oil, gas oils and similar distillates, it may be necessary to hold the condenser bath temperature in the 38 to 60°C range.

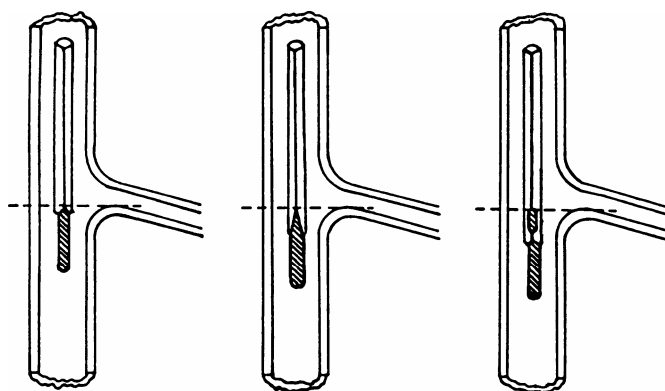


FIG. 5 Position of Thermometer in Distillation Flask

D402 - 02 Procedure Section



Designation: D402-02

Standard Test Method for Distillation of Cut-Back Asphaltic (Bituminous) Products¹

8. Procedure

8.1 Correct the temperatures to be observed in the distillation if the elevation of the laboratory at which the distillation is made deviates 150 m or more from sea level. Corrected temperatures for the effect of altitude are shown in Table 1 and Table 2. If the prevailing barometric pressure in millimetres of mercury is known, correct the temperature to be observed with the corrections shown in Table 3. *Do not correct for the emergent stem of the thermometer.*

NOTE 2—Table 3 covers a wide range of temperatures from 160 to 360°C (320 to 680°F) and is to be preferred for world-wide specifications other than ASTM/IP specifications.

8.2 Apply heat so that the first drop of distillate falls from the end of the flask side-arm in 5 to 15 min. Conduct the distillation so as to maintain the following drop rates, the drop count to be made at the tip of the adapter:

50 to 70 drops per minute to 260°C (500°F)
20 to 70 drops per minute between 260 and 316°C (500 and 600°F)
Not over 10 min to complete distillation from 316 to 360°C (600 to 680°F)

8.2.1 Record the volumes of distillate to the nearest 0.5 mL in the receiver at the corrected temperatures. If the volume of distillate recovered is critical, use receivers graduated in 0.1-mL divisions and immersed in a transparent bath maintained at $15.6 \pm 3^\circ\text{C}$.

NOTE 3—Some cut-back asphaltic products yield either no distillate or very little distillate over portions of the temperature range to 316°C (600°F). In this case it becomes impractical to maintain the above distillation rates. For such cases the intent of the method shall be met if the rate of rise of temperature exceeds 5°C (9°F)/min.

8.3 When the temperature reaches the corrected temperature of 360°C (680°F), cut off the heat and remove the flask and thermometer. With the flask in a pouring position, remove the thermometer and immediately pour the contents into the residue container. The total time from cutting off the heat to starting the pour shall not exceed 30 s. When pouring, the side-arm should be substantially horizontal to prevent condensate in the side-arm from being returned to the residue.

NOTE 4—The formation of skin on the surface of a residue during cooling entraps vapors which will condense and cause higher penetration results when they are stirred back into the sample. If skin begins to form during cooling, it should be gently pushed aside. This can be done with a spatula with a minimum of disturbance to the sample.

8.4 Allow the condenser and any distillates trapped in the condenser neck to drain into the receiver and record the total volume of distillate collected as total distillate to 360°C (680°F).

8.5 When the residue has cooled until fuming just ceases, stir thoroughly and then, when the material reaches $135 \pm 5^\circ\text{C}$ ($275 \pm 9^\circ\text{F}$), pour into the receptacles for testing for properties such as penetration, viscosity, or softening point. Proceed as required by the appropriate ASTM or IP method from the point that follows the pouring stage.

8.6 If desired, the distillate, or the combined distillates from several tests, may be submitted to a further distillation, in accordance with Test Method D86 – IP 123, or, when the distillate is of coal-tar origin, Method C.O.3.

TABLE 1 Corrected Distillation Temperatures for Various Altitudes, °C

Elevation above Sea Level, m	Distillation Temperatures for Various Altitudes, °C				
-300	192	227	262	318	362
-150	191	226	261	317	361
0	190	225	260	316	360
150	189	224	259	315	359
300	189	223	258	314	358
450	188	223	257	313	357
600	187	222	257	312	356
750	186	221	256	311	355
900	186	220	255	311	354
1050	185	220	254	310	353
1200	184	219	254	309	352
1350	184	218	253	308	351
1500	183	218	252	307	351
1650	182	217	251	306	350
1800	182	216	250	306	349
1950	181	216	250	305	348
2100	180	215	249	304	347
2250	180	214	248	303	346
2400	179	214	248	303	346

TABLE 2 Corrected Distillation Temperatures for Various Altitudes, °F

Elevation above sea level, m (ft)	Distillation Temperatures for Various Altitudes, °F				
-300	377	440	503	604	684
-150	375	438	502	602	682
0	374	437	500	600	680
150	373	436	499	598	678
300	371	434	497	597	676
450	370	433	495	595	675
600	369	431	494	593	673
750	368	430	493	592	671
900	366	429	491	590	669
1050	365	427	490	589	668
1200	364	426	488	587	666
1350	363	425	487	586	665
1500	362	424	486	584	663
1650	360	422	484	583	661
1800	359	421	483	581	660
1950	358	420	482	580	658
2100	357	419	481	579	657
2250	356	418	479	577	655
2400	355	416	478	576	654

TABLE 3 Factors for Calculating Temperature Corrections

Nominal Temperatures, °C (°F)	Correction ^A per 10 mm Hg Difference in Pressure, °C (°F)
160 (320)	0.514 (0.925)
175 (347)	0.531 (0.957)
190 (374)	0.549 (0.989)
225 (437)	0.591 (1.063)
250 (482)	0.620 (1.116)
260 (500)	0.632 (1.138)
275 (527)	0.650 (1.170)
300 (572)	0.680 (1.223)
315.6 (600)	0.698 (1.257)
325 (617)	0.709 (1.277)
360 (680)	0.751 (1.351)

^A To be subtracted in case the barometric pressure is below 760 mm Hg; to be added in case barometric pressure is above 760 mm Hg.

D850 - 03 Procedure Section



Designation: D850-03

Standard Test Method for Distillation of Industrial Aromatic Hydrocarbons and Related Materials¹

10. Procedure

10.1 *Manual Distillation Procedure:*

10.1.1 Connect the flask to the condenser apparatus as described in Section 9. Fit the thermometer to the flask as described in 9.1.

10.1.2 Heat the flask slowly, especially after boiling has begun, so as to allow the mercury column of the thermometer to become fully expanded before the first drop distills over. Regulate the rate of heating so that the ring of condensing vapor on the wall of the flask reaches the lower edge of the side arm in not less than 90 s, and preferably approximately 120 s, from the start of the rise of the vapor ring. The total time from the start of heating until the first drop falls into the receiver should be not less than 5 nor more than 10 min. Avoid major changes in heating rate. Even operation is best gained through experience with the method. When distillation starts, adjust the receiver to allow condensation to flow down its inner wall to prevent loss by spattering; then adjust the heater to continue the distillation at the rate of 5 to 7 mL/min (about 2 drops/s). Maintain this rate, and continue the distillation to dryness. The total yield of distillate when testing close boiling benzenes, toluenes, and xylenes shall be not less than 97 %, and when testing wider boiling refined products and light oils, shall be not less than 95 %; otherwise, the test shall be repeated.

10.1.3 Take the temperature reading when the first drop of distillate falls into the receiving cylinder and report as the initial boiling point (IBP). If necessary, take additional readings when 5, 10, each additional 10 up through 90, and 95 % of the specimen has just distilled over. Take a final reading when the liquid just disappears from the lowest point in the flask, and report this reading as the dry point temperature. When testing crude materials, a decomposition point, rather than a dry point, may be obtained. When a decomposition point is reached at the end of a distillation, the temperature will frequently cease to rise and begin to fall. In this case, take the temperature at the decomposition point as the maximum temperature observed. The decomposition point may also be indicated by the appearance of heavy fumes in the flask. Should that occur, record the temperature at the time the bulb of the flask becomes substantially full of fumes. If a decomposition rather than a dry point is observed, so note when recording results.

10.1.4 Observe and record any correction for inaccuracy of the thermometer at the time and place of the distillation test.

10.2 *Automatic Distillation Procedure:*

10.2.1 Connect the distillation flask to the automatic distillation equipment as described in 9.2. Fit the temperature measuring device to the flask for automatic distillation equipment according to the manufacturer's instructions.

10.3 *Barometer Reading and Temperature of the Barometer*—The observed barometric pressure shall be corrected by reference to standard tables and reported in terms of millimeters of mercury at 0°C.

D1078 - 03 Procedure Section



Designation: D1078-03

Standard Test Method for Distillation Range of Volatile Organic Liquids¹

9. Procedure

9.1 Manual Distillation Procedure:

9.1.1 Using the graduated receiver measure 100 ± 0.5 mL of the temperature-adjusted sample. Remove the flask from the apparatus and transfer the fresh specimen directly to the flask, allowing the graduate to drain for 15 to 20 s.

NOTE 6—For viscous liquids, a longer drainage period may be necessary to complete the transfer of the specimen to the flask, but the drainage time should not exceed 5 min. Do not allow any of the specimen to enter the vapor tube.

9.1.2 Connect the flask to the condenser by inserting the vapor tube of the flask into the condenser, making a tight connection with a well-rolled cork or similar material. Adjust the position of the heat shield so that the neck of the flask is vertical and the vapor tube extends into the condenser tube a distance of 25 to 50 mm. Have the bottom of the flask resting firmly in the hole of the heat shield. Insert the thermometer as described in 8.1.2. Place the receiver, without drying, at the outlet of the condenser tube in such a position that the condenser tube extends into the graduate at least 25 mm but does not extend below the 100-mL mark. If the initial boiling point of the material is below 70°C, immerse the cylinder in a transparent bath and maintain at a temperature of 10 to 20°C throughout the distillation. Place a flat cover on the top of the graduate to prevent condensed moisture from entering the graduate.

9.1.3 A certain amount of judgment is necessary in choosing the best operating conditions to get acceptable accuracy and precision for materials having different distilling temperatures. As a general guide, it is recommended that:

9.1.3.1 For materials having an initial boiling point below 150°C, the following conditions be established:

Heat Shield—Hole size, 32-mm diameter.

Heating Rate—Time from application of heat to first drop of distillate, 5 to 10 min, and time of rise of vapor column in neck of flask to side arm, 2½ to 3½ min.

9.1.3.2 For materials having an initial boiling point above 150°C, the following conditions should be established:

Heat Shield—Hole size, 38-mm diameter.

Heating Rate—Time from application of heat to first drop of distillate, 10 to 15 min, and time of rise of vapor column in neck of flask to side arm, sufficiently rapid to permit collection of the first drop of distillate within 15 min of the start of heating.

9.1.4 Adjust the heat input so that the distillation proceeds at a rate of 4 to 5 mL/min (approximately 2 drops per second), and move the receiving cylinder so that the tip of the condenser tube touches one side of the cylinder after the first drop falls (initial boiling point). Record the readings of the distillation thermometer after collecting 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 95 mL of distillate.

9.1.5 Without changing the heater setting, continue distillation beyond the 95 % point until the dry point is observed. Record the temperature at this point as the dry point (Section 3). If a dry point is not obtained (that is, if active decomposition should occur before the dry point is reached, as evidenced by a rapid evolution of vapor or heavy fumes; or if there is liquid remaining on the bottom of the flask when the maximum temperature is observed on the distillation thermometer), record this fact.

9.1.6 When a dry point cannot be obtained, report as the end point the maximum temperature observed on the distillation thermometer or final boiling point (Section 3). When active decomposition is encountered, the rapid evolution of vapor and heavy fumes is usually followed by a gradual decrease in the distillation temperature. Record the temperature and report as the decomposition point (Section 3). If the expected drop in temperature does not occur, record the maximum temperature observed on the distillation thermometer 5 min after the 95 % point has been reached, and report as “end point, 5 min.” This notation shows that a true end point could not be reached within the given time limit. In any event, the end point should not exceed 5 min after the 95 % point.

9.1.7 Read and record the barometric pressure.

9.1.8 After the condenser tube has drained, read the total volume of distillate and record it as recovery. The total yield of distillate from a material having a distillation range of 10°C or less should be not less than 97 % for

nonviscous liquids. For viscous liquids and materials having a wider distillation range than 10°C, a yield of 95 volume % is satisfactory. If yields are not obtained within these limits, repeat the test.

9.1.9 If any residue is present, cool to room temperature and pour into a small cylinder graduated in 0.1-mL subdivisions. Measure the volume and record it as residue. Record the difference between 100 and the sum of the residue plus recovery as distillation loss.

9.2 Automatic Distillation Procedure:

9.2.1 Using the automatic distillation receiver measure 100 ± 0.5 mL of the temperature-adjusted sample. Transfer the fresh specimen directly to the flask, allowing the receiver to drain for 15 to 20 s (see Note 6).

NOTE 6—For viscous liquids, a longer drainage period may be necessary to complete the transfer of the specimen to the flask, but the drainage time should not exceed 5 min. Do not allow any of the specimen to enter the vapor tube.

9.2.2 Connect the distillation flask to the condenser and fit the temperature measuring device to the flask according to the instrument manufacturer's instruction.

9.2.3 Start the distillation following the instrument manufacturer's instruction.

D1160-06 Procedure Section



Designation: D1160-06

Standard Test Method for Distillation of Petroleum Products at Reduced Pressure¹

10. Procedure

10.1 Determine when the temperature sensor was last calibrated. Recalibrate according to Annex A1 if more time has elapsed than that specified in Annex A1.

10.2 Set the temperature of the condenser coolant to at least 30°C below the lowest vapor temperature to be observed in the test.

NOTE 3—A suitable coolant temperature for distillation of many materials is 60°C.

10.3 From the density of the sample determine the weight, to the nearest 0.1 g, equivalent to 200 mL of the sample at the temperature of the receiver. Weigh this quantity of oil into the distillation flask.

10.4 Lubricate the spherical joints of the distillation apparatus with a suitable grease (Note 4). Make certain that the surfaces of the joints are clean before applying the grease, and use only the minimum quantity required. Connect the flask to the lower spherical joint of the distilling head, place the heater under the flask, put the top mantle in place and connect the rest of the apparatus using spring clamps to secure the joints.

NOTE 4—Silicone high-vacuum grease has been used for this purpose. An excess of this lubricant applied to the flask joint can cause the sample to foam during distillation.

10.5 Place a few drops of silicone oil in the bottom of the thermowell of the flask and insert the temperature sensor to the bottom. The sensor can be secured with a wad of glass wool at the top of the thermowell.

10.6 Start the vacuum pump and observe the flask contents for signs of foaming. If the sample foams, allow the pressure on the apparatus to increase slightly until the foaming subsides. Apply gentle heat to assist the removal of dissolved gas. For general directions for suppression of excessive foaming of the sample, see A6.2.

10.7 Evacuate the apparatus until the pressure reaches the level prescribed for the distillation (Note 5). Failure to reach the distillation pressure, or the presence of a steady increase in pressure in the apparatus with the pump blocked off, is evidence of significant leakage into the system. Bring the system to atmospheric condition using a nitrogen bleed and relubricate all joints. If this does not result in a vacuum-tight system, examine other parts of the system for leaks.

NOTE 5—The most commonly prescribed pressure is 1.3 kPa (10 mm Hg). For heavy products with a substantial fraction boiling above 500°C, an operating pressure of 0.13 kPa (1 mm Hg) or 0.26 kPa (2 mm Hg) is generally specified.

10.8 After the desired pressure level has been attained, turn on the heater and apply heat as rapidly as possible to the flask, without causing undue foaming of the sample. As soon as vapor or refluxing liquid appears at the neck of the flask, adjust the rate of heating so that the distillate is recovered at a uniform rate of 6 to 8 mL/min (Note 6).

NOTE 6—It is extremely difficult to achieve the desired rate at the very beginning of the distillation, but this rate should be attainable after the first 10 % of the distillate has been recovered.

