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Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester¹

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This standard has been approved for use by agencies of the U.S. Department of Defense.

^{ε1} NOTE—Editorially revised 15.1 in February 2014.

INTRODUCTION

This flash point test method is a dynamic test method which depends on specified rates of heating to be able to meet the precision of the test method. The rate of heating may not in all cases give the precision quoted in the test method because of the low thermal conductivity of some materials. There are flash point test methods with slower heating rates available, such as Test Method D3941 (for paints, resins, and related products, and high viscosity products in the range of 0 to 110°C), where the test conditions are closer to equilibrium.

Flash point values are a function of the apparatus design, the condition of the apparatus used, and the operational procedure carried out. Flash point can therefore only be defined in terms of a standard test method, and no general valid correlation can be guaranteed between results obtained by different test methods, or with test apparatus different from that specified.

1. Scope*

1.1 These test methods cover the determination of the flash point of petroleum products in the temperature range from 40 to 370°C by a manual Pensky-Martens closed-cup apparatus or an automated Pensky-Martens closed-cup apparatus, and the determination of the flash point of biodiesel in the temperature range of 60 to 190°C by an automated Pensky-Martens closed cup apparatus.

NOTE 1—Flash point determinations above 250°C can be performed, however, the precision has not been determined above this temperature. For residual fuels, precision has not been determined for flash points above 100°C. The precision of in-use lubricating oils has not been determined. Some specifications state a D93 minimum flash point below 40°C, however, the precision has not been determined below this temperature.

1.2 Procedure A is applicable to distillate fuels (diesel, biodiesel blends, kerosine, heating oil, turbine fuels), new and in-use lubricating oils, and other homogeneous petroleum liquids not included in the scope of Procedure B or Procedure C.

1.3 Procedure B is applicable to residual fuel oils, cutback residua, used lubricating oils, mixtures of petroleum liquids with solids, petroleum liquids that tend to form a surface film under test conditions, or are petroleum liquids of such kinematic viscosity that they are not uniformly heated under the stirring and heating conditions of Procedure A.

1.4 Procedure C is applicable to biodiesel (B100). Since a flash point of residual alcohol in biodiesel is difficult to observe by manual flash point techniques, automated apparatus with electronic flash point detection have been found suitable.

1.5 These test methods are applicable for the detection of contamination of relatively nonvolatile or nonflammable materials with volatile or flammable materials.

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

NOTE 2—It has been common practice in flash point standards for many decades to alternately use a C-scale or an F-scale thermometer for temperature measurement. Although the scales are close in increments, they are not equivalent. Because the F-scale thermometer used in this procedure is graduated in 5° increments, it is not possible to read it to the 2°C equivalent increment of 3.6°F. Therefore, for the purposes of application of the procedure of the test method for the separate temperature scale thermometers, different increments must be used. In this test method, the following protocol has been adopted: When a temperature is intended to be a converted equivalent, it will appear in parentheses following the SI unit, for example 370°C (698°F). When a temperature is

¹ These test methods are under the joint jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and are the direct responsibility of Subcommittee D02.08 on Volatility. In the IP, these test methods are under the jurisdiction of the Standardization Committee.

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*A Summary of Changes section appears at the end of this standard

intended to be a rationalized unit for the alternate scale, it will appear after “or,” for example, 2°C or 5°F.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific warning statements, see 6.4, 7.1, 9.3, 9.4, 11.1.2, 11.1.4, 11.1.8, 11.2.2, and 12.1.2.

2. Referenced Documents

2.1 ASTM Standards:²

- D56 Test Method for Flash Point by Tag Closed Cup Tester
- D3941 Test Method for Flash Point by the Equilibrium Method With a Closed-Cup Apparatus
- D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
- D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
- E1 Specification for ASTM Liquid-in-Glass Thermometers
- E300 Practice for Sampling Industrial Chemicals
- E502 Test Method for Selection and Use of ASTM Standards for the Determination of Flash Point of Chemicals by Closed Cup Methods

2.2 ISO Standards³

- Guide 34 Quality Systems Guidelines for the Production of Reference Materials
- Guide 35 Certification of Reference Material—General and Statistical Principles

3. Terminology

3.1 Definitions:

3.1.1 *biodiesel, n*—a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100.

3.1.2 *biodiesel blends, n*—a blend of biodiesel fuel with petroleum-based diesel fuel.

3.1.3 *dynamic, adj*—in petroleum products—in petroleum product flash point test methods—the condition where the vapor above the test specimen and the test specimen are not in temperature equilibrium at the time that the ignition source is applied.

3.1.3.1 *Discussion*—This is primarily caused by the heating of the test specimen at the constant prescribed rate with the vapor temperature lagging behind the test specimen temperature.

3.1.4 *equilibrium, n*—in petroleum products—in petroleum product flash point test methods—the condition where the vapor above the test specimen and the test specimen are at the same temperature at the time the ignition source is applied.

3.1.4.1 *Discussion*—This condition may not be fully achieved in practice, since the temperature may not be uniform throughout the test specimen, and the test cover and shutter on the apparatus can be cooler.

3.1.5 *flash point, n*—in petroleum products, the lowest temperature corrected to a barometric pressure of 101.3 kPa (760 mm Hg), at which application of an ignition source causes the vapors of a specimen of the sample to ignite under specified conditions of test.

4. Summary of Test Method

4.1 A brass test cup of specified dimensions, filled to the inside mark with test specimen and fitted with a cover of specified dimensions, is heated and the specimen stirred at specified rates, using one of three defined procedures (A, B, or C). An ignition source is directed into the test cup at regular intervals with simultaneous interruption of the stirring, until a flash is detected (see 11.1.8). The flash point is reported as defined in 3.1.5.

5. Significance and Use

5.1 The flash point temperature is one measure of the tendency of the test specimen to form a flammable mixture with air under controlled laboratory conditions. It is only one of a number of properties which must be considered in assessing the overall flammability hazard of a material.

5.2 Flash point is used in shipping and safety regulations to define *flammable* and *combustible* materials. One should consult the particular regulation involved for precise definitions of these classifications.

NOTE 3—The U.S. Department of Transportation (DOT)⁴ and U.S. Department of Labor (OSHA) have established that liquids with a flash point under 37.8°C (100°F) (see Note 1) are flammable, as determined by these test methods, for those liquids which have a kinematic viscosity of 5.8 mm²/s (cSt) or more at 37.8°C or 9.5 mm²/s (cSt) or more at 25°C (77°F), or that contain suspended solids, or have a tendency to form a surface film while under test. Other classification flash points have been established by these departments for liquids using these test methods.

5.3 These test methods should be used to measure and describe the properties of materials, products, or assemblies in response to heat and an ignition source under controlled laboratory conditions and should not be used to describe or appraise the fire hazard or fire risk of materials, products, or assemblies under actual fire conditions. However, results of these test methods may be used as elements of a fire risk assessment which takes into account all of the factors which are pertinent to an assessment of the fire hazard of a particular end use.

5.4 These test methods provide the only closed cup flash point test procedures for temperatures up to 370°C (698°F).

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

³ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

⁴ For information on U.S. Department of Transportation regulations, see Codes of U.S. Regulations 49 CFR Chapter 1 and the U.S. Department of Labor, see 29 CFR Chapter XVII. Each of these items is revised annually and may be procured from the Superintendent of Documents, Government Printing Office, Washington, DC 20402.

6. Apparatus

6.1 *Pensky-Martens Closed Cup Apparatus (manual)*—This apparatus consists of the test cup, test cover and shutter, stirring device, heating source, ignition source device, air bath, and top plate described in detail in [Annex A1](#). The assembled manual apparatus, test cup, test cup cover, and test cup assembly are illustrated in [Figs. A1.1-A1.4](#), respectively. Dimensions are listed respectively.

6.2 *Pensky-Martens Closed Cup Apparatus (Automated)*⁵—This apparatus is an automated flash point instrument that is capable of performing the test in accordance with Section 11 (Procedure A), Section 12 (Procedure B), and 13 (Procedure C) of these test methods. The apparatus shall use the test cup, test cover and shutter, stirring device, heating source, and ignition source device described in detail in [Annex A1](#).

6.3 *Temperature Measuring Device*—Thermometer having a range as shown as follows and conforming to the requirements prescribed in Specification E1 or in [Annex A3](#), or an electronic temperature measuring device, such as resistance thermometers or thermocouples. The device shall exhibit the same temperature response as the mercury thermometers.

