Distillation and Vapor Pressure Measurement in Petroleum Products

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Editor

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Distillation and Vapor Pressure Measurement in Petroleum Products

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Foreword

THIS PUBLICATION, Manual on *Distillation and Vapor Pressure Measurement in Petroleum Products*, was sponsored by ASTM International Committee D02 on Petroleum Products and Lubricants, and edited by Rey G. Montemayor, Imperial Oil Ltd., Sarnia, Ontario, Canada. This publication is Manual 51 of ASTM International's Manual Series.

Preface

ASTM International has been developing standards that is widely used world-wide since 1898. The technical content and quality of these standards are excellent, and these are largely due to the thousands of technical experts who volunteer and devote considerable amount of their time and effort in the standards development activities.

In ASTM Committee D02 on Petroleum Products and Lubricants, one of the largest ASTM committees, a tremendous amount of activity is spent in developing new test methods, and revising existing test methods to meet ever increasing demands for high quality standards in the industry. ASTM D02 is blessed with a considerable number of technical experts who, in one way or another, have contributed tremendously to standards development related to petroleum products and lubricants. This manual is the result of the selfless effort, time, dedication, and considerable expertise of some of these experts.

Acknowledgment

This manual would not have been possible without the help and contribution from a number of individuals. I would like to sincerely thank the authors of the different chapters who have been very responsive in submitting their manuscripts, and who have been very patient in waiting for all the publication protocols to be satisfied. Their time, effort, dedication and expertise have proven to be invaluable in the preparation of this manual. To the anonymous reviewers who have provided very helpful and constructive suggestions on their review of the content of the various chapters thereby making them easier to understand and minimize any potential misunderstanding, I would like to extend my heartfelt gratitude. Special thanks to a number of ASTM Staff who are instrumental in bringing this work to become a reality: to Lisa Drennen of Committee D02 who provided a number of ASTM historical documents; and to Monica Siperko and Kathy Dernoga of the ASTM Publications Department who provided support, guidance, and encouragement throughout the preparation of the various chapter manuscripts. I wish to thank Imperial Oil Ltd., for its continued support in the time and effort spent with this work, and other ASTM International activities. I would also like to acknowledge ASTM International and Committee D02 for sponsoring this work. And last, but not least, to Susanna, my sincere thanks for being so understanding and supportive of my involvement with ASTM International.

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Contents

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Introduction and a Brief Historical Background

Rey G. Montemayor[1]

Coverage Of The Manual

THOSE OF US ASSOCIATED WITH THE PETROLEUM industry know that crude oil and the various petroleum fractions and products derived from it consist of a complex mixture of various components, mostly hydrocarbons. Some of these components are quite volatile, and some are not so volatile. It is fairly recognized that the different petroleum fractions and products have inherent volatility characteristics. Volatility is defined as the tendency or ability of a material to change from a liquid state to gaseous state. When dealing with petroleum products, the principal volatility characteristics that are significant are distillation, vapor pressure, and flammability.

This manual deals with the practice of distillation and vapor pressure measurement either in the laboratory or at on-line facilities. Although flammability characteristics of various petroleum products measured by flash point determination provide significant volatility information, this work specifically excludes discussion of flash point measurement because there is a separate manual currently being written on the subject of flash point measurement in petroleum products. The chapters that follow provide information and discussions on the different aspects of measuring distillation and vapor pressure characteristics, with the purpose of clarifying and providing a better understanding of the various test methods. This work focuses on current standard test methods used by practitioners of distillation and vapor pressure measurements in the petroleum industry world-wide. Specifically, the standard test methods discussed are American Society for Testing and Materials (ASTM International) test methods, recognizing that there are equivalent and/or similar standard test methods in other countries as well. A cross reference of ASTM with other national standards from various countries (if known or available) are given in the appropriate chapters. The significance and use of the measured distillation and vapor pressure characteristics are covered in the chapters on specific petroleum products, such as spark-ignition engine fuels, diesel and other middle distillate fuels, aviation fuels, crude oil, liquefied petroleum gas, and hydrocarbon solvents.

Laboratory testing or measurement of the various properties and characteristics of various petroleum fractions and products serves to provide information about these materials, which can be used for research purposes, refinery plant control, and verifying the conformance to specified values in product specifications. Necessarily, the complexity of the test methods used must be consistent with the accuracy required to provide convenient and timely data about the characteristics of the materials being tested. The test methods must be standardized so that reproducible results may be obtained by different operators in various region or parts of the world using similar test equipment. ASTM test methods are widely used all over the world, and the test methods and specifications covered in this work are prime examples of standardized test methods that have withstood the test of time since their early inception.

This work is intended to be a hands-on, practical reference manual for test operators, laboratory technicians, laboratory technologists, research workers, laboratory managers, and others, who need to have a good understanding of the routine measurement test method and procedures used to determine the characteristics and properties of various petroleum products. There is no intention to elaborate the physical chemistry and thermodynamic concepts of these chemical properties. There are other works that deal with these properties in much greater technical detail, but such technical details are outside the scope of this manual. This manual aims to provide information that will be helpful for the practitioners of routine petroleum test measurements, provide better understanding of the standard test methods used to characterize these types of materials, and offer insight on how these measured properties apply to and affect the performance of these products.

Distillation Measurement

The distillation measurement test methods covered in this manual are: ASTM D86 "Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure" [1], ASTM D402 "Standard Test Method for Distillation of Cutback Asphaltic (Bituminous) Products" [2], ASTM D850 "Standard Test Method for Distillation of Industrial Aromatic Hydrocarbons and Related Materials" [3], ASTM D1078 "Standard Test Method for Distillation Range of Volatile Organic Liquids" [3], ASTM D1160 "Standard Test Method for Distillation of Petroleum Products at Reduced Pressure" [1], ASTM D2892 "Standard Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)" [4], and ASTM D5236 "Standard Test Method for Distillation

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of Heavy Hydrocarbon Mixtures (Vacuum Potstill Method)" [5].

Vapor Pressure Measurement

The vapor pressure measurement test methods covered in this manual are: ASTM D323 "Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method)" [1], ASTM D1267 "Standard Test Method for Gage Vapor Pressure of Liquefied Petroleum (LP) Gases (LP-Gas Method)" [1], ASTM D4953 "Standard Test Method for Vapor Pressure of Gasoline and Gasoline-Oxygenate Blends (Dry Method)" [5], ASTM D5190 "Standard Test Method for Vapor Pressure of Petroleum Products (Automated Method)" [5], ASTM D5191 "Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method)" [5], ASTM D5482 "Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method—Atmospheric)" [5], ASTM D6377 "Standard Test Method for Determination of Vapor Pressure of Crude Oil: VPCRx (Expansion Method) [6], D6378 "Standard Test Method for Determination of Vapor Pressure (VPx) of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method)" [6], and D6897 "Standard Test Method for Vapor Pressure of Liquefied Petroleum Gas (LPG) (Expansion Method)" [6]. Two other test methods very closely associated with vapor pressure, i.e., ASTM D2533 "Standard Test Method for Vapor-Liquid Ratio of Spark-Ignition Engine Fuels" [1] and ASTM D5188 "Standard Test Method for Vapor-Liquid Ratio Temperature Determination of Fuels (Evacuated Chamber Method)" [5], are discussed. Some lesser known vapor pressure measurement test methods mainly for very low vapor pressure materials such as solvents, lubricating oils, and pure compounds are also dealt with, albeit briefly. These are: ASTM E1194 "Standard Test Method for Vapor Pressure" [7], ASTM E1719 "Standard Test Method for Vapor Pressure of Liquids by Ebulliometry" [8], and ASTM D2879 "Standard Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope" [4].

Simulated Distillation Measurement

A separate chapter on simulated distillation is also included in this manual. Simulated distillation by gas chromatography has gained acceptance as a measure of the boiling point distribution of the various components making up petroleum products. It provides distillation data that are much more sensitive to compositional variation than what a conventional distillation test method such as D86 would give, and a number of correlation equations have been developed to give excellent correlated D86 distillation data. The simulated distillation test methods that are discussed are: ASTM D2887 "Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography" [4], ASTM D3710 "Standard Test Method for Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography" [4], ASTM D5307 "Standard Test Method for Determination of Boiling Range Distribution of Crude Petroleum by Gas Chromatography" [5], ASTM D5399 "Standard Test Method for Boiling Point Distribution of Hydrocarbon Solvents by Gas Chromatography" [3], and ASTM D6352 "Standard Test Method for Boiling Range Distribution of Petroleum Distillates in Boiling Range from 174 ° to 700 °C by Gas Chromatography" [6].

This manual will also present updated data from a recent interlaboratory study [9] conducted in 2001 to determine the relative bias (if any) of manual and automated D86 distillation results. In addition, data from the recently concluded interlaboratory study (2003) [10] comparing vapor pressure results using D5191 and D6378 test methods will be presented. These data on D86, D5191, and D6378 are in the process of being included in the existing standards.

A Bit Of History

Distillation Measurement at Atmospheric Pressure

A patent search for a test method approximating what is known today as ASTM D86 failed to yield any patent registered in the United States or in Europe. D86 was first approved in 1921 as a tentative test method and issued as D86-21T "Tentative Method of Test for Distillation of Gasoline, Naphtha, Kerosene, and Similar Petroleum Products" [11]. It is said [12] to have been first published as a standard test method in 1930 and was based on tests developed for "casinghead" or natural gasoline by the predecessor organization of the Gas Processors Association. A probable predecessor to D86-21 as a standard test method is ASTM D28-17 "Standard Tests for Paint Thinners Other than Turpentine" [13], first proposed as a tentative test method in 1915, and adopted in 1917. It prescribes the use of the Engler flask (100 mL) and condenser specifications as that required by D86-21. The D28-17 distillation apparatus is shown in Fig. 1 [12]. It is important to note that the specifications for the Engler distillation flask and condenser are very similar to the specifications indicated in the latest version of D86 with the exception that in the modern D86, a 125 mL flask is indicated for materials other than natural gasoline. The test parameters stated in D28-17 are very similar to the present day D86 test method including the rate of distillation and the flask support hole (at least for natural gasoline). The prescribed thermometer is similar to the high temperature distillation range thermometer in D86. A major difference of D28-17 relative to D86-21 and the present D86 is that the results are given in terms of the volume recovered in the receiving cylinder at the next 10 °C point after the initial boiling point and for every 10 °C interval thereafter, whereby D86 reports the temperature reading at various volumes of material recovered. For example, if the initial boiling point occurs at 144 °C, the first reading of the quantity in the receiver shall be made at 150 °C, and thereafter at 160 °C, 170 °C, etc. This is akin to the E 200 or E 300 results in current D86 reporting requirements. Another major difference is that the results in D28-17 are reported solely in °C, while in D86-21 and the current version, results are given in °F or °C. There were no precision statements in D28-17.

At the time that D86-21 was published in 1930, similar standard test methods for gasoline distillation were developed in Great Britain (IPT G3) and in France (AFNOR B6-11) [14]. In Germany, the Engler-Ubbelohde apparatus (similar to the D86-21 apparatus) was used [14], [15]. D86-21 has withstood the test of time, with all of the critical test parameters having been carried over to the present version of the test method. Because the main product of concern at the time was "natural gasoline," only a 32 mm flask support hole

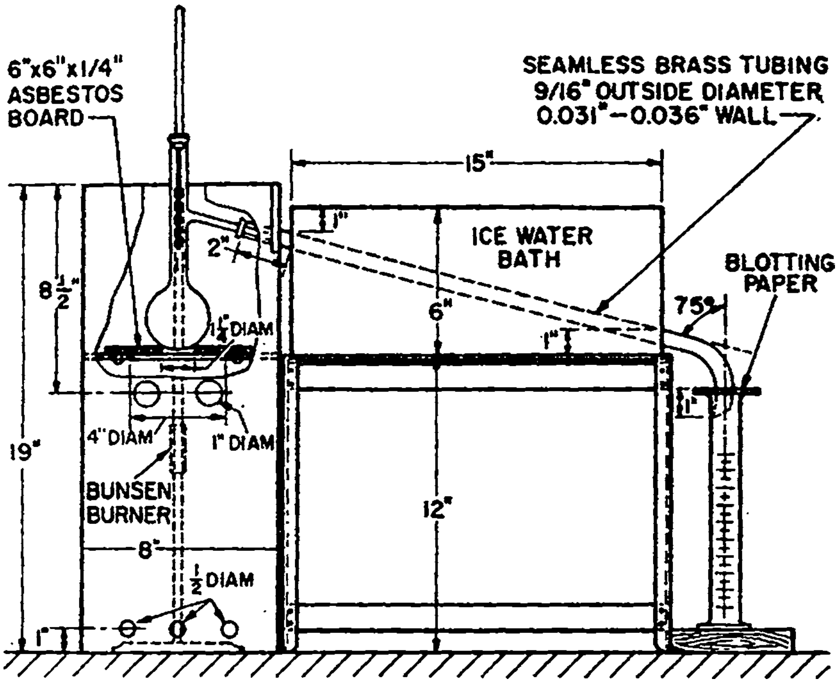

Fig. 1—The Engler distillation unit described in D28-17T.

and a 100 mL flask were specified, similar to that required by Group 0 of the present D86. There were no separate requirements for samples belonging to the Groups 0, 1, 2, 3, and 4 of today's D86. The initial boiling point, and temperature at each 10 mL mark of the graduated cylinder, the maximum temperature or end point, the recovery, residue, and distillation loss were the results reported. A precision statement under repeatability conditions was reported to be 6 °F (3.33 °C), although this was referred to as "accuracy." From the initial publication in 1920 to 1956, several revisions of D86 occurred. Correction of reported distillation temperatures to standard atmospheric pressure using the Sydney Young equation, constants "A" and "B" for calculating corrected distillation loss, and a nomograph showing the precision (repeatability and reproducibility) as a function of the rate of change of temperature reading per percent recovered were incorporated in the test method (see Fig. 2). Between 1956 and 1962, further revisions included the Group 1 to 4 classification of materials to be distilled, calculating and reporting percent evaporated in addition to percent recovered, and a table that gave comparative data for manual and automated distillation results for gasoline, kerosene, and diesel distillate fuel. In 1996, an extensive re-write of D86 was done and one of the notable changes involved the replacement of the precision nomographs with equations for manual and automated results for Groups 1 to 4. Other historical test methods dealing with distillation of petroleum products are ASTM D158-59 "Method of Test for Distillation of Gas Oil and Similar Distillate Fuels Oils" [16] and ASTM D216-77 "Method of Test for Distillation of Natural Gasoline" [17]. These have since been replaced by D86.

ASTM D850 is a distillation test method at atmospheric pressure for industrial aromatic materials with narrow boiling ranges. It was first published in 1945 as a tentative test method ASTM D850-45T "Tentative Test Method for Distillation of Industrial Aromatic Hydrocarbons" [18]. The flask dimensions specified in D850-45 are slightly different than the current version of the standard, with no precision statements. No definitions of the required boiling points were given. However, by and large, the test method is very similar to the current test method. Revisions to D850-45T have been made over the years, and it has undergone extensive rewrites in the mid-1990s to include automated and manual distillation as well as precision for both distillation techniques. ASTM D1078 is an atmospheric pressure distillation test method to determine the distillation range of volatile organic liquids boiling between 30 °C and 350 °C, and is applicable to organic liquids such as hydrocarbons, oxygenated compounds, and chemical intermediates. It was first published in 1949 as D1078-49T as "Tentative Test Method for Distillation Range of Lacquer Solvents and Diluents" [19]. It was specifically indicated not to be used for mineral spirits and similar petroleum solvents. The distillation flask dimensions specified in D1078-49T are slightly different than the current standard, and only a 32 mm (1.25 in.) flask support hole was required. Other than these differences, the original version of the standard is very similar to the current standard. The standard has undergone various revisions over the years, and in 1999 a major revision was made to include precision statements for automated and manual D1078 distillation.

Distillation Measurement at Reduced Pressure

In 1938, Fenske described in a review [20] of laboratory and small-scale distillation of petroleum products, and several apparatuses and procedures for distillation at reduced pressure. These have evolved in a number of standard test methods to determine the distillation characteristics of petroleum products and fractions that would decompose if distilled at atmospheric pressure. ASTM D1160 was first

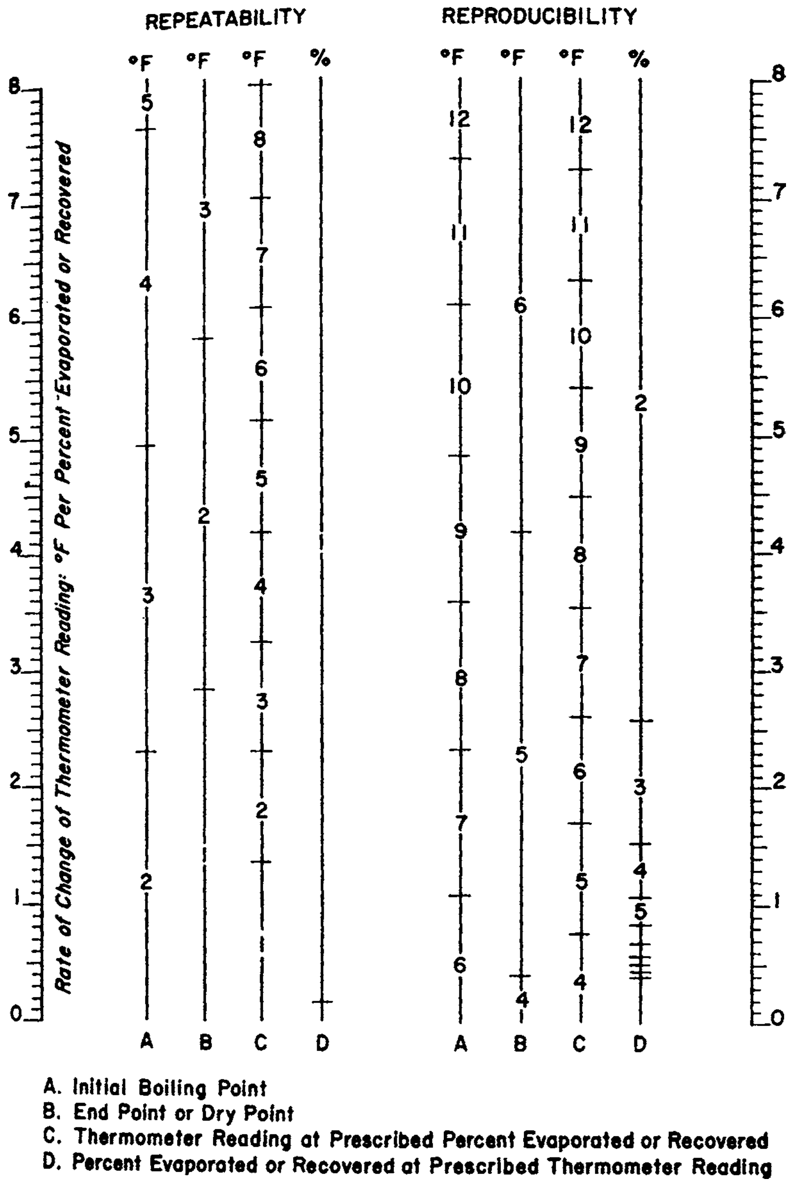

Fig. 2—Nomograph showing precision of D86-52.

published in 1951; ASTM D2892 for crude oil distillation first approved and published in 1970; and ASTM D5236 for heavy hydrocarbon mixtures such as heavy crude oils, petroleum distillates, and residues, was originally published in 1992. The original versions of these test methods are essentially very similar to the current versions, although these standards have undergone revision over time.

Simulated Distillation

In 1960, Eggerston et al. [21] demonstrated that a low resolution, temperature programmed gas chromatographic analysis could be used to simulate the data obtained by a time consuming boiling point distillation method like D2892. The gas chromatographic method was based on the observation that hydrocarbons eluted from a nonpolar column in the order of their boiling points. In essence, the gas chromatograph was operating as a very efficient microdistillation apparatus involving a much greater number of theoretical plates than the batch distillation process in conventional distillation. Because of the regularity of the elution order of hydrocarbon components, the retention times can be converted to distillation temperatures, thereby providing a fast method of obtaining boiling point distribution data. Green et al. [22] in 1964 confirmed that low resolution gas chromatographic analysis does provide distillation data that are in very good agreement with D2892 results. These authors coined the term “simulated distillation by gas chromatography” and thus a very useful analytical tool, especially for petroleum analysis, was born. Simulated distillation achieved a formal status as an ASTM standard when ASTM D2887-73 [23] was issued as “Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography.” Other simulated distillation test methods followed.

The development of simulated distillation as a routine procedure has been made possible by technological advances in gas chromatography. Beginning with the capability of automatic temperature programming, and continuing through stable and sensitive detectors, automatic instrumental parameter controls, automatic injectors and samplers, electronic integration and data processing software, the technique has developed into a very powerful analytical tool for the petroleum refining industry.

Vapor Pressure Measurement

It is said that the Reid vapor pressure test method was the result of a competition in the 1920s to improve upon the original U.S. Bureau of Mines "vapor tension" method (essentially a pressure gage on a specified length of 2 in. pipe) to measure the vapor pressure of gasoline [24]. The competition was won by W. Reid, and the resulting test method was tentatively approved as ASTM D323-30T "Tentative Test Method for Vapor Pressure of Natural Gasoline" [25]. As the title indicates, it was specifically written for natural gasoline. It required reporting in psi units and the temperature is in °F. The apparatus is essentially the same as in the current version of the method. No requirement for air saturation is made in the standard, and no precision statement is included. A correction was necessary to take into account the increase in air and water vapor pressure at the test temperature. This correction is no longer made in the current D323. ASTM D417-35T "Vapor Pressure of Motor and Aviation Gasoline (Reid Method)" [26], was approved as a tentative method in 1935. It was essentially an upgraded version of D323-30T to include aviation gasoline. The apparatus was the same, but air saturation was required and a precision statement was included (although stated to be "Accuracy"). A correction factor was still required. These earlier vapor pressure standards have withstood the test of time, and an examination of the current D323 reveals that very little change has occurred, with the exception of the correction factor and its application to products other than motor and aviation gasoline.

D4953, the dry Reid vapor pressure test method, was first approved in 1989. The other vapor pressure test methods, all of which use automated instruments, were approved shortly afterward in the early 1990s. More recent vapor pressure test methods came into existence in the late 1990s, namely, D6377 for crude oil and D6378 for gasoline, which did not require air saturation or chilling to 0 °C (32 °F).

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Distillation Measurement at Atmospheric Pressure

Rey G. Montemayor[1]

THIS CHAPTER INCLUDES THE DETAILS OF DIStillation measurement test methods for petroleum products performed at atmospheric pressure. The test methods covered are ASTM D86-04b "Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure" [1], D850-03 "Standard Test Method for Distillation of Industrial Aromatic Hydrocarbons and Related Materials" [2], and D1078 "Standard Test Method for Distillation Range of Volatile Organic Liquids" [2]. The salient features of these test methods are discussed in detail to provide information that is essential to a fuller understanding of the test procedure and to allow the practitioners of this measurement to perform the test in a manner assuring conformance to the method. Examples are given for calculations required to illustrate how reported distillation results are obtained, and explanations are provided for details of the test method that may not be obvious to users of the method. A brief discussion of D402-02 "Standard Test Method for Distillation of Cut-Back Asphaltic (Bituminous) Products" [3] will be given at the end of the chapter to complete the discussion on distillation measurements for petroleum products.

ASTM D86—Distillation At Atmospheric Pressure

Scope

This test method covers the atmospheric distillation of petroleum products using a laboratory batch distillation unit to determine quantitatively the boiling range characteristics of such products as natural gasoline, light and middle distillates, automotive spark-ignition fluids, aviation gasoline, aviation turbine fuels, diesel fuels, petroleum spirits, naphthas, white spirits, kerosines, and Grades 1 and 2 burner fuels. Hydrocarbon solvents are also included in the scope of D86. The test method is designed for distillate fuels; it is not applicable to products containing appreciable quantities of residual materials. This test method includes both manual and automated instruments.

Terminology

There are a number of terms frequently used in the distillation measurement of petroleum products. Some of the terms pertinent to the discussions in this manual are described below. For a more complete definition and discussion of other terms, the reader is referred to D86 or at subsequent discussions that follow.

Initial Boiling Point (*IBP*)—The corrected temperature reading that is observed at the instant the first drop of condensate falls from the lower end of the condenser tube.

X % Boiling Point (*e.g., 5 % boiling point*)—The corrected temperature reading corresponding to when *X* % of the distillate has been recovered in the receiving flask.

End Point (*EP*) *or Final Boiling Point* (*FBP*)—The maximum corrected temperature reading obtained during the test. This usually occurs after the evaporation of all liquid from the bottom of the flask.

Dry Point (*DP*)—The corrected temperature reading that is observed at the instant the last drop of liquid (exclusive of any drops or film of liquids on the side of the flask or on the temperature measuring device), evaporates from the lowest point in the distillation flask.

The end point or final boiling point, rather than dry point, is intended for general use. The dry point is normally reported for special purpose naphthas such as hydrocarbon solvents used in the paint and coatings industry. Dry point is also substituted for the end point (final boiling point) whenever the sample is of such nature that the precision of the end point (final boiling point) cannot consistently meet the requirements given in the precision section of the method.

Front End Loss—Loss due to evaporation during transfer from the receiving cylinder to the distillation flask, vapor loss during the distillation, and uncondensed vapor in the flask at the end of the distillation.

Percent Recovered—The volume of condensate observed in the receiving cylinder, expressed as a percentage of the charge volume associated with a simultaneous temperature reading.

Percent Recovery—The maximum amount of condensate recovered in the receiving cylinder expressed as a percentage of the charge volume.

Percent Total Recovery—The combined percent recovery and the residue in the flask.

Percent Loss—The difference between 100 and the percent total recovery.

Percent Evaporated—The sum of the percent recovered and the percent loss.

Summary of the Method

Based on its composition, vapor pressure, expected IBP or expected EP (FBP), or combination thereof, the sample is classified into one of five Groups. Apparatus arrangements,

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condenser temperature, and other operational variables are defined by the Group into which the sample falls. A 100 mL specimen of the sample is distilled under prescribed conditions for the Group in which the sample falls. The distillation is performed in a laboratory batch distillation unit at ambient atmospheric pressure under conditions that are designed to provide approximately one theoretical plate fractionation. Systematic observations of temperature readings and volumes of condensate are made, depending on the needs of the user of the data. The volume of the residue and the losses are also recorded. At the conclusion of the distillation, the observed vapor temperatures can be corrected for barometric pressure and the data are examined for conformance to procedural requirements such as distillation rates. The test is repeated if any specified condition has not been met. The results are commonly expressed as percent evaporated or percent recovered versus corresponding temperature readings.

The detailed procedure section (Sec. 10) of D86 is given in the Appendix for reference.

Significance and Use

The distillation characteristics of petroleum products have an important effect on their safety and performance, especially in the case of fuels and hydrocarbon solvents. The boiling range gives information on the composition, the properties, and the behavior of the fuel during storage and use. The distillation characteristics are critically important for both automotive and aviation gasoline, affecting starting, warm-up, and the tendency to vapor lock at high operating temperature or at high altitude, or both. The presence of high boiling components in these and other fuels can significantly affect the degree of formation of solid combustion deposits. Volatility, as it affects the rate of evaporation, is an important factor in the application of many solvents, particularly in the paints and coatings industry. Distillation limits are often included in petroleum product specifications, in commercial contract agreement, process refinery/control applications, and for compliance to various regulations.

Sampling

It has often been said the laboratory measurement result is only as good as the sample with which the test has been done. This is particularly true for petroleum products because of the complex nature of the components making up the sample. If precautions are not taken to get a representative sample of the product being tested, then the reported test results may not give an accurate value of the property being measured. ASTM D4057 "Standard Practice for Manual Sampling of Petroleum and Petroleum Products" [4] is often quoted as the standard practice for the manual sampling of petroleum and petroleum products, and ASTM D4177 "Standard Practice for Automatic Sampling of Petroleum and Petroleum Products" [4] is the standard practice for the automated sampling of petroleum and petroleum products. Detailed discussion of these sampling practices is outside the scope of this manual and the reader is referred to these ASTM standards for details. This chapter assumes that the sample that gets to the laboratory is a good and representative sample of the product being tested for distillation by D86.

TABLE 1—Group characteristics.

	Group 0	Group 1	Group 2	Group 3	Group 4
Sample characteristics					
Distillate type	Natural gasoline				
Vapor pressure at					
37.8 °C, kPa		⩾65.5	<65.5	<65.5	<65.5
100 °F, psi		⩾9.5	<9.5	<9.5	<9.5
(Test Methods D323, D4953, D5190, D5191, D5482, IP69 or IP394)					
Distillation, IBP °C				⩽100	>100
°F				⩽212	>212
EP °C		⩽250	⩽250	>250	>250
°F		⩽482	⩽482	>482	>482

Group Characteristic

When the representative sample arrives at the lab, the first thing that the test operator needs to know is to what group category or characteristic the sample belongs in order to determine the applicable operational and test parameters necessary to do the distillation. The group characteristics are based on the sample composition, vapor pressure, expected initial boiling point (IBP), or expected final boiling point (FBP), or combination thereof. Table 1 gives the various parameters that are used to determine into which group a particular sample belongs.

Group 0—If the sample is natural gasoline, i.e., a volatile hydrocarbon liquid extracted from natural gas, such as condensates that have properties somewhat similar to but more volatile than refinery gasoline, then the sample is classified as a Group 0. Natural gasolines were popular during the early days of petroleum refining, but are limited to specific markets these days. These materials are generally not sold to the general public. They are intermediate products suitable for transport and storage, but intended for further processing.

Group 1—If the sample has a vapor pressure of ⩾65.5 kPa (9.5 psi) at 37.8 °C (100 °F) and a FBP or EP of ⩽250 °C (482 °F), then the sample is classified as a Group 1 material. Most spark-ignition engine gasolines that have been made by blending components fall into this category. Most refinery intermediate streams such as catalytic cracker light naphtha and similar materials are also Group 1 distillation material.

Group 2—If the sample has a vapor pressure of <65.5 kPa (9.5 psi) at 37.8 °C (100 °F) and a FBP or EP of ⩽250 °C (482 °F), then the sample is classified as a Group 2 material. Most hydrocarbon solvents are in this category. Aviation gasoline also falls into this group. Some intermediate refinery streams such as atmospheric and vacuum debutanizer bottoms, fluid catalytic naphtha, power former feed, are classified as Group 2 distillation materials.

Group 3—If the sample has a vapor pressure of <65.5 kPa (9.5 psi) at 37.8 °C (100 °F), an IBP of ⩽100 °C (212 °F), and a FBP or EP of >250 °C (482 °F), then the sample is classified as a Group 3 material.

Group 4—If the sample has a vapor pressure of <65.5 kPa (9.5 psi) at 37.8 °C (100 °F), an IBP of >100 °C (212 °F), and a FBP or EP of >250 °C (482 °F), then the

TABLE 2—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	Ambient or above pour point[b]
	°F	<40	<50	<50	Ambient or 48 to 70 °F	Ambient or above pour point[b]
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.

sample is classified as a Group 4 material. Examples of Group 4 materials are aviation turbine (Jet-A) gasoline, kerosene, and diesel fuels. Intermediate refinery streams such as atmospheric and vacuum heavy naphtha, heavy atmospheric gas oil, light atmospheric gas oil, hydrocracker distillate, and similar material belong to Group 4. Some heavy isoparaffinic and aromatic solvents also fall into this category.

Sample Storage and Conditioning

After deciding which distillation Group the sample belongs to, Table 2 should be consulted for the correct temperature required for sample storage or conditioning as may be required. It is important that these sample storage and conditioning temperatures be adhered to if the results are to be reported as having been run according to ASTM D86.

Group 0—Requires sample storage and conditioning at <5 °C (40 °F).

Group 1—Requires sample storage and conditioning at <10 °C (50 °F).

Group 2—Requires sample storage and conditioning at <10 °C (50 °F).

Group 3—Requires sample storage at ambient temperature, and sample conditioning at ambient or 9 to 21 °C (48 to 70 °F) above pour point.

Group 4—Requires sample storage at ambient temperature, and sample conditioning at ambient or 9 to 21 °C (48 to 70 °F) above pour point.

Wet Samples

Table 2 also gives some guidance on what to do regarding wet samples. If the sample is wet when it is delivered to the lab, another sample should be obtained that is free from suspended water (resample). If the resample is still wet, or if the sample is known to be wet, dry the sample by following 7.5.2 or 7.5.3 of D86-04b using anhydrous sodium sulfate or other suitable drying agent. Once the sample shows no visible signs of water, use a decanted portion of the sample maintained at <10 °C (50 °F) for Groups 0, 1, and 2 or ambient temperature for Groups 3 and 4. The report shall note that the sample has been dried by the addition of a desiccant.

Manual and Automated D86 Apparatus

In the last 10 to 15 years, the use of the automated D86 distillation instrument has grown by leaps and bound simply because of the advantages provided by the automated instrument. In Chap. 1, the brief historical account indicated that the manual distillation instrument began in the 1920s. The original manual distillation instrument used a Bunsen burner as the heat source, specified a mercury-in-glass thermometer as the temperature measuring device, and manual reading of the temperature at specified percent recovered. The electric heater replaced the Bunsen burner as the heat source in later years, but controlling the distillation rate was still a major problem. The advent of the automated distillation instrument solved a lot of problems associated with the manual test method. The automated distillation instrument does everything that is done using the manual distillation equipment, except automatically. The sample must still be conditioned, measured, and added to the distillation flask manually. However, after the distillation unit is set up for a specific temperature profile, there is minimal involvement from the test operator and everything else proceeds automatically. The temperature at specific percent recovered is determined by a temperature measuring device, and the test results can be printed automatically after the distillation is completed. Some automated instruments have dry point sensors that allow the detection of the dry point of the sample. The use of automated distillation instrument has reduced the test operator involvement time from about 45 min to about 10 min per sample. This operator time savings can be used to do other tests in the laboratory. Hence, the use of automated D86 distillation instruments has increased productivity in the laboratory and has gained popularity and acceptance, especially in North America, Europe, the Middle East, and Asia Pacific. To be sure, there will always be some laboratories that will use a manual distillation instrument, especially those with smaller number of distillation requirements. Hence, a discussion of the manual instrument is still pertinent to users of the test method.

Figure 1 shows a schematic illustration of the early manual D86 distillation unit. Figure 2 shows a schematic diagram of a setup using electric heaters. Figure 3 shows an example of the many automated D86 distillation units currently available on the market.

Once the Group category of a given sample received in the laboratory is determined, and the sample is stored and conditioned as required, the next step is to set up the apparatus. Regardless of whether the manual or automated distillation units is used, the basic components of the distillation

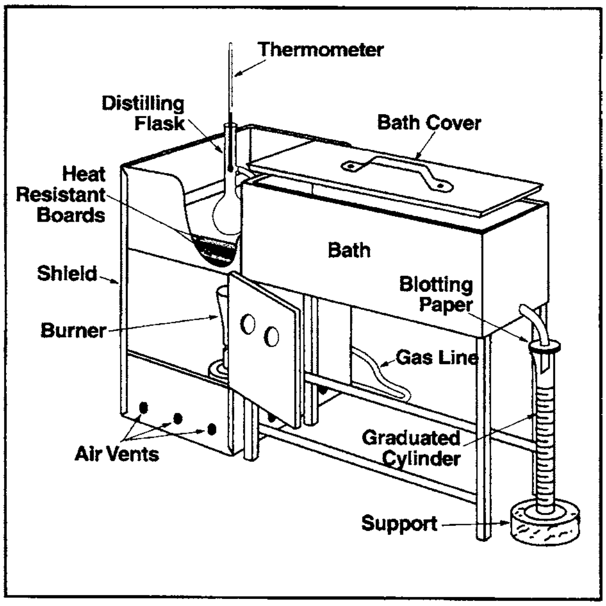


Fig. 1—Apparatus assembly using gas burner.

units are the same; namely, the distillation flask, the flask support board, the condenser and associated cooling system, the heat source, the temperature measuring device, and the receiving cylinder to collect the distillate.

Distillation Flask

Figure 4 shows the distillation flask dimensions for three type of flasks specified in D86: Flask A (100 mL) is for Group 0 materials (natural gasoline), Flask B (125 mL) for Group 1 to 4, and Flask B with ground glass joint for Groups 1 to 4. Figure 5 gives the detail of the upper neck section of the distillation flask with a ground glass joint.

Flask Support Hole Dimension

Table 3 gives the flask support board hole diameter for Group 0 to 4 material. For Group 0, the support board hole is indicated to be Type A with a diameter of 32 mm (1.25 in.). Groups 1 and 2 require a Type B support board with a hole diameter of 38 mm (1.5 in.). Type C support board for Groups 3 and 4 have a hole diameter of 50 mm (2.0 in.). The flask support board and hole diameter shall be of the prescribed dimension for each Group to ensure that the thermal heat to the flask comes only from the central opening and that extraneous heat to the flask other than through the central opening hole is minimized.

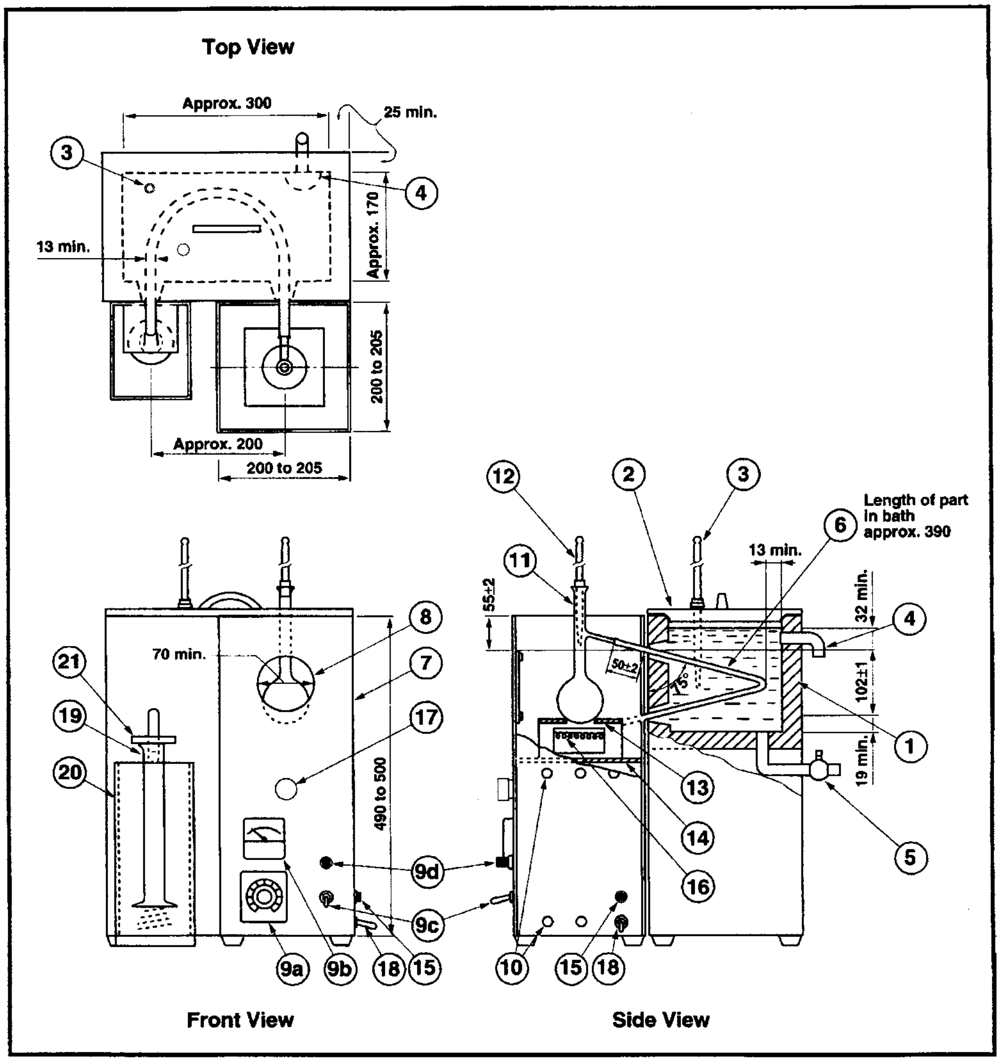
It is important that the right size flask support hole is used for a material classified as belonging to a particular group. If a flask support hole larger than specified for a given group is used, more heat than what is required would be directed onto the flask, thus making the distillation go faster with possible lower distillation temperatures being recorded. Conversely, if a smaller flask support hole than specified for a given group is used, less heat than what is required would be directed onto the flask, thus making the distillation go more slowly with possible higher distillation temperatures being recorded. Using the wrong flask support hole diameter can also affect the time from the start of distillation to IBP, the time from IBP to 5 %, the average rate of distillation, and the EP rate/or temperature.

In addition to giving the correct flask support hole diameter for each Group, Table 3 also gives information on the temperature of the flask and specimen at the start of the test and the receiving cylinder. Maintaining the temperature of the receiving cylinder at the prescribed temperature is easily done with automated instruments. However, such is not the case with the manual instrument. If the receiver cylinder temperature is much greater than what is prescribed, this could cause a loss of distillate, resulting in potentially higher distillation temperatures being reported. If no losses occur, potentially lower distillation temperature could be reported due to thermal expansion. Conversely, if the receiver temperature is much less than what is prescribed, the distillation temperatures may be higher due to thermal contraction.

Condenser and Cooling Systems

Table 4 gives the critical conditions that have to be met in order to be in compliance with the test requirements of D86. One of the parameters indicated is the temperature of the condenser, which is controlled by the cooling bath or cooling system employed in the apparatus. For Groups 0 and 1, the condenser temperature is required to be 0 °C to 1 °C (32 °F to 34 °F). Groups 2 and 3 require a condenser temperature of 0 °C to 5 °C (32 °F to 40 °F), while Group 4 would need to be maintained from 0 °C to 60 °C (32 °F to 140 °F). Sometimes, the importance of maintaining the correct condenser temperature is not appreciated, and using the incorrect condenser temperature can cause erroneous distillation results to be reported. If the condenser temperature in distilling a Group 0 or 1 material is greater than 1 °C (33 °F), the condensation process in the condenser could be affected in such a way that the first drop of condensate is delayed, thereby resulting in a higher IBP value.

In the early days of manual distillation, pieces of cracked ice were introduced into the condenser bath to maintain the proper condenser temperature. This practice was later replaced by the use of cooling coils connected to recirculating cooling baths in the condenser bath assembly to ensure conformance to the required condenser temperature. The more modern automated distillation units have very efficient refrigeration and cooling systems such that control of the condenser temperature for specific Group distillation is no problem. In most automated distillation instruments, when a test procedure is designated for a particular distillation Group, the required condenser temperature settings are automatically set and controlled. The minimum temperature that permits satisfactory operation is used. In general, a condenser temperature in the 0 °C to 4 °C is suitable for kerosine, No. 1 Grade fuel oil, and No. l-D diesel fuel oil. In some cases involving No. 2 Grade fuel oil, No. 2 Grade diesel fuel oil, gas oils, and similar middle distillates, it may be necessary to hold the condenser bath temperature in the 38 °C to 60 °C (100 °F to 140 °F) range. When distilling samples that have appreciable naphthalene content, if the condenser temperature is much lower than 60 °C (140 °F), there is the danger that the subliming naphthalene can plug the condenser tube, creating a back pressure in the distillation system that could result in a fire or worse situation.



1–Condenser bath
2–Bath cover
3–Bath temperature sensor
4–Bath overflow
5–Bath drain
6–Condenser tube
7–Shield
8–Viewing window
9a–Voltage regulator
9b–Voltmeter or ammeter
9c–Power switch
9d–Power light indicator
10–Vent
11–Distillation flask
12–Temperature sensor
13–Flask support board
14–Flask support platform
15–Ground connection
16–Electric heater
17–Knob for adjusting level of support platform
18–Power source cord
19–Receiver cylinder
20–Receiver cooling bath
21–Receiver cover

Fig. 2—Apparatus assembly using electric heater.

Heat Source and Heat Control

In addition to the condenser temperature requirements for each distillation Group materials, Table 4 also gives other critical conditions that have to be met during the test in order to ensure conformance with the test method. These are: (1) time from the first application of heat to the IBP, in minutes; (2) time from IBP to 5 % recovered in seconds or to 10 % recovered for Group 0, in minutes; (3) average rate of distillation from 5 % recovered to about 5 mL in the flask, in mL/min; and (4) time recorded from 5 mL residue to EP or FBP, in minutes. Satisfying all these requirements during the early days of manual distillation was very difficult, especially when the heat source was a Bunsen burner. When D86-21T was published, both a gas burner as well as an electric heater were indicated to be acceptable heat sources. The critical parameter was the time from initial application of heat to IBP, and the distillation rate. Later versions of the test method introduced the other parameters. With electric heaters as the heat source, heat control was done mainly by adjusting the wattage setting. Considerable test operator time was spent in adjusting wattage settings to meet the required parameters.

The amount of heat emanating from the heat source obviously affects how much time elapses from the first application of heat to the first drop of condensate into the receiving cylinder. Hence, careful determination of the required wattage setting was required when electric heaters were used. If

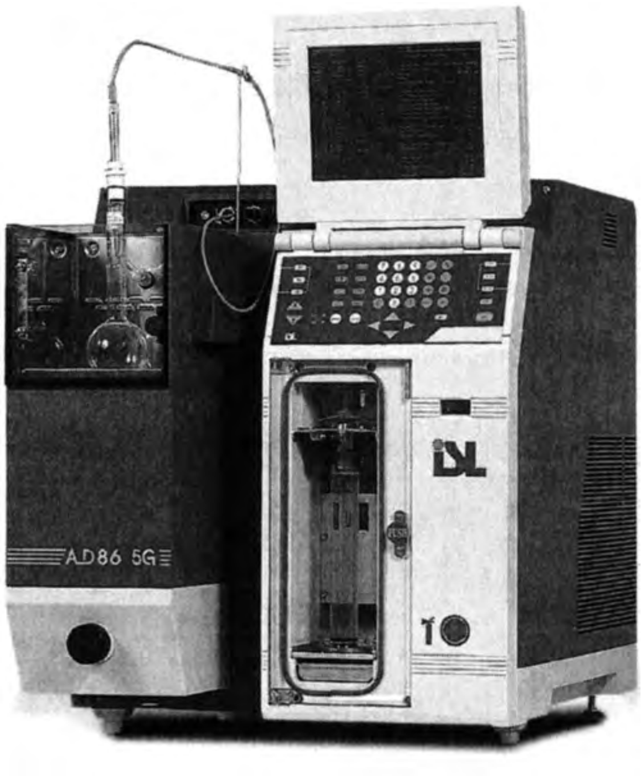


Fig. 3—An example of an automated distillation instrument. (Images courtesy of Petroleum Analyzer Company L.P. PAC LP.)

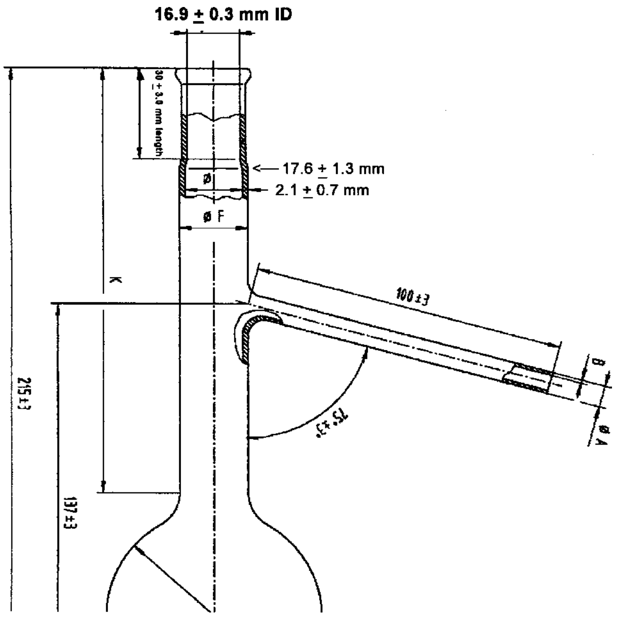
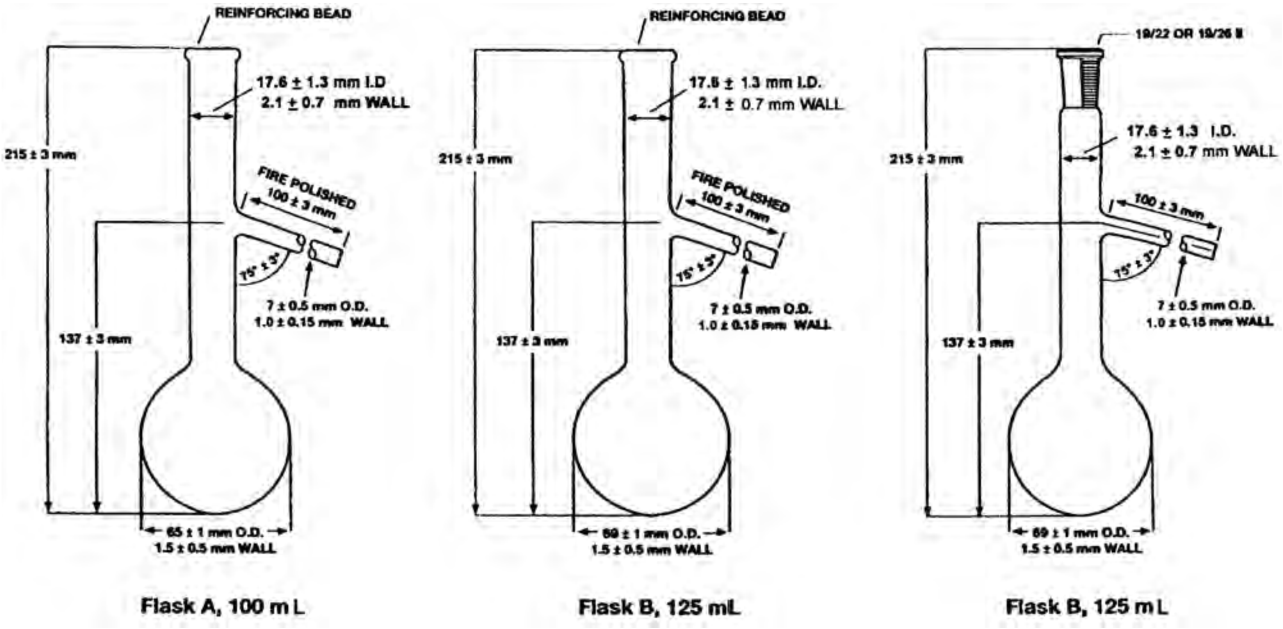


Fig. 5—Detail of upper neck section.

the initial heat is too much, the rate of boiling would be too fast, resulting in a potentially lower initial boiling point reading. If the initial heat is too little, the rate of boiling would be too slow, resulting in a potentially higher boiling point. Further adjustments were required to maintain an average distillation rate of 4 to 5 mL/min from the 5 % recovered to approximately 5 mL residue in the flask. It has to be emphasized that the required distillation rate is an average distillation rate of 4 to 5 mL/minute. Thus, it is quite possible that at some point during the distillation, the rate could be less than this or more than this. One would be in conformance with the test as long as the average distillation rate from 5 % recovered to approximately 5 mL residue in the flask, although the ideal situation is to keep the distillation rate as constant as possible throughout the test.

Since it is difficult to determine when there is 5 mL of residual material in the flask, this occurrence is estimated by observing the amount of liquid recovered in the receiving



Flask A, 100 mL

Flask B, 125 mL

Flask B, 125 mL

Fig. 4—Flask A, 100 mL; Flask B, 125 mL; and Flask B with ground glass joint, 125 mL.

TABLE 3—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	0–5	13–18	13–18	13–18	Not above
Flask °C	32–40	55–65	55–65	55–65	Ambient
°F					
Flask support and shield	Not above ambient	Not above ambient	Not above ambient	Not above ambient	
Receiving cylinder 100 mL charge	0–5	13–18	13–18	13–18[a]	13-ambient[a]
°C	32–40	55–65	55–65	55–65[a]	55-ambient[a]
°F					

[a] See 10.3.1.1 for exceptions.

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 of the material being left in the flask can be assumed to correspond with an amount of 93.5 mL in the receiving cylinder. Hence, when approximately 93.5 mL has been recovered, it is necessary to adjust the heat to recover the higher boiling components. The time required from this final heat adjustment to the FBP needs to be less than 5 min. If any of the time requirements given in Table 4 are not met, it is necessary to repeat the test, making the necessary adjustment to conform to the prescribed test parameters.

With the advent and use of computer software in modern automated distillation instruments, heat control during distillation is very efficient and a distillation rate of 4 to 5 mL/min can often be attained with minimal problems. Automated distillation equipment was mentioned in the standard as early as in the D86-62 edition. However, the degree of sophistication of their ability to control the heat during distillation cannot compare with the modern automated distillation units. Algorithms now exist that allow the instrument software to monitor and control heat parameters during distillation. Preliminary electric heater settings can be obtained when developing a temperature profile for given samples, and some automated distillation instrument can be run in a "learn mode" that allows recommended temperature profiles to be determined. With the modern automated distillation units, it is much easier to do distillation measurement of samples satisfying all the parameters required by D86.

TABLE 4—Conditions during test procedure.

	Group 0	Group 1	Group 2	Group 3	Group 4
Temperature of cooling	0–1	0–1	0–5	0–5	0–60
bath °C	32–34	32–34	32–40	32–40	32–140
°F					
Temperature of bath	0–4	13–18	13–18	13–18	±3
around °C	32–40	55–65	55–65	55–65	±5
receiving cylinder °F					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		
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 °C to 40 °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 °C to 60 °C range.

TABLE 5—Expected 50 % boiling point value for toluene for 7C and 8C thermometers.

Thermometer	ASTM IP	7C 5C	8C 6C
Toluene	50 % boiling point	109.3±0.2 °C	109.9±0.2 °C

Temperature Measurement Device

The manual D86 distillation procedure specifies two mercury-in-glass thermometers: ASTM 7C/IP 5C and ASTM 7F for low range distillation; i.e., −2 °C to 300 °C (30 °F to 580 °F), and ASTM 8C/IP 6C and ASTM 8F for high range distillation; i.e., −2 °C to 400 °C (30 °F to 760 °F). The automated D86 distillation procedure uses temperature measurement devices or systems other than the specified mercury-in-glass thermometers. Examples are thermocouples or platinum-resistance temperature probes. These other temperature measurement devices shall exhibit the same temperature lag, emergent stem effect, and accuracy as the equivalent mercury-in-glass thermometer. The electronic circuitry or algorithms, or both, used shall include the capability to simulate the temperature lag of a mercury-in-glass thermometer. More recently, other liquid-in-glass thermometer (non-mercury due to health exposure concerns) have become available. However, no published data comparing D86 results obtained using non-mercury liquid-in-glass thermometer and the specified mercury-in-glass thermometer is readily available.

The mercury-in-glass thermometers specified in the manual procedure are full immersion thermometers. However, during the distillation measurement process, the thermometer is only partially immersed. This results in readings that are lower than those that would be obtained using partial immersion thermometers. Table 5 shows that the boiling point of toluene (used as a verification fluid) is determined to be 109.3±0.2 °C when the distillation is done with an ASTM 7C thermometer relative to the 110.6 °C reading obtained by a partial immersion thermometer, and 109.9±0.2 °C for an ASTM 8C thermometer. The same is true with the other types of temperature measuring device. Therefore, similar readings for the toluene boiling point should be obtained.

The positioning of the temperature measuring device in the distillation flask is very important in order to get accurate results. Figure 6 shows the proper positioning of the thermometer in the distillation flask. Similar precaution needs to be observed for the other types of temperature measuring devices. For automated distillation instruments, follow the manufacturer's instructions as to the proper placement position. In a major rewrite of D86 in 1996, the requirement for a temperature sensor centering device was introduced. The intent was to ensure that the temperature sensor is centered within the interior walls of the flask. Figure 7 shows an example of a centering device used for straight-bore neck flasks, and Fig. 8 shows a polytetrafluoroethylene (PTFE) centering device for flasks with a ground glass joint. Other centering devices are acceptable as long as they position and hold the temperature measurement device in the proper position in the neck of the distillation flask, as shown in Fig. 6. It is important to note that when running a distillation test using the manual procedure, products with a low IBP may have one or more readings obscured by the centering device.

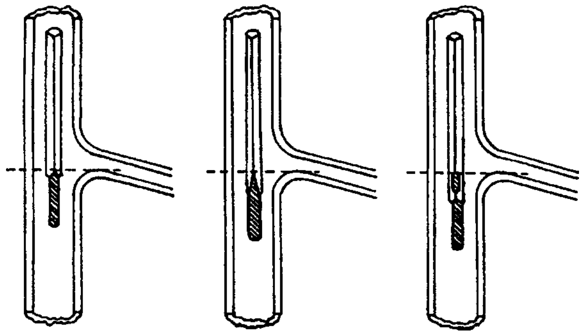


Fig. 6—Position of thermometer in distillation flask.

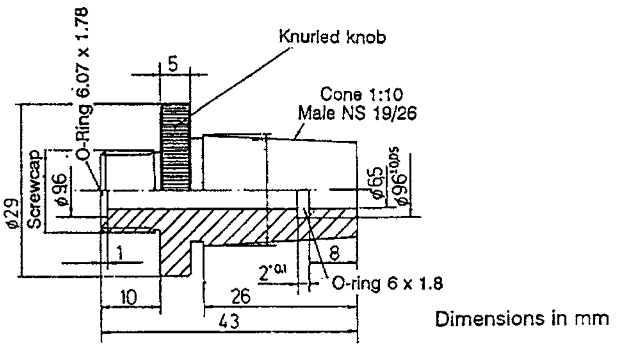


Fig. 7—Example of centering device designs for straight-bore neck flasks.

Calibration

Temperature Measuring Device

One critical apparatus that needs calibration is the temperature measurement device. The temperature measuring device provides the temperature reading at a given percent recovered, and the barometer gives the barometric pressure

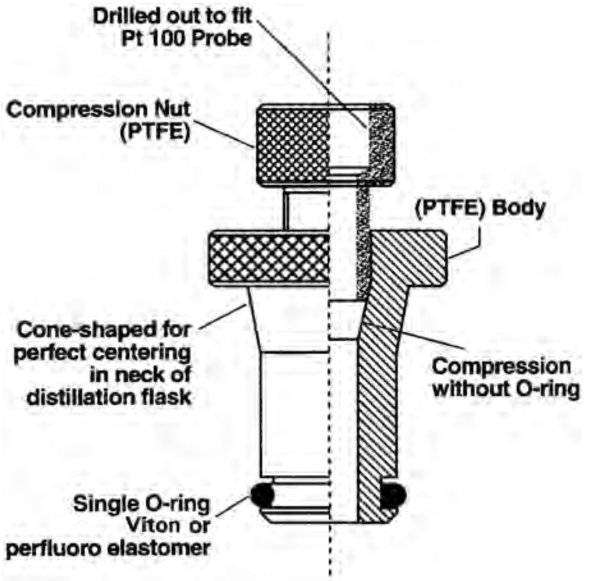


Fig. 8—PTFE Centering device for ground glass joint.

TABLE 6—Expected 50 % boiling point of *n*-hexadecane for 7C and 8C thermometers.

Thermometer	ASTM	7C	8C
	IP	5C	6C
n-hexadecane	50 % boiling point	275.0±1.0 °C	278.6±1.0 °C

used to correct the temperature reading to atmospheric pressure. The manual procedure specifies the ASTM 7C/IP 5C and 7F for low range distillation, and ASTM 8C/IP 6C and 8F for high range distillation. The calibration of these mercury-in-glass thermometers are checked using ASTM E77 "Standard Test Method for Inspection and Verification of Thermometers" [5]. The automated procedure uses temperature measuring devices other than mercury-in-glass thermometers. The accuracy and the calibration of the electronic circuitry or computer algorithms, or both, is verified by the use of a standard precision resistance bench. When performing the temperature verification, no algorithms shall be used to correct the temperature for lag and emergent stem effect. Confirmation of the calibration of thermometers and other temperature measuring devices shall be made at intervals of not more than six months, and after the system has been replaced or repaired.