10.9 Record the vapor temperature, time, and the pressure at each of the following volume percentage fractions of the charge collected in the receiver: IBP, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95, and at the end point. If the liquid temperature reaches 400°C, or if the vapor reaches a maximum temperature before the end point is observed, record the vapor temperature reading and the total volume recovered at the time the distillation is discontinued. When a product is tested for conformity with a given specification, record all requested observations, whether or not they are listed above.

NOTE 7—The maximum vapor temperature will result either from complete distillation of the oil or from the onset of cracking.

10.10 If a sudden increase in pressure is observed, coupled with the formation of white vapors and a drop in the vapor temperature, the material being distilled is showing significant cracking. Discontinue the distillation immediately and record the fact on the run sheet. If necessary, rerun the distillation with a fresh sample at lower operating pressure.

10.11 Lower the flask heater 5 to 10 cm and cool the flask and heater with a gentle stream of air or, preferably, with a stream of carbon dioxide (Note 8). Repressure the contents of the still with dry nitrogen (**Warning**—Repressuring the contents of the still with air while it contains hot oil vapors can result in fire or explosion.) if it is necessary to dismantle the apparatus before it has cooled below 200°C. Carbon dioxide can also be used for repressuring, provided liquid nitrogen traps are not in use. (**Warning**— In addition to other precautions, it is recommended to discontinue the distillation at a maximum vapor temperature of 350°C. Operating the distillation flask at temperatures above 350°C for prolonged periods at pressures below 1 kPa may also result in thermal deformation of the flask. In this case, discard the flask after use. Alternatively, use a quartz flask.)

NOTE 8—A gentle stream of carbon dioxide is preferred to cool the flask to prevent fire in the event the flask cracks during the test or during the cooling cycle.

10.12 Bring the temperature of the cold trap mounted before the vacuum source back to ambient temperature. Recover, measure, and record the volume of the light products collected in the trap.

10.13 Remove the receiver, empty it, and place it back into the instrument for the cleaning cycle, or use a separate, empty receiver. Remove the flask and replace with a flask filled with a cleaning solvent (Note 9). Run a distillation at atmospheric pressure to clean the unit. At the end of this cleaning run, remove the flask and receiver and blow a gentle stream of air or nitrogen to dry the unit.

NOTE 9—Toluene or cyclohexane can be used as cleaning solvent.

D2892-05 Procedure Section



Designation: D2892-05

Standard Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)¹

10. Procedure

10.1 *Charging:*

10.1.1 The charge size shall be such that the dynamic hold up as determined in accordance with Annex A2 is between 1 and 4 % of the charge when operating at 75 % of maximum boilup (see Table 1). Chill the flask to a temperature not lower than 0°C.

10.1.2 Insert the stirring device or place some pieces of glass or porcelain into the flask to control bumping.

10.1.3 Determine the density of the sample by Test Method D941, D1217, or D1298.

10.1.4 Calculate to within $\pm 5\%$ the mass of crude petroleum corresponding to the desired volume of the charge. Weigh to the nearest 1 % this quantity of sample into the flask.

10.1.5 Attach the flask to the column and connect the pressure drop measuring device. Install the heating system, stirrer, and support device. (**Warning**—Poisonous H_2S gas is frequently evolved from crude oil and precautions must be taken either to absorb the gas that passes through the cold trap or to vent it to a safe place.)

10.2 Debutanization:

10.2.1 For necessary apparatus refer to 6.1.5 and 6.1.6.

10.2.2 Begin circulation of refrigerant at a temperature no higher than -20°C in the condenser, distillate cooler, and receiver, if so equipped.

10.2.3 Record the barometric pressure at the beginning and periodically throughout the distillation.

10.2.4 Apply heat to the flask at such a rate that vapors reach the top of the column between 20 and 50 min after startup. Adjust heat input so as to achieve a pressure drop of less than 0.13 kPa/m (1.0 mm Hg/m) in packed columns or less than 0.065 kPa (0.5 mm Hg) in real plate columns. Program automated equipment in accordance with the preceding directions. Turn on the stirring device if used.

10.2.5 Allow the column to operate at total reflux until the vapor temperature reaches equilibrium but not longer than 15 min after the first drop of condensate appears in the reflux divider.

10.2.6 Record the vapor temperature as the initial vapor temperature.

10.2.7 Stop the circulation of the refrigerant and observe the vapor temperature. When the vapor temperature reaches 15°C , start the circulation of refrigerant again.

10.2.8 If the vapor temperature drops below 15°C , continue refluxing for at least 15 min. Repeat 10.2.7. If the vapor temperature remains at 15°C or rises, continue with the atmospheric distillation. (**Warning**—The following three steps should not be done until after the first naphtha cut has been removed to ensure that all the light gases have been recovered.)

10.2.9 Remove and weigh the dry ice traps containing light hydrocarbon liquid after carefully wiping them dry.

10.2.10 Sample the contents of the first dry ice trap using a 10 to 50 mL pressure vessel evacuated to no lower than 26.6 kPa (200 mm Hg). Keep all containers at the temperature of dry ice to ensure no loss of volatiles. The first trap next to the condenser should contain all of the sample. If condensate is found in the second trap, sample both traps or combine the contents before sampling.

10.2.11 Submit the trap sample and gas balloon, if used, for analysis by a suitable gas chromatographic test method to be reported on a fixed-gas free basis. Test Methods D6729, D6730, and D6733, equipped with liquid or gas sampling valves, or both, for sample introduction equipment have been used successfully for this analysis.

10.3 Distillation at Atmospheric Pressure:

10.3.1 Maintain a temperature below -20°C in the lines of the distillate cooler and receiver as well as in the condenser. Turn on the column mantle heat controller and maintain the column jacket temperature 0 to 5°C below the vapor temperature.

10.3.2 Regulate the heat input as necessary to establish and maintain a boilup rate approximately 75 % of maximum. Fig. 3 can be used as a guide for Propak. Rates for other sizes can be estimated by multiplying the boilup rate in Table 1 by the cross-sectional area of the column and dividing by the sum of the reflux ratio + 1.

10.3.3 Commence takeoff at a reflux ratio of 5:1 and total cycle time of not over 30 s nor less than 18 s.

10.3.4 Take off distillate in separate and consecutive fractions of suitable size. The recommended size of fraction is that corresponding to 5 or 10°C in vapor temperature. Collect fractions boiling below 65°C in receivers cooled to 0°C or below. When the vapor temperature reaches 65°C , refrigerant in the condenser and related coolers can be discontinued and water at ambient temperature substituted.

10.3.5 At the end of each fraction and at each cut point, record the following observations:

10.3.5.1 Time in hours and minutes,

10.3.5.2 Volume in millilitres,

10.3.5.3 Vapor temperature in $^\circ\text{C}$ to the nearest 0.5°C ,

10.3.5.4 Temperature of the boiling liquid in $^\circ\text{C}$ to the nearest 1°C ,

10.3.5.5 Atmospheric pressure in kPa (mm Hg), and

10.3.5.6 Pressure drop in the column in kPa (mm Hg).

10.3.6 If signs of flooding are observed, reduce the heating rate while continuing takeoff until steady conditions are restored. If a cut point is encountered during this period, stop the distillation, cool the charge, and recombine the off-condition cuts. Restart the distillation with a period at total reflux, not to exceed 15 min, to restore operating conditions before continuing takeoff. Do not make a cut within 5°C of startup.

10.3.7 Continue taking cuts until the desired maximum vapor temperature is reached or until the charge shows signs of cracking. Pronounced cracking is evidenced by a fog appearing in the flask and later at the reflux divider. Do not allow the vapor temperature to exceed 210°C nor the temperature of the boiling liquid to exceed 310°C.

10.3.8 Shut off the reflux valve and the heating system. Allow the contents to cool to such a temperature that the distillation can be commenced at 13.3 kPa (100 mm Hg) without flooding. This temperature can be estimated by adding the ΔT between the liquid and vapor temperatures found for the column during atmospheric operation to the expected initial vapor temperature at the reduced pressure, or by subtracting the ΔT from the last recorded liquid temperature.

NOTE 4—Cooling of the liquid in the flask can be accelerated by blowing a gentle stream of compressed air onto the flask after its heating mantle has been removed. Avoid strong jets of cold air. Alternately, turn on coolant in the quench coil of the flask, if used.

10.3.9 Weigh all fractions and determine their densities.

10.3.10 Submit the first distillate fraction for analysis by gas chromatography.

10.4 *Distillation at 13.3 kPa (100 mm Hg):*

10.4.1 If further cuts at higher temperatures are required, distillation can be continued at reduced pressures, subject to the maximum temperature that the boiling liquid will stand without significant cracking. This is about 310°C in most cases. Notable exceptions are crude oils containing heat-sensitive sulfur compounds. In any case, do not make a cut within 5°C of the temperature at startup because the column will not be at equilibrium.

10.4.2 Connect a vacuum pumping and control system to the apparatus as shown in Fig. 1.

10.4.3 Start the vacuum pump and adjust the pressure downward gradually to the value of 13.3 kPa (100 mm Hg) or set the pressure regulator at this value. The temperature of the liquid in the flask must be below that at which it will boil at 13.3 kPa (100 mm Hg). If the liquid boils before this pressure is reached, increase the pressure and cool further until the desired pressure can be achieved without boiling.

10.4.4 Apply heat to the boiler and reestablish reflux at any moderate rate in the reflux divider for about 15 min to reheat the column to operating temperature. Momentarily stop heat input and raise the pressure with N₂ for 1 min to drop the holdup into the distillation flask.

10.4.5 Reapply heat to the distillation flask and adjust the rate of heating to maintain a constant pressure drop equivalent to the boilup rate of approximately 75 % of the maximum rate for this pressure and begin takeoff without delay. The approximate pressure drops required for this purpose are indicated in Fig. 3. Maintain a column insulation temperature 0 to 5°C below the vapor temperature throughout the operation.

10.4.6 Remove separately, cuts of suitable size as in 10.3.4.

10.4.7 At the end of each distillate fraction and at each cut point, record the following observations:

10.4.7.1 Time in hours and minutes,

10.4.7.2 Volume in millilitres observed at ambient temperature,

10.4.7.3 Vapor temperature in °C to the nearest 0.5°C with correction, if any,

10.4.7.4 Temperature of the boiling liquid in °C to the nearest 1°C,

10.4.7.5 Pressure drop in the column in kPa (mm Hg),

10.4.7.6 Operating pressure measured at the top of the column in kPa (mm Hg) absolute with correction, if any, and

10.4.7.7 AET using the equations given in Annex A8.

10.4.8 Continue taking cuts until the desired maximum point is reached or until the charge shows signs of cracking. Pronounced cracking is evidenced by the evolution of gases as indicated by rising pressure as well as a fog appearing in the flask (see Note 4). Do not allow the temperature of the boiling liquid to exceed 310°C.

(**Warning**—Automatic vacuum controllers could mask a slight rise in pressure due to cracking. Vigilance is required to avoid this.)

10.4.9 Shut off the reflux valve and the heating system. Allow the contents to cool to such a temperature that the distillation can be commenced at a lower pressure without boiling. This temperature can be estimated by adding the ΔT between the liquid and vapor temperatures found for the column during operation to the expected initial vapor temperature at the lower pressure, or by subtracting the ΔT from the last recorded liquid temperature.

10.4.10 Weigh all fractions and determine their densities at 15°C.

10.5 *Distillation at Lower Pressures:*

10.5.1 If the final cut point has not been reached, distillation can be continued at a lower pressure subject to the same limitation as before (see 10.4.1). Only one pressure level between 13.3 kPa (100 mm Hg) and 0.266 kPa (2 mm Hg) is permitted. Where the maximum cut point is 400°C AET, the minimum pressure is recommended.

10.5.2 Adjust the pressure to the desired level. If the liquid boils before the pressure is reached, increase the pressure and cool further until the desired pressure can be achieved without boiling. Follow the procedure in 10.4.4.

10.5.3 Circulate cooling water in the condenser and liquid cooler either at ambient temperature or warmed to a temperature that will ensure that wax does not crystallize in the condenser or takeoff lines. Alternatively, leave the cooling coils full of water but vented and not circulating, or else circulate a stream of air instead of water as a coolant.

10.5.4 Continue vacuum operation as in 10.4.5 through 10.4.8. During this operation, a reflux ratio of 2:1 is allowed if mutually agreed upon in advance and noted in the report. Correct observed and corrected vapor temperatures to AET using the equations given in Annex A8.

10.5.5 Check periodically that the condensate drips normally in the condenser and that the distillate flows smoothly into the takeoff line. If crystallization is observed, allow the coolant in the condenser to warm as in 10.5.3.

10.5.6 When the final cut point has been reached, or when limits of boiling liquid temperature and column pressure prevent further distillation, turn off the reflux valve and heating system and allow to cool with the vacuum still applied.

10.5.7 When the temperature of the residue in the flask has fallen below 230°C, shut off the vacuum pump. Vent the fractionating unit with nitrogen or other inert gas. Do not use air. (**Warning**—Air is suspected of initiating explosions in fractionating units that are vented while too hot, such as at the end of a run.)

10.5.8 Stop circulation of coolant in the condenser and ancillary equipment. Disconnect the flask. Recover the static holdup of the column (wettage) by distilling a small quantity of solvent such as toluene in a separate flask to wash the column, condenser, and takeoff system. Evaporate the solvent from the collected residue at 10°C above the boiling point of the solvent, using a small purge of nitrogen. For distillations not involving disagreement, or by mutual consent, the holdup can be estimated using a graph similar to Fig. 4. The density of the holdup is estimated by extrapolation of the density line for the preceding cuts. The static holdup can be treated as a separate small cut or blended into the bottoms before inspections are made. The latter must be done if other analyses besides density are to be performed on the residue.

10.5.9 Weigh all fractions and the residue in the flask and determine their densities at 15°C by Test Method D4052 or by another suitable method. Convert the density to 15°C, if necessary.

NOTE 5—Heavier flasks, such as those for 50 and 70-mm diameter columns, are not normally removed for weighing. In these cases the residue can be discharged at a temperature not over 200°C into a tared container for weighing. Nitrogen pressure of approximately 6.7 kPa (50 mm Hg) will be sufficient for this. Wettage in these cases will include that of the column and the flask together.

D5236-03 Procedure Section



Designation: D5236-03

Standard Test Method for Distillation of Heavy Hydrocarbon Mixtures (Vacuum Potstill Method)¹

9. Procedure

9.1 Determine the density of the sample by one of the following test methods: Test Method D941, D1217, D1480, D5002, or D1298. Refer to Guide D1250 to correct densities to 15°C.

9.2 Insert the stirring bar.

9.3 From Table 1, determine the volume of the charge and calculate the mass to be charged by multiplying its density by the desired volume.

9.4 Weigh this mass of charge into the flask to the nearest 0.1 %. In the case of flasks too large to handle, the flask can be put in place and the charge drawn in from a container (weighed with its transfer line) using a pressure of 90 to 95 kPa in the still. The charge may need to be warmed to facilitate transfer. Its mass can be determined from the difference.

9.5 Attach the flask to the column (in the case of smaller flasks), and put on all the heating mantles. Put the stirring device in place and turn it on. (**Warning**—Ensure that the safety shield is in place.)

9.6 A contiguous cutting scheme may be achieved in one of two ways, while remaining within the scope of the key aspects of this method. It may be achieved by gradually reducing the pressure over the course of the distillation (dynamic) or done stepwise, by slowing (or stopping) the takeoff rate to allow lowering of the operating pressure to achieve the final cut temperature. In each case, this must be done keeping in mind the necessity to avoid starving the distillation (due to a slow takeoff rate), while at the same time avoiding entrainment (by reducing too quickly the pressure applied to the system).

9.7 Apply heat to the flask at a rate that will raise the temperature of the charge quickly, but no faster than 300°C/h (540°F/h). Do not exceed a skin temperature on the flask of 400°C (750°F) or cracking may result on the walls of the flask. (**Warning**—Some hydrocarbon mixtures cannot tolerate 400°C for any useful length of time. Reducing the skin temperature may be necessary in these cases.)

9.8 Turn on the head compensation mantle and maintain the outer wall of the glass vacuum jacket at a temperature approximately 40°C below the temperature of the liquid in the flask.