Temperature Range	Thermometer Number	
	ASTM	IP
−5 to +110°C (20 to 230°F)	9C (9F)	15C
+10 to 200°C (50 to 392°F)	88C (88F)	101C
+90 to 370°C (200 to 700°F)	10C (10F)	16C

6.4 *Ignition Source*—Natural gas flame, bottled gas flame, and electric ignitors (hot wire) have been found acceptable for use as the ignition source. The gas flame device described in detailed in [Fig. A1.4](#) requires the use of the pilot flame described in [A1.1.2.3](#). The electric ignitors shall be of the hot-wire type and shall position the heated section of the ignitor in the aperture of the test cover in the same manner as the gas flame device. (**Warning**—Gas pressure supplied to the apparatus should not be allowed to exceed 3 kPa (12 in.) of water pressure.)

6.5 *Barometer*—With accuracy of ± 0.5 kPa.

NOTE 4—The barometric pressure used in this calculation is the ambient pressure for the laboratory at the time of the test. Many aneroid barometers, such as those used at weather stations and airports, are precorrected to give sea level readings and would not give the correct reading for this test.

7. Reagents and Materials

7.1 *Cleaning Solvents*—Use suitable solvent capable of cleaning out the specimen from the test cup and drying the test cup and cover. Some commonly used solvents are toluene and acetone. (**Warning**—Toluene, acetone, and many solvents are flammable and a health hazard. Dispose of solvents and waste material in accordance with local regulations.)

8. Sampling

8.1 Obtain a sample in accordance with instructions given in Practices [D4057](#), [D4177](#), or [E300](#).

8.2 At least 75 mL of sample is required for each test. Refer to Practice [D4057](#). When obtaining a sample of residual fuel oil, the sample container shall be from 85 to 95 % full. For other types of samples, the size of the container shall be chosen such that the container is not more than 85 % full or less than 50 % full prior to any sample aliquot being taken. For biodiesel (B100) samples, a typical one liter container filled to 85% volume is recommended.

8.3 Successive test specimens can be taken from the same sample container. Repeat tests have been shown to be within the precisions of the method when the second specimen is taken with the sample container at least 50 % filled. The results of flash point determinations can be affected if the sample volume is less than 50 % of sample container capacity.

8.4 Erroneously high flash points may be obtained if precautions are not taken to avoid the loss of volatile material. Do not open containers unnecessarily, to prevent loss of volatile material or possible introduction of moisture, or both. Avoid storage of samples at temperatures in excess of 35°C or 95°F. Samples for storage shall be capped tightly with inner seals. Do not make a transfer unless the sample temperature is at least the equivalent of 18°C or 32°F below the expected flash point.

8.5 Do not store samples in gas-permeable containers, since volatile material may diffuse through the walls of the enclosure. Samples in leaky containers are suspect and not a source of valid results.

8.6 Samples of very viscous materials shall be heated in their containers, with lid/cap slightly loosened to avoid buildup of dangerous pressure, at the lowest temperature adequate to liquefy any solids, not exceeding 28°C or 50°F below the expected flash point, for 30 min. If the sample is then not completely liquefied, extend the heating period for additional 30 min periods as necessary. Then gently agitate the sample to provide mixing, such as orbiting the container horizontally, before transferring to the specimen cup. No sample shall be heated and transferred unless its temperatures is more than 18°C or 32°F below its expected flash point. When the sample has been heated above this temperature, allow the sample to cool until its temperature is at least 18°C or 32°F below the expected flash point before transferring.

NOTE 5—Volatile vapors can escape during heating when the sample container is not properly sealed.

NOTE 6—Some viscous samples may not completely liquefy even after prolonged periods of heating. Care should be exercised when increasing the heating temperature to avoid unnecessary loss of volatile vapors, or heating the sample too close to the flash point.

8.7 Samples containing dissolved or free water may be dehydrated with calcium chloride or by filtering through a qualitative filter paper or a loose plug of dry absorbent cotton. Warming the sample is permitted, but it shall not be heated for prolonged periods or greater than a temperature of 18°C/32°F below its expected flash point.

NOTE 7—If the sample is suspected of containing volatile contaminants, the treatment described in [8.6](#) and [8.7](#) should be omitted.

9. Preparation of Apparatus

9.1 Support the manual or automated apparatus on a level steady surface, such as a table.

⁵ Supporting data regarding a variant of the cover locking mechanism have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1706.

9.2 Tests are to be performed in a draft-free room or compartment. Tests made in a laboratory hood or in any location where drafts occur are not reliable.

NOTE 8—A shield, of the approximate dimensions 460 mm (18 in.) square and 610 mm (24 in.) high, or other suitable dimensions, and having an open front is recommended to prevent drafts from disturbing the vapors above the test cup.

NOTE 9—With some samples whose vapors or products of pyrolysis are objectionable, it is permissible to place the apparatus along with a draft shield in a ventilation hood, the draft of which is adjustable so that vapors can be withdrawn without causing air currents over the test cup during the ignition source application period.

9.3 Prepare the manual apparatus or the automated apparatus for operation in accordance with the manufacturer's instructions for calibrating, checking, and operating the equipment. (**Warning**—Gas pressure should not be allowed to exceed 3 kPa (12 in.) of water pressure.)

9.4 Thoroughly clean and dry all parts of the test cup and its accessories before starting the test, to ensure the removal of any solvent which had been used to clean the apparatus. Use suitable solvent capable of removing all of the specimen from the test cup and drying the test cup and cover. Some commonly used solvents are toluene and acetone. (**Warning**—Toluene, acetone, and many solvents are flammable. Health hazard. Dispose of solvents and waste material in accordance with local regulations.)

10. Verification of Apparatus

10.1 Adjust the automated flash point detection system (when used) in accordance with the manufacturer's instructions.

10.2 Verify that the temperature measuring device is in accordance with 6.3.

10.3 Verify the performance of the manual apparatus or the automated apparatus at least once per year by determining the flash point of a certified reference material (CRM) such as those listed in Annex A4, which is reasonably close to the expected temperature range of the samples to be tested. The material shall be tested according to Procedure A of these test methods and the observed flash point obtained in 11.1.8 or 11.2.2 shall be corrected for barometric pressure (see Section 14). The flash point obtained shall be within the limits stated in Table A4.1 for the identified CRM or within the limits calculated for an unlisted CRM (see Annex A4).

10.4 Once the performance of the apparatus has been verified, the flash point of secondary working standards (SWs) can be determined along with their control limits. These secondary materials can then be utilized for more frequent performance checks (see Annex A4).

10.5 When the flash point obtained is not within the limits stated in 10.3 or 10.4, check the condition and operation of the apparatus to ensure conformity with the details listed in Annex A1, especially with regard to tightness of the lid (A1.1.2.2), the action of the shutter, the position of the ignition source (A1.1.2.3), and the angle and position of the temperature measuring device (A1.1.2.4). After any adjustment, repeat the

test in 10.3 using a fresh test specimen, with special attention to the procedural details prescribed in these test methods.

PROCEDURE A

11. Procedure

11.1 Manual Apparatus:

11.1.1 Ensure that the sample container is filled to the volume capacity requirement specified in 8.2. Fill the test cup with the test specimen to the filling mark inside of the test cup. The temperature of the test cup and test specimen shall be at least 18°C or 32°F below the expected flash point. If too much test specimen has been added to the test cup, remove the excess using a syringe or similar device for withdrawal of fluid. Place the test cover on the test cup and place the assembly into the apparatus. Be sure the locating or locking device is properly engaged. If the temperature measuring device is not already in place, insert the device into its holder.

11.1.2 Light the test flame, and adjust it to a diameter of 3.2 to 4.8 mm (0.126 to 0.189 in.), or switch on the electric igniter and adjust the intensity in accordance with the manufacturer's instructions. (**Warning**—Gas pressure should not be allowed to exceed 3 kPa (12 in.) of water pressure.) (**Warning**—Exercise care when using a gas test flame. If it should be extinguished it will not ignite the vapors in the test cup, and the gas for the test flame that then enters the vapor space can influence the result.) (**Warning**—The operator should exercise and take appropriate safety precautions during the initial application of the ignition source, since test specimens containing low-flash material can give an abnormally strong flash when the ignition source is first applied.) (**Warning**—The operator should exercise and take appropriate safety precautions during the performance of these test methods. The temperatures attained during these test methods, up to 370°C (698°F), are considered hazardous.) (**Warning**—As a safety practice, when using automated or manual apparatus, it is strongly advised, before heating the test cup and specimen, to dip the ignitor to check for the presence of unexpected volatile material.)