The magnitude of any bias by these temperature measuring devices is determined by distilling pure toluene and comparing the 50 % recovered temperature with the values given in Table 5. Reagent grade toluene (generally >99.9 % purity) conforming to the specifications of the Committee on Analytical Reagents of the American Chemical Society is used for this verification. At 101.3 kPa, toluene is shown in reference manuals as boiling at 110.6 °C when measured using a partial immersion thermometer. Because D86 uses thermometers calibrated for total immersion, the results will be lower as shown in Table 5. For distillation of Group 3 or 4 materials, verify the performance of the temperature measuring device by distilling *n*-hexadecane (cetane). Table 6 gives the expected 50 % boiling point of *n*-hexadecane when using 7C and 8C thermometer or equivalent temperature measuring device.

No data that could be found to support the values for the 50 % boiling point of toluene and *n*-hexadecane given in Tables 5 and 6, although the difference between partial immersion and total immersion boiling points have been recognized in the standard as early as in the D86-90 edition [6]. A recent interlaboratory study on the relative bias of automated versus manual D86 distillation included toluene and *n*-hexadecane as samples. From the statistical evaluation of results for automated and manual D86 distillation, updated 50 % boiling points for toluene and *n*-hexadecane have been obtained. These updated values are shown in Table 7, and are in the process of being incorporated in D86. From Table 7, it can be seen that the updated tolerances given for the manual distillation are quite large for toluene (108.9±3 °C) for ASTM 7C/IP 5C thermometer, and similarly for *n*-hexadecane (277.7±5.5 °C) for ASTM 8C/IP6C thermometer. This might seem to be too wide a tolerance to use for checking the calibration of the instrument, but this is what the interlaboratory study shows. The updated tolerances for toluene and *n*-hexadecane for automated instruments are more in line with the previously used values, with toluene giving a tolerance value of 109.1±0.6 °C, and with *n*-hexadecane giving a tolerance value of 278.5±1.5 °C.

TABLE 7—Updated 50 % boiling points of toluene and *n*-hexadecane[a].

	Manual	Automated
Toluene	ASTM 7C/IP 5C	Groups 1, 2, and 3
	108.9±3.0 °C	109.1±0.6 °C
n-hexadecane	ASTM 8C/IP 6C	Group 4
	277.7±5.5 °C	278.5±1.5 °C

[a] Data from RR:D02-XXXX.

Receiving Cylinder and Level Follower

The receiving cylinder provides information on how much of the distillate has been recovered. Hence, it is important that the calibration of the receiving cylinder be verified for accurate results. For the manual procedure, the common practice of verifying the volumetric calibration of the receiving cylinder is to fill the tared cylinder to the 5.0 mL mark with water at ambient temperature and determining the weight of the water. Assuming that the ambient temperature is 22 °C, and that the density of water at this temperature is 0.9978 g/mL, the weight of water in the receiving cylinder when filled to the 5.0 mark should be 4.989 g. The weight of the water added during the volumetric verification obviously depends on the accuracy by which the volume of water added is read. The cylinder can also be filled to the 100 mL mark and the weight of water determined, if so desired.

In automated distillation apparatus, the air-liquid meniscus is detected using an optical-electronic device or photocell driven by a stepper motor to measure the distillate volume in the receiving cylinder. For automated distillation apparatus, the level follower/recording mechanism should have a resolution of 0.1 mL or better with a maximum error of 0.3 mL between the 5 mL and 100 mL points. The calibration of the assembly shall be verified in accordance with manufacturer's instructions at intervals of not more than 3 months, and after the system has been repaired or replaced. The typical calibration procedure involves verifying the output with the receiver containing 5 mL and 100 mL of material, respectively.

Barometer or Pressure Measuring Device

The barometric pressure is determined by means of a barometer in the case of the manual distillation procedure. The barometric pressure is required to correct the observed distillation temperature to atmospheric pressure. Hence, the calibration and proper performance of the barometer needs to be verified. Calibration of a barometer is not easily done since it involves comparing the reading of a barometer being verified with another barometer certified and traceable to a primary standard. The best way is to ensure that the barometer is set up correctly. For the Fortin type mercury barometer, the reader is referred to ASTM D3631 "Standard Test Method for Measurement of Surface Atmospheric Pressure" [7].

Automated distillation apparatus use pressure transducers to measure the prevailing atmospheric pressure. The pressure transducer reading can be verified against a mercury barometer. Most, if not all, of the automated distillation apparatus on the market today can automatically report

TABLE 8—Example of automated D86 distillation data for a Group 1 sample.

	Barometric pressure						
	Observed 98.6 kPa (740 Torr)		Corrected 101.3 kPa (760 Torr)		Arithmetical procedure		
% Recovered	°C	°F	°C	°F	% Evaporated	°C	°F
IBP	25.5	78	26.2	79.2	IBP		
5	33.0	91	33.7	92.7	5	26.7	80.0
10	39.5	103	40.3	104.5	10	34.1	93.4
15	46.0	115	46.8	116.2	15	40.7	105.2
20	54.5	130	55.3	131.5	20	47.3	117.1
30	74.0	165	74.8	166.7	30	65.7	150.2
40	93.0	199	93.9	201.0	40	84.9	184.9
50	108.0	226	108.9	228.0	50	101.9	215.3
60	123.0	253	124.0	255.1	60	116.9	242.4
70	142.0	288	143.0	289.4	70	134.1	273.3
80	166.5	332	167.6	333.6	80	156.0	312.8
85	180.5	357	181.6	358.9	85	168.4	335.1
90	200.0	393	201.6	394.8	90	182.8	361.0
EP (FBP)	215.0	419	216.2	421.1	EP (FBP)		
% Recovered	94.2		95.3				
% Residue	1.1		1.1				
% Loss	4.7		3.6				

TABLE 9—Approximate thermometer reading correction.

Temperature Range		Correction[a] per 1.3 kPa (10 Torr) Difference in Pressure	
°C	°F	°C	°F
10–30	50–86	0.35	0.63
30–50	86–122	0.38	0.68
50–70	122–158	0.40	0.72
70–90	158–194	0.42	0.76
90–110	194–230	0.45	0.81
110–130	230–266	0.47	0.85
130–150	266–302	0.50	0.89
150–170	302–338	0.52	0.94
170–190	338–374	0.54	0.98
190–210	374–410	0.57	1.02
210–230	410–446	0.59	1.07
230–250	446–482	0.62	1.11
250–270	482–518	0.64	1.15
270–290	518–554	0.66	1.20
290–310	554–590	0.69	1.24
310–330	590–626	0.71	1.28
330–350	626–662	0.74	1.33
350–370	662–698	0.76	1.37
370–390	698–734	0.78	1.41
390–410	734–770	0.81	1.46

[a] Values to be added when barometric pressure is below 101.3 (760 Torr)and to be subtracted when barometric pressure is above 101.3 kPa.

both the uncorrected distillation temperatures as well as the distillation temperatures corrected for the prevailing atmospheric pressure.

Calculations

There are a number of calculations required before the results of a distillation measurement can be reported. Sample calculations are given in this section to illustrate how observed distillation temperatures are converted to percent recovered or percent evaporated temperatures. These calculations are generally required when using the manual distillation procedure. Most, if not all, automated distillation apparatus do all these calculations automatically. Table 8 shows an example of automated D86 distillation data on a Group 1 sample. These data will be used to illustrate the various calculations.

Correcting Temperature Readings to 101.3 kPa (760 mm Hg) Pressure

When doing a manual D86 distillation, it is required to correct the observed distillation temperature to the temperature at atmospheric pressure; i.e., 101.3 kPa (760 Torr). A correction to be applied to each temperature reading is calculated using the Sydney Young equation, as given in Eqs (1)–(3) or by the use of Table 9. For Celsius temperatures:

$$C_c = 0.0009(101.3 - P_k)(273 + t_c) \tag{1}$$

$$C_c = 0.000\,12(760 - P)(273 + t_c) \tag{2}$$

For Fahrenheit temperatures:

$$C_f = 0.000\,12(760 - P)(460 + t_f) \tag{3}$$

where:

t_c = observed temperature reading in ° C,

t_f = observed temperature reading in °F,

C_c and C_f = corrections to be added algebraically to the observed temperature readings,

P_k = prevailing barometric pressure at the time and location of test, in kPa, and

P = prevailing barometric pressure at the time and location of test, in Torr.

Sample Calculation

Using the observed 50 % recovered temperature in the sample report given in Table 8, the observed Celsius temperature reading is 108.0 °C, and the prevailing barometric pressure is 98.6 kPa. Thus, $t_c = 108.0$ and $P_k = 98.6$. Using Eq (1):

$$C_c = 0.0009(101.3 - 98.6)(273 + 108.0) = 0.0009(2.7)(381.0)$$
$$= 0.0009(1028.7) = 0.9\ ^\circ\mathrm{C}$$

Corrected Celsius temperature reading: $108.0 + 0.9 = 108.9\ ^\circ\mathrm{C}$.

From Table 8, the observed Fahrenheit temperature reading for the 50 % recovered is 226.0 °F, and the prevailing barometric pressure is 740 Torr. Thus, $t_f = 226.0$ and $P = 740$. Using Eq (3):

$$C_f = 0.00012(760 - 740)(460 + 226.0) = 0.00012(20)(686.0)$$
$$= 0.00012(13720) = 1.7\ ^\circ\mathrm{F}$$

Corrected Fahrenheit temperature reading: $226.0 + 1.7 = 227.7\ ^\circ\mathrm{F}$.

To use Table 9 in the Celsius temperature reading example above, first determine how many 1.3 kPa units the difference between 101.3 kPa and the prevailing barometric pressure is. To get the correction, multiply that number by the value given in the table for the corresponding °C temperature range. In the example, $P_k = 98.6$ kPa and $t_c = 108.0$ °C:

Difference from 101.3 = (101.3 − 98.6) = 2.7 kPa

2.7/1.3 = 2.08 units of 1.3 kPa pressure difference

$C_c = 2.08(0.45) = 0.9$ °C.

To use Table 9 in the Fahrenheit temperature reading example above, first determine how many 10 Torr units the difference between 760 and the prevailing barometric pressure is. To get the correction, multiply that number by the value given in the table corresponding for the corresponding °F range. In the example, $P = 740$ Torr and $t_f = 226.0$ °F:

Difference from 760 = (760 − 740) = 20 Torr.

20/10 = 2.0 units of 10 Torr pressure difference

$C_f = 2(0.81) = 1.6$ °F.

After applying the corrections and rounding each result to the nearest 0.5 °C (1.0 °F) for manual distillation or 0.1 °C (0.2 °F) for automated distillation, use the corrected temperature readings in all further calculations and reporting unless product definitions, specifications, or agreements between parties involve specifically indicate that such correction is not required.

Percent Total Recovery and Percent Loss

The percent total recovery is the sum of the percent recovery and the percent residue. Percent recovery is the volume of distillate in the receiving cylinder at the end of the distillation. The percent residue is the volume of the liquid remaining in the distillation flask after the flask has cooled, determined by using a 5 mL cylinder. Percent loss is obtained by subtracting the percent total recovery from 100. For the data given in Table 8:

$$\text{Percent recovery} = 94.2\%$$

$$\text{Percent residue} = 1.1\%$$

$$\text{Percent total recovery} = \text{percent recovery} + \text{percent residue} = 94.2 + 1.1 = 95.3\ \% \tag{4}$$

$$\text{Percent loss} = 100 - \text{percent total recovery} = 100 - 95.3 = 4.7\ \% \tag{5}$$

Corrected Percent Loss and Corrected Percent Recovery

When the temperature readings are corrected to 101.3 kPa (760 Torr) pressure, correct the percent loss to 101.3 kPa by using Eq (6) or (7):

$$L_c = 0.5 + (L - 0.5)/\{1 + (101.3 - P_k)/8.00\} \tag{6}$$

$$L_c = 0.5 + (L - 0.5)/\{1 + (760 - P)/60.0\} \tag{7}$$

where:

L = percent loss,

L_c = corrected percent loss,

P_k = pressure in kPa, and

P = pressure in Torr.

For the data given in Table 8 where the percent loss is given to be 4.7 and the barometric pressure is 98.6 kPa:

$$\text{Corrected \% loss} = L_c = 0.5 + (4.7 - 0.5)/\{1 + (101.3 - 98.6)/8.0\} = 3.6\ \%$$

The observed percent recovery can be corrected to 101.3 kPa (760 Torr) by using Eq (8):

$$R_c = R + (L - L_c) \tag{8}$$

where:

L = observed percent loss,

L_c = corrected percent loss,

R = observed percent recovery, and

R_c = corrected percent recovery.

From the data given in Table 8 with an observed percent recovery of 94.2 %, a percent loss of 4.7 %, and a corrected loss of 3.6 %, the corrected percent recovery is:

$$R_c = 94.2 + (4.7 - 3.6) = 95.3\ \% \tag{9}$$

Percent Evaporated and Percent Recovered

It is evident that adding the percent loss to the percent recovered will give the percent evaporated. Hence:

$$P_e = P_r + L \quad \text{or} \quad P_r = P_e - L \tag{10}$$

where:

L = percent observed loss,

P_e = percent evaporated, and

P_r = percent recovered.

Temperature Readings at Prescribed Percent Evaporated

To obtain temperature readings at prescribed percent evaporated, D86 prescribes two procedures: the arithmetical procedure or the graphical procedure.

Arithmetical procedure—Subtract the observed loss from each prescribed percent evaporated to obtain the corresponding percent recovered. Calculate each required temperature reading using Eq (11) as follows:

$$T = T_L + [(T_H - T_L)(R - R_L)/(R_H - R_L)] \tag{11}$$

where:

T = temperature reading at the prescribed percent evaporated,

T_H = temperature reading recorded at R_H,

T_L = temperature reading recorded at R_L,

R = percent recovered corresponding to the prescribed percent evaporated (from Eq (10)),

R_H = percent recovered adjacent to, and higher than R, and

R_L = percent recovered adjacent to, and lower than R.

In order to provide an example calculation, the data given in Table 8 will be used. To make it simpler, only the temperature reading at 50 % evaporated will be calculated. Temperature readings at other prescribed percent evaporated will follow similar calculations. The required data from Table 8 are:

L = observed percent loss = 4.7 %,

$R = (50 - 4.7) = 45.3$ % (from Eq (10)),

R_H = 50 % recovered = percent recovered adjacent to, and higher than R,

R_L = 40 % recovered = percent recovered adjacent to, and lower than R,

T_L = 93.9 °C or 201 °F, and

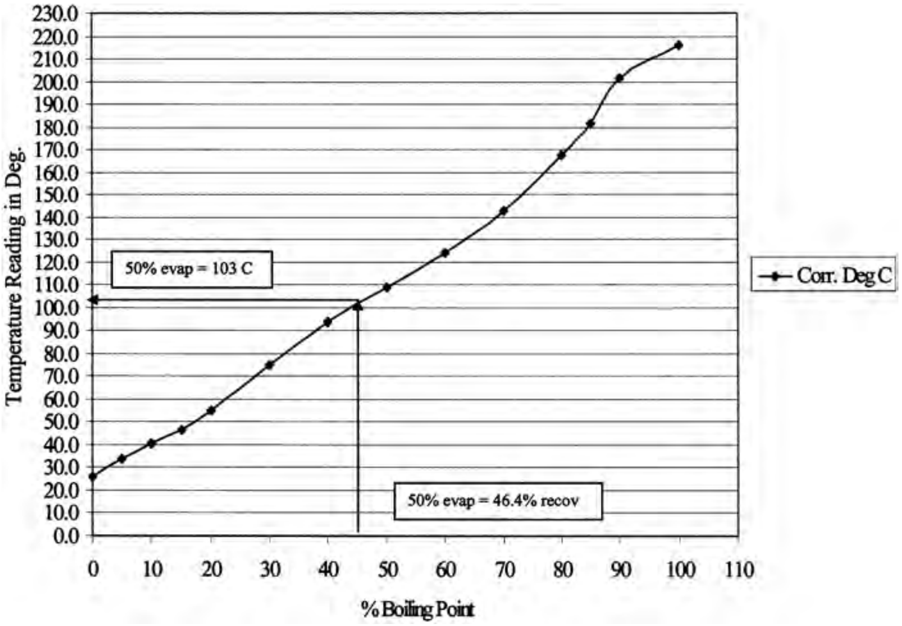


Fig. 9—Example of the graphical procedure for determining percent evaporated temperatures.

$T_H = 108.9$ °C or 228 °F.

Substituting these values into Eq (11) gives:

$$T_{50\mathrm{E}}(^\circ\mathrm{C}) = 93.9 + [(108.9 - 93.9)(45.3 - 40)/(50 - 40)] = 93.9 + [(15)(5.3)/10] = 101.9\ ^\circ\mathrm{C}$$

$$T_{50\mathrm{E}}(^\circ\mathrm{F}) = 201 + [(228 - 201)(45.3 - 40)/(50 - 40)] = 201 + [(27)(5.3)/10] = 215.3\ ^\circ\mathrm{F}$$

Because the temperature readings used were corrected for barometric pressure, the resulting temperature reading at the prescribed percent evaporated will be the temperature reading corrected to 101.3 kPa (760 Torr). If the uncorrected temperature reading at the prescribed percent evaporated is desired, the same calculation can be used with the exception that the uncorrected temperature reading values would be substituted into the equation.

It is important to note that it is not possible to calculate IBP and FBP temperatures on a percent evaporated distillation data using the discussion in this section. For that reason, IBP and FBP temperatures are generally reported the same for percent recovered or percent evaporated distillation data.

Graphical procedure—Using graph paper with uniform subdivisions, plot each temperature reading corrected for barometric pressure (if required) against its corresponding percent recovered. Plot the IBP at 0 % recovered. Draw a smooth curve connecting the points. For each prescribed percent evaporated, subtract the distillation loss to obtain the corresponding percent recovered and read the temperature reading corresponding to the calculated percent recovered.

Figure 9 gives an example of the graphical procedure as described, using the data in Table 8, showing an estimate of the 50 % evaporated temperature which is equivalent to 46.4 % recovered. The extrapolated 50 % evaporated temperature is approximately 103 °C, which is fairly close to the 101.9 °C obtained by the arithmetical procedure. A better estimate can be obtained by using graph paper with smaller subdivisions.

Percent Evaporated or Percent Recovered at a Prescribed Temperature Reading

Many specifications require specific percentages evaporated or recovered at prescribed temperature readings, either as a maximum value, minimum value, or ranges. These values are frequently designated by the terms Exxx or Rxxx, where xxx is the desired temperature. Regulatory standards on the certification of reformulated gasoline under the complex model procedure require the determination of E200 and E300, defined as percent evaporated fuel at 93.3 °C (200 °F) and 148.9 °C (300 °F). E158, the percent evaporated at a distillation temperature of 70.0 °C (158 °F) is also used in describing fuel volatility characteristics. Other typical temperatures are R200 for kerosines, and R250 and R350 for gas oils, where R200, R250, and R350 are the percent recovered at 200 °C, 250 °C, and 350 °C, respectively.

As an example of how the E200 value is obtained, the data given in Table 8 is used. From the barometric pressure during the distillation, calculate the correction to the desired temperature reading using Eq (1) and (2), or (3):

$$P_k = 98.6\ \mathrm{kPa},\ P = 740\ \mathrm{Torr},\ t_c = 93.3\ ^\circ\mathrm{C},\ \text{and}\ t_f = 200\ ^\circ\mathrm{F}$$

$$C_c = 0.0009(101.3 - 98.6)(273 + 93.3) = 0.9\ ^\circ\mathrm{C}$$

Expected t_c after taking into account correction = 93.3 − 0.9 = 92.4 °C.

$$C_f = 0.000\,12(760 - 740)(460 + 200) = 1.6\ ^\circ\mathrm{F}$$

Expected t_f after taking into account correction = 200 − 1.6 = 198.4 °F.

To get the R93.3 (R200), report the observed vol % corresponding to the temperature closest to the expected temperature reading; i.e., expected t_c or t_f. The data given in

TABLE 10—Data points for determining slope S_C or S_F.

Stope at %	IBP	5	10	20	30	40	50	60	70	80	90	95	EP
T_L at %	0	0	0	10	20	30	40	50	60	70	80	90	95
T_U at %	5	10	20	30	40	50	60	70	80	90	90	95	V_{EP}
$V_U - V_L$	5	10	20	20	20	20	20	20	20	20	10	5	$V_{EP} - 95$

Table 8 show that the R93.3 (R200) approximately 40 %. However, the data shown in Table 8 only report temperature readings at 5 % and 10 % recovered intervals, and therefore the calculated R93.3 (R200) from these data is not very accurate. If a more accurate R93.3 (R200) result is needed, D86 requires (see Annex A4.5 and A4.6 of D86-04b) that in the region between ±10 °C of the expected temperature reading, temperature-volume data are to be collected in intervals of 1 vol % for manual distillation and 0.1 vol % for automated distillation. The sample calculation given here is for illustration only and will be applicable if narrower vol % interval temperature readings are available.

To get the E93.3 (E200), add the observed loss to the R93.3 (R200). From the data given in Table 8, the E93.3 (E200) is approximated to be $40 + 3.6 = 43.6$ %. However the data shown in Table 8 only reports temperature readings at 5 % and 10 % recovered intervals, and therefore the calculated E93.3 (E200) from these data is not very accurate. If a more accurate E93.3 (E200) result is needed, D86 requires (see Annex A4.5 and A4.6 of D86-04b) that in the region between ±10 °C of the expected temperature reading, temperature-volume data are to be collected in intervals of 1 vol % for manual distillation and 0.1 vol % for automated distillation. The sample calculation given here is for illustration only and will be applicable if narrower vol % interval temperature readings are available.

A similar calculation can be done for any Rxxx or Exxx value that is required.

Slope or Rate of Change of Temperature

To determine the precision of a result, it is generally necessary to determine the slope or rate of change of the temperature at that particular point. This variable, denoted as S_C or S_F is equal to the change in temperature, either in °C or °F, respectively, per percent recovered or evaporated.

For Group 1 in the manual method, and for all Groups in the automated method, the precision of the IBP and FBP does not require any slope calculation. Other than these, the slope at any point during the distillation is calculated using Eq (12) and the values given in Table 10.

$$S_C(\text{or } S_F) = (T_U - T_L)/(V_U - V_L) \qquad (12)$$

where:

S_C = is the slope, °C/vol %,

S_F = is the slope, °F/vol %,

T_U = is the upper temperature, °C (or °F),

T_L = is the lower temperature, °C (or °F),

V_U = is the vol % recovered or evaporated corresponding to T_U, and

V_L = is the vol % recovered or evaporated corresponding to T_L.

Using the data given in Table 8, and Table 10, the slope S_C (or S_F) at 50 % recovered can be calculated using Eq. (12) as follows:

$$S_C = (124.0 - 93.9)/(60 - 40) = 1.51$$

$$S_F = (255.1 - 201.0)/(60 - 40) = 2.71$$

In the event that the distillation end point occurs prior to the 95 % point, the slope at the end point is calculated as follows:

$$S_C(\text{or } S_F) = (T_{EP} - T_{HR})/(V_{EP} - V_{HR}) \qquad (13)$$

where:

V_{EP} = is the vol % recovered or evaporated corresponding to the end point,

V_{HP} = is the vol % recovered or evaporated corresponding to the highest reading, either 80 % or 90 % prior to end point,

T_{EP} = is the temperature, in °C or °F at the distillation end point, and

T_{HP} = is the temperature at the highest reading, either 80 % or 90 % recovered or evaporated prior to the end point.

For points between 10 % and 85 % recovered not shown in Table 10, the slope is calculated as follows:

$$S_C(\text{or } S_F) = 0.05(T_{(V+10)} - T_{(V-10)}) \qquad (14)$$

For samples in Group 1, the precision data reported are based on slope values calculated from percent evaporated data. For samples in Groups 2, 3, and 4, the precision data reported are based on slope values calculated from percent recovered data. In general, when results are reported as vol % recovered, slope values for the calculation of precision are to be determined from percent recovered data; when results are reported as vol % evaporated, slope values are to be determined from percent evaporated data.

Calculation of Precision

To complete this section on calculations, examples of calculated repeatability and reproducibility at 50 % recovered temperature will be given. The data shown in Table 8, which is a Group 1 sample run on an automated distillation apparatus will be used. A detailed discussion on precision will be given in a subsequent section.

Repeatability at 50 % recovered—The repeatability equation for a 50 % recovered temperature for a Group 1 material using automated distillation and °C is:

$$r = 1.1 + 0.67S_C \qquad (15)$$

Using the $S_C = 1.51$ at 50 % recovered calculated earlier with the Table 8 data, the repeatability is estimated to be:

$$r = 1.1 + 0.67(1.51) = 2.1 \ {}^\circ\text{C}$$

The repeatability equation for a 50 % recovered temperature for a Group 1 material using automated distillation and °F is:

$$r = 2.0 + 0.67S_F \qquad (16)$$

Using the $S_F = 2.71$ at 50 % recovered calculated earlier with the Table 8 data, the repeatability is estimated to be:

$$r = 2.0 + 0.67(2.71) = 3.8 \ {}^\circ\text{F}$$

Reproducibility at 50 % recovered—The reproducibility equation for 50 % recovered temperature for a Group 1 material using automated distillation and ° C is:

$$R = 2.6 + 2.0S_C \tag{17}$$

Using the $S_C = 1.51$ at 50 % recovered calculated earlier with the Table 8 data, the reproducibility is estimated to be:

$$R = 2.6 + 2.0(1.51) = 5.6\ ^\circ\mathrm{C}$$

The reproducibility equation for a 50 % recovered temperature for a Group 1 material using automated distillation and °F is:

$$R = 4.7 + 2.0S_F \tag{18}$$

Using the $S_F = 2.71$ at 50 % recovered calculated earlier with the Table 8 data, the reproducibility is estimated to be:

$$R = 4.7 + 2.0(2.71) = 10.1\ ^\circ\mathrm{F}$$

Report

Manual Method—Report the volumetric readings to the nearest 0.5 mL, and all temperature readings to the nearest 0.5 °C (1.0 °F). Unless otherwise specified, the reported temperature readings are corrected to 101.3 kPa (760 Torr).

Automated Method—Report the volumetric readings to the nearest 0.1 mL, and all temperature readings to the nearest 0.1 °C (0.2 °F). Unless otherwise specified, the reported temperature readings are corrected to 101.3 kPa (760 Torr).

If the reported temperature readings have not been corrected to 101.3 kPa (760 Torr), this should be stated explicitly in the report. It is recommended that when the sample is gasoline, or any other products classified under Group 0 or 1, or in which the percent loss is greater than 2.0, percent evaporated temperatures should be reported. Otherwise, report either as percent evaporated or percent recovered, or as required by relevant specification. The report must indicate clearly which basis has been used. If reporting percent evaporated temperature readings using the manual method, indicate whether the arithmetical or the graphical procedure was used.

The general practice is to report the corrected IBP, 5 %, 10 %, 20 %, 30 %, 40 %, 50 %, 60 %, 70 %, 80 %, 90 %, 95 %, and EP (FBP) recovered or evaporated (see above). However, other percent recovered or evaporated intervals can be reported, as required.

Precision

Versions of D86 prior to 1996 estimated precision by using nomograph similar to the one shown in the previous chapter. During the 1996 major rewrite of the standard, the nomographs were reduced to various equations in order to make the estimation of precision values easier. In the preceding section on Calculations, examples were given to determine repeatability and reproducibility of the 50 % recovered temperature of a Group 1 material. It was seen that the precision value is dependent on the rate of temperature change per percent recovered or evaporated, or slope. Once the slope S_C or S_F of a given Group material is determined, the precision for either automated or manual distillation data can be calculated. There are three tables that can be used to calculate precision depending on whether distillation is done using the manual or automated procedure, whether the material is a Group 1, or whether the material belongs to Group 2, 3, and 4.

TABLE 11—ASTM Thermometers for distillation test of industrial aromatic hydrocarbons.

ASTM Theremometer No.	Name	Range, °C	Subdivision, °C
39C	Solvents distillation	48 to 102	0.2
40C	Solvents distillation	72 to 126	0.2
41C	Solvents distillation	98 to 152	0.2
42C	Solvents distillation	95 to 255	0.5
102C	Solvents distillation	123 to 177	0.2
103C	Solvents distillation	148 to 202	0.2
104C	Solvents distillation	173 to 227	0.2
105C	Solvents distillation	198 to 252	0.2

Table 11 gives the repeatability and reproducibility equations for Group 1 materials using manual and automated procedure. Table 12 shows the precision for manual procedure on Group 2, 3, and 4 materials. For the automated procedure on Groups 2, 3, and 4 materials, precision is calculated using equations shown in Table 13. As part of a new interlaboratory study currently under way, new precision statements for D86 will be determined.

Bias

There are no reference materials with certified D86 distillation results with which to establish an absolute bias for the test method. However, there are so-called "certified reference materials," which are normally either a specific petroleum product, or blends of products, which have been subjected to a rigorous interlaboratory study. The resulting D86 values are consensus values and not "certified values." Since

TABLE 12—Boiling points of hydrocarbons.

	Boiling Point, ° C
Cyclohexane	78.0
Benzene	80.1
Ethylbenzene	136.2
Pyridine	115.5
Toluene	110.6
m-Xylene	139.1
o-Xylene	144.4
p-Xylene	138.3

TABLE 13—Constants for correction for variations in barometric pressure (600 to 800 Torr).

Material	A	B
Benzene	0.0427	0.000 025
Toluene	0.0463	0.000 027
Ethylbenzene	0.0490	0.000 028
o-Xylene	0.0497	0.000 029
m-Xylene	0.0490	0.000 029
p-Xylene	0.0492	0.000 029
Mixed xylenes Grade xylene	0.0493	0.000 029
Solvent naphtha	0.0493	0.000 029
Hi-flash solvent	0.0530	0.000 032

calibration of D86 distillation apparatus is done using pure compounds like toluene and *n*-hexadecane, relative to these calibrating fluids, it is possible to determine some sort of bias statements (see discussion on Temperature Measuring Device, and Tables 5–7).

Relative bias is any systematic difference between manual D86 distillation results and results using an automated instrument. It was mentioned in the previous chapter that as early as the D86-62 edition [8], a table was included in the test method showing manual and automated D86 distillation results for gasoline, kerosine, and diesel fuels from cooperative studies among various laboratories. Other comparative data were included in the test method as they became available. A more recent interlaboratory study was conducted in 2001, specifically to determine an updated measure of the relative bias between manual and automated D86 distillation to take into account the considerable technical advancement in use with current automated D86 distillation instruments. The study was conducted under a tightly controlled and stringent testing protocol involving five petroleum products; namely, gasoline, mineral spirits, jet fuel, summer diesel, and winter diesel; as well as two pure materials; namely, toluene and *n*-hexadecane. Eleven laboratories participated in the manual D86 distillation and 30 laboratories participated in the automated D86 distillation procedure. Statistical evaluation of the results by ASTM D6708 [9] indicated that there was no statistically significant bias between manual and automated D86 distillation results. Details of the interlaboratory study can be found in RR:D02-1566 [10] available from ASTM International.

ASTM D850 And D1078: Distillation At Atmospheric Pressure For Aromatic Materials And Volatile Organic Solvents

Other distillation measurements at atmospheric pressure are performed using ASTM D850 and D1078. The discussion of these two test methods will not be as extensive as those given for D86.

ASTM D850

D850 covers the distillation of industrial aromatic hydrocarbons and related materials of relatively narrow boiling range from 30 to 250 °C. The terminology used in the test method is very similar to that used in D86. However, the EP (FBP) is not recorded. Instead, the dry point is noted and reported. A 100 mL specimen of the sample is distilled under prescribed distillation parameters very similar to D86. However, a 200 mL flask is used rather than the 100 mL or 125 mL flask required in D86. D850 is suitable for setting specifications and for use in development or research work on industrial aromatic hydrocarbons and related materials. The method includes both manual and automated distillation procedures. For the manual distillation, thermometers other than an ASTM 7C/IP5C and ASTM 8C/IP6C are prescribed. Table 11 gives the list of ASTM thermometers used for distillation by D850. For automated apparatus using temperature measuring device, verification of the temperature calibration is done using 50 % boiling points of toluene and other specified pure compounds (see Table 12). Temperature measuring devices are also used in conjunction of centering devices similar to those specified in D86. Condenser temperature is controlled between 10 and 20 °C and distillation rate is from 5 mL/min to 7 mL/min. Flask support board hole diameter varies from 25 mm for benzene and toluene; 38 mm for materials boiling above toluene but below 145 °C; and 50 mm for higher boiling material. Controlling the temperature of the receiving cylinder is not indicated.

TABLE 14—Summary of D850 distillation precision (°C).

	Manual		Automated					
			I.P.[a]			R[b]		
Compound	I.P.[a]	R[b]	IBP	50 %	DP	IBP	50 %	DP
Benzene	0.16	0.42	···	···	···	···	···	···
Toluene	0.23	0.47	0.24	0.10	0.23	0.58	0.16	0.46
Xylene	0.26	0.42	0.41	0.24	0.26	0.96	0.44	0.29
Cyclohexane	0.17	···	···	···	···	···	···	···
Cresol	···	···	0.68	0.42	0.68	···	···	···

[a] I.P. = Intermediate precision.

[b] R = Reproducibility.

Temperature readings at various percent recovered and the dry point are corrected for barometric pressure using Eq (19) as follows:

$$C = \{A + [B(760 - P)]\}(760 - P) \qquad (19)$$

where:

C = correction in °C,

A, B = constants from Table 13, and

P = the measured barometric pressure in Torr.

The constants A and B are given in Table 13.

The IBP, 5 %, 10 %, 20 %, 30 %, 40 %, 50 %, 60 %, 70 %, 80 %, 90 %, and 95 % recovered temperature, and DP (dry point) are reported to 0.1 °C. Distillation range, defined as the difference between the dry point and initial boiling point, is also reported as required. No statistically significant bias between automated and manual D850 distillation results was observed in the interlaboratory crosscheck program carried out to determine the current precision statement of the method. A summary of the D850 precision statement is given in Table 14. The details of the procedure section of D850 is found in the Appendix of this manual.

ASTM D1078

D1078 covers the determination of the distillation range of liquids boiling between 30 and 350 °C, that are chemically stable during the distillation process, by manual or automated distillation procedures at atmospheric pressure. The test method is applicable to organic liquids such as hydrocarbons; oxygenated solvents such as ketones, alcohols, and esters, glycols; plasticizers; and chemical intermediates generally used in the paint and coatings industry. The terminology used in the test method is very similar to that used in D86. However, the EP (FBP) is not recorded. Instead, the dry point (DP) is noted and reported. The distillation range is defined as the difference between the IBP and DP. This test method provides a method of measuring the distillation range of volatile organic liquids. The relative volatility of organic liquids can be used with other tests for identification and measurement of quality. As such, this test method provides a means of assessing compliance with relevant specifications.

TABLE 15—Thermometers.

ASTM Thermometer number	IP	Range, °C	Subdivision, °C
2C[a]	62C[a]	−5 to +300	1.0
3C[a]	73C[a]	−5 to +400	[b]
14C	···	38 to 82	0.1
37C	77C	−2 to +52	0.2
38C	78C	24 to 78	0.2
39C	79C	48 to 102	0.2
40C	80C	72 to 126	0.2
41C	81C	98 to 152	0.2
42C[a]	82C[a]	95 to 255	0.5
102C	83C	123 to 177	0.2
103C	84C	148 to 202	0.2
104C	85C	173 to 227	0.2
105C	86C	198 to 252	0.2
106C	87C	223 to 277	0.2
107C	88C	248 to 302	0.2

[a] These thermometers have more temperature lag than the other thermometers listed herein and are satisfactory for use with narrow-boiling range liquids.
[b] 1 to 301 °C; 1.5 °C above 301 °C.

A 100 mL specimen of the sample is distilled under prescribed distillation parameters very similar to D86. However, a 200 mL flask is used rather than the 100 mL or 125 mL flask required in D86. Distillation temperatures observed using partial immersion thermometer are corrected to standard atmospheric pressure. The list of ASTM thermometers that can be used with manual D1078 distillation is given in Table 15. Thermocouples or resistance thermometers are temperature measurement devices used with automated D1078 distillation. Just as in D86, these non-mercury-in-glass temperature measurement devices have to exhibit the same temperature lag and accuracy as the calibrated mercury-in-glass thermometers. Confirmation of the calibration of these temperature sensors shall be done at regular intervals. This can be accomplished potentiometrically by the use of a standard resistance decade box or by distilling pure (99.9+ % purity) toluene. The 50 % distillation temperature of toluene, corrected to standard atmospheric pressure, is shown in various reference manuals as 110.6 °C obtained under conditions of a manual D1078 distillation that uses a partial immersion thermometer.

The required condenser temperature depends on the IBP of the material being distilled. Table 16 shows that it can be from 0 °C to 50 °C depending on whether the material's IBP is below 50 °C or above 150 °C. The flask support hole dimension (referred to as heat shield hole in D1078) specified is also dependent on the IBP of the material: for those with IBP < 150 °C, a hole size of 32 mm diameter is specified; for those with IBP > 150 °C, a 38 mm diameter hole is required. The required heating rate also depends on the IBP of the material. When the IBP is < 150 °C, the time from the first application of heat to IBP should be 5 min to 10 min with the time of rise of vapor column in the neck of the flask to side arm being 2.5 min to 3.5 min. When the IBP is > 150 °C, the time from the first application of heat to IBP should be 10 min to 15 min with the time of rise of vapor column in the neck of the flask to side arm being 15 min. Distillation rate is specified to be 4 to 5 mL/min.

TABLE 16—Temperatures.

Initial Boiling Point, °C	Condenser, °C	Sample, °C
Below 50	0 to 3	0 to 3
50 to 70	0 to 10	10 to 20
70 to 150	25 to 30	20 to 30
Above 150	35 to 50	20 to 30

TABLE 17—Change of boiling point with pressure.

Compound	Value of K, °C per Torr at boiling point	K, °C per mbar at boiling point	Boiling point at 760 Torr, °C
Acetone	0.039	0.029	56.1
n-Amyl alcohol	0.041	0.031	138.0
n-Amyl acetate	0.048	0.036	149.5
Aromatic solvent naphtha	0.049	0.037	···
Benzene	0.043	0.032	80.1
Isobutyl acetate	0.045	0.035	117.3
n-Butyl acetate	0.045	0.035	126.1
sec-Butyl acetate	0.045	0.034	112.4
Isobutyl alcohol	0.036	0.027	107.9
n-Butyl alcohol	0.037	0.028	117.7
sec-Butyl alcohol	0.035	0.026	99.5
Diacetone alcohol	0.050	0.037	···
Diethylene glycol	0.050	0.037	245.0
Dipropylene glycol	0.051	0.038	232.8
Ethyl acetate	0.041	0.030	77.2
Ethyl alcohol	0.033	0.025	78.3
Ethylene glycol	0.045	0.033	197.6
2-Butoxyethanol	0.047	0.035	171.2
2-Ethoxyethanol	0.044	0.033	135.1
2-Ethoxyethyl acetate	0.046	0.035	156.3
Hexylene glycol	0.045	0.033	197.1
n-Hexyl acetate	0.050	0.037	171.6
Isophorone	0.057	0.043	215.3
Methyl alcohol	0.033	0.025	64.5
Methyl ethyl ketone	0.043	0.032	79.6
Methyl isoamyl acetate	0.048	0.036	146.2
Methyl isoamyl ketone	0.048	0.036	144.9
Methyl isobutyl carbinol	0.041	0.030	131.8
Methyl isobutyl ketone	0.046	0.035	116.2
Percholoroethylene	0.048	0.036	121.2
Isopropyl alcohol	0.033	0.025	82.3
Isopropyl acetate	0.041	0.030	88.5
Propylene glycol	0.043	0.032	187.6
Pyridine	0.046	0.035	115.4
Toluene	0.046	0.035	110.6
Trichloroethylene	0.043	0.032	87.1
Vinyl acetate	0.040	0.030	72.7
Xylene (mixed isomers)	0.049	0.037	···

The observed temperature readings at IBP, 5 %, 10 %, 20 %, 30 %, 40 %, 50 %, 60 %, 70 %, 80 %, 90 %, and 95 %, and DP (dry point) are corrected for the prevailing barometric pressure. The correction can be calculated using Eq (20):

$$\text{Correction} = K(760 - P) \qquad (20)$$

where:

K = rate of change of boiling point with pressure in °C per Torr pressure as given in Table 17, and

TABLE 18—Summary of D1078 precision data, °C.

	Manual D1078		Automatic D1078	
Parameter	Repeatability *r*	Reproducibility *R*	Repeatability *r*	Reproducibility *R*
IBP	0.005 28 *X*	0.010 7 *X*	0.004 50 *X*	0.015 6 *X*
50 %	0.004 71 *X*	0.006 47 *X*	0.002 09 *X*	0.006 83 *X*
DP	0.006 84 *X*	0.013 01 *X*	0.003 96 *X*	0.010 70 *X*
Boiling range	0.0405 $(X+5)$	0.1163 $(X+5)$	0.0445 $(X+5)$	0.1294 $(X+5)$

X=the mean of two results being compared.

P = barometric pressure in Torr.

The value of K given in °C per millibar is also given in Table 17 if the barometric pressure is in millibar. The applicable equation is given by Eq (21):

$$\text{Correction} = K(1013 - P) \tag{21}$$

where:

K = rate of change of boiling point with pressure in °C per millibar pressure as given in Table 17, and

P = barometric pressure in millibars.

For other pure compounds not listed in Table 17, the value of K can be approximated to be 0.000 12 times the normal IBP on the absolute temperature scale.

The percent recovery should not be less than 97 % for nonviscous liquids with distillation range of <10 °C. For viscous liquids and materials having a distillation range of >10 °C, the percent recovery should not be less than 95 %. If percent recoveries are outside these limits, the test should be repeated. D1078 does not specify specific parameters to report. It simply states that the results shall be reported in a manner conforming with the specifications of the material test. If no definite manner of reporting is specified, report the corrected temperatures at each percent recovered including IBP and dry point. Distillation range is also generally reported.

An interlaboratory study in 2000 indicated that there is no significant difference in D1078 automated versus manual results. The study also provided data showing that the precision is dependent on the boiling point temperature. Tables 18 and 19 give a summary of D1078 precision and sample calculation of D1078 Precision value for IBP, 50 % boiling point, DP (dry point), and boiling point range. Details of the D1078 procedure section can be found in the Appendix section of this manual.

Comparison Of ASTM D86, D850, And D1078

Table 20 provides an easy comparison of the important features and parameters of D86, D850, and D1078.

Potential Troubleshooting Guide

When the results of a distillation measurement deviate from the normally expected values, the operator often times has to determine a possible explanation for the abnormal results. It could be that the distillation results are correct and valid with changes in composition of the material being tested giving different results than previous samples. However, there are occasions when the abnormal result(s) can be due to specific problems during the distillation measurement process itself, and when corrected, can provide results which are more in line with normally expected values (or range of values). Such is the purpose of Table 21, which is generally applicable to Group 0, 1, and 2 materials. When a problem with a distillation result is encountered, Table 21 may help in potentially pinpointing the cause of abnormal test results. Correcting the suspected cause, could provide distillation results which would be closer to expected values.

It has to be recognized that Table 21 is not meant to cover all possible scenarios that can be encountered during a distillation measurement. Sometimes the effect of a deviating test parameter is not straightforward, especially when distilling higher boiling point materials like Group 4 samples. For example, as a result of faster rate of condensa-

TABLE 19—Sample calculation of D1078 precision values, °C.

Manual D1078 RR—IBP Data			Auto D1078 RR—IBP Data		
IBP	*r*	*R*	IBP	*r*	*R*
50	0.3	0.5	50	0.2	0.8
75	0.4	0.8	75	0.3	1.2
100	0.5	1.1	100	0.5	1.6
125	0.7	1.3	125	0.6	2.0
150	0.8	1.6	150	0.7	2.3
175	0.9	1.9	175	0.8	2.7

Manual D1078 RR—50 % Data			Auto D1078 RR—50 % Data		
50 %	*r*	*R*	50 %	*r*	*R*
50	0.2	0.3	50	0.1	0.3
75	0.4	0.5	75	0.2	0.5
100	0.5	0.6	100	0.2	0.7
125	0.6	0.8	125	0.3	0.9
150	0.7	1.0	150	0.3	1.0
175	0.8	1.1	175	0.4	1.2

Manual D1078 RR—DP Data			Auto D1078 RR—DP Data		
DP	*r*	*R*	DP	*r*	*R*
50	0.3	0.7	50	0.2	0.5
75	0.5	1.0	75	0.3	0.8
100	0.7	1.3	100	0.4	1.1
125	0.9	1.6	125	0.5	1.3
150	1.0	2.0	150	0.6	1.6
175	1.2	2.3	175	0.7	1.9

Manual D1078 RR—BPR[a] Data			Auto D1078 RR—BPR Data		
BPR	*r*	*R*	BPR	*r*	*R*
0.5	0.2	0.6	0.5	0.2	0.7
5	0.4	1.2	5	0.4	1.3
10	0.6	1.7	10	0.7	1.9
15	0.8	2.3	15	0.9	2.6
20	1.0	2.9	20	1.1	3.2
25	1.2	3.5	25	1.3	3.9
30	1.4	4.1	30	1.6	4.5

[a] BPR=boiling point range.

TABLE 20—Comparison of D86, D850, and D1078 Test Methods.

Item	D86	D850	D1078
Basis for test parameters	Groups (0–4)	IBP	IBP
Specimen size	100 mL	100 mL	100 mL
Distillation Flask	100 mL (Group 0) 125 mL (Groups 1–4)	200 mL	200 mL
Flask support hole diameter	32 mm (Group 0) 38 mm (Groups 1 and 2) 50 mm (Groups 3 and 4)	25 mm (benz and toluene) 38 mm (IBP$<$145 °C) 50 mm (IBP$>$145 °C)	32 mm (IBP$<$150 °C) 38 mm (IBP$>$150 °C)
# Specified thermometers	2	8	15
Condenser temperature	0–1 °C (Group 0 and 1) 0–5 °C (Group 2 and 3) 0–60 °C (Group 4)	10–20 °C	0–3 °C (IBP$<$50 °C) 0–10 °C (IBP 50–70 °C) 25–30 °C (IBP 70–150 °C) 35–50 °C (IBP$>$150 °C)
Rate of heat to IBP	2–5 min (Group 0) 5–10 min (Group 1–3) 5–15 min (Group 4)	5–10 min	5–10 min (IBP$<$150° C) 10–15 min (IBP$>$150°C)
Time from IBP to 5 % recovered	60–100 s (Group 1 and 2)	···	···
Time vapor ring to flask side-arm	···	90–120 s	2.5–3.5 min (IBP$<$150 °C)
Rate of distillation	4–5 mL/min	5–7 mL/min	4–5 mL/min
95 % to EP	5 min max	···	5 min max
EP (FBP) or DP	EP (FBP)	DP	DP
Precision for 50 % recovered for toluene (manual)	r=1.0 °C R=1.8 °C	I.P.[a] =0.23 °C R=0.47 °C	r=0.5 °C R=0.6 °C
Precision for 50 % recovered for Toluene (auto)	r=1.2 °C R=2.9 °C	I.P.[a] =0.10 °C R=0.16 °C	r=0.2 °C R=0.7 °C

[a] I.P.=Intermediate precision.

tion of the vapors in the condenser tube, the effect of a lower condenser temperature would be to give a lower distillation temperature reading than if the correct condenser temperature is used for Groups 0–2 materials. However, for Group 4 material, the condensate flow through the condenser tube would be reduced to such an extent that the temperature reading at a given percent volume recovered would be higher than if the correct condenser temperature is employed. For a lighter boiling material, if the receiver temperature is higher than indicated in the method, evaporation loss could become substantial such that the observed distillation temperature could be higher than if the correct receiver temperature is used. However, for higher boiling material, warmer receiver temperature could be sufficient to cause expansion of the recovered liquid such that the observed distillation temperature could be lower than if the receiver temperature is set correctly. Hence, Table 21 is indicated only to be a potential troubleshooting guide.

Safety

In the early days of D86 distillation, a common occurrence was a fire resulting from breakage or cracking of the distillation flask. The use of an open flame when Bunsen burners were the heat source provided the ignition source for such fires. Even when Bunsen burners were replaced with electric heaters, the heater element still provides a good ignition source for the material being distilled whenever the flask breaks. Even today with the use of automated equipment, such risk still exists, and because the distillation setup is often left unattended, there is the added danger that such a fire can go undetected. Quartz distillation flasks have become available that have minimized the risk of flask breakage. Most, if not all, automated distillation instruments are now equipped with automatic fire detection and suppression mechanisms. As such, if a fire is detected as a result of a flask breakage, the heater system is automatically shut off, and a fire suppression mechanism is activated. Of course, in order to work properly, the fire suppression mechanism has to be properly installed and connected to a source of nitrogen or carbon dioxide gas.

Another source of safety incident involving distillation equipment is wrongly labeled samples. Occasionally, a sample is delivered to the laboratory with a label indicating that the sample is a higher boiling material when in fact it is a lower boiling material. When the heater setting for a higher boiling material is used, it would normally cause the wrongly labeled low boiling material to boil too fast, potentially causing an overpressure in the distillation assembly. This could cause the stopper assembly to be loosened in such a way that the boiling material can spill over onto the heater elements and catch fire. Again, the fire detection and suppression mechanism would help in such an incident. Sometimes the condenser tube could become plugged with materials that sublime under the distillation condition or waxes. When this happens, extreme back pressure can be created causing the stopper to be loosened, and a fire could start. On occasion, especially when performing a distillation on a low boiling material, if the condenser temperature controller

TABLE 21—Potential troubleshooting guide for distillation measurement.

Problem	Symptom	Probable cause	Suggested corrective action
Lower distillation temperature results than expected	Initial to IBP time <5 min	Heater temperature too high	Adjust heater temperature
		Flask support hole diameter too big	Use correct flask support hole size
	Time from IBP to 5 % point <60 s	Heater temperature too high	Adjust heater temperature
		Flask support hole diameter too big	Use correct flask support hole size
	Distillation rate >4–5 mL/min	Heater temperature too high	Adjust heater temperature
		Flask support hole diameter too big	Use correct flask support hole size
		Thermometer or probe position too high	Adjust position of thermometer or probe
		Condenser temperature too low[a]	Adjust condenser temperature
	Temperature measuring device reading low	Temperature measuring device out of calibration	Perform calibration check
	Condenser temperature giving low reading	Faulty condenser temperature controller	Correct or repair condenser temperature controller
		Barometer reading too high	Check barometer calibration and operation
Higher distillation temperature results than expected	Initial to IBP time >5 min	Heater temperature too low	Adjust heater temperature
		Flask support hole diameter too small	Use correct flask support hole size
	Time from IBP to 5 % point >100 s	Heater temperature too low	Adjust heater temperature
		Flask support hole diameter too small	Use correct flask support hole size
	Distillation rate <4–5 mL/min	Heater temperature too low	Adjust heater temperature
		Flask support hole diameter too small	Use correct flask support hole size
		Thermometer or probe position too low	Adjust position of thermometer or probe
		Condenser temperature too high[a]	Adjust condenser temperature
	Temperature measuring device reading high	Temperature measuring device out of calibration	Perform calibration check
	Condenser temperature giving high reading	Faulty condenser temperature controller	Correct or repair condenser temperature controller
		Barometer reading too low	Check barometer calibration and operation
		Receiver temperature too high[a]	Check receiver temperature controller

[a] See discussion after this Table.

malfunctions such that the condenser temperature is below the freezing point of the material being distilled, the condenser tube plugs up and a similar back pressure can develop and cause a fire.

Just like any test method, there are inherent risks, though minimal, associated with performing a distillation procedure. It is important that practitioners of distillation measurement be aware of the safety aspects of doing the procedure. Distillation measurements can be done safely with proper attention to details.

Statistical Quality Control

Although D86, D850, and D1078 do not mandate the use of statistical quality control tools to ensure that the test procedure utilized in generating distillation data is in statistical control, it has become an increasingly prevalent good laboratory practice in various organizations to do so. Samples representative of the products being manufactured should be used as the quality control (QC) sample to monitor the “in-control” status of the instrument and the test method. The

TABLE 22—Cross-reference of distillation at atmospheric pressure test methods.

Test Method	Europe	UK	France	Germany	Japan
ASTM D86	ISO 3405	IP 123	AFNOR M07-002	DIN 51751	K 2254
ASTM D402	···	IP 27	···	···	···
ASTM D850	···	···	···	···	···
ASTM D1078	···	IP 195	···	···	···

QC sample should be stable and not subject to deterioration over a reasonable period of time. Standard statistical quality control procedures can be used, and a good example of such a standard is ASTM D6299 [9]. Out-of-control situations encountered when monitoring the QC data helps in identifying instrumental conditions that could produce erroneous distillation results. Causes for out-of-control statistical data need to be investigated, and corrective action(s) implemented to correct the identified cause(s) and return the instrument to statistical control. If necessary, a calibration check may be required as a result of monitoring QC data.

Cross-Reference Of Distillation At Atmospheric Pressure Test Methods

ASTM D86, D850, and D1078 are used in North America and other countries that use ASTM standards. However, because the petroleum industry is a world wide industry, there are test methods very similar to D86 and D1078 that are used in other parts of the world in testing petroleum and related materials. Table 22 gives a cross-reference to other test methods used in the distillation measurement at atmospheric pressure.

New Test Methods For Distillation At Atmospheric Pressure

Two new distillation test methods are currently under development: a Mini distillation method and a Micro distillation method. Both test methods aim to provide distillation data comparable to D86 data but using much smaller specimen sizes and shorter turnaround time. No procedural details will be given in this manual regarding these new distillation test methods. Only the important features of each of these test methods will be given. Preliminary data indicate that the distillation results from these two methods give comparable D86 distillation results. An interlaboratory study is being organized to generate precision statements for these new test methods. When the precision statements for these test methods become available, two new ASTM standards will be balloted for approval. These new standards will have new ASTM designations, and will be separate and distinct from D86, D850, or D1078 test methods.

Micro Method

- Sample size = 10 mL
- Manual introduction of sample to distillation flask
- Sample analysis time of less than 10 min
- Measures vapor and liquid temperature by fast-response, low inertia sensor
- Monitors pressure in the distillation flask during atmospheric distillation, which is converted to distilled volume percent by a patented algorithm

Fig. 10—An Example of a micro distillation instrument. (Images courtesy of Petroleum Analyzer Company L.P. PAC LP.)

- Allows determination of distillation characteristics of petroleum products with atmospheric boiling ranges between 20 °C and 400 °C
- Eliminates condenser cooling, receiver and volume measurement; distillate condenses into waste bottle
- Portable design

Figure 10 shows an example of a Micro distillation instrument.

Mini Method

- Sample size = 6 mL
- Automatic transfer of sample into disposable metal sample cup
- Sample analysis time = 15 min
- Allows determination of distillation characteristics of petroleum products with atmospheric boiling ranges between 20 °C to 400 °C
- Samples need to be identified by Groups (similar to D86)
- Sample is heated, evaporated, and condensed into receiver cell
- Vapor temperature is monitored with a thermoelectric sensor
- Distillate volume is determined by a stationary diode array detector
- Operator initiated automatic cleaning cycle via an automatic acetone distillation cycle
- Portable design

Figure 11 shows an example of a Micro distillation instrument.

ASTM D402 Distillation Of Cut-Back Asphaltic Product

This distillation test method is under the jurisdiction of ASTM Committee D04 on Road and Paving Materials. This test method is also a batch distillation similar to D86 with the exception that 200 mL of the sample is distilled in a 500 mL flask, at a controlled rate, to a liquid temperature of 360 °C (680 °F). The volumes of distillate obtained at specified temperatures are measured. The residue from the distil-

Fig. 11—An example of a mini distillation instrument. (Images courtesy of Grabner Instruments.)

lation, as well as the distillated, may also be tested as required.

This test method measures the amount of the more volatile components in cut-back asphaltic product. A standard 100 mL graduated cylinder or a 100 mL Crow receiver is used in this test method. An ASTM 8C or IP 6C thermometer is used to measure the liquid temperature during the test, although an other equivalent thermometric device can be used. The thermometer is immersed in the liquid sample about 6 mm from the bottom of the flask. Because of the nature of the sample, the calculated amount of sample to give 200 mL is transferred gravimetrically into the 500 mL flask.

The following parameters are calculated from the test results:

$$\mathit{Asphaltic\ Residue}(\text{vol } \%) = [200 - TD/200] \times 100 \quad (22)$$

$$\mathit{Total\ Distillate}(\text{vol } \%) = (TD/200) \times 100 \quad (23)$$

where:

TD = total volume of distillate recovered to 360 °C (680 °F)

In addition, distillate fractions to 190 °C (374 °F), 225 °C (437 °F), 260 °C (500 °F), and 316 °C (600 °F) are also reported.

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3

Distillation Measurement at Reduced Pressure

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THIS CHAPTER INCLUDES A DISCUSSION ON THE details of distillation measurement test methods for petroleum products performed at reduced pressure. The test methods covered are ASTM D2892-03 “Standard Test Method for Distillation of Crude Petroleum (15 Theoretical Plate Column)” [1], D5236-03 “Standard Test Method for Distillation of Heavy Hydrocarbon Mixtures (Vacuum Pot-still Method)” [2], and D1160-03 “Standard Test Method for Distillation of Petroleum Products at Reduced Pressure” [3].

Distillation Of Crude Petroleum By ASTM D2892

Introduction

ASTM D2892 “Standard Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)” as the full title reads, is different from other ASTM Standard Test Methods, as it does not yield a defined set of standard numbers. The scope reads: “This test method details *procedures for the production* of a liquefied gas, distillate fractions, and residuum *of standardized quality* on which analytical data can be obtained, *and the determination of yields of the above fractions* by both mass and volume.” From this description it is evident that ASTM D2892 is a preparative method, to produce fractions of standardized quality. However, it does not specify the “fractions,” and “quality” is only indirectly specified. Moreover, this standard test method does not provide for detailed design specifications of the equipment used. Instead D2892 provides for equipment performance specifications. In this respect, the scope reads: “*Performance* criteria for the necessary equipment is specified.” Hence, ASTM D2892 is rather a framework, a standard guideline for laboratory distillation of crude oils, than a true test method. This approach has significant bearing on the interpretation and comparison of results produced by this test method.

Field Of Application

ASTM D2892 does not appear in any official international fuel or product specification, but is widely used in contracts and other types of internal, or mutually voluntary specifications. The main application areas are:

1. Assessment of crude oil processability and other engineering applications commonly referred to as “Crude Oil Evaluation.”
2. Assessment of crude oil value. D2892, and subsequent analytical characterization of the produced fractions form the basis of many internal “crude oil evaluation” tools as well as part of crude oil trade contracts.
3. Value reconciliation in common pipeline systems. Crude oil production in offshore and remote areas is usually not contained to one field, or one company, but to multiple fields, all with varying crude oil quality, and operated by multiple companies. However, for logistic and economic reasons, transport of the produced crude oil to a gathering or processing area is frequently accomplished through one common pipeline. In such cases, it is evident that every company involved wants to get the value of the crude oil produced back at the other end of the pipeline. ASTM D2892 is frequently applied in contracts to assure such value reconciliation.

Since crude oil is produced, transported, traded, and processed in very large quantities, it is evident that accuracy and precision of ASTM D2892 can, and usually will have, a large economic impact.

Important Parameters

The most important operational parameters, having the largest impact on accuracy and precision, are temperature and pressure, both defining cut point (boiling point) and yield. Separation sharpness, column efficiency, largely defines fraction quality.

Cut point and yield is generally regarded as the most important “product” of ASTM D2892. The scope says about this: “From the preceding information, a graph of temperature versus mass percent distilled can be produced. This distillation curve corresponds to a laboratory technique, which is defined at 15/5 (15 theoretical plate column, 5:1 reflux ratio) or True Boiling Point (TBP).” However, both the reported temperature and the designation “TBP” need some closer inspection, as these terms are not as unambiguous as the text suggests.

Temperature

The key to understanding the true nature of “temperature” is in the very first sentence of the scope, reading: “This test method covers the procedure for the distillation of stabilized crude petroleum to a final cut temperature of 400 °C Atmospheric Equivalent Temperature (AET).” The relationship, and conversion, between observed temperature and AET is described in detail in Annex A8: “Practice for Conversion of Observed Temperature to Atmospheric Equivalent Tempera-

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[1] Daco-Antech, Werkendelslaan 53, Heiloo 1851 VB, The Netherlands.

ture (AET).” By implication, it says quite clearly that the temperature observed is not necessarily the temperature reported!