9.9 Reduce the pressure in the system gradually to a suitable starting pressure. Choose from Table 2 the highest pressure that is consistent with the expected initial boiling point as well as the lowest pressure that is consistent with the maximum cutpoint, using Fig. 7 as a guide. A pressure of 0.133 kPa (1.0 mm Hg) has been found satisfactory for starting a material having an initial boiling point of 343°C (650°F) AET, such as residues from Test Method D2892 distillations.

NOTE 2—Degassing of the charge is sometimes evident before the actual distillation begins. This appears as bubbling at the surface without generation of condensable vapors.

9.10 When distillation begins, evidenced by vapors entering the neck of the flask, reduce the heat input to a level that will maintain the chosen distillation rate from Table 2 (see Note 2). Adjust the heat compensator on the head to maintain the outer wall of the glass vacuum jacket at a temperature 5°C below the vapor temperature.

NOTE 3—Although a range of distillation rates is permitted, 80 % of the maximum allowed is recommended.

9.11 In cases in which the observed initial vapor temperature will be 150°C (302°F) or lower, it is desirable to refrigerate the first fraction receiver to ensure the retention of light ends. If solid waxy material appears on the walls, warm the receiver with an infrared heat lamp or hot air gun to liquify the product in the receiver in order to improve the accuracy of the reading. In automatic operation, the receivers must be thermostated at a temperature high enough to ensure that no solidification takes place and low enough to prevent evaporation of light material.

9.12 When using the dynamic method of pressure reduction, calculate a projected final cutpoint using the operating pressure and the differential between the vapor and pot temperature as the operating envelope. Estimating that the difference between the vapor and the pot temperature remain *relatively* constant, determine if the final vapor temperature can be achieved at this pressure while remaining within the recommended limitations of the flask temperature (see 9.18). If the final cutpoint cannot be achieved at the starting pressure, the pressure should be gradually lowered toward an operating pressure that will allow the final cut to be taken. This must be done bearing in mind the associated takeoff rates for the vacuum pressures indicated in Table 2 and the limitations of the pot temperature. The pressure should be lowered enough to allow the takeoff rate to accelerate briefly while the operator is remaining vigilant to avoid entrainment. The distillation rate at the operating pressure should fall within the recommendations stated in Table 2 and should be allowed to stabilize for at least 2 min before arriving at a cutpoint. Experience has shown that reduced crude oil samples typically run well at 0.133 kPa for up to 25 - 30 % of the charge volume. Subsequent lowering of the operating pressure, as described above, has yielded satisfactory results. Repeat this procedure throughout the remainder of the distillation until an operating pressure has been attained that will allow the final cut temperature to be reached while remaining within the recommended confines of the maximum pot temperature and temperature/time constraints of flask temperature (see 9.18).

9.13 When the receiver is full, or when a cutpoint is reached, isolate the receiver or move to the next one, as the case may be.

9.13.1 In manual operation, isolate the receiver using the vacuum adaptor and vent it to atmospheric pressure before replacing it with another tared receiver. Apply vacuum, and when the new receiver is at approximately system pressure, reconnect it to the system.

9.13.2 In automatic operation, receivers are changed automatically and do not normally need further attention.

9.14 Record the following observations:

9.14.1 Time in hours and minutes,

9.14.2 Volume of distillate in millilitres,

- 9.14.3 Vapor temperature to nearest 0.5°C,
- 9.14.4 Liquid temperature in the flask in °C,
- 9.14.5 Pressure in the head to nearest 1 %, and
- 9.14.6 Atmospheric equivalent temperature by calculation as prescribed in Annex A4.
- 9.15 Proceed to 9.18.

9.16 Alternatively, the stepwise method can be achieved by initializing the distillation and operating at the pressure at which the distillation stabilizes (see 9.9). Continue taking product and making cuts until the final cutpoint is achieved or until the temperature of the boiling liquid reaches approximately 290°C (554°F).

9.17 At this point, if the final cutpoint cannot be achieved before reaching 320°C (608°F) in the boiling liquid, reduce the heat input to zero until the distillation slows or stops. This will take 2 to 10 min depending on the amount of material in the flask. Reduce the pressure slowly to a level that will allow for a reasonable amount of overhead product to evolve at the new pressure level. A pressure reduction by a factor of five or six has been shown to be necessary to produce a viable quantity of overhead at the new pressure level.

9.18 Restore the heat to about 90 % of the previous level and then adjust to give the desired rate at the lower level (see Table 2). Do not take any cuts until the pressure has stabilized at the new level for at least 2 min. Repeat 9.16 and 9.17 until a pressure level has been reached that will allow for achieving the final cutpoint before the boiling liquid reaches a temperature of 320°C (608°F).

9.19 Continue taking product as long as there is no indication of incipient cracking. Addition of heat to the flask to maintain product rate should be done with great care. It is recommended to achieve the final cutpoint in less than 1 h after the flask temperature has risen above 310°C (590°F).

9.20 The distillation shall be discontinued immediately as soon as signs of incipient cracking are observed (see Note 4).

NOTE 4—Cracking will significantly affect the quality of the cuts and the residue, for example, the densities and viscosities would be significantly lower than those obtained without cracking.

NOTE 5—Incipient cracking is usually first observed from a distinct and persistent rise in pressure (for example, >10 % of pressure set point) or an increase of the demand on the vacuum pump capacity. However, automatic vacuum controllers tend to mask these phenomena. Other signs of incipient cracking are the accumulation of thin black deposits on the glassware through the column or the appearance of a smoke-like vapor in the system after the condenser.

9.21 When either the final cutpoint or 90 volume % has been distilled or incipient cracking is observed, discontinue the distillation. Discontinue heat input to the flask and heating jacket at once and slightly raise the pressure of the system by reducing the vacuum pump capacity. Allow the residue to cool while stirring.

NOTE 6—Beyond 90 volume % distilled, the flask may be too near dryness for safe operation.

9.22 Remove the flask compensating mantle, or in the case of steel flasks, turn on the air in the quench coil.

9.23 When the temperature of the residue has fallen below 150°C (302°F), remove and weigh the flask and contents to determine the mass of the residue. For larger stills, the residue can be discharged through the charging line using a positive pressure of about 10 kPa in the still.

9.24 Weigh all overhead fractions to within 0.1 % of the charge mass.

9.25 Determine the relative density of all fractions and convert to 15°C (59°F) using Guide D1250 where applicable.

9.26 In the case of the smaller stills, recover the wettagage by boiling up a small quantity of solvent such as toluene in a separate flask to wash the head and condenser. Evaporate the solvent in a hood assisted by a stream of air and weigh directly. This wettagage may be treated as a separate fraction and its density estimated or blended into the residue before inspections are made. The latter must be done if the residue is to be analyzed for other than density. For larger stills, follow instructions given in Annex A5. Note that the holdup in the latter case includes both the overhead wettagage and the wettagage of the flask with residue and must be considered a separate fraction. Density must be measured in this case.

VAPOR PRESSURE AND V/L RATIO TEST METHODS

D323 - 99a Procedure Section



Designation: D323–99a

Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method)¹

PROCEDURE A FOR PETROLEUM PRODUCTS HAVING REID VAPOR PRESSURES BELOW 180 kPa (26 psi)

11. Procedure

11.1 *Sample Transfer*— Remove the sample from the cooling bath, uncap, and insert the chilled transfer tube (see Fig. 1). Remove the liquid chamber from the cooling bath, and place the chamber in an inverted position over the top of the transfer tube. Invert the entire system rapidly so that the liquid chamber is upright with the end of the transfer tube approximately 6 mm (0.25 in.) from the bottom of the liquid chamber. Fill the chamber to overflowing (see Note 6). Withdraw the transfer tube from the liquid chamber while allowing the sample to continue flowing up to complete withdrawal.

NOTE 6—**Precaution:** In addition to other precautions, make provision for suitable containment and disposal of the overflowing sample to avoid fire hazard.

11.2 *Assembly of Apparatus*—Immediately remove the vapor chamber from the water bath and couple the filled liquid chamber to the vapor chamber as quickly as possible without spillage. When the vapor chamber is removed from the water bath, connect it to the liquid chamber without undue movement that could promote exchange of room temperature air with the 37.8°C (100°F) air in the chamber. Not more than 10 s shall elapse between removing the vapor chamber from the water bath and completion of the coupling of the two chambers.

11.3 *Introduction of the Apparatus into Bath*—Turn the assembled apparatus upside down and allow all the sample in the liquid chamber to drain into the vapor chamber. With the apparatus still inverted, shake it vigorously eight times up and down. With the gage end up, immerse the assembled apparatus in the bath, maintained at $37.8 \pm 0.1^\circ\text{C}$ ($100 \pm 0.2^\circ\text{F}$), in an inclined position so that the connection of the liquid and vapor chambers is below the water level and carefully examine for leaks (see Note 7). If no leaks are observed, further immerse the apparatus to at least 25 mm (1 in.) above the top of the vapor chamber. Observe the apparatus for leaks throughout the test and discard the test at anytime a leak is detected.

NOTE 7—Liquid leaks are more difficult to detect than vapor leaks; and because the coupling between the chambers is normally in the liquid section of the apparatus, give it particular attention.

11.4 *Measurement of Vapor Pressure*—After the assembled apparatus has been in the water bath for at least 5 min, tap the pressure gage lightly and observe the reading. Withdraw the apparatus from the bath and repeat the instructions of 11.3. At intervals of not less than 2 min, tap the gage, observe the reading, and repeat 11.3 until a total of not less than five shakings and gage readings have been made. Continue this procedure, as necessary, until the last two consecutive gage readings are the same, indicating that equilibrium has been attained. Read the final gage pressure to the nearest 0.25 kPa (0.05 psi) and record this value as the uncorrected vapor pressure of the sample. Without undue delay, remove the pressure gage from the apparatus (see Note 8) without attempting to remove any liquid that may be trapped in the gage, check its reading against that of the pressure measuring device (see A1.6) while both are subjected to a common steady pressure that is within 1.0 kPa (0.2 psi) of the recorded uncorrected vapor pressure. If a difference is observed between the pressure measuring device and the pressure gage readings, the difference is added to the uncorrected vapor pressure when the pressure measuring device reading is higher, or subtracted from the uncorrected vapor pressure when the pressure measuring device reading is lower, and the resulting value recorded as the Reid vapor pressure of the sample.

NOTE 8—Cooling the assembly prior to disconnecting the gage will facilitate disassembly and reduce the amount of hydrocarbon vapors released into the room.

11.5 Preparation of Apparatus for Next Test:

11.5.1 Thoroughly purge the vapor chamber of residual sample by filling it with warm water above 32°C (90°F) and allowing it to drain. Repeat this purging at least five times. Purge the liquid chamber in the same manner. Rinse both chambers and the transfer tube several times with petroleum naphtha, then several times with acetone, then blow dry using dried air. Place the liquid chamber in the cooling bath or refrigerator in preparation for the next test.

11.5.2 If the purging of the vapor chamber is done in a bath, be sure to avoid small films of floating sample by keeping the bottom and top openings of the chamber closed as they pass through the water surface.

11.5.3 *Preparation of Gage*—Disconnect the gage from its manifold connection with the pressure measuring device and remove trapped liquid in the Bourdon tube of the gage by repeated centrifugal thrusts. This is accomplished in the following manner: hold the gage between the palms of the hands with the right palm on the face of the gage and the threaded connection of the gage forward. Extend the arms forward and upward at an angle of 45°. Swing the arms rapidly downward through an arc of about 135° so that centrifugal force aids gravity in removing trapped liquid. Repeat this operation at least three times or until all liquid has been expelled from the gage. Connect the gage to the vapor chamber with the liquid connection closed and place in the 37.8°C (100°F) bath to condition for the next test. (see Note 9).

NOTE 9—**Caution:** Do not leave the vapor chamber with the gage attached in the water bath for a longer period of time than necessary to condition for the next test. Water vapor can condense in the Bourdon tube and lead to erroneous results.

PROCEDURE B
FOR PETROLEUM PRODUCTS HAVING REID
VAPOR PRESSURES BELOW 180 kPa (26 psi),
(HORIZONTAL BATH)

14. Procedure

14.1 *Sample Transfer*—Remove the sample from the cooling bath, uncap, and insert the chilled transfer tube (see Fig. 1). Remove the liquid chamber from the cooling bath, and place the chamber in an inverted position over the top of the transfer tube. Invert the entire system rapidly so that the liquid chamber is upright with the end of the transfer tube approximately 6 mm (0.25 in.) from the bottom of the liquid chamber. Fill the chamber to overflowing (see Note 6). Withdraw the transfer tube from the liquid chamber while allowing the sample to continue flowing up to complete withdrawal.

14.2 *Assembly of Apparatus*—Immediately remove the vapor chamber from the water bath. Disconnect the spiral tubing at the quick action disconnect. Couple the filled liquid chamber to the vapor chamber as quickly as possible without spillage or movement that could promote exchange of room temperature air with the 37.8°C (100°F) air in the vapor chamber. Not more than 10 s shall elapse between removing the vapor chamber from the water bath and completion of the coupling of the two chambers.

14.3 *Introduction of the Apparatus into the Bath*—While holding the apparatus vertically, immediately reconnect the spiral tubing at the quick action disconnect. Tilt the apparatus between 20 and 30° downward for 4 or 5 s to allow the sample to flow into the vapor chamber without getting into the tube extending into the vapor chamber from the gage, or pressure transducer. Place the assembled apparatus into the water bath maintained at $37.8 \pm 0.1^\circ\text{C}$ ($100 \pm 0.2^\circ\text{F}$) in such a way that the bottom of the liquid chamber engages the drive coupling and the other end of the apparatus rests on the support bearing. Turn on the switch to begin the rotation of the assembled liquid-vapor chambers. Observe the apparatus for leakage throughout the test (see Note 7). Discard the test at anytime a leak is detected.

14.4 *Measurement of Vapor Pressure*—After the assembled apparatus has been in the bath for at least 5 min, tap the pressure gage lightly and observe the reading. Repeat the tapping and reading at intervals of not less than 2 min, until two consecutive readings are the same. (Tapping is not necessary with the transducer model but the reading intervals should be the same.) Read the final gage or transducer pressure to the nearest 0.25 kPa (0.05 psi) and record this value as the uncorrected vapor pressure. Without undue delay, disconnect the gage from the apparatus. Connect the gage or pressure transducer to a pressure measuring device. Check its reading against that of the pressure measuring device while both are subjected to a common steady pressure that is within 1.0 kPa (0.2 psi) of

the recorded uncorrected vapor pressure. If a difference is observed between the pressure measuring device and gage or transducer readings, the difference is added to the uncorrected vapor pressure when the pressure measuring device reading is higher, or subtracted from the uncorrected vapor pressure when the pressure measuring device reading is lower, and the resulting value recorded as the Reid vapor pressure of the sample.

14.5 Preparation of Apparatus for Next Test:

14.5.1 Thoroughly purge the vapor chamber of residual sample by filling it with warm water above 32°C (90°F) and allowing it to drain. Repeat this purging at least five times. Purge the liquid chamber in the same manner. Rinse both chambers and the transfer tube several times with petroleum naphtha, then several times with acetone, then blow dry using dried air. Place the liquid chamber in the cooling bath or refrigerator in preparation for the next test (see Note 9).

14.5.2 If the purging of the vapor chamber is done in a bath, be sure to avoid small films of floating sample by keeping the bottom and top openings of the chamber closed as they pass through the water surface.

14.5.3 *Preparation of Gage or Transducer*—In the correct operation of this procedure, liquid should not reach the gage or transducer. If it is observed or suspected that liquid has reached the gage, purge the gage as described in 11.5.3. The transducer has no cavity to trap liquid. Ensure that no liquid is present in the T handle fitting or spiral tubing by forcing a stream of dry air through the tubing. Connect the gage or transducer to the vapor chamber with the liquid connection closed and place in the 37.8°C (100°F) bath to condition for the next test.

PROCEDURE C

FOR PETROLEUM PRODUCTS HAVING REID VAPOR PRESSURES ABOVE 180 kPa (26 psi)

20. Procedure

20.1 Paragraphs 11.1 and 11.2 shall not apply.

20.2 Connect the 6.35-mm (0.25-in.) valve of the chilled liquid chamber to the ice-cooled coil. With the 12.7-mm (0.5 in.) valve of the liquid chamber closed, open the outlet valve of the sample container and the 6.35-mm (0.25-in.) valve of the liquid chamber. Open the liquid chamber 12.7-mm (0.5-in.) valve slightly and allow the liquid chamber to fill slowly. Allow the sample to overflow until the overflow volume is 200 mL or more. Control this operation so that no appreciable drop in pressure occurs at the liquid chamber 6.35-mm (0.25-in.) valve. In the order named, close the liquid chamber 12.7-mm (0.5-in.) and 6.35-mm (0.25-in.) valves; and then close all other valves in the sample system. Disconnect the liquid chamber and the cooling coil.