11.1.3 Apply the heat at such a rate that the temperature, as indicated by the temperature measuring device, increases 5 to 6°C (9 to 11°F)/min.

11.1.4 Turn the stirring device at 90 to 120 rpm, stirring in a downward direction. (**Warning**—Meticulous attention to all details relating to the ignition source, size of test flame or intensity of the electric ignitor, rate of temperature increase, and rate of dipping the ignition source into the vapor of the test specimen is desirable for good results.)

11.1.5 Application of Ignition Source:

11.1.5.1 If the test specimen is expected to have a flash point of 110°C or 230°F or below, apply the ignition source when the temperature of the test specimen is $23 \pm 5^\circ\text{C}$ or $41 \pm 9^\circ\text{F}$ below the expected flash point and each time thereafter at a temperature reading that is a multiple of 1°C or 2°F. Discontinue the stirring of the test specimen and apply the ignition source by operating the mechanism on the test cover which controls the shutter so that the ignition source is lowered into

the vapor space of the test cup in 0.5 s, left in its lowered position for 1 s, and quickly raised to its upward position.

11.1.5.2 If the test specimen is expected to have a flash point above 110°C or 230°F, apply the ignition source in the manner described in 11.1.5.1 at each temperature increase of 2°C or 5°F, beginning at a temperature of 23 ± 5°C or 41 ± 9°F below the expected flash point. (**Warning**— As a safety practice, when using automated or manual apparatus, it is strongly advised that, for an expected flash point above 130°C, to dip the ignitor every 10°C throughout the test until the sample temperature reaches 28°C below the expected flash point and then follow the prescribed dipping procedure. This practice has been shown to reduce the possibility of a fire, and, on average, not to significantly affect the result. A limited study⁶ has shown that this dipping practice has no observable effect on test method repeatability.)

11.1.6 When testing materials to determine if volatile material contamination is present, it is not necessary to adhere to the temperature limits for initial ignition source application as stated in 11.1.5.

11.1.7 When testing materials where the expected flash point temperature is not known, bring the material to be tested and the tester to a temperature of 15 ± 5°C or 60 ± 10°F. When the material is known to be very viscous at this temperature, heat the specimen to a starting temperature as described in 8.6. Apply the ignition source, in the manner described in 11.1.5.1, beginning at least 5°C or 10°F higher than the starting temperature.

NOTE 10—Flash Point results determined in an “unknown expected flash point mode” should be considered approximate. This value can be used as the expected flash point when a fresh specimen is tested in the standard mode of operation.

11.1.8 Record as the observed flash point the reading on the temperature measuring device at the time ignition source application causes a distinct flash in the interior of the test cup. The sample is deemed to have flashed when a large flame appears and instantaneously propagates itself over the entire surface of the test specimen. (**Warning**—For certain mixtures containing halogenated hydrocarbons, such as, methylene chloride or trichloroethylene, no distinct flash, as defined, is observed. Instead a significant enlargement of the test flame (not halo effect) and change in color of the test flame from blue to yellowish-orange occurs. Continued heating and testing of these samples above ambient temperature can result in significant burning of vapors outside the test cup, and can be a potential fire hazard. See [Appendix X1](#) and [Appendix X2](#) for more information.)

11.1.9 When the ignition source is a test flame, the application of the test flame can cause a blue halo or an enlarged flame prior to the actual flash point. This is not a flash and shall be ignored.

11.1.10 When a flash point is detected on the first application, the test shall be discontinued, the result discarded, and the test repeated with a fresh test specimen. The first application of the ignition source with the fresh test specimen

shall be 23 ± 5°C or 41 ± 9°F below the temperature at which a flash point was detected on the first application.

11.1.11 When a flash point is detected at a temperature which is greater than 28°C or 50°F above the temperature of the first application of the ignition source, or when a flash point is detected at a temperature which is less than 18°C or 32°F above the temperature of the first application of the ignition source, the result shall be considered approximate, and the test repeated with a fresh test specimen. Adjust the expected flash point for this next test to the temperature of the approximate result. The first application of the ignition source with the fresh test specimen shall be 23 ± 5°C or 41 ± 9°F below the temperature at which the approximate result was found.

11.1.12 When the apparatus has cooled down to a safe handling temperature, less than 55°C (130°F), remove the test cover and the test cup and clean the apparatus as recommended by the manufacturer.

NOTE 11—Exercise care when cleaning and positioning the lid assembly so not to damage or dislocate the flash detection system or temperature measuring device. See the manufacturer’s instructions for proper care and maintenance.

11.2 Automated Apparatus:

11.2.1 The automated apparatus shall be capable of performing the procedure as described in 11.1, including control of the heating rate, stirring of the test specimen, application of the ignition source, detection of the flash point, and recording the flash point.

11.2.2 Start the automated apparatus in accordance with the manufacturer’s instructions. (**Warning**—Failure to install the sample temperature measuring device correctly, when using automated apparatus, can result in uncontrolled heating of the test portion and potentially a fire. Some automated apparatus include provisions to avoid this occurrence.) The apparatus shall follow the procedural details described in 11.1.3 through 11.1.8.

PROCEDURE B

12. Procedure

12.1 Manual Apparatus:

12.1.1 Ensure that the sample container is filled to the volume capacity requirement specified in 8.2. Fill the test cup with the test specimen to the filling mark inside of the test cup. The temperature of the test cup and test specimen shall be at least 18°C or 32°F below the expected flash point. If too much test specimen has been added to the test cup, remove the excess using a syringe or similar device for withdrawal of fluid. Place the test cover on the test cup and place the assembly into the apparatus. Be sure the locating or locking device is properly engaged. If the temperature measuring device is not already in place, insert the device into its holder.

12.1.2 Light the test flame and adjust it to a diameter of 3.2 to 4.8 mm (0.126 to 0.189 in.), or switch on the electric igniter and adjust the intensity in accordance with the manufacturer’s instructions. (**Warning**—Gas pressure should not be allowed to exceed 3 kPa (12 in.) of water pressure.) (**Warning**—Exercise care when using a gas test flame. If it should be extinguished it will not ignite the vapors in the test cup and the gas for the test flame that then enters the vapor space can

⁶ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1652.

influence the result.) (**Warning**—The operator should exercise and take appropriate safety precautions during the initial application of the ignition source, since test specimens containing low-flash material may give an abnormally strong flash when the ignition source is first applied.) (**Warning**—The operator should exercise and take appropriate safety precautions during the performance of these test methods. The temperatures attained during these test methods, up to 370°C (698°F), are considered hazardous.)

12.1.3 Turn the stirring device at 250 ± 10 rpm, stirring in a downward direction.

12.1.4 Apply the heat at such a rate that the temperature as indicated by the temperature measuring device increases 1 to 1.6°C (2 to 3°F)/min.

12.1.5 Proceed as prescribed in Section 11, with the exception of the preceding requirements for rates of stirring and heating.

12.2 Automated Apparatus:

12.2.1 The automated apparatus shall be capable of performing the procedure as described in 12.1, including control of the heating rate, stirring of the test specimen, application of the ignition source, detection of the flash point, and recording the flash point.

12.2.2 Start the automated apparatus in accordance with the manufacturer's instructions. The apparatus shall follow the procedural details in accordance with 12.1.3 through 12.1.5.

Procedure C

13. Procedure

13.1 *Automated Apparatus*—Ensure that the apparatus is equipped with an electronic measuring system for the detection of the flash point.

13.2 Ensure that the sample container is filled to the volume capacity requirement specified in 8.2. Fill the test cup with the test specimen to the filling mark inside of the test cup. The temperature of the test cup and test specimen shall be at least 24°C below the expected flash point. If too much test specimen has been added to the test cup, remove the excess using a syringe or similar device for withdrawal of fluid. Place the test cover on the test cup and place the assembly into the apparatus. Be sure the locating or locking device is properly engaged. If the temperature measuring device is not already in place, insert the device into its holder.