When processing crude oils in a distiller in a refinery, the whole process is continuous and under atmospheric pressure. ASTM D2892, however, is a batch process. Whereas in the continuous refinery process, residence time for the hottest fraction (the residue) is usually only minutes, in a batch process the whole material might “see” a high temperature for hours. As a rule of thumb, it is recognized that temperatures above 340 °C might lead to severe thermal degradation if sustained for a prolonged time beyond the “minutes.” Moreover, since it is a batch process utilizing a flask to hold the batch of feedstock (crude oil) attached to a column, where the actual separation takes place, there is a strong temperature gradient from the boiling liquid in the flask up to the upper side of the column, where the distillate is withdrawn and the boiling point temperature is measured. The temperature gradient over the column depends on the relative distillation speed (specified in D2892), the pressure drop over the column (depending on the packing employed) and the composition of the crude petroleum itself. Whereas for light crude oils (about 50 API-gravity) the temperature difference between top and bottom might be in the order of 40 °C to 60 °C, for heavy crude oils (about 15 API-gravity) the difference might be as high as 100 °C to 150 °C difference. ASTM D2892 specifies (Sec. 10.3.7): “Do not allow the vapour temperature to exceed 210 °C nor the temperature of the boiling liquid to exceed 310 °C.” This implies that only up to a maximum observed (top) temperature of 210 °C, or even lower for heavy crude oils, the distillation takes places at atmospheric pressure. It is only under these conditions that the observed temperature is equivalent to the reported temperature.

Beyond 210 °C, or even lower for heavier crude oils, the distillation needs to be carried out under reduced pressure, and consequently the observed vapor temperature at reduced pressure, has to be converted into “Atmospheric Equivalent Temperature.” This conversion, described in detail in Annex A8, is based on a *correlation* of vapor pressure with temperature for multi-component systems, as developed by Maxwell and Bonnell [4]. This correlation is widely used in the oil industry for vapor pressure (boiling point)—temperature conversions. There is one snag, though: the accuracy of the correlation is dependent on the chemical composition of the vapor! For this reason, Maxwell and Bonnell also included a “correction” for chemical type based on Watson K-factor. However, this correction is hardly employed in practice, and usually only the original equation based on a Watson K-factor of 12.0 is employed. ASTM D2892 says about this (Sec. A8.3.2): “The equations are correct only for fractions that have a Watson K-factor of 12.0 ± 0.2. The K-factor shall be assumed to be 12 and any effect of K-factor ignored unless there is *mutual agreement* to the contrary.” The term “mutual agreement” not only applies to the application of a K-factor correction, but also to the cut points as such. ASTM D2892 has no standard cut points! It clearly states (Sec. 4.2): “In cooperative testing or in cases of dispute, the stages of low pressure, the reflux ratios, and the temperatures of cut points must be mutually agreed upon by the interested parties prior to beginning the distillation.”

TABLE 1—Effect of operating pressure on distillation time for D2892.

Operating pressure, kPa (Torr)	Take-off rate, at 5:1 reflux	Distillation time, min	Take off rate, at 2:1 reflux	Distillation time, min
100 (760)	530	110	—	—
13.3 (100)	400	150	—	—
1.33 (10)	150	400	300	200
0.266 (2)	100	600	200	300

All other aspects of how to meet the required precision and accuracy of the observed temperature is governed in ASTM D2892 in several Annexes, e.g.: Annex A4 “Test Method for the Verification of Temperature Sensor Location,” Annex A5 “Test Method for the Determination of the Temperature Response Time,” and Annex A6 “Practice for the Calibration of Sensors.”

Distillation Pressure

When either the observed vapor temperature or the charge has reached the allowed maximum temperature, D2892 requires, that the distillation is continued at a lower pressure of 13.3 kPa (100 Torr). Reducing the pressure has several effects. First of all, the apparent boiling point is lowered and thus the charge and vapor temperature as well. However, reducing the pressure also has a pronounced effect on the vapor velocity through the column. Linear vapor velocity is proportional to pressure; the lower the pressure, the higher the vapor velocity for the same mass of liquid evaporated. The increased vapor velocity will create more resistance in the column and thus the pressure drop increases and the maximum throughput of the column decreases. Consequently, it takes longer to distill a certain mass of crude oil under low pressure than under atmospheric pressure. As stated before, with the column running at reduced pressure, the observed vapor temperature has to be converted to Atmospheric Equivalent Temperature using Annex A8 to allow comparison of boiling points. The maximum AET that can be achieved under reduced pressure conditions also depends on the composition of the charge, but is subject to the same limitations on maximum temperatures as the atmospheric part. Usually, a maximum boiling point of 300 °C (AET) should be attainable under 13.3 kPa pressure conditions. However, the scope of the method reads: “…to a final cut temperature of 400 °C.” In order to reach that maximum temperature, the pressure has to be reduced even further. Unfortunately, the method leaves some degrees of freedom for this lower reduced pressure, it states: “Only one pressure level between 13.3 kPa (100 Torr) and 0.266 kPa (2 Torr) is permitted.” However, the method does not specify which level. Moreover, Sec. 10.5.4 states: “During this operation, a reflux ratio of 2:1 is allowed if mutually agreed upon in advance and noted in the report.” The reason behind this is the anticipated duration of the distillation, i.e., time efficiency. Lowering the pressure will decrease the maximum throughput in the column and thus the time required to distill a certain amount of crude oil. Table 1 shows the effect of pressure on the time it takes to produce 1 L of distillate using a 25 mm column packed with Propak.

It is clear that lowering the pressure has significant consequences for distillation time. Whereas under atmospheric

TABLE 2—Operating pressure and pressure drop (at 80% of maximum throughput; Pro-pak packing).

Operating (vapor) pressure, kPa	Pressure drop, kPa	Total pressure at bottom, kPa
13.3	0.54	13.8
1.33	0.84	2.17
0.266	1.14	1.41

pressure it takes slightly less than 2 h to produce 1 L of distillate, that time requirement is increased to 10 h when running under 0.266 kPa and a 5:1 reflux ratio. Moreover, since a conversion is required to calculate AET under reduced pressure conditions, it also implies that the variance of the reported boiling point increases, because now the error in the pressure measurement is also included in the uncertainty. Because the conversion is a correlation, it also implies that when comparing AETs obtained at different pressure levels, the variance also increases as the extrapolation error increases if the pressure level is farther away from atmospheric.

Since vapor velocity creates pressure drop over the column, not only is there a temperature gradient over the column, but also a pressure gradient. The pressure relevant for cut point definition is the vapor pressure as measured as close as possible to the point where the vapor temperature is measured, i.e., the top of the column. However, the boiling action of the liquid, i.e., where evaporation takes place, is in the flask at the bottom of the column. As can be seen from the Table 2 below, the absolute pressure at the bottom of the column is disproportional to the pressure at the top of the column where the vapor temperature is measured. For example, a fivefold decrease in top pressure, going down from 1.33 to 0.266 kPa, results in less than a factor of 2 decrease in the pressure at the bottom. This implies that the temperature difference between top and bottom increases and consequently, the gain in maximum attainable final cut point is usually very marginal (less than 20 °C) under 0.266 kPa operating pressure. Changing the reflux ratio will improve on distillation time under these conditions, but the price to pay is a decrease in separation sharpness and thus potential differences in quality of the produced distillates and residuum.

Separation Sharpness (Efficiency)

The separation sharpness (efficiency) of a fractionating column defines the quality of the distillates. The scope of ASTM D2892 says that the columns allowed for this method are defined as: "…having an efficiency of 14 to 18 theoretical plates…." For D2892, this requirement is further defined in Annex A1: "Test Method for the Determination of the Efficiency of a Distillation Column." However, this test is carried out utilizing two pure components, reasonably close in boiling point, and under total reflux (no takeoff). As such, it only serves to characterize the column, but it yields no information on the actual performance of the column distilling a crude oil under a 5:1 reflux ratio.

Theoretically, the "True Boiling Point" of a compound can only be determined under infinite theoretical plates and total reflux (perfect equilibrium between liquid and vapor). As a rule of thumb, when distilling multi-component mixtures, a boiling curve produced under 14 to 18 theoretical plates will be hardly distinguishable from a boiling curve produced under infinite theoretical plates. However, this only holds if the reflux ratio at least matches the number of theoretical plates. In the case of ASTM D2892, that would imply a 15:1 ratio. However, applying a 15:1 reflux ratio would increase distillation time by a factor of 3. Therefore, ASTM D2892 says, the 5:1 ratio is a compromise between efficiency and time. A consequence of the lower reflux ratio is that the actual separation sharpness is lower than the 14 to 18 theoretical plates suggest. In other words, the overlap in fractions is larger than would be expected. As an example, a residuum cut at 350 °C would still contain significant amounts of material boiling below 350 °C, and the preceding fraction will contain material with a boiling point larger than 350 °C.

A true comparison and a more realistic "standard" of separation sharpness is given in Appendix X2: "Practice for performance check." This practice is based on a system to characterize the separation sharpness of distillation columns developed by Butler and Pasternak [5]. Similarly as for temperature, the pressure level employed affects the actual separation sharpness (N_{actual}). To allow comparison between column performance, Butler and Pasternak introduced a correction to account for the operating pressure. This corrected efficiency (N_{minimum}) ranges for a D2892 standard column from four theoretical plates at a 50 °C cut point to eight theoretical plates at a 350 °C cut point; i.e., approximately a quarter to a half of the theoretical number of plates (15 to 18) achievable with this column. Moreover, the data pertain to a reflux ratio of 5:1, application of a 2:1 reflux ratio will lower the actual and minimum efficiency even further. This might have severe consequences for the interpretation of the cut points and fraction qualities produced by this method. A lower actual efficiency automatically implies a larger deviation from the True Boiling Point. Differences in fraction qualities will be evident from front end and back end sensitive properties. As such, the viscosity is strongly affected by the amount of light and low viscosity material in the fraction, whereas the heavy tail of a fraction might have a pronounced effect on cold properties such as freezing point. Figure 1 demonstrates the expected shifts in yield for various actual efficiencies.

The overlap at cut point of a 15 theoretical plate column operated at 5:1 reflux ratio is approximately 15–20 °C at both sides. When running the column is in dynamic equilibrium, i.e., since "light" material is removed all the time, the liquid-vapor equilibrium inside the column is adjusting all the time. If the distillation is interrupted, e.g., by changing to another pressure level, a new equilibrium will be established. However, since that new equilibrium is now obtained under total reflux, the column attains its maximum theoretical separation power. That is, the enrichment of light material in the top of the column is significantly higher than under a 5:1 ratio. The noticeable effect is that the vapor temperature indicated is significantly lower than the final temperature achieved prior to interruption. Taking cuts under such circumstances (i.e., smaller than the overlap), which existed under 5:1 ratio, will result in an irregular and bumpy temperature-yield curve. Moreover, the fraction qualities at these stages will be significantly corrupted.

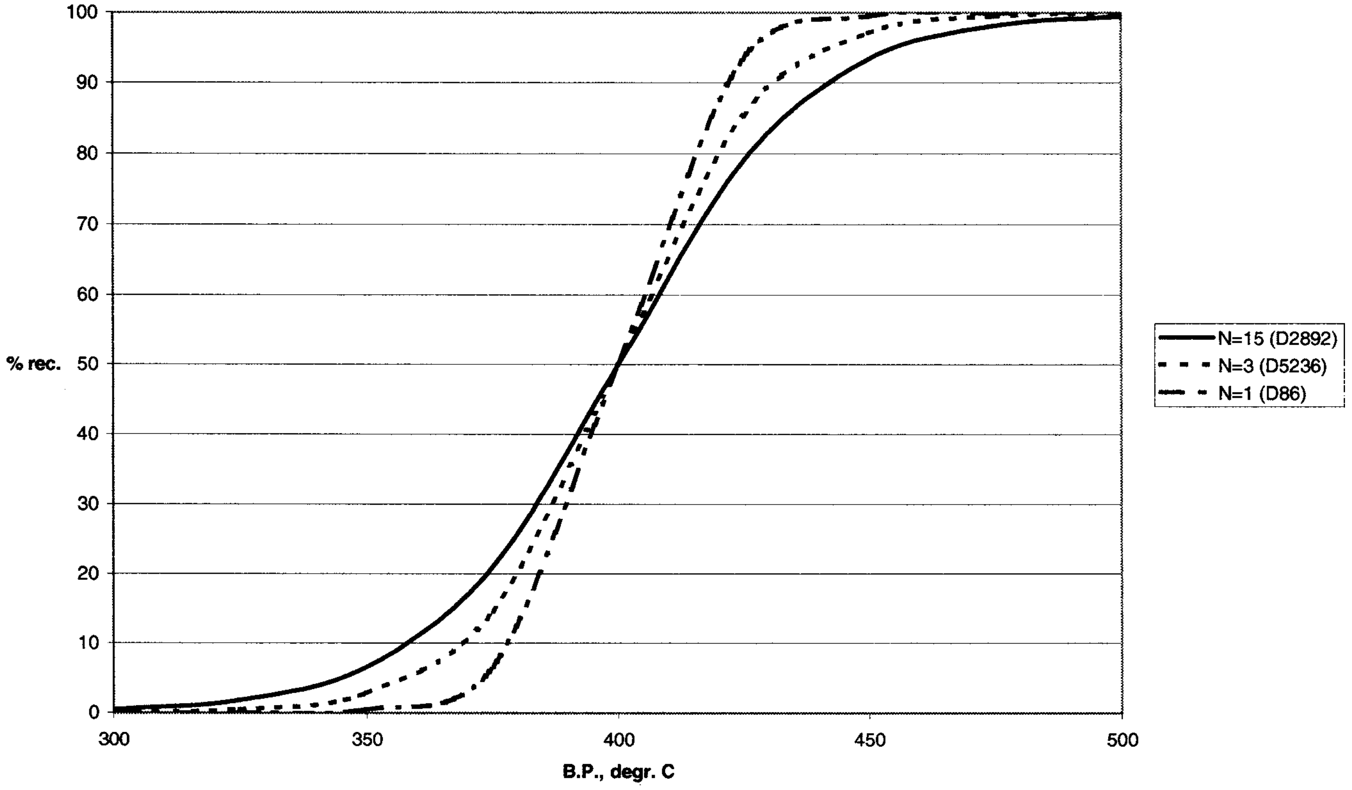

Fig. 1—Effect of efficiency on yield.

Therefore, it is strongly recommended not to determine cut points at a distance, or produce fractions of a size, smaller than the overlap.

Other Factors Affecting Results

It has already been mentioned that reflux ratio is an important factor, both in the accuracy and precision of the boiling point curve, but also with respect to fraction quality. Therefore, it is important that the correct reflux ratio is applied. ASTM D2892 Annex A7 describes a "Test Method for the Verification of Reflux Dividing Valves." Compliance to this standard will ensure correct reflux ratios.

Another factor that affects the amount of reflux running down the column, and thus separation sharpness, is heat loss. ASTM D2892 distillation is supposed to be carried out under adiabatic conditions. Adiabaticity is defined under Terminology, Sec. 3.1.1 states: "adiabaticity—the condition in which there is no significant gain or loss of heat throughout the length of the column;" this is further explained in Sec. 3.1.1.1: "Discussion—When distilling a mixture of compounds as is the case of crude petroleum, there will be a normal increase in reflux ratio down the column. In the case where heat losses occur in the column, the internal reflux is abnormally greater than the reflux in the head. The opposite is true when the column gains heat, as with an overheated mantle." Therefore, it is of the utmost importance that Annex A3 "Test Method for the Determination of the Heat Loss in a Distillation Column" is in full compliance. It is recommended never to run a column without automatic heat loss compensation, i.e., each column should preferably be equipped with a heating mantle. ASTM D2892 states in note 2: "For certain types of columns there is no significant difference in yields and fraction qualities between an uncompensated and a heat-compensated column. In such a case, by mutual agreement between parties concerned, the application of a heated insulating system can be omitted." It should be noted, though, that columns without heat loss are virtually non-existent and parasitic heat losses will lead to significant tailing of the cuts, and thus corrupt fraction quality.

The presence of water in a crude oil sample can, and usually will, lead to significant distortions in the TBP curve over the range 50–150 °C. ASTM D2892 contains an Appendix X1 (non-mandatory), which describes a possible procedure for dehydration prior to distillation. Other dehydration methods are also allowed, but care should be taken that no light material is lost during this process.

Although ASTM D2892 allows (internal) column diameters ranging from 25 to 70 mm, and flask sizes from 1 to 30 L, the choice of the two is not independent. The relationship between column size, flask size depends on packing type employed and is determined by the dynamic holdup of the column. The dynamic holdup is the amount of liquid (reflux) which is present in the column during actual distillation and is determined through Annex A2: "Test Method for the Determination of the Dynamic Holdup of a Distillation Column." ASTM D2892 (Sec. 10.1.1) requires that: "The charge size shall be such that the dynamic holdup 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)." Table 1 in ASTM D2892, lists the known performance data for the more popular column dimensions and packing materials. Another important safety issue to consider in relation to flask and charge size is the requirement that a minimum amount of liquid of at least 10 % of flask size should remain in the flask at all times. Failure to adhere to this, can lead to local overheating and implosion of the flask.

From the above it will be clear that ASTM D2892 is a rather complicated performance based method. To assure best results, it is recommended to pay due attention to Sec. 7 "Verification of Apparatus Performance." It refers to the non-mandatory Appendix X2 "Practice for Performance Check." Appendix X2 provides for an overall performance check on column performance under real dynamic conditions and might provide clues on any significant deviations from the specified performance and operational aspects of ASTM D2892. A periodic, say once a year, check on compliance is strongly recommended.

Precision

The precision of ASTM D2892 is primarily determined by the combined accuracy of the (vapor) temperature and pressure measurement. The uncertainty in cut point is thus factually an uncertainty in temperature (AET). However, ASTM D2892 states precision in terms of yield (% mass and volume). Yield does not equal temperature, except under very specific conditions. Note 7 states: "The crude oil used for this precision statement had a density at 15 °C equal to 0.859 and an average slope equal to 6 °C per percent distilled." Therefore, it should be stressed that, similar to D86, precision is actually a function of slope and thus the precision quoted in ASTM D2892 only pertains to an average crude oil with an average slope of 6 °C per percent distilled.

Summary

ASTM D2892 provides for a rather complicated performance based framework to carry out crude oil distillations to produce a TBP curve and obtain fractions of defined quality for further characterization.

The many degrees of freedom in the choice of equipment and operational conditions, makes strict adherence to various performance specifications a must. For the best results in repeatability and reproducibility and reliable comparison and exchange of data produced by this method, it is imperative that parties concerned agree in detail of the exact procedure to be employed in the contracts. Precision can be further improved by also specifying column diameter and the packing material to be employed.

ASTM D2892 is a rather lengthy test, which only for average crude oils with a limited maximum cut point (e.g., 350 °C) can be accomplished within an 8 h shift. There will be a natural tendency to speed up the distillation, but it should be remembered that any attempt in short cuts, almost inevitable will lead to a degradation in precision and accuracy.

Vacuum Distillation

Subcommittee ASTM D02.08 on Volatility has two methods for the vacuum distillation of petroleum products under its jurisdiction; viz: ASTM D1160 "Standard Test Method for Distillation of Petroleum Products at Reduced Pressure" and ASTM D5236 "Standard Test Method for Distillation of Heavy Hydrocarbon Mixtures (Vacuum Potstill Method)." Although at first sight both methods look rather similar, they are fundamentally different: the only thing in common they have is that both perform a distillation under reduced pressure.

ASTM D5236

Introduction

ASTM D5236 "Standard Test Method for Distillation of Heavy Hydrocarbon Mixtures (Vacuum Potstill Method)" has many similarities to ASTM D2892 "Distillation of Crude Petroleum (15-Theoretical Plate Column)." In fact, many in the industry regard D5236 as the logical extension of D2892 distillation. The maximum attainable cut point in D2892 is 400 °C. The maximum attainable cut point in D5236 is specified in the scope at around 565 °C, depending on the heat sensitivity of the sample. The scope of D5236 lists as applicable products heavy crude oils, petroleum distillates, residues, and synthetic mixtures.

Similar to ASTM D2892, D5236 is different from other ASTM Standard Test Methods by the fact that it does not yield a defined set of standard numbers. The scope reads: "This test method details the *procedures for the production* of distillate fractions of standardized quality in the gas oil and lubricating oil range as well as the production of standard residue. In addition, it provides for the determination of standard distillation curves to the highest atmospheric equivalent temperature possible by conventional distillation." Moreover, D5236 also does not provide for detailed design specifications of the equipment used and equipment performance specifications are specified instead. In contrast to ASTM D2892, performance specifications are not so rigidly defined, which might lead to a large variability in results obtained by this method and might have significant bearing on the comparison of results produced.

Although many in the industry regard D5236 as a logical extension of the boiling range produced by D2892, the results do not match! This is caused by the large difference in separation sharpness (efficiency). Whereas D2892 is defined at a relatively high efficiency of 15 theoretical plates, and results therefore hardly distinguishable from the TBP, ASTM D5236 employs a low efficiency, 1 theoretical plate column. It is only under very specific circumstances outlined later on that the results approach the TBP curve. On the relationship of D5236 with D2892, the scope of D5236 says: "However, distillation curves and fraction qualities obtained by these methods are not comparable."

Field of Application

ASTM D5236 does not appear in any official international fuel or product specification, but is used in contracts and other types of internal, or mutually agreed upon voluntar specifications. The main application areas are:

1. Assessment of crude oil processability and other engineering applications, commonly referred to as "Crude Oil Evaluation." In such a case it pertains to an extension of ASTM D2892, and uses the residuum produced by ASTM D2892 as the test specimen.
2. Occasionally, ASTM D5236 is used for assessment of crude oil, or feedstock, value. ASTM D5236 and subsequent analytical characterization of the produced fractions in some cases form the basis of internal "crude oil and feedstock valuation" tools. It also might be incorporated as part of crude oil/feedstock trade contracts.

Although some companies utilize ASTM D5236 as a tool to produce a boiling point curve of heavy petroleum and other high boiling products, it should be noted that if such a characterization is the only purpose, ASTM D1160 is the preferred, and usually specified, tool to produce analytical boiling point curves of such products.

Important Parameters

As for any distillation method, the most important parameters having the largest impact on accuracy and precision are (vapor) temperature and operating pressure, as both define cut point (boiling point) and yield. Separation sharpness, defining fraction quality, is not explicitly specified, but is implicitly contained in the procedure. However, it is much more subject to variability than for ASTM D2892.

Temperature

The required measurement precision and accuracy of the vapor temperature is covered in several Annexes to D5236: Annex A1 "Test Method for Determination of Temperature Response Time," Annex A2 "Practice for Calibration of Sensors," Annex A4 "Practice for Conversion of Observed Vapour Temperature to Atmospheric Equivalent Temperature (AET)."

When processing "heavy products" in a refinery in a High Vacuum Unit, the whole process is continuous and thus residence time at high temperature is relatively short. ASTM D5236, however, is a batch process. In a batch process, the whole material might "see" a high temperature for hours. As a rule of thumb, it is recognized that temperatures above 340 °C might lead to severe thermal degradation if sustained for a prolonged time beyond "minutes." In contrast to ASTM D2892, D5236 employs a "potstill" with a low pressure drop entrainment separator operated under total takeoff conditions. As a result, the temperature gradient, top—bottom, in D5236 is significantly lower than for D2892. It is these features, i.e., low pressure drop, very low pressures, and total takeoff, which allow distillation up to significantly higher temperatures (AET) than D2892. At the same time, it also implies significantly different fraction qualities.

The applicable operating pressures range from 50 Torr down to 0.1 Torr. At these very low pressures, the heat content of the vapor is very low, and together with the rather fast changing vapor temperature, it is of the utmost importance that the requirements for temperature response time (Annex A1) of the temperature sensor are met. Failure to do so will inevitably lead to significant underestimation of vapor temperature.

Since the whole distillation takes place under reduced pressure, the observed vapor temperature at reduced pressure has to be converted into "Atmospheric Equivalent Temperature." This conversion, described in detail in Annex A4, is based on a *correlation* of vapor pressure with temperature for multi-component systems, as developed by Maxwell and Bonnell [4]. The correlation is widely used in the oil industry for vapor pressure (boiling point) temperature conversions. However, the "linearized" vapour pressure correlation is starting to deviate from "linear" below 2 Torr (2.66 kPa). The authors recognized this fact and the correlation curve was split into two linear parts: The part governing the range from atmospheric down to 2 Torr and a part from 2 Torr down to 0.1 Torr. ASTM D5236 gives two sets of equations governing these ranges. At 2 Torr both equations yield exactly the same result in AET. Extrapolating the correlations beyond 0.1 Torr will lead to significant distortions as the distillation enters the area of molecular distillation, where vapor pressure becomes subordinate to temperature differences between a heated (oil containing) surface and a cooling (vapor collection) surface in combination with the split diameter between both surfaces, so-called short path distillation.

TABLE 3—Effect of operating pressure on distillation time for D5236.

Operating pressure, kPa (Torr)	Take-off rate (25 mm column), mL/h	Distillation time for 1 L, min
6.67 (50)	450–750	130–80
1.33 (10)	375–625	160–95
0.133 (1)	225–375	265–160
0.0400 (0.3)	150–250	400–240
0.0133 (0.1)	50–100	1200–600

Distillation Pressure

ASTM D5236 is rather vague on the operating pressures to be applied. The correct choice depends on many factors such as the Initial Boiling Point (IBP) of the charge, the required final cut point (AET) and time required to achieve a complete distillation.

A high starting pressure will yield a short distillation time, but restricts the maximum attainable cut point. A low starting pressure puts restrictions on the IBP of the charge, but allows for maximum attainable cut point, although distillation time required will significantly increase. Usually a stepwise change in operating pressure is employed as a compromise to maximise "reach" in a minimum of time. However, in between changing the pressure level has significant consequences for both yield and fraction quality.

Section 9.9 of ASTM D5236 has specific instruction about operating pressure: "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 cut point. A pressure of 1.0 mm Hg has been found satisfactory for starting a material having an initial boiling point of 343 °C, such as residues from Test Method D2892 distillations." An excerpt of Table 2 of D5236 is given below (Table 3) together with an estimate of the time required to produce 1 L of distillate.

It is clear that lowering the pressure has significant consequences for distillation time. Moreover, since D5236 operates under total takeoff under a dynamic equilibrium, in between, interruption of the distillation has a large effect on the boiling point curve produced and should be avoided if possible. The yield shifts, and the changing actual separation sharpness will also significantly effect cut quality. Figure 2 illustrates the effect on the yield curve produced by direct distillation, without interruption, up to a maximum cut point of 600 °C, in comparison to a curve distilled directly up to 525 °C, interrupted and, with a cold column, restarted to obtain the 600 °C endpoint.

Furthermore, it should be kept in mind that decreasing the operating pressure by a factor of 10, at the same time linear vapor velocity increases by a factor of 10. In fact, running

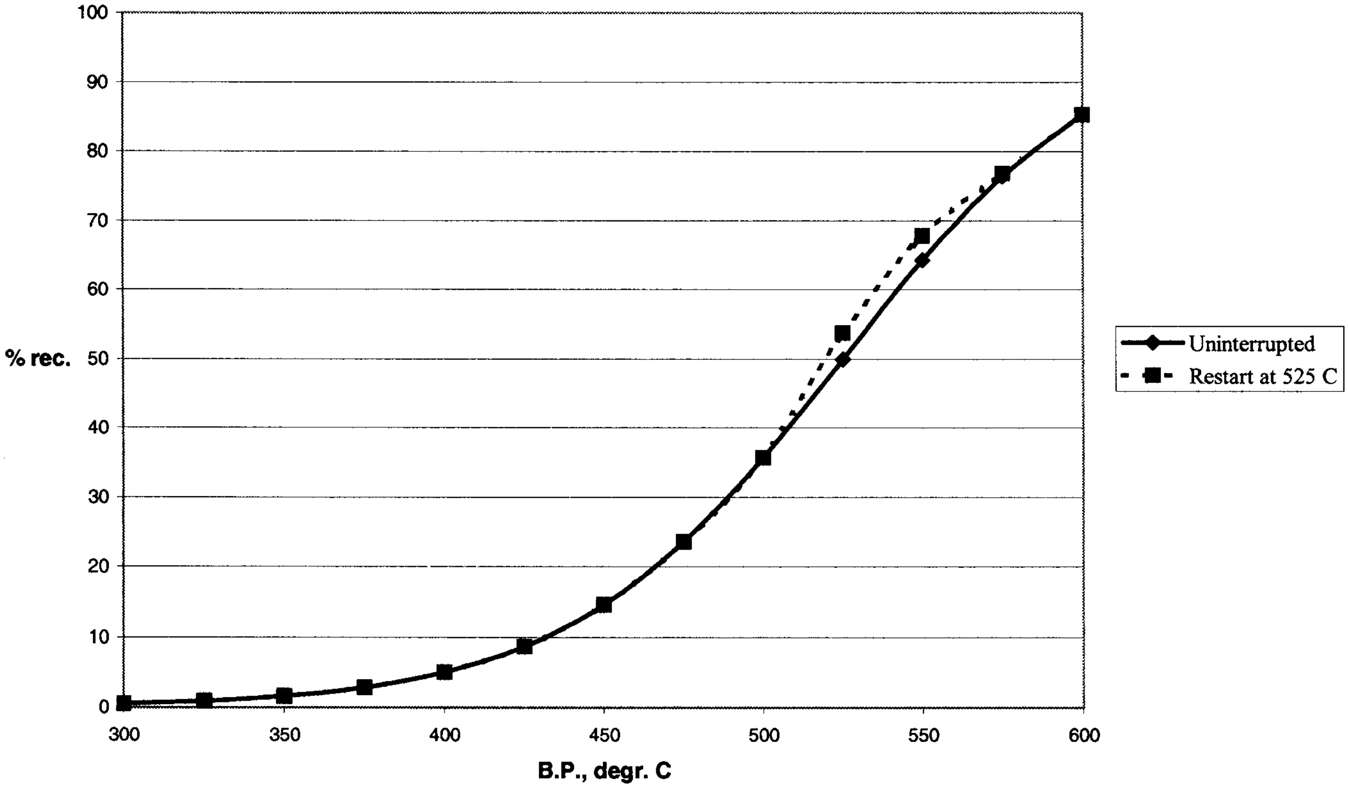

Fig. 2—Effect of interruption and (cold column) restart on yield.

at high (liquid) distillation rate at (very) low pressure will cause the vapor velocity to exceed supersonic speed and thus create heavy turbulence and significant pressure drop, even in relatively large diameter tubing, but specifically in the column head containing a low pressure drop entrainment separator. The pressure drop thus created might be two to three times of the order of the absolute pressure running at 0.013 kPa and thus might lead to a very significant underestimation of the vapor pressure at the head where vapor temperature is measured. Operating pressure level also affects the separation sharpness. As a rule of thumb, lowering the operating pressure will result in an apparent increase in separation sharpness (actual efficiency) because of a more favorable relative volatility of the components.

Separation Sharpness

The separation sharpness (efficiency) of a column defines the quality of the distillates. ASTM D5236 employs a one theoretical plate column. It runs under adiabatic total takeoff conditions; hence, theoretically there is no reflux and no mass exchange between the up-flowing vapors and downcoming fluids. However, columns without heat loss do not exist; there always is some heat loss, which will result in some condensation of vapor on the walls of the column. Thus, in actual practice the separation sharpness will be slightly higher than 1. Moreover, separation sharpness (actual efficiency) increases if the operating pressure decreases. The present version of ASTM D5236 has no defined requirements for separation sharpness. Implicitly, however, actual efficiency is contained in the requirements for distillation rate in combination with operating pressure and the requirement for adiabaticity. Actual efficiency is estimated at about 2 to 3 theoretical plates.

A non-adiabatic column (either losing or gaining heat) will significantly affect the amount of "reflux" running down the column walls and thus the separation sharpness. ASTM D5236, Sec. 6.5.2 states: "The head shall be enclosed in a heat insulating system such as a glass fabric mantle capable of maintaining the outer wall of the glass vacuum jacket at a temperature of 5 °C below the internal vapour temperature of the head." This is to ensure that during operation the column indeed runs under adiabatic conditions. Under start-up conditions, however, the head will be relatively cold and thus the amount of condensation might be substantial. During the distillation the mandatory temperature compensation employed assures that no significant heat flow from inside to outside or vice versa will occur. Since the distillation is run under total takeoff conditions, interruption of the distillation will result in cool-down of the head, and thus restart in "cold head" conditions again. This will yield a very irregular distillation curve (see Fig. 2).

ASTM D5236 is rather vague in how to proceed when distilling up to the maximum cut point, which cannot be met within a reasonable time under one single pressure level. The current version of D5236 gives two options under such circumstances (Sec. 9.6):

1. "It may be achieved by gradually reducing the pressure over the course of the distillation (dynamic), or
2. done stepwise, by slowing (or stopping) the takeoff rate to allow lowering of the operating pressure to achieve the final cut temperature."

Both approaches have their drawbacks and both have consequences for cut quality. Option 1, in principle, is in violation of Sec. 5.4 "Details of cut points (i.e., operating pressure and AET) must be mutually agreed upon before the test begin." It will be clear that this requirement is almost impossible to meet with a dynamic pressure reduction system. Moreover, precision and accuracy are also a function of operating pressure and distillation conditions at the cut point. Thus, dynamic reduction essentially leaves both precision and cut quality rather undefined. The main drawback of option 2 is that some skill, experience, or both are needed to achieve the requirements further outlined in Sec. 9.6: "…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)." Moreover, during the pressure reduction, and the time it requires to establish a new (dynamic) equilibrium, no cuts can be taken with any confidence. This period of "uncertainty" might take some 10 min, so it is of the utmost importance to choose the pressure reduction points carefully in order not to interfere with the agreed cut points.

Other Factors

Especially when running under a very low operating pressure of 0.0133 kPa, it should be realized that the pressure exerted by the static liquid head in the flask is of the same order of magnitude as the operating pressure itself. Hence, evaporation rate at the liquid surface, might and will be significantly higher than at the bottom of the liquid. Therefore, ASTM D5236 requires that a stirrer is employed to ensure active renewal of the liquid surface and thus even evaporation of the liquid.

Similar to ASTM D2892, ASTM D5236 allows (internal) column diameters ranging from 25 mm to 70 mm, and flask sizes from 3 L to 24 L. Unlike D2892, D5236 has no direct performance related equipment specifications; hence, the dimensions of various pieces of the equipment in relation to each other are given in a number of tables. Failure to adhere to these relative dimensions will lead to significant performance distortions.

Boiling Point, TBP, and AET

There is a lot of misunderstanding on the true meaning of these terms. Here are some facts.

Boiling Point is defined as: "That temperature where the vapour pressure of a compound equals its ambient pressure." The Atmospheric Boiling Point (ABP) thus is the temperature at which a compound shows a true vapor pressure of 760 Torr (101.3 kPa). Most, if not all, organic compounds cannot tolerate temperatures exceeding 400 °C for more than seconds. At such temperatures they will almost immediately decompose. Hence, it is impossible to measure a vapor pressure of 101.3 kPa for such compounds, and thus there is no way of a direct determination of ABP in these cases. The only alternative is to measure the vapor pressure of such compounds at a number of temperatures significantly lower than 400 °C and subsequently extrapolate the data to a vapor pressure of 101.3 kPa. The temperature achieved in such a way is called the Atmospheric Equivalent Temperature (AET). Maxwell and Bonnell, on basis of many vapor pressure data on hydrocarbons and hydrocarbon mixtures derived a general correlation formula to convert vapor pressures measured at a specific temperature to any other temperature. Most of the time this conversion is used the other way around; i.e., the boiling point of a compound and its associated vapor pressure is measured and subsequently converted (extrapolated) to a temperature where its vapor pressure would equal 101.3 kPa, which yields the AET. In this respect, it should be mentioned that measuring the vapor pressure of a compound with an AET beyond 400 °C is not an easy task. The available temperature measurement range is small (somewhere between 150 °C and 300 °C) and true vapor pressures extremely low in this range ($\ll$0.01 kPA) for these compounds. Consequently, any extrapolation over such a small range, far outside that range, is prone to significant uncertainty and "error."

The correct definition of True Boiling Point would be: "That temperature where the vapor pressure of the compound equals its ambient temperature and the rate of evaporation of the liquid phase equals the rate of condensation of the vapor phase." In other words, in terms of distillation, a boiling liquid in perfect equilibrium with its vapor under total reflux conditions. Unfortunately, the term TBP is usually employed as being equivalent to ABP. Nobody ever measured a boiling point of a hydrocarbon greater than 400 °C, regardless of pressure! Any quotation of boiling points over 400 °C is the result of a mathematical conversion, correlation, and extrapolation of vapor pressure data measured well below 400 °C. In the oil industry, the most widely used boiling point (vapor pressure) "conversion-equation" for multicomponent mixtures is the equation developed by Maxwell and Bonnell.

In summary, Atmospheric Equivalent Temperature (AET) is a very useful *convention* for scientific applications, exchange of data, and discussions on volatility properties of hydrocarbons. True Boiling Point is, in most cases, no more than a theoretical concept, often misused in the wrong context. Moreover, the designation "true" in this context is highly disputable.

Comparison of ASTM D5236 and D2892

ASTM D2892 employs a high theoretical plate column and ASTM D5236 a low theoretical plate column, and never the two boiling curves shall meet! Figure 3 shows an (ideal) D5236 and D2892 boiling point curve in comparison to a theoretical TBP curve. The input for the D5236 distillation is the residue (>350 °C) of the preceding D2892 distillation. From this figure, it is clear that the ASTM D2892 curve practically matches the theoretical TBP curve, but that the ASTM D5236 curve, especially at the beginning and at the end of the distillation, shows very significant deviations. Moreover, it is obvious that any attempt to connect the two curves, to reconstruct a full TBP curve on, e.g., a crude oil, will result in a heavily distorted combined curve and a very questionable representation of a crude oil's volatility distribution.

As explained in the previous chapter, the "overlap" at cut point of a 15 theoretical plate column as employed in D2892 is approximately 15–20 °C at both sides. For the low efficiency D5236 column this overlap amounts to approximately 50–70 °C at both sides. Figure 3 shows what will happen if a residue from D2892, in order to extend the boiling curve, is further distilled in a D5236 column, taking 10 °C cuts. It is clear that if the first cut point in D5236 is

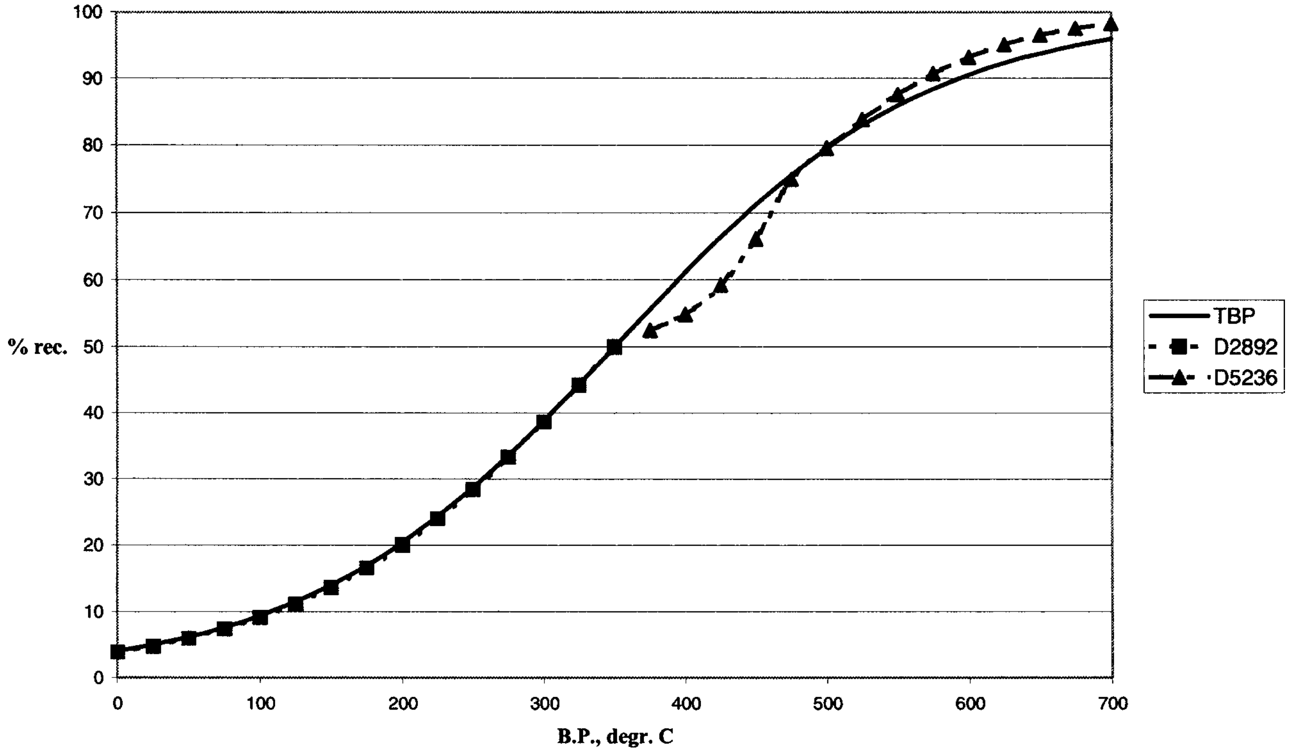

Fig. 3—Combining ASTM D2892 with ASTM D5236 boiling point data.

within the noted overlap range with the final cut point of D2892, there will be a "strange" bump in the boiling point curve. It is rather common practice to "match" D2892 with D5236 curves, but failure to understand the consequences of the significantly different efficiencies of both columns will yield some very unrealistic boiling curves.

Precision

Both for ASTM D5236 and D2892 the precision is primarily determined by the combined accuracy of the (vapor) temperature and pressure measurement. The uncertainty in cut point thus is factually an uncertainty in temperature (AET). Although ASTM D5236 shows a precision statement, which looks vaguely familiar to a D86 precision statement, i.e., a temperature uncertainty as a function of percent volume distilled, it does not include the "slope" of the distillation either. Moreover, precision would also be dependent on pressure, the parameter for which is not included in the D5236 precision statement either. Since D5236 is applied to products of widely different slopes (such as D2892 residues on the one hand and lube oil cuts on the other hand), and run under rather vaguely defined operating pressure conditions, the stated precision should be regarded as very unrealistic and with hardly any significance.

Both precision statements (D2892 and D5236) were developed a long time ago, and are in urgent need of upgrading. However, the wide range of products covered, the large sample volumes required, and the long distillation times, significantly hamper the execution of an interlaboratory study and the subsequent development of more realistic statements.

ASTM D1160

Introduction

In contrast to D5236 and D2892, ASTM D1160 "Standard Test Method for Distillation of Petroleum Products at Reduced Pressure" is a true analytical method for (Sec. 1.1): "…the determination, at reduced pressures, of the range of boiling points for petroleum products that can be partially or completely vaporized at a maximum liquid temperature of 400 °C…." As such, it has much more resemblance with ASTM D86 than with the aforementioned preparative methods.

On the other hand, many of the features and peculiarities of D5236 also appear in D1160. Both methods share similar "performance" Annexes such as

Annex A1 "Practice for Calibration of Temperature Sensors," Annex A2 "Practice for Determination of Temperature Response Time," Annex A3 "Practice for Calibration of Vacuum Gages," and Annex A7 "Practice for Converting Observed Vapour Temperatures to Atmospheric Equivalent Temperatures (AET)."

However, there are also significant differences. The most important difference is that D1160 is operated at a fixed distillation rate (Sec. 10.8): "…adjust the rate of heating so that the distillate is recovered at a uniform rate of 6 to 8 mL/min." Moreover, interruption of the distillation is not permitted; the maximum end point is essentially dictated by the chosen operating pressure and the requirement that the liquid temperature shall not exceed 400 °C.

Field of Application

The field of application of ASTM D1160 is contained in its "Significance and Use" section, from which the following excerpts are taken: "The boiling range obtained can be used

1. …in engineering calculations to design distillation equipment.
2. …to prepare appropriate blends for industrial purposes.
3. …to determine compliance with regulatory rules.
4. …to determine the suitability of the product as feed to a refining process."

In addition, "Significance and Use" list the following applications:

1. Petroleum product specifications often include distillation limits based on data by this test method.
2. Many engineering design correlations have been developed on data by this test method.

Obviously, ASTM D1160 is the preferred, and usually specified, analytical tool to produce boiling point curves of products, which by their nature, require distillation under reduced pressure conditions.

Important Parameters

As for any distillation method, the most important parameters having the largest impact on accuracy and precision are (vapor) temperature and operating pressure. For ASTM D1160, in addition, accurate volume measurement is also an important factor.

Temperature

ASTM D1160 devotes many clauses related to the accurate and precise measurement of vapor temperature such as:

Section 6.1.3: "The system must produce readings with an accuracy of ±0.5 °C over the range to 400 °C and have a response time of less than 200 s as described in Annex A2. The location of the vapour temperature sensor is extremely critical. …The vapour temperature measuring device can consist of different configurations depending if it is a platinum resistance in glass or metal, or if it is a thermocouple in glass or metal."

Annex A2: "Practice for Determination of Temperature Response Time"

Section A2.2: "This practice is performed to ensure that the sensor is able to respond sufficiently rapidly to changes in temperature such that no significant error due to lag is introduced in a rapidly rising temperature curve."

Section A2.2.1: "The importance of this test is greatest under the lowest pressure conditions when the heat content of the vapours is minimal."

In fact, since ASTM D1160 is a "fast" test, response time of the sensor is much more important than the accuracy of the device itself. The response time of a temperature sensor is dependent on many factors, but in essence it is a function of heat content of the vapors, mass of the sensor, surface area of the sensor, heat transfer characteristics of the vapor to the sensing element, and the temperature difference between the vapor and the sensing element.

Let us suppose we want to distill a product with a temperature span of 200 °C (final-initial BP) at the highest allowable rate of 8 mL/min. This equates to a distillation time of 25 min and an average rate of change of 0.133 °C/s. Annex A2, defines as response time the time it takes to cool down a sensor in still air at atmospheric pressure from 30 °C to 5 °C above the air temperature. Hence, at a maximum response time of 200 s, this equates to a rate of change of 0.125 °C/s. This implies that under such circumstances, the rate of change of the vapor temperature is faster than the response time of the sensor. Moreover, the temperature difference conditions for the response time measurement are at least 5 °C and a smaller difference would increase the response time far above the 200 s and at the same time decrease the rate of change of the sensor. From these "facts" it can be concluded that a temperature lag between vapor temperature and observed vapor temperature is inevitable. As ASTM D1160 is a *standard* test method, that would not matter if all factors governing sensor response were rigidly specified. However, as is obvious from Sec. 6.1.3, neither the mass, surface area, nor the heat transfer characteristics of the sensor is defined (…*depending…it is a platinum resistance in glass or metal, or if it is a thermocouple in glass or metal*…). Consequently, significant "noise" in precision data might be expected on basis of the use of a non-standardized temperature-measuring device. As shown above, specification of a maximum response time, will only take out a marginal part of this "variance."

Distillation Pressure

Pressure is the second most important parameter to take care of, to assure reasonable reproducibility. The scope says (1.2): "In cases of dispute, the referee test method is the manual test method at a *mutually agreed upon pressure*." In contrast, D1160 is rather vague about the pressure to be applied. Section 4.1 states: "The sample is distilled at an accurately controlled pressure between 0.13 and 6.7 kPa (1 and 50 mm Hg)…;" further information is contained in (informative!) note 5: "The most commonly applied pressure is 1.3 kPa (10 mm Hg). For heavy products with a substantial fraction boiling above 500 °C, an operating pressure of 0.15 kPa (1 mm Hg) or 0.26 kPa (2 mm Hg) is generally specified."

As shown under "Temperature" and Sec. A2.2.1, the pressure level also affects the temperature lag due to a rapidly rising vapor temperature in relation to sensor response time, thus introducing more "noise" in precision variance.

Volume Measurement

The boiling curve produced by ASTM D1160 is a plot of vapor temperature (AET) versus volume recovered. Volume is a function of temperature. Consequently, it is important that the intake volume measured (200 mL) has the same temperature as the distillate collected in the receiver. Furthermore, it goes without saying that accurate calibration and reading of the distillate receiver have a significant bearing on precision of ASTM D1160 results.

Precision

The precision of ASTM D1160 is expressed the same way as in ASTM D86: as a function of slope. However, here it should also be recognized that the most important factor is the accuracy of temperature and pressure measurement. As outlined above, ASTM D1160 has a relatively fast distillation rate; therefore, the temperature sensor response time (Annex A2) has a very pronounced effect on temperature accuracy. A slow response time will lead to a significant lag between temperature reading and actual vapor temperature. It should also be noted that precision is pressure level dependent, which is recognized in ASTM D1160. However, the precision statement only covers the pressure range of 0.13 kPa to 1.3 kPa (1 to 10 Torr).

Accuracy

Section 12.4 states: "Bias—since there is no accepted reference material suitable for determining the bias for the procedure in this test method, no statement is being made."

However, in a qualitative sense, the following statement can be made regarding *relative bias*: Distillation curves by D1160, obtained under different pressure conditions, will NOT match! Distillation curves by D1160, obtained with temperature measuring devices of significantly different response times, will NOT match! Distillation curves by D1160 and D86, on the same material, will NOT match! Distillation curves by D1160 and D5236, on the same material, will NOT match!

The quantitative magnitude of the relative bias will depend strongly on (1) The slope of the distillation curve, (2) temperature sensor response time differences, and (3) Differences in operating pressure.

Closing Remarks

Both D2892 and D5236, in principle, determine the mass boiling point distribution of petroleum products. The mass curves can be converted to volumetric boiling point curves, using the densities of the fractions. Therefore, volumetric curves produced by those two methods are defined at a specific temperature, depending on the density definition employed. D1160 and D86 on the other hand, determine a volumetric curve, and the volume recovered is determined by the temperature of the charge introduced in the flask and the temperature of the distillate in the receiver. Deviations, between labs, in those temperatures, will further increase the uncertainty in the curves produced and inflate the stated reproducibility of the D1160 test method.

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Simulated Distillation Measurement

D. Susan Workman[1]

Introduction

DISTILLATION IS THE MOST WIDELY USED SEPARAtion process in the petroleum industry. Knowledge of the boiling range of crude oils, refined fractions, and finished products has been an essential part of quality determination since the beginning of the refining industry. Routine laboratory scale physical distillation tests have been extensively used for determining the boiling ranges of crude feedstocks, distillation fractions, and a complete slate of refinery products (ASTM methods D86, D1160, D2892, and D5236) [1–4].

An alternative to physical distillation or true boiling point distillation is simulated distillation by gas chromatography. Eggerston et al. first described simulated distillation in 1960 [5]. Simulated distillation (SD) is equivalent to a 100 theoretical-plate physical distillation, is very rapid, reproducible, and easily automated, requires only a small microlitre sample volume, and can better define initial and final boiling points.

Boiling range distribution data are used to evaluate new crude oils, to confirm crude quality, to monitor crude quality during transportation, and to provide information for the optimization of refinery processes. The ability to quickly and reliably evaluate crude oils and fractions has important economic implications. The full development of simulated distillation methods as routine procedures has had a significant impact on the ability to determine boiling point information for crude oils and petroleum products.

Gas Chromatography and Simulated Distillation

Gas chromatography (GC) (also referred to as gas-liquid chromatography, GLC) is a chromatography method for separating the volatile components of mixtures. It is a highly efficient fractionating technique, which is ideally suited to the rapid determination of the amount present of specific known components.

In traditional GC, a small amount (1 – 5 microlitres) of a liquid sample is injected by means of a syringe into a heated injection port, where the liquid is vaporized. An inert carrier gas (helium, nitrogen, or hydrogen) transports the volatilized sample into a column where separation of the injected mixture occurs by partitioning between the gas stream and the liquid phase in the column. The gas stream, containing the separated compounds, is then passed through a detector. The detector signal is monitored continuously by a recording device (such as an analogue to digital converter) that records the components as a function of time. The resulting individual peaks are Gaussian in shape.

On the other hand, simulated distillation (SD) is a low-resolution chromatographic method that has been developed to simulate true boiling point or physical distillation. It is based on the experience that hydrocarbons elute from a nonpolar adsorbent or liquid phase in order of their boiling points. In simulated distillation analysis, the components are not separated as individual peaks but as one large Gaussian-shaped peak that resembles a lump. Figure 1 illustrates a typical simulated distillation chromatogram.

SD is based on the correlation of the normal boiling point and retention time data for a normal paraffin mixture, often referred to as the calibration mixture. The retention time data for the normal paraffins are gathered using a specified temperature program. A mathematical relationship between the boiling points of the normal paraffins and retention or elution time is determined. This relationship is essentially linear for the hydrocarbons that are retained by the column. The output from a sample chromatogram, analyzed under the same conditions, is divided into equal individual area slices and compared to the calibration equation. Each area slice has a retention time associated with it and therefore a boiling point is determined from the calibration equation (boiling point versus retention time). The area slices are then summed to generate the area or weight percent off by temperature report. Therefore, the amount at any interval on the chromatogram can be determined. Normal-paraffin calibration chromatograms are shown in Figs. 2 and 3. Table 1 contains the retention time versus boiling point calibration report. Figure 4 illustrates the normal-paraffin calibration chromatogram showing the calibration equation. Figure 5 is an example of a simulated distillation chromatogram for a sample analyzed using ASTM D7213. The chromatogram also shows the calibration line. Table 2 is a typical simulated distillation report.

ASTM Simulated Distillation Methods

One of the most widely used characterizations of complex hydrocarbon mixtures is the determination of boiling-point distribution. The measurement of this distribution is carried out by guidelines established in the methods of ASTM International. Currently there are nine standard ASTM methods, D3710, D7096, D2887, D5399, D7213, D6352, D6417, D5307, and D7169 [6–14]. A summary of the ASTM simulated and physical distillation methods in found in Fig. 6.

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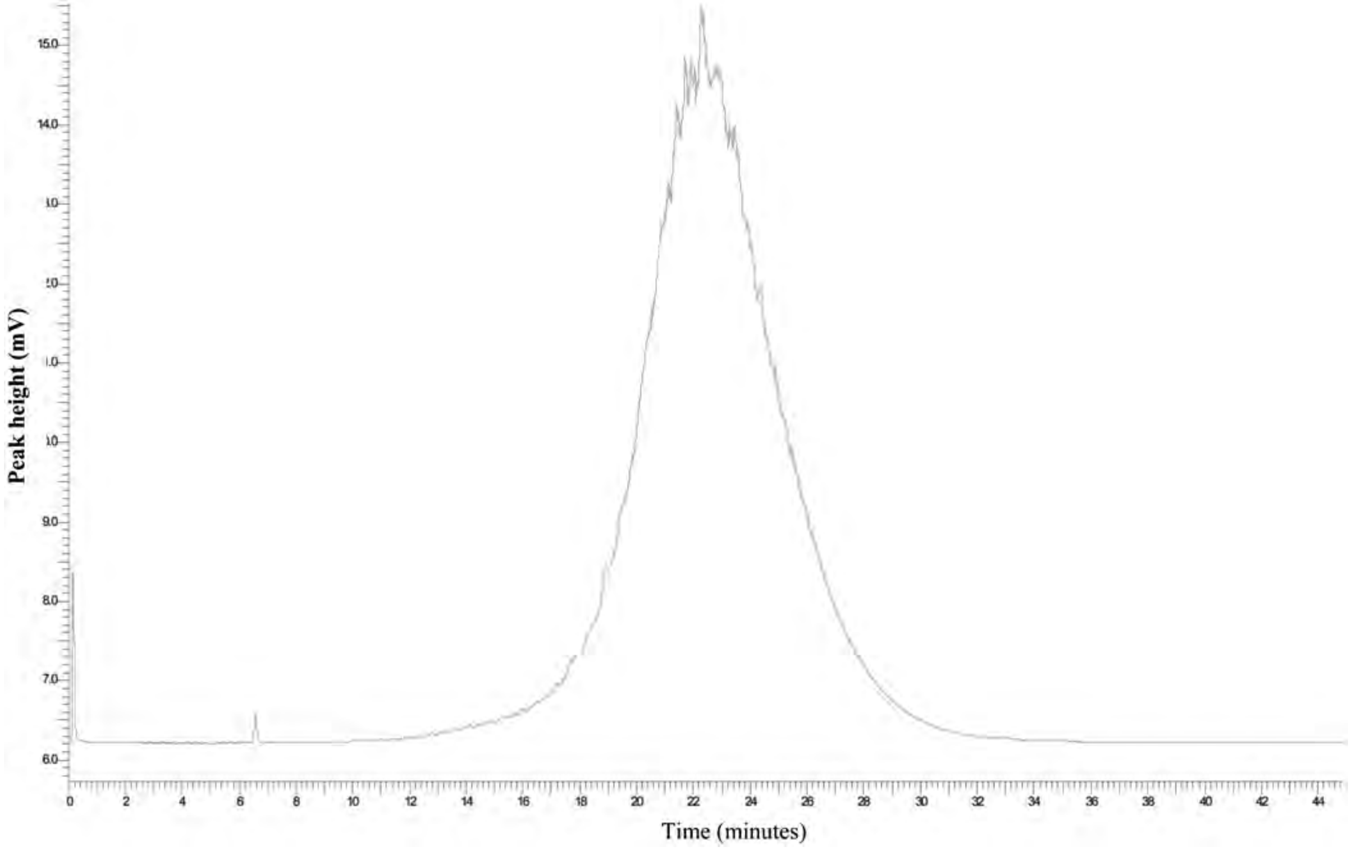

Fig. 1—Typical simulated distillation Chromatogram.

Method D3710-99 covers the determination by packed column GC of the boiling range distribution of gasoline and gasoline components with a final boiling point (FBP) of 260°C (500°F) or lower. This method uses a Thermal Conductivity Detector. Method D7096 is one of the newest simulated distillation methods and uses a Flame Ionization Detector. It covers the boiling range distribution of gasoline and liquid gasoline blending components using wide-bore capillary GC. It is applicable to petroleum products and fractions with a final boiling point of 280°C (536°F). This method has also been validated for gasoline containing ethanol. Method D2887 covers the determination by GC of the boiling range distribution of petroleum products and fractions having an FBP of 538°C (1000°F) or lower at atmospheric pressure. Method D5399 covers the determination of the boiling point distribution of hydrocarbon solvents by capillary GC. This test method is limited to samples having a minimum initial boiling point (IBP) of 37°C (97°F), a maximum FBP of 285°C (545°F), and boiling range of 5 to 150°C (9 to 270°F). Method D7213 is applicable to petroleum distillates having an initial boiling point of 100°C and a final boiling point less than 615°C. This test method should not be used for analysis of petroleum distillates containing low molecular weight components (such as naphtha, gasoline, or crude oils) or materials containing heterogeneous components (such as alcohols, ethers, acids, or esters) or residue. Method D6352 covers the determination by capillary GC of petroleum distillate fractions having an IBP greater that 174°C (345°F) and a FBP of less than 700°C (1292°F) at atmospheric pressure. Method D6417 uses the principles of simulated distillation to provide an estimation of the amount of engine oil volatilized at 371°C (700°F) by GC. It is limited to samples having an IBP greater than 126°C (259°F). Method D5307-97 is for the determination by packed column GC of boiling range distribution of crude petroleum through 538°C (1000°F), with material boiling above 538°C being reported as residue.

D5307 uses older packed column technology and internal standard methodology. Limitations of the column packing do not allow for material to be eluted from the column above 538°C, which corresponds to the elution of approximately n-C_{42}. Material above 538°C is reported as residue. Method D7169, “Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography,” covers the determination of the boiling point distribution and cut point intervals of crude oils and residues using capillary columns and high temperature gas chromatography. The amount of residue (or sample recovery) is determined using an external standard. This method extends the applicability of simulated distillation to petroleum samples that do not completely elute from the chromatographic system. This test method is used to determine the boiling point distribution through 720°C (1328°F), which corresponds to the elution of n-C_{100}.