20.2.1 To avoid rupture because of the liquid-full condition of the liquid chamber, the liquid chamber must be quickly attached to the vapor chamber and the 12.7-mm (0.5-in.) valve opened.

20.3 Immediately attach the liquid chamber to the vapor chamber and open the liquid chamber 12.7-mm (0.5-in.) valve. Not more than 25 s shall pass in completing the assembly of the apparatus after filling the liquid chamber, using the following sequence of operations:

20.3.1 Remove the vapor chamber from the water bath.

20.3.2 Connect the vapor chamber to the liquid chamber.

20.3.3 Open the liquid chamber 12.7-mm (0.5-in.) valve.

20.4 If a dead-weight tester is used instead of the mercury manometer as a pressure measuring device (see 16.2), apply the calibration factor in kilopascals (pounds-force per square inch) established for the pressure gage to the uncorrected vapor pressure. Record this value as the calibrated gage reading and use in Section 8 in place of the pressure measuring device reading.

PROCEDURE D

FOR AVIATION GASOLINES APPROXIMATELY 50 kPa (7 psi) REID VAPOR PRESSURE

25. Procedure

25.1 Refer to Section 11.

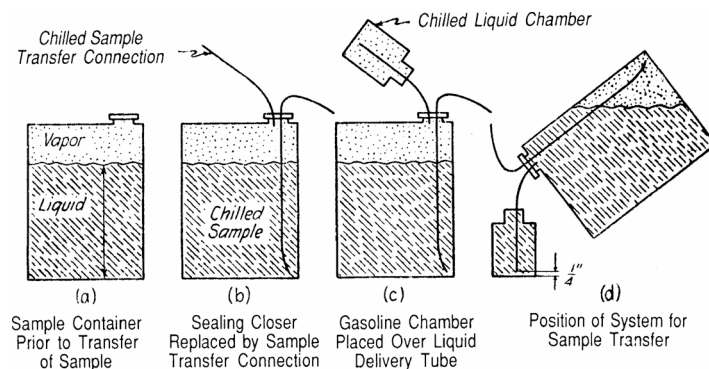


FIG. 1 Simplified Sketches Outlining Method Transferring Sample to Liquid Chamber from Open-Type Containers

D1267 - 02 Procedure Section



Designation: D1267-02

Standard Test Method for Gage Vapor Pressure of Liquefied Petroleum (LP) Gases (LP-Gas Method)¹

9. Procedure

9.1 Safe means for the disposal of vapors and liquids during this operation and in the subsequent sampling operation must be provided.

9.2 *Purging*—With the assembled apparatus in an upright position, connect the inlet valve of the lower chamber to the sample source with the sampling connection (7.2). Open the sample source valve to the apparatus. Cautiously open the bleeder valve on the upper chamber, permitting the air or vapors, or both, in the apparatus to escape until the apparatus is full of liquid. Close the lower chamber inlet valve and open the bleeder valve to its wide open position. Allow the contained liquid to evaporate until the apparatus is covered with white frost (may require more than one chilling), then invert the assembly, and expel any residual material through the bleeder valve. Allow the residual vapors to escape until the pressure in the apparatus is essentially atmospheric, then close the bleeder valve.

9.3 *Sampling*—Return the apparatus, now containing only vapors, to its normal upright position and open the inlet valve. As soon as the apparatus attains essentially the same pressure as the pressure of the sample source, momentarily open the bleeder valve. If liquid does not promptly emerge, repeat the purging step (9.2). If liquid appears immediately, close the bleeder and inlet valves in that order (Note 1). Close the valve on the sample source, and disconnect the sampling line. Immediately close the straight-through valve between the two chambers and open the inlet valve, with the apparatus in an upright position. Close the inlet valve as soon as no more liquid escapes, and immediately open the straight-through valve.

NOTE 1—Transfer of the sample is facilitated by chilling the apparatus with a portion of the material under test.

9.3.1 When using the 33 1/3 % lower chamber (A1.1.3) proceed to 9.4.

9.3.2 When using the 20 % lower chamber (Appendix A1.1.4), close the straight-through valve and again open the inlet to permit expulsion of the lower chamber contents. As soon as no more liquid escapes from the lower chamber, close the inlet valve and immediately open the straight-through valve.

9.3.3 The upper chamber, prior to this operation, is liquid full at some temperature that is normally below the environmental temperature. Since any warming of the apparatus would cause expansion of the liquid content of the

upper chamber, leading to possible rupture of the chamber, it is necessary that the procedural steps of providing free space in the apparatus be completed promptly.

9.4 Vapor Pressure Determination:

9.4.1 Invert the apparatus and shake it vigorously. Return the apparatus to its normal upright position and immerse it in the constant-temperature water bath maintained at the test temperature (4.1). The apparatus including the bleeder valve coupling, but not the pressure gage, must be immersed. Throughout the determination, the temperature of the water bath shall be checked periodically by means of the bath thermometer.

9.4.1.1 At test temperatures of 50°C (122°F) or below, maintain the bath at $\pm 0.1^\circ\text{C}$ (0.2°F). At test temperatures above 50°C (122°F), up to and including 70°C (158°F), maintain the bath at $\pm 0.3^\circ\text{C}$ (0.5°F).

9.4.1.2 Observe the apparatus assembly throughout the test period to ensure freedom from leaks. Discontinue the test and discard the results at any time a leak is detected.

9.4.2 After 5 min have elapsed, withdraw the apparatus from the water bath, invert it, shake it vigorously, and then return it to the bath. Perform the shaking operation quickly to avoid excessive cooling of the apparatus and its contents. Thereafter, at intervals of not less than 2 min, withdraw the apparatus from the bath, invert, shake it vigorously, and then return it to the bath. Prior to each removal of the apparatus from the water bath, tap the gage lightly and observe the pressure reading. These operations will normally require 20 to 30 min to ensure equilibrium. After this time, if consecutive observed gage readings are constant, record the pressure reading as the Uncorrected LP-Gas Vapor Pressure of the sample at the test temperature.

9.4.3 If a pressure gage is used that is not calibrated against a dead-weight tester, it is necessary to determine if a gage correction needs to be applied to the pressure gage reading. Without removing the pressure gage from the apparatus or the apparatus from the bath, attach a test gage, previously calibrated against a dead-weight tester, to the bleeder valve outlet and open the bleeder valve. At the end of 5 min, compare the readings of the two gages. Record any correction thus determined as gage correction.

9.4.3.1 Alternatively, if a pressure gage is used that has been calibrated against a dead-weight tester, then the gage correction is zero and it is not necessary to determine a gage correction as per 9.4.3, using a second test gage that has been calibrated against a dead-weight tester.

D2533 -99 Procedure Section



Designation: D2533–99

Standard Test Method for Vapor-Liquid Ratio of Spark-Ignition Engine Fuels¹

11. Procedure

11.1 Read and record the barometric pressure.

11.2 With the V/L buret at room temperature or somewhat above (Note 12) and everything in readiness, carry out the following steps as quickly as possible. Open the chilled sample container, tip it so as to reach the liquid with the hypodermic syringe needle, taking caution to prevent water from reaching the sample and partially fill the syringe. Point the needle upward and dispel the contents to eliminate all air bubbles. Immediately refill the syringe from the sample container and check for air or vapor in the syringe (Note 13).

NOTE 12—If a film is noted in the buret, clean it further with sodium dichromate-sulfuric acid solution. **Warning**—Causes severe burns. A recognized carcinogen. A strong oxidizer. Contact with organic material may cause fire.

NOTE 13—Glycerol (mercury) in the buret may be somewhat above room temperature due to warming in the previous test, but should not be so warm as to cause the sample to vaporize when injected.

NOTE 14—Vapor may form if the sample is drawn in too rapidly. If this happens, repeat the sampling with a clean, chilled syringe.

NOTE 15—Use cotton gloves to reduce heat transfer from the hands to the syringe.

11.2.1 Depress the plunger exactly to the mark for the sample size desired, then, taking care not to disturb the plunger position, insert the needle through the rubber septum full length into the V/L buret. Depress the plunger all the way to inject the sample, and withdraw the needle. Use a 1-mL sample if the highest V/L ratio expected for the sample is less than 35. For higher V/L ratios, use a smaller sample sufficient to give 20 to 35 mL of vapor at the highest temperature to be tested.

11.3 Record the volume of sample charged, corrected by means of the calibration specified in 9.1 and 9.2.

11.4 Transfer the charged buret to the water bath set at the desired temperature and position so that the water level comes above the stopcock barrel.

11.5 As vapor forms in the buret, adjust the height of the leveling bulb to give the desired pressure on the sample. If glycerol is used as the confining medium, raise the level of glycerol in the reservoir 10.80 mm above the level of the glycerol in the buret for every mm of mercury that the barometric pressure is below 760 mm Hg; or lower it by a like amount for every mm that the barometric pressure is above 760 mm Hg. If mercury is used as the confining medium, raise the level of the mercury in the reservoir 1.0 mm above the level of the mercury in the buret for every mm of mercury that the barometric pressure is below 760 mm Hg; or lower it by a like amount for every mm that the barometric pressure is above 760 mm Hg.

NOTE 16— If the difference between the atmospheric pressure in the laboratory and the pressure for which the V/L measurement is desired is too great for convenient correction by means of the leveling bulb alone, use the mercury-filled manometer described in 6.2.4 to set the pressure. Keep the level of glycerol in the leveling bulb the same as that in the buret and apply pressure or vacuum gently to the air space in the leveling bulb as needed to obtain the desired pressure on the manometer.

NOTE 17—With some narrow boiling gasoline fractions, super heating may occur and no vapors are formed in the buret, even after immersion for as long as 15 min or more. When vaporization takes place, it does so rapidly and sometimes explosively. With these samples, it is recommended that injection be carried out with warm glycerol in the buret, such that a few millilitres of vapor are formed immediately after injection. The temperature of the glycerol is dependent on the sample composition but in general should not be more than 50°F (28°C) above ambient. With mercury as the confining medium this phenomenon has not been observed.

11.6 Without removing the buret from the water bath, shake it sufficiently to agitate the liquid sample, but not so vigorously as to disperse droplets of sample into the glycerol.

NOTE 18—Shaking is not necessary if mercury is used as the confining liquid because the superior heat transfer properties of the mercury will result in rapid thermal equilibrium of the system. With mercury as the confining liquid shaking is discouraged because of the danger of breakage of the glass caused by accidental impact.

11.7 Readjust the height of the leveling bulb, if necessary, to give the desired pressure on the sample. Because of mercury's high density, the use of a cathetometer or similar optical leveling device is necessary to minimize pressure errors.

NOTE 19—Any spilled mercury, and any that may be purged from the equipment, should be placed in an airtight closed vessel. This recovered mercury may be sent to a reprocessor, who can provide shipping instructions. (Names of mercury reproducers are available from ASTM Headquarters.) To minimize spillage, a catch pan that is large enough to contain all the mercury in case of failure should be placed under the apparatus.

It is useful to have a 1 L vacuum flask available connected to a vacuum source. Introduce a few ounces of a solid mercury vapor absorbent in the flask. Connect one end of a piece of tubing to the top of the flask and insert a glass eyedropper at the other end. Use the eyedropper end to pick up spilled mercury and to remove the spent sample and excess mercury from the top of the burets at the end of the run.

11.8 Read the volume of vapor to the nearest 0.1 mL. Repeat until the volume remains constant for at least 2 min. Record the volume, corrected by means of the calibration specified in 9.1 and 9.3, the bath temperature, and the pressure.

11.9 If the vapor-liquid ratio is also desired at another temperature, either adjust the temperature of the bath accordingly, or transfer the buret to another bath at the desired temperature. Repeat the operations described in 11.5 and 11.8.

NOTE 20—During the cleaning procedure note that small amounts of hydrocarbons can be trapped between the glass and the Hg column. If they are not removed, they may contaminate the next sample. After removal of the spent sample at the end of the

run, close the valve at the top of the tube and immerse the tube in the hottest bath available at that moment for about 5 min. Then raise the tube 50 to 75 cm and hold in this position for 5 to 10 s. The trapped hydrocarbons will rise to the top of the tube, from where they can be removed.

D2879 - 97 (Reapproved 2002)



Designation: D2879 -97 (Reapproved 2002)

Standard Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope¹

8. Procedure

8.1 Add to the isoteniscope a quantity of sample sufficient to fill the sample bulb and the short leg of the manometer section (**Warning**—Poison. Can be harmful or fatal if inhaled or swallowed. Vapor harmful; emits toxic fumes when heated. Vapor pressure at normal room temperature exceeds threshold limit value for occupational exposure. See A1.1.) to point *A* of Fig. 1. Attach the isoteniscope to the vacuum system as shown in Fig. 3, and evacuate both the system and the filled isoteniscope to a pressure of 13.3 Pa (0.1 torr) as measured on the McLeod gage. Break the vacuum with nitrogen (**Warning**—Compressed gas under high pressure. Gas reduces oxygen available for breathing. See A1.2.). Repeat the evacuation and purge of the system twice to remove residual oxygen.

8.2 Place the filled isoteniscope in a horizontal position so that the sample spreads out into a thin layer in the sample bulb and manometer section. Reduce the system pressure to 133 Pa (1 torr). Remove dissolved fixed gases by gently warming the sample with an alcohol (**Warning**—Flammable. Denatured alcohol cannot be made non-toxic. See A2.3.) lamp until it just boils. Continue for 1 min.

NOTE 3—During the initial evacuation of the system, it may be necessary to cool volatile samples to prevent boiling or loss of volatiles.

NOTE 4—If the sample is a pure compound, complete removal of fixed gases may readily be accomplished by vigorous boiling at 13.3 Pa (0.1 torr). For samples that consist of mixtures of substances differing in vapor pressure, this procedure is likely to produce an error due to the loss of volatile components. Gentle boiling is to be preferred in such cases. The rate of boiling during degassing may be controlled by varying both the pressure at which the procedure is carried out and the amount of heating. In most cases, satisfactory degassing can be obtained at 133 Pa (1 torr). However, extremely viscous materials may require degassing at lower pressures. Samples of high volatility may have to be degassed at higher pressures. In the event that the vapor pressure data indicate that the degassing procedure has not completely removed all dissolved gases, it may be necessary to apply a correction to the data or to disregard data points that are so affected (see 8.7). The degassing procedure does not prevent the loss of volatile sample components completely. However, the described procedure minimizes such losses, so that for most purposes the degassed sample can be considered to be representative of the original sample less the fixed gases that have been removed.

8.3 After the sample has been degassed, close the vacuum line valve and turn the isoteniscope to return the sample to the bulb and short leg of the manometer so that both are entirely filled with the liquid. Create a vapor-filled, nitrogen-free space between the bulb and the manometer in the following manner: maintain the pressure in the isoteniscope at the same pressure used for degassing; heat the drawn-out tip of the sample bulb with a small flame until sample vapor is released from the sample; continue to heat the tip until the vapor expands sufficiently to displace part of the sample from the upper part of the bulb and manometer arm into the manometer section of the isoteniscope.

8.4 Place the filled isoteniscope in a vertical position in the constant-temperature bath. As the isoteniscope approaches temperature equilibrium in the bath, add nitrogen to the gas-sampling system until its pressure equals that of the sample. Periodically adjust the pressure of the nitrogen in the gas-handling system to equal that of the sample. When the isoteniscope reaches temperature equilibrium, make a final adjustment of the nitrogen pressure to equal the vapor pressure of the sample. Pressure balance in the system is indicated by the manometer section of the isoteniscope. When the liquid levels in the manometer arms are equal in height, balance is indicated. Read and

record the nitrogen pressure in the system at the balance point. Use the McLeod gage to measure pressures below 2.00 kPa (15 torr) and the mercury manometer for pressures from 2.00 kPa (15 torr) to 101 kPa (760 torr).