13.3 Light the test flame, and adjust it to a diameter of 3.2 to 4.8 mm (0.126 to 0.189 in.) or switch on the electric igniter and adjust the intensity in accordance with the manufacturer's instructions. (**Warning**—Gas pressure should not be allowed to exceed 3 kPa (12 in. of water pressure.) (**Warning**—Exercise care when using a gas test flame. If it should be extinguished it will not ignite the vapors in the test cup, and the gas for the test flame that then enters the vapor space can influence the result.) (**Warning**—The operator should exercise and take appropriate safety precautions during the initial application of the ignition source, since test specimens containing low-flash material can give an abnormally strong flash when the ignition source is first applied.) (**Warning**—The operator should exercise and take appropriate safety precau-

tions during the performance of these test methods. The temperatures attained during these test methods, up to 370°C (698°F), are considered hazardous.)

13.4 Apply the heat at such a rate that the temperature as indicated by the temperature measuring device increases $3.0 \pm 0.5^\circ\text{C}/\text{min}$.

13.5 Turn the stirring device at 90 to 120 rpm, stirring in a downward direction. (**Warning**—Meticulous attention to all details relating to the ignition source, size of test flame, rate of temperature increase, and rate of dipping the ignition source into the vapor of the test specimen is desirable for good results.)

13.6 *Application of Ignition Source*—The first test on the sample shall use an expected flash point of 100°C.

13.7 Apply the ignition source when the temperature of the test specimen is approximately 24°C below the expected flash point and each time thereafter at a temperature reading that is a multiple of 2°C. Discontinue the stirring of the test specimen and apply the ignition source by operating the mechanism on the test cover which controls the shutter so that the ignition source is lowered into the vapor space of the test cup in 0.5 s, left in its lowered position for 1 s, and quickly raised to its upward position.

13.8 Record as the flash point the reading on the temperature measuring device at the time the ignition source application causes a distinct flash in the interior of the test cup which is detected by the electronic device.

13.9 The application of the test flame can cause a blue halo or an enlarged flame prior to the actual flash point. This is not a flash and shall be ignored.

13.10 When a flash point is detected on the first application, the test shall be discontinued, the result discarded, and the test repeated with a fresh test specimen. The first application of the ignition source with the fresh test specimen shall be approximately 24°C below the temperature at which a flash point was detected on the first application.

13.11 When a flash point is detected at a temperature which is greater than 30°C above the temperature of the first application of the ignition source, or when a flash point is detected at a temperature which is less than 16°C above the temperature of the first application of the ignition source, the result shall be considered approximate, and the test repeated with a fresh test specimen. Adjust the expected flash point for this next test to the temperature of the approximate result. The first application of the ignition source with the fresh test specimen shall be approximately 24°C below the temperature at which the approximate result was found.

13.12 When the apparatus has cooled down to a safe handling temperature, less than 55°C, remove the test cover and the test cup and clean the apparatus as recommended by the manufacturer.

NOTE 12—Exercise care when cleaning and positioning the lid assembly so not to damage or dislocate the flash detection system or temperature measuring device. See the manufacturer's instructions for proper care and maintenance.

PRECISION, CALCULATION, AND REPORT FOR PROCEDURES A, B, OR C

14. Calculation

14.1 Observe and record the ambient barometric pressure (see **Note 4**) at the time of the test. When the pressure differs from 101.3 kPa (760 mm Hg), correct the flash point as follows:

$$\text{Corrected flash point} = C + 0.25 (101.3 - K) \quad (1)$$

$$\text{Corrected flash point} = F + 0.06 (760 - P) \quad (2)$$

$$\text{Corrected flash point} = C + 0.033 (760 - P) \quad (3)$$

where:

C = observed flash point, °C,

F = observed flash point, °F,

P = ambient barometric pressure, mm Hg, and

K = ambient barometric pressure, kPa.

14.2 After correction for barometric pressure, round the temperature to the nearest 0.5°C (1°F) and record.

15. Report

15.1 Report the corrected flash point as the ASTM D93 or IP 34, whichever is applicable, Procedure A or Procedure B or Procedure C Pensky-Martens Closed Cup Flash Point of the test specimen.

16. Precision and Bias (Procedure A)

16.1 *Precision*—The precision of this procedure as determined by the statistical examination of the interlaboratory test results, is as follows:

16.1.1 *Repeatability*—The difference between successive results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values in 1 case in 20.

$$r = AX, \quad (4)$$

$$A = 0.029,$$

X = mean result in °C, and

r = repeatability.

16.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical material, would in the long run, in the normal and correct operation of the test method, exceed the following values only in 1 case in 20.

$$R = BX, \quad (5)$$

$$B = 0.071,$$

X = mean result in °C, and

R = reproducibility.

16.1.3 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in these test methods, bias has not been determined.

16.1.4 *Relative Bias*—Statistical evaluation of the data did not detect any significant difference between the reproducibility variances of manual and automated Pensky-Martens flash point results for the samples studied. Evaluation of the data did not detect any significant difference between averages of manual and automated Pensky-Martens flash point for the samples studied with the exception of cycle oil and fuel oil which showed some bias. In any case of dispute, the manual procedure shall be considered the referee test.

NOTE 13—The precision statements were derived on clear liquids only. Refer to the research report⁷ for information regarding relative bias and types of samples. Additional studies are in progress concerning relative bias.

16.1.5 The precision data were developed from a combined 1991 ASTM cooperative test program⁷ using 5 samples of fuel and lubricating oils (Twelve laboratories participated with the manual apparatus and 21 laboratories participated with the automated equipment) and a 1994 IP cooperative test program using 12 fuel samples and 4 pure chemicals. (Twenty-six laboratories participated with manual and automated equipment. The apparatus used either a gas test flame or an electric resistance (hot wire) device for the ignition source. Information on the type of samples and their average flash point are in the research report.⁷

17. Precision and Bias (Procedure B)

17.1 *Precision*—The precision of this procedure, as determined by the statistical examination of the interlaboratory test results, is as follows:

17.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the following value in 1 case in 20:

Residual fuel oil 2°C
Other types 5°C

17.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical material would, in the long run, exceed the following value only in 1 case in 20:

Residual fuel oil 6°C
Other types 10°C

NOTE 14—The precisions of these standards were derived from interlaboratory studies conducted in degrees Celsius.

17.1.3 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in these test methods, bias has not been determined.

17.1.4 The precision data for residual fuel oils were developed in a 1996 cooperative test program conducted by the IP using 12 samples of residual fuel and 40 laboratories worldwide using both the manual and automated apparatus. Information on the type of samples and their average flash point are in the research report.

⁷ Supporting data (the results of the 1991 interlaboratory cooperative test program) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:S15-1008.

17.1.5 The precision data for other sample types in Procedure B is not known to have been developed in accordance with RR:D02-1007.

NOTE 15—Procedure B was not tested in the 1991 interlaboratory program.

18. Precision and Bias (Procedure C)⁸

18.1 *Precision*—The precision of this procedure, as determined by the statistical examination of the interlaboratory test results, is as follows:

18.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the following value in 1 case in 20:

8.4°C

18.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical material would, in the

⁸ Supporting data (the results of the 2008 interlaboratory cooperative test program) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1683.

long run, in the normal and correct operation of the test method, exceed the following value only in 1 case in 20:

14.7°C

NOTE 16—The precisions of these standards were derived from interlaboratory studies conducted in degrees Celsius.

18.1.3 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in these test methods, bias has not been determined.

18.1.4 The precision data for biodiesel were developed in a 2008 cooperative interlaboratory test program⁸ using 9 samples of biodiesel (B100) of various source and 17 samples of the same biodiesel dosed with concentrations of alcohol from 0.1 to 0.3%. Various automated apparatus in 11 laboratories participated. The precision was calculated on the flash point range from 60 to 190°C. The alcohol concentrations were verified in separate laboratories using EN 14110. Information on the type of samples and their average flash point are in the research report.