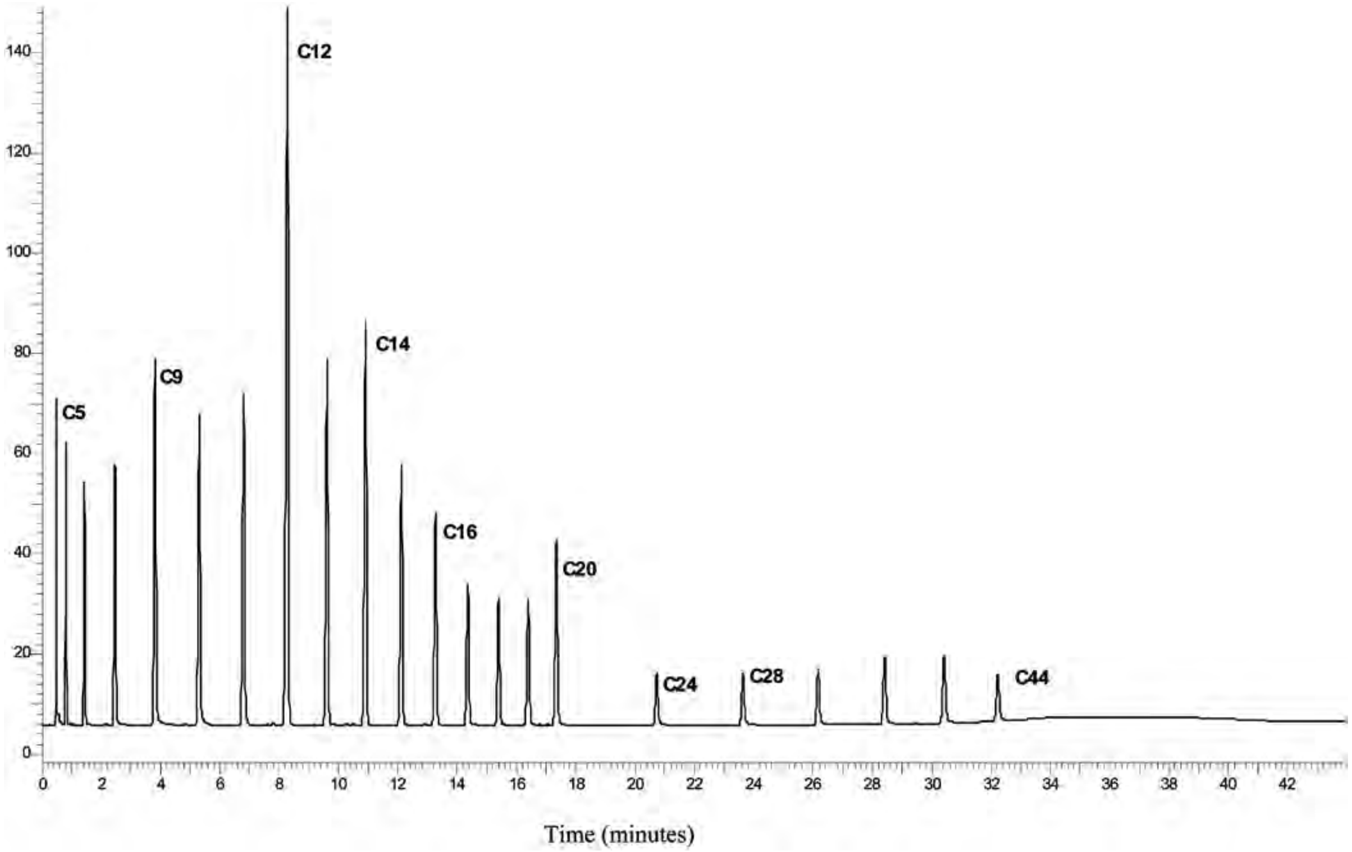

Fig. 2—D2887 normal-paraffin calibration standard chromatogram.

Important Considerations

There are six important factors to consider when establishing a simulated distillation procedure; instrument and injection requirements, column selection, carrier gas, data collection, analysis software, and data interpretation.

Instrument Requirements

The gas chromatograph selected for simulated distillation analysis requires a programmable oven, a suitable inlet, a flame ionization detector or thermal conductivity detector, and an autosampler. The oven and inlet temperature profiles must be reproducible. The autosampler must provide consistent delivery of the sample into the injector or onto the column.

The introduction of liquid samples into a gas chromatograph has been a difficulty ever since the beginning of the use of this technique in routine laboratories. Especially in capillary gas chromatography, extraordinary demands are placed on the sample introduction system. An extremely small sample amount has to be introduced accurately and rapidly in a reproducible manner into the smallest possible vaporized gas volume. This gas plug must be transferred into or onto the column without any losses by degradation, adsorption, or discrimination. This can only be achieved by employing very sophisticated inlet devices.

When using capillary columns for simulated distillation analysis, there are two injectors that are most commonly used: the cool on-column injector (COCI) and the programmable temperature vaporization (PTV) inlet. The COCI introduces liquid sample directly onto a capillary column. To do this both the inlet and the oven must be cool at injection. On-column injection allows accurately known volumes to be very reproducibly introduced directly onto the column. This greatly reduces the chance for discrimination and thermal degradation. On-column injection is very suitable for high boiling components because no vaporization takes place during the injection period. Since no intermediate vaporization step is present during on-column injection, the composition of the sample that is introduced onto the column must be equivalent to the original. Since the sample does not vaporize immediately in the inlet, problems with sample discrimination and sample alteration are minimized.

The PTV combines the advantages of various well known injection methods and can be used for all tasks which previously required a split or on-column injection system. The sample is injected into a glass liner, which is not heated until injection has been completed. Heating rates between 2 and 25°C/s may be selected. The inlet is usually programmed at such a rate that during the analysis the inlet is 15 to 25°C ahead of the column temperature.

Column Selection

Simulated distillation is based on the fundamental assumption that individual nonpolar hydrocarbon components of a sample elute in the order of their boiling points from a GC column. The column is coated with a nonpolar stationary phase. The elution or retention time is dependent upon va-

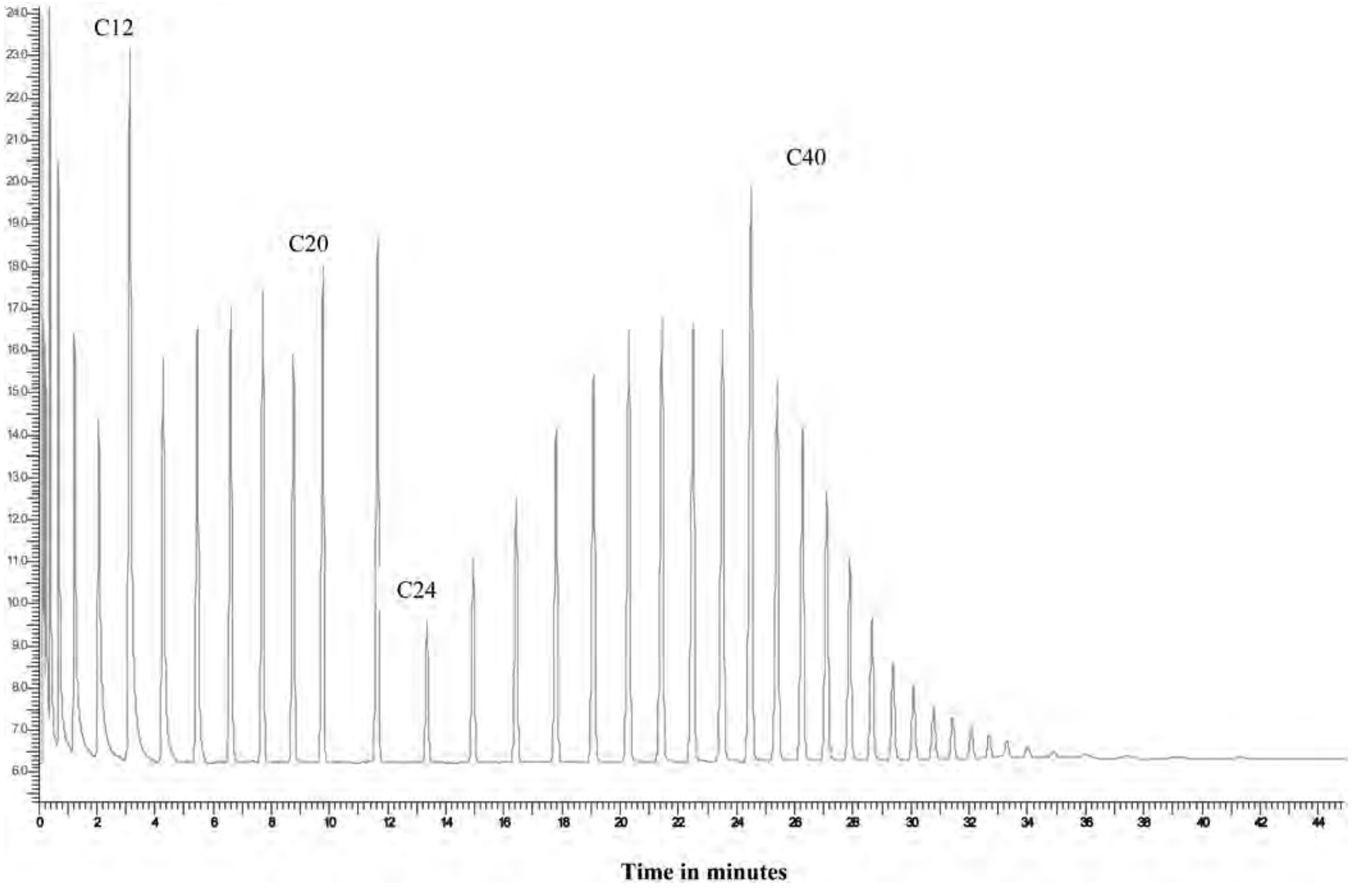

Fig. 3—D7213 normal-paraffin calibration standard chromatogram.

por pressure of the component and its affinity for the stationary phase. GC columns require two phases, a flowing or moving gas phase and a liquid phase held stationary on an inert solid support. Older packed columns were made of glass, copper, or stainless steel and were 3 to 6 mm in diameter and 1 to 2 m in length. The column was packed with a large surface area solid, usually a diatomaceous earth or crushed firebrick, and coated with a liquid phase. Separation occurs as the vaporized sample molecules partition themselves among the stationary phase and the moving gas phase. Since this partitioning is dependent on the solubility of the molecule in the two phases, a differential migration occurs through the column. The solubility of the lower boiling components is greater at lower column temperature than for the higher boiling molecules. In other words, the smaller the molecule the faster it moves through the column. Therefore, as the column temperature is increased, the solubility of the higher boiling molecules is increased, resulting in their elution from the column. Since the liquid phase for simulated distillation is nonpolar, the net result is that the molecules are eluted from the column in accordance with their boiling point.

During the past 20 years, chromatographers have witnessed an evolution in column technology. The developments of open tubular capillary columns have revolutionized gas chromatography. Capillary gas chromatography provides high resolution, which is significantly better than required by simulated distillation methods. However, these better efficiencies offer advantages for simulated distillation. The capillary column liquid phases are cross-linked, which has significantly reduced column bleed, and therefore reduced detector maintenance. This also provides very stable baselines, reducing the number of calibration runs, quality control samples, and blanks that are required. Consistency in column manufacturing has also increased the precision of the simulated distillation methods. This, along with the other features mentioned previously, amount to a near doubling of productivity and precision [15]. It is important to note that capillary columns have a limited sample capacity due to their very thin films and in the majority of SD samples must be diluted prior to injection.

Also, with capillary columns, resolution of the sample is more precise, particularly at the beginning and end of the chromatography. The characteristic of higher column resolution causes higher signal to noise ratios which yield a more accurate determination of the beginning and end of the chromatogram. The simulated distillation data are dependent to a great extent upon the accuracy of determination of the initial boiling point (IBP) and the final boiling point temperatures (FBP). Since the start and end of elution is better defined using capillary columns, more accurate simulated distillation data are produced.

Gas chromatographic columns may have the equivalent of 1,000,000 theoretical plates compared with conventional physical distillation which normally operates in the range of 1 to 10 theoretical plates. In physical or chromatographic

TABLE 1—D7213 normal-paraffin and retention time calibration report.

No.	Name	RT (min)	BP (C)
1	n-C5	0.13	36.1
2	n-C6	0.17	68.7
3	N-C7	0.24	98.4
4	N-C8	0.39	125.7
5	N-C9	0.69	150.8
6	N-C10	1.23	174.1
7	N-C11	2.07	195.9
8	N-C12	3.14	216.3
9	N-C13	4.29	235.4
10	N-C14	5.46	253.9
11	N-C15	6.61	270.6
12	N-C16	7.71	287.2
13	N-C17	8.76	301.9
14	N-C18	9.78	316.1
15	N-C20	11.66	343.9
16	N-C22	13.36	368.3
17	N-C24	14.95	391.1
18	N-C26	16.43	412.2
19	N-C28	17.80	431.1
20	N-C30	19.09	449.7
21	N-C32	20.30	466.1
22	N-C34	21.43	481.1
23	N-C36	22.50	496.1
24	N-C38	23.52	508.9
25	N-C40	24.51	522.2
26	N-C42	25.40	533.9
27	N-C44	26.27	545.0
28	N-C46	27.09	556.1
29	N-C48	27.89	566.1
30	N-C50	28.65	575.0
31	N-C52	29.38	583.9
32	N-C54	30.09	592.2
33	N-C56	30.77	600.0
34	N-C58	31.43	607.8
35	N-C60	32.07	615.0
36	N-C62	32.68	622.2

distillation, the column is considered to contain a number of theoretical plates and in each plate equilibrium between vapor and liquid will exist. A theoretical plate is actually a hypothetical zone or stage in which two phases, such as the *liquid* and *vapor* phases of a substance, establish an *equilibrium* with each other. Each theoretical plate or tray can be represented by a mathematical equation. The performance of physical and chromatographic distillation separation processes depends on having a series of equilibrium stages and is enhanced by providing more such stages. Therefore, the more theoretical plates in the column, the more equilibrium stages are present and the more efficient the separation. Unlike other gas chromatographic methodologies which aim for highly efficient conditions that achieve high resolution separation of components, chromatographic conditions for simulated distillation are selected to give limited column efficiency and resolution. The lower resolution analysis conditions provide boiling point data that generally agree with physical distillation.

Carrier Gas Flow Control

High purity helium, nitrogen, or hydrogen should be used for the carrier gas for SD analysis. These gases may not exceed more than 5 mL/m^3 of oxygen. The total amount of impurities should not exceed 10 mL/m^3. Additional purification may be required to remove excess water, oxygen, or hydrocarbons. The delivery pressure of the carrier gas must be sufficient to ensure a constant carrier gas flow rate. The gas chromatograph must be equipped with carrier gas pressure or flow control capable of maintaining constant carrier gas flow control throughout the entire column temperature program cycle. Constant flow is required in order to maintain constant response for the flame ionization detector.

Data Collection

A 0 to 1 mV range recording potentiometer or equivalent, with a full-scale response of two seconds or less may be used to provide a graphical display of the analysis. However, modern simulated distillation systems use an electronic integrator or a computer-based chromatography data system. The integrator/computer system must have normal chromatographic software for measuring the retention time and areas of eluting peaks (peak detection mode). The system must also be capable of converting the continuously integrated detector signal into area slices of a fixed duration (area slice mode). These contiguous area slices, collected over the entire analysis, are stored for later processing. The electronic range of the integrator/computer system must be operated within the linear range of the detector system used.

Analysis Software

Prior to 1973 strip chart recorders and ball integrators were used to process SD data. During the past ten years there has been considerable development of commercial software packages for SD. The current technology of PC-based software systems, Microsoft Windows environment software, and universal data formats have provided many third-party software programs which can provide fast and accurate SD reports. The need for industry standardization became apparent after the 1991 ASTM D2887 round-robin to confirm the published precision data. It was found that the actual precision was much lower than the published data. After several discussions it was determined that the most significant factor affecting the poor precision in the study was the lack of a standard SD calculation algorithm for determining the start and end of sample elution. Standard calculation algorithms are now incorporated in almost all of the ASTM SD methods previously described. Each specific SD method has its own algorithm, which contains the instructions for calculating the boiling point distribution data. Many of the commercial software products contain these algorithms. Table 3 contains the necessary features for a good SD software program.

Data Interpretation

There are four important tools that can be used when interpreting simulated distillation data to ensure consistent results. These are: visual inspection of the chromatograms, calibration equation, baselines/blanks, and sample area. Once the analysis is complete and the electronic data stored, the analyst must prepare the simulated distillation report. Before beginning any simulated distillation data work up, a quick visual inspection of the chromatograms should be completed. There is no point in beginning to analyze data that does not look “right.” The analyst can confirm with a

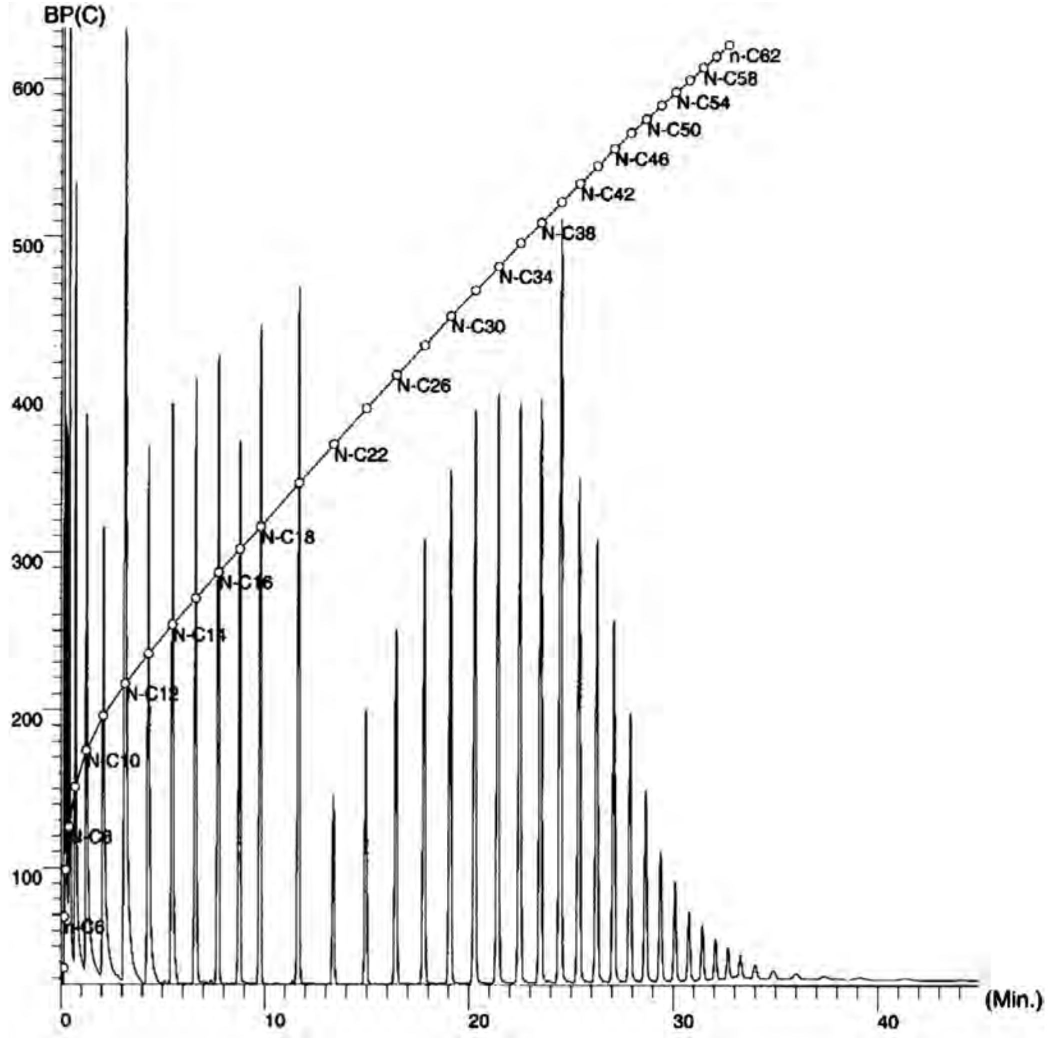

Fig. 4—D7213 normal-paraffin calibration chromatogram with boiling point versus retention time relationship.

quick look that the data appear as expected and therefore determine that no instrument malfunctions occurred during the run. The next thing to consider is the calibration. All normal paraffin peaks must be correctly integrated and identified. Secondly, ensure that all peaks are not overloaded by following a skewness criterion. A skewed peak will distort the calibration. The calibration line should appear as a relatively straight line. All baseline blanks (whether solvent injection or software compensation) must be clean and represent a normal column temperature profile. Some gas chromatographs and integrator systems have an algorithm built into their operating software that allows a mathematical model of the baseline profile to be stored in memory. This profile is automatically subtracted from the detector signal on subsequent sample runs to compensate for the column bleed. Otherwise, using the chromatographic software, a solvent blank may be subtracted from each sample to correct for column bleed and solvent interference from early eluting components. This provides a point-by-point or slice-by-slice subtraction of the baseline. ASTM SD methods prefer to use a solvent blank correction and contain a warning in the calculation algorithm section of the method that automatic baseline compensation may not give the same results as slice-by-slice blank subtraction. Most chromatographic systems use an autosampler for introduction of the sample into the gas chromatograph. Monitoring the sample area is a simple tool that can ensure that the autosampler or syringe is providing repeatable injections. This can be extremely important when using an external standard methodology. One mistake analysts often make is assuming that because the quality control sample is within the established limits, data from the next sample will be valid. It is important to ensure that every sample analyzed meets the interpretation criterion outlined.

Comparison To Physical Distillation TBP

Crude assay distillation refiners need improved accuracy and precision of boiling-point data to optimize overall refining margins. Simulated distillation offers tighter precision than conventional crude assay distillation (ASTM D2892 and D5236). It also provides faster turnaround and boiling-point data to a much higher final boiling point. Simulated distillation is a very valuable business tool for evaluation of new crudes and ensuring crude product integrity from purchase through transportation and delivery.

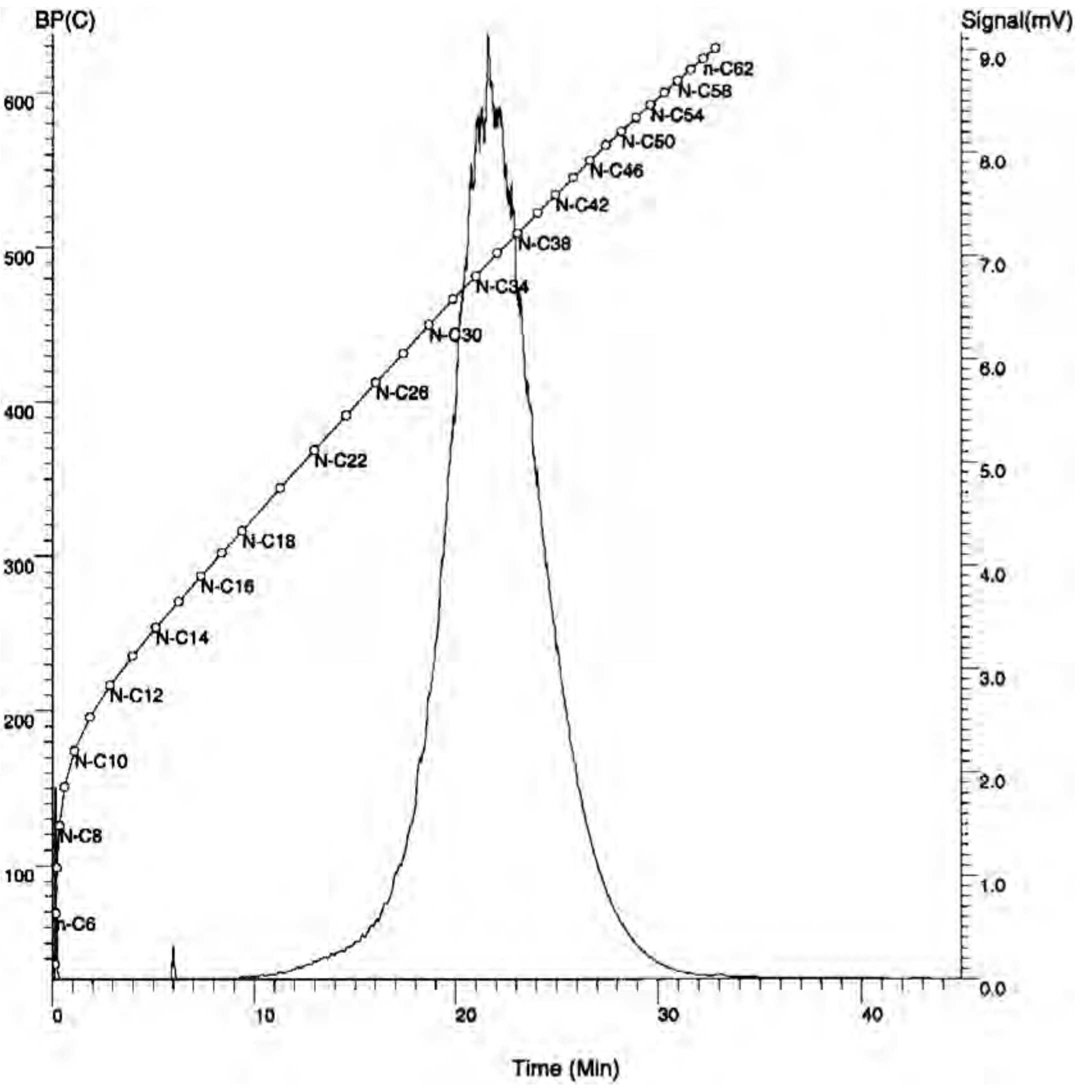

Fig. 5—D7213 simulated distillation chromatogram with calibration line.

Crude assay distillation using D2892 uses a 15-plate distillation column operating under a reflux ratio of 5:1 to produce true boiling point data. The distillation starts at ambient pressure (760 mm Hg) and then switches to vacuum conditions to extend the method to 343°C atmospheric equivalent boiling point. The remaining charge is transferred to a vacuum potstill method (D5236) in which the distillation continues at 0.5 mm Hg to obtain an atmospheric equivalent boiling point limit of 545°C. The true boiling point curve can be built from simulated distillation data using a combination of the ASTM methods and physically distilled fractions or the whole crude sample can be analyzed directly using D7169. Figure 7 compares the boiling point curves from volume and weight percent physical distillation (D5236), D7213, and combined ASTM simulated distillation methods on physically distillated fractions.

Correlations Using Simulated Distillation Data

D86 Correlated Data from D2887 Data

There are three calculations for determining D86 correlated data from D2887. The first is the *ASTM Special Technical Publication* (*STP*) *577* which is also called the Atlantic Richfield correlation. The second is the American Petroleum Institute (API) Procedure 3A3.2. The calculations for both of these correlations are found in Appendix X4 of D2887. The third correlation was developed specifically for jet and diesel fuel.

Both D975, "Standard Specification for Diesel Fuel Oils" and D1655, "Standard Specification for Aviation Turbine Fuels," require the use of D86 distillation to determine compliance with the distillation requirement of the specification. In 1999 a proposal was made to allow the use of D2887 as an alternative method to D86 distillation for diesel and jet fuel specification testing [16]. A mathematical model was developed to calculate D86 equivalent data from D2887 data [17]. This third correlation is found in Appendix X5 of D2887.

Correlation of Flash Point and D2887

Construction of a correlation model for the prediction of flash point from boiling range distribution data by gas chromatography obtained by simulated distillation was undertaken by ASTM Committee D02.04 Section K. This correlation is currently under ballot consideration as an ASTM

TABLE 2—Typical D7213 simulated distillation data report.

% Off	BP (C)	% Off	BP (C)	% Off	BP (C)	% Off	BP (C)
IBP-0.5	364.3						
1.0	383.1	26.0	473.7	51.0	494.5	76.0	516.6
2.0	405.3	27.0	474.6	52.0	495.3	77.0	517.7
3.0	418.1	28.0	475.5	53.0	496.1	78.0	519.0
4.0	426.3	29.0	476.5	54.0	496.9	79.0	520.2
5.0	432.5	30.0	477.3	55.0	497.6	80.0	521.6
6.0	437.7	31.0	478.2	56.0	498.4	81.0	523.0
7.0	442.0	32.0	479.0	57.0	499.1	82.0	524.4
8.0	445.3	33.0	479.8	58.0	499.9	83.0	525.9
9.0	448.4	34.0	480.7	59.0	500.6	84.0	527.4
10.0	451.0	35.0	481.5	60.0	501.4	85.0	529.1
11.0	453.3	36.0	482.4	61.0	502.2	86.0	530.8
12.0	455.4	37.0	483.2	62.0	503.1	87.0	532.6
13.0	457.3	38.0	484.0	63.0	503.9	88.0	534.5
14.0	459.1	39.0	484.8	64.0	504.7	89.0	536.5
15.0	460.7	40.0	485.7	65.0	505.5	90.0	538.6
16.0	462.2	41.0	486.5	66.0	506.4	91.0	541.0
17.0	463.6	42.0	487.3	67.0	507.2	92.0	543.5
18.0	464.9	43.0	488.1	68.0	508.1	93.0	546.4
19.0	466.1	44.0	489.0	69.0	509.0	94.0	549.9
20.0	467.3	45.0	489.7	70.7	510.0	95.0	553.8
21.0	468.5	46.0	490.5	71.0	511.0	96.0	558.4
22.0	469.6	47.0	491.2	72.0	512.1	97.0	564.1
23.0	470.7	48.0	492.0	73.0	513.1	98.0	571.3
24.0	471.7	49.0	492.8	74.0	514.2	99.0	583.0
25.0	472.7	50.0	493.6	75.0	515.4	FBP-99.5	593.6

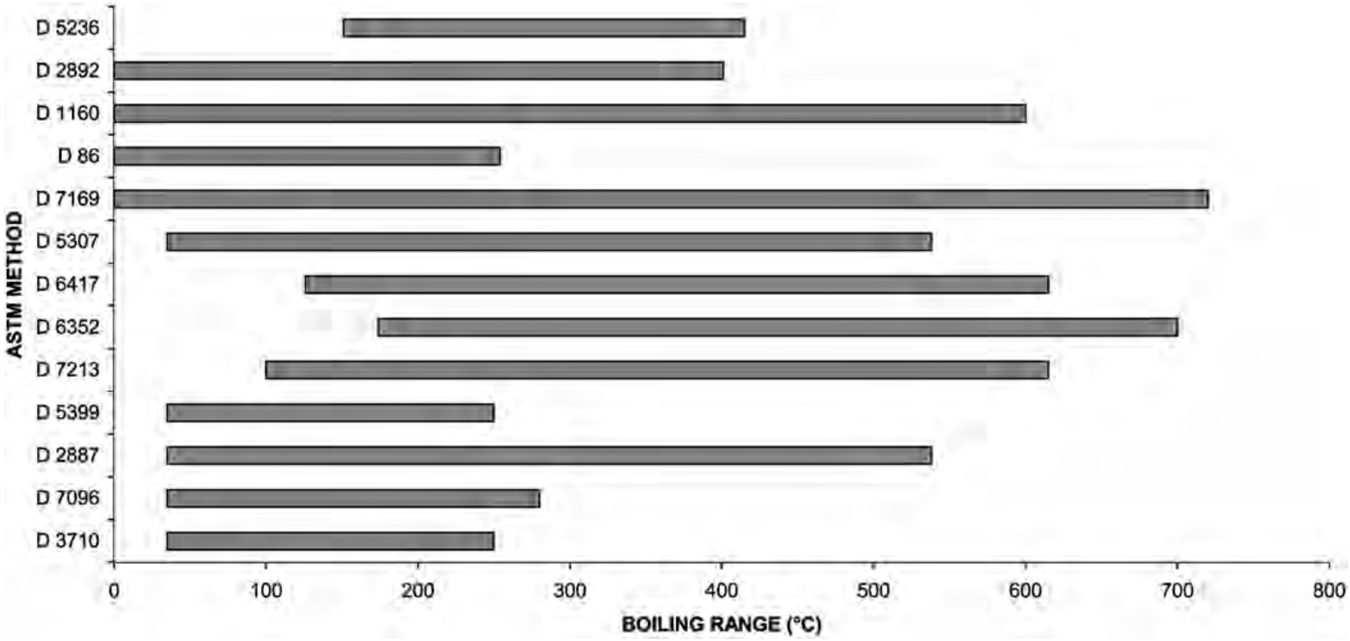

Fig. 6—Summary of ASTM physical and simulated distillation methods.

TABLE 3—Suggested important features of simulated distillation software.

1. ASTM calculation algorithm
2. External standard analysis
3. Batch analysis with single analysis features
4. Baseline subtraction
5. Record the analysis method used
6. Auto calibration and carbon number identification
7. On-line recalibration
8. Visual IBP/FBP and calibration information
9. On-line help
10. CDF compatible
11. Milivolt start/stop display
12. Separates data collection from data analysis
13. On-screen reanalysis
14. User definable cut-points
15. Built-in calculation for ASTM motor oil volatility
16. User definable CS2 quenching factor
17. D86/D1160 correlation
18. Recovery calculations (for residual)
19. Other correlations under development
20. Column resolution and skewness factors

standard method. The correlation model used closed cup flash point data from three ASTM standards, D56, D93, and D3828 and simulated distillation data from D2887 [18–20]. The boiling point temperatures at the initial boiling point, 5 and 10% are required for the flash point calculation. The experimental flash point data and simulated distillation data were obtained from American, Canadian, and European interlaboratory studies. These studies included diesel and jet fuels. The correlation model was constructed by applying a partial least squares regression on experimental flash point data and a selection of variables from the simulated distillation data. The regression calculation results in a correlation model containing a set of correlation coefficients and data for model error predication. The correlation model was validated by applying the D6708 procedure [21]. This procedure tests for significant bias between the experimental and calculated flash point from a validation dataset [22].

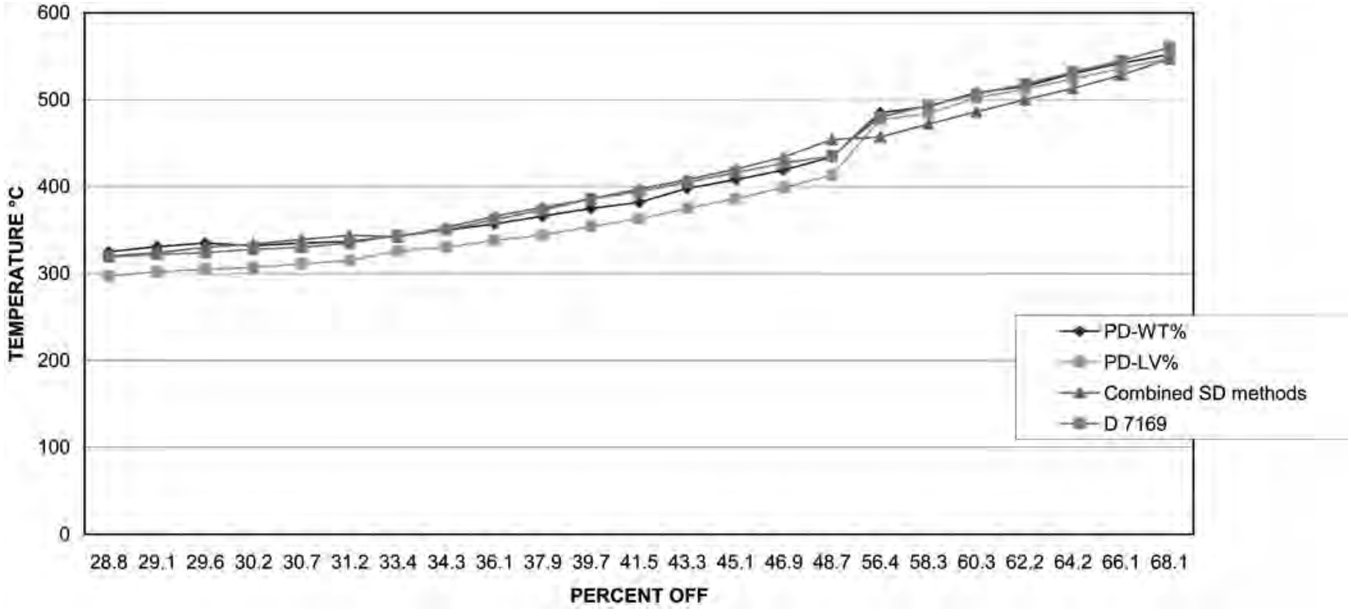

Fig. 7—Comparison of physical distillation and simulated distillation.

Future Work In The Area Of Simulated Distillation

Accelerated Simulated Distillation

Accelerated simulated distillation is a fast gas chromatographic technique in which short columns with a narrow diameter, high flow rates, and fast heating rates are used to carry out accelerated chromatography. The analysis time may be reduced to seconds. The results show boiling-point distribution values nearly the same as those obtained with standard methods. In the past ten years there has been quite a lot of interest and effort into reducing analysis times of simulated distillation analyses. In 1997 Giarroco carried out D2887 analysis in seven minutes using a fast oven program at 40°C and a very narrow capillary column [23]. Lubkowitz also published work showing a seven-minute D2887 using a 0.32-mm i.d., 0.5 μm film thickness dimethylpolysiloxane capillary column, and a high flow rate of 30 mL/min [24]. Workman used narrow bore capillary columns and fast oven temperature program rates for a 15-minute simulated distillation analysis based on D7213 [25]. All of these papers and many others show the applicability of fast chromatographic techniques for the determination of boiling-point distribution using simulated distillation. As technology advances, these fast techniques will become the new industry standards for simulated distillation analyses.

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5

Vapor Pressure Measurement

Rey G. Montemayor[1]

ANOTHER PROPERTY CHARACTERISTIC OF PETROleum products that is closely associated with distillation parameters is vapor pressure. More often than not, the performance of various petroleum products, especially those used in transportation fuel applications, are very much dependent on synergistic parameters involving distillation and vapor pressure data.

As mentioned in Chapter 1, the measurement of vapor pressure characteristics of petroleum products began with ASTM D323-30T "Standard Test Method for Vapor Pressure of Natural Gasoline (Reid Method)" [1]. This test method has withstood the test of time and exists today essentially as the same test method originally published as a tentative method 75 years ago. Various test methods for measuring vapor pressure have come into use within the petroleum industry since that time. In 1991, a number of automatic test methods for vapor pressure measurement have gained approval in the industry, and technological advances in automatic vapor pressure measurements have dominated the market place, especially with the stringent requirements of regulations to protect the environment.

This chapter will discuss the relevant details of the latest versions of the various vapor pressure measurement test methods currently available and in use in the petroleum industry. Details that would serve to provide a better understanding or clarification of the test methods will be discussed.

ASTM D323—Vapor Pressure Measurement By The Reid Method [2]

Before the advent of automatic vapor pressure measurement instruments, ASTM D323 "Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method)" was the workhorse standard for this test. As such, a detailed discussion of D323 is presented here.

Scope

The scope of this test method now includes gasoline, volatile crude oil, and other volatile petroleum products. The original test method was only for natural gasoline, but was later expanded in 1935 to include aviation gasoline [3]. Because the external atmospheric pressure is counteracted by the atmospheric pressure initially present in the vapor chamber, the Reid vapor pressure (RVP) measured by this test method gives the absolute pressure at 37.8 °C (100 °F) in Pa (psi). The Reid vapor pressure differs from the true vapor pressure of the sample due to some small sample vaporization and the presence of water vapor and air in the confined space used in the test method.

Procedure A—This is a manual procedure applicable to gasoline and other petroleum products with a vapor pressure of less than 180 kPa (26 psi). This procedure is not applicable to liquefied petroleum gases or for gasoline-oxygenate blends.

Procedure B—This is a semi-automated procedure applicable to gasoline and other petroleum products with a vapor pressure of less than 180 kPa (26 psi) using a horizontal bath with automatic capability of rotating the vapor pressure test chamber on its axis 350° in one direction, then 350° in the opposite direction in a repetitive fashion. Only gasoline was used in the interlaboratory study to generate the precision of this procedure. This procedure is not applicable to liquefied petroleum gases or for gasoline-xygenate blends.

Procedure C—This manual procedure is applicable to materials with vapor pressure greater than 180 kPa (26 psi) and utilizes a liquid chamber with two valved openings.

Procedure D—This manual procedure is limited to aviation gasoline with a vapor pressure of approximately 50 kPa (7 psi), and requires a more stringent limit on the ratio of the vapor and liquid chambers (3.95–4.05 to 1).

Summary and Significance of the Test Method

The liquid chamber of the vapor pressure apparatus is filled with the chilled, air-saturated sample, and connected to the vapor chamber that has been heated to 37.8 °C (100 °F) in a bath. The assembled apparatus is immersed in a bath maintained at 37.8 °C (100 °F) until a constant pressure is observed. The reading, after correction due to gage error (if any), is reported as the Reid vapor pressure. The nominal vapor/liquid ratio V/L during the test is required to be 4:1. The procedural details of measuring vapor pressure using procedures A, B, C, and D are given in the Appendix of this manual.

Vapor pressure is critically important for both automotive and aviation gasolines. It affects starting performance, warm-up, and tendency to vapor lock with high temperature or high altitudes. Maximum vapor pressure limits for gasoline are legally mandated in various parts of the world as a measure of air pollution control and environmental protection. Vapor pressure of crude oils is of importance to the crude producer and the refiner for general handling, storage, distribution, and initial refinery treatment. Vapor pressure is also used as an indirect measure of the evaporation rate of volatile petroleum solvents, although other vapor pressure

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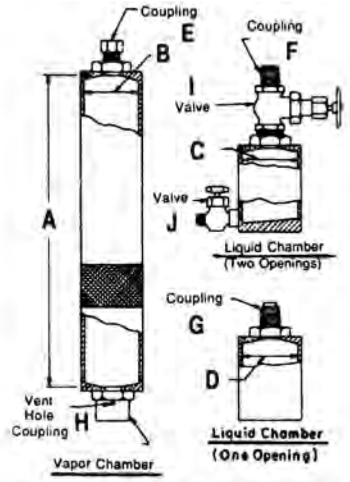

DIMENSIONS OF VAPOR PRESSURE APPARATUS

Key	Description	mm	in.
A	Vapor chamber, length	254 ± 3	10 ± 1/8
B, C, D	Vapor and gasoline chambers, Liquid ID	51 ± 3	2 ± 1/8
E	Coupling, ID min	4.7	3/16
F, G	Coupling, OD	12.7	1/2
H	Coupling, ID	12.7	1/2
I	Valve	12.7	1/2
J	Valve	6.35	1/4

Fig. 1—Vapor and liquid chamber of reid vapor pressure apparatus.

measurement techniques may be required to measure the low vapor pressure values of some of these solvents. The details of the procedure section of this test method can be found in the Appendix of this manual.

Apparatus

Vapor Chamber—For procedures A, B, C, and D, the vapor chamber is the chamber into which the liquid specimen is allowed to drain and vaporize at the prescribed temperature. Figure 1 shows the schematic diagram and required dimensions for the vapor chamber specified for the four procedures. This vapor chamber design is almost identical to the original vapor chamber specified in D323-30T, confirming the robustness of the original test method designed for natural gasoline.

Liquid Chamber With One Opening—For procedures A, B, and D, the liquid chamber with one opening is the chamber into which the air-saturated liquid specimen is transferred to from the chilled bulk sample. When the liquid chamber is full of the chilled liquid specimen for testing, the vapor chamber is coupled to the liquid chamber and the measurement process is begun. Figure 1 also shows the diagram and dimension of the liquid chamber with one opening.

Liquid Chamber With Two Openings—For Procedure C dealing with samples under pressure, a liquid chamber with two openings is required. This is shown in Fig. 1, and it is very similar to the liquid chamber with one opening except that a second opening at the base of the chamber is present. This allows for the safe isolation of the specimen under pressure.

Pressure Gage—The pressure gage shall be a Bourdon type spring gage of test gage quality 100 mm to 150 mm (4.5 in. to 6.5 in.) in diameter provided with a nominal 6.35 mm (0.25 in.) male thread connection with a passageway not less than 4.7 mm (3/16 in.) in diameter from the Bourdon tube to the atmosphere. The range and graduations of the pressure gage is dictated by the vapor of the sample being tested, as shown in Table 1. In Procedure B, a suitable transducer with digital readout can be used in place of a pressure gage.

TABLE 1—Pressure gage range and graduations.

Reid vapor pressure kPa	psi	Gage to be used Scale range kPa	psi	Maximum numbered intervals kPa	psi	Maximum intermediate graduations kPa	psi
⩽27.5	⩽4	0–35	0–5	5.0	1	0.5	0.1
20.0–75.0	3–12	0–100	0–15	15.0	3	0.5	0.1
70.0–180.0	10–26	0–200	0–30	25.0	5	1.0	0.2
70.0–250.0	10–36	0–300	0–45	25.0	5	1.0	0.2
200.0–375.0	30–55	0–400	0–60	50.0	10	1.5	0.25
⩾350.0	⩾50	0–700	0–100	50.0	10	2.5	0.5

Cooling Bath or Refrigerator—A cooling bath or a refrigerator capable of maintaining a temperature between 0 °C and 1 °C (32 °F and 34 °F) is required to cool the sample and the liquid chamber. The cooling bath must be of such dimensions to allow the sample container and the liquid chamber to be fully immersed. Solid carbon dioxide ("dry ice") is not to be used to cool the sample being tested because carbon dioxide is appreciably soluble in gasoline and its use has been found to be a cause of erroneous vapor pressure data.

Water Bath—The water bath must be of sufficient dimension so that the vapor pressure apparatus can be immersed to at least 25.4 mm (1 in.) above the top of the vapor chamber. The water bath must be able to control the bath temperature at 37.8 ± 0.1 °C (100 ± 0.2 °F). For Procedure B, provision shall be made to rotate the apparatus on its axis 350° in one direction and then 350° in the opposite direction in a repetitive fashion. A suitable bath is shown in Fig. 2.

Thermometer—To monitor the temperature of the water bath during the test, a thermometer is required. It is essential that the bath thermometer be immersed to the 37 °C (98 °F) mark throughout the vapor pressure determination. An ASTM 18C (18F) thermometer having a range of 34 °C to 42 °C (94 °F to 108 °F) is specified for the Reid vapor pressure determination.

Pressure Measuring Device—To check the accuracy of the pressure gage, a measuring device having a suitable range is required. The pressure measuring device must have a minimum accuracy of 0.5 kPa (0.07 psi) with increments no larger than 0.5 kPa (0.07 psi). A mercury manometer is suitable as a pressure measuring device. When a mercury manometer is not used, the calibration of the pressure measuring device used has to be checked periodically. A deadweight tester can be used instead of a mercury manometer for checking gage pressure reading above 180 kPa (26 psi).

Sample Transfer Connection—A device for transferring sample from the sample container without interfering with the vapor space. The device consists of two tubes inserted

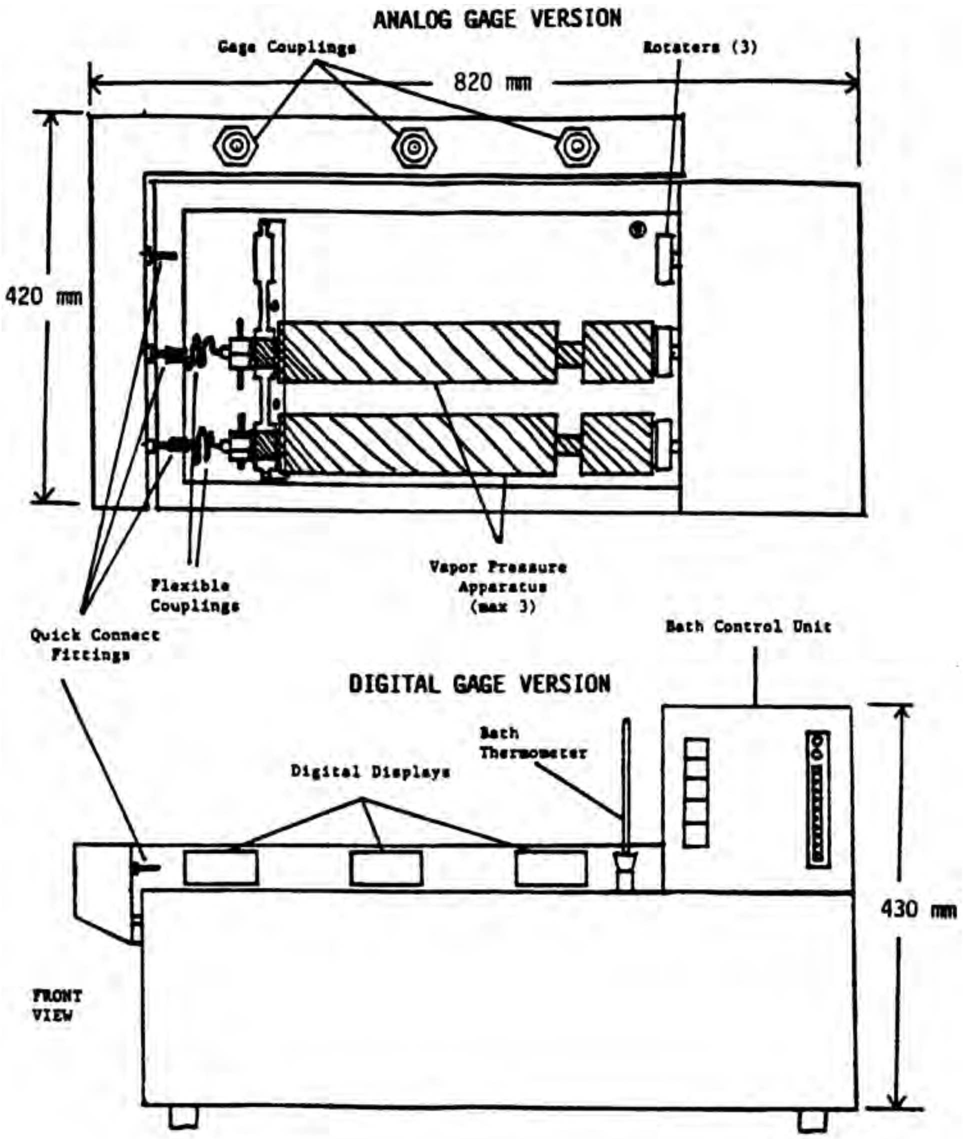

Fig. 2—Apparatus for ASTM D323 Procedure B.

into a two-hole stopper of appropriate dimensions to fit the opening of the sample container. One of the tubes is short for delivery of the sample, and the other is long enough to reach the bottom corner of the sample container. See Fig. 3 for a schematic diagram.

Sampling

Vapor pressure measurement is extremely sensitive to losses of light components through evaporation such that utmost precautions in the sampling and sample handling are necessary to minimize compositional changes that will affect the measured vapor pressure. Sampling shall be done in accordance with ASTM D4057 "Standard Practice for Manual Sampling of Petroleum Products" [4]. Section 10.3 of D4057 specifies that when isolating samples for vapor pressure measurements, ASTM D5842 "Standard Practice for Sampling and Handling of Fuels for Volatility Measurements" [5] shall be used. The sample shall be taken in a 1 L (1 qt) container filled 70 % to 80 % with sample for Procedures A, B,

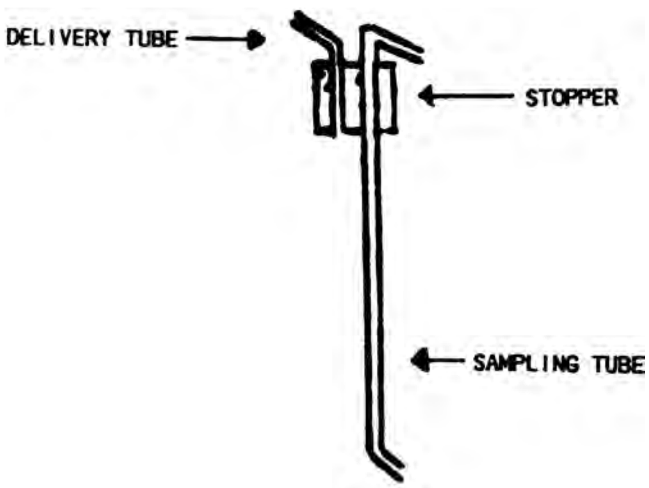

Fig. 3—Sample transfer connection device.

and D, although containers of other sizes can be used as long as it is recognized that precision can be affected. RVP determination is required to be performed on the first specimen isolated from the sample container. The remaining sample in the sample container shall not be used for a second vapor pressure determination. If another RVP determination is necessary, obtain a new sample. The sample container and its contents has to be cooled to a temperature of 0–1 °C (32–34 °F) before the container is opened. Sufficient time to reach this temperature shall be ensured by direct measurement of the temperature of a similar sample in a similar container placed in the cooling bath or refrigerator at the same time as the sample. Because Procedure C is for the determination of vapor pressure greater than 180 kPa (26 psi), some of the sampling and procedural requirements applicable to Procedures A, B, and D may not be applicable. The reader is referred to the actual test method itself, i.e., D323, or the excerpted procedure sections in the Appendix of this manual.

Calibration

Volumetric Capacity of the Vapor and Liquid Chambers—The specified limits of vapor chamber to liquid chamber ratio for this method are 3.8 to 4.2. Therefore, it is a requirement to check the volume of the vapor chamber and the liquid chamber. This can be done by determining the amount of water required to completely fill the liquid chamber to determine the volume of the liquid chamber. Afterward, the vapor chamber is connected to the liquid chamber, and the additional amount of water required to fill the vapor chamber to the seat of the gage connection is determined. A dispensing burette of 10 mL capacity will allow this measurement to be done easily. The theoretical volume of the liquid chamber based on the prescribed dimensions is 64.86 mL. For the vapor chamber, the specified dimensions amount to a theoretical volume of 259.44 mL. For Procedure D determination, the prescribed volume of the vapor chamber to the liquid chamber ratio is given to be 3.95 to 4.05. To maintain the correct volume ratio between vapor chamber and the liquid chamber, paired chambers shall not be interchanged without a recalibration check to ascertain that the volume ratio is within the required limit.

Pressure Gage—The accuracy of the pressure gage must be checked against a mercury manometer or other calibrated pressure measuring device. If the gage reading differs from a calibrated pressure measuring device or a deadweight tester by more than 1 % of the scale range of the gage, the gage shall be considered inaccurate. For example, for a 0–30 kPa (0–15 psi gage), the allowed pressure reading difference of the pressure gage and a calibrated pressure measuring device should be less than 0.3 kPa (0.15 psi).

Thermometer or Temperature Measuring Device—The calibration of the prescribed thermometer, ASTM 18C, can be checked following the procedure described in ASTM E77 "Standard Test Method for Inspection and Verification of Thermometers" [6]. The calibration of other temperature measuring devices such as thermocouples or resistance thermometer can be done using standard resistance benches.

Report, Precision, and Bias

Report—Report the observed vapor pressure corrected for any difference between the gage and pressure measuring device reading to the nearest 0.25 kPa (0.05 psi) as the Reid vapor Pressure (RVP).

TABLE 2—Repeatability of ASTM D323.

	Range		Repeatability	
Procedure	kPa	psi	kPa	psi
A Gasoline[a]	35–100	5–15	3.2	0.46
B Gasoline[a]	35–100	5–15	1.2	0.17
A[b]	0–35	0–5	0.7	0.1
A[b]	100–180	16–26	2.1	0.3
C[b]	>180	>26	2.8	0.4
D (Aviation gasoline)[b]	50	7	0.1	0.1

[a] From a 1987 ILS data analyzed by ASTM D6300 [9]. See RR: D02-1245 [7].

[b] Developed in the early 1950s prior to statistical evaluation method.

Precision—Tables 2 and 3 give respectively, the repeatability and reproducibility of the various procedures included in this test method.

Absolute Bias—Since there is no accepted reference material suitable for determining the bias for this test method, absolute bias cannot be determined. The amount of bias between the Reid vapor pressure determined by this method and the true vapor pressure is not known.

Relative Bias—There is no statistically significant difference between Procedures A and B for gasoline as determined in the 1987 interlaboratory study (ILS; see RR: D02-1245) [7].

ASTM D4953—Vapor Pressure By The Dry Reid Method [5]

Scope

ASTM D4953 "Standard Test Method for Vapor Pressure of Petroleum Products (Dry Method)" is a modification of ASTM D323. It provides two procedures for determining the vapor pressure of gasoline and gasoline-oxygenate blends utilizing the same apparatus as described for Procedures A and B of D323. The modification requires that the interior surfaces of the liquid and vapor chambers be free of water. Hence, this method is often referred to as the Dry Reid method. Just like D323, this method measures an absolute pressure at 37.8 °C (100 °F) because the external atmospheric pressure is counteracted by the atmospheric pres-

TABLE 3—Reproducibility of ASTM D323.

	Range		Reproducibility	
Procedure	kPa	psi	kPa	psi
A Gasoline[a]	35–100	5–15	5.2	0.75
B Gasoline[a]	35–100	5–15	4.5	0.66
A[b]	0–35	0–5	2.4	0.35
A[b]	100–180	16–26	2.8	0.4
C[b]	>180	>26	4.9	0.7
D (Aviation gasoline)[b]	50	7	1.0	0.15

[a] From a 1987 ILS data analyzed by ASTM D6300 [9]. See RR: D02-1245 [7].

[b] Developed in the early 1950s prior to statistical evaluation method.

TABLE 4—Repeatability and reproducibility of ASTM D4953.

Procedure	Repeatability, kPa (psi)	Reproducibility, kPa (psi)
Procedure A	3.65 (0.53)	5.52 (0.50)
Procedure B:		
Gage	4.00 (0.58)	5.38 (0.78)
Transducer (Herzog)	2.14 (0.31)	2.90 (0.42)
Transducer (Precision Scientific)	3.58 (0.52)	4.27 (0.62)

sure initially present in the air chamber. The vapor pressure differs from the true vapor pressure of the sample due to some small vaporization of the sample and the presence of water vapor and air.

The vapor pressure of gasoline or gasoline-oxygenate blends below 35 kPa (5 psi) or greater than 100 kPa (15 psi) can be determined by this test method. However, the precision and bias statement for this test method may not apply.

Procedure A—Uses the same apparatus and procedure as does Procedure A of D323. Extreme measures are utilized to ensure that the interior surfaces of the liquid and vapor chamber are maintained free from moisture.

Procedure B—Uses the same apparatus and procedure as does Procedure B of D323. Extreme measures are utilized to ensure that the interior surfaces of the liquid and vapor chamber are maintained free from moisture.

Summary of the Test Method, Significance and Use, and Apparatus

As mentioned in the discussion of the scope of ASTM D4953, the test method is almost identical to ASTM D323 with the exception that precautions are required to ensure that the interior surfaces of the liquid and vapor chambers are maintained completely free of water. Hence, the discussion given in the D323 portion of this chapter regarding the summary, significance and use, and applicable apparatus apply. Similarly, the sampling, calibration, and report requirements for this method are the same as for D323. The vapor pressure determined by this method is oftentimes referred to as the Dry Reid vapor pressure. The procedural details of the test method are given in the Appendix of this manual.

Precision and Bias

Precision—The precision for this test method was developed in a 1991 interlaboratory study (ILS) involving 14 types of hydrocarbon and hydrocarbon-oxygenate blends, and summarized in research report RR:D02-1286. The repeatability and reproducibility for Procedures A and B are given in Table 4.

Absolute Bias—Since there is no accepted reference material suitable for determining the bias for this test method, absolute bias cannot be determined. The amount of bias between the vapor pressure determined by this method and the true vapor pressure is not known.

Relative Bias—Statistically significant bias has been observed in the 1991 interlaboratory study (see RR: D02-1286) [8] between Procedure A and Procedure B of this test method. These biases can be corrected by applying the appropriate correlation equations given below:

For Procedure B, gage:

$$\text{DVPE}, \ _{\text{Procedure A}} = 1.029X \tag{1}$$

For Procedure B, transducer (Herzog):

$$\text{DVPE}, \ _{\text{Procedure A}} = 0.984X \tag{2}$$

where:

DVPE, $_{\text{Procedure A}}$ = dry vapor pressure equivalent to Procedure A value, and

X = vapor pressure obtained by Procedure B.

For example, if the vapor pressure obtained by Procedure B (gage) is 68.0 kPa (9.96 psi), using Eq (1), the dry vapor pressure equivalent (DVPE) to Procedure A is:

$$(1.029)(68.0) = 70.0 \text{ kPa}$$

A similar calculation can be made for a vapor pressure obtained by Procedure B (transducer) using Eq (2).

For Procedure B, transducer (Precision Scientific), there was no relative bias observed relative to Procedure A results.