8.4.1 It is extremely important that adjustments of the nitrogen pressure be made frequently and carefully. If the nitrogen pressure is momentarily too great, a bubble of nitrogen may pass through the manometer and mix with the sample vapor. If the nitrogen pressure is momentarily too low, a bubble of sample vapor may escape. If either action occurs, the test is terminated immediately and restarted from 8.3.

NOTE 5—Because the densities of most samples are very much less than that of mercury, small errors in the final adjustment of the levels of the liquid level in the manometer have a negligible effect on the measured values of vapor pressure above 133 Pa (1 torr).

8.5 Increase the temperature of the constant-temperature bath 25 K. As the temperature rises, maintain pressure balance in the system in the manner described in 7.4. When temperature equilibrium is reached, make a final adjustment of pressure to establish balance. Read and record the system pressure. Repeat at intervals of 25 K until the system pressure exceeds 101 kPa (760 torr).

8.6 Plot the logarithm and the measured vapor pressure at each temperature versus the reciprocal of the absolute temperature, $(K)^{-1}$.

NOTE 6—Three or four-cycle semilog graph paper is useful for making this type of plot.

8.7 If the slope of the vapor pressure curve at its low-temperature end indicates that the sample contains fixed gases as a result of incomplete degassing, one of three procedures must be followed. (For examples, see Fig. 4 and Fig. 5.)

8.7.1 Repeat the determination of vapor pressure in the manner described in 8.1–8.7, but employ a more vigorous degassing procedure. This procedure is recommended for pure compounds and mixtures that do not have a vapor pressure greater than 133 Pa (1 torr) at 323 K.

NOTE 7—In general, vapor pressure determinations are made after both temperature equilibrium in the air bath and pressure equilibrium in the isoteniscope and measuring system are attained. However, when a sample begins to decompose, the observed vapor pressure of the sample usually increases even at constant temperature. In such cases, the measured pressure of the system is no longer a function only of the temperature and is not a vapor pressure in the usual sense of the term. It is sometimes useful to continue to take pressure readings even after a system has become unstable. In such cases, the pressure reading is taken after temperature equilibrium is reached in the air bath, regardless of whether a stable pressure balance can be maintained.

8.7.2 In many cases, despite the presence of fixed gases in the sample, the plot of the vapor pressure may be linear over a rather wide range of temperature (see Fig. 4). Extrapolate the linear section to lower temperatures to estimate the vapor pressure even though the presence of fixed gases prevents the direct determination. Extrapolation over more than one decade of pressure is not recommended.

8.7.3 If the lack of a suitable region of linearity prevents the use of the procedure described in 8.7.2 (see Fig. 5), the following arithmetic correction procedure is used: Assume that the pressure at the lowest temperature, K_1 , at which measurements were made is predominantly due to fixed gases. Calculate the pressure that would be developed at constant volume if this volume of fixed gases were to be heated to the temperature, K_2 , of the next data point.

$$P_{a2} = P_{a1} \times K_2/K_1 \quad (2)$$

Repeat this procedure for each data point. Calculate the corrected vapor pressure of the sample by subtracting each value of P_a from the corresponding P_e for each successive data point.

$$P_c = P_e - P_a \quad (3)$$

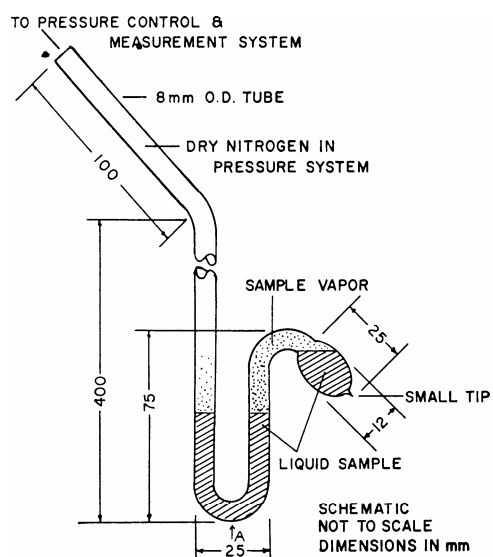


FIG. 1 Isoteniscope

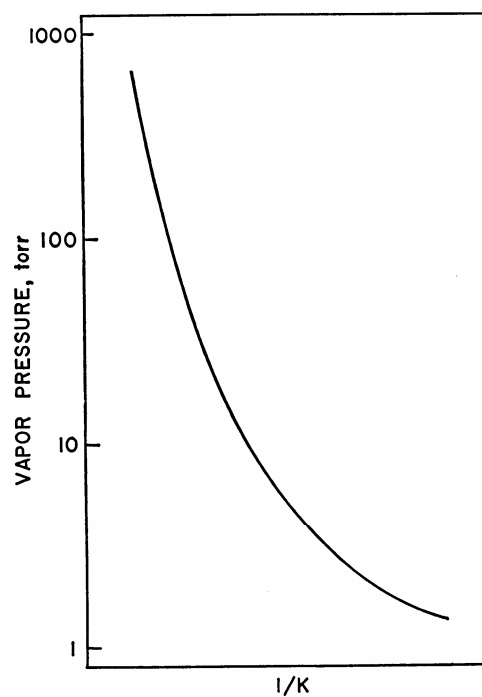


FIG. 5 Log P_e versus $1/K$ Without Linear Region

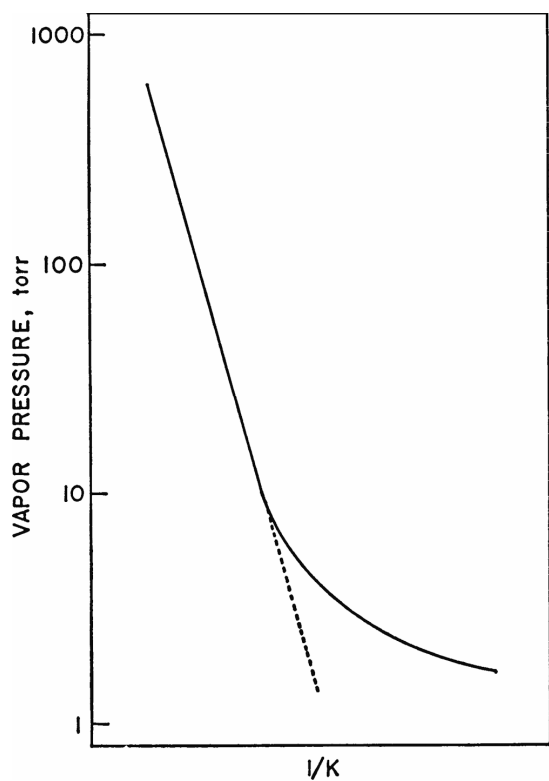


FIG. 4 Log P_e versus $1/K$ with Linear Region

A1.1 Scope

A1.1.1 This annex describes a procedure for the determination of the decomposition temperature of liquids whose vapor pressure can be measured in the apparatus described in the standard method.

A1.2 Summary of Test Method

A1.2.1 Dissolved and entrained gases are removed from the sample in the same manner described in the standard method. The isothermal rate of pressure change with respect to time is measured for several temperatures above the expected decomposition temperature of the sample. The logarithms of the rates of pressure rise are plotted against the reciprocals of the absolute temperatures at which the rates were measured. The decomposition temperature is defined as the temperature at which the rate of pressure increase of the sample is equivalent to a rise of 67 kPa (500 torr) in 10 h (1.85 Pa/s).

A2.3 Alcohol

Warning—Flammable.

Denatured alcohol cannot be made nontoxic.

Keep away from heat, sparks, and open flame.

Keep container closed.

Use with adequate ventilation.

Avoid prolonged breathing of vapor or spray mist.

Avoid contact with eyes and skin.

Do not take internally.

D4953 - 99a Procedure Section



Designation: D4953–99a

Standard Test Method for Vapor Pressure of Gasoline and Gasoline-Oxygenate Blends (Dry Method)¹

8. Procedure

8.1 *Sample Transfer*—Remove the sample from the cooling bath, dry the exterior of the container with absorbent material, uncap, and insert the chilled transfer tube (see Fig. 1). Remove the liquid chamber from the cooling bath and, using an absorbent material, dry the threaded top and place the chamber in an inverted position over the top of the transfer tube. Invert the entire system rapidly so that the liquid chamber is upright with the end of the transfer tube approximately 6 mm (0.25 in.) from the bottom of the liquid chamber. Fill the chamber to overflowing. Withdraw the transfer tube from the liquid chamber while allowing the sample to continue flowing up to complete withdrawal.

NOTE 8—**Warning:** Provision shall be made for suitable containment and disposal of the overflowing sample to avoid fire hazard.

8.2 *Assembly of Apparatus*—Immediately remove the vapor chamber from the water bath and, as quickly as possible, dry the exterior of the chamber with absorbent material with particular care given to the connection between the vapor chamber and the liquid chamber. Remove the closure from the vapor chamber and couple the filled liquid chamber to the vapor chamber as quickly as possible without spillage. When the vapor chamber is removed from the water bath and dried and the closure is removed, connect it to the liquid chamber without undue movement that could promote exchange of room temperature air with the 37.8°C (100°F) air in the chamber. Not more than 10 s should elapse between removing the vapor chamber from the water bath and completion of the coupling of the two chambers. With Procedure B it is necessary to disconnect the spiral tubing at the quick action disconnect after removing from the water bath and before making the connection to the vapor chamber.

8.3 Introduction of the Apparatus into Bath:

8.3.1 *Procedure A*—Turn the assembled apparatus upside down and allow all the sample in the liquid chamber to drain into the vapor chamber. With the apparatus still inverted, shake it vigorously eight times lengthwise. With the gage end up, immerse the assembled apparatus in the bath, maintained at $37.8 \pm 0.1^\circ\text{C}$ ($100 \pm 0.2^\circ\text{F}$), in an inclined position so that the

connection of the liquid and vapor chambers is below the water level. Carefully examine for leaks. If no leaks are observed, further immerse the apparatus to at least 25 mm (1 in.) above the top of the vapor chamber. Observe the apparatus for leaks throughout the test and discard the test at anytime a leak is detected.

8.3.2 Procedure B—While holding the apparatus in a vertical position immediately reconnect the spiral tubing at the quick action disconnect. Tilt the apparatus to 20 to 30° downward for 4 or 5 s to allow the sample to flow into the vapor chamber without getting into the tube extending into the vapor chamber from the gage or pressure transducer. Place the assembled apparatus into the water bath maintained at $38.7 \pm 0.1^\circ\text{C}$ ($100 \pm 0.2^\circ\text{F}$) in such a way that the bottom of the liquid chamber engages the drive coupling and the other end of the apparatus rests on the support bearing. Observe the apparatus for leakage throughout the test. Discard the test anytime a leak is detected.

8.4 Verification of Single Phase Sample—After the apparatus has been immersed in the bath, check the remaining sample for phase separation. If the sample is contained in a transparent container, this observation can be made prior to sample transfer (8.1). If the sample is contained in a non-transparent container, mix the sample thoroughly and immediately pour a portion of the remaining sample into a clear glass container and observe for evidence of phase separation. A hazy appearance is to be carefully distinguished from separation into two distinct phases. The hazy appearance shall not be considered grounds for rejection of the fuel. If a second phase is observed, discard the test and the sample. Hazy samples may be analyzed (see Report section).

8.5 Measurement of Vapor Pressure:

8.5.1 Procedure A—After the assembled apparatus has been in the water bath for at least 5 min, tap the pressure gage lightly and observe the reading. Withdraw the apparatus from the bath and repeat the instructions of 8.3. At intervals of not less than 2 min, tap the gage, observe the reading and repeat the instructions given in 8.3 until a total of not less than five shakings and gage readings have been made and continuing thereafter if necessary until the last two consecutive gage readings are constant, indicating that equilibrium has been attained. Read the final gage pressure to the nearest 0.25 kPa (0.05 psi) and record this value as the uncorrected vapor pressure of the sample. Without undue delay remove the pressure gage from the apparatus and, without attempting to remove any liquid that may be trapped in the gage, check its reading against that of the pressure measuring device while both are subjected to a common steady pressure that is not more than 1.0 kPa (0.2 psi) from the recorded uncorrected vapor pressure. If a difference is observed between the gage and the pressure measuring device readings, add to or subtract the difference from the uncorrected vapor pressure and record the resulting value as the vapor pressure of the sample.

8.5.2 Procedure B—After the assembled apparatus has been in the bath for at least 5 min, tap the pressure gage lightly and observe the reading. Repeat the tapping and reading at intervals of not less than 2 min, until 2 consecutive readings are constant. (Tapping is not necessary with transducer model but the reading intervals are the same.) Read the final gage or transducer pressure to the nearest 0.25 kPa (0.05 psi) and record this value as the uncorrected vapor pressure. Without undue delay, disconnect the gage or pressure transducer from the apparatus and check its reading against that of the pressure measuring device while both are subjected to a common steady pressure that is not more than 1.0 kPa (0.2 psi) different from the recorded uncorrected vapor pressure. If a difference is observed between the gage or transducer and the pressure measuring device, add to or subtract the difference from the uncorrected vapor pressure and record the resulting value as the vapor pressure of the sample.

NOTE 9—If it is suspected that phase separation of the sample may have occurred during the test procedure, the following procedure can be performed to verify the integrity of the test sample. Perform the following operations as quickly as possible after removing the apparatus from the water bath in order to maintain the temperature of the sample at or near the test temperature. Quickly dry the exterior surfaces of the liquid and vapor chambers with absorbent material. With the apparatus in an upright position, disconnect the vapor and liquid chambers. Quickly drain the contents of the liquid chamber into a dry, clear, glass container and observe the sample. If the sample is not clear and bright and free of a second phase, cap the container, reheat the sample to 37.8°C (100°F), mix the sample well, and observe the sample again. If the sample is still not clear and bright and free of a second phase, phase separation has occurred and the test may not be valid.

8.6 Preparation of Apparatus for Next Test—Thoroughly purge the vapor chamber of residual sample by filling it with warm water above 32°C (90°F) and allowing it to drain. Repeat this purging at least five times. Purge the liquid chamber in the same manner. Rinse both chambers and the transfer tube several times with petroleum naphtha, then several times with acetone, then blow dry using dried air. Appropriately close the liquid chamber and place it in the cooling bath or refrigerator in preparation for the next test. Use an appropriate closure for the bottom connection (where liquid chamber attaches) of the vapor chamber and attach the gage after the gage has been prepared in accordance with 8.6.2.

8.6.1 If the purging of the vapor chamber is done in a bath, be sure to avoid small films of floating sample by keeping the bottom and top openings of the chamber closed as they pass through the water surface.

8.6.2 Preparation of Gage—Procedure A—Disconnect the gage from its manifold connection with the pressure measuring device, remove trapped liquid in the Bourdon tube of the gage by repeated centrifugal thrusts. Accomplish this in the following manner: hold the gage between the palms of the hands with the right palm on the face of the gage and the threaded connection of the gage forward, extend the arms forward and upward at an angle of 45° , and swing the arms rapidly downward through an

arc of about 135° so that centrifugal force aids gravity in removing trapped liquid. Repeat this operation at least 3 times or until all liquid has been expelled from the gage. Connect the gage to the vapor chamber with the liquid connection closed and place in the 37.8°C (100°F) bath to condition for the next test.

8.6.3 Preparation of Gage or Transducer—Procedure B—In the correct operation of Procedure B liquid does not reach the gage or transducer. If it is observed or suspected that liquid has reached the gage, purge the gage as described in 8.6.2. The transducer has no cavity to trap liquid. Ensure that no liquid is present in the T-handle fitting or spiral tubing by forcing a stream of dry air through the tubing. Connect the gage or transducer to the vapor chamber with the liquid connection closed and place in the 37.8°C (100°F) bath to condition for the next test.