19. Keywords

19.1 automated flash point; automated Pensky-Martens closed cup; flammability; flash point; Pensky-Martens closed cup

ANNEXES

(Mandatory Information)

A1. APPARATUS SPECIFICATIONS⁵

A1.1 A typical assembly of the apparatus, gas heated, is shown in Fig. A1.1. The apparatus shall consist of a test cup, cover, and stove conforming to the following requirements:

A1.1.1 *Cup*—The cup shall be of brass, or other nonrusting metal of equivalent heat conductivity, and shall conform to the dimensional requirements in Fig. A1.2. The flange shall be equipped with devices for locating the position of the cup in the stove. A handle attached to the flange of the cup is a desirable accessory. The handle shall not be so heavy as to tip over the empty cup.

A1.1.2 *Cover*:

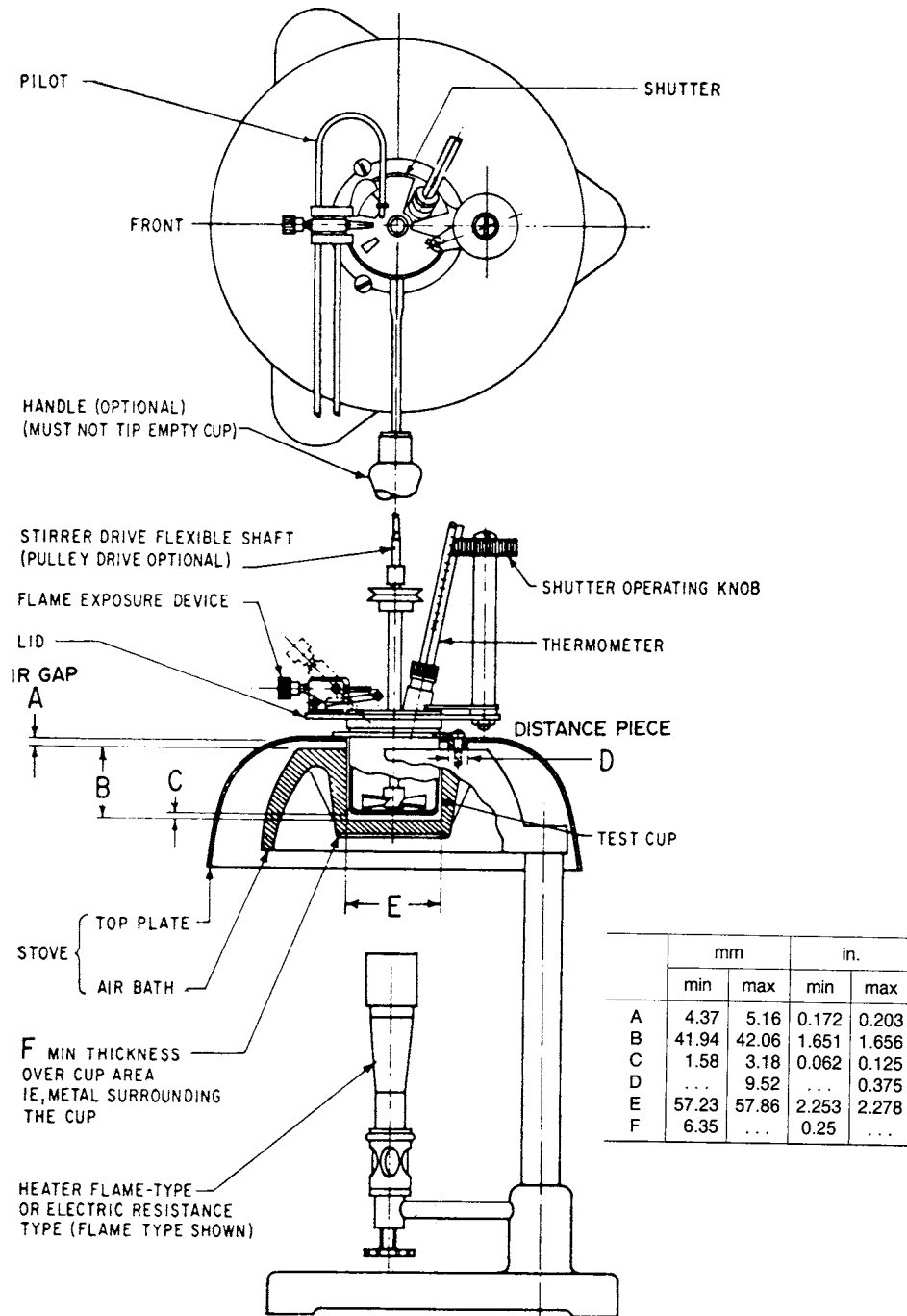
A1.1.2.1 *Cover Proper*—The cover shown in Fig. A1.3 shall be of brass (A1.1.1) and shall have a rim projecting downward almost to the flange of the cup. The rim shall fit the outside of the cup with a clearance not exceeding 0.36 mm (0.014 in.) on the diameter. There shall be a locating or locking device, or both, engaging with a corresponding device on the cup. The upper edge of the cup shall be in close contact with the inner face of the cover throughout its circumference.

A1.1.2.2 *Shutter*—The cover shall be equipped with a brass shutter (Fig. A1.1 and Fig. A1.4), approximately 2.4 mm ($\frac{3}{32}$ in.) thick, operating on the plane of the upper surface of the cover. The shutter shall be so shaped and mounted that it rotates on the axis of the horizontal center of the cover between two stops, so placed, that when in one extreme position, the

openings A, B, and C in the cover are completely closed, and when in the other extreme position, these openings are completely opened. The mechanism operating the shutter should be of the spring type and constructed so that when at rest the shutter shall exactly close the three openings. When operated to the other extreme, the three cover openings shall be exactly open and the tip of the exposure tube shall be fully depressed.

A1.1.2.3 *Flame-Ignition Device*—The flame-ignition device (Fig. A1.4) shall have a tip with an opening 0.69 to 0.79 mm (0.027 to 0.031 in.) in diameter. This tip shall be made preferably of stainless steel, although it may be fabricated of other suitable metals. The flame-exposure device shall be equipped with an operating mechanism which, when the shutter is in the open position, depresses the tip so that the center of the orifice is between the planes of the under and upper surfaces of the cover proper at a point on a radius passing through the center of the larger opening A (Fig. A1.3). An electric ignitor is also suitable. The electric ignitors shall be of the electric resistance (hot-wire) type and shall position the heated section of the ignitor in the aperture of the test cover in the same manner as the gas flame device.

A1.1.2.4 *Pilot Flame*—A pilot flame shall be provided for automatic relighting of the exposure flame. A bead 4 mm ($\frac{5}{32}$ in.) in diameter can be mounted on the cover so that the size of the test flame can be regulated by comparison. The tip of the



NOTE 1—Lid assembly can be positioned either right or left-handed.

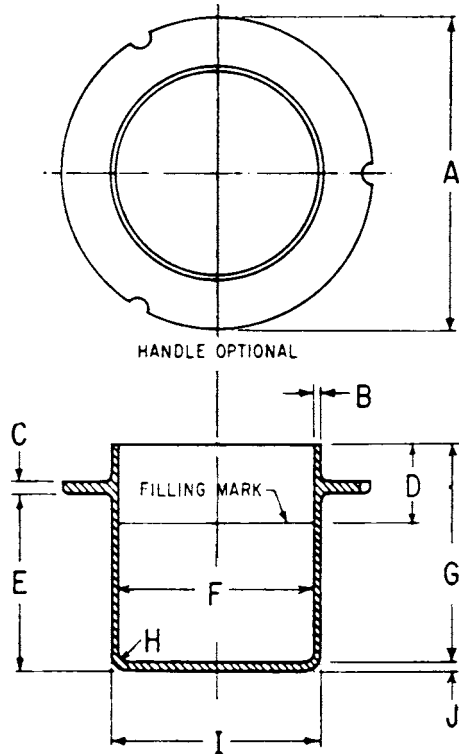
FIG. A1.1 Pensky-Martens Closed Flash Tester

pilot flame shall have an opening the same size as the tip of the flame exposure device (0.69 to 0.79 mm (0.027 to 0.031 in.) in diameter).

A1.1.2.5 *Stirring Device*—The cover shall be equipped with a stirring device (Fig. A1.4) mounted in the center of the cover and carrying two 2-bladed metal propellers. In Fig. A1.4 lower propeller is designated by the letters *L*, *M*, and *N*. This propeller shall measure approximately 38 mm from tip to tip, with each of its two blades 8 mm in width with a pitch of 45°. The upper propeller is designated by the letters *A*, *C*, and *G*. This propeller measures approximately 19 mm, tip to tip, each

of its two blades is also 8 mm in width with a pitch of 45°. Both propellers are located on the stirrer shaft in such a manner that, when viewed from the bottom of the stirrer, the blades of one propeller are at 0 and 180° while the blades of the other propeller are at 90 and 270°. A stirrer shaft may be coupled to the motor by a flexible shaft or a suitable arrangement of pulleys.