Based on the 1987 interlaboratory study (see RR:D02-1245), there was no statistically significant bias observed between D323 and procedure A of this method for samples containing hydrocarbons only or hydrocarbons and methyl *t*-butyl ether (MTBE).

ASTM D5191—Vapor Pressure of Petroleum Products (Mini Method) [5]

In the early 1990s, a number of automatic vapor pressure measurement instruments appeared in the petroleum industry. D323 provided vapor pressure data, but the test was not easy to do, time consuming, and not applicable to gasoline-oxygenate blends. Hence, when automatic instruments became readily available, there was a substantial interest in having an ASTM method involving these instruments developed. A number of emergency ASTM standards were approved to meet the industry need at the time. In 1991, an extensive interlaboratory study [8] including a number of the available automatic vapor pressure instruments, as well as D4953, was conducted on a number of petroleum products. ASTM D5191 "Standard Test Method of Vapor Pressure of Petroleum Products (Mini-Atmospheric Method)" is one of the automatic vapor pressure test method that was approved shortly thereafter. In addition to D5191, ASTM D5190 "Standard Test Method for Vapor Pressure of Vapor Pressure of Petroleum Products (Automatic Method)" [5] and ASTM D5482 "Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method)" [5] were also approved as ASTM test methods. Because D5191 is almost identical to the Environmental Protection Agency (EPA) Test Method 3, which is the designated vapor pressure test method for regulatory compliance, D5191 will be discussed in greater detail than D5190 and D5482.

Scope

This test method covers the use of automatic vapor pressure instrument to determine the total vapor pressure exerted in a vacuum by air-containing, volatile, liquid petroleum products. This test method is suitable for testing samples with boiling points above 0 °C (32 °F) that exert a vapor pressure between 7 kPa and 130 kPa (1.0 psi and 18.6 psi) at 37.8 °C (100 °F) at a 4:1 vapor-to-liquid ratio. Sample sizes used are in the range of 1 mL to 10 mL. Dissolved water in the sample is not taken into account.

Samples can be tested at other vapor-liquid ratios, other temperatures, and vapor pressures. However, the precision of the test does not apply to these other testing parameters. In the interlaboratory study to determine the precision of the method, no crude oil samples were included. Hence, the use of this method for crude oil vapor pressure measurement is specifically outside the scope. Nonetheless, there are a number of users that determine the vapor pressure of crude oil by this method. ASTM D6377 "Standard Test Method for Vapor Pressure of Crude Oil (Expansion Method)" [9] and IP 481 "Test Method for Determination of the Air Saturated Vapor Pressure (ASVP) of Crude Oil" [10] have been shown to be suitable for vapor pressure measurement of crude oils.

The dry vapor pressure equivalent (DVPE) of gasoline and gasoline-oxygenate blends can be calculated using this test method by means of a correlation equation (see discussion on relative bias). The calculated DVPE very closely approximates the dry vapor pressure that would be obtained on the same sample when tested by Procedure A of D4953.

Summary and Significance of the Test Method

A known volume of chilled, air-saturated sample is introduced into a thermostatically controlled, evacuated test chamber, or a chamber that is evacuated by means of a moveable piston, with an internal volume that is five times that of the total test specimen introduced into the chamber. After being introduced into the test chamber, the specimen is allowed to reach thermal equilibrium at the test temperature of 37.8 °C (100 °F). The resulting rise in pressure in the test chamber is measured using a pressure transducer sensor and indicator. Only total pressure measurements (sum of the partial pressure of the sample and the partial pressure of the dissolved air) are used in this test method. The measured total vapor pressure is converted to a dry vapor pressure equivalent (DVPE) using a correlation equation. The details of the Procedure section of this method can be found in the Appendix.

The discussion on the significance and use of D323 is also applicable to this test method. This method measures the vapor pressure of gasoline and gasoline-oxygenate blends, which is regulated by various government agencies. Specifications for volatile petroleum products generally include vapor pressure to ensure products of suitable volatility performance.

Apparatus

Vapor Pressure Apparatus—The type of apparatus used in this test method employs a small volume test chamber incorporating a transducer for pressure measurements, and associated equipment for thermostatically controlling the temperature of the chamber and creating an evacuated test chamber. The test chamber is designed to contain between 5 mL to 50 mL of liquid and vapor, and capable of maintaining a vapor-to-liquid ratio between 3.95:1 and 4.05:1. The pressure transducer will have a minimum operational range of 0 to 177 kPa (0 to 25.7 psi) with a minimum resolution of 0.1 kPa (0.01 psi) and a minimum accuracy of ±0.8 kPa (±0.12 psi). Resulting pressure readings are displayed. A thermostatically controlled heater capable of maintaining the temperature of the test chamber at 37.8 ± 0.1 °C (100 ± 0.2 °F) is used. A platinum resistance temperature measuring device is used to measure and monitor the test chamber temperature. The minimum temperature range of the temperature measuring device is from ambient to 75 °C (167 °F) with a resolution and accuracy of 0.1 °C (0.2 °F).

Fig. 4—An example of an automatic vapor pressure instrument for D5191. (Used with permission from Grabner Instruments).

Vacuum Pump—For instruments that require evacuation of the test chamber when using this method, the vacuum pump should be capable of reducing the pressure in the test chamber to less than 0.01 kPa (0.001 psi).

Syringe—(Optional, depending on the sample introduction system of the instrument.) A gas tight syringe, 1 mL to 20 mL capacity with a ±1 % or better accuracy and precision, is suitable. The capacity of the syringe should not exceed two times the volume of the test specimen being dispensed.

Water Bath, Air Bath, or Refrigerator—To chill the samples and syringe to temperatures between 0 °C and 1 °C (32 °F and 34 °F), a water bath, air bath, or refrigerator capable of controlling the temperature to the desired value, is required.

McLeod Vacuum Gage or Calibrated Electronic Vacuum Measuring Device—For checking calibration of pressure transducer. It has to cover the range from 0.01 to 0.67 kPa (0.1 to 5 Torr).

An example of an automatic vapor pressure instrument for this test method is shown in Fig. 4.

Sampling and Sample Handling

Vapor pressure measurement is extremely sensitive to volatile component losses through evaporation. The resulting changes in composition from such losses dictates the utmost precaution and the most meticulous care in the isolation and handling of samples for testing. The test method indicates that sampling be done by D4057. However, D4057 has specific instructions that, for samples being obtained for vapor pressure measurements, D5842 has to be used. As indicated in the sampling section of the D323 discussion, samples in 1 L (1 qt) containers filled to 70 % to 80 % of capacity, are generally used for manual vapor pressure measurements.

TABLE 5—ASTM D5191 P_{tot} accepted reference values (ARV) for reference fuels.

Reference fluids	ARV [P_{tot}], kPa	Tolerance, kPa[a]	Tolerance Interval, kPa[a]
44/56 Blend (pentane/toluene) wt %	69.99	±2.36	67.63 to 72.35
n-Pentane	112.75	±2.48	110.27 to 115.23
2,2-Dimethyl butane	74.10	±2.11	71.99 to 76.21
2,3-Dimethyl butane	56.48	±2.11	54.37 to 58.59
	ARV [P_{tot}], psi	Tolerance, psi[a]	Tolerance Interval, psi[a]
44/56 Blend (pentane/toluene) wt %	10.15	±0.34	9.81 to 10.49
n-Pentane	16.35	±0.36	15.99 to 16.71
2,2-Dimethyl butane	10.75	±0.31	10.44 to 11.06
2,3-Dimethyl butane	8.19	±0.31	7.88 to 8.50
Reference fluids	ARV [P_{tot}], kPa	Tolerance, kPa[b]	Tolerance Interval, kPa[b]
44/56 Blend (pentane/toluene) wt %	70.0	±1.2	68.8 to 71.2
n-Pentane	112.8	±1.2	111.6 to 114.0
2,2-Dimethyl butane	74.1	±1.2	72.9 to 75.3
2,3-Dimethyl butane	57.1	±1.2	55.9 to 58.3
	ARV [P_{tot}], psi	Tolerance, psi[b]	Tolerance Interval, psi[b]
44/56 Blend (pentane/toluene) wt %	10.15	±0.17	98.8 to 10.32
n-Pentane	16.35	±0.17	16.19 to 16.53
2,2-Dimethyl butane	10.75	±0.17	10.58 to 10.92
2,3-Dimethyl butane	8.19	±0.17	8.11 to 8.45

[a] From 2003 ILS of D5191/D6378. For additional details, see RR:D02-1619.
[b] Balloted at ASTM D02.08 in 2006. Tolerance include uncertainty values.

However, D5842 allows the use of smaller sample size, i.e., 125 mL (4 oz) for automated vapor pressure measurements. It is to be recognized that the precision statement of this test method was obtained using samples obtained in 1 L (1 qt) container. In the case of referee testing, the 1 L (1 qt) sample container is required.

Vapor pressure measurement is to be performed on the first test specimen withdrawn from the sample container. The remaining sample in the container should not be used for a second vapor pressure determination. If a second determination is necessary, obtain a new sample. The sample container and its contents has to be cooled to a temperature of 0–1 °C (32–34 °F) before the container is opened. Sufficient time to reach this temperature shall be ensured by direct measurement of the temperature of a similar sample in a similar container placed in the cooling bath or refrigerator at the same time as the sample. A verification of the 70 % to 80 % filling of the sample container has to be done. Before testing, the sample has to be air saturated. This is done by removing the sample container cap momentarily, taking care that no water enters, resealing the cap, and shaking the container vigorously. Return the container with the air saturated sample to the cooling bath or refrigerator for a minimum of 2 min. Verify that there is no phase separation in the sample. After introduction of the specimen to the instrument, check the remaining sample for phase separation. If phase separation is evident, discard the test and the sample. Resample as necessary.

Calibration

Instrument Verification—The 2003 interlaboratory study on D5191 and D6378 provided data for four reference fuels, which can be used to verify the performance of the test instrument. D5191 is being modified to include a new section on instrument verification using the accepted reference value (ARV) for the P_{tot}, total vapor pressure, for these four reference fuels. However, the topic of corresponding tolerance limits for these reference fuels is still currently under consideration, and will be incorporated in the test method once a final decision is made. Table 5 gives the ARVs for the total vapor pressure of *n*-pentane, 2,2-dimethyl butane, 2,3-dimethyl butane, and a 44/56 wt % blend of *n*-pentane and toluene, and the tolerance limits under consideration.

Pressure Transducer—The calibration of the pressure transducer has to be checked at least once every 6 months or sooner, as indicated from the quality control program for the instrument. The calibration is checked using two reference points: zero pressure (<0.1 kPa) and the ambient barometric pressure. For the zero pressure calibration check, connect a McLeod gage or a calibrated electronic vacuum measuring device to the vacuum source in line with the test chamber. Apply vacuum to the test chamber. When the vacuum measuring device registers a pressure of less than 0.1 kPa (0.9 Torr), adjust the indicator or readout to zero or to the actual reading on the vacuum measuring device as dictated by the instrument design or manufacturer's instructions. If additional detail is required for the zero pressure calibration check, consult Section A6.3 of ASTM D2892 "Standard Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)." For the ambient barometric pressure check, open the test chamber of the apparatus to the atmosphere and observe the readout value of the transducer. Ensure that the total pressure is displayed, not a corrected or calculated value. Compare the pressure readout of the instrument with the value obtained from the pressure measuring device. Adjust the pressure reading as necessary, following the instrument manufacturer's instructions. Many aneroid barometers such as those used at weather stations or airports are pre-corrected to give sea level readings; these must not be used for checking the ambient atmospheric pressure calibration of the apparatus.

TABLE 6—Summary of existing and new ASTM D5191 precision.

Existing precision				New precision			
Repeatability		Reproducibility		Repeatability		Reproducibility	
kPa	psi	kPa	psi	kPa	psi	kPa	psi
0.008 07 (DVPE+124)	0.008 07 (DVPE +18.0)	0.0161 (DVPE +124)	0.0161 (DVPE +18.0)	0.006 DVPE+160	0.006 (DVPE +23.2)	0.010 14 (DVPE +160)	0.010 14 (DVPE +23.2)

Temperature Measuring Device—The calibration of the temperature measuring device, generally a platinum resistance thermometer, has to be checked at least every 6 months against a NIST (or other nationally recognized certification body) traceable thermometer.

Calculation

The dry vapor pressure equivalent (DVPE) is calculated from the observed total vapor pressure reading that has not been corrected by any automatically programmed correction factor by using Eq (3), either manually or automatically by the instrument.

$$\mathrm{DVPE}_{\mathrm{D5191}},\mathrm{kPa\ (psi)} = (0.965X) - A \qquad (3)$$

where:

X = measured total pressure in kPa (psi), and

A = 3.78 kPa (0.548 psi).

As an example, if the observed total pressure is 74.0 kPa (10.73 psi), the calculated $\mathrm{DVPE}_{\mathrm{D5191}}$ according to Eq (3) is:

$$\mathrm{DVPE}_{\mathrm{D5191}} = (0.965)(74.0) - 3.78 = 67.6\ \mathrm{kPa}$$

A similar calculation can be made using Eq (3) if the total pressure reading is in psi.

Report, Precision, and Bias

Report—Record the observed total vapor pressure to the nearest 0.1 kPa (0.01 psi). Report the dry vapor pressure equivalent to the nearest 0.1 kPa (0.01 psi) without reference to temperature. If the sample was observed to be hazy, indicate by adding the letter "H" to the reported DVPE value.

Precision—The 2003 interlaboratory study (ILS) [11] produced new precision statement for this method. The study involved 27 laboratories, 4 types of instruments, and 20 types of hydrocarbon and hydrocarbon-oxygenate blends. However, since the new precision statement is just in the process of being incorporated into the method, the existing precision statements are given in Table 6 as well as the new proposed precision statements. Sample calculations for repeatability and reproducibility for various DVPE values are given in Table 7.

Bias—Since there is no accepted reference material suitable for determining the bias of this test method, absolute bias cannot be determined.

Relative Bias—There is a statistically significant bias between the total vapor pressure obtained by this method and the dry Reid vapor pressure (D4953 Procedure A) based on the results of the interlaboratory study conducted in 1991 (see RR: D02-1286). The magnitude of the relative bias is given by Eq (3) in the Calculation section of this method, where the dry vapor pressure equivalent (DVPE) is calculated from the observed total vapor pressure of the sample.

The EPA Method 3 DVPE equation is slightly different than the DVPE equation for this method. It is important to note that the EPA correlation equation corrects the bias of D5191 results to D4953 Procedure B and not D4953 Procedure A. The EPA Method 3 DVPE equation is given by Eq (4):

$$\mathrm{DVPE}_{\mathrm{EPA\text{-}Method\ 3}} = (0.956X) - B \qquad (4)$$

where:

X = total vapor pressure measured in kPa (psi), and

B = 2.39 kPa (0.347 psi).

The California Air Resources Board (CARB) uses the total vapor pressure measured by D5191 to calculate a correlated D323 Reid vapor pressure equivalent (RVPE) by Eq (5):

$$\mathrm{RVPE}_{\mathrm{CARB}} = (0.972X) - C \qquad (5)$$

where:

X = total vapor pressure measured in kPa (psi), and

C = 4.93 kPa (0.715 psi).

A summary of these DVPE D5191 total vapor pressure correlations to D4953 Procedure A, D4953 Procedure B, and D323 is given in Table 8 for comparison. It is interesting to

TABLE 7—Sample calculation for ASTM D5191 precision.

	Existing precision		New precision	
DVPE	Repeatability	Reproducibility	Repeatability	Reproducibility
kPa				
25	1.20	2.40	1.11	1.88
50	1.40	2.80	1.26	2.13
70	1.57	3.12	1.38	2.33
80	1.65	3.28	1.44	2.43
105	1.85	3.69	1.59	2.69
120	1.97	3.93	1.68	2.84
psi				
3.63	0.17	0.35	0.16	0.27
7.25	0.20	0.41	0.18	0.31
10.15	0.23	0.45	0.20	0.34
11.60	0.24	0.48	0.21	0.35
15.23	0.27	0.53	0.23	0.39
17.40	0.29	0.57	0.24	0.41

TABLE 8—Summary of correlated ASTM D5191 total vapor pressure.

D5191 P_{tot}	D5191 to D4953 Procedure A	EPA Method 3 to D4953 Procedure B	CARB to D323
74.90 kPa	68.50 kPa	69.21 (68.21)[a] kPa	67.87 kPa
10.86 psi	9.93 psi	10.04 (9.88)[a] psi	9.84 psi

[a] Correlated D4953 A using Eq (2).

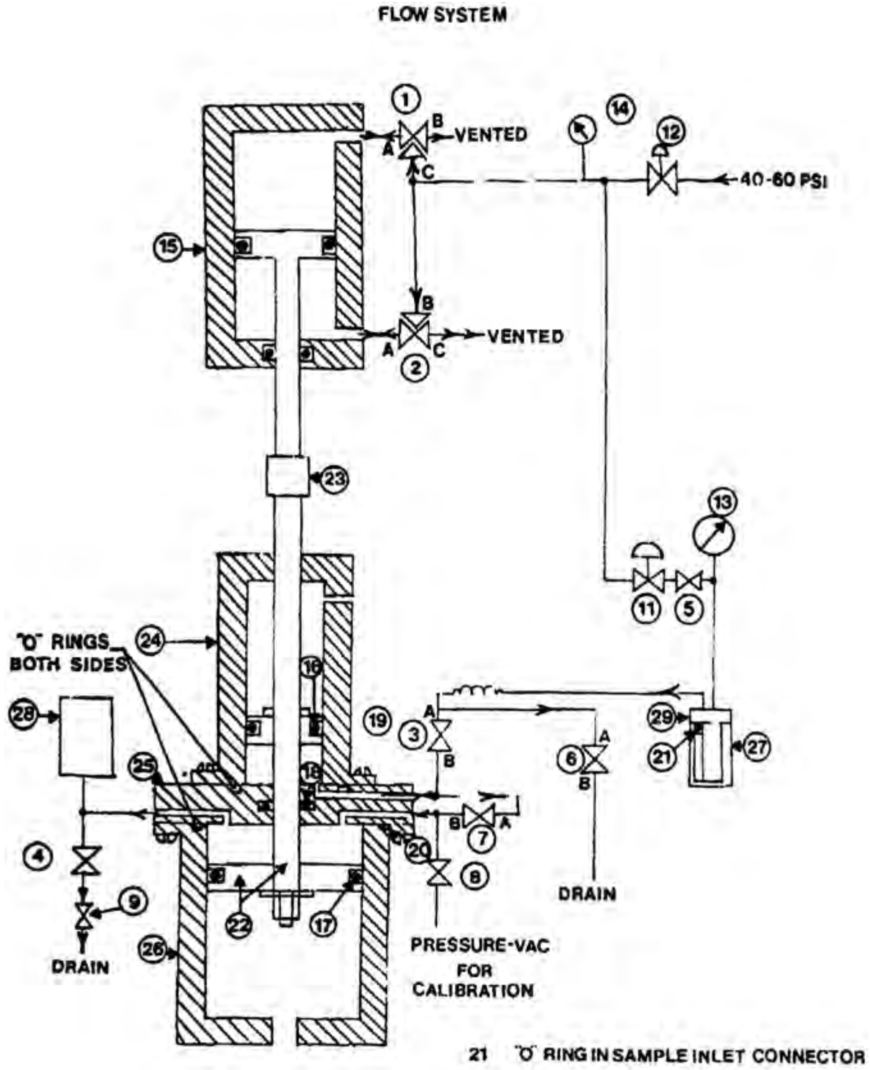

Fig. 5—Schematic diagram of the D5190 automatic vapor pressure instrument.

note that the difference between the D5191 DVPE and the EPA Method 3 DVPE is only 0.38 kPa (0.06 psi) relative to D4953 Procedure A.

ASTM D5190—Vapor Pressure Of Petroleum Products (Automatic Method) [5]

Another automatic vapor pressure measurement test method that was developed along with D5191 in 1991 is D5190 "Vapor Pressure of Petroleum Products (Automatic Method)." The scope of this method is very similar to D5191, with the exception that the test chamber is not evacuated at the start of the test. The discussions on the significance and use of the method, sampling, and reporting of results given in D5191 are applicable to this method as well. Hence, only the sections of the method that are different from D5191 will be discussed below.

Summary of the Test Method

The chilled sample cup of the instrument is filled with chilled sample and is coupled to the instrument inlet fitting. The specimen is automatically forced from the sample chamber to the expansion chamber, where it is held until thermal equilibrium at 37.8 °C (100 °F) is attained. During this process, the specimen is expanded to five times its volume to give a 4:1 vapor-to-liquid ratio. The vapor pressure is measured to be a pressure transducer. The measured vapor pressure is automatically converted to a DVPE value using a correlation equation. The procedure section of this test method is given in the Appendix of the manual.

Apparatus

Vapor Pressure Instrument—The essential components of the instrument are indicated in Fig. 5. The detailed operational procedure using the instrument is given in the Appendix of this manual. Sample cup is capable of holding up to 125 mL of sample.

Pressure Transducer—The pressure transducer for this test method is capable of operating in the range of 0 to 172 kPa (0 to 25.0 psi) with a resolution of 0.1 kPa (0.01 psi) and a minimum accuracy of ±0.7 kPa (±0.10 psi).

The information given in D5191 related to the thermostatically controlled heater/bath for maintaining the required test temperature and the water or air bath or refrigerator for chilling the sample, is also applicable to this method.

Calibration

Pressure Transducer—The calibration of the pressure transducer should be checked at least every month, or sooner when needed, as indicated by the quality control program for the instrument. The calibration check for the transducer is accomplished using three reference materials to cover the range above and below 34 kPa (5.0 psi). *n*-Hexane is used for 34 kpa (5 psi); *n*-Pentane for 106 kPa (15.4 psi); and 2,2-dimethyl butane for 68 kPa (9.9 psi).

Temperature Measuring Device—Check the calibration of the temperature measuring device used to monitor the temperature of the thermostatically controlled bath at lease every 6 months against a NIST (or other nationally recognized certifying body) traceable thermometer. Check the capability of the bath to maintain a temperature of $37.8 \pm 0.1\ ^\circ\mathrm{C}$ $(100 \pm 0.2\ ^\circ\mathrm{F})$.

Calculation

The total vapor pressure determined by this method is transformed to a DVPE value to give a dry vapor pressure equivalent value relative to D4953 Procedure A, by using Eq (6):

$$\mathrm{DVPE}_{\mathrm{D5190}}, \mathrm{kPa\ (psi)} = (0.954X) + A \tag{6}$$

where:

X = measured total vapor pressure with this method in kPa (psi), and

A = 1.94 kPa (0.281 psi).

Precision and Bias

Precision—The precision for D5190 was developed as part of a 1991 interlaboratory cooperative study and is described in RR: D02-1286. The study included 14 types of hydrocarbon and hydrocarbon-oxygenate blends, and a total of 60 participating laboratories.

$$\text{Repeatability} = 2.48\ \text{kPa}\ (0.36\ \text{psi})$$

$$\text{Reproducibility} = 3.45\ \text{kPa}\ (0.50\ \text{psi})$$

Bias—Since there is no accepted reference material suitable for determining the bias for the procedure in this test method, bias cannot be determined.

Relative Bias—A statistically significant relative bias was observed in the 1991 ILS between the total pressure obtained using this test method and the dry vapor pressure obtained from using D4953 Procedure A. The magnitude of this relative bias is given by the DVPE equation given by Eq (6).

ASTM D5482—Vapor Pressure Of Petroleum Products (Mini Method-Atmospheric) [5]

A third automatic vapor pressure test method approved in 1991 is ASTM D5482 "Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method-Atmospheric)." The scope of this method is very similar to D5191, with the exception that the test chamber is not evacuated at the start of the test. The discussions on the significance and use of the method, sampling, and reporting of results given in D5191 are applicable to this method as well. Hence, only the sections of the method that are different from D5191 will be discussed below.

TABLE 9—Summary of D5482 precision.

	Repeatability		Reproducibility	
Units	Herzog SC970	ABB Model 4100	Herzog SC970	ABB Model 4100
kPa	1.31	1.79	2.69	4.14
psi	0.19	0.26	0.39	0.60

Summary of the Test Method

A known volume of chilled, air-saturated sample is introduced into a thermostatically controlled chamber with an internal volume that is five times that of the total test specimen introduced into the chamber. The test chamber is at atmospheric pressure prior to the introduction of the sample. After being introduced into the test chamber, the specimen is allowed to reach thermal equilibrium at the test temperature of 37.8 °C (100 °F). The resulting rise in pressure in the test chamber is measured using a pressure transducer sensor and indicator. The measured total vapor pressure is converted to a dry vapor pressure equivalent using a correlation equation. The details of the Procedure section of this method can be found in the Appendix.

Apparatus

Vapor Pressure Apparatus—The type of apparatus used in this test method employs a small volume test chamber incorporating a transducer for pressure measurements, and associated equipment for thermostatically controlling the temperature of the chamber. The test chamber is designed to contain between 2 mL and 50 mL of liquid and vapor, and capable of maintaining a vapor-to-liquid ratio between 3.95:1 and 4.05:1. The pressure transducer will have a minimum operational range of 0 to 172 kPa (0 to 25.0 psi) with a minimum resolution of 0.1 kPa (0.01 psi) and a minimum accuracy of ±0.3 kPa (±0.05 psi).

The information given in D5191 related to the thermostatically controlled heater for maintaining the required test temperature, syringe, the water or air bath or refrigerator for chilling the sample, and pressure measuring devices is also applicable to this method.

Calculation

The total vapor pressure determined by this method is transformed to a DVPE value to give a dry vapor pressure equivalent value relative to D4953 Procedure A, by using Eq (7):

$$\mathrm{DVPE}_{\mathrm{D5482}}, \mathrm{kPa\ (psi)} = (0.954X) + A \tag{7}$$

where:

X = measured total vapor pressure with this method in kPa (psi), and

A = 0.538 kPa (0.078 psi) for Herzog SC 970, or

A = 1.937 kPa (0.281 psi) for ABB Model 4100.

Precision and Bias

Precision—The precision for D5482 was developed as part of a 1991 interlaboratory cooperative study and described in RR: D02-1286. The study included 14 types of hydrocarbon and hydrocarbon-oxygenate blends. Table 9 gives a summary of the D5482 precision.

Bias—Since there is no accepted reference material suitable for determining the bias for the procedure in this test method, bias cannot be determined.

Relative Bias—A statistically significant relative bias was observed in the 1991 ILS between the total pressure obtained using this test method and the dry vapor pressure obtained from using D4953 Procedure A. The magnitude of this relative bias is given by the DVPE equation given by Eq (7).

ASTM D6377—Vapor Pressure Of Crude Oil: VPCR$_X$ (Expansion Method) [9]

It was mentioned in the D323 discussion that its scope include the determination of vapor pressure of volatile crude oil. Before the advent of automatic vapor pressure instruments, vapor pressure data for crude oil has been obtained using D323. However, after D5191 was approved, a number of organization began using D5191 although crude oil was never part of the sample set used to generate the precision statement for the method. In fact, D5191 gives information that this is the case in Note 2 of the method and references ASTM D6377 "Standard Test Method for Vapor Pressure of Crude Oil: VPCR$_x$ (Expansion Method)" as well as IP 481 "Test Method for Determination of the Air Saturated Vapor Pressure (ASVP) of Crude Oil" as test methods that have been shown to be suitable for crude oil vapor pressure measurement. In this section, D6377 will be discussed.

Scope

This test method covers the use of automatic vapor pressure instruments to determine the vapor pressure of crude oils at temperatures between 5 °C and 80 °C (41 °F and 176 °F) for vapor-liquid ratios from 4:1 to 0.02:1. The range of applicable vapor pressure is from 7 kPa to 500 kPa (1 psi to 70 psi). When the vapor pressure measurement is done for a 4:1 vapor-liquid ratio at 37.8 °C, the observed vapor pressure can be correlated to the vapor pressure obtained by D323.

Terminology

There are several terms used in this test method that needs to be defined.

Dead Crude—Term usually employed for crude oils that will not result in actual boiling of the sample when exposed to normal atmospheric pressure at room temperature. The use of pressure cylinders, mandatory for live crude, is recommended for dead crude, although sampling in normal sample containers such as cans is acceptable.

Live Crude—Term usually employed for crude oils contained in pressurized system that will result in actual boiling of the sample when brought to normal atmospheric pressure at room temperature.

REID Vapor Pressure Equivalent (*RVPE*)—A value calculated by a correlation equation from VPCR$_x$ when $x = 4:1$ and the test temperature is 37.8 °C (100 °F), which is related to the vapor pressure of the sample using D323.

VPCR$_x$—The pressure exerted in an evacuated chamber at a vapor-liquid ratio of $x:1$ exerted by conditioned or unconditioned crude oil which may contain gas, air, or water, or a combination thereof. x can vary from 4 to 0.02.

Summary and Significance of the Test Method

Using a chamber with a built-in piston, a sample of known volume is drawn from a pressurized sampling system (floating piston cylinder) is drawn into the chamber. The temperature of the chamber is maintained at 20 °C (68 °F) or higher. After sealing the chamber, the volume is expanded by moving the piston until the final volume produces the desired V/L value. The temperature of the chamber is then regulated to the desired measuring temperature. After equilibration, the measured pressure is recorded as the VPCR$_x$ of the sample. To determine the RVPE, the V/L ratio has to be 4:1 and the test temperature is 37.8 °C (100 °F).

The vapor pressure of crude oil at various V/L ratios is an important physical property for shipping, distribution, and storage. It is important for crude oil producers and refiners for general handling and distribution. A V/L of 0.02:1 represents closely the situation of an oil tanker. This test method does not require chilling and air saturation of the sample prior to the vapor pressure measurement. The details of the procedure section of the test method can be found in the Appendix.

Apparatus and Calibration

The apparatus suitable for this test method employs a small volume, cylindrically shaped measuring chamber with associated equipment to control the chamber temperature from 5 °C to 80 °C. The measuring chamber shall contain a movable piston with a maximum dead volume of less than 1 % of the total volume at the lowest position to allow sample introduction into the measuring chamber and expansion to the desired V/L. A static pressure transducer shall be incorporated in the piston. An inlet/outlet valve is required for sample introduction and expulsion. The measuring chamber is designed to have a total volume of 5 mL to 15 mL and shall be capable of maintaining a V/L of 4:1 to 0.02:1 within 0.01.

The discussions covered in D5191 regarding the description and calibration of the pressure transducer, electronic temperature control, and pressure measuring devices is also applicable to this test method.

Sampling

Sampling of live crude oil shall be made in accordance with Practice D3700 "Standard Practice for Containing Hydrocarbon Fluid Samples Using a Floating Piston Cylinder" [4]. Sampling dead crude oil shall be made in accordance with D4057 or D4177 or when the use of D3700 is impractical. Floating piston cylinders with a minimum sample volume of 200 mL is required if the volume of test specimen required to do the test is less than 20 mL. Sampling and storage temperature should not exceed 30 °C. To prevent losses of high volatile material in the sample, the sample is always maintained at a pressure at least 100 kPa (14.5 psi) higher than the vapor pressure. Compressed air or any compressed gas can be used as back-pressuring agent. The floating piston cylinder shall have provisions for mechanical stirring of the sample and a second valve at the inlet for rinsing.

If the sample is contained in a pressurized source such as a pipeline, use a floating piston cylinder and obtain the sample directly from the source under pressure. If the sample is taken from a non-pressurized source such as a storage tank, oil tanker, drum, or other small container, obtain the sample according to D4057 or D4177 and fill the sample into an open floating piston at the prevailing pressure. Transfer the sample from the cylinder to the measuring chamber at room temperature but at least 5 °C above the pour point (determined by D5853 "Standard Test Method for Pour Point of Crude Oil" [5]).

Report, Precision, and Bias

The observed vapor pressure is reported to the nearest 0.1 kPa (0.02 psi), specifying the test temperature and V/L ratio, as:

$$\text{VPCR}_x(T_m) = \#\#\#.\#\ \text{kPa}\ (\#\#\#.\#\#\ \text{psi}) \tag{8}$$

where:
$x = V/L$ ratio, and
T_m = test temperature in °C.

A preliminary precision under repeatability condition is given for V/L ratios of 4:1 and 0.02:1 derived for more than 30 different crude oil samples in three different laboratories. For the V/L of 4:1, the vapor pressure ranges were 2.8 kPa to 16.6 kPa; and vapor pressures up to 240 kPa at a V/L of 0.02:1. An interlaboratory study is under way to determine repeatability and reproducibility of the test method.

$$V/L = 4{:}1 \text{ and } T_m = 37.8\ ^\circ\text{C};\ \text{repeatability} = 0.015\text{VPCR}_x \tag{9}$$

$$V/L = 0.02{:}1 \text{ and } T_m = 37.8\ ^\circ\text{C};\ \text{repeatability} = 0.055\text{VPCR}_x \tag{10}$$

The reproducibility of this test method is not known at this time, but is the subject of a current ASTM interlaboratory study.

Bias—Since there is no accepted reference material suitable for determining the bias of this test method, bias cannot be determined.

Relative Bias—For a V/L ratio of 4:1 and a test temperature of 37.8 °C, a correlation equation to relate the VPCR_x at these test parameters to the D323 RVP is given by:

$$\text{RVPE}_{\text{D6377}} = (A)\text{VPCR}_4 + B \tag{11}$$

where:
RVPE = Correlated D323 RVP,
$A = 0.752$, and
$B = 6.07$ kPa (0.88 psi).

ASTM D6378—Vapor Pressure (VP_X) Of Petroleum Products, Hydrocarbons, And Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method) [9]

This recently approved test method, ASTM D6378 "Standard Test Method for the Determination of Vapor Pressure of Petroleum Products, Hydrocarbons, and Hydrocarbon-oxygenate Mixtures (Triple Expansion Methods)" has generated a lot of interest in the petroleum industry because it does not require the air-saturation and chilling requirements of D5191. The vapor pressure of these materials is a parameter that is subject to environmental regulation; hence, simplification of the test methodology to provide the required data is welcomed. However, this test method has not been incorporated into the spark-ignition fuel specification because there is no data to compare the result of this test method with the current specification test for vapor pressure (D5191). A cooperative interlaboratory study was recently completed designed to compare the results of the vapor pressure results using D5191 and this test method using 20 different types of fuels, hydrocarbons, and hydrocarbon-oxygenate mixtures.

The discussion of this test method is based on the existing D6378-03 version. This test method is currently being revised within ASTM to incorporate the results of the recently concluded 2003 ILS. A separate discussion of the proposed revision to this test method is given at the end of this section.

Scope

The scope of this test method is very similar to that discussed in D5191. The exception is the fact that air-saturation and chilling of the sample is not required. A V/L ratio of 4:1 and a test temperature of 37.8 °C (100 °F) are prescribed. However, it is claimed that the method is suitable for test temperatures of 0 °C to 100 °C and V/L ratios from 4:1 to 1:1, although the precision for the test method may not be applicable. The vapor pressure (VP_x) determined by this test method can be correlated to the dry vapor pressure equivalent or DVPE value relative to D5191 (see Relative bias section). The partial pressure of air in the liquid at the designated V/L ratio is subtracted from the measured total pressure.

Summary and Significance of the Test Method

The discussion given in D6377 regarding the summary of the test method is also valid for D6378. Notable difference it that after the chamber is sealed, an expansion is performed in three steps to a final volume of $(X+1)$ times that of the test specimen. After each expansion step, the observed pressure is determined. The partial pressure of air (PPA) is calculated from the observed pressures during the three expansion steps. The temperature of the chamber is increased to a specified value and the resulting pressure is measured. The VP_X or the vapor pressure of the sample is calculated by subtracting the partial pressure of air (PPA) that has been corrected for the test temperature. For DVPE relative to D5191 results, the V/L is set to 4:1 and the test temperature is at 37.8 °C. All volume expansion steps, recording of observed pressures, and calculations are all done automatically. The procedure section of this test method is in the Appendix of this manual.

The significance of the test is similar to those given in the previously discussed vapor pressure test methods. It is important to note that in this test method, the air-saturation step is not required, thus eliminating potential losses of highly volatile materials.

Apparatus and Calibration

The apparatus suitable for this test method employs a small volume, cylindrically shaped measuring chamber with associated equipment to control the chamber temperature from 5 °C to 100 °C. The measuring chamber shall contain a movable piston with a maximum dead volume of less than 1 % of the total volume at the lowest position to allow sample introduction into the measuring chamber and expansion to the desired V/L. A static pressure transducer shall be incorporated in the piston. An inlet/outlet valve is required for sample introduction and expulsion. The measuring chamber is designed to have a total volume of 5 mL to 15 mL and shall be capable of maintaining a V/L of 4:1 to 1:1 within 0.05.

The discussions covered in D5191 regarding the description and calibration of the pressure transducer, electronic temperature control, and pressure measuring devices are also applicable to this test method.

Sampling and Sample Handling

The sampling and sample handling discussion on D5191 are applicable to D6378 as well, with the exception that the air saturation step is not required. Chilling the sample to a temperature between 0 °C and 1 °C (32 °F and 34 °F) is still required, just like in D5191. However, there is a provision that the chilling of the sample may be omitted if steps are taken to avoid loss of high volatile components during sample introduction.

Calculation

The derivation of the equations used to calculate the vapor pressure of the sample as a result of the triple expansion and pressure observation is given in detail in the Appendix of D6378. The interested reader is referred to that section of the test method for the details. It would suffice to give the relevant equation for the vapor pressure calculation in this section.

Firstly, the partial pressure of air (PPA_i) is calculated from the three observed pressure readings resulting from the three volume expansion after the sample has been introduced into the test chamber. The equation is:

$$\mathrm{PPA}_i = \frac{(\mathrm{TP}_{X,1} - \mathrm{TP}_{X,3})(\mathrm{TP}_{X,2} - \mathrm{TP}_{X,3})}{\dfrac{(V_3 - V_1)}{(V_2 - V_1)}(\mathrm{TP}_{X,1} - \mathrm{TP}_{X,2}) - (\mathrm{TP}_{X,1} - \mathrm{TP}_{X,3})} \tag{12}$$

where:

$\mathrm{TP}_{X,1}$ = total pressure after first expansion,
$\mathrm{TP}_{X,2}$ = total pressure after second expansion,
$\mathrm{TP}_{X,3}$ = total pressure after third expansion,
V_1 = volume after first expansion,
V_2 = volume after second expansion, and
V_3 = volume after third expansion.

Secondly, the calculated PPA_i is corrected to the test temperature to give PPA_t using Eq (13):

$$\mathrm{PPA}_t = \mathrm{PPA}_i\ (273.2 + t)/(273.2 + t_i) \tag{13}$$

where:

PPA_t = corrected partial pressure of air,
t_i = temperature of the test chamber after sample introduction and expansion, °C, and
t = test temperature, °C.

Lastly, the vapor pressure of the sample is calculated as follows:

$$\mathrm{VP}_{X,t} = \mathrm{TP}_{X,t} - \mathrm{PPA}_t \tag{14}$$

where:

$\mathrm{VP}_{X,t}$ = vapor pressure of the sample,
$\mathrm{TP}_{X,t}$ = total pressure at test temperature t, and
PPA_t = corrected partial pressure of air.

TABLE 10—ASTM D6378 P_{tot} accepted reference values (ARVs) for reference fuels.

Reference fluids	ARV [P_{tot}], kPa	Tolerance kPa[a]	Tolerance interval, kPa[a]
n-Pentane	107.9	±1.2	106.7 to 109.1
2,2-Dimethyl butane	68.8	±1.2	67.6 to 70.0
2,3-Dimethyl butane	51.7	±1.2	50.5 to 52.9

	ARV [P_{tot}], psi	Tolerance, psi[a]	Tolerance interval, psi[a]
n-Pentane	16.35	±0.17	16.19 to 16.53
2,2-Dimethyl butane	10.75	±0.17	10.58 to 10.92
2,3-Dimethyl butane	8.19	±0.17	8.11 to 8.45

[a] Balloted at ASTM D02.08 in 2006. Tolerance include uncertainty values.

All required calculations are done automatically by the instrument.

Report, Precision, and Bias

The calculated vapor pressure is reported to the nearest 0.1 kPa (0.02 psi), specifying the test temperature and V/L ratio, as:

$$\mathrm{VP}_{X,t} = \#\#\#.\#\ \mathrm{kPa}\ (\#\#\#.\#\#\ \mathrm{psi}) \tag{15}$$

where:

$X = V/L$ ratio, and
t = test temperature in °C.

The existing repeatability and reproducibility of this method at a $V/L = 4:1$, is given to be:

$$\text{Repeatability} = 0.05\ \text{kPa}\ (0.07\ \text{psi})$$

$$\text{Reproducibility} = 1.63\ \text{kPa}\ (0.22\ \text{psi})$$

Relative bias relative to D5191 is given by Eq (16):

$$\mathrm{DVPE}_{(\text{relative to D5191})} = \mathrm{VP}_{4,37.8\ ^\circ\mathrm{C}} - B \tag{16}$$

where:

$\mathrm{VP}_{4,37.8\ ^\circ\mathrm{C}}$ = calculated vapor pressure of sample at 37.8 °C and $V/L = 4:1$, and
B = 1.027 kPa (0.15 psi).

Proposed Revision to ASTM D6378 Being Considered

As part of the 2003 ILS comparing D5191 and D6378 vapor pressure results, a number of modification is currently being considered to D6378, which is anticipated to be completed after this manual has been published. Hence, a brief discussion will be given on the proposed revision of D6378.

(1) Chilling the sample to a temperature of 0 °C to 1 °C is no longer required.
(2) After the sample introduction step, and before the first expansion step, the test chamber temperature is adjusted to the test temperature. As a consequence, PPA_i is now the same as PPA_t, and a corrected PPA_i is no longer required.
(3) A new instrument verification section is created where accepted reference values (ARVs) for $\mathrm{VP}_{4,37.8\ ^\circ\mathrm{C}}$ and tolerance values are given (see Table 10).

TABLE 11—Summary of existing and new D6378 precision.

Existing precision				New precision			
Repeatability		Reproducibility		Repeatability		Reproducibility	
kPa	psi	kPa	psi	kPa	psi	kPa	psi
0.50	0.07	1.63	0.22	0.015 (VP_X+9)	0.015 $(VP_X+1.31)$	0.0273 (VP_X+9)	0.0273 $(VP_X+1.31)$

(4) A revised Quality Control section would require the use of samples representative of the actual sample analyzed as Quality Control standards.
(5) New precision statements will be incorporated into the method (see Tables 11 and 12).
(6) The relative bias equation correlating D6378 to D5191 results will be revised with the new equation given by Eq (17):

$$DVPE_{(\text{relative to D5191})} = VP_{4,37.8\ °C} - B \qquad (17)$$

where:
$VP_{4,37.8\ °C}$ = calculated vapor pressure of sample at 37.8 °C and $V/L = 4:1$, and
$B = 1.005$ kPa (0.15 psi).

Other that the aforementioned proposed revision, the test method is the same as the current D6378.

ASTM D1267—Vapor Pressure Of Liquefied Petroleum (LP) Gases (LP-Gas Method) [2]

Historically, for liquefied petroleum gas (LPG) products, vapor pressure was the most critical specification parameter due to the fact that most of the serious incidents during the early days of the LPG industry was related to the extreme volatility of these materials. Vapor pressure was, and is, invariably tied to pressure vessel and safety valve certification and transportation regulation. ASTM D1267 "Standard Test Method for Vapor Pressure of Liquefied Petroleum (LP) Products (LP Gas Method)" was adapted from D323.

TABLE 12—Sample calculation for ASTM D6378 precision.

	Existing precision		New precision	
DVPE	Repeatability	Reproducibility	Repeatability	Reproducibility
kPa				
25	0.50	1.63	0.51	0.93
50	0.50	1.63	0.89	1.61
70	0.50	1.63	1.19	2.33
80	0.50	1.63	1.34	2.43
105	0.50	1.63	1.71	3.11
120	0.50	1.63	1.89	3.52
psi				
3.63	0.07	0.22	0.07	0.14
7.25	0.07	0.22	0.13	0.23
10.15	0.07	0.22	0.17	0.31
11.60	0.07	0.22	0.19	0.35
15.23	0.07	0.22	0.25	0.45
17.40	0.07	0.22	0.28	0.51

Scope

This test method covers the determination of the gage vapor pressure of liquefied petroleum (LP) gas products at temperatures of 37.8 °C (100 °F) up to and including 70 °C (158 °F). Liquefied petroleum gases (LPGs) are narrow boiling range hydrocarbon mixtures consisting mainly of propane or propylene, or both; butanes and butylenes or both; in which the hydrocarbon compounds with boiling point greater 0 °C (32 °F) is less than 5 % by liquid volume, and whose gage vapor pressure at 37.8 °C (100 °F) is not greater than 1550 kPa (225 psi). This is a manual test method of determining the vapor pressure of LPG.

Summary and Significance of the Test Method

The test apparatus, consisting of two interconnected chambers and equipped with a suitable pressure gage, is purged with the sample to be tested, then filled completely with the test specimen. $33\frac{1}{3}$ to 40 vol % of the sample content of the apparatus is immediately discarded to provide adequate free space for product expansion. The apparatus is immersed in a water bath maintained at 37.8 °C (100 °F), or at some other higher test temperature up to and including 70 °C (158 °F). After temperature equilibrium, the observed gage pressure (corrected for gage error and standard barometric pressure) is reported as the LPG vapor pressure at the test temperature. Procedural details of this test method are found in the Appendix of the manual.

Information on the vapor pressure of LPG products at 37.8 °C (100 °F) to 70 °C (158 °F) is important in the selection of properly designed storage vessels, shipping containers, and customer utilization equipment to ensure the safe handling of these products. The determination of the vapor pressure of LPG is essential for safety reasons to ensure that the maximum operating design pressures of storage, handling, and fuel systems will not be exceeded under normal operating temperature conditions. For LPG, vapor pressure is an indirect measure of the most extreme low temperature conditions under which initial vaporization can be expected to occur. It can be considered as a semi-quantitative measure of the amount of the most volatile material present in the product.

Apparatus

The apparatus for this test method is very similar to that specified for D323 with the exception of a bleeder valve between the upper chamber and the gage (see Fig. 6). The pressure gage is a Bourdon type spring gage of test gage quality 114 mm to 140 mm $\left(4\frac{1}{2}\text{ in. to }5\frac{1}{2}\text{ in.}\right)$ in diameter provided with a nominal 6 mm $\left(\frac{1}{4}\text{ in.}\right)$ male thread connection with a passageway not less than 5 mm (3/16 in.) in diameter. The range and graduations of the pressure gage used is dictated by the vapor pressure of the sample being tested (see Table 13). There are two possible lower chambers: (a)

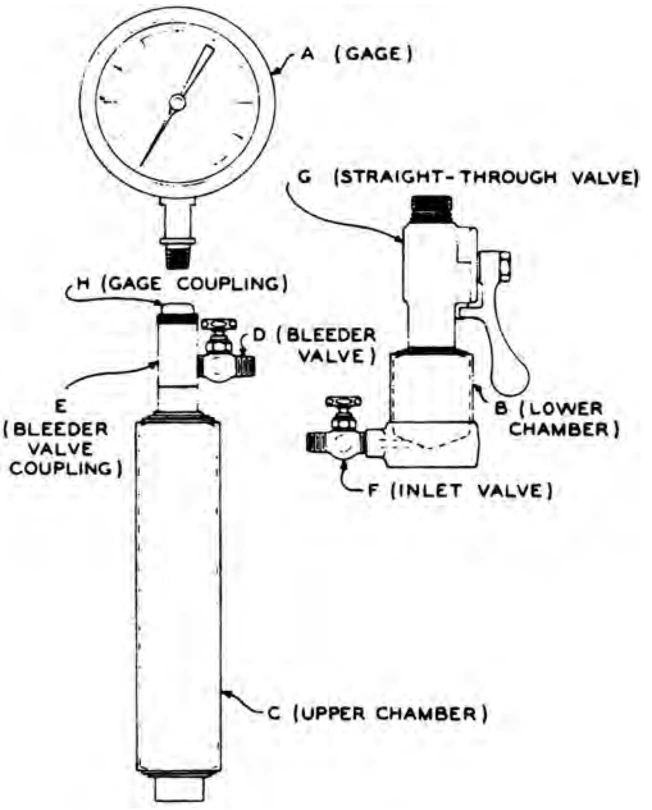

Fig. 6—Typical LPG manual vapor pressure apparatus.

$33\frac{1}{3}$ %—cylindrical vessel of such a volume such that the ratio of the volume of the upper chamber to the lower chamber is between the limits of 1.97 and 2.03; and (b) 20 %—cylindrical vessel of such a volume such that the ratio of the volume of the upper chamber to the lower chamber is between the limits of 3.95 and 4.05. The water bath temperature should be capable of being maintained within 0.1 °C (0.2 °F) at 50 °C (122 °F) or 0.3 °C (0.5 °F) at higher temperatures. ASTM thermometers 18C, 18F, 65C, or 65F are the thermometers suitable for this test method. A dead-weight tester of satisfactory range can be used to checking the accuracy of the vapor pressure gages.

Sampling and Calculation

Samples shall be obtained and stored in accordance with D1265 "Standard Practice for Sampling Liquefied Petroleum Gases (LP) Gases (Manual Method)" [2], unless the samples can be taken directly from the source of the material to be tested.

TABLE 13—Pressure gage range and graduations for ASTM D1267.

LPG vapor pressure, kPa (psi)	Scale range, kPa (psi)	Numbered intervals, kPa (psi)	Intermediate graduations, kPa (psi)
655 (95) and under	0–700 (100)	70 (10)	3.4 (0.5)
620 (240) to 1750 (250)	0–1750 (250)	172 (25)	7 (1)
1660 (240) to 3460 (500)	0–3500 (500)	344 (50)	35 (5)

The observed vapor pressure has to be corrected for gage errors. The corrected vapor pressure should then be converted to a standard barometric pressure of 760 Torr (29.92 in. of Hg) using the following equations:

$$\text{Vapor pressure, kPa} = \text{corrected vapor pressure} - (760 - P_1)0.1333 \qquad (18)$$

$$\text{Vapor pressure, psi} = \text{corrected vapor pressure} - (760 - P_1)0.0193 \qquad (19)$$

$$\text{Vapor pressure, kPa} = \text{corrected vapor pressure} - (29.92 - P_2)3.3864 \qquad (20)$$

$$\text{Vapor pressure, psi} = \text{corrected vapor pressure} - (29.92 - P_2)0.4912 \qquad (21)$$

where:

P_1 = observed barometric pressure, Torr.
P_2 = observed barometric pressure, in. Hg.

Report, Precision, and Bias

Report—The test results should be reported to the nearest 5 kPa or 0.5 psi, and the test temperature.

Precision—The repeatability of the test method is 12 kPa (1.8 psi), and the reproducibility is 19 kPa (2.8 psi).

Bias—The method has no bias because the value of the vapor pressure is defined only in terms of this test method.

ASTM D6897—Vapor Pressure Of Liquefied Petroleum Gases (LPG) (Expansion Method) [9]

ASTM D6897 "Standard Test Method for Vapor Pressure of Liquefied Petroleum Gases (LPG) (Expansion Method)" uses an automatic instrument to measure the vapor pressure of LPG, and was first approved in 2003. The method is not intended to determine the true vapor pressure of LPG samples, but rather to determine and report a vapor pressure value that corresponds to the vapor pressure measured by the manual D1267 test method.

Scope

This test method covers the use of automatic vapor pressure instruments to measure the vapor pressure of liquefied petroleum gas (LPG) products at a temperature of 37.8 °C at a V/L ratio of 0.5:1 and pressures from 200 to 1550 kPa on a sample volume of 3.33 mL. The method is said to be applicable for the determination of vapor pressure of LPG products from 37.8 °C to 70 °C at V/L ratios from 0.1:1 to 4:1, and pressures up to 3500 kPa. However, it is important for the user of the method to recognize that the precision of the test method has only been determined for V/L ratio of 0.5:1 at 37.8 °C, and a pressure range of 300 kPa to 1500 kPa.

Summary and Significance of the Test Method

After rinsing a measuring chamber equipped with a built-in piston with a portion of the sample, a test specimen of defined volume is drawn from a pressurized sampling system into a chamber controlled at 5 °C by moving the piston to the filling position. After sealing the chamber, the volume is expanded by moving the piston until the final volume produces the desired V/L ratio of 0.5:1. The temperature of the test chamber is then regulated to the test temperature of interest. After equilibrium is established, the total pressure measured is corrected to 101.3 kPa and reported as the vapor pressure of the sample at the test temperature. All the operational steps are done automatically by the instrument.

The discussion given in the Significance of Test section of D1267 is also applicable to this test method, and the reader is referred to that section.

Apparatus and Calibration

The apparatus suitable for this test method employs a small volume, cylindrically shaped measuring chamber with associated equipment to control the chamber temperature from 5 °C to 70 °C. The measuring chamber shall contain a movable piston with a maximum dead volume of less than 1 % of the total volume at the lowest position to allow sample introduction into the measuring chamber and expansion to the desired V/L. A static pressure transducer shall be incorporated in the piston. An inlet/outlet valve is required for sample introduction and expulsion. The measuring chamber is designed to have a total volume of 5 mL and shall be capable of maintaining a V/L of 0.5:1 with a maximum deviation of 0.01. Because of the extended pressure range of this method, the pressure transducer has to have a range of 0 to 3500 kPa with a minimum resolution of 1 kPa. Minimum accuracy for pressures up to 700 kPa is ±1 kPa, ±2 kPa for pressures up to 1750 kPa, and ±4 kPa for pressures up to 3500 kPa.

The discussions covered in D5191 regarding the description and calibration of the pressure transducer, electronic temperature control, and pressure measuring devices are also applicable to this test method. Possible verification materials to check the instrument calibration are:

$$\text{Propane with } VP_{tot}(37.8\ ^\circ C) = 1301 \pm 7 \text{ kPa}$$

$$\text{Butane with } VP_{tot}(37.8\ ^\circ C) = 357 \pm 6 \text{ kPa}$$

$$\text{Pentane with } VP_{tot}(70\ ^\circ C) = 310 \pm 6 \text{ kPa}$$

These values are the total vapor pressure values, uncorrected to 101.3 kPa. If the instrument is configured to read the vapor pressure corrected to 101.3 kPa automatically, add 101.3 to the displayed vapor pressure reading before comparing the results with the values indicated above for the verification materials.

Calculation, Report, Precision, and Bias

Calculation—The observed total pressure reading of the instrument after thermal equilibrium has been established is corrected to standard atmospheric pressure of 101.3 kPa by using Eq (19). It is important to ensure that the instrument reading used in this equation is the absolute pressure (relative to vacuum) and has not been corrected by an automatically programmed correction factor. The calculation and correction of the observed total vapor pressure is normally done automatically by the instrument, if so equipped.

$$\text{Corrected VP} = P_{tot} - 101.3 \text{ kPa} \tag{22}$$

where:

P_{tot} = observed total vapor pressure, kPa.

Report—Report the corrected total pressure to the nearest 1 kPa as the LPG vapor pressure and indicate the test temperature as well as the V/L ratio if it is not equal to 0.5:1.

$$\text{VP } (T_m\ ^\circ C) = \#\#\#\# \text{ kPa}$$

where:

T_m = test temperature, °C.

Precision—A preliminary precision under repeatability condition was obtained from triplicate determinations of 20 samples of propane covering the range of 300 to 1463 kPa at 37.8 °C and a V/L ratio of 0.5:1. No reproducibility value is available at the present time.

$$\text{Repeatability} = 7.4 \text{ kPa } (1.1 \text{ psi})$$

Relative Bias—The bias of the results of this test method relative to the manual D1267 test method has not been determined at the present time.

Vapor-Liquid Ratio Temperature Measurements

There are two ASTM test methods that, although related to the vapor pressure of petroleum products, do not give vapor pressure data. Instead, these test methods give results on the ratio of the vapor to liquid volume of a material at a given temperature and pressure. A brief discussion of these two test method will be given in this section.

ASTM D2533—Vapor-Liquid Ratio of Spark-Ignition Fuels [2]

Scope

This test method describes a manual procedure for determining the volume of vapor formed at atmospheric pressure from a given volume of gasoline. The ratio of these measured volumes is reported as the vapor-liquid (V/L) ratio of the gasoline at the test temperature. This test method also allows the calculation of the temperature corresponding to a given V/L ratio at a specified pressure. For example, $T_{(V/L=20)}$ is the temperature at which the partial pressure of the sample is equal to 101.3 kPa when the V/L ratio is 20. Dry glycerol is used as the containing liquid for non-oxygenated fuel (due to the partial solubility of the oxygenates in glycerol), while mercury can be used for both oxygenated and non-oxygenated fuels.

Summary and Significance of the Test Method

A measured volume of an air saturated sample kept at 0 °C to 4 °C (32 °F to 34 °F) is introduced through a rubber septum into a vapor-liquid burette filled with glycerol or mercury. The burette containing the sample is placed in a temperature controlled water bath. The volume of vapor in equilibrium with the liquid fuel is measured at the desired test temperature(s) and pressure (usually 760 Torr), and the V/L ratio is calculated. If the temperature corresponding to a given V/L ratio and pressure is required, the V/L ratio is determined at several temperatures at the given pressure. The results are plotted and the temperature at the desired V/L ratio is determined. The Procedure section of this

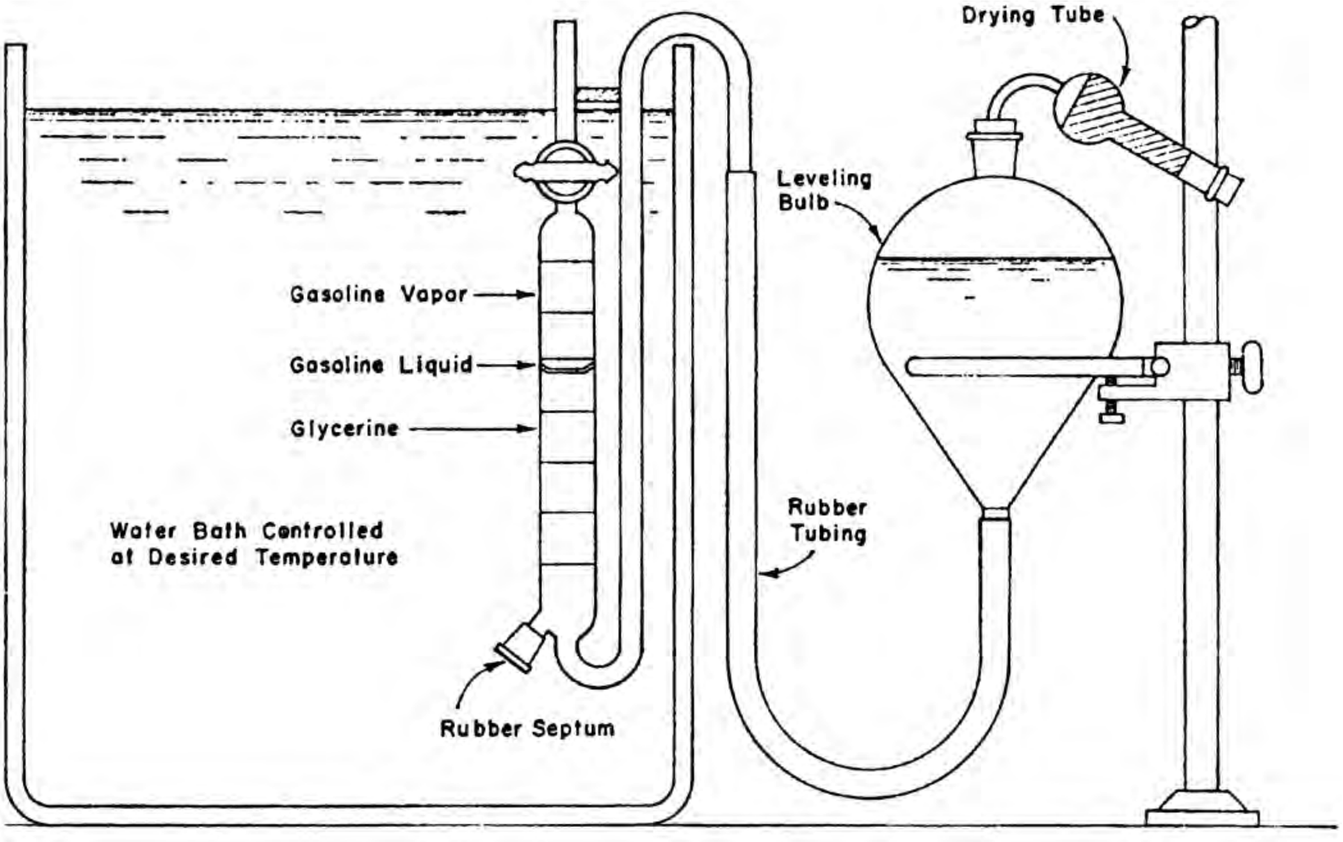

Fig. 7—*V*/*L* ratio apparatus set up in D2533.

method can be found in the Appendix of this manual.