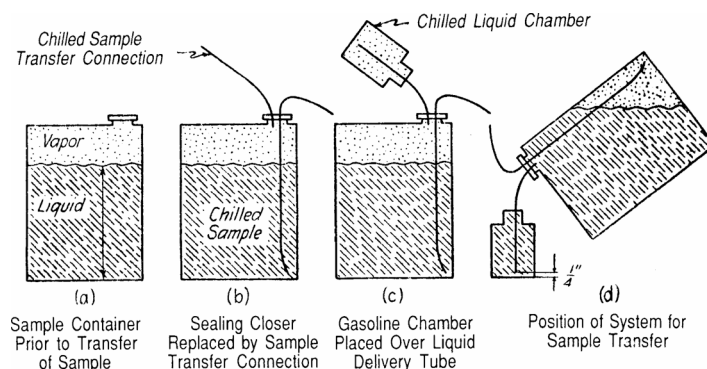


FIG. 1 Simplified Sketches Outlining Method Transferring Sample to Liquid Chamber from Open-Type Containers

D5188 - 99 Procedure Section



Designation: D5188–99

Standard Test Method for Vapor-Liquid Ratio Temperature Determination of Fuels (Evacuated Chamber Method)¹

11. Procedure

11.1 Calculate the volume of sample required to give the desired vapor-liquid ratio using Eq. 1 (12.1).

11.2 Remove the sample from the cooling bath or refrigerator, dry the exterior of the container with absorbent material, unseal and insert a chilled transfer tube or gas-tight syringe (9.4). Draw a bubble-free aliquot of sample into the syringe or transfer tube and deliver this sample to the test chamber as rapidly as possible. The total time between opening the chilled sample container and inserting/securing the syringe into the sealed test chamber shall not exceed 1 min.

11.3 Perform the analysis in accordance with the manufacturer's instructions for operation of the instrument.

11.4 Record the temperature reading from the instrument to the nearest 0.1°C (0.2°F) after the pressure indicator has remained stable at 101.3 kPa (14.69 psia) for 1 min.

NOTE 10—If the measurement is made at a pressure other than 101.3 kPa (14.69 psia) the pressure must be noted.

11.5 *Verification of Single Phase Sample*—Check the remaining sample from 8.3 for phase separation. If the sample is contained in a transparent container, this observation can be made prior to sample transfer (11.2). If the sample is contained in a non-transparent container, mix the sample thoroughly and immediately pour a portion of the remaining sample into a clear glass container and observe for evidence of phase separation. A hazy appearance is to be carefully distinguished from separation into two distinct phases. The hazy appearance shall not be considered grounds for rejection of the fuel. If a second phase is observed, discard the test and the sample. Hazy samples may be analyzed (see Report section).

12. Calculations

12.1 Use the following equation to calculate vapor-liquid ratio:

$$V/L = \frac{V - v}{v} \quad (1)$$

where:

V/L	=	vapor-liquid ratio
V	=	volume of test chamber, mL, and
v	=	volume of sample at 0°C (32°F), mL.

13. Report

13.1 Report $T_{(V/L)}$ temperature to the nearest 0.1°C (0.2°F) and the vapor-liquid ratio without reference to pressure.

13.2 If the sample was observed to be hazy in 11.5, report the test result as in 13.1, followed by the letter H.

NOTE 11—The precision and bias statements have not been determined for hazy samples, since these types of samples have not been evaluated as part of an interlaboratory study.

NOTE 12—The inclusion of the letter H in 13.2 is intended to alert the data recipient that the sample analyzed was hazy. In the event a laboratory has a computer system that is incapable of reporting alphanumeric results in accordance with the requirements in 13.2, it is permissible for the laboratory to report the result obtained as in 13.1, along with a statement or annotation that clearly conveys to the data recipient that the sample analyzed was hazy.

D5190 -01 Procedure Section



Designation: D5190-01

Standard Test Method for Vapor Pressure of Petroleum Products (Automatic Method)¹

12. Procedure

12.1 *Sample Transfer*—Remove the sample from the cooling bath or refrigerator, dry the exterior of the container with absorbent material, uncap, and insert a chilled transfer tube apparatus (see Fig. 1). Quickly take the chilled sample cup and place it, in an inverted position, over the sample delivery tube of the transfer apparatus. Invert the entire system rapidly so that the sample cup is upright with the end of the delivery tube touching the bottom of the sample cup. Fill the sample cup to overflowing. Withdraw the delivery tube from the sample cup while allowing the sample to continue flowing up to the moment of complete withdrawal.

NOTE 7—Precaution: In addition to other precautions make provisions for suitable restraint (for example, catch pan) and disposal of the overflowing or spilled gasoline to avoid fire hazard.

12.2 Quickly couple the sample cup to the instrument and start the analysis in accordance with the manufacturer's instructions for operation of the instrument. The total time between opening the chilled sample container and securing the sample cup to the instrument shall not exceed 1 min.

12.3 At the completion of the test, record the uncorrected dry vapor pressure reading from the digital meter to the nearest 0.1 kPa (0.01 psi). If the instrument does not automatically calculate the DVPE, record the uncorrected vapor pressure reading and calculate the DVPE using Eq. 1 (see 13.1).

13. Calculation

13.1 Calculate a DVPE, using the following equation. This corrects the instrument reading for the relative bias found in the 1991 interlaboratory cooperative test program (see Note 10) between the dry vapor pressure measured in accordance with Test Method D4953, Procedure A and this test method:

$$DVPE = (0.954 X) + A \quad (1)$$

where:

X = measured total vapor pressure, in units consistent with A , and
 A = 1.94 kPa (0.281 psi).

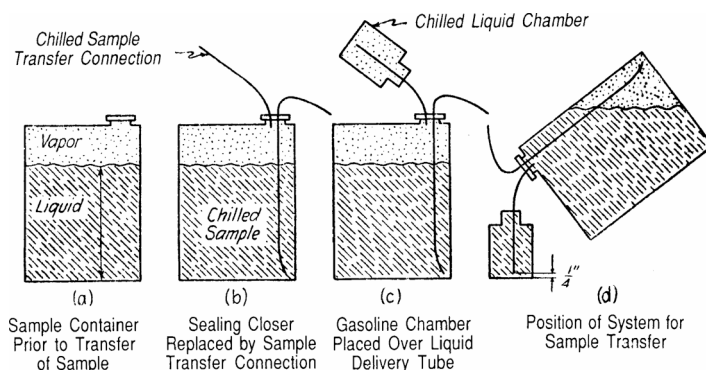


FIG. 1 Simplified Sketches Outlining Method Transferring Sample to Liquid Chamber from Open-Type Containers

D5191 - 04a Procedure Section



Designation: D5191-04a

Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method)¹

12. Procedure

12.1 Remove the sample from the cooling bath or refrigerator, dry the exterior of the container with absorbent material, uncap, and insert a chilled transfer tube or syringe (see 9.3). Draw a bubble-free aliquot of sample into a gas tight syringe or transfer tube, and deliver this test specimen to the test chamber as rapidly as possible. The total time between opening the chilled sample container and inserting/securing the syringe into the sealed test chamber shall not exceed 1 min.

12.2 Follow the manufacturer's instructions for injection of the test specimen into the test chamber, and for operation of the instrument to obtain a total vapor pressure result for the test specimen.

12.3 Set the instrument to read the result in terms of total vapor pressure. If the instrument is capable of calculating a dry vapor pressure equivalent value, make sure that only the parameters in 13.2 are used.

13. Calculation

13.1 Record the total vapor pressure reading from the instrument to the nearest 0.1 kPa (0.01 psi). For instruments that do not automatically record a stable pressure value, manually record the pressure indicator reading

every minute to the nearest 0.1 kPa. When three successive readings agree to within 0.1 kPa, record the result to the nearest 0.1 kPa (0.01 psi).

13.2 Calculate the DVPE using Eq. 1. Ensure that the instrument reading used in this equation corresponds to the total pressure and has not been corrected by an automatically programmed correction factor:

$$DVPE, \text{ kPa (psi)} = (0.965 X) - A \quad (1)$$

where:

X	=	measured total vapor pressure in kPa (psi), and
A	=	3.78 kPa (or 0.548 psi).

NOTE 10—The correlation equation was derived from the results of the 1988 cooperative program¹ and confirmed in the 1991 interlaboratory study.²

9.3 If a syringe is used for introduction of the sample specimen, chill it to between 0 and 4.5°C (32 and 40°F) in a refrigerator or ice bath before drawing in the sample. Avoid water contamination of the syringe reservoir by sealing the outlet of the syringe during the cooling process.

D5482 - 01 Procedure Section



Designation: D5482–01

Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method—Atmospheric)

12. Procedure

12.1 Remove the sample from the cooling bath or refrigerator, dry the exterior of the container with absorbent material, uncap, and insert a chilled syringe. Draw a bubble-free aliquot of sample into the gas tight syringe, and deliver this test specimen to the test chamber as rapidly as possible. The total time between opening the chilled sample container and securing the syringe into the test chamber shall not exceed 1 min.

12.2 Follow the manufacturer's instructions for injection of the test specimen into the test chamber and for operation of the instrument to obtain a vapor pressure result for the test specimen.

12.3 If the instrument is capable of calculating the dry vapor pressure equivalent automatically, ensure that the equation in 13.2 is used.

13. Calculation

13.1 Record the vapor pressure reading from the instrument to the nearest 0.1 kPa (0.01 psi). For instruments that do not automatically record a stable pressure value, manually record the pressure indicator reading every minute to the nearest 0.1 kPa. When three successive readings agree to within 0.1 kPa, record the result to the nearest 0.1 kPa (0.01 psi).

13.2 Calculate the DVPE using Eq. 1. Ensure that the instrument reading used in this equation corresponds to the total pressure and has not been corrected by an automatically programmed correction factor. Use the variable pertaining to the type of equipment utilized.

$$DVPE, \text{ kPa (psi)} = (0.965 X) + A \quad (1)$$

where:

X	=	measured total vapor pressure in kPa (psi),
A	=	0.538 kPa (0.078 psi) for HERZOG Model SC 970,
		and
A	=	1.937 kPa (0.281 psi) for ABB Model 4100.

NOTE 5—The correlation equations were derived from data obtained in a 1991 interlaboratory cooperative test program.⁷ The equations correct for the relative bias between the measured vapor pressure and the dry vapor pressure obtained in accordance with Test Method D4953, Procedure A.

D6377 - 99 Procedure Section



Designation: D6377–99

Standard Test Method for Determination of Vapor Pressure of Crude Oil: VPCR_x (Expansion Method)¹

12. Procedure

12.1 Set the sample introduction temperature of the measuring chamber between 20 and 37.8°C. For crude oil samples with a pour point higher than 15°C, set the injection temperature at least 5°C above the pour point temperature of the sample.

12.2 Set the V/L to the desired value X:1 (For test results related to Test Method D323, set the V/L to 4:1).

12.3 Mix the sample in the pressurized floating piston cylinder vigorously with the mechanical stirrer to ensure a homogenous sample, and connect the outlet of the cylinder to the inlet of the apparatus.

12.4 Follow the manufacturer's instructions for introducing the test specimen into the measuring chamber. The volume of the specimen shall be such that after the expansion to the final volume the programmed V/L is achieved.

12.5 After closing the inlet valve, expand the volume of the measuring chamber to the final volume.

12.6 Switch-on the shaker, and leave it on during the entire measuring procedure

12.7 Adjust the temperature control to the measuring temperature (for results related to Test Method D323, adjust to a temperature of 37.8°C). The measuring temperature shall not be lower than at least 10°C above the pour point temperature of the sample.

12.8 Wait for temperature equilibrium between measuring chamber and specimen, and monitor the total vapor pressure every 30 ± 5 s. When three successive readings agree within 0.3 kPa, record this resulting vapor pressure as VPCR_x(Tm°C).

D6378 - 03 Procedure Section



Designation: D6378–03

Standard Test Method for Determination of Vapor Pressure (VP_x) of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method)¹

12. Procedure

12.1 Set the sample introduction temperature of the measuring chamber between 20 and 37.8°C.

12.2 Set the vapor-liquid ratio to the desired value X:1 (for test results related to Test Method D5191, set the vapor-liquid ratio to 4:1).

12.3 Connect an aliquot of sample either in a syringe, pressurized sample container, or a tubing immersed in the sample to the inlet of the apparatus. Make provisions to avoid loss of high volatiles in the sample. The overall volume of the sample shall exceed the volume of three rinsing cycles plus the final test volume. Follow the manufacturer's instructions for introducing the test specimen into the measuring chamber.

12.4 Perform the three rinsing cycles (see 9.3) immediately after connecting the sample.

12.5 Introduce the test specimen into the measuring chamber by a stroke of the piston. The volume of the specimen shall be such that after the expansion to the final volume the programmed vapor-liquid ratio is achieved.

12.6 Close the inlet valve, and make the first expansion by a stroke of the piston.

12.7 Monitor the TP_X every 20 ± 2 s. When three successive readings agree within 0.1 kPa, record this resulting total pressure as $TP_{X,1}$.

12.8 Make the second expansion, and monitor the TP_X every 20 ± 2 s. When three successive readings agree within 0.1 kPa, record this resulting total pressure as $TP_{X,2}$.

12.9 Repeat 12.8 for the third expansion, and record the resulting total pressures as $TP_{X,3}$.

12.10 Allow the temperature of the measuring chamber to increase to within 0.1°C of the desired test temperature. Monitor the TP_X every 20 ± 2 s. When three successive readings agree within 0.1 kPa, record this resulting total pressure as $TP_{X,t}$.

12.11 *Check for Sample Separation*—After introducing the test specimen into the instrument for analysis, check the remaining sample for sample separation (see 8.4)

8.4 *Verification of Single Phase Sample*—After drawing the test specimens and transferring them into the instrument for analysis, check the remaining sample for phase separation. If the sample is contained in a transparent container, this observation can be made prior to sample transfer. If the sample is contained in a non-transparent container, shake the sample thoroughly and immediately pour a portion of the remaining sample into a glass container and observe for evidence of phase separation. A hazy appearance is to be carefully distinguished from separation into distinct phases. If the sample separates into two distinct phases with a discernible common boundary, then discard the test and the sample. If the sample has a hazy appearance, but does not have two distinct phases, then phase separation has not occurred. The test is valid, but the precision and bias in Section 15 may not apply (see Section 14).

D6897 - 03 Procedure Section



Designation: D6897–03

Standard Test Method for Vapor Pressure of Liquefied Petroleum Gases (LPG) (Expansion Method)¹

12. Procedure

12.1 Connect the pressurized sample container to the inlet of the apparatus and position it in such a way that the outlet valve of the container is below the liquid level. Open the outlet valve of the pressurized sample container.

12.2 *Rinsing*—Open the inlet valve and draw in the sample by moving the piston from zero-volume to the filling position. Close the inlet valve and open the outlet valve, move the piston to zero-volume position. Close the outlet valve. Repeat this procedure two more times.

12.3 *Filling*—Regulate the measuring chamber to the filling temperature of $5 \pm 0.5^\circ\text{C}$. When the measuring chamber is at the filling temperature, close the outlet valve and open the inlet valve. Draw in the sample from the pressurized sample container by moving the piston from zero-volume to the filling position. Close the inlet valve.

12.4 *Expansion*—Move the piston to the final volume to provide the necessary vapor to liquid ratio (the overall volume of the measuring chamber is 1.5 times the fill volume of liquid for a vapor to liquid ratio of 0.5:1).

12.5 *Total Pressure Determination*—Adjust the temperature regulator of the measuring chamber to the test temperature of interest, such as 37.8°C . After the temperature equilibrium observe the pressure reading. If two

consecutive readings remain constant within ± 3 kPa after 1 min, record the observed pressure as total pressure of the sample at test temperature.

E1194 - 01 Procedure Section



Designation: E1194-01

Standard Test Method for Vapor Pressure¹

8. Procedures

8.1 *Isotenoscope Procedure*—Refer to Test Method D2879.

8.2 *Gas-Saturation Procedure:*

8.2.1 The test sample can be (1) coated onto clean silica sand, glass beads, or other suitable inert support from solution; (2) in solid granular form; or (3) a liquid. If using a coated-support procedure, the thickness of the coating must be sufficient to ensure that surface energy effects will not impact vaporization. Following volatilization the surface must remain completely coated with the test compound.

8.2.2 Coat the support prior to column loading, to ensure the support is properly coated. Use sufficient quantity of material on the support to maintain gas saturation for the duration of the test.

8.2.3 Put the support into a suitable saturator column. The dimensions of the column and gas velocity through the column should allow complete saturation of the carrier gas and negligible back diffusion.

8.2.4 Connect the front and back-up traps to the column discharge line downstream from the saturator column. Use the back-up trap to check for breakthrough of the compound from the front trap. For example systems, see Figs. 1-4.

8.2.5 Surround the saturator column and traps by a thermostated chamber controlled at the test temperature within $\pm 0.05^\circ\text{C}$ or better.