A1.1.2.6 *Stove*—Heat shall be supplied to the cup by means of a properly designed stove which is equivalent to an air bath. The stove shall consist of an air bath and a top plate on which the flange of the cup rests.

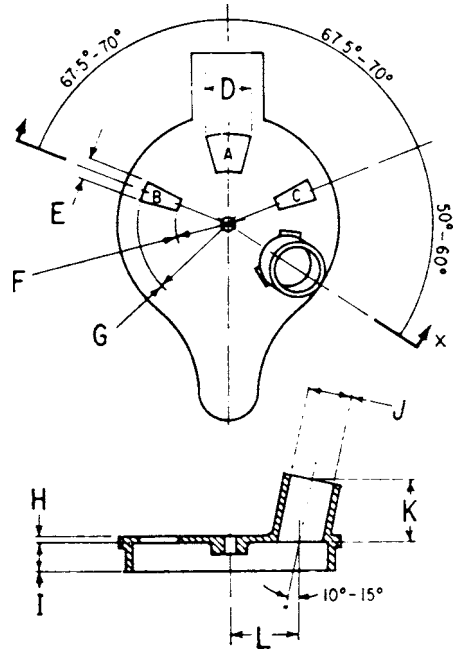


	mm		(in.)	
	min	max	(min)	(max)
A	79.0	79.8	(3.11)	(3.14)
B	1.0	...	(0.04)	(...)
C	2.8	3.6	(0.11)	(0.14)
D	21.72	21.84	(0.855)	(0.860)
E	45.47	45.72	(1.790)	(1.800)
F	50.72	50.85	(1.997)	(2.002)
G	55.75	56.00	(2.195)	(2.205)
H	3.8	4.0	(0.15)	(0.16)
I	53.90	54.02	(2.122)	(2.127)
J	2.29	2.54	(0.090)	(0.100)

FIG. A1.2 Test Cup

A1.1.2.7 *Air Bath*—The air bath shall have a cylindrical interior and shall conform to the dimensional requirements in Fig. A1.1. The air bath may be either a flame or electrically heated metal casting (A1.1.2.8), or an electric-resistance element (A1.1.2.9). In either case, the air bath must be suitable for use at the temperatures to which it will be subjected without deformation.

A1.1.2.8 *Heater, Flame or Electric*—If the heating element is a flame or an electric heater, it shall be so designed and used that the temperatures of the bottom and the walls are approximately the same. In order that the air bath internal surfaces should be at a uniform temperature, it should not be less than 6.4 mm (1/4 in.) in thickness unless the heating element is designed to give equal heat flux densities over all the wall and bottom surfaces.

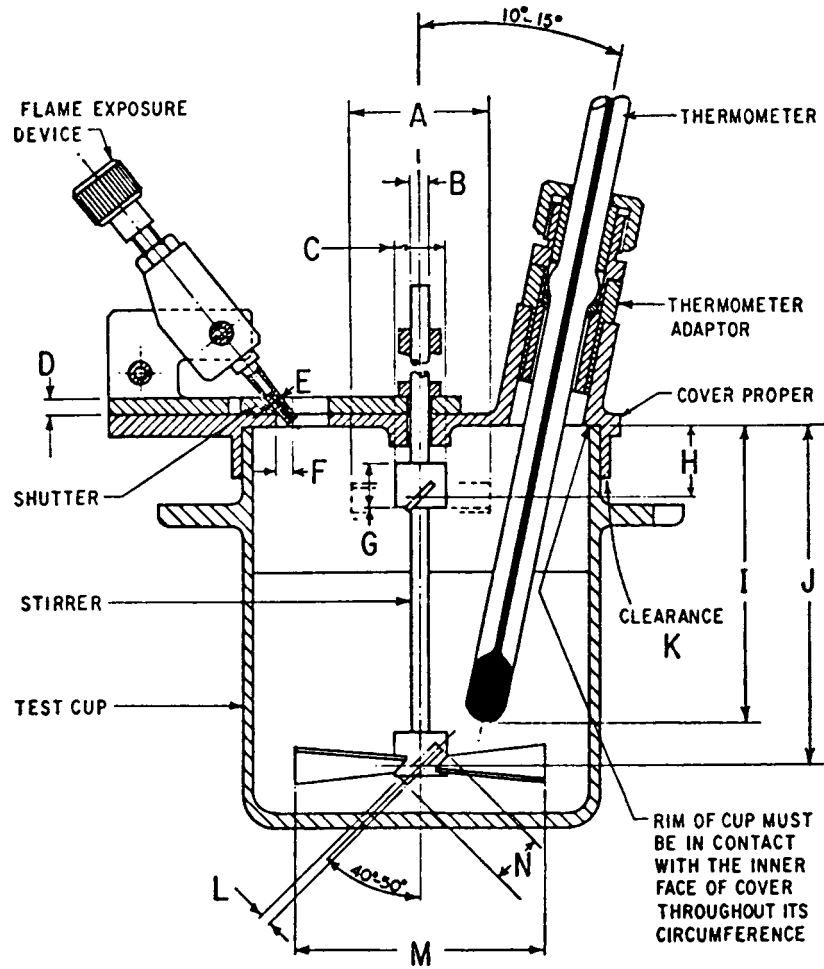


	mm		(in.)	
	min	max	(min)	(max)
D	12.7	13.5	(0.50)	(0.53)
E	4.8	5.6	(0.19)	(0.22)
F	13.5	14.3	(0.53)	(0.56)
G	23.8	24.6	(0.94)	(0.97)
H	1.2	2.0	(0.05)	(0.08)
I	7.9	...	(0.31)	(...)
J	12.00	12.32	(0.472)	(0.485)
K	16.38	17.00	(0.645)	(0.669)
L	18.65	19.45	(0.734)	(0.766)

FIG. A1.3 Cover Proper

A1.1.2.9 *Heater, Electric Resistance*—If the heater is of the electric resistance type, it shall be constructed so that all parts of the interior surface are heated uniformly. The wall and bottom of the air bath shall not be less than 6.4 mm (1/4 in.) in thickness unless the resistance heating elements are distributed over at least 80 % of the wall and all the bottom of the air bath. A heater having such a distribution shall have the heating elements positioned at least 4.0 mm (5/32 in.) away from the internal surface of the air bath in conjunction with a minimum thickness of 1.58 mm (1/16 in.) for the wall and bottom of the air bath.

A1.1.2.10 *Top Plate*—The top plate shall be of metal, and shall be mounted with an air gap between it and the air bath. It may be attached to the air bath by means of three screws and spacing bushings. The bushings should be of proper thickness to define an air gap of 4.8 mm (3/16 in.), and they shall be not more than 9.5 mm (3/8 in.) in diameter.



	mm		(in.)	
	min	max	(min)	(max)
A	18.3	19.8	(0.72)	(0.78)
B	2.38	3.18	(0.094)	(0.125)
C	7.6	8.4	(0.30)	(0.33)
D	2.0	2.8	(0.08)	(0.11)
E	0.69	0.79	(0.027)	(0.031)
F	2.0	2.8	(0.08)	(0.11)
G	6.4	10.4	(0.25)	(0.41)
H	9.6	11.2	(0.38)	(0.44)
I ^A	43.0	46.0	(1.69)	(1.81)
J	50.0	51.6	(1.97)	(2.03)
K	...	0.36	(...)	(0.014)
L	1.22	2.06	(0.048)	(0.08)
M	31.8	44.4	(1.25)	(1.75)
N	7.6	8.4	(0.30)	(0.33)