The tendency of a fuel to vaporize in common spark-ignition fuel system is indicated by the *V*/*L* ratio of that fuel at conditions approximating those in critical parts of the fuel system. Automotive fuel specifications generally include $T_{(V/L=20)}$ limits to ensure products of suitable volatility performance. A fuel with a high $T_{(V/L=20)}$ is generally specified for high ambient temperatures, and low ambient temperatures would require a fuel with low $T_{(V/L=20)}$ value.

Critical Apparatus, Calibration, Sampling, and Sample Handling

The *V*/*L* ratio apparatus set up is given in Fig. 7 showing the *V*/*L* ratio burette. The calibration of the burette is done by gravimetrically weighing a specified volume of distilled water dispensed from the burette. A water bath capable of controlling the bath temperature between 3 °C to 82 °C (90 °F to 180 °F) to within 0.1 °C (0.2 °F) is required. ASTM thermometers 64C and 65C (64F or 65F) is specified, although digital temperature measuring devices are also acceptable.

Sampling and sample handling are similar to those discussed in D323 and D5191. Chilling the sample to 0 °C to 1 °C (32 °F to 34 °F) as well as air saturation are required.

Calculation, Report, Precision, and Bias

Calculation—The *V*/*L* ratio is obtained by simply dividing the measured volume of the vapor by the volume of the sample injected into the buret, or

$$V/L = A/B \tag{23}$$

where:

A = volume of the vapor, mL, and

B = volume of the sample injected, mL.

Report—The *V*/*L* ratio(s) is reported to the nearest 0.1, and the corresponding test temperature to 0.1 °C or °F. If the pressure is other than 760 Torr, report the pressure in Torr.

Precision—The precision of this method is reported in terms of $T_{(V/L=20)}$. Table 14 gives the repeatability and reproducibility of the method for glycerol and mercury.

Relative Bias—For non-oxygenated gasoline, no relative bias was observed when using glycerol or mercury as the containing liquid. For 15 vol % MTBE-gasoline blend, glycerol showed a 0.5 °C (0.9 °F) bias when glycerol was the containing liquid. No relative bias has been observed between results from this method using mercury as the containing liquid and D5188 "Standard Test Method for Vapor-Liquid Ratio Temperature of Fuels (Evacuated Chamber Method)" [5].

TABLE 14—Precision of D2533.

Containing liquid	Repeatability	Reproducibility
Glycerol	1.0 °C (1.8 °F)	1.3 °C (2.3 °F)
Mercury	1.4 °C (2.5 °F)	1.6 °C (3.0 °F)

ASTM D5188—Vapor-Liquid Ratio Temperature of Fuels (Evacuated Chamber Method)

Scope

This test method describes a procedure for the determination of the temperature at which the vapor of a given volume of an air-saturated volatile petroleum product introduced at 0 °C to 1 °C (32 °F to 34 °F) produces a pressure of 101.3 kPa (14.69 psia) in an evacuated chamber of fixed volume. The test method is applicable to samples for which the determined temperature is between 36 °C and 80 °C (97 °F and 176 °F) and the vapor-liquid ratio is between 8:1 and 75:1. This test method is applicable to both gasoline and gasoline-oxygenate blends. $T_{(V/L=20)}$, which is the equilibrium temperature at which the partial pressure of a sample under test condition equals one atmosphere when the vapor-liquid ratio is 20, is often determined. Under this specific V/L condition, the test result from this method is intended to be comparable to the results obtained by D2533.

Summary and Significance of the Test

A known volume of chilled, air saturated sample is introduced into an evacuated chamber of known volume. The test chamber is thermostatically controlled. The amount of sample introduced into the chamber is calculated to give the desired vapor-liquid ratio for the chamber volume in use. After the sample introduction, the chamber temperature is adjusted until a stable chamber pressure of 101.3 kPa (14.69 psia) is established.

The tendency of a fuel to vaporize in common spark-ignition fuel system is indicated by the V/L ratio of that fuel at conditions approximating those in critical parts of the fuel system. Automotive fuel specifications generally include $T_{(V/L=20)}$ limits to ensure products of suitable volatility performance. A fuel with a high $T_{(V/L=20)}$ is generally specified for high ambient temperatures, and low ambient temperatures would require a fuel with low $T_{(V/L=20)}$ value. The details of the Procedure section are found in the Appendix of this manual.

Apparatus, Calibration, Sampling, and Sample Handling

The information given in D5191 regarding the test chamber, pressure transducer, heater, temperature and pressure measuring devices, vacuum pump, water bath and/or refrigerator for chilling the sample are applicable to this method. Calibration, sampling, and handling of the sample after isolation are the same as well, with the exception that *n*-pentane is used as a calibration verification material with an expected $T_{(V/L=20)}$ of 36.1 ± 0.5 °C (96.9 ± 1.0 °F).

Calculation, Report, Precision, and Bias

Calculation—Equation (24) is indicated in the method as the equation to be used in calculating the volume of the specimen required to give the desired V/L ratio for a given chamber volume:

$$(V/L) = (V - v)/v \tag{24}$$

which can be rearranged to give

$$v = V/[(V/L) + 1] \tag{25}$$

where:

(V/L) = vapor-liquid ratio,

V = volume of the test chamber, mL, and

v = volume of sample charged at 0 °C (32 °F).

Report—The $T_{(V/L)}$ temperature is reported to the nearest 0.1 °C (0.2 °F) and the vapor-liquid ratio without reference to pressure. Typically, the $T_{(V/L=20)}$ is reported in the petroleum industry.

Precision—Based on a 1999 interlaboratory study involving gasoline and gasoline-oxygenate blends (ethanol and MTBE, 0 vol % to 15 vol %), the precision of this test method is as follows;

$$\text{Repeatability, } r = 0.6\ ^\circ\text{C}\ (1.1\ ^\circ\text{F})$$

$$\text{Reproducibility, } R = 0.9\ ^\circ\text{C}\ (1.6\ ^\circ\text{F}).$$

Bias—No absolute bias has been established for this test method since there is no accepted reference material suitable for determining the bias.

Relative Bias—No statistically significant bias was determined between the results using this test method and D2533 using a V/L ratio of 20 and using mercury as the containing fluid.

Other Vapor Pressure Measurements

There are several ASTM test methods purportedly used in the measurement of vapor pressure properties of materials. However, these test methods are seldom used in the petroleum industry either due to the complexity of the test method, or the availability of easier/more convenient ways of measuring the vapor pressure. These test methods will be described very briefly, and not much detail will be given. Users who are interested in the details of these test methods are referred to the test methods themselves.

ASTM D2878—Estimating Apparent Vapor Pressures and Molecular Weights of Lubricating Oils [4]

This test method describes a calculation procedure for converting evaporation loss data obtained by ASTM D972 "Standard Test Method for Evaporation Loss of Lubricating Greases and Oils" [2] to apparent vapor pressures and molecular weights at temperatures 121 °C to 260 °C (250 °F to 500 °F). The test is run at the selected temperature for a sufficient length of time to give the desired evaporation loss. The evaporation rate is compared with the standard value of pure *m*-terphenyl to give an apparent vapor pressure value for the material using the equations given in the test method. There is no associated precision statement for the calculated apparent vapor pressure, but the repeatability and reproducibility of evaporation loss by D972 are given as a guide.

ASTM D2879—Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope [4]

This test method covers the determination of the vapor pressure of pure liquids or mixtures in a closed vessel at a 40 ± 5 % ullage, i.e., where the volume of the vapor is 40 % of the total volume of the sample container. The test method is purportedly applicable to vapor pressures of 133 Pa to 101.3 kPa at temperatures of ambient to 475 °C. The detailed procedure is quite complex and this test method is used probably to generate vapor pressure data for materials with very low vapor pressures such as hydrocarbons and petroleum solvents. Because of the complex nature of the test method and the expensive equipment involved, there has not been a sufficient number of organizations that are willing to volunteer in conducting a comprehensive interlaboratory study to determine the precision and bias of the method.

ASTM E1194—Vapor Pressure [12]

This test method specifies the Isoteniscope method by D2879 and a gas saturation test method for measuring low vapor pressure of materials. D2879 is described previously. The gas saturation procedure is applicable to vapor pressures from 1×10^{-11} to 1 kPa from 10 °C to 60 °C. For the description of the test method, this is not a procedure that can be done routinely in a quality control laboratory and is probably suited under research laboratory environment. The estimated precision for several test compounds are given in the method, none of which is generally encountered in the petroleum industry.

ASTM E1719—Vapor Pressure of Liquids by Ebulliometry [13]

This test method covers the determination of the vapor pressure of liquids having an atmospheric boiling point between 12 °C and 302 °C by ebulliometry. A specimen is introduced into an ebulliometer boiler that is attached to a manostat. The manostat is set at a low pressure, and the specimen is heated to the boiling temperature. A suitable number of boiling temperatures at successively higher pressure settings are determined. The pressure-temperature data are fitted into an equation specified in the method, and the vapor pressure values are calculated. The test method is limited to materials that boil smoothly under the operational conditions of the ebulliometer. Materials that "bump" continually, boil erratically, or eject material through the condenser are not suitable for this measurement procedure. Similar to E1194, this test method is more suited to be performed under a research laboratory environment rather than a routine quality control setting. Precision statements are given for *n*-pentane and an equimolar mixture of ethanol and propanol.

Comparison Of Vapor Pressure And Vapor/Liquid Ratio Test Methods

Table 15 summarizes the different ASTM vapor pressure test methods for easy comparison. The scope, applicable vapor pressure range, test temperature, vapor-liquid ratio, and the test results are compared. Table 16 gives a summary of the precision of these same vapor test methods.

Cross-Reference Of ASTM Vapor Pressure Methods With Other International Standards

Table 17 gives a cross-reference of the various ASTM vapor pressure and *V*/*L* ratio test methods with other known international standards.

TABLE 15—Comparison of ASTM vapor pressure and vapor/liquid ratio test methods.

ASTM designation	Test method	Scope	Vapor pressure range, kPa	Test temperature, °C	Vapor-to-liquid ratio	Result
D323 Proc. A	Reid method	Gasoline, volatile crude oil, and other volatile petroleum products	<180	All at 37.8	4:1	Vapor pressure
D323 Proc. B	Reid method	″	<180			
D323 Proc. C	Reid method	″	>180			
D323 Proc. D	Reid method	Aviation gasoline	50			
D4953 Proc. A	Dry Reid method	Gasoline and gasoline-oxygenate blends, other air-containing volatile petroleum products	35 to 100	37.8	4:1	Vapor pressure
D4953 Proc. B	Dry Reid semi-automatic					
D5190	Automatic method	″	7 to 172	37.8	4:1	DVPE[a]
D5191	Mini method	″	7 to 130	37.8	4:1	DVPE[a]
D5482	Mini method, atmospheric	″	7 to 110	37.8	4:1	DVPE[a]
D6377	Expansion method	Crude oils		5 to 80	4:1 to 0.021:1	Vapor pressure
D6378	Triple expansion method	Volatile petroleum products, hydrocarbons, and hydrocarbon-oxygenate mixtures	7 to 150	37.8	4:1	Vapor pressure
D5188	Evacuated chamber method	Gasoline and gasoline oxygenate blends	101.3	36 to 80	8:1 to 75:1	*V*/*L* temperature
D2533	Evacuated chamber method	Gasoline	101.3	36 to 80	20:1	*V*/*L* and temperature
D1267	LP-gas method	Liquefied petroleum products		37.8 to 70		Vapor pressure

[a] DVPE = dry vapor pressure equivalent (see discussion under individual test method).

TABLE 16—Precision of various vapor pressure and V/L ratio test methods.

ASTM designation	Method name	Procedure/model	Range	Repeatability	Reproducibility
D323	Reid method	A (Gasoline)	35–100 kPa (5–15 psi)	3.2 kPa (0.46 psi)	5.2 kPa (0.75 psi)
		B (Gasoline)	35–100 kPa (5–15 psi)	1.2 kPa (0.17 psi)	4.5 kPa (0.66 psi)
		A	0–35 kPa (0–5 psi)	0.7 kPa (0.10 psi)	2.4 kPa (0.35 psi)
		A	110–180 kPa (16–26 psi)	2.1 kPa (0.30 psi)	2.8 kPa (0.40 psi)
		C	>180 kPa (>26 psi)	2.8 kPa (0.40 psi)	4.9 kPa (0.70 psi)
		D	50 kPa (7 psi)	0.7 kPa (0.10 psi)	1.0 kPa (0.15 psi)
D4953	Dry Reid method	A		3.65 kPa (0.53 psi)	5.52 kPa (0.80 psi)
		B (Gage)		4.00 kPa (0.58 psi)	5.38 kPa (0.78 psi)
		B (Herzog)		2.14 kPa (0.31 psi)	2.90 kPa (0.42 psi)
		B (Precision)		3.58 kPa (0.52 psi)	4.27 kPa (0.62 psi)
D5190	Automatic method			2.48 kPa (0.36 psi)	3.45 kPa (0.50 psi)
D5191	Mini method			0.008 07(DVPE+B) B=124 kPa (18.0 psi)	0.0161(DVPE+B) B=124 kPa (18.0 psi)
D5482	Mini method, atmospheric	Herzog SC970		1.31 kPa (0.19 psi)	2.69 kPa (0.39 psi)
		ABB 4100		1.79 kPa (0.26 psi)	4.14 kPa (0.60 psi)
D6377	VPRC_x, expansion method	Crude	V/L=4 and 37.8 °C	0.015 VPCR_4	To be determined
			V/L=0.1 and 37.8 °C	0.055 $\text{VPCR}_{0.1}$	
			V/L=0.02 and 37.8 °C	0.065 $\text{VPCR}_{0.02}$	
D6378	VP_x, expansion method	Petroleum Products		0.50 kPa (0.07 psi)	1.63 kPa (0.22 psi)
D5188	Evacuated chamber	V/L		0.6 °C	0.9 °C
D2533	Evacuated chamber	V/L	Glycerol	1.0 °C	1.3 °C
			Mercury	1.4 °C	1.6 °C
D1267	LP-gas method			12 kPa (1.8 psi)	18 kPa (2.8 psi)

TABLE 17—Cross-reference of international vapor pressure standards relative to ASTM test methods.

ASTM U.S.	ISO Europe	IP U.K.	BS U.K.	AFNOR France	DIN Germany	FTM	JIS Japan
D323	3007	69	2000	M41-007	51 754	791-1201	K2258
D4953							
D5190							
D5191		394		M07-079			
D5482							
D6377							
D6378							
D5188							
D2533							
D1267	4256	161			51 616		

Refernces

[1] ASTM D323-30t, Historical Document, ASTM International, West Conshohocken, PA.

[2] ASTM, *Annual Book of ASTM Standards*, Vol. 5.01, ASTM International, West Conshohocken, PA.

[3] ASTM D417-35t, Historical Document, ASTM International, West Conshohocken, PA.

[4] ASTM, *Annual Book of ASTM Standards*, Vol. 5.02, ASTM International, West Conshohocken, PA.

[5] ASTM, *Annual Book of ASTM Standards*, Vol. 5.03, ASTM International, West Conshohocken, PA.

[6] ASTM, *Annual Book of ASTM Standards*, Vol. 14.03, ASTM International, West Conshohocken, PA.

[7] ASTM, Research Report, RR:D02-1245, ASTM International, West Conshohocken, PA.

[8] ASTM, Research Report RR:D02-1286, ASTM International, West Conshohocken, PA, 2001.

[9] ASTM, *Annual Book of ASTM Standards*, Vol. 5.04, ASTM International, West Conshohocken, PA.

[10] IP 481: "Test Method for Determination of Air Saturated Vapor Pressure (ASVP) of Crude Oil," Energy Institute, London, U.K.

[11] ASTM, Research Report RR:D02-1619, ASTM International, West Conshohocken, PA, 2001.

[12] ASTM, *Annual Book of ASTM Standards*, Vol. 11.05, ASTM International, West Conshohocken, PA.

[13] ASTM, *Annual Book of ASTM Standards*, Vol. 14.02, ASTM International, West Conshohocken, PA.

6

An Overview of On-Line Measurement for Distillation and Vapor Pressure

Alex T. C. Lau[1] and Michael A. Collier[2]

AS WE HAVE SEEN IN PREVIOUS CHAPTERS, THE measurement of distillation and vapor pressure characteristics are vital pieces of information for the classification and volatility property certification of petroleum products. While these measurements are typically conducted under standard laboratory conditions and practices, there also exists a need for measurement of these same parameters under the dynamic conditions encountered during the actual production process of these fuels and other products. This chapter provides a high level, non-technical overview to introduce readers to the subject matter.

Measurements under these types of dynamic conditions are generally accomplished through the application of on-line analytical instrumentation systems. These systems are designed to tap, either directly or indirectly, into the process streams contained within a refineries production facility. These systems are generally capable of making continuous or periodic measurements of the distillation or vapor pressure characteristic during the actual dynamic production of the product. This provides for near continuous feedback of information about the volatility characteristics of a product directly to the process plant operators, such that the necessary adjustments to key process parameters can be made in order to have the final product meet the desired (or targeted) volatility properties. In modern day refineries, this process control function is typically carried out through automated control systems based on complex mathematical models of the manufacturing process, with the plant operators acting primarily in a supervisory role and to deal with unexpected disturbances. Last but not least, the on-line measurement system produced results can be used in providing continuous quality control and statistical analysis of the volatility properties of the monitored product stream.

The design of these on-line measurement systems is non-trivial. For most applications, the design considerations begin with the process control requirement and objective. Since these systems are intended to operate continuously, unsupervised, and within the production facility, system hardware design must meet specific safety requirements and standards developed through ASTM, ISA, and other industry consortiums.

In general, an on-line analytical instrumentation system comprises four major functional modules (see Figs. 1 and 2, reproduced from Standard Practice D3764).

Sample Transport Module

This typically comprises a sample probe which "taps" into the process, motive force such as pumps if necessary, and suitable lengths of small bore piping (<1 in.) to deliver the live process material to the Sample Conditioning Module location.

Sample Conditioning Module

The primary function of this module is to condition the pressure and temperature of the live process material into more "analytical instrument friendly" states since most manufacturing processes operate at high pressure and temperatures. As well, undesirable materials such as rust, water, and dirt are removed.

Analysis and Report Module

This typically comprises the analytical instrumentation that actually performs the volatility property analysis. There is a plethora of different, well understood, and time-proven techniques for volatility property measurements. Most (but not all) are designed to mimic the corresponding ASTM test methods. The mainstream techniques utilized are: Gas Chromatography (GC), physical distillation by heat, and vapor pressure measurement by pressure transducer.

Popular ASTM test methods that are mimicked by on-line measurement systems include: Vapor pressure: D323, D5191, D6378; Physical Distillation: D86, D1160; and GC: D3710, D2887.

GC-based techniques are often referred to as "Sim-Dis," a short form for "simulated distillation." While results for some Sim-Dis applications agree reasonably well with actual physical distillation results, in general, there will be systematic differences between the two techniques as they are based on fundamentally different principles.

After conducting the volatility analysis, the calculations and reporting are performed mostly by microprocessors (although there is still some analog instrumentation available) and transmitted to the process control command center via a variety of data telemetry means.

Sample Disposal Module

After the analysis is completed, the spent sample will need to be collected and disposed of. Most if not all analytical instrumentation modules operate at somewhat lower internal

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[1] Imperial Oil-Eng Service, 90 Wynford Drive, Toronto, Ontario, M3C 1K5, Canada.

[2] Petroleum Analyzer Company LP, P.O. Box 206, Wilmington, IL 60481

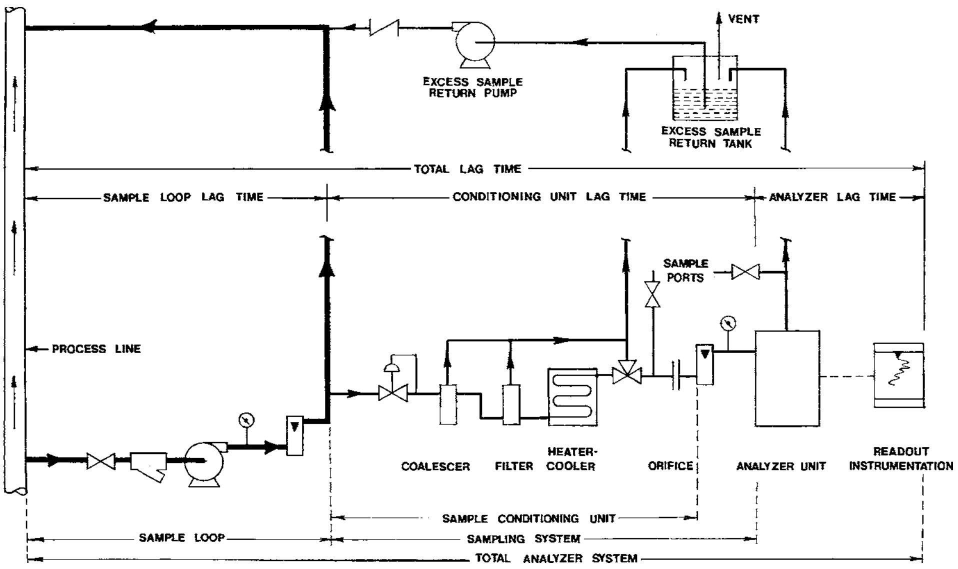

Fig. 1—Typical on-line analytical instrumentation system (ASTM Practice D3764, Fig. 1).

pressure than the manufacturing process; if re-injection into the manufacturing process stream is required, external motive force such as a pump will be necessary. It is not at all uncommon to have the spent sample return to a local sump at atmospheric pressure, with a periodic pump out of the sump back into the process system.

Performance Validation of On-Line Analytical Instrumentation Systems

Since most on-line systems are intended to mimic ASTM laboratory-based test methods, validation of on-line system performances are typically conducted by comparison of on-line system results against laboratory results using the corresponding ASTM test methods on the same process material. In general, there are two types of validations: (a) validation using a line sample taken at the process stream and (b) validation using a reference material.

ASTM Practice D3764 describes the necessary procedures and mathematics to carry out both types of validations. This practice can be used to quantify the performance of a process stream analyzer system or its subsystem in terms of precision and bias relative to the corresponding ASTM test methods.

Results from analytical instrumentation systems validated in accordance with this practice can be used as a prediction of what the ASTM test method result would be, within a specified tolerance, if the ASTM test method was conducted on the materials that are within the validated property range and type.

In addition, this practice provides the user of a process stream analyzer system with useful information for ongoing quality assurance testing designed to update or revalidate an analyzer system through the application of statistical quality control techniques.

In general, due to the highly automated and application-specific nature of on-line systems, precision is expected to be much better than the corresponding ASTM test methods. However, due to differences in sample treatment, analytical conditions (temperature, pressure), and techniques, systematic biases are often observed between on-line systems and their corresponding laboratory counterpart methods. Due to the predictable nature of these biases, mathematical compensations can easily be carried out prior to actual use of the on-line system results. ASTM Practice D6708 describes detailed protocol to estimate such biases.

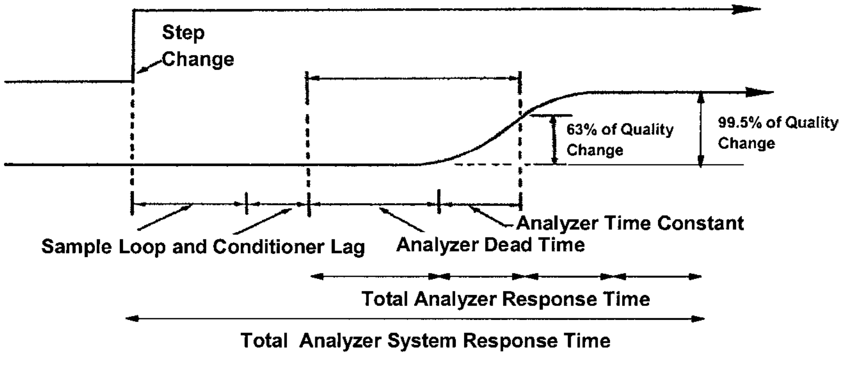

Fig. 2—Typical on-line analytical system response time (ASTM Practice D3764, Fig. 2).

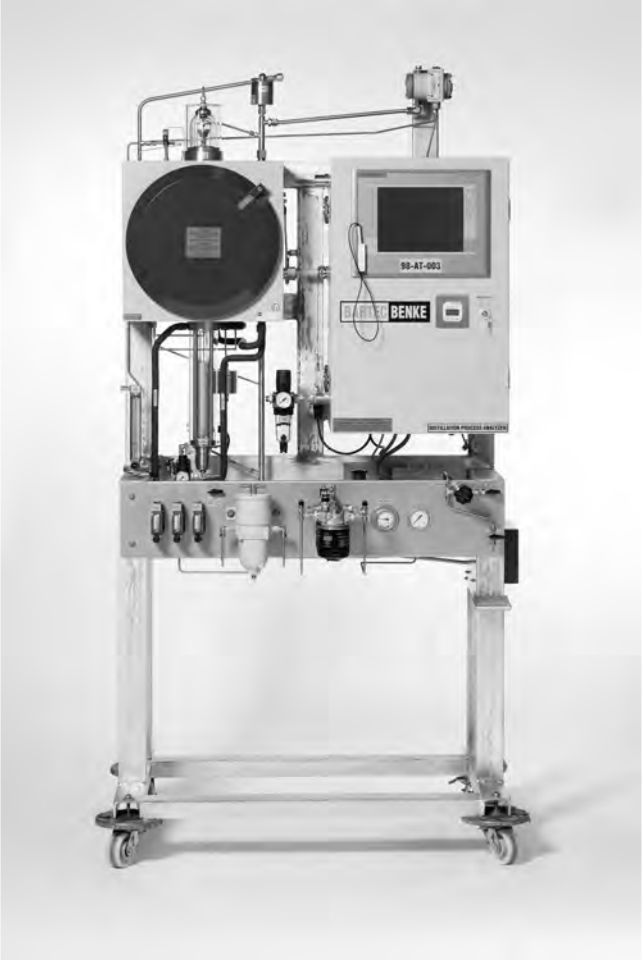

Fig. 3—On-line atmospheric distillation system. (Images courtesy of Bartec Benke GmbH Reinbek, Germany)

Following are descriptions of operation of some typical on-line analytical instrumentation systems.

Atmospheric Distillation

The typical on-line atmospheric distillation system (Fig. 3) is usually capable of either providing information on temperature at selected percent distilled, or percent distilled at selected temperatures. The sample is metered into a evaporation chamber; here, a fraction of the sample is vaporized by heating and condensed into an overhead collection. The unvaporized sample temperature and flow rate is monitored. Depending on which mode of operation is chosen, the flow rate at a selected temperature is then correlated to percent distilled at the selected temperature, or the heating of the evaporation chamber is regulated to maintain a selected constant flow rate and the temperature of the unvaporized sample is converted to distillation temperature at a selected percent distilled. Another type of on-line atmospheric distillation system (Fig. 4) only measures the temperature at a pre-selected percent distilled, usually 90 %, which can be converted to correlate to the final boiling point of the product being monitored. This type of monitor establishes an equilibrium distillation condition based on pressure and flow rate through selected orifices connected to the vaporized and unvaporized portions of the evaporation chamber, these are pre-determined prior to final assembly of the monitor.

Fig. 4—On-line boiling point monitor. (Images courtesy of Petroleum Analyzer Company LP. PAC LP.)

Vacuum Distillation

A typical on-line vacuum distillation system (Fig. 5) is very similar to the single point, percent distilled (again usually 90 %), atmospheric distillation system described previously. The difference with this monitor is that the pressure within the system is reduced by vacuum pumps to the desired levels needed to efficiently vaporize the sample without causing decomposition. A schematic of a typical on-line vacuum distillation system is shown in Fig. 6. These types are needed for those samples that have increasingly higher boiling points.

Simulated Distillation

The on-line Sim-Dis system (Fig. 7) correlates to physical distillation by separating hydrocarbons in boiling point

Fig. 5—On-line vacuum distillation monitor. (Images courtesy of Petroleum Analyzer Company LP. PAC LP.)

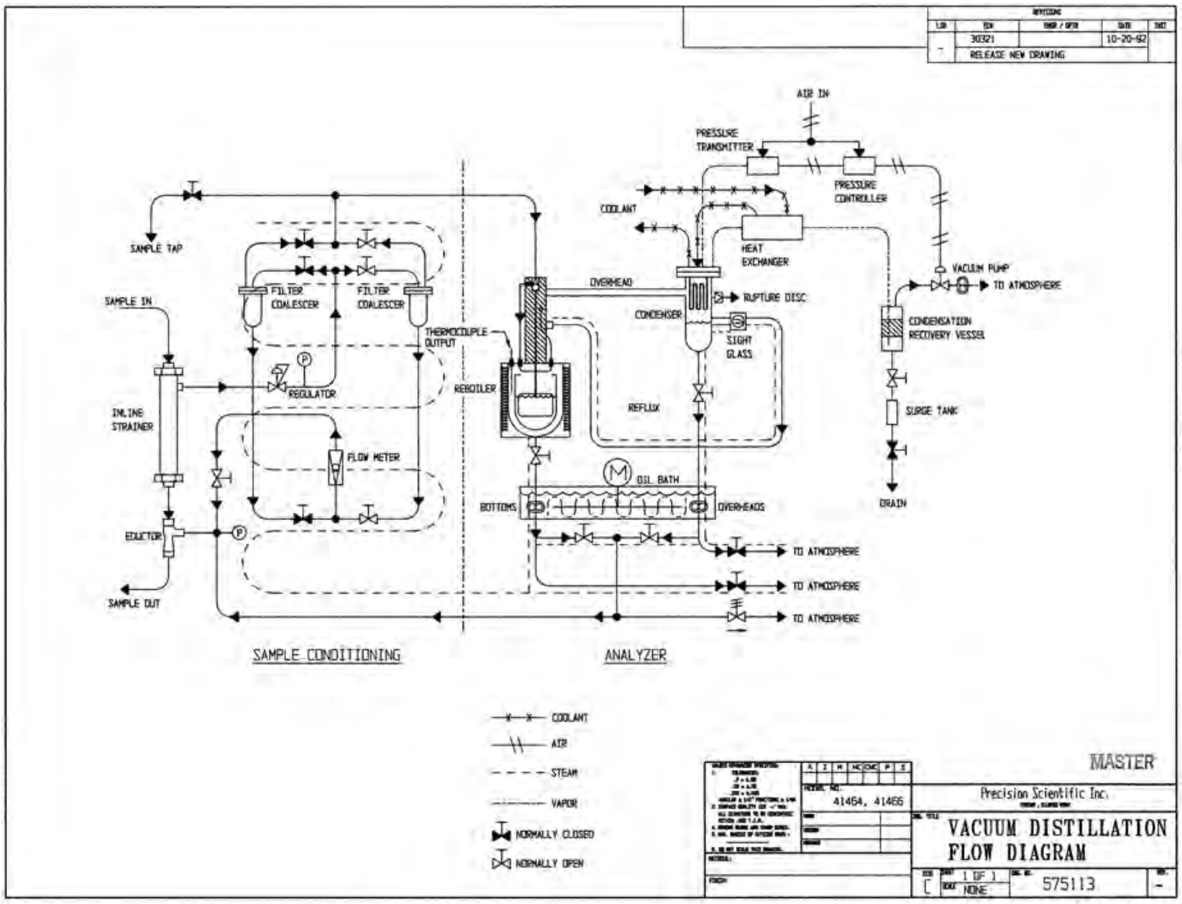

Fig. 6—Schematic flow diagram vacuum distillation. (Images courtesy of Petroleum Analyzer Company LP. PAC LP.)

order through a gas chromatography column. The column is heated at a reproducible rate and the boiling temperatures are assigned to the elution time of the component. These data are then converted into distillation information.

Reid Vapor Pressure

The on-line Reid vapor system (Fig. 8), as the name implies, measures the vapor pressure of the sample at specified con-

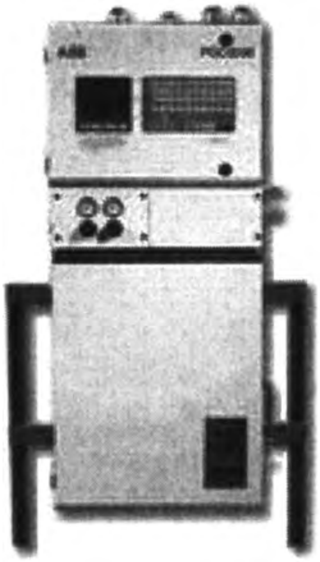

Fig. 7—On-line simulated distillation system. (Images courtesy of ABB Inc.)

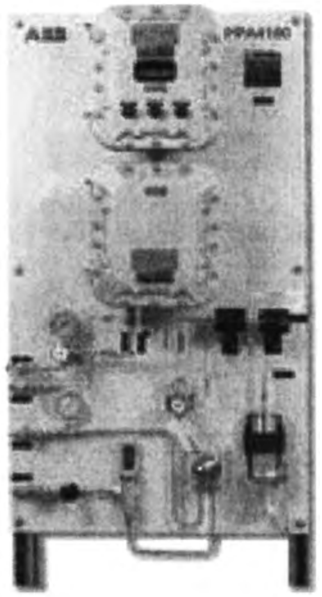

Fig. 8—On-line Reid vapor pressure monitor. (Images courtesy of ABB Inc.)

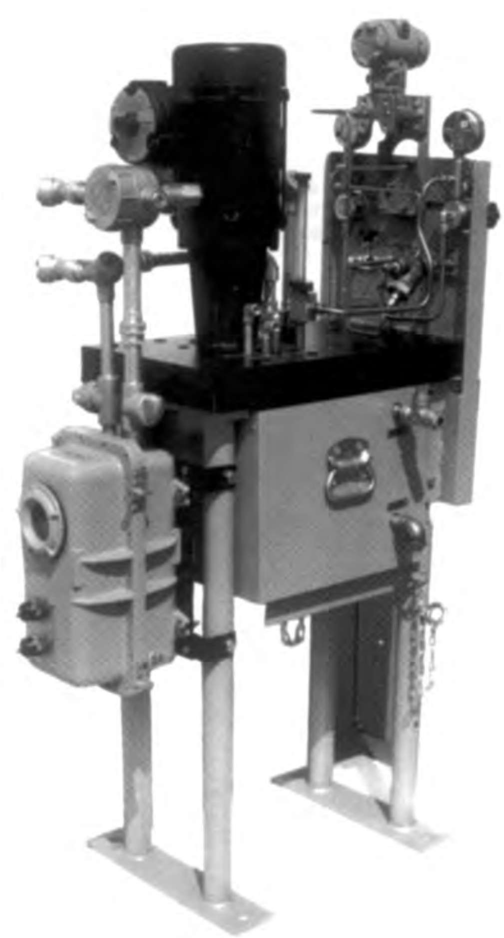

Fig. 9—On-line absolute vapor pressure monitor. (Images courtesy of Petroleum Analyzer Company LP. PAC LP.)

ditions. This measurement is very similar to the techniques utilized by the laboratory versions of the mini methods for vapor pressure, however, with the modifications necessary for on-line remote locations. A small volume of sample is captured from the process stream and is then contained within a chamber at the specified temperature and vapor-to-liquid ratio. Once the pressure of the sample being measured stabilizes, the results are transmitted back to the control center.

Absolute Vapor Pressure

These on-line vapor pressure systems (Fig. 9) are designed to provide the absolute vapor pressure of the sample by measuring the pressure at a specified temperature when the flow of the sample through a jet pump causes the pump to cavitate. This type of monitor is able to measure the process stream continuously.

7

Distillation and Vapor Pressure Data of Crude Oil

Rey G. Montemayor[1]

Introduction [1–3]

CRUDE OIL IS A HIGHLY COMPLEX MIXTURE OF MOlecular species made up of hydrogen and carbon (commonly referred to as hydrocarbons), heterocyclic molecular species (hydrocarbons with cyclic structures containing other chemical species such as oxygen, nitrogen, or sulfur or a combination thereof), organometallic compounds (hydrocarbons containing metal chemical species), inorganic sediments, and water. Crude oil can vary greatly in composition, and can exhibit highly variable physical and chemical characteristics. This is due to the fact that crude oils are not pure materials, but usually contain colloidally suspended components, dispersed solids, and emulsified water. No two crude oils will be chemically or physically identical. The composition of crude oil can vary from highly flammable light ends to highly viscous and heavy tar-like materials. The chemical composition of crude oil varies from field to field, between regions, and even within the same geologic formation.

The physical and chemical analyses of crude oil to determine its quality and processability is known as a crude oil assay. The results of a crude oil assay testing can provide extensive detailed data useful for refiners, oil traders, and producers. Assay data can help refineries determine if a crude oil is compatible for a particular petroleum refiner, or if the crude oil can cause yield, quality, production, environmental, and other problems. To determine the desired information, two different analytical schemes are commonly used, namely an inspection assay and a comprehensive assay. Inspection assays generally involve a few limited properties such as API gravity or density, sulfur content, sediment, and water. Occasionally pour point is determined to determine the fluidity of the crude oil. There is very limited agreement on what constitutes an inspection assay. Different oil companies generally do additional tests that will provide information that can be used in the processing of a given crude oil. Comprehensive assays involve more tests than what are performed on an inspection assay. The overriding issue in doing a comprehensive assay on a given crude oil is economics. Comprehensive assays of crude oil are done to determine: (a) the slate of products that can be produced with a given refinery's process technology, (b) processing difficulties that may arise as a result of the inherent composition and impurities of the crude oil, and (c) downstream processing and upgrading activities to optimize yields of high-value products. Since this manual is concerned mainly with distillation and vapor pressure measurements of crude oil, the focus of this chapter is on the distillation and vapor pressure data. There are a number of other tests which are performed during an inspection assay or a comprehensive assays. These are discussed in detail elsewhere [1].

Distillation Data of Crude Oil

Invariably, a comprehensive assay will require that the crude oil be subjected to a fractional distillation, and the fractions characterized by the appropriate tests. This is necessary so that the refiner can assess the quantity and quality of potential products that can be recovered from a given crude oil, and determine if that product slate would be economically viable to meet the market requirements of a particular refinery. The following fractions provide the basis for a moderately thorough evaluation:

C_2–C_4(−89 to −0.5°C)	Gas
C_5(36°C)–79°C	Light Naphtha
79–121°C	Medium Naphtha
121–191°C	Heavy Naphtha
191–277°C	Kerosine
277–343°C	Distillate Fuel Oil
343–455°C	Light Vacuum Gas Oil (LVGO)
455–566°C	Heavy Vacuum Gas Oil (HVGO)
344°C+	Atmospheric Residuum
566°C+	Vacuum Residuum

ASTM D2892 "Standard Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)" [4] describes the procedure for the distillation of crude petroleum to a final cut temperature of 400°C AET (Atmospheric Equivalent Temperature). The test method employs a fractionating column having an efficiency of 14 to 18 theoretical plates operated at a reflux ratio of 5:1. The performance criteria for the necessary equipment are specified. Detailed procedure is described for the production of a liquefied gas, distillate fractions, and residuum of standardized quality on which analytical data can be obtained, and the determination of yields of the fractions (both in mass and volume %). From this information, a graph of the temperature versus mass % distilled can be generated. This distillation curve corresponds to a laboratory technique defined at 15/5 (15 theoretical column, 5:1 reflux ratio) or TBP (true boiling point).

Above a 400°C AET, it is necessary to do the distillation at reduced pressures under conditions that provide approxi-

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mately one theoretical plate fractionation. ASTM D1160 "Standard Test Method for Distillation of Petroleum Products at Reduced Pressure" [5] covers the determination, at reduced pressures, of the range of boiling points for petroleum products that can be partially or completely vaporized at a maximum liquid temperature of 400°C. Both manual and automatic procedures are specified. ASTM D5236 "Standard Test Method for Distillation of Heavy Hydrocarbon Mixtures (Vacuum Potstill Method)" [6] covers the procedure for distillation of heavy hydrocarbon mixtures having initial boiling points greater than 150°C such as heavy crude oils, petroleum distillates, residues, and synthetic mixtures. It uses a potstill with a low pressure drop entrainment separator operated under total takeoff conditions. Additionally, this test method describes the procedures for the production of distillate fractions of standardized quality in the gas oil and lubricating oil range for further characterization, as well as the production of standard residua. It also provides for the determination of standard distillation curves to the highest atmospheric equivalent temperature. For most crude oils, a temperature of up to 565°C AET can be attained by D5236. D2892 is the recommended distillation method for crude oils up to cut point 400°C AET, and although D5236 can be used for testing similar materials, the distillation curves and fraction qualities obtained by D2892 relative to those obtained by D5236 are not comparable. These three methods of distillation of crude oil materials under reduced pressure, namely D1160, D2892, and D5236 are discussed in detail in Chapter 3 of this manual.

There is also a high temperature simulated distillation test method for crude oil, ASTM D7169 "Standard Test Method for Samples with Residues Such as Crude Oil and Atmospheric and Vacuum Residues by High Temperature GC" [7] which covers up to temperatures of 720°C. A study [8] reported a comparison of the results using D2892 and D5236 with the results using high temperature simulated distillation (HTSD) method using 85 crude oils grouped into light, intermediate, and heavy categories according to their API gravities. The results of the study indicated that in general, the difference observed at each cutpoint is <2 weight %. The estimated precision of the correlation between crude assay distillation and HTSD at each cutpoint showed standard deviation of <2 weight %. The precision of cutpoints up to 538°C is better than 0.5 weight%. The study reported that an exception occurs at the 400°C AET cutpoint for light and intermediate crudes, and the region from 400 to 482°C AET for heavy crudes. The authors speculated that this can be due to the fact that the 400°C cutpoint is the first cutpoint following the crossover from D2892 (15-theoretical plate distillation) and D5236 (1-theoretical plate distillation). Simulated distillation measurement is discussed in Chapter 4 of this manual.

Vapor Pressure Data of Crude Oils [9,10]

Underground crude oil contains many lighter hydrocarbons in solution. When the oil is brought to the surface and processed, many of the dissolved lighter hydrocarbons (as well as water) are removed through a series of high pressure and low pressure separators. The crude oil is then introduced into a storage tank for shipping and transportation off site. The remaining hydrocarbons are emitted as vapors into the tank. These vapors are either vented, flared, or recovered by vapor recovery units. Lighter crude oils (API gravity $>36°$) flash more hydrocarbon vapors than heavier crudes (API gravity $<36°$). Nonstabilized crude oil cannot be stored in storage tanks because the extreme vapor pressure exerted by the light hydrocarbons can blow off the roof. The degree of stabilization required depends on the prevailing temperature and the intrinsic vapor pressure of the crude oil at that temperature. For example, if crude oil is stored in the Houston area, the amount of stabilization will be greater than that required if the crude oil is stored in Alaska. In storage tanks where the oil is frequently cycled and the overall throughput is high, more working vapors will be released than in tanks with low throughput and where the oil is held for longer periods and allowed to "weather." Stabilized crude oil can be defined as a crude oil where the vapor pressure at the prevailing temperature does not exceed the ambient vapor pressure in the vessel used to contain the material. Once the crude oil is stabilized where a sufficient amount of these lighter hydrocarbons have been removed, it can then be safely transported by pipeline or crude oil tankers to locations where they can be processed. The vapor pressures of the light hydrocarbons present in the stabilized crude constitute the vapor pressure of the crude oil.

In various sites all over the world, local and regional regulations mandate vapor pressure values which are applicable to crude oil in storage, or when they are being transported from one site to another. In many areas of the world, vapor pressure of crude oil is used to assess the "breathing loss" from a storage tank and verify conformance to mandated levels. Regulatory bodies usually require the "true vapor pressure (TVP)" at a specified temperature or a set of temperatures. True vapor pressure at the required temperatures is estimated from the Reid vapor pressure determined by ASTM D323 "Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method)" [5]. The scope of D323 indicates that it is applicable to volatile crude oil and gives the Reid vapor pressure (RVP) at 37.8°C of petroleum products and crude oil. Although D323 is not applicable to all crude oil samples, it has historically been used to determine the RVP of crude oil.

Regulations in various parts of the world require the reporting of "breathing losses" of organic liquids in storage including crude oil. In the calculation of these "breathing losses" the true vapor pressure (TVP) is required. In the United States (and probably for most part of the world), TVP is estimated from the RVP. Historically, TVP is estimated from the RVP and crude temperature values using the API Bulletin 2517 nomograph (Fig. 1) [11,13]. An equation [11], derived from a regression analysis of points read off the API Bulletin 2517 nomograph over the full range of RVP, slopes of the ASTM distillation curve at 10 % evaporated, and temperature of the liquid is given by:

$$\mathrm{TVP} = e^{\{[(2.799/(T+459.6))-2.227]\log(\mathrm{RVP})-(7.261/(T+459.6))+12.82\}} \qquad (1)$$

where TVP = estimated TVP, RVP = Reid vapor pressure in psi, and T = temperature of the liquid in degrees F.

In general, the equation yields TVP values which are within 0.05 psi of the values obtained directly from the API Bulletin 2517.

In California, emissions losses are covered under the Air Toxics Information and Assessment Act (AB2588). True va-

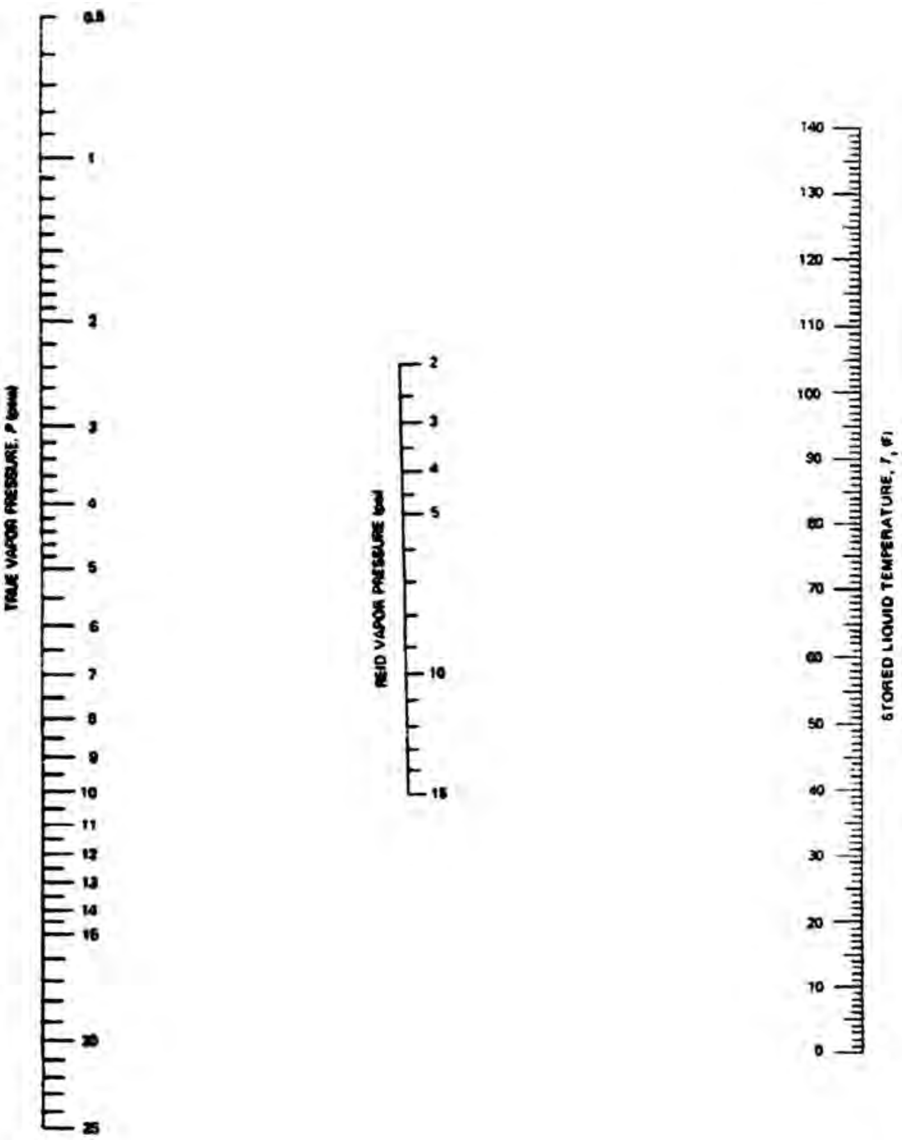

Fig. 1—API Bulletin 2517 nomograph for crude oil [11,13].

por pressure (TVP) which are required by the emission losses calculations is similarly estimated from the Reid vapor pressure (RVP) using the API Bulletin 2517. The relevant TVP–RVP equation from the Technical Guidance Document and Guidelines Regulation for AB2588 is given by the following equation [12,13]:

$$\mathrm{TVP} = (\mathrm{RVP})e^{C_o(\mathrm{IRTEMP}-\mathrm{ITEMP})} \quad (2)$$

where C_o = constant dependent upon the value of RVP, ITEMP = (1/559.69 °R), IRTEMP = [1/(T_s + 459.69 °R)], and T_s = temperature of the stored fluid in °F

Note: °R is degree Rankin scale, which is the Fahrenheit equivalent of degree Kelvin scale in degree Celsius. Table 1 gives the C_o values corresponding to different RVP numbers.

However, the Technical Guidance Document to the Criteria and Guidelines for AB2588 [12,13] contained a provision to correct the calculated TVP values from the API Bulletin 2517 nomograph. The correction might have been predicated by a perceived error in the API nomograph calcu-

TABLE 1—C_o values for different RVP [12].

RVP	C_o
0 < RVP < 2	−6622.5
2 < RVP < 3	−6439.2
RVP = 3	−6255.9
3 < RVP < 4	−6212.1
RVP = 4	−6169.2
4 < RVP < 5	−6177.9
RVP = 5	−6186.5
5 < RVP < 6	−6220.4
RVP = 6	−6254.3
6 < RVP < 7	−6182.1
RVP = 7	−6109.8
7 < RVP < 8	−6238.9
RVP = 8	−6367.9
8 < RVP < 9	−6477.5
RVP = 9	−6587.9
9 < RVP < 10	−6910.5
RVP = 10	−7234.0
10 < RVP < 15	−8178.0
RVP = 15	−9123.2

lated values of TVP based on the interpretation that the RVP is supposed to be equal to the TVP at 100 °F. Correction factors (C_F) were developed using linear regression techniques, and are to be added to the calculated values of TVP in order to obtain reasonable TVP numbers. The relationship between the three values is given as follows:

$$\text{Corrected TVP} = \text{Calculated TVP (from nomograph)} + C_F \tag{3}$$

The correction factor C_F was found to be dependent upon the RVP according to the following equations:

$$C_F = (0.04) \times \text{RVP} + 0.1 \quad (\text{if RVP} < 3 \text{ psi}) \tag{4}$$

$$C_F = e^{[(2.3452061 \log(\text{RVP})) - 4.132622]} \quad (\text{if RVP} > 3 \text{ psi}) \tag{5}$$

Since 1991, vapor pressure of crude oils has been measured by organizations using ASTM D5191 "Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method)" [5], although crude oil is not in the scope of the method. This method gives a dry vapor pressure equivalent (DVPE) value corresponding to the vapor pressure determined by ASTM D4953 "Standard Test Method for Vapor Pressure of Petroleum Products (Dry Reid)" [5] at 37.8°C with a 4+1 V/L ratio. It has to be emphasized that the DVPE value obtained by D5191 is not the RVP and should not be used as such. It may be the case that D5191 DVPE is interpreted to be equivalent to RVP by some, but this is definitely technically incorrect! Some regulations may require TVP to be measured by D5191, and this too, is not correct! A more recent test method developed specifically for measuring the vapor pressure of crude oil is ASTM D6377 "Standard Test Method for Determination of Vapor Pressure of Crude Oil: VPCR_x (Expansion Method)" [6]. This test method covers the use of automated instruments to measure the vapor pressure of crude oil at temperatures between 5 and 80°C for V/L = 4:1 to 0.02:1 (X=4 to 0.02) and pressures from 7 to 500 kPa (1 to 70 psi). Sampling is done using a pressurized sampling system (floating piston cylinder), and vapor pressure results are reported as VPCR_x where x = the V/L ratio with the measurement temperature. A correlation equation (which is not part of the mandatory text of the method has been included only for informational purposes) of VPCR_x results to D323 values was developed using data at 37.8°C and V/L = 4:1 of Norwegian North Sea crude oils. The correlated D323 vapor pressure is called the *RVPE* or Reid vapor pressure equivalent, and can be obtained using the equation:

$$RVPE = A \times VPR_4 \text{ (at } 37.8\,^\circ\text{C)} + B \tag{6}$$

where *RVPE* is the Reid vapor pressure equivalent (correlated D323 value), A = 0.752, and B = 6.07 kPa (0.88 psi).

Some organizations have found considerable bias using the correlation equation given by Eq. (6) for highly stabilized crude oil [14], and this is being addressed. Additional precision studies on D6377 have just been recently concluded. The precision and bias statements of the method will be updated as data becomes available. A similar test method in Europe specific to crude oil is IP 481 "Test Method for Determination of Air Saturated Vapor Pressure (ASVP) of Crude Oil" [15]. Details regarding D323, D5191, and D6377 test methods are given in Chapter 5 of this manual.

API Nomographs and True Vapor Pressure (TVP) [15]

It was mentioned earlier in this chapter that it has been a common practice to estimate the true vapor pressure (TVP) of a liquid in storage using the Reid vapor pressure and temperature of the liquid and the API Bulletin 2517 nomograph. There is an on-going controversy regarding this practice, which has contributed to incorrect references to TVP and RVP in regulations, disputes on crude/condensate quality in various parts of the world, and an international "billion dollar bias" on imported offshore crude from excess stabilization. Although, it has potentially great ramifications on the oil industry, it is a subject matter that is outside the scope of this manual. Only a brief overview of the situation will be given, but the subject matter obviously needs to be discussed or resolved elsewhere.

The problem seems to arise by the application of the API Bulletin 2517 TVP/RVP nomograph, originally developed on weathered crude oils containing light ends, to highly stabilized crude oils that contain very little light ends requiring 2–3 % volume extra butane removal to meet the API TVP requirements. It would appear that the correct nomograph to use is the "products" API nomograph, and not the weathered crude nomograph to be technically correct for highly stabilized crude. Using the "products nomograph," a 10 psi RVP naphtha, gasoline, or condensate would yield a predicted 10.5 psi TVP. However, if the crude oil nomograph is used for the same materials, a predicted TVP of 13.5 psi would be obtained. A highly stabilized crude would have similar component distribution as a naphtha, condensate, or gasoline blend and therefore is expected to behave similarly. This situation is being pursued for resolution at the ASTM/API stage, and hopefully will be eventually communicated and resolved with various regulatory bodies in the near future.

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8

Distillation and Vapor Pressure Data in Spark-Ignition Fuels

B. R. Bonazza[1] and L. M. Gibbs[2]

Introduction

THE VOLATILITY CHARACTERISTICS OF A SPARK-ignition engine fuel are of prime importance to the driveability of vehicles under all conditions encountered in normal service. The large variations in operating conditions and wide ranges of atmospheric temperatures and pressures impose many requirements on a fuel if it is to give satisfactory vehicle performance. Fuels that vaporize too readily in pumps, fuel lines, carburetors, or fuel injectors will cause decreased fuel flow to the engine, resulting in hard starting, rough engine operation, or stoppage (vapor lock). Under certain atmospheric conditions, fuels that vaporize too readily can also cause ice formation in the throat of a carburetor, resulting in rough idle and stalling. This problem occurs primarily in older vehicles. Conversely, fuels that do not vaporize readily enough may cause hard starting and poor warm-up driveability and acceleration. These low-volatility fuels may also cause an unequal distribution of fuel to the individual cylinders in vehicles with carburetors or throttle body fuel injection systems. Similar problems would not be expected in vehicles with port fuel injection systems.

The volatility of automotive spark-ignition engine fuel must be carefully "balanced" to provide the optimum compromise among performance features that depend upon the vaporization behavior. Superior performance in one respect may give serious trouble in another. Therefore, volatility characteristics of automotive fuel must be adjusted for seasonal variations in atmospheric temperatures and geographical variations in altitude. ASTM D4814-04b, "Standard Specification for Automotive Spark-Ignition Engine Fuel," defines the volatility requirements for gasolines sold in the United States. Volatility of fuels is varied for seasonal climatic changes and for conformance to U.S. EPA volatility regulations by providing six vapor pressure/distillation classes and six vapor lock protection classes for fuel [1,2].

The four common volatility properties, i.e., vapor pressure, distillation, driveability index,and vapor-liquid ratio at temperature or vapor lock index, are described below. The effect of these volatility parameters on the performance of the vehicle is also discussed.

Vapor Pressure

Vapor pressure is one of the single most important properties for vehicle cold-start and warm-up driveability. It is the vapor pressure at 37.8 °C (100 °F) measured in a chamber having 4:1 ratio of air to liquid fuel. ASTM D323-99a, "Test Method for Vapor Pressure of Petroleum Products (Reid Method)," can be used for hydrocarbon-only gasolines and gasoline-ether blends, but not for gasoline-alcohol blends because traces of water in the apparatus can extract the alcohol from the blend and lead to incorrect results. Therefore, this method is no longer listed as an acceptable test method for spark-ignition engine fuels in Specification D4814 [3].

To avoid the alcohol-water interaction problem in Test Method D323, a similar method using the same apparatus and procedure, but maintaining dry conditions, has been developed. It is ASTM D4953, "Test Method for Vapor Pressure of Gasoline and Gasoline-Oxygenate Blends (Dry Method)." For hydrocarbon-only gasolines, there is no statistically significant difference in the results obtained by Test Methods D323 and D4953. Advances in instrumentation have led to the development of three other methods that can be used for both gasolines and gasoline-oxygenate blends. They are ASTM D5190, "Test Method for Vapor Pressure of Petroleum Products (Automatic Method)," D5191, "Test Method for Vapor Pressure of Petroleum Products (Mini Method)," and D5482, "Test Method for Vapor Pressure of Petroleum Products (Mini Method-Atmospheric)." The precision (repeatability and reproducibility) of these three methods is much better than that for D4953. A fourth method, ASTM D6378, "Test Method for Determination of Vapor Pressure (VPx) of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method)" is being evaluated by ASTM, and if repeatability and reproducibility are acceptable, it will very likely also be included in Specification D4814. Today, D4814 accepts the following test methods for measuring vapor pressure of gasoline: D4953, D5190, D5191, and D5482.

Test procedures for all of the methods listed above are basically the same. A chilled fixed volume of gasoline is placed in a test chamber and heated to 37.8 °C (100 °F). The pressure developed by gasoline vapors is measured in units of pounds per square inch (psi) or kilopascals (kPa). The methods differ in the design of the apparatus, including the design of the test chamber. D323 yields the Reid Vapor Pressure (RVP); the other methods yield the Dry Vapor Pressure Equivalent (DVPE) [4]. The RVP is nearly the same as the

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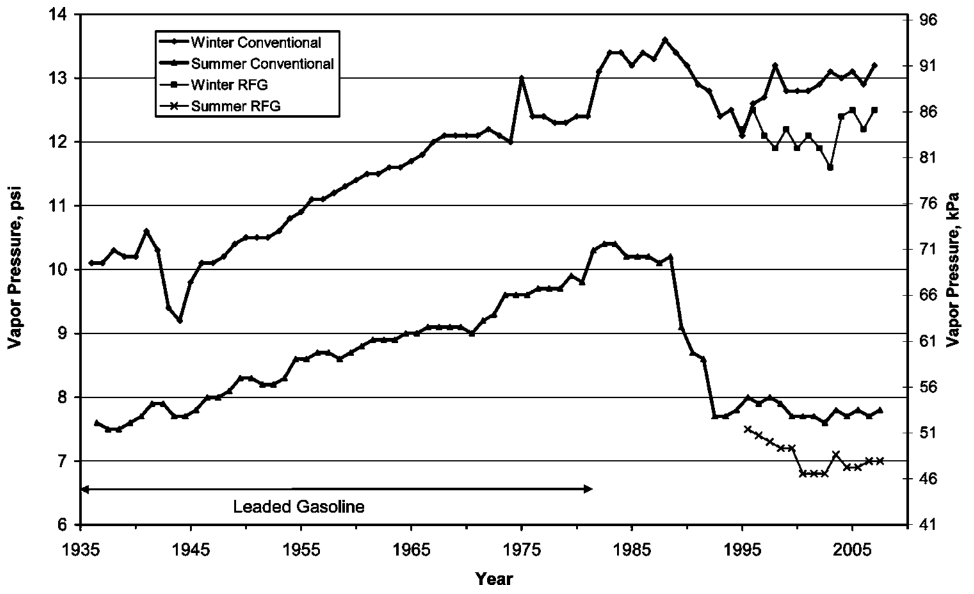

Fig. 1—United States regular grade national average vapor pressure trends.