8.2.6 If any test material is detected in the second trap, breakthrough has occurred and the measured vapor pressure may be too low. To eliminate breakthrough, take one or both of the following steps:

8.2.6.1 Increase trapping efficiency by using more efficient traps, such as a larger higher capacity or a different type of trap.

8.2.6.2 Decrease the quantity of material trapped by decreasing the flow rate of carrier gas or reduce the sampling period.

8.2.7 After temperature equilibration, the carrier gas passes through the specimen and the sorbent (or cold) traps and exits from the thermostated chamber. The thermostatically-controlled chamber should utilize liquid baths. Liquid (water or oil) baths are suggested because of the difficulty in controlling temperatures in accordance with the tight specifications required (7) using air baths. Variations in the ambient temperature in facilities designed for hazardous chemical work make this a critical need.

8.2.8 Measure the flow rate of the effluent carrier gas at the adiabatic saturation temperature with a bubble meter or at ambient temperature for other, nonhumidifying devices considered suitable. Check the flow rate frequently during the procedure to ensure that the total volume of carrier gas is accurately measured. Use the flow rate to calculate the total volume (at room temperature) of gas that has passed through the specimen and sorbent or trap. $((\text{volume}/\text{time}) (\text{time}) = \text{volume})$.

8.2.9 Measure the pressure at the outlet of the saturator. Determination of the saturator operating pressure is critical because it will always be above ambient pressure due to a pressure drop through the system. Measure either by including a pressure gage between the saturator and traps or by determining the pressure drop across the particular trapping system used in a separate experiment for each flow rate.

8.2.10 Calculate the test specimen vapor pressure (which is its partial pressure in the gas stream) from the total gas volume (corrected to the volume at the temperature at the saturator) and the mass of specimen vaporized.

8.2.11 Record the ambient pressure frequently during the test to ensure an accurate saturator pressure value. Laboratories are seldom at normal atmospheric pressure of 760 torr and this fact is often overlooked.

8.2.12 Determine the time required for collecting the quantity of test specimen necessary for analysis in preliminary runs or by estimates based on experience. Before calculating the vapor pressure at a given temperature, carry out preliminary runs to determine the flow rate that will completely saturate the carrier gas with sample vapor.

To check, determine whether another flow rate at the same system temperature gives a different calculated vapor pressure.

8.2.13 Measure the desorption efficiency for every combination of sample, sorbent, and solvent used. To determine the desorption efficiency, inject a known mass of sample onto a sorbent. Then desorb and analyze it for the recovered mass.

8.2.14 For each combination of sample, sorbent and solvent used, make triplicate determinations at each of three concentrations. Desorption efficiency may vary with the concentration of the actual sample and it is important to measure the efficiency at or near the concentration of the sample under gas saturation test procedure conditions. It is usually necessary to interpolate between two measured efficiencies.

8.2.15 If the test specimen vapor pressure is very low, check and make sure significant amounts of the test specimen are not lost on the surface of the apparatus. This is checked by a material compatibility test prior to loading the sorbent into the traps or saturation column. If the tested chemical has a significant affinity for the traps or saturation column material of construction, select and test an alternative material of construction.

8.2.16 When testing elevated temperature conditions, it is necessary that the system is operating at a uniform temperature. Contaminant condensation on cold spots will give low vapor pressure values.

8.2.17 The choice of the analytical method, trap, and desorption solvent depends upon the nature of the test specimen and the temperature conditions of interest.

8.2.18 Advantages of this test method when used with an analysis specific for the compound of interest are:

8.2.18.1 Minor impurities are not likely to interfere with either the test protocol or the accuracy of the vapor pressure results.

8.2.18.2 Pressures of two or more compounds may be obtained simultaneously, providing the compounds do not have significant vapor/liquid activity interaction.

E1719 - 97 Procedure Section



Designation: E1719–05

Standard Test Method for Vapor Pressure of Liquids by Ebulliometry¹

9. Procedure

9.1 Start with clean, dry apparatus. Verify the operation and capability of the apparatus as described in Annex A1 for a new ebulliometer setup or an ebulliometer setup that has not been used recently.

9.2 Charge a specimen of appropriate volume to the ebulliometer boiler. Charge 75 ± 1 mL for the vapor-lift ebulliometer (Fig. 1). Close all stopcocks on the vapor-lift ebulliometer. Charge 125 ± 1 mL for the stirred-flask ebulliometer (Fig. 2). Add a magnetic stirring bar to the stirred-flask ebulliometer. Connect the stirred-flask ebulliometer to the reflux condenser.

9.3 Connect the ebulliometer reflux condenser to the cold trap. Connect the cold trap exit to a glassware T-connection. Connect one side of the T-connection to the manostat and the other side to the manometer. If a comparative ebulliometer is used as the manometer, charge the reference fluid to the comparative ebulliometer and connect it through a cold trap to the T-connection.

9.4 Start the condenser coolant flow. Set the manostat for the lowest pressure to be studied. (This pressure should produce a boiling temperature at least 30 K above the condenser coolant temperature.) Turn on the magnetic stirrer if using a stirred-flask ebulliometer. Turn on the electrical heater, and heat the specimen to produce steady-state reflux. A 30-mm reflux zone should be visible in the bottom of a 200-mm long reflux condenser at steady-state. Decrease the heating power if the reflux zone extends above half the height of the condenser. The reflux return rate from the condenser at steady-state should be at least two drops/s.

9.5 See 6.2 if the specimen “bumps”. If “bumping” invalidates the test, two remedies can be tried to see whether it is eliminated: the test can be repeated at a higher initial pressure, or a stirred-flask ebulliometer can be tried in place of the vapor-lift-pump ebulliometer.

NOTE 4—“Bumping” in the ebulliometer boiler is usually caused by the inability of the apparatus to dissipate the effects of superheating of the specimen. This problem occurs more often at lower pressures, approximately 1 to 15 kPa (8 to 110 torr).

NOTE 5—Some materials may “bump” a few times and then boil smoothly. These materials can be studied provided that material is not ejected from the condenser during the “bumping” period.

9.6 Record the temperature and manostat pressure after the boiling point temperature is at a steady-state (± 0.10 K) for at least 10 min. Raise the manostat pressure to the next highest pressure to be studied, and repeat the steady-state measurement. Continue until five or more pressure-temperature data points are determined.

9.6.1 Vary the heater power, and observe the effect on the boiling temperature before recording the first data point. If increasing the heater power raises the boiling temperature, this indicates that there is insufficient reflux to the thermometer well. Raise the power level in this case until a “heater power plateau” is reached at which the observed temperature is independent of the heater power.

9.6.2 At steady-state, the boiling temperature should be independent of the heater power (applied voltage) over a modest range (approximately 5 V for an ebulliometer with a variable transformer).

9.7 Discontinue the test if the specimen begins to decompose or polymerize. Decomposition may be indicated by a decreasing boiling point temperature, smoking or extreme discoloration of the specimen, or failure to reach a steady-state. Polymerization of the specimen usually causes the temperature to continue to increase instead of reaching a steady-state.

9.8 Check the cold trap for the presence of condensed volatiles from the specimen upon completion of the test. Discard the results from the test if condensate is found in the cold trap.

NOTE 6—If the test material is a pure chemical (99.9 % by weight) or an azeotropic mixture, a small amount (approximately 2 mL) of cold trap condensate is allowable.

NOTE 7—Take care not to permit water from humid laboratory air to condense inside the cold traps. Analyze the cold trap condensate in a questionable case to verify that it is from the specimen under study.

SIMULATED DISTILLATION METHODS

D2887 - 04a Procedure Section



Designation: D2887–04a

Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography^{1, 2}

11. Procedure

11.1 *Sample Preparation:*

11.1.1 The amount of sample injected must not overload the column stationary phase nor exceed the detector linear range. A narrow boiling range sample will require a smaller amount injected than a wider boiling range sample.

11.1.1.1 To determine the detector linear range, refer to Practice E594 for flame ionization detectors or Practice E516 for thermal conductivity detectors.

11.1.1.2 The column stationary phase capacity can be estimated from the chromatogram of the calibration mixture (see 9.3.2). Different volumes of the calibration standard can be injected to find the maximum amount of a component that the stationary phase can tolerate without overloading (see 10.3.1). Note the peak height for this amount of sample. The maximum sample signal intensity should not exceed this peak height.

11.1.2 Samples that are of low enough viscosity to be sampled with a syringe at ambient temperature may be injected neat. This type of sample may also be diluted with CS₂ to control the amount of sample injected to comply with 11.1.1.

11.1.3 Samples that are too viscous or waxy to sample with a syringe may be diluted with CS₂.

11.1.4 Typical sample injection volumes are listed below.

Packed Columns:		Neat Sample Volume, μL	
Stationary Phase Loading, %		1.0	
10		0.5	
5			
Open Tubular Columns:		Neat Sample Volume, μL	
Film Thickness, μ		0.1 to 0.2	
0.8 to 1.5		0.1 to 0.5	
1.8 to 3.0		0.2 to 1.0	
3.0 to 5.0			

11.2 *Sample Analysis*—Using the analysis sequence protocol, inject a sample aliquot into the gas chromatograph. Collect a contiguous time slice area record of the entire analysis.

9.3.2 *Detector Response Calibration*—This test method assumes that the detector response to petroleum hydrocarbons is proportional to the mass of individual components. This must be verified when the system is put in service, and whenever any changes are made to the system or operational parameters. Analyze the calibration mixture using the identical procedure to be used for the analysis of samples (see Section 10). Calculate the relative response factor for each *n*-paraffin (relative to *n*-decane) in accordance with Practice D4626 and Eq. 2:

$$F_n = (M_n / A_n) / (M_{10} / A_{10}) \quad (2)$$

where:

F_n	=	relative response factor,
M_n	=	mass of the <i>n</i> -paraffin in the mixture,
A_n	=	peak area of the <i>n</i> -paraffin in the mixture,
M_{10}	=	mass of the <i>n</i> -decane in the mixture, and
A_{10}	=	peak area of the <i>n</i> -decane in the mixture.

The relative response factor (F_n) of each *n*-paraffin must not deviate from unity (1) by more than $\pm 10\%$.

10.3.1 Inspect the chromatogram of the calibration mixture for evidence of skewed (non-Gaussian shaped) peaks. Skewness is often an indication of overloading the sample capacity of the column that will result in displacement of the peak apex relative to nonoverloaded peaks. Distortion in retention time measurement and hence errors in boiling point temperature determination will be likely if column overloading occurs. The column liquid phase loading has a direct bearing on acceptable sample size. Reanalyze the calibration mixture using a smaller sample size or a more dilute solution to avoid peak distortion.

D3710 - 95 (Reapproved 2004) Procedure Section



Designation: D3710–95 (Reapproved 2004)

Standard Test Method for Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography¹

10. Procedure

10.1 *Blank*—After conditions have been set to meet performance requirements, program the column temperature upward to the maximum temperature to be used. Following a rigorously standardized schedule, cool the column to the selected starting temperature. At the exact time set by the schedule, without injecting a sample, start the column temperature program. Measure and record the area in each time interval from the start of the run until the end of the run as specified in 8.7. Make a blank run at least daily.

10.1.1 In order for the blank run to be valid, it must meet the drift requirement specified in 8.3. In addition, no peaks must be found such that the difference in area readings per second in consecutive time intervals be greater than five times the noise. If the noise is not detectable, assume it to be 1 count per second.

NOTE 13—The identification of a constant baseline at the end of the run is critical to this test method. Constant attention must be given to all factors that influence baseline stability, such as substrate bleed.

NOTE 14—Some gas chromatographs have an algorithm built into their operating software, which causes a mathematical model of the column bleed profile to be stored in memory. This profile is subtracted automatically from the detector signal on subsequent runs to compensate for the column bleed.

10.2 Calibration:

10.2.1 Using the same conditions described in 10.1, inject the calibration mixture into the chromatograph. Record the data in such a manner that retention time of peak maxima and peak area of the individual components are obtained. As noted in 8.7, this can be done by means of a computer or integrator.

NOTE 15—When determination of peak maxima and peak area is done by the time slice technique, the following algorithms can be used to verify the start of peak, end of peak, and peak maxima: A peak is defined as starting in that time slice in which the rate of change of the chromatographic signal is greater than a specified value (0.05 mV/min and 0.001 %/s have been used successfully). This criterion must be confirmed for two consecutive time segments in order to be valid. Once a peak is detected, the end is determined by one of two criteria. The first applies when there is good resolution between peaks. The peak can be defined as ending when the rate of change of the chromatographic signal is less than the value specified above. The second criterion applies when resolution between peaks is not complete. The first peak ends when, after the apex has passed, the area per time segment reaches a minimum and starts to increase. The retention time of peak maxima can be determined by the following equation, as shown in Fig. 3:

$$t_{\max} = t_i + (t_{i+1} - t_i) A_{i+1} / (A_{i-1} + A_{i+1}) \quad (3)$$

where:

t_{\max}	=	retention time of peak maxima,
t_i	=	time to start of segment i ,
t_{i+1}	=	time to start of segment $i + 1$,
A_{i+1}	=	area of segment that starts at t_{i+1} , and
A_{i-1}	=	area of segment that starts at t_{i-1} .

For systems in which the output is in units other than millivolts, an equivalent measure of the slope may be used.

10.2.2 Plot the retention time of the maxima of each peak versus the corresponding normal boiling point in degrees Celsius (or Fahrenheit) as shown in Fig. 4. If the sample is known to contain less than 5.0 % aromatics, do not include aromatic compounds in the retention time calibration curve.

NOTE 16—For best precision, the calibration curve should be essentially a linear plot of boiling point versus retention time. In general, the lower the initial boiling point of the sample, the lower will be the starting temperature of the chromatographic column. If the starting temperature is too high, there will be considerable curvature at the lower end of the curve, and loss of precision in that boiling range. Since it is impractical to operate the column so as to eliminate curvature completely at the lower end of the curve where initial boiling points below ambient temperature are encountered, at least one point on the curve should have a boiling point lower than or equal to the initial boiling point of the sample. Extrapolation of the curve at the upper end is more accurate, but for best accuracy, calibration points should bracket the boiling range of the sample at both the low and high ends.

10.2.3 The boiling point retention time calibration curve must be checked at least daily by either the calibration mixture or a secondary standard of known boiling point characteristics.

NOTE 17—If peaks in the sample are used as boiling point calibration marks, the calibration mixture need not be run. However, it may prove helpful in establishing identity of peaks in the sample to run the calibration mixture once. Furthermore, precision may be improved in some cases by adding to the sample an *n*-paraffin, selected so as to be resolved completely from

the sample, to serve as an additional boiling point calibration. Plot the retention times of the peaks versus the corresponding atmospheric boiling points to obtain the calibration curve.

10.3 Sampling:

10.3.1 Using the exact conditions and time basis as were used in the blank and calibration, inject the sample into the chromatograph. Disregarding peaks (if any) before propane, measure and record the area of each time segment at time intervals as specified in 8.7.

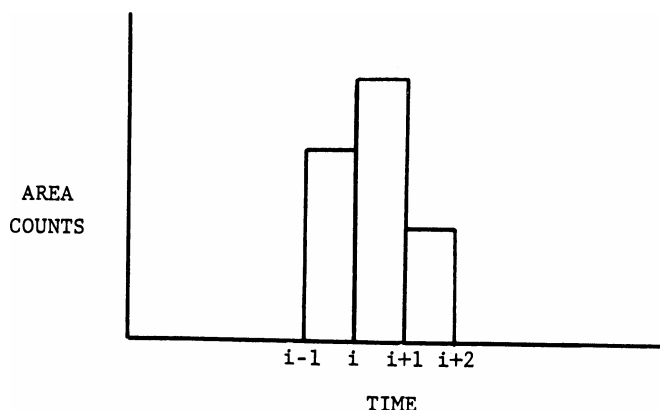


FIG. 3 Determination of Time to Peak Maxima

D5307 - 97 (Reapproved 2002) Procedure Section



Designation: D5307–97 (Reapproved 2002) ⁸¹

Standard Test Method for Determination of Boiling Range Distribution of Crude Petroleum by Gas Chromatography¹

11. Procedure

11.1 *Baseline Compensation Analysis*—To compensate for baseline drift and signal offset, subtract an area slice profile of a blank run from the sample run to obtain corrected area slices. This profile is obtained as follows:

11.1.1 After conditions have been set to meet performance requirements, program the column oven temperature upward to the maximum temperature to be used and hold for at least ten minutes.