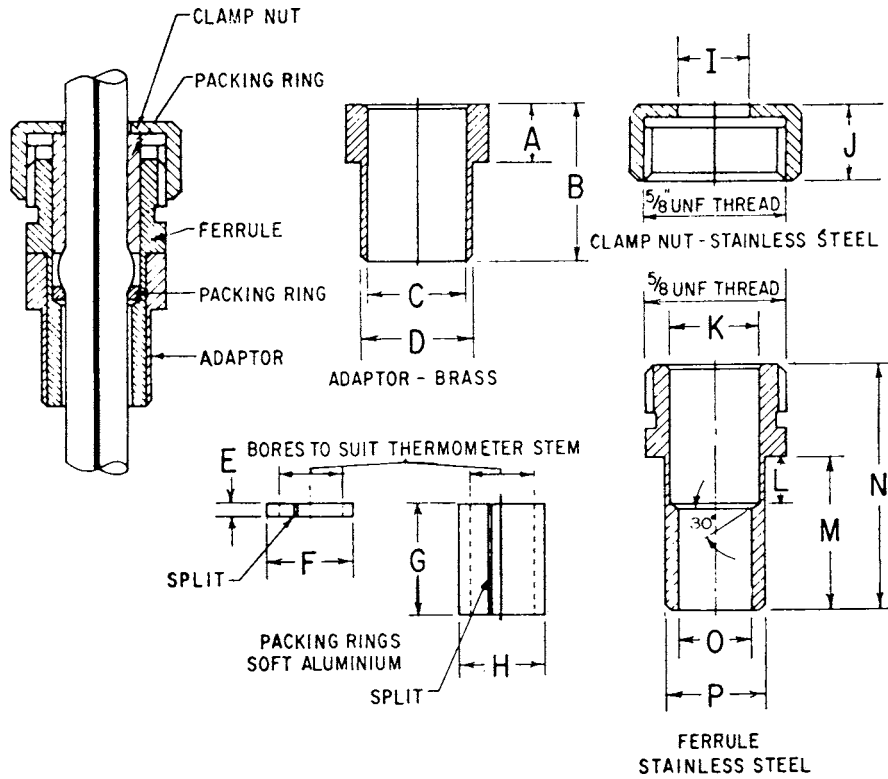
^A Includes tolerance for length of thermometer given in Specification E1.

FIG. A1.4 Test Cup and Cover Assembly

A2. MANUFACTURING STANDARDIZATION OF THERMOMETER AND FERRULE

A2.1 The low-range thermometer, which conforms also to the specification for the cup thermometer in the tag closed tester (Test Method **D56**) and which frequently is fitted with a metal ferrule intended to fit the collar on the cover of the tag flash tester, can be supplemented by an adapter (**Fig. A2.1**) to be used in the larger diameter collar of the Pensky-Martens apparatus. Differences in dimensions of these collars, which do not affect test results, are a source of unnecessary trouble to manufacturers and suppliers of instruments, as well as to users.

A2.2 Dimensional requirements are shown in **Fig. A2.1**. Conformity to these requirements is not mandatory, but is desirable to users as well as suppliers of Pensky-Martens testers.



	mm		(in.)	
	min	max	(min)	(max)
A	6.20	6.50	(0.244)	(0.256)
B	17.0	18.0	(0.67)	(0.71)
C	9.80	9.85	(0.386)	(0.388)
D	11.92	12.24	(0.469)	(0.482)
E	1.40	1.65	(0.055)	(0.065)
F	8.56	8.61	(0.337)	(0.339)
G	12.4	13.0	(0.49)	(0.57)
H	8.56	8.61	(0.337)	(0.339)
I	8.1	8.6	(0.32)	(0.34)
J	9.9	10.7	(0.39)	(0.42)
K	8.64	8.69	(0.340)	(0.342)
L	5.1	5.6	(0.20)	(0.22)
M	17.0	17.5	(0.67)	(0.69)
N	27.4	28.2	(1.08)	(1.11)
O	7.11	7.16	(0.280)	(0.282)
P	9.73	9.78	(0.383)	(0.385)

FIG. A2.1 Dimensions for Thermometer Adapter, Ferrule, and Packing Ring

A3. THERMOMETER SPECIFICATIONS

A3.1 See Fig. A3.1 and Tables A3.1-A3.4.

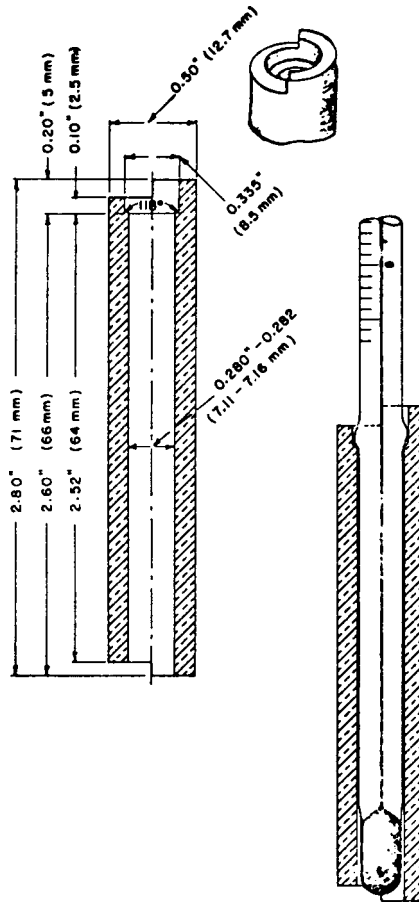


FIG. A3.1 Test Gage for Checking Enlargements on Thermometers

TABLE A3.1 IP Thermometer Specifications

NOTE 1—The stem shall be made with an enlargement having a diameter of 1.5 to 2.0 mm greater than the stem and a length of 3 to 5 mm, the bottom of the enlargement being 64 to 66 mm from the bottom of the bulb. These dimensions shall be measured with the test gage shown in Fig. A3.1.

Name	IP 15C	IP 16C	IP 101C
	Pensky-Martens Low	Pensky-Martens High	Pensky-Martens Medium
Range	-5 to + 110°C	90 to 370°C	20 to 150°C
Graduation	0.5°C	2°C	1°C
Immersion, mm	57	57	57
Overall length ±5 mm	290	280 ± 10	290
Stem diameter, mm	6.0 to 7.0	6.0 to 7.0	6.0 to 7.0
Bulb shape	cylindrical	cylindrical	cylindrical
Bulb length, mm	9 to 13	7 to 10	9 to 13
Bulb diameter, mm	not less than 5.5 and not greater than stem	not less than 4.5 and not greater than stem	not less than 5.5 and not greater than stem
Length of graduated portion, mm	140 to 175	143 to 180	140 to 175
Distance bottom of bulb to, mm	0°C 85 to 95	90°C 80 to 90	20°C 85 to 95
Longer lines at each	1 and 5°C	10 and 20°C	5°C
Figured at each	5°C	20°C	5°C
Expansion chamber	required	required	required
Top finish	ring	ring	ring
Scale error not to exceed ±	0.5°C	1 to 260°C 2°C above 260°C	1°C
See notes	1 and Table A3.2 for emergent stem temperatures	1 and Table A3.2 for emergent stem temperatures	1 and Table A3.2 for emergent stem temperatures

TABLE A3.3 Standardization Temperatures

NOTE 1—The emergent column temperatures are those attained when using the thermometers in the test equipment for which the thermometers were originally designed. In some cases these temperatures are markedly different from those realized during standardization.

Temperature	Average Temperature of Emergent Column	Temperature	Average Temperature of Emergent Column	Temperature	Average Temperature of Emergent Column	Temperature	Average Temperature of Emergent Column
Thermometer 9C (–5 to + 100°C)		Thermometer 9F (20 to 230°F)		Thermometer 10C (90 to 370°C)		Thermometer 10F (200 to 700°F)	
0°C	19°C	32°F	66°F	100°C	61°C	212°F	141°F
35°C	28°C	100°F	86°F	200°C	71°C	390°F	159°F
70°C	40°C	160°F	106°F	300°C	87°C	570°F	180°F
105°C	50°C	220°F	123°F	370°C	104°C	700°F	220°F
IP 15C (–7 to 110°C)		IP 15F (20 to 230°F)		IP 16C (90 to 370°C)		IP 16F (20 to 700°F)	
0°C	19°C	32°F	66°F	100°C	61°C	200°F	140°F
20°C	20°C	70°F	70°F	150°C	65°C	300°F	149°F
40°C	31°C	100°F	86°F	200°C	71°C	400°F	160°F
70°C	40°C	150°F	104°F	250°C	78°C	500°F	175°F
100°C	48°C	212°F	118°F	300°C	87°C	600°F	195°F
				350°C	99°C	700°F	220°F