DVPE. Test method D5191 contains an equation for calculating DVPE from the instrument's reported total vapor pressure. U.S. EPA and the California Air Resources Board each have similar equations that provide slightly different values.

Figure 1 shows how gasoline vapor pressure has changed over time [5]. For both summer and winter gasolines, the vapor pressure showed a steady increase until 1989 when there was a sudden drop as a result of the EPA Phase I vapor pressure summertime regulations. EPA Phase II regulations came into effect in 1992 and caused an additional reduction. The regulations do not apply in wintertime, but initially caused wintertime vapor pressure also to be reduced. However, for conventional gasolines, wintertime vapor pressure is again showing a trend upward. Reformulated summertime and wintertime gasolines (introduced beginning in 1995) have lower vapor pressures than corresponding conventional gasolines.

Beginning in 1987, several states required the addition of oxygenates to gasoline during the winter months in certain geographic areas to reduce vehicle carbon monoxide emissions. The oxygenated components used in spark-ignition fuel include aliphatic ethers, such as methyl tertbutyl ether (MTBE) and ethanol. The addition of ethanol has a unique effect on the vapor pressure of the blend. Ethanol vapor pressure does not blend linearly with gasoline vapor pressure, as shown in Fig. 2 [6]. The vapor pressure of neat ethanol is about 2.3 psi (15.9 kPa), but at 10 volume %, it blends as if it had a vapor pressure of 18 to 20 psi (124 to 138 kPa). As shown in Fig. 2, a small amount of ethanol blended into gasoline causes a large increase in vapor pressure. The curve then levels out. The blending vapor pressure effect of ethanol is greater as the vapor pressure of the gasoline decreases. As illustrated in Fig. 2, adding 10 volume % ethanol to a 6 psi (41 kPa) gasoline results in an increase

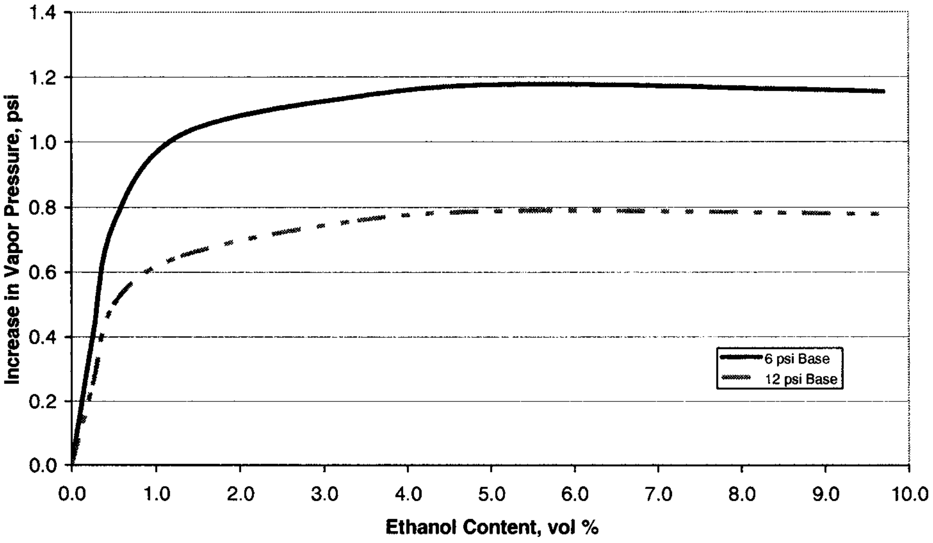

Fig. 2—Effect of ethanol addition on vapor pressure.

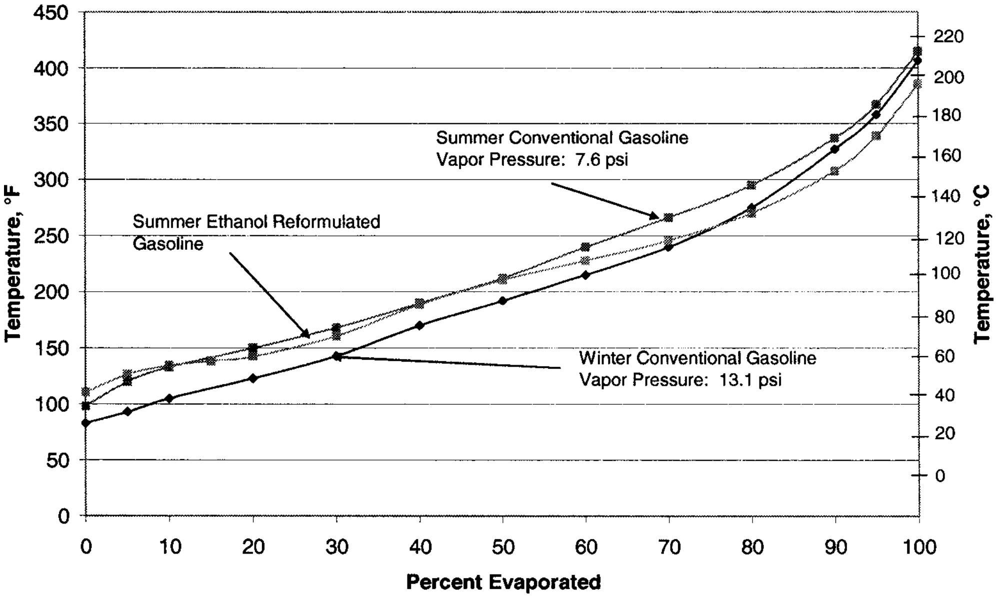

Fig. 3—Typical distillation profiles of summer and winter gasolines (ASTM D86).

in vapor pressure of nearly 1.2 psi (8.3 kPa) while the addition to a 12 psi (83 kPa) gasoline results in about a 0.8 psi (5.5 kPa) increase.

Distillation

Gasoline is a mixture of hundreds of hydrocarbon compounds, each with its distinctive boiling point. Therefore, gasoline boils over a range of temperatures and its tendency to vaporize is characterized by determining a series of temperatures at which various percentages of the fuel have evaporated, as described in ASTM D86, "Test Method for Distillation of Petroleum Products at Atmospheric Pressure." A plot of the results is commonly called the distillation curve. The 10, 50, and 90 volume % evaporated temperatures are often used to characterize the volatility of gasoline. According to this procedure, a 100 mL sample of gasoline is placed in a round-bottom flask and heated at a rate specified for samples with its vapor pressure characteristics. Temperatures are recorded when the first drop is collected (initial boiling point), at recovered volumes of 5 mL, 10 mL, every subsequent 10 mL interval to 90 mL, 95 mL, and at the end of the test (end point). For gasoline samples, the temperatures associated with each incremental volume percentage recovered are converted to temperatures for each incremental volume percentage evaporated by correcting for any sample loss during the test [4]. Two gas chromatographic methods can be used to determine the distillation characteristics of gasoline: ASTM D3710, "Test Method for Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography" and ASTM D7096 "Test Method for Determination of the Boiling Range Distribution of Gasoline by Wide-Bore Capillary Gas Chromatography." The ASTM D3710 and D7096 test methods do not directly provide the same results as the ASTM D86 test method. The ASTM D3710 test method has not been validated for blends containing oxygenates, while the ASTM D7096 test method has been validated for gasolines containing ethanol, but no other oxygenates.

Figure 3 shows typical gasoline ASTM D86 distillation curves for summer and winter conventional gasolines and also for a summer reformulated gasoline containing ethanol [4]. Figure 4 illustrates the importance to vehicle performance of the various parts of the curve [4]. The front end of the distillation curve is important for cold starting with a more volatile curve (lower temperatures) providing easier starting. However, if it is too volatile, hot-starting and hot-fuel-handling driveability can be a problem. The midrange is important for cold starting and warm-up driveability. This in turn helps with short-trip fuel economy. In older vehicles with carburetors, too much midrange volatility can contribute toward carburetor icing. A high tail end of the distillation curve contributes to better fuel economy, but if too high it can contribute to combustion chamber and other engine deposits. A high tail end also can contribute to cold-start fuel dilution of the engine oil.

Figure 5 shows how various distillation points have changed over the years [7–10]. Early on in the history of gasoline, the 10 %, 50 %, and 90 % evaporated distillation points increased as the demand for gasoline increased. Since the early 1920s, the trend has been downward with a leveling off beginning in the 1960s. With the implementation of the EPA Phase I regulations in 1989, the 10 % evaporated point began to increase as the vapor pressure was reduced since the two properties are highly correlated. With their introduction in 1995, the reformulated gasolines have higher 10 % evaporated points and lower 50 % and 90 % evaporated points than conventional gasolines.

In the U.S. EPA complex model and other specifications, distillation is addressed in terms of the percent evaporated at prescribed temperatures rather than the percent evaporated at prescribed temperatures. For example, when the result is reported as percent evaporated at 93 °C (200 °F), it is referred to as E 93 (E 200). This term is illustrated on Fig. 4. Annex A4 in ASTM D86 describes how to report results in E terms.

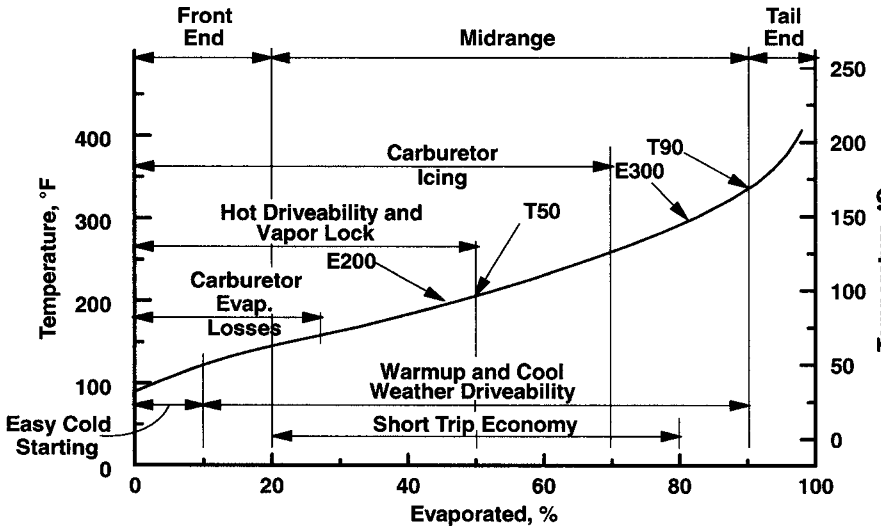

Fig. 4—Correlation of distillation curve with vehicle performance.

Driveability Index

While each area of the distillation curve is important, the combination of the various points that describe the whole curve must be taken into account to adequately describe vehicle driveability. The ASTM Driveability Task Force, using data from the Coordinating Research Council (CRC) and others, has developed a correlation between various distillation points and vehicle cold-start and warm-up driveability. This correlation is called Driveability Index (DI) and is defined as follows:

$$DI = 1.5(T_{10}) + 3.0(T_{50}) + 1.0(T_{90}) + 1.33\ ^\circ C(2.4\ ^\circ F) \times \text{Ethanol Volume }\%,$$

where T_{10}, T_{50}, and T_{90} are the temperatures at the 10 %, 50 %, and 90 % evaporated points of a Test Method D86 distillation, respectively, 1.33 is the coefficient for the volume % ethanol present when the distillation results are determined in degrees Celsius and 2.4 is the coefficient when distillation results are determined in degrees Fahrenheit[2,11].

Figure 6 shows the historical trend for DI [7–10]. The DI has shown a steady decrease over the years, except that around 1980 the summertime DI leveled out while the wintertime DI continued its decreasing trend until the mid-1990s, when it leveled out. The DI for both summertime and wintertime reformulated gasolines is lower than for conventional gasolines.

Adding ethanol to hydrocarbon-only gasoline lowers the DI. However, vehicle testing by the CRC has shown that at equal DI values ethanol blends provide poorer cold-start and warm-up driveability. This effect has recently been addressed in Specification D4814 with a change in the DI equation.

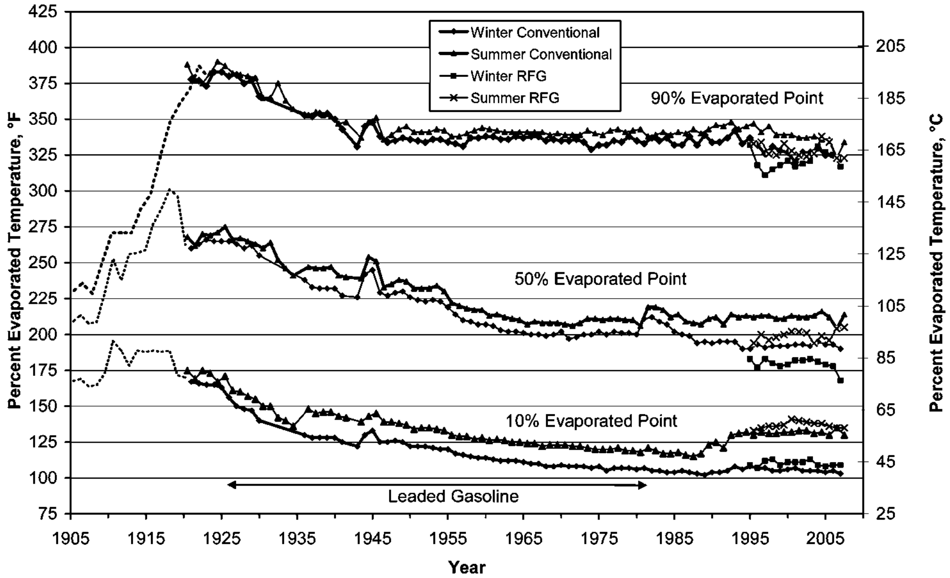

Fig. 5—United States regular grade national average distillation trends.

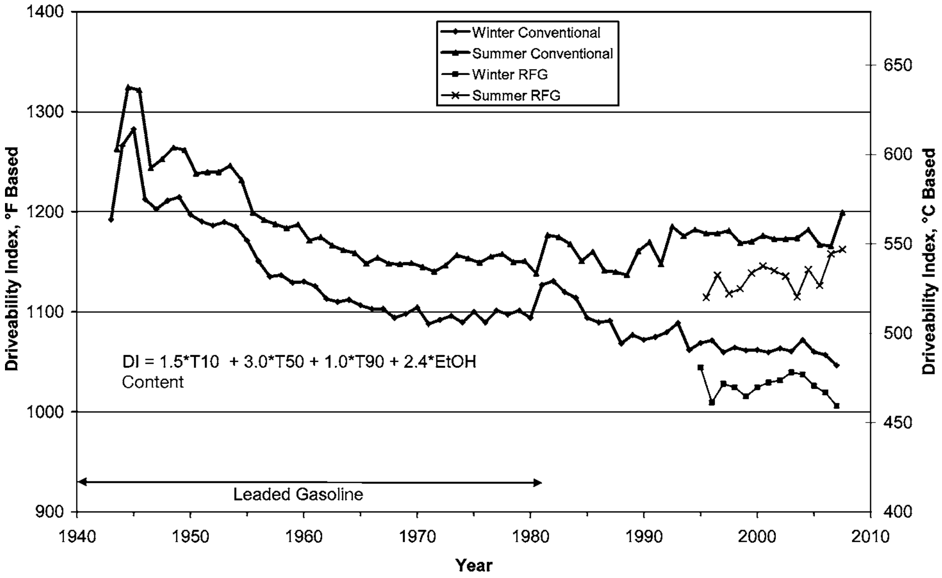

Fig. 6—United States regular grade national average driveability index trends.

Vapor-Liquid Ratio

Vapor pressure and distillation properties alone are not sufficient to define the volatility of spark-ignition engine fuel. At high operating temperatures, fuels can boil in fuel pumps, lines, or carburetors. If too much vapor is formed, the fuel flow to the engine can be decreased, resulting in poor engine performance or even engine stoppage. These conditions are known as "vapor lock." In fuel injected vehicles, the malfunctions encountered are hard starting after a hot soak, idle roughness, no-start, hesitation, etc., which are referred to as hot-fuel-handling driveability problems. Although the hot-fuel-handling problems and vapor locking tendency of gasoline are influenced both by the temperatures at the front end of its distillation profile and by its vapor pressure, the single property that correlates best with vehicle malfunction is the temperature at which the gasoline forms a vapor-liquid ratio of twenty ($T_{V/L=20}$). This is the temperature at which 20 volumes of vapor is in equilibrium with one volume of liquid at atmospheric pressure. Although this correlation was originally developed with carbureted vehicles, it has been shown to still predict hot-fuel-handling problems with fuel injected vehicles.

One standard test method for measuring vapor-liquid ratio is ASTM D2533, "Test Method for Vapor-Liquid Ratio of Spark-Ignition Engine Fuels." This method allows the use of either of two confining fluids: glycerin or mercury. Glycerin should be used as the confining fluid for gasolines that do not contain oxygenates. Mercury must be used as the confining fluid for gasolines that do contain oxygenates, and can also be used for gasolines that do not contain oxygenates. In D2533, a measured volume of liquid fuel at 0 °C (32 °F) is introduced into a glass buret filled with glycerol (nonoxygenated fuel) or mercury (for all fuels). The buret is heated to the desired temperature and the volume of vapor in equilibrium with the liquid is recorded after the pressure for the system has been adjusted to the desired pressure, usually one atmosphere. If the temperature corresponding to a given vapor-liquid ratio is desired—usually a $V/L = 20$—the vapor-liquid ratio is determined at several temperatures, the results plotted, and the temperature at the desired vapor-liquid ratio is read from the plot [4].

Another instrumental method that does not use a confining fluid and can be used for both gasolines and gasoline-oxygenate blends is ASTM D5188, "Test Method for Vapor-Liquid Ratio Temperature Determination of Fuels (Evacuated Chamber Method)." This method is applicable to samples for which the determined temperature is between 36 °C and 80 °C (97 °F and 176 °F) and the vapor-liquid ratio is between 8:1 and 75:1. In D5188, a calculated volume of air-saturated sample (all fuels) at 0 °C (32 °F) is introduced into an evacuated, thermostatically controlled test chamber of known volume. The sample volume is calculated to obtain the desired vapor-liquid ratio in the chamber. After injection, the chamber temperature is adjusted until a stable chamber pressure of 101.3 kPa (760 Torr) is achieved [4].

Appendix X2 of Specification D4814 includes a computer method, a linear equation method, and a nomograph method that can be used for estimating the temperature for a $T_{V/L=20}$ of gasolines from vapor pressure and distillation test results. However, these estimation methods are not applicable to gasoline-oxygenate blends.

Adding ethanol to hydrocarbon-only gasoline lowers the $T_{V/L=20}$ and increases the chances to encounter hot-fuel-handling and vapor lock problems. Vehicle testing by the CRC has shown that at equal $T_{V/L=20}$ values ethanol blends provide poorer hot-fuel-handling driveability. This effect is being addressed for incorporation into Specification D4814.

Figure 7 shows a histogram for the calculated temperature for a vapor-liquid ratio of 20 ($T_{V/L=20}$) [7–10]. Like vapor pressure with which it is highly correlated, $T_{V/L=20}$ decreased with time as vapor pressure increased. When vapor pressure was reduced by the EPA Phase I and Phase II regulations, $T_{V/L=20}$ increased. Summertime reformulated gasoline with its more restrictive vapor pressure has higher $T_{V/L=20}$ values than conventional gasoline.

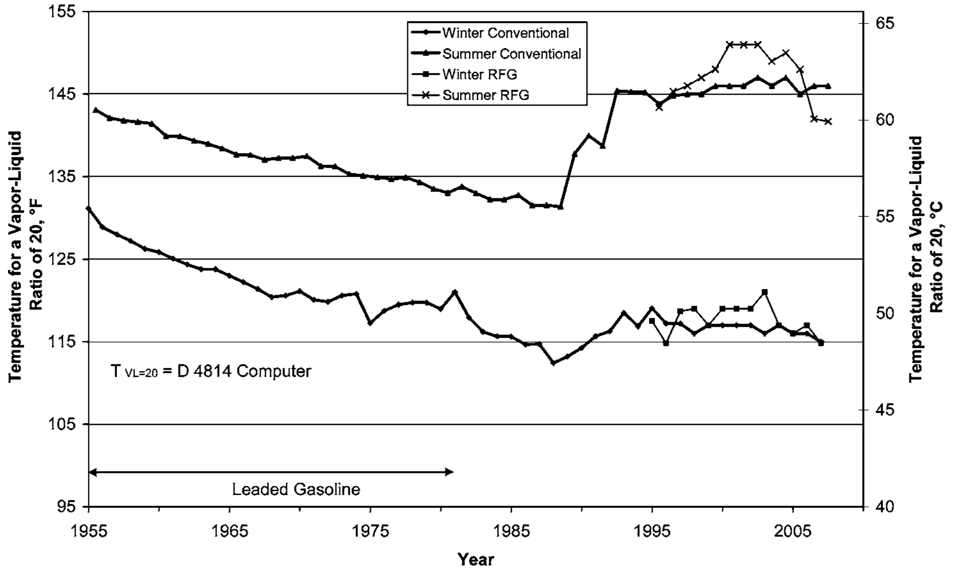

Fig. 7—United States regular grade national average temperature for a vapor-liquid ratio of 20 trends.

Vapor-Lock Index (VLI)

Outside the United States, Vapor Lock Index (VLI) is often used to control vapor lock and other hot-fuel handling problems. VLI is a calculated index using vapor pressure in kPa (VP) and distillation profile percent evaporated at 70 °C (158 °F) (E 70) fuel inspection data as follows:

$$\mathrm{VLI} = 10(\mathrm{VP}) = 7(\mathrm{E}\ 70)$$

VLI varies with the season. The normal range is 800 to 1250. Lower values provide greater protection against vapor lock and hot-fuel handling problems [4].

Volatility and Performance

In general terms, the following relationships between volatility and performance apply [1]:

1. High vapor pressures and low 10 % evaporated temperatures are both conducive to easy cold starting. However, under hot operating conditions, they are also conducive to increased vapor formation in fuel tanks, carburetors, and fuel injectors resulting in hot-fuel-handling and vapor lock problems. The amount of vapor formed in fuel tanks and carburetors, which must be contained by the evaporative emissions control system, is related to the vapor pressure and distillation temperatures. Thus, a proper balance must be maintained and seasonally adjusted for good overall performance.
2. Although vapor pressure is a factor in the amount of vapor formation under hot-fuel-handling driveability and vapor locking conditions, vapor pressure alone is not a good index. A better index for measuring the vapor locking performance of gasolines in cars equipped with carburetors is the temperature at which the V/L is 20 at atmospheric pressure. The lower the $T_{V/L=20}$, the greater the tendency to cause vapor lock and hot-fuel-handling problems. Vapor lock is much less of a problem for fuel injected cars, which have pressurized fuel systems. Instead if a too-volatile fuel is used in a fuel injected car, hard starting, rough idling, and in the extreme, no-start conditions are encountered.
3. The temperature for 50 % evaporated is a broad indicator of warm-up and acceleration performance under cold-starting conditions. The lower the 50 % evaporated temperature, the better the performance. (This statement is not always valid for gasoline-oxygenate blends, especially those containing alcohol.) The temperatures for 10 % and 90 % evaporated are also indicators of warm-up performance under cold-starting conditions, but to a lesser degree than the 50 % evaporated temperature. Lowering the 50 % evaporated point, within limits, also has been shown to reduce exhaust hydrocarbon emissions.
4. The temperature for 90 % evaporated and the final boiling point, or end point, indicate the amount of relatively high-boiling components in gasoline. A high 90 % evaporated temperature, because it is usually associated with higher density and high-octane number components, may contribute to improved fuel economy and resistance to knock. If the 90 % evaporated temperature and the end point are too high, they can cause poor mixture distribution in the intake manifold and combustion chambers (carbureted or port fuel injected vehicles), increased hydrocarbon emissions, excessive combustion chamber deposits, and dilution of the crankcase engine oil.
5. The Driveability Index represents the entire distillation curve. Lower values of DI mean greater volatility, which equates to better cold-start and warm-up driveability until some minimum level is reached at which no further improvement is observed. If the DI is too high, vehicle cold-start and warm-up driveability can be adversely affected. The maximum DI for each volatility class is limited by Specification ASTM D4814. A DI specification limit allows a refiner more flexibility in blending gasoline that provides proper cold-start and warm-up driveability compared to tight restrictions on

TABLE 1—Vapor pressure and distillation class requirements.

		Distillation temperatures, °C(°F), at % Evaporated[b]						
			50 vol %					
Vapor pressure/ distillation class	Vapor pressure,[a] max, kPa (psi)	10 vol %, max	min	max	90 vol %, max	End Point, max	Distillation Residue, vol. % max	Driveability index[c] max, °C(°F) Derived[d,e]
AA	54 (7.8)	70 (158)	77 (170)	121 (250)	190 (374)	225 (437)	2	597 (1250)
A	62 (9.0)	70 (158)	77 (170)	121 (250)	190 (374)	225 (437)	2	597 (1250)
B	69 (10.0)	65 (149)	77 (170)	118 (245)	190 (374)	225 (437)	2	591 (1240)
C	79 (11.5)	60 (140)	77 (170)	116 (240)	185 (365)	225 (437)	2	586 (1230)
D	93 (13.5)	55 (131)	66 (150)	113 (235)	185 (365)	225 (437)	2	580 (1220)
E	103 (15.0)	50 (122)	66 (150)	110 (230)	185 (365)	225 (437)	2	569 (1200)

[a] Consult EPA for approved test methods for compliance with EPA vapor pressure regulations.

[b] At 101.3 kPa pressure (760 mm Hg).

[c] Driveability index $(\mathrm{DI}) = 1.5T_{10} + 3.0T_{50} + 1.0T_{90} + 1.33\ ^\circ\mathrm{C}(2.4\ ^\circ\mathrm{F}) \times \mathrm{Ethanol\ Volume\ \%}$,, where T_{10} = distillation temperature, °C(°F) at 10 % evaporated, T_{50} = distillation temperature, °C(°F) at 50 % evaporated, and T_{90} = distillation temperature, °C(°F) at 90 % evaporated, and 1.33 is the coefficient of the volume % ethanol present when the distillation results are determined in degrees Celsius and 2.4 is the coefficient when distillation results are determined in degrees Fahrenheit.

[d] The DI specification limits are applicable at the refinery or import facility as defined by 40 CFR part 80.2 and are not subject to correction for precision of the test method.

[e] Since DI is an index and has no units, the standard temperature conversion from U.S. customary to SI units is not appropriate. The following equation is to be used to make the conversion: $\mathrm{DI}_{^\circ\mathrm{C}} = (\mathrm{DI}_{^\circ\mathrm{F}} - 176)/1.8$.

individual distillation points. As the ambient temperature is reduced, fuels with lower DI are required. The impact of oxygenates on DI and driveability has been under investigation. The addition of ethanol reduces DI, but driveability is not improved as might be expected. The DI equation has been modified to reflect the ethanol effect. The oxygenate effect may depend on the type of oxygenate, the ambient temperature, and the DI level of the fuel. The CRC continues to investigate this issue.

ASTM D4814, "Specification for Automotive Spark-Ignition Engine Fuel," includes a table of six volatility classes for vapor pressure, distillation temperatures, and Driveability Index (Table 1) and a separate table of six volatility classes for $T_{V/L=20}$ (Table 2). A combination of limits from these two tables defines the fuel volatility requirements for each month and geographic area of the United States. The specification also accounts for EPA regulations on vapor pressure and state implementation plan vapor pressure limits approved by EPA. These volatility characteristics have been established on the basis of broad experience and cooperation among gasoline and oxygenate suppliers, additive vendors, state and federal regulators, and manufacturers and suppliers of automobile vehicles and equipment. Fuels meeting this specification have usually provided satisfactory performance in typical passenger car service. However, certain equipment or operating conditions may require or permit variations from these limits.

TABLE 2—Vapor-lock protection class requirements.

Vapor-lock protection class	Temperature, °C(°F) for a Vapor/Liquid ratio of 20, min
1	60 (140)
2	56 (133)
3	51 (124)
4	47 (116)
5	41 (105)
6	35 (95)

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188 PPS 95/1, 193 PPS 96/1, 198 PPS 97/1, and 205 PPS 98/1; TRW 208 PPS 99/1, 213 PPS 2000/1, 218 PPS 2001/1, and 223 PPS 2002/1; NGMS 228 PPS 2003/1, 233 PPS 2004/1, 238 PPS 2005/3, 245 PPS 2006/3, and 250 PPS 2007/3 2008/3, Bartlesville, OK, 1986–2007.

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9

Distillation and Vapor Pressure Data of Diesel Fuels

Rey G. Montemayor[1]

Introduction and History [1,2]

THE DIESEL ENGINE IS A TYPE OF INTERNAL COMBUSTION engine. More specifically, it is a compression ignition engine in which the fuel is ignited by exposure to the high temperature and pressure of a compressed gas instead of a separate source of ignition such as a spark plug, as is the case of gasoline engines. The diesel cycle was invented in 1892 by Rudolf Diesel, and he received a patent for the diesel engine in 1893. Diesel experimented and built working models of his engine, the first model running under its own power with a 26 % efficiency. By 1897, he ran the "first diesel engine suitable for practical use," which operated at a 75 % efficiency. In 1898, he demonstrated his engine at the Exhibition Fair in Paris, fueled by peanut oil, a renewable biomass fuel, which was his original intent.

The early diesel engines were not small or light enough for anything but stationary use due to the size of the fuel injection pump. Diesel engines were produced primarily for industry and shipping in the early 1900s. Ships and submarines benefited greatly from the efficiency of the new diesel engine which began gaining popularity. The 1920s brought a new injection pump design that allowed the introduction of fuel as it entered the engine without the need of pressurized air and its accompanying tank. The engine was now manageable in size and small enough to be used in vehicles. During the mid-1920s, trucks using diesel engines became available. In 1936, Mercedez Benz built the first automobile with a diesel engine.

The development and the use of diesel engines in North America were largely due to the efforts of Clessie L. Cummins who, after he purchased the rights to the diesel engine in 1919, had worked with diesel engine problems prevailing at the time. Over the years, Cummins, founder of the Cummins Corporation, has continued to improve the efficiency of the diesel engine, providing technological innovations that set a high standard for the industry, exceeding the requirements of the Clean Air Act of 1970.

Rudolf Diesel intended the diesel engine to use a variety of fuels, and he envisioned the use biomass fuels in the 1890s. In the 1920s, the growth of the petroleum industry brought about alterations of diesel engines to utilize the lower viscosity of fossil fuel residue rather than a biomass based fuel. Before the 1970s, automobiles with diesel engines were not popular in the United States. They were traditionally perceived as heavier, noisier, having performance characteristics that made them slower to accelerate, and as being more expensive than gasoline vehicles. When the OPEC crisis came in 1973, the American public looked to diesel fuel, which was more efficient and more economical, and diesel-powered automobiles became attractive. European and Japanese diesel vehicles became prevalent at the time and even American manufacturers began producing diesel powered automobiles. However, the crude oil crisis stabilized in the 1980s and American diesel automobile production ceased in 1985. Present day diesel-powered automobiles continue to be manufactured mostly in Europe and Japan. In Europe and Asia Pacific, where tax rates make diesel fuel much cheaper than gasoline, diesel vehicles are very popular and newer designs have significantly narrowed performance differences between gasoline and diesel vehicles. Diesel engine efficiency and durability has kept it the engine of choice for trucks, heavy machinery, and marine engines. More recently, the use of alkyl esters of fatty acids derived from natural oils (biodiesels) have gathered momentum, especially in Europe. In the United States, there appears to be an urgency in developing the use of biodiesel fuels. Rudolf Diesel's vision of using renewable biomass fuel to run the diesel engine may be realized after all.

Diesel Engine Applications

There are many applications that use diesel engines other than automotive engines. Diesel engines vary greatly in size, power output, and operating speeds. Depending on the speed required for the application, the range of diesel engines can be roughly classified according to:

1. High speed application: approximately >1200 rpm. Examples are diesel engines that are used to power trucks, buses, locomotives, tractors, cars, yachts, compressors, pumps, and small generators. Conditions under these applications are frequent and wide variation in load and speed.
2. Medium speed application: approximately 300 to 1200 rpm. Large electrical generators, pumping units, and marine auxiliaries are examples.
3. Low speed application: generally <300 rpm. The largest diesel engines are used to power ships and other larger marine transport. Electric power generation also uses low speed diesel engines.

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Grades and Specification of Diesel Fuel

There are seven grades of diesel fuels suitable for the various types of diesel engines. These are covered in ASTM D975-06 "Standard Specification for Diesel Fuel Oils" [3]. These grades are described as follows:

1. Grade No. 1-D S15: A special purpose, light middle distillate fuel for use in diesel engine applications requiring a fuel with 15 wppm sulfur (maximum) and higher volatility than that provided by Grade No. 2-D S15 fuel.
2. Grade No. 1-DS 500: A special purpose, light middle distillate fuel for use in diesel engine applications requiring a fuel with 500 wppm sulfur (maximum) and higher volatility than that provided by Grade No. 2-D S500 fuel.
3. Grade No. 1-DS 5000: A special purpose, light middle distillate fuel for use in diesel engine applications requiring a fuel with 5000 wppm sulfur (maximum) and higher volatility than that provided by Grade No. 2-D S5000 fuel.
4. Grade No. 2-DS15: A general purpose, middle distillate fuel for use in diesel engine applications requiring a fuel with 15 wppm sulfur (maximum). It is especially suitable for use in applications with conditions of varying speed and load.
5. Grade No. 2-DS 500: A general purpose, middle distillate fuel for use in diesel engine applications requiring a fuel with 500 wppm sulfur (maximum). It is especially suitable for use in applications with conditions of varying speed and load.
6. Grade No. 2-DS 5000: A general purpose, middle distillate fuel for use in diesel engine applications requiring a fuel with 5000 wppm sulfur (maximum). It is especially suitable for use in applications with conditions of varying speed and load.
7. Grade No. 4-D: A heavy distillate fuel, or blend of distillate and residual oil, for use in low and medium speed diesel engines in applications involving predominantly constant speed and load.

Table 1 shows the detailed specification requirements for diesel fuel oils.

Distillation Data of Diesel Fuels

The distillation parameter specified in D975 is the 90 % recovered temperature by ASTM D86 "Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure" [3]. The minimum specified 90 % distillation temperature is 282 °C for Grade No. 2-D S15, for Grade No. 2-D S500, and for Grade No. 2-D S5000 fuels. The maximum specified 90 % distillation temperature is 288 °C for Grade No. 1-D S15, for Grade No. 1-D S500, for Grade No. 1-D S500; and 338 °C for Grade No. 2-D S15, for Grade No. 2-D S500, and for Grade No. 2-D S5000 fuels. For all grades, D2887 "Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography" [4] can be used as an alternate distillation test method, although the numerical requirement is changed to reflect the fact that this test method uses a different principle than D86 (the referee method). Grade No. 4-D does not have any distillation requirement.

Distillation characteristics are related to the volatility of the diesel fuel. The average volatility requirements for diesel fuels vary with use and depend on engine speed, size, and design. Fuels having too low volatility tend to reduce power output and fuel economy as a result of poor atomization. Those having too high volatility may reduce power output and fuel economy through vapor lock in the fuel system or inadequate droplet penetration from the nozzle. In general, the distillation range should be as low as possible without adversely affecting the flash point, burning quality, heat content, or viscosity of the fuel. If the 10 % boiling point temperature is too high, poor starting may result. An excessive boiling range from 10 % to 50 % boiling point may increase warm-up time. A low 50 % boiling point temperature is desirable to minimize smoke and odor. Low 90 % boiling point temperature and final boiling point (FBP) tend to ensure low carbon residues and minimum crankcase dilution [5]. Although the 90 % boiling point temperature is a specification parameter in D975, D86 10 % boiling point, 50 % boiling point (commonly referred to as mid-boiling point), 90 % boiling point, 95 % boiling point, and the FBP also contribute to the characterization of diesel fuel oils.

Distillation data for the various grades of diesel fuels to determine conformance to D975 specification are obtained primarily using the conventional D86 distillation procedure. However, as mentioned earlier, correlation equations have been developed to obtain correlated D86 distillation data from D2887 results. Generalized equations to give correlated D86 distillation values are given in Appendix X6 of D2887; namely, the STP 577 [6] and the API Procedure 3A3.2 correlations [7]. A recent version of D2887 gives an updated correlation equation developed for Jet Fuel and Diesel Fuel that gives correlated D86 distillation values from D2887 results. This is discussed in detail in Appendix X5 of D2887, and is summarized here for easy reference:

$$t_n = a_0 + a_1 T_{n-1} + a_2 T_n + a_3 T_{n+1} \tag{1}$$

where:

t_n = nth, boiling point temperature of correlated D86 boiling point,

a_i = ith coefficient from Table 2, and

T_n = nth boiling point temperature of D2887.

Table 2 is the same as Table X5.1 of D2887. The cross-method reproducibility between the correlated D86 values for Jet Fuel and Diesel Fuel and D2887 are given in Table X5.2 of D2887. In case of dispute, test method D86 has been designated as the referee method.

A specification requirement that uses D86 50 % boiling point temperature (T_{50}), is Cetane Index by ASTM D976 "Standard Test Method for Calculated Cetane Index of Distillate Fuels" [3]. This Cetane Index (also called the Two-Variable Cetane Index) gives a calculated value that is part of a requirement, originating with the U.S. Environmental Protection Agency, for control of aromatics content. The D976 Cetane Index requires density at 15 °C obtained by ASTM D1298 "Standard Practice for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method" [3] or D4052 "Standard Test Method for Density and Relative Density of Liquids by Digital Density Meter" [4], and D86 50 % boiling point temperature. The equation is given below:

TABLE 1—Detailed requirements for diesel fuels (from ASTM 975-05). [a]

Property	ASTM Test method[b]	Grade						
		No. 1-D S15	No. 1-D S500[c]	No. 1-D S5000[d]	No. 2-D S15	No. 2-D S500[c,e]	No. 2-D S5000[d,e]	No. 4-D[d]
Flash point, °C, min.	D93	38	38	38	52[e]	52[e]	52[e]	55
Water and sediment, % vol, max	D2709	0.05	0.05	0.05	0.05	0.05	0.05	…
	D1796	…	…	…	…	…	…	0.50
Distillation:								
one of the following requirements shall be met:								
1. Physical distillation	D86							
Distillation Temperature, °C 90 %, % vol recovered								
min		…	…	…	282[e]	282[e]	282[e]	…
max		288	288	288	338	338	338	…
2. Simulated distillation	D2887							
Distillation Temperature, °C 90 %, %vol recovered								
min						300[e]	300[e]	
max		304	304			356	356	
Kinematic viscosity, mm^2/S at 40 °C	D445							
min		1.3	1.3	1.3	1.9[e]	1.9[e]	1.9[e]	5.5
max	…	2.4	2.4	2.4	4.1	4.1	4.1	24.0
Ash % mass, max	D482	0.01	0.01	0.01	0.01	0.01	0.01	0.10
Sulfur, ppm (μg/g)[f] max	D5453	15	…	…	15	…	…	…
% mass, max	D2622[g]	…	0.05	…	…	0.05	…	…
% mass, max	D129	…	…	0.50	…	…	0.50	2.00
Copper strip corrosion rating max 3 h at 50 °C	D130	No. 3	No. 3	No. 3	No. 3	No. 3	No. 3	…
Cetane number, min[h]	D613	40[i]	40[i]	40[i]	40[i]	40[i]	40[i]	30[i]
One of the following properties must be met:								
(1) Cetane index, min.	D976-80[g]	40	40	…	40	40	…	…
(2) Aromaticity, % vol, max	D1319[g]	35	35	…	35	35	…	…
Operability Requirements								
Cloud point, °C, max	D2500	[j]	[j]	[j]	[j]	[j]	[j]	…
or								
LTFT/CFPP, °C, max	D4539/D6371							
Ramsbottom carbon residue on 10 % distillation residue, % mass, max	D524	0.15	0.15	0.15	0.35	0.35	0.35	…
Lubricity, HFRR @ 60 °C, micron, max	D6079	520	520	520	520	520	520	…

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[a] To meet special operating conditions, modifications of individual limiting requirements may be agreed upon between purchaser, seller, and manufacturer.

[b] The test methods indicated are the approved referee methods. Other acceptable methods are indicated in 4.1.

[c] Under United States regulations, if Grades No. 1-D S500 or No. 2-D S500 are sold for tax exempt purposes then, at or beyond terminal storage tanks, they are required by 26 CFR Part 48 to contain the dye Solvent Red 164 at a concentration spectrally equivalent to 3.9 lb per thousand barrels of the solid dye standard Solvent Red 26, or the tax must be collected.

[d] Under United States regulations, Grades No. 1-D S5000, No. 2-D S5000, and No. 4-D are required by 40 CFR Part 80 to contain a sufficient amount of the dye Solvent Red 164 so its presence is visually apparent. At or beyond terminal storage tanks, they are required by 26 CFR Part 48 to contain the dye Solvent Red 164 at a concentration spectrally equivalent to 3.9 lb per thousand barrels of the solid dye standard Solvent Red 26.

[e] When a cloud point less than -12°C is specified, as can occur during cold months, it is permitted and normal blending practice to combine Grades No. 1 and No. 2 to meet the low temperature requirements. In that case, the minimum flash point shall be 38°C, the minimum viscosity at 40°C shall be 1.7 mm2/s, and the minimum 90 % recovered temperature shall be waived.

[f] Other sulfur limits can apply in selected areas in the United States and in other countries.

[g] These test methods are specified in 40 CFR Part 80.

[h] Where cetane number by Test Method D613 is not available, Test Method D4737 can be used as an approximation.

[i] Low ambient temperatures as well as engine operation at high altitudes may require the use of fuels with higher cetane ratings.

[j] It is unrealistic to specify low temperature properties that will ensure satisfactory operation at all ambient conditions. In general, cloud point (or wax appearance point) Low Temperature Flow Test, and Cold Filter Plugging Point Test may be used as an estimate of operating temperature limits for Grades No. 1D S500; No. 2 D S500; and No. 1D S5000 and No. 2D S5000 diesel fuel oils. However, satisfactory operation below the cloud point (or wax appearance point) may be achieved depending on equipment design, operating conditions, and the use of flow-improver additives as described in X4.1.2. Appropriate low temperature operability properties should be agreed upon between the fuel supplier and purchaser for the intended use and expected ambient temperatures. Test Methods D4539 and D6371 may be especially useful to estimate vehicle low temperature operability limits when flow improvers are used. Due to fuel delivery system, engine design, and test method differences, low temperature operability tests may not provide the same degree of protection in various vehicle operating classes. Tenth percentile minimum air temperatures for U.S. locations are provided in Appendix X4 as a means of estimating expected regional temperatures. The tenth percentile minimum air temperatures may be used to estimate expected regional target temperatures for use with Test Methods D2500, D4539, and D6371. Refer to X4.1.3 for further general guidance on test application.

TABLE 2—Correlation coefficients for correlated D86 from D2887 equations.

t_n °C	a_0	a_1	a_2	a_3	T_{n-1}	T_n °C	T_{n+1}
IBP	25.350 6	0.322 16	0.711 87	–0.042 21	T_{IBP}	T_5	T_{10}
5 %	18.822 10	0.066 02	0.158 03	0.778 98	T_{IBP}	T_5	T_{10}
10 %	15.172 60	0.201 49	0.306 06	0.482 27	T_5	T_{10}	T_{20}
20 %	12.29 92	0.227 681	0.291 586	0.462 078	T_{10}	T_{20}	T_{30}
30 %	9.666 87	0.365 291	0.297 52	0.305 422	T_{20}	T_{30}	T_{50}
50 %	5.418 90	0.077 63	0.689 84	0.183 02	T_{30}	T_{60}	T_{70}
70 %	0.352 46	0.161 36	0.415 11	0.377 15	T_{50}	T_{70}	T_{80}
80 %	–0.215 36	0.256 14	0.409 25	0.279 95	T_{70}	T_{60}	T_{90}
90 %	0.099 66	0.243 35	0.320 51	0.373 57	T_{80}	T_{90}	T_{96}
95 %	0.898 80	–0.097 90	1.038 16	–0.008 94	T_{90}	T_{95}	T_{FBP}
FBP	21.631 1	–0.363 78	1.064 99	0.169 01	T_{90}	T_{95}	T_{FBP}

$$\text{Calculated Cetane Index (CCI)} = 454.74 - 1641.416\,D + 774.74\,D^2 - 0.554\,B + 97.803(\log_{10} B)^2 \tag{2}$$

where:

CCI = calculated Cetane index,

D = density at 15 °C by D1298 or D4052, in g/Ml, and

B = 50 % recovered boiling point temperature by D86, in °C, and corrected to standard barometric pressure.

A second test method for calculating CCI is ASTM 4737 “Standard Test Method for Calculating Cetane Index by Four Variable Equation” [4]. D4737 can be used to determine an approximation of the Cetane number, a critical measure of the ignition quality of the diesel fuel and influences combustion roughness. This method requires the density at 15 °C obtained by D1298 or D4052, and D86 10 % recovered, 50 % recovered, and 90 % recovered temperature. The equation for Grade No. 1-D S500, Grade No. 1-D S5000, Grade No. 2-D S5000, and Grade No. 4-D is given below:

$$\text{Calculated Cetane Index (CCI)} = 45.2 + (0.0892)T_{10N} + [0.131 + (0.901)B](T_{50N}) + [0.0523 - (0.420)B](T_{90N}) + [0.00049][(T_{10N})^2 - (T_{90N})^2] + 107\,B + 60\,B^2 \tag{3}$$

where:

CCI = calculated Cetane index,

D = density at 15 °C by D1298 and D4052, in g/ Ml,

$DN = D - 0.85$,

$B = [e^{(-3.5)/DN}] - 1$,

T_{10} = 10 % recovered boiling point temperature by D86, in °C, and corrected to standard barometric pressure,

$T_{10N} = T_{10} - 215$,

T_{50} = 50 % recovered boiling point temperature by D86, in °C, and corrected to standard barometric pressure,

$T_{50N} = T_{50} - 260$,

T_{90} = 90 % recovered boiling point temperature by D86, in °C, and corrected to standard barometric pressure, and

$T_{90N} = T_{90} - 310$.

The equation for Grade No. 2-D S500 is:

$$\text{CCI} = -386.25\,D + 0.1740\,T_{10} + 0.1215\,T_{50} + 0.01850\,T_{90} + 297.42 \tag{4}$$

where D, T_{10}, T_{50} and T_{90} have the same definition as those given in Eq (3).

There are limitations to the cetane index calculated by these methods. These are:

(1) It is not applicable to fuels containing cetane improving additives.

(2) It is not applicable to pure hydrocarbons, synthetic fuels such as certain products derived from shale oils and tar blends, alkylates, or coal-tar products, or fuels containing biodiesel.

(3) Inaccurate results may occur if used for crude oils, residuals, or products having a D86 FBP temperature below 250 °C.

For biodiesel, the applicable specification is given by ASTM D6751 “Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels” [8]. A 360 °C maximum 90 % recovered atmospheric equivalent temperature by ASTM D1160 “Standard Test Method for Distillation of Petroleum Products at Reduced Pressure” [3] is specified in D6751.

Vapor Pressure Data of Diesel Fuels

Because of the relatively low volatility of the various grades of diesel fuel, vapor pressure is not part of the specifications covering diesel fuels or biodiesel. The low volatility of diesel fuel would mean fairly low vapor pressure, and would not be a concern for environmental regulators. As a result, there are no data available on the vapor pressure of diesel fuel or on any characteristics of these fuels requiring vapor pressure data.

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10

Distillation and Vapor Pressure in Aviation Fuels

Kurt H. Strauss[1]

Aviation Gasoline

Distillation

HISTORY—UNTIL THE START OF WORLD WAR II, there were as many as 12 grades of aviation gasoline on the market, including three military and a number of proprietary specifications. However, distillation characteristics differed only slightly between the various grades, the main differences being in the octane requirements. To meet new performance requirements and to rationalize supplies during WW II, a single set of distillation requirements was adopted by the military specification AN-F-28, later MIL-G-5572. These same requirements were accepted for civil fuels in D910 in 1945 and are listed in Table 1. They have remained unchanged until the present. Because aviation gasoline is in very limited use in the U.S. military, Specification MIL-G-5572 was dropped in March 1988 and any military purchases of aviation gasoline are to specification D910.

Performance—Aviation gasoline volatility is controlled by a combination of distillation and vapor pressure limits. (Vapor pressure limits are discussed later on in this chapter.) Because of the extreme operating requirements of aviation gasoline, the volatility range has to allow for fuel evaporation, i.e., engine starting, at very low temperatures, but at the same time protect against vapor lock at elevated fuel system temperatures as well as help prevent carburetor icing at low temperatures. Additional limitations can be placed on the fuel by high altitude conditions where very low ambient pressures in unpressurized aircraft tankage could lead to high evaporation losses. Because of major differences in the performance of specific engines and aircraft, an aircraft designer is forced to adjust the design to accommodate existing fuel specifications. Any new aircraft/engine system has to be tested over a wide range of operating conditions to assure safe operation. Ultimately, the combination of fuel volatility and specific aircraft/engine designs becomes a rather inflexible operating system with little permissible variability. To simplify world-wide usage, other international specifications have incorporated the same volatility limits.

As in automotive engines, the front end distillation limits define the evaporability of the gasoline, with lower distillation limits representing more volatile fuel. However, because the same distillation limits apply to systems ranging from simple carburetors to complex injection systems in supercharged engines, clear-cut relationships between front end volatility and aircraft performance exist only for specific systems and do not apply across the aircraft/engine spectrum.

TABLE 1—Volatility specifications for aviation gasolines.

Property	Requirements		
	D910, all grades		D6227, 82 UL
Distillation, °C			
Initial boiling point, °C	Report		—
Fuel evaporated			
10 volume % at °C	Max	75	70
40 volume % at °C	Min	75	—
50 volume % at °C	Max	105	121
90 volume % at °C	Max	135	190
Final boiling point, °C	Max	170	225
Sum of 10% + 50% evaporated temperatures, °C	Min	137	—
Recovery volume, %	Min	97	95
Residue volume, %	Max	1.5	2
Loss volume, %	Max	1.5	3.0
Vapor Pressure, 38 °C, kPa	Min	38	38
	Max	49	62

Composition—Distillation limits also have to reflect compositional differences, particularly for the high octane grades where only a limited number of hydrocarbon compounds have the necessary knock characteristics. One limit intended specifically to control composition is the sum of the temperatures of the 10 and 50 percentage points, which guards against a fuel consisting of only a very light and a heavy component: so-called dumbbell blends. Such blends have caused performance problems and are therefore not allowed.

Testing—Distillation characteristics of aviation gasoline have been and continue to be established by D86. A typical distillation curve for aviation gasoline is in Fig. 1.

Vapor Pressure

History—Vapor pressure limits were developed in parallel with front end distillation limits. While the two properties are interrelated, compositional effects and measurement scatter mitigate against an accurate estimation of vapor pressure based on distillation data. By limiting both properties, the evaporation rate and vapor lock characteristics of gasolines are controlled more precisely. Thus, the maximum vapor pressure, together with an initial boiling point, was set

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[1] Consultant, 640 Ocean Avenue, Portland ME 04103.

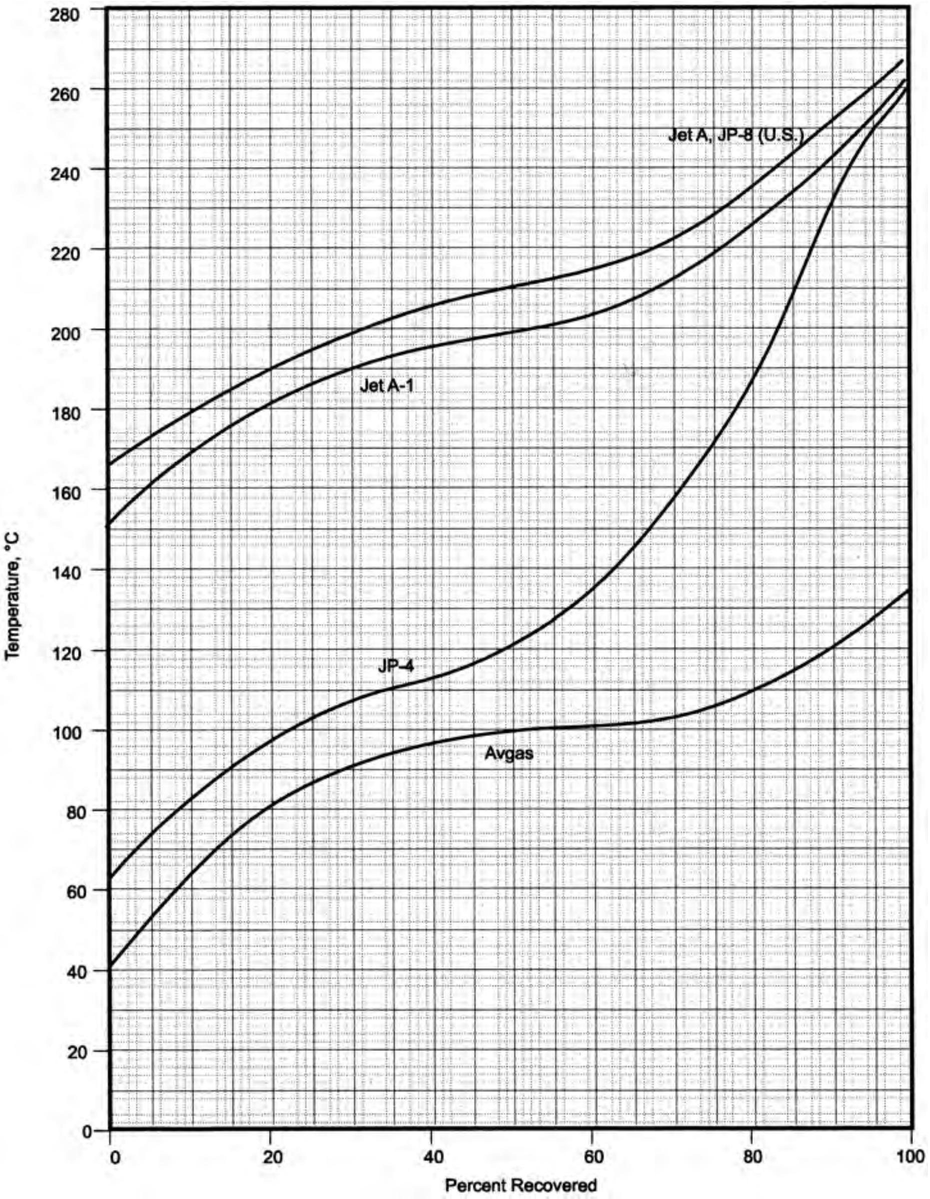

Fig. 1—Aviation fuel distillation curves (part 1) taken from CRC Report 635.

to minimize carburetor icing and prevent vapor lock. While carburetor icing is caused by the temperature drop across the throttle plate due to fuel evaporation and depends on the moisture in the air, fuel volatility does affect the temperature decrease across the carburetor plate. Vapor lock occurs when the absolute pressure in a fuel line is lower than the vapor pressure of the fuel, causing fuel vapor formation that exceeds the fuel pump's capacity. The minimum vapor pressures assured adequate evaporation for low temperature starting. Vapor pressure specification limits are also listed in Table 1. Unlike motor gasoline the vapor pressure for aviation gasoline is not adjusted for climatic or seasonal changes but remains constant regardless of geographic location or seasonal conditions.

Testing—Aviation gasoline vapor pressure or Reid vapor pressure is measured by D323, D5191, or D5190, all performed at 38 °C. Proper sampling is essential to obtaining valid test results.

Aviation Gasoline Versus Motor Gasoline

Comparisons of aviation gasoline and motor gasoline volatilities show the distillation and vapor pressures of motor gasoline to have a wider range than those for aviation gasoline. The approved use of motor gasoline in aircraft systems therefore depends on the specific aircraft design and has to be substantiated by extensive performance tests, particularly under hot takeoff conditions. Once substantiated, such use is legalized by Supplemental Type Certificates (STCs), which are issued by civil air authorities for each aircraft/engine combination. A new aviation gasoline specification, D6227, is based on blends of motor gasoline components, but use of this fuel is limited to aircraft systems designed for this fuel. D6227 must be listed or referenced in the aircraft's Type Certificate or in an appropriate STC. Distillation and vapor pressure limits for this fuel, Grade 82 UL, are shown in Table 1.

TABLE 2—Volatility specifications for current U.S. Military aviation turbine fuels.

Specification	MIL-DTL-5624		MIL-PRF-38219	MIL-PRF-83133	MIL-PRF-25524
Grade	JP-4	JP-5	JP-7	JP-8	JP-TS
Distillation, °C by ASTM D86					
Initial boiling point	Report	Report	182 min	Report	157 (105)[a] min
Fuel recovered					
10%	Report	206 (185)[a] max	196 min	205 (186)[a] max	193 (174)[a] max
20%	100 min	Report	206 min	Report	—
50%	125 min	Report	Report	Report	204 (207)[a] max
90%	Report	Report	260 max	Report	238 (250)[a] max
End point	270 max	300 (330)[a] max	288 max	300 (330)[a] max	260 (288)[a] max
Residue, %, max	1.5	1.5	1.5	1.5	1.5
Loss, %, max	1.5	1.5	1.5	1.5	1.5
Vapor pressure, kPa, 38 °C					
Min —	14	—	—	—	
Max —	21	—	—	—	
Vapor pressure, kPa					
at 149 °C	—	—	20.7 max	—	
at 260 °C	—	—	331 max	—	
Flash point, °C, min	—	50	50	38	43

[a] Limits in parentheses are by D2887.

Quality Protection of Aviation Gasoline Volatility

Handling and Storage Effects—Inadvertent mixing with a higher vapor pressure product is the most likely reason for an increase in vapor pressure above the maximum allowed. Tank venting from storage tanks or drums can result in the loss of light ends. This, in turn, can drop the vapor pressure below the allowed minimum level but can also decrease the gasoline's octane rating. Lead content may also increase beyond its maximum specified concentration on loss of light ends. Mixing with lower vapor pressure products such as jet fuel or heating oil will cause other properties, particularly octane ratings, to fail first. Experience indicates that vapor pressure is the more sensitive volatility parameter compared to distillation and is more likely to go off specification first. It is important to note that all aviation fuels must meet the fuel specification at the time of aircraft fueling and changes in vapor pressure or distillation above or below specification limits therefore make the product unsuitable for aircraft use.

Non-Petroleum Fuels for Reciprocating Aircraft Engines

Non-petroleum fuels such as ethanol are in extremely limited use and are not covered in this discussion. Their volatility can be significantly different from the conventional aviation gasolines.

Aviation Turbine Fuels

A major difference between gasoline and turbine fuels is in their respective volatilities. While gasolines have to evaporate at relatively low temperatures to be in gaseous form when entering the combustion chamber, turbine fuels can have lower volatilities because they are injected as a fine mist into high pressure systems where evaporation takes place virtually at the flame front. In turn, the lower volatility becomes advantageous in reducing evaporation at the low pressures of high altitudes.