11.1.2 Following a rigorously standardized schedule, cool the column to the selected starting temperature, and allow it to equilibrate at this temperature for at least 3 min. At the exact time set by the schedule, without injecting a sample, start the column temperature program.

11.1.3 Acquire the data in area slice mode (see 6.2.2), recording the area slices for each time interval from the start of the run until the end of the run. It is essential that all measurements be on the same time basis for the blank and sample runs.

11.1.4 Perform a blank analysis at least once each day analyses are performed.

NOTE 1—A completely satisfactory baseline is difficult to obtain when compensation for column bleed is attempted with matched dual columns and detectors. In actual practice, the best compensation can be obtained by directly subtracting the area profile of the blank run derived from a single column.

NOTE 2—Some commercially available gas chromatographs have the capability to make baseline corrections (from a stored blank analysis) directly on the detector signal. Further correction of area slices may not be required with such systems. However, if an electronic offset is added to the signal after baseline compensation, additional area slice correction may be required in the form of offset subtraction. Consult the specific instrumentation instructions to determine if an offset is applied to the signal.

11.2 *Retention Time Versus Boiling Point Calibration:*

11.2.1 Using the same conditions as for the blank run, and following the same rigorously standardized schedule (see 11.1), inject an appropriate aliquot of the calibration mixture (see 7.4) into the chromatograph. Record the data in such a manner that retention times and areas for each component are obtained (peak detection mode).

11.2.1.1 The volume of the calibration mixture injected must be selected to avoid distortion of any component peak shapes caused by overloading the sample capacity of the column. Distorted peaks will result in displacement of peak apexes (that is, erroneous retention times) and hence errors in boiling point determination. The column liquid phase loading has a direct bearing on acceptable sample size.

11.2.2 Plot the retention time of each peak versus the corresponding boiling point for that component, as shown in Fig. 2. Boiling points of *n*-paraffins are listed in Table 2. Tabulate these same data and save for later calculations.

11.2.3 The calibration curve should be essentially a linear plot of boiling point versus retention time. Since it is not practical to operate the column so as to completely eliminate curvature at the lower end of the curve, the calibration mixture must contain at least one *n*-paraffin with a boiling point equal to or lower than the IBP of the sample. Extrapolation of the curve at the upper end (to 538°C) is more accurate provided extrapolation is not made outside the temperature-programmed portion of the run. However, for best accuracy, calibration points should bracket the boiling range to be measured at both low and high ends. If normal paraffins can be unambiguously identified in the sample, these retention times may be used for calibration.

11.2.4 Perform a boiling point-retention time calibration at least once each day analyses are performed.

11.3 *Sample Preparation:*

11.3.1 Store very light samples to between 0 and 5°C. Allow the unopened sample to remain within this temperature range for at least 4 h (preferably overnight) before opening.

11.3.2 Shake or stir the sample to ensure homogeneity and pour out a small portion (approximately 100 mL) for subsequent weighing and analysis.

11.3.3 Heavy, viscous crude may require warming as well as stirring to ensure homogeneity.

11.3.4 Since water is not measured by the FID, a portion of the sample must be dried before the sample can be weighed. Add 2 to 3 g of drying agent, such as anhydrous calcium chloride, to a 50-mL vial and fill the vial about half full with sample. Cap the vial tightly and shake the vial vigorously. Allow the mixture to stand several minutes to allow the drying agent to settle out. By means of a disposable pipette, remove the dried oil layer for sample weighing and analysis.

11.3.5 Weigh at least 10 g of dried sample to the nearest 0.1 mg into a 25-mL vial.

11.3.6 Add approximately 1 g of internal standard mixture into the same vial. Determine the weight to the nearest 0.1 mg.

11.3.7 Dilute the mixture with an approximately equal volume of carbon disulfide.

11.3.8 Cap the vial tightly and shake the mixture vigorously for 3 min, or until the mixture is solubilized completely. Use this solution for the crude oil plus internal standard analysis (see 11.4.1).

11.3.9 In a second vial, dissolve approximately the same amount of dried sample as 11.3.5 with an approximately equal volume of carbon disulfide. Use this solution for the separate crude oil without internal standard analysis (see 11.4.4).

11.4 *Sample Analysis:*

11.4.1 Using the exact conditions that were used in the blank and calibration runs (see 11.1 and 11.2), and following the rigorously defined schedule (see 11.1), inject 1 μ L of the diluted crude oil plus internal standard mixture into the chromatograph. Record the area slices of each time interval through the end of the run.

11.4.2 Continue the run until the retention time equivalent to a boiling point of 538°C (1000°F) is reached. Stop recording area slices under the chromatogram at this point.

11.4.3 To remove as much as possible of the heavy components remaining on the column, continue heating the column until the FID signal returns to baseline. The column temperature may be increased to speed this process.

11.4.4 Cool the column to the starting temperature. Use identical conditions as used in 11.4.1. Inject 1 μ L of the crude oil sample without internal standard (see 11.3.9). Record the area slices of each time interval through the end of the run.

11.4.5 The sample plus internal standard analysis (see 11.4.1) and the sample only analysis (see 11.4.4) may be made in either order.

6.2.2 *Integrator*—Electronic integrator or computer-based chromatography data system must be used for detector signal integration and accumulation. The integrator/computer system must have normal chromatographic software for measuring retention time and areas of eluting peaks (peak detection mode). In addition, the system must be capable of converting the continuously integrated detector signal into area slices representing contiguous fixed duration time intervals (area slice mode). The recommended time interval is 1 s. No time interval shall be greater than 12 s. The system must be capable of subtracting the area slice of a blank run from the corresponding area slice of a sample run. Alternatively, the baseline chromatogram can be subtracted from the sample chromatogram and the net resulting chromatogram can be processed in the slice mode. A computer program that performs the slice calculation as a post-run calculation is also used.

7.4 *Calibration Mixture*—A mixture of *n*-paraffins dissolved in carbon disulfide (**Warning**—see 7.5) covering the boiling range of the sample through 538°C (1000°F). At least one compound in the mixture must have a boiling point equal to or lower than the IBP of the sample. Methane, ethane, propane, or butane can be added to the calibration mixture, if necessary, by injecting about 1 mL of the pure gaseous compound into a septum-capped, sealed vial containing the rest of the calibration mixture, using a gas syringe. If *n*-paraffin peaks can be unambiguously identified in the sample chromatogram, their retention times can be used for calibration.

TABLE 2 Boiling Points of Normal Paraffins ^A

Carbon Number	BP, °C	BP, °F	Carbon Number	BP, °C	BP, °F
1	-162	-259	23	380	716
2	-89	-128	24	391	736
3	-42	-44	25	402	756
4	0	32	26	412	774
5	36	97	27	422	792
6	69	156	28	431	808
7	98	208	29	440	825
8	126	259	30	449	840
9	151	304			
10	174	345	31	458	856
			32	466	871
11	196	385	33	474	885
12	216	421	34	481	898
13	235	455	35	489	912
14	254	489	36	496	925
15	271	520	37	503	937
16	287	549	38	509	948
17	302	576	39	516	961
18	316	601	40	522	972
19	330	626			
20	344	651	41	528	982
			42	534	993
21	356	674	43	540	1004
22	369	695	44	545	1013

^ASee Footnote 7.

D5399 - 04 Procedure Section



Designation: D5399-04

Standard Test Method for Boiling Point Distribution of Hydrocarbon Solvents by Gas Chromatography¹

9. Procedure

9.1 *Calibration*—After preparing the apparatus as in Section 8, inject the calibration mixture into the gas chromatograph. Record the data in such a manner that the retention times of peak maxima and the peak areas for each component are obtained.

9.1.1 The sample size of the calibration mixture must be chosen as to avoid distortion of the individual component peak shape caused by overloading the sample capacity of the column. Distortion in retention time measurement and hence errors in boiling point distribution will be likely with column overloading. Sample size of 0.1 to 0.5 μL have been shown to give good results.

9.1.2 This test method requires the use of commercially available “Simulated Distillation” softwares³ to process the chromatographic data in order to obtain good precision of results. Calibration of the gas chromatographic method can be done by inputting the retention times, and the normal boiling points of each of the components of the calibration mixture. The equation for the temperature versus retention time calibration curve is automatically generated by the software.

9.1.3 Insure a rigorous syringe cleaning step between samples where multiple volumes of the next sample are flushed through the syringe and deposited to waste prior to actual injection. If an autosampler or injector is used, the syringe flushing feature has to be programmed so that syringe carryover is minimized. If injections are made manually, insure that the syringe needle is thoroughly wiped clean before injection.

9.1.4 A typical calibration curve using a 30-m column is shown in Fig. 3.

9.1.5 For best precision, make sure that the calibration curve is essentially a linear plot of boiling point versus retention time. It is essential that at least one point on the calibration curve be at a lower boiling point than the IBP of the sample. Extrapolation of the curve at the upper end is more accurate, but for best accuracy, make sure that calibration points bracket the boiling range of the sample at both the low and high ends.

9.1.6 The calibration must be checked at least once a day.

9.2 *Sample Analysis*—Using identical instrument parameters and conditions used in the calibration run, inject the sample into the gas chromatograph. Record the data in such a manner that the retention times and areas of chromatographic peaks are obtained.

9.2.1 The same software used to process the calibration run must be used to process the sample gas chromatographic data. The software must be able to process the data and report IBP, and FBP, as well as boiling point data for any percent recovered (at 1 % interval) between the initial and the final boiling point.

9.2.2 Care must be taken that the sample size chosen does not allow some peaks to exceed the linear range of the detector. Choose the detector range and the sample size such that all peaks are fully integrated.

9.2.3 Baseline stability is generally not a problem for these types of samples. If problems with baseline is encountered, constant attention must be given to all factors that influence baseline stability such as column bleed, septum bleed, detector temperature control, carrier gas flow, leaks, etc. Baseline correction is generally not required for these types of samples.

9.2.4 Make periodic blank runs in the normal manner without injection of sample to insure that the system is free from contamination. If the blank run shows sample carryover contamination, steps must be taken to eliminate the source of contamination.

D6352 - 04 Procedure Section



Designation: D6352–04 ^{e1}

Standard Test Method for Boiling Range Distribution of Petroleum Distillates in Boiling Range from 174 to 700°C by Gas Chromatography¹

9. Procedure

9.1 *Analysis Sequence Protocol* —Define and use a predetermined schedule of analysis events designed to achieve maximum reproducibility for these determinations. The schedule shall include cooling the column oven and

³Beckman CALS Simulated Distillation software was used in developing this test method. There are other Simulated Distillation softwares available in the market. Such softwares are marketed by Hewlett Packard, Perkin Elmer-Nelson, Analytical Controls, VG, Separation Systems, and others.

injector to the initial starting temperature, equilibration time, sample injection and system start, analysis, and final high temperature hold time.

9.1.1 After chromatographic conditions have been set to meet performance requirements, program the column temperature upward to the maximum temperature to be used and hold that temperature for the selected time. Following the analysis sequence protocol, cool the column to the initial starting temperature.

9.1.2 During the cool down and equilibration time, ready the integrator/computer system. If a retention time calibration is being performed, use the peak detection mode. For samples and baseline compensation (with or without solvent injection), use the area slice mode operation. The recommended slice rate for this test method is 1.0 Hz (1 s). Other slice rates may be used if within the limits from 0.02 to 0.2 % of the retention time of the final calibration component (C90). Larger slice rates may be used, as may be required for other reasons, if provision is made to accumulate (bunch) the slice data to within these limits prior to determination of the boiling range distribution.

9.1.3 At the exact time set by the schedule, inject either the calibration mixture, solvent, or sample into the chromatograph; or make no injection (perform a baseline blank). At the time of injection, start the chromatograph time cycle and the integrator/computer data acquisition. Follow the analysis protocol for all subsequent repetitive analyses or calibrations. Since complete resolution of sample peaks is not expected, do not change the sensitivity setting during the analysis.

9.2 *Baseline Blank*— A blank analysis (baseline blank) shall be performed at least once per day. The blank analysis may be without injection or by injection of an equivalent solvent volume as used with sample injections, depending upon the subsequent data handling capabilities for baseline/solvent compensation. The blank analysis is typically performed prior to sample analyses, but may be useful if determined between samples or at the end of a sample sequence to provide additional data regarding instrument operation or residual sample carry over from previous sample analyses.

NOTE 4—If automatic baseline correction (see Note 2) is provided by the gas chromatograph, further correction of area slices may not be required. However, if an electronic offset is added to the signal after baseline compensation, additional area slice correction may be required in the form of offset subtraction. Consult the specific instrumentation instructions to determine if an offset is applied to the signal. If the algorithm used is unclear, the slice area data can be examined to determine if further correction is necessary. Determine if any offset has been added to the compensated signal by examining the corrected area slices of those time slices that precede the elution of any chromatographic unretained substance. If these corrected area slices (representing the true baseline) deviate from zero, subtract the average of these corrected area slices from each corrected area slice in the analysis.

9.3 *Retention Time versus Boiling Point Calibration*—A retention time versus boiling point calibration shall be performed on the same day that analyses are performed. Inject an appropriate aliquot (0.2 to 2.0 μL) of the calibration mixture (see 7.5) into the chromatograph, using the analysis schedule protocol. Obtain a normal (peak detection) data record to determine the peak retention times and the peak areas for each component. Collect a time slice area record if a boiling range distribution report is desired.

9.3.1 Inspect the chromatogram of the calibration mixture for evidence of skewed (non-Gaussian shaped) peaks. Skewness is often an indication of overloading the sample capacity of the column, which will result in displacement of the peak apex relative to non-overloaded peaks. Skewness results obtained by one laboratory are presented in Table 6. Distortion in retention time measurement and, hence, errors in boiling point temperature determination will be likely if column overloading occurs. The column liquid phase loading has a direct bearing on acceptable sample size. Reanalyze the calibration mixture using a smaller sample size or a more dilute solution if peak distortion or skewness is evident.

9.3.1.1 *Skewness Calculation*—Calculate the ratio A/B on specified peaks in the calibration mixture as indicated by the designations in Fig. 3. A is the width in seconds of the portion of the peak eluting prior to the time of the apex peak and measured at 10 % of peak height (0.10- H), and B is the width in seconds of the portion of the peak eluting after the time of the peak apex at 10 % of peak height (0.10- H). This ratio for the n-pentacotane (normal C_{50}) peak in the calibration mixture shall not be less than 0.5 or more than 2.0. Results of analysis in one laboratory are presented in Table 6.

9.3.2 Prepare a calibration table based upon the results of the analysis of the calibration mixture by recording the time of each peak maximum and the boiling point temperature in $^{\circ}\text{C}$ (or $^{\circ}\text{F}$) for each component in the mixture. A typical calibration table is presented in Table 7. n-Paraffin boiling point (atmospheric equivalent temperatures) are listed in Table 1. Fig. 1 illustrates a graphic plot of typical calibration data.

9.4 *Sample Preparation*—Sample aliquots are introduced into the gas chromatograph as solutions in a suitable solvent (for example, CS₂).

9.4.1 Place approximately 0.1 to 1 g of the sample aliquot into a screw-capped or crimp-cap vial.

9.4.2 Dilute the sample aliquot to approximately 1 weight % with the solvent.

9.4.3 Seal (cap) the vial, and mix the contents thoroughly to provide a homogeneous mixture. It may be necessary to warm the mixture initially to affect complete solution of the sample. However, the sample shall be in stable solution at room temperature prior to injection. If necessary, prepare a more dilute solution.

9.5 *Sample Analysis*— Using the analysis sequence protocol, inject a diluted sample aliquot into the gas chromatograph. Collect a contiguous time slice record of the entire analysis.

9.5.1 Be careful that the injection size chosen does not exceed the linear range of the detector. The typical sample size ranges from 0.2 to 2.0 µL of the diluted sample. The maximum sample signal amplitude should not exceed the maximum calibration signal amplitude found in 9.3.1. A chromatogram for round robin sample 95-3 is presented in Fig. 4.

9.5.2 Ensure that the system's return to baseline is achieved near the end of the run. If the sample chromatogram does not return to baseline by the end of the temperature program, the sample apparently has not completely eluted from the columns, and the sample is considered outside the scope of the test method.