TABLE A3.4 Specifications for Medium-Range Pensky-Martens

ASTM No. 88F (88C) Vegetable Oil Flash Thermometer		Medium-Range Pensky-Martens	
Name		5	
Reference Fig. No.			
Range	10–200°C		50–392°F
For test at			
A Immersion, mm		57	
Graduations:			
Subdivisions	0.5°C		1°F
Long lines at each	1°C and 5°C		5°F
Numbers at each	5°C		10°F
Scale error, max	0.5°C		1°F
Special inscription		ASTM 88F (88C) 57 mm IMM	
Expansion chamber:			
Permit heating to	205°C		400°F
B Total length, mm		285 to 295	
C Stem OD, mm		6.0 to 7.0	
D Bulb length, mm		8.0 to 12.0	
E Bulb OD, mm		>4.5 and <stem ^A	
Scale location:			
Bottom of bulb to line at	20°C		68°F
F Distance, mm		80 to 90	
G Length of graduated portion, mm		145 to 180	
Ice-point scale:			
Range			
H Bottom of bulb to ice-point, mm			
Contraction chamber:			
I Distance to bottom, min, mm			
J Distance to top, max, mm			
Stem enlargement:			
K OD, mm		7.5 to 8.5	
L Length, mm		2.5 to 5.0 ^A	
M Distance to bottom, mm		64 to 66	

^A Bulb OD shall be greater than 4.5 mm and less than the outside diameter of the stem (C).

A4. VERIFICATION OF APPARATUS PERFORMANCE

A4.1 *Certified Reference Material (CRM)*—CRM is a stable, pure (99 + mole % purity) hydrocarbon or other stable petroleum product with a method-specific flash point established by a method-specific interlaboratory study following ASTM RR:D02-1007 guidelines or ISO Guide 34 and 35.

A4.1.1 Values of the flash point corrected for barometric pressure for some reference materials and their typical limits are given in [Table A4.1](#)⁹ (see [Note A4.1](#)). Suppliers of CRMs will provide certificates stating the method-specific flash point

⁹ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:S15-1010.

TABLE A4.1 D93 Typical Flash Point Values and Typical Limits for CRM

NOTE 1—Supporting data for the interlaboratory study to generate the flash point in [Table A4.1](#) can be found in research report RR:S15-1010.⁹

Hydrocarbon	Purity, mole %	Flash Point, °C	Limits, °C
<i>n</i> -decane	99 +	52.8	±2.3
<i>n</i> -undecane	99 +	68.7	±3.0
<i>n</i> -tetradecane	99 +	109.3	±4.8
<i>n</i> -hexadecane	99 +	133.9	±5.9

for each material of the current production batch. Calculation of the limits for these other CRMs can be determined from the reproducibility value of these test methods, reduced by interlaboratory effect and then multiplied by 0.7. See Research Report RR:S15-1008.⁷

NOTE A4.1—Materials, purities, flash point values, and limits stated in [Table A4.1](#) were developed in an ASTM interlaboratory program to determine suitability of use for verification fluids in flash point test methods. Other materials, purities, flash point values, and limits can be suitable when produced according to the practices of ASTM RR:D02-1007 or ISO Guides 34 and 35. Certificates of performance of such materials should be consulted before use, as the flashpoint value will vary dependent on the composition of each CRM batch.

A4.2 *Secondary Working Standard (SWS)*—SWS is a stable, pure (99 + mole % purity) hydrocarbon, or other petroleum product whose composition is known to remain appreciably stable.

A4.2.1 Establish the mean flash point and the statistical control limits (3σ) for the SWS using standard statistical techniques. (See ASTM MNL 7).¹⁰

¹⁰ *Manual on Presentation of Data and Control Chart Analysis, ASTM MNL*, 6th ed., ASTM International, W. Conshohocken, 1990.

APPENDIXES

(Nonmandatory Information)

X1. FLASH POINT MASKING PHENOMENON

X1.1 A condition during flash point testing can occur with certain mixtures whereby the nonflammable component of the sample tends to inert the vapor space above the liquid, thus preventing a flash. Under this condition, the flash point of the material is masked resulting in the reporting of incorrect high flash point or no flash point.

X1.2 This flash point masking phenomenon most frequently occurs with ignitable liquids that contain certain halogenated hydrocarbons such as dichloromethane (methylene chloride) and trichloroethylene.

X1.3 Under this condition, no distinct flash as defined in [3.1.5](#) of these test methods is observed. Instead a significant enlargement of the test flame and a change in the color of the

test flame from blue to yellow-orange laminar flame is observed.

X1.4 Under this condition, continued heating and testing for flash point at temperatures above ambient temperature, have resulted in significant burning of the ignitable vapor outside the test cup, often above the test flame. This can be a potential fire hazard if not recognized.

X1.5 It is recommended that if this condition is encountered during the flash point testing of these type of materials, testing should be discontinued.

X1.6 Further commentaries regarding flash point test and flammability of mixtures can be found in Test Method [E502](#).

X2. FLASH POINT TEST AND FLAMMABILITY OF MIXTURES

X2.1 While the flash point can be used to indicate the flammability of liquid materials for certain end uses, flash point does not represent the minimum temperature at which a material can evolve flammable vapors.

X2.2 There are instances with pure materials where the absence of a flash point does not ensure freedom from flammability. Included in this category are materials that require large diameters for flash propagation, such as trichloroethylene. This material will not propagate a flame in apparatus the size of a flash point tester, however, its vapors are flammable and will burn when ignited in apparatus of adequate size.

X2.3 When a liquid contains flammable and nonflammable components, there are cases where this liquid can evolve

flammable vapors under certain conditions and yet will not exhibit a close-cup flash point. This phenomenon is noted when a nonflammable component is sufficiently volatile and present in sufficient quantity to inert the vapor space of the closed cup, thus preventing a flash. In addition, there are certain instances where an appreciable quantity of the nonflammable component will be present in the vapor, and the material will exhibit no flash point.

X2.4 Liquids containing a highly volatile nonflammable component or impurity, which exhibit no flash point because of the influence of the nonflammable material, may form flammable mixtures if totally flash vaporized in air in the proper proportions.

SUMMARY OF CHANGES

Subcommittee D02.08 has identified the location of selected changes to this standard since the last issue (D93 – 12) that may impact the use of this standard. (Approved July 15, 2013.)

(1) Change of 360°C to 370°C in the Scope.

(2) Addition of reference to **Note 1** in **Note 3**.

Subcommittee D02.08 has identified the location of selected changes to this standard since the last issue (D93 – 11) that may impact the use of this standard. (Approved Nov. 1, 2012.)

(1) New warning in **11.1.2**.

(2) Revised wording of the warning in **11.1.5.2**.

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Designation: D 2500 – 05

An American National Standard
British Standard 4458



Designation: 219/82

Standard Test Method for Cloud Point of Petroleum Products¹

This standard is issued under the fixed designation D 2500; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope*

1.1 This test method covers only petroleum products and biodiesel fuels that are transparent in layers 40 mm in thickness, and with a cloud point below 49°C.

NOTE 1—The interlaboratory program consisted of petroleum products of Test Method D 1500 color of 3.5 and lower. The precisions stated in this test method may not apply to samples with ASTM color higher than 3.5.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 7.

2. Referenced Documents

2.1 ASTM Standards:²

D 1500 Test Method for ASTM Color of Petroleum Products (ASTM Color Scale)

E 1 Specification for ASTM Liquid-in-Glass Thermometers

2.2 *Energy Institute Standard:*
Specifications for IP Standard Thermometers³

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *biodiesel, n*—a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100.

3.1.1.1 *Discussion*—Biodiesel is typically produced by a reaction of vegetable oil or animal fat with an alcohol such as

methanol or ethanol in the presence of a catalyst to yield mono-esters and glycerin. The fuel typically may contain up to 14 different types of fatty acids that are chemically transformed into fatty acid methyl esters (FAME).

3.1.2 *biodiesel blend, n*—a blend of biodiesel fuel with petroleum-based diesel fuel designated BXX, where XX is the volume % of biodiesel.

3.1.3 *cloud point, n*—*in petroleum products and biodiesel fuels*, the temperature of a liquid specimen when the smallest observable cluster of hydrocarbon crystals first occurs upon cooling under prescribed