Volatility of Military Fuels

History of Military Turbine Fuels—Early gas turbines were developed on special kerosine-type fuels defined by U.S. military grade JP-1. To drastically increase fuel availability, the U.S. Air Force changed in 1947 to a wide boiling range fuel consisting of blends of kerosine and heavy naphtha. This JP-3 grade (Military Specification AN-F-58) had relatively few distillation limits and had the same vapor pressure limits as aviation gasoline. When high speed jet fighters of the 1960s experienced large fuel losses during rapid climbs to cruising altitude, the vapor pressure limits of the JP-3 grade were reduced to 14–31 kPa (2–3 psi) in a new JP-4 grade and have remained at that level. The U.S. Air Force has now changed from the JP-4 grade to the JP-8 grade whose volatility matches the civil grades Jet A and A-1. Volatility limits for various military fuels are listed in Table 2. This table also lists the applicable military specifications for these grades. Typical distillation curves for various turbine fuels are shown in Figs. 1 and 2.

When changing from piston-engined to jet powered aircraft on aircraft carriers, the U.S. Navy modified the carrier fuel systems from water displacement to conventional pumping systems, leaving empty tank vapor spaces as jet fuel was withdrawn. If these systems were to contain JP-4 fuel, the vapor spaces could be flammable. To avoid the problem, the Navy developed its own shipboard fuel, Grade JP-5, a lower volatility fuel with higher flash points and distillation limits than contemporary Air Force fuels.

As a specialty fuel for very high speed aircraft the U.S. Air Force maintains Grade JP-7, a very low volatility fuel. A different specialty fuel, Grade JP-TS, is for use in the U-2 aircraft. Volatility limits for both grades are also listed in Table 2.

Volatility of Civil Fuels

History of Civil Turbine Fuels—The first civil turbine fuel specification, D1655, issued in 1959, listed three grades. Jet A and Jet A-1 were kerosine-type fuels with differing freezing

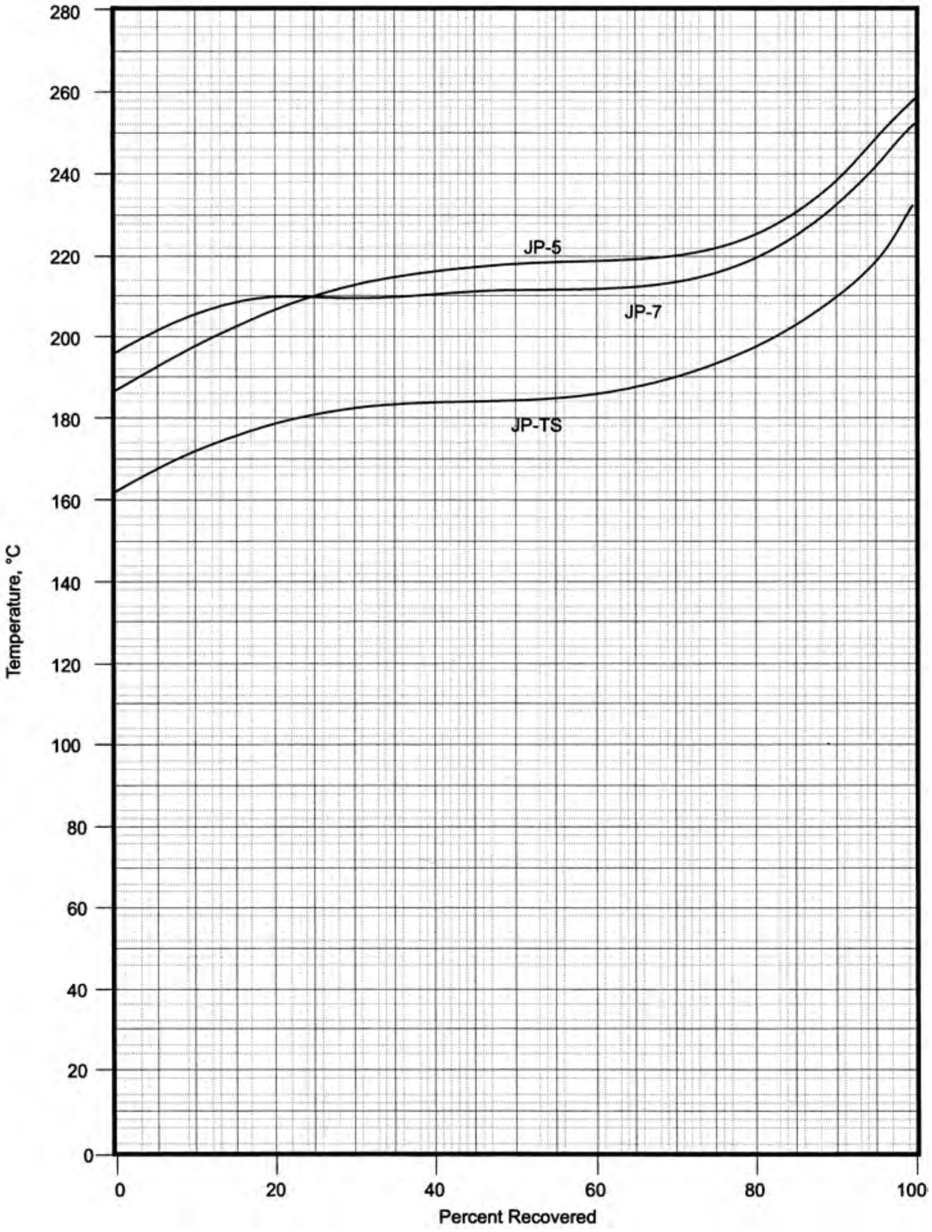

Fig. 2—Aviation fuel distillation curves taken from CRC Report 635.

points, while Jet B was a wide-boiling fuel directly comparable to JP-4. In actual, practice Jet B was only in limited airline use and today neither JP-4 nor Jet B exist in significant volumes.

At this point it is pertinent to digress to a discussion of kerosine fuel volatility control. As mentioned earlier, distillation controls on these fuels are few and do not significantly affect kerosine volatility. Because the Reid vapor pressures of kerosine-type fuels are very low (on the order of 1.4–2.8 kPa or 0.2–0.4 psi), volatility is controlled by flash point limits and vapor pressure does not appear in the specifications for these grades. In turn, the maximum boiling range and therefore the availability for these fuels is limited by flash point and freezing point. However, vapor pressure plays an important part in fuel system design, particularly at elevated temperatures. In such cases the designer resorts to true vapor pressure, which is not called out in specifications but will be found in various handbooks, particularly the CRC *Handbook for Aviation Fuel Properties*.

Current Status for Civil Aircraft Turbine Fuels—Today, Jet A is in general use in the United States and limited use in Canada; Jet A-1 is the turbine fuel grade available in the rest of the world. Distillation and flash point limits for these grades are shown in Table 3. As mentioned above, the military fuel JP-8 corresponds to Jet A-1 except for additive content. The Jet B grade has been dropped from D1655 because of limited use and is incorporated in a separate specification, D6615.

While a number of research efforts are exploring the suitability of different fuels such as biofuels or fuels from synthetic stocks, there is little reason to expect that the volatility of these materials will differ significantly from existing

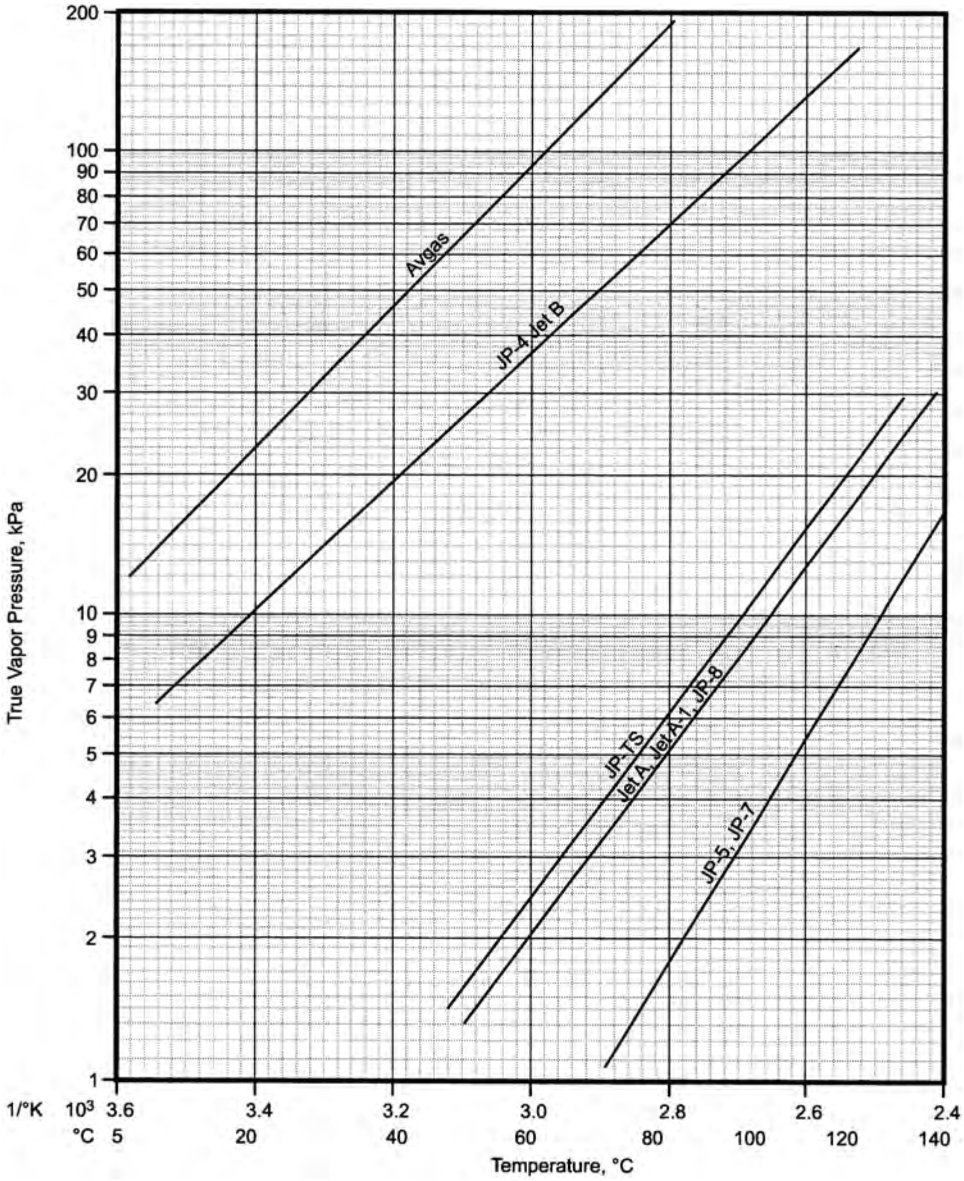

Fig. 3—Absolute vapor pressures of aviation fuels taken from CRC Report 635.

turbine fuels because these fuels will have to be operable in existing engine/airframe systems.

Test Methods—The distillation characteristics of aviation turbine fuels have been measured by D86. However, refinery automation has seen the increasing use of D2887. This method uses a chromatographic method to measure fuel boiling points. The results tend to differ from D86, particularly in the initial and the final parts of the distillation. Consequently some limits in the specifications are different for D2887 than for D86. Both sets of limits are shown in Tables 2 and 3.

Vapor Pressure

As mentioned above, Reid vapor pressure for the wide boiling JP-4 fuel is measured by D323. The test methods for the estimation of absolute vapor pressure for JP 7 are detailed in the appendices of Specification MIL-PRF-38219. When true vapor pressures at elevated temperatures are required for design purposes, typical vapor pressure versus temperature data can be found in the CRC *Handbook of Aviation Fuel Properties*. Figure 3 is taken from this source and shows typical true vapor pressures for a variety of military and civil fuels over a range of temperatures.

Quality Protection of Aviation Turbine Fuel Volatility

Handling and Storage Effects—Mixing with a higher vapor pressure or lower flash point product is the most likely reason for a decrease in flash point below minimum requirements. It is the most common cause for product specification failure in multi-product transport systems. Such mixing is even more critical for the high flash products such as JP-5 or JP-7. The inadvertent addition of heavier products is unlikely to affect kerosine volatility, but can adversely impact other properties such as freezing point. Extended storage

TABLE 3—Volatility specifications for current civil aviation turbine fuels.

Specification Grade	ASTM D1655 Jet A/Jet A-1	ASTM D6615 Jet B
Distillation, °C by D86		
Fuel recovered		
10%	205 max	—
20%	—	145 max
50%	Report	190 max
90%	Report	245 max
End point	300 max	—
Residue, %, max	1.5	1.5
Loss, %, max	1.5	1.5
Distillation, °C by D2887		
Fuel recovered		
10%	185 max	
50%	Report	
90%	Report	
Final boiling point	340 max	
Vapor pressure, kPa, 38 °C		
Min	—	14
Max	—	21
Flash point, °C, min	38	

normally has no effect on volatility but can cause other properties to deteriorate.

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Distillation and Vapor Pressure Data of Solvents

Rey G. Montemayor[1] and John W. Young[2]

Solvents

THE TERM "SOLVENT" REFERS TO A SUBSTANCE, usually a liquid, which is able to dissolve or disperse a particular substance or ingredient. Solvents are used in numerous industrial, commercial, and consumer products.

Specifications for solvents and chemical intermediates (a substance with a distinct molecular composition that is produced or consumed in a chemical process) invariably include volatility parameters such as initial and final boiling points as well as boiling point range. In this chapter, solvent volatility properties and how they relate to evaporation rate will be covered.

Characterization of Solvent Volatility

Background

Atmospheric laboratory batch distillation test methods are widely recognized and accepted as a means of determining quantitatively the boiling range characteristics of fuels, solvents, and related materials. Three commonly used and cited batch distillation test methods are:

- ASTM D86 "Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure" [1]
- ASTM D850 "Standard Test Method for Distillation of Industrial Aromatic Hydrocarbons and Related Materials" [2]
- ASTM D1078 "Standard Test Method for Distillation Range of Volatile Organic Liquids" [2]

These test methods are used to characterize organic liquids such as hydrocarbons, oxygenated compounds, chemical intermediates, and blends thereof, and to determine conformance to specific industry standard specifications, commercial contract agreements, refinery control specifications, and compliance to regulatory requirements. When distillation data are required to determine conformance to a specific standard or specification, it is critical that the "correct" distillation test method be used.

Test Method D86 is used to determine quantitatively the boiling range characteristics of products as such natural gasolines, light and middle distillates, automotive fuels, aviation gasolines, aviation turbine fuels, diesel fuels, petroleum spirits, naphthas, white spirits, kerosene, and burner fuels. Test Method D1078 is used to determine the distillation range of organic liquids such as hydrocarbons, oxygenated compounds, chemical intermediates, and blends thereof boiling between 30 °C and 350 °C (that are chemically stable during the distillation process). Test Method D850 is used to determine the distillation range of industrial aromatic hydrocarbons and related materials of relatively narrow boiling ranges from 30 °C to 250 °C.

In general, Test Method D86 is applicable to materials with broad (wide) boiling ranges. Test Methods D1078 and D850 are applicable to materials with narrower boiling ranges and the manual procedures generally use thermometers with smaller subdivisions and narrower temperature measurement ranges than thermometers specified for use in Test Method D86 (see Tables 1–3). Although Test Methods D86, D850, and D1078 use relatively simple equipment (much of which is common for all three test methods), rigorous attention to procedural details in the individual test methods is required to ensure that repeatable and reproducible distillation data are produced.

Solvent Types

Hydrocarbon Solvents

Hydrocarbon solvents are composed of carbon and hydrogen. The primary source of hydrocarbon solvents is the petroleum industry. Petroleum solvents are often derived from liquid fractions collected during the refining of crude oil (petroleum).

Heteroatom-Containing Hydrocarbon Solvents

Solvents consisting of carbon and hydrogen as well as other heteroatoms such as oxygen, halogens (chlorine, bromine, etc.), nitrogen, and sulfur. Solvents containing heteroatoms are generally manufactured in petrochemical plants.

Hydrocarbon Solvents

Petroleum solvents derived from liquid fractions of crude oil are typically complex mixtures of *n*-paraffins, *i*-paraffins, cycloparaffins, and aromatic hydrocarbons. Liquid petroleum fractions often undergo additional processing (refining) to remove undesirable components such as sulfur and nitrogen species, traces of olefinic compounds, and aromatic hydrocarbons. The type of process-ing that petroleum fractions undergo ultimately determines the physical prop-

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erties of the "solvent" and its chemical composition. A key physical property used in the characterization of these products is the boiling point range of the material. Boiling ranges of petroleum solvents and petrochemical products are generally characterized using atmospheric laboratory batch distillation test methods.

Naphtha

Naphtha products are derived from petroleum and are volatile to moderately volatile hydrocarbon solvents—mainly aliphatic (composed of a mixture of *n*-paraffins, *i*-paraffins, cycloparaffins) and some aromatic hydrocarbons. These products are fractionally distilled under refinery operating conditions to yield various kinds of naphtha solvents. Common examples are: "petroleum ether" (with various boiling point ranges) and Varnish Makers and Painters Naphtha (VM&P). VM&P naphthas as specified in the ASTM D3735 "Standard Specification for VM&P Naphthas" [2] cover four types; Type I–Regular, Type II–High flash, Type III–Odorless, and Type IV–Low aromatics.

Mineral Spirits

Mineral Spirits (Stoddard solvents) are aliphatic solvents composed of a mixture of *n*-paraffins, *i*-paraffins, cycloparaffins, and aromatic hydrocarbons. ASTM D235 "Standard Specification for Mineral Spirits (Petroleum Spirits) (Hydrocarbon Dry Cleaning Solvent)" [2], covers four types of hydrocarbon solvent used primarily in the coatings, industrial cleaning and dry-cleaning industries. In Standard D235, Mineral Spirits are classified as Type I–Full Range, Type II–High Flash Point, Type III–Odorless and Type IV–Low Dry Point. Mineral spirits are further differentiated based on aromatics content as Class A–8 to 22 volume % aromatics, Class B–2 to 8 max volume % aromatics and Class C–less than 2 volume % aromatics.

Low Boiling Aliphatic Solvents

Low boiling aliphatic solvents are volatile aliphatic hydrocarbon solvents, (composed of a mixture of *n*-paraffins, *i*-paraffins, cycloparaffins, and some aromatic hydrocarbons). Hydrocarbon solvents consist mainly of saturated hydrocarbons species. Specific low boiling fractions from petroleum refining operations can undergo hydroprocessing to reduce the aromatics content. Examples include solvents such as iso-pentane pentane, mixed-hexane, and commercial (mixed) heptane. These types of solvents are usually mixtures of isomers (with a limited carbon number distribution). End uses for these materials includes coatings, inks, adhesives, oil seed extraction, and components for formulated products.

Naphthenic/Cycloparaffinic Solvents

These are hydrocarbon solvents are composed primarily of cycloparaffins. Although cycloparaffins are present in a small quantity in naphtha solvents, pure cycloparaffins such as cyclohexane are used as a chemical intermediate in the manufacture of nylon fibers, engineering resins, plasticizers, polyurethane, polyester, and epoxy resins.

Isoparaffinic Solvents

These are composed primarily of *i*-paraffins. Isoparaffinic solvents are used as reaction diluents, formulation components for industrial and consumer products, coatings, inks, and adhesive. Isoparaffinic solvents typically have a very low odor.

Aromatic Solvents

The more common aromatic hydrocarbon solvents are benzene, toluene, and xylenes. Typically, these "pure" aromatics are recovered from refinery feed streams (such as reformate) via extraction processes. Pure aromatic solvents such as benzene, toluene, and mixed xylene (a mixture of *o*-xylene, *m*-xylene, *p*-xylene, and ethyl benzene) typically have very narrow boiling ranges. Benzene is used as a chemical intermediate in the manufacture of styrene. Isopropyl benzene (cumene) is used as a chemical intermediate in the manufacture of other chemicals including phenol and acetone. *o*-Xylene is used as a feedstock for phthalic anhydride manufacture, *m*-xylene is used in the manufacture of isophthalic acid, and *p*-xylene (the most important commercial isomer) is used in the manufacture of polyester fibers and films. Toluene and xylene (and heavier aromatic solvents) are commonly used formulation components in coatings and adhesives.

Heteroatom-Containing Hydrocarbon Solvents

Oxygenated Solvents

The largest group of heteroatom-containing hydrocarbon solvents is the oxygenated solvents. The various types of oxygen-containing solvents are discussed below.

Ketones—Examples of ketones include acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK). Acetone is often used in aerosols and spray coatings. MEK and MIBK are extensively used as active solvents in synthetic lacquers and paint resins. In the petroleum industry, MEK and MIBK are also used in the dewaxing of lube oils.

Esters—Esters used as solvents include alkyl acetates and propionates, as well as glycol ether acetates. Glycol ether acetates are used as retarder (tail) solvents in solvent-based coatings and as coalescers in latex paints.

Glycol ethers—These are the type of oxygenated solvents that contains the ether and hydroxyl functional group. Glycol ethers are used in the coatings industry as coupling agents in water-based coating formulations. Examples of glycol ethers include: 2-methoxyethanol and 2-ethoxyethanol.

Alcohols—Alcohols including methyl alcohol, propyl alcohol, ethyl alcohol, isopropyl alcohol, and sec-butyl alcohol find applications as solvents for nitrocellulose lacquers, melamine-formaldehyde and urea formaldehyde resins, and other alkyd resins. Alcohols are also used as chemical raw materials in the manufacture of ketones, esters, monomers, and synthetic polymers.

Chlorinated and Other Heteroatom-Containing Hydrocarbon Solvents

Another type of heteroatom-containing solvents are chlorinated solvents such as methylene chloride (used in many paint removers) and trichloroethylene (used widely in industrial and metal cleaning in vapor degreasing operations).

TABLE 1—Typical distillation specifications of hydrocarbon solvents [3].

Solvent	ASTM Specification	IBP-Dry Point, °C	ASTM Test Method
Hexanes	D1836	64–70	D86
Heptanes		94–99	D86
Mineral spirits			
Type I-Regular	D235	149–213	D86
Type II-High flash	D235	177–213	D86
Type III-Odorless	D235	149–213	D86
Type IV-Low dry point	D235	149–185	D86
VM&P Naphtha			
Type I-Regular	D3735	113–154	D86
Type II-High flash	D3735	138–177	D86
Type III-Odorless	D3735	113–154	D86
Type IV-Low aromatics	D3735	113–154	D86
Cyclohexane	D5309	79–81	D86
Toluene	D841	110–111	D850
Mixed xylenes	D843	137–142	D850
o-Xylene	D5471	143–145	D850
p-Xylene	—	139–140	D850
m-Xylene	D5136	138–139	D850
Ethyl benzene	—	136–137	D850
High flash aromatics			
Type 1-Arom 100	D3734	149 -179	D86
Type II–Arom 150	D3734	177–216	D86

There other solvents containing other heteroatoms such as nitrogen and sulfur. However, their applications as solvents are fairly limited, and are therefore beyond the scope of this chapter.

Distillation Specification in Solvents

Hydrocarbon solvents are essential formulation ingredients for many coating, ink, and adhesive products. In these products, solvents function in a fugitive manner; that is to say, that they do the job they are designed for (solvating or dispersing resins, additives, dyes, pigments, etc.) then leave by evaporation, diffusion, or biodegradation. How quickly a solvent product leaves a coating, ink, or adhesive product is dependent on the volatility of the fluid (e.g., evaporation rate, dry time). Normally, the distillation range of a solvent product dictates solvent volatility. Solvents with low initial boiling points and dry points tend to be more volatile than solvents having higher initial boiling points and dry points. In addition, solvents with narrow distillation ranges typically are more volatile (i.e., evaporate more rapidly) than materials with broad distillation ranges (for materials of the same chemical composition with comparable initial boiling points). In addition to impacting the evaporation rate of a product, volatility affects a solvent products flash point. The flash point is defined as the lowest temperature at which solvent vapors will ignite in the presence of air/oxygen and an ignition source. Materials with high initial boiling points have higher flash points. Materials with low initial boiling points have lower flash points. This is an important consideration for most facilities, since fire codes, and regulations focus on flash point as a means of establishing if materials or products can be stored in warehouse facilities, special fire containment facilities, environmentally controlled containment facilities, or stored outdoors. However, the topic of flash point is covered in another ASTM International manual currently being written.

Most of the solvents discussed have distillation specifications that need to be met when marketed as a commercial solvent. Table 1 gives information on the various distillation specification or typical boiling points of a number of hydrocarbon solvents. Table 2 provides information for various oxygenated solvents. Table 3 provides information on chlorinated solvents.

Significance of Distillation Data For Solvents

Distillation limits are often key requirements in specifications for hydrocarbon and oxygenated solvents and chemical intermediates. For hydrocarbon and oxygenated solvents, distillation data in combination with other physical properties (such as density, refractive index, and color) can provide valuable information on product. For those solvents used to dissolve active components of formulations such as those in the paint and coatings, adhesives, and similar industries, the initial and dry boiling points are important parameters in addition to the solvency characteristics of the solvent. Invariably, the boiling point parameters of a solvent are intimately tied to its evaporation rate or volatility properties. There are applications that require fast evaporation rates and the low boiling solvents often fit these requirements. The lower the boiling point of a solvent, the faster its evaporation rate. There are applications in which the evaporation rate needs to be controlled. For these applications, product formulators can select from a broad family of hydrocarbon and oxygenated solvents with an almost infinite range of volatilities (to provide the required solvency, evaporation rate, dry time, etc.).

TABLE 2—Typical Distillation Specifications of Oxygenated Solvents [3].

Solvent	ASTM Specification	Distillation Range, °C	Typical Boiling Point, °C	ASTM Test Method
Ketones				
Acetone	D329	1	56	D1078
Methyl ethyl ketone (MEK)	D740	78.5–81.0	80	D1078
Methyl isobutyl ketone (MIBK)	D1153	114–117	116	D1078
Methyl isoamyl ketone (MIAK)	D2917	140–148	145	D1078
Methyl amyl ketone (MAK)	D4360	147–153.5	151	D1078
Diacetone alcohol	D2627	135–172	170	D1078
Isophorone	D2916	210–218	215	D1078
Esters				
Methyl acetate	—		55	D1078
Ethyl acetate	D4614		77	D1078
Isopropyl acetate	D3131	85–90	88	D1078
n-Propyl acetate	D3130	96–103	101	D1078
Isobutyl acetate	D1718	112–119	115	D1078
n-Butyl Acetate	D4615		126	D1078
n-Amyl Acetate	D3540	142–152		D1078
Methyl amyl acetate	D2634	142.5–149.5	148	D1078
n-Hexyl acetate	D5137	162–176	165	D1078
n-Butyl propionate	—		145	D1078
n-Pentyl propionate	—		168	D1078
Ethylene glycol monomethyl Ether acetate	D3728	150–160	156	D1078
Propylene glycol monomethyl Ether acetate	D4835	140–150	146	D1078
Glycol Ethers				
2-Methoxyethanol	D3128	123–126	125	D1078
2–Ethoxyethanol	D331	134–136	136	D1078
2-Butoxyethanol	D330	168–173	171	D1078
PGM ether	D4837	117–125	121	D1078
DPGM ether	D4836	184–195	188	D1078
Alcohols				
Methanol	D1152	1.0	64	D1078
Ethanol (anhydrous)	—		78	D1078
Isopropanol	D770	1.5	82	D1078
n-Propanol	D3622	2.0	97	D1078
Sec-Butanol	D1007	98–101	99	D1078
Iso Butanol	D1719	2.0	108	D1078
n-Butanol	D304	1.5	118	D1078
Methyl isobutyl carbinol	D2635	130–133	131	D1078

Significance of Vapor Pressure Data of Solvents

The vapor pressure of solvents is obviously related to their volatility characteristics. The higher the vapor pressure of a given solvent, the lower its initial boiling point and the greater its evaporation rate. Distillation and vapor pressure data are intimately linked together since a material would start to boil only when the vapor pressure of the liquid equals the atmospheric pressure. Vapor pressure values are given as the vapor pressure exerted by a material at a given temperature. A common reference temperature is 37.8 °C (100 °F), and vapor pressure values are in psia. Low boiling point solvents will have high vapor pressure at the reference temperature, and conversely, high boiling point solvents will have low vapor pressure.

TABLE 3—Typical distillation specification of some chlorinated solvents [3].

Solvent	ASTM Specification	Distillation Range, °C	Typical Boiling Point, °C	ASTM Test Method
Methylene chloride	D4079	39–45	39	D1078
Trichloroethylene	D4080	85–90	86	D1078
Perchloroethylene	D4081	120–122	121	D1078

TABLE 4—Vapor pressure data of solvents [4].

Solvent	Vapor pressure at 37.8 °C (100° F) in psia	Notes
Hydrocarbons		
Hexane	4.96	Commercial solvents are isomeric mixtures
Heptane	1.62	Commercial solvents are isomeric mixtures
Nonene	0.22	Commercial solvents are isomeric mixtures
Cyclopentane	9.92	Commercial solvents are isomeric mixtures
Cyclohexane		Commercial solvents are isomeric mixtures
Benzene	3.21	Measured value
Toluene	1.03	Measured value
o-Xylene	0.26	Measured value
m-Xylene	0.33	Measured value
p-Xylene	0.35	Measured value
Ketones		
Acetone	7.50	Extrapolated value
Methyl ethyl ketone (MEK)	3.25	Extrapolated value
Methyl isobutyl ketone (MIBK)	0.76	Extrapolated value
Esters		
Methyl acetate	7.11	Extrapolated value
Ethyl acetate	3.27	Extrapolated value
n-Propyl acetate	1.24	Extrapolated value
Isopropyl acetate	2.13	Extrapolated value
n-butyl acetate	0.45	Extrapolated value
Isobutyl acetate	0.15	Extrapolated value
Alcohol		
Methanol	4.61	Extrapolated value
Ethanol	2.31	Extrapolated value
Isopropanol	1.84	Extrapolated value
n-Propanol	0.88	Extrapolated value
Sec. butanol	0.80	Extrapolated value
Isobutanol	0.49	Extrapolated value
n-Butanol	0.32	Extrapolated value
Chlorinated hydrocarbons		
Methylene chloride	13.66	Extrapolated value
1,1,1-Trichloroethane	4.11	Extrapolated value

Table 4 gives a listing of typical vapor pressures of some of the solvents discussed earlier in this chapter. The low vapor pressures of some solvents are given as extrapolated values, and probably have been determined by ebulliometry or isoteniscope methods (see Chap. 5).

References

[1] ASTM, *Annual Book of ASTM Standards*, Vol. 5.01, ASTM International, West Conshohocken, PA.

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[3] Montemayor, R. G., and Yuhas, S. A., "Solvents," ASTM International, West Conshohocken, PA, to be published.

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12

Distillation and Vapor Pressure Data in Liquefied Petroleum Gas (LPG)

R. J. Falkiner[1] and R. G. Montemayor[2]

Introduction

LIQUEFIED PETROLEUM GAS (LPG) IS A GENERIC term for ethane (C2) to butane (C4) hydrocarbon mixtures that can exist as liquids under modest pressures at ambient temperatures. Methane (C1, natural gas) must be refrigerated to less than −162°C (−259°F) to be condensed by compression to liquefied natural gas (LNG). Pentane and heavier hydrocarbons (C5+, condensate) are liquids at ambient temperature and pressure, and are used in the manufacture of gasoline, naphtha fuels, and solvents. Ethane, propane, and butane are gases at standard temperature and pressure, but can be liquefied by compression and condensation of the vapor at or below ambient temperature. Propane (C3), butane (C4), and butane/propane mixtures (C3/C4 or B-P mix) have ideal properties for a fuel, widely used throughout the world in an amazing variety of applications. They are stable, high energy content, relatively low sulfur, clean burning fuels that can be transported economically as a liquid, and be used either as a liquid or a gas. Propane can be used from about −40 to 45°C, and butane from 0°C to about 110°C (about 0 to 250 psig vapor pressure) or higher depending on the pressure ratings of the equipment being used. The contents of the LPG tank are always under pressure at temperatures above the normal boiling point of about −42°C for propane and 0°C for butane, so there is no need for a fuel pump or electrical components for most applications. This makes LPG ideally suited to a wide variety of portable, mobile, or remote applications, using mechanically reliable and simple equipment. Propane applications tend to be robust and reliable as a result.

This chapter deals mostly with ASTM D1835 "Standard Specification for Liquefied Petroleum (LP) Gases" [1] Liquefied Petroleum Gas (LPG), "Commercial Propane," and "Special Duty Propane" grades (commonly known as "spec" products). The same sampling and test methods can apply to other Natural Gas Liquids (NGLs) that can have a wider range of compositions. The same distribution equipment, rail/truck tanks, and storage vessels can be used for propane or B-P mixtures so it is not outwardly apparent what grade of LPG is being used in a particular region or application. The terms "propane," "LPG," and "HD5"[3] are commonly used interchangeably in North America (although this is not technically correct). ASTM D1835 and Gas Processors Association GPA 2140 specifications exist for "Commercial B-P Mixtures," but this is rarely used for consumer applications in North America. There is no current Canadian General Standards Board (CGSB) specification for B-P mixtures, as the winter temperatures are too cold, and butane demand is high for winter gasoline production. Polar climates must use propane year round for low-temperature operability. Tropical climates (no winter temperatures, no winter gasoline) tend to use B-P mixtures year round to utilize the butane. Temperate climates with large seasonal temperature changes could use propane in the winter and B-P mixtures in the summer. However, the logistics of seasonal distribution and air/fuel calibration changes, coupled with a more than adequate propane supply generally favors the use of propane throughout the year.

The same properties that make LPG so useful contribute to some of the unique challenges in using it safely. Water/ice/hydrate properties are unique. Pressurized systems are more prone to leaks, even when the equipment is idle. The heavier than air vapor density allows accumulation in low points and cavities in the absence of ventilating air flow. When mixed with air in the right ratio in the narrow range, it has the potential for high destructive power in the event of an ignition source that results in an explosion or fire. Consequently, persons handling LPG and installing equipment are typically required to be trained and licensed. A variety of safety devices and procedures are used, and LPG is odorized to help detect potentially dangerous leaks.

History—LPG Properties and Thermodynamics

Many people consider the work conducted in this area during the 1920s and 30s to be synonymous with the development of chemical engineering as a separate discipline. High pressure crude, condensates and LPG have physical properties and a commercial importance that made them the principle target of early research in thermodynamics and chemical processing. LPG and NGL were probably the first commercially important, large volume materials that were handled and processed near or above the critical temperature of components or mixtures.

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[3] HD5 is GPA 2140 grade (Heavy Duty, 5 % max propylene) which is functionally equivalent to ASTM D1835 Standard Specification for "Special Duty Propane," and CAN/CSA-3.14 "Grade 1," differing only in certain sampling and test method details.

Critical phenomena had been observed in single components as early as 1823. In 1861, Thomas Andrews observed the similar phenomena when he found that carbon dioxide could not be liquefied at any pressure at temperatures higher than 31 °C. He hypothesized that such a state existed for all fluids and called it the "critical point" [2]. Andrews' experiments were first made public in the 1863 edition of W. A. Miller's textbook entitled *Elements of Chemistry* [3]. The phenomena of isothermally condensing a gas mixture to form liquid by decreasing pressure or isobarically increasing temperature of a gas-liquid mixture to form a liquid phase, were first observed by J. D. Kuenen in 1892 when he was studying the phase behavior of the binary system (carbon dioxide + chloromethane). He called these phenomena "retrograde condensation" of the first kind and the second kind, respectively [4].

In the mid 1920s, Walter Podbielniak developed the first practical low temperature fractional distillation test that allowed the composition of NGL mixtures to be accurately determined [5]. The "Pod" column was quickly adopted by the industry and improved over the years both in accuracy and automated operation. It was the industry standard until it was eventually replaced by gas chromatographic analysis in the mid 1950s. "Downhole" samples from high pressure formations taken at underground temperature and pressure were found to contain substantial amounts of dissolved "liquid" methane. This violated the then accepted principle within the industry that no material could be a liquid above its critical temperature. The theories on retrograde condensation in gas processing by Lacy in a 1932 API paper was greeted with a great deal of skepticism by the gas processing industry [6], but it certainly put technology development into high gear. This caused quite a stir at the time, as retrograde condensation was, as the name implies, the exact opposite of what was expected. This created a great need to understand the phase behavior of high-pressure and supercritical mixtures, both for crude oil reservoir pressure management and for production of high-pressure condensate. Within a decade of intensive research and development, cycling plants for methane reinjection, liquefaction (refrigerated liquid natural gas), LPG dehydration, and sweetening processes were all commercialized.

A large amount of technical data generated in this era is still used today. For example, the tables and graphs in the last published edition of the *Handbook of Butane-Propane Gases* were essentially unchanged from the first edition, published in 1932. Similarly, the *GPSA* (*Gas Processors Suppliers Association*) *Engineering Data Book* has been in continuous publication, and the eleventh edition is now available in U.S. engineering or metric versions, and on CD-ROM. Tables of information for installers that are derived from these data are still in use today in publications such as NFPA 58 (National Fire Protection Agency) and CAN/CSA B149-2 (Canadian Standards Association) (the respective USA and CDN "propane installation codes"). There is a large amount of related work on other vapor-liquid equilibria for the LPG gases, their mixtures, and other materials that are commercially important for manufacture and use of LPG. This includes water [7], H_2S, CO_2, COS, N_2, mercaptan, and others [8].

Development of Thermodynamic Equation of State (EOS) methods now allows calculation of most properties of even complex mixtures directly from composition [9]. In most cases, properties such as vapor pressures, enthalpies, bubble points, dew points, adiabatic flash compositions, and the like, can be calculated about as accurately as they can be measured directly. This includes LPG mixtures around their critical points, and "retrograde" condensation, and more recently ternary solid/liquid/vapor and hydrate systems [10].

Distillation and Composition of LPG by Low Temperature Fractional Distillation

Distillation is no longer used as a specification criterion for LPG, having been replaced by gas chromatography in the mid 1950s. Unlike other fuels, the purpose of distillation of liquefied petroleum gases (LPG) and natural gas liquids (NGL) was more to determine the composition of the mixture, and less to relate to the performance of the blend in end user equipment. Distillation was an important criterion for the various grades of "cassinghead" or "natural" gasoline, where the distillation (and density) specifications were intended to limit the amount of ethane, propane, and butane that could be in the blend. It was the enforcement of these specifications in 1921 that resulted in a large oversupply of propane and butane, and establishment of propane, butane, and propane-butane (BP) mixtures as separate grades of LPG in 1932 [11]. More historical information on the low temperature fractional distillation of LPG can be found in various editions of the *Handbook of Propane and Butane Gases*, technical articles in early archives of Butane-Propane News, U.S. Bureau of Mines and Gas Processor Association (GPA) and other earlier publications.

Composition by GC

Very little history was found on D2163 "Standard Test Method for Analysis of Liquefied Petroleum (LP) Gases and Propane Concentrates by Gas Chromatography" [12]. Since LPG is a fairly simple mixture of predominately C2 to C5 hydrocarbons, the composition of any mixture can be used as an indirect control of the volatility of the mixture. Control of the lightest components indirectly controls the vapor pressure. Control of the heavier components indirectly controls the evaporative residue of the mixture. The D2163 GC method was originally based on up to four different packed columns and thermal conductivity detectors using gravimetric standard reference fluids ("calibrant gas" or "cal-gas") for external calibration procedures. Two of the column packings were discontinued due to toxicity. ASTM Committee D02 is currently developing a replacement method for D2163. The method was expanded to allow other capillary/PLOT)[4] columns that provided improved resolution and separation of components, as well as FID (flame ionization detector) response factors referenced to methane, and other detectors.

Some precautions must be made for application of GC analysis to either vapor pressure or volatility (distillation). For example, if the LPG sample contains appreciable amounts of dissolved gases that are not detected by flame ionization detectors (FID), then the contribution of this gas

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[4] PLOT is Porous Layer Open Tubular (usually KCL deactivated alumina for LPG analysis).

to the total vapor pressure will not be determined. This can be important in cases where inert gases are used to either provide an incombustible atmosphere (“inerting”), or to provide additional pressure for removing liquid from the sample container (commonly called a “pad” gas).

Some raw or unprocessed gas contains appreciable amounts of CO_2 or N_2, so the use of FID detectors is generally restricted to finished “Spec” LPG products that normally do not contain these materials. However, this can occur under certain circumstances. For example, nitrogen is commonly used to displace air from new or reconditioned tanks prior to going back into service, and nitrogen, helium or other gases are commonly used to pressurize common 80 % fill cylinders as used in ASTM D1265 “Standard Practice for Sampling Liquefied Petroleum (LP) Gases” [13] for injecting samples into GCs and other equipment. ASTM D3700 “Standard Practice for Containing Hydrocarbon Fluid Samples Using a Floating Piston Cylinder” [14] will be the recommended sampling procedure, but D1265 will be allowed for routine use, except where highly accurate results are required for trace gases (see *History of LPG, ASTM Manual on Fuels and Lubricants*, [11] and Appendix of ASTM D3700 [14] and D6849 “Standard Practice for Storage and Use of Liquefied Petroleum (LPG) in Samples for LPG Analysis” [15] for more information on sampling and use of cylinders for various LPG analysis).

Vapor Pressure

History

The LPG VP specifications limit the maximum pressure that will be experienced in pressure vessels at high ambient temperature, and indirectly control the maximum concentration of light ends, principally ethane in propane and propane in butane.

Historically, vapor pressure was the most critical LPG specification, being responsible for most of the serious problems in the early days of the industry [11]. Vapor pressure is invariably tied to pressure vessel and safety valve certification and transportation regulations, so it is generally viewed to be critical for regulatory compliance. However, modern pressure vessel standards as well as LPG production equipment and analyzers have all but eliminated vapor pressure as a significant operational problem.

Certification standards vary by jurisdiction, but typically, a large safety margin is built into the system. For example, a typical consumer cylinder pressure rated for 250 psig “working pressure” would be pressure tested after manufacture to twice this (500 psig) and equipped with a “pressure relief valve” (pressure safety valve or vent) range of 250–500 psig, 50–100 % of the test pressure. Propane, at the maximum specification pressure, would have to be heated to over 60°C (140°F) to even reach the opening (“cracking”) pressure of the safety relief valve. In addition, the actual burst pressure is controlled to typically at least three times the working pressure (manufacturers are required to pressure test one cylinder out of each lot to destruction as a quality control procedure for the quality of steel and welds). It is common practice for the manufacturer to “over-build” cylinders to eliminate any uncertainty in the costly certification process. For example, sample cylinders rated for 1800 psig working pressure are often tested at about 5000 psig, and have burst pressures far in excess of minimum three times the working pressure, often in the 12 000–15 000 psig range. Finally, all consumer cylinders, storage vessels, trucks, and rail cars require periodic inspection and recertification. These considerations have essentially eliminated LPG vapor pressure (VP), per se, as a significant problem.

The manual “Reid” vapor pressure test method D323 “Standard Test Method of Petroleum Products (Reid Method)” [16] was developed in a competition in the 1920s to improve upon the original U.S. Bureau of Mines “vapor tension” method (essentially a pressure gage on a length of 2-in. diameter pipe). The competition was won by Reid (D323 Reid method), and an adaptation of this is used in D1267 “Standard Test Method for Gage Vapor Pressure of Liquefied Petroleum (LP) Gases” [17] for higher VP (>26 psi) LPGs. The test has changed little over the years. Many laboratories are no longer equipped to run the LPG Reid Method. It is now much more common to calculate VP from composition by D2163 using calculations in D2598 “Standard Practice for Calculation of the Properties of Liquefied Petroleum (LP) Gas from Compositional Analysis” [18] than it is to run a manual D1267 Reid VP. However, until recently, the D2598 method did not have component VP data for methane (if it is present), which could force the use of the manual method in some circumstances for strict compliance to LPG product standards for production/release. In addition, the D2598 VP calculation was biased high (e.g., conservative) at high ethane contents, due to the use of a component VP extrapolated from above the critical point of ethane. Both methane and ethane component blending values were updated in the 2003 published standard based on thermodynamic calculations.

There is no universally accepted criterion for setting the maximum VP specification for propane, and this is an area for future research and international standardization. The first GPA VP specification was 225 psig at 105°F set to meet the insulated rail tank car requirements of the Interstate Commerce Commission (ICC). In 1955, the specification was revised to 215 psig at 100°F, mainly to use a single water bath for both natural gasoline and propane. Still later in 1955, the VP was lowered to 210 psig at 100°F to meet United States DOT safety standards for rail tank cars [19]. A variety of other regulatory limits also exist. This includes DOT 173.301 (f) (2), which limits VP in cylinders to 300 psig at 130°F, Section 170.314 (c) 225 psig at 105°F, and Section 173.315 (c) (1) cargo and portable tanks at 100 psig at 115°F [20].

Other regulatory requirements would be expected in different jurisdictions. The original HD5 VP specification was 200 psig to promote heavy-duty engine applications, but was reset to the current 208 psig limit when this market failed to develop as expected.

Higher vapor pressure specifications allow slightly more ethane to be included in the blend, which increases supply slightly, and is potentially beneficial for very low (< −35°C) temperature operations. However, higher ethane content in the gas phase can cause overly lean air/mixtures for some appliance applications during first vapor withdrawal from a full tank, and rich operation from essentially pure propane when the tank is near empty. This wide swing in air/fuel ratio and the attendant problems of calibrating the air/fuel ratio in vapor withdrawal service also prompted the industry to reduce the VP from 215 to 210 psig in 1955.

Current ISO 9162 specifications have a maximum VP of 1550 kPa at 40°C, compared to 208 psig (1435 kPa) at 37.8°C (100°F) for ASTM, GPA, and CGSB. This difference is larger than the difference in VP due to the small difference in test temperature. Equation of state calculations indicate that the ISO standard would correspond to about 213 psig at 100°F, making the ASTM standard more conservative by about 5 psig. This difference is generally not significant in day-to-day operations.

The practical maximum for a universal multi-use fuel probably lies somewhere between the current ASTM limits of 208 and the estimated ISO limit of 213 psig at 100°F. This is a possible area of future research and standardization.

Testing

By historical convention, the VP of LPG is reported in "gage" or "gauge" pressure in pounds per square inch relative to atmospheric pressure (psig). The pressure gage used in the D1267 LPG Reid method reads zero at the start of the test, but unlike D323 or D4953 the apparatus starts out liquid filled, and no air is introduced into the test apparatus during the test. The test result is essentially the partial pressure of the LPG relative to atmosphere, and the absolute pressure is higher by the barometric pressure at the time of the test. This has caused significant confusion over the years when using pressure transducers calibrated in psia units, or when reporting in metric units (kPa), which by definition would be interpreted as being an absolute pressure. As a result, the specifications require reporting in kPa (gage), which is not a true SI unit. Also, this difference was sometimes confused with the high bias at high ethane contents when using the D2598 calculation, prior to the value for ethane being modified in the 2003 revision to D2598.

ASTM has recently published a standard test method D6897-03 "Standard Test Method for the Vapor Pressure of Liquefied Petroleum Gas (Expansion Method" [21]) based on newer instrumentation similar to D5191 and D6378 for gasoline. This method measures the vapor pressure at 37.8°C, at a liquid to vapor ratio of 0.5 to 1, from 200 to 1550 kPa on a sample volume of 3.33 mL. The instrument is capable of measuring vapor pressure over a wider range of temperatures, pressures, and V/L ratios, but the temperature of 37.8°C and V/L range specified conforms to the original D1267 method with single or double venting options using one of the two allowed liquid chambers. Like D1267, the reported value will include the contribution of any dissolved gases that may be present, including inert gases that may be present from field or lab operations (see Appendix section of D3700 or D6849 for a more complete discussion of these effects).

Quality Protection of LPG Volatility

LPG is always stored in pressurized sealed tanks and fuel systems, so fugitive losses are rarely sufficient to change the composition of the mixture. However, the composition of the LPG changes slightly due to vaporization of the remaining liquid to create an equilibrium vapor as the contents of the tank are consumed.

The extent of the composition change depends upon whether equilibrium liquid or vapor is withdrawn from the storage tank or cylinder, the initial composition of the liquid, the temperature, and the remaining liquid content of the tank at the time.

The change in the composition of the remaining liquid is:

1. Larger if vapor versus liquid is removed from the cylinder, since this is the equivalent of one complete single plate distillation of the entire contents.
2. Larger at lower temperatures, since the difference in relative volatility of the components is larger. In the extreme, above the critical temperature of the mixture, there is no difference between liquid or vapor withdrawal, since only a single composition supercritical fluid exists.
3. Larger at low remaining liquid level, since a higher fraction of the remaining liquid must vaporize to create the equilibrium vapor.

These factors are taken into account in ASTM D6849 "Standard Practice for the Storage and Use of Liquefied Petroleum Liquid (LPG) in Sample Cylinders for LPG Test Methods" [15] to allow use of an ordinary 80 % fill tank or cylinder for storage and use of QC reference fluids in various test methods for volatility and composition (see Appendix section of D3700 and D6849 for a more detailed discussion of these effects).

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Appendix

Rey G. Montemayor[1]

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 Pressure[1]

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).

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

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

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 ambient
	°F	32–40	55–65	55–65	55–65	
Flask support and shield		not above ambient	not above ambient	not above ambient	not above 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

		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	ambient or
					9 to 21°C above pour point [B]	
	°F	<40	<50	<50	ambient or	ambient or
					48 to 70°F above pour point [B]	
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	°C	0–4	13–18	13–18	13–18	±3
receiving cylinder	°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		
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.

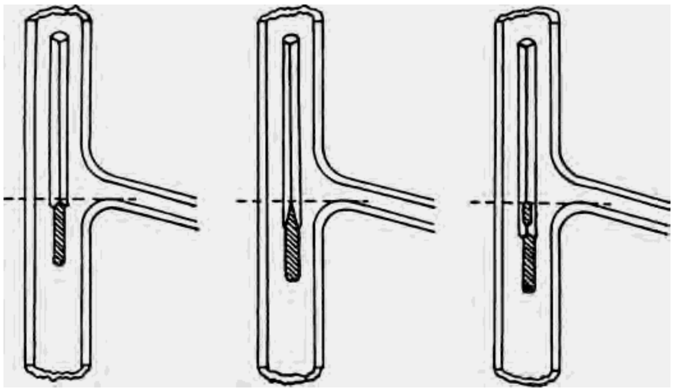


FIG. 5 Position of Thermometer in Distillation Flask

D402 - 02 Procedure Section

Designation: D402–02

Standard Test Method for Distillation of Cut-Back Asphaltic (Bituminous) Products[1]

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 ± 3°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 ± 5°C (275 ± 9°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 Materials[1]

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 Liquids[1]

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 3½min.

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 Pressure[1]

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 then 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 ±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 °C to the nearest 0.5°C,

10.3.5.4 Temperature of the boiling liquid in °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 N_2 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 wettage 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 wettage 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 wettage and the wettage 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± 0.1°C (100 ± 0.2°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 ± 0.1°C (100 ± 0.2°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 appartaus. 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.

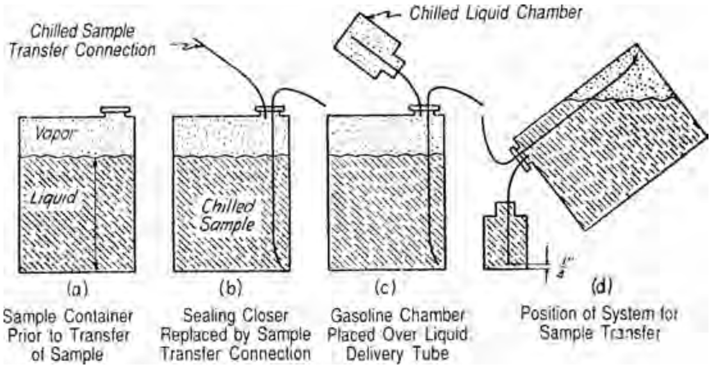
20.4 If a dead-weight tester is used instead of the mercury manometer as a pressure measuring device (see 16.2), apply the calibration factor in kilopascals (pounds-force per square inch) established for the pressure gage to the uncorrected vapor pressure. Record this value as the calibrated gage reading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



(a) Sample Container Prior to Transfer of Sample

(b) Sealing Closer Replaced by Sample Transfer Connection

(c) Gasoline Chamber Placed Over Liquid Delivery Tube

(d) Position of System for Sample Transfer

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 ±0.1°C (0.2°F). At test temperatures above 50°C (122°F), up to and including 70°C (158°F), maintain the bath at ±0.3°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 Fuels[1]

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 reprocessors 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 Isoteniscope [1]

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.

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

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.

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

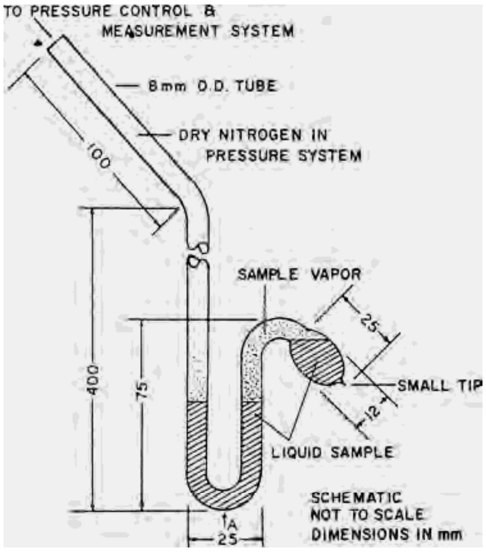


FIG. 1 Isoteniscope

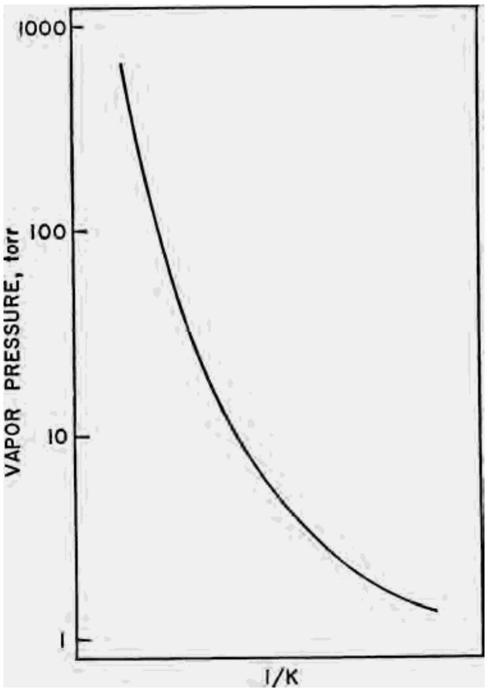


FIG. 5 Log P_e versus 1/K Without Linear Region

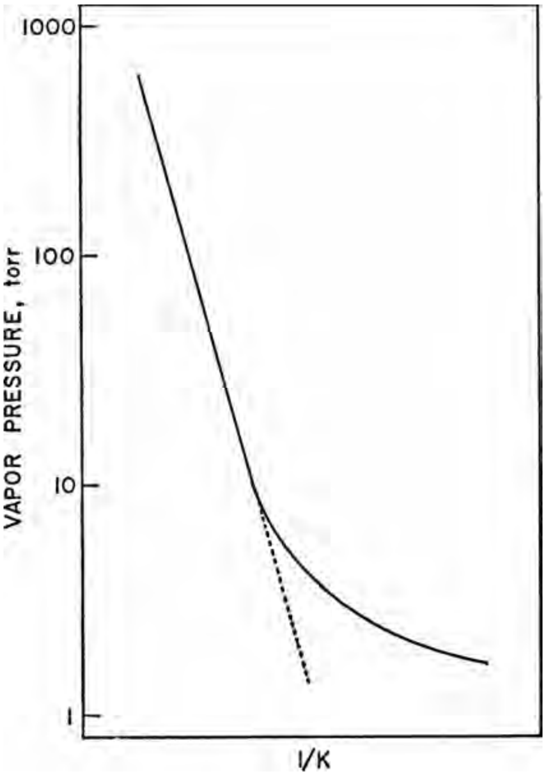


FIG. 4 Log P_e versus 1/K with Linear Region

A1.1 Scope

A1.1.1 This nnex 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 ± 0.1°C (100 ± 0.2°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 ± 0.1°C (100 ± 0.2°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.

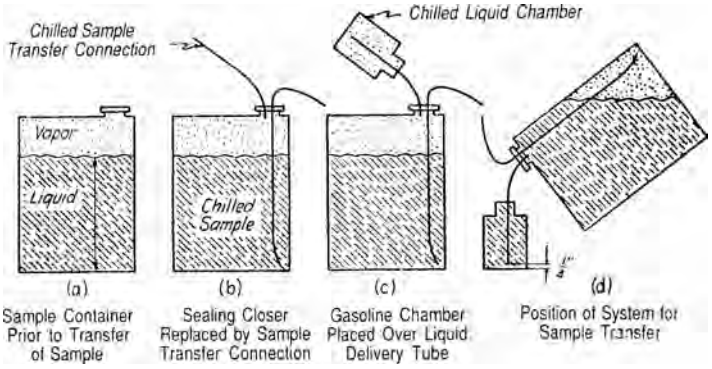


FIG. 1 Simplified Sketches Outlining Method Transferring Sample to Liquid Chamber from Open-Type Containers

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:

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

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.l 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:

$$DVPE = (0.954\,X) + A \qquad (1)$$

where:

X = measured total vapor pressure, in units consistent with A, and

A = 1.94 kPa (0.281 psi).

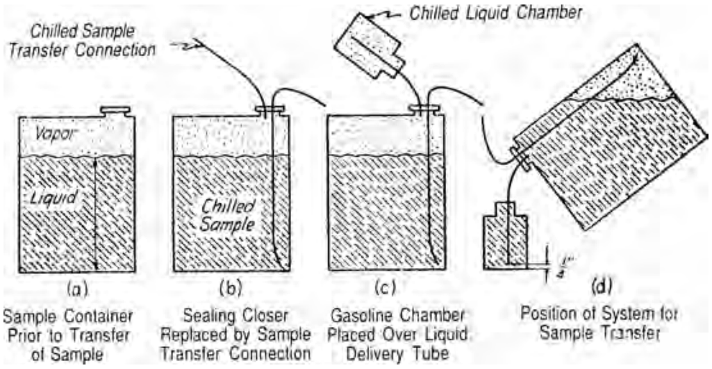


FIG. 1 Simplified Sketches Outlining Method Transferring Sample to Liquid Chamber from Open-Type Containers

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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:

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

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 program[i] 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.

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

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 ± 0.5°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 Pressure[1]

8. Procedures

8.1 *Isoteniscope 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 comple+-te 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 ±0.05°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. ((volume/time) (time) = 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 Ebulliometry[1]

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. A30-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 CS_2 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 CS_2.

11.1.4 Typical sample injection volumes are listed below.

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

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:

$$F_n = \left(M_n / A_n\right) / \left(M_{10} / A_{10}\right) \qquad (2)$$

where:

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

The relative response factor (F_n) of each *n*-paraffin must not deviate from unity (1) by more than ±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 Chromatography[1]

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:

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

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.

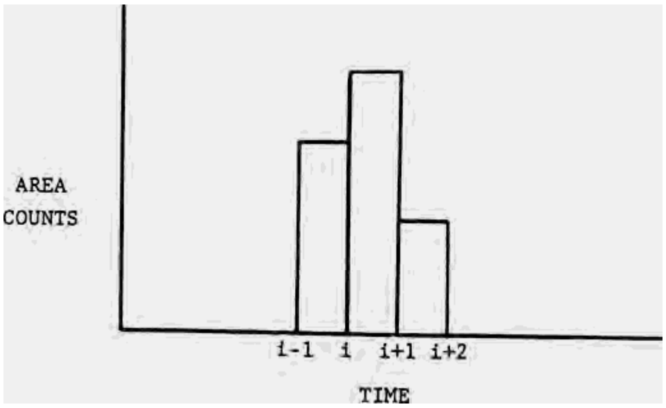

FIG. 3 Determination of Time to Peak Maxima

D5307 - 97 (Reapproved 2002) Procedure Section

Designation: D5307–97 (Reapproved 2002) $^{\varepsilon 1}$

Standard Test Method for Determination of Boiling Range Distribution of Crude Petroleum by Gas Chromatography[1]

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 μL 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 μL 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

[A] See Footnote 7.

D5399 - 04 Procedure Section

Designation: D5399–04

Standard Test Method for Boiling Point Distribution of Hydrocarbon Solvents by Gas Chromatography[1]

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” softwares[3] 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 $^{\varepsilon 1}$

Standard Test Method for Boiling Range Distribution of Petroleum Distillates in Boiling Range from 174 to 700°C by Gas Chromatography[1]

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

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[3] Beckman 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-pentacontane (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 °C (or °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, CS_2).

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.

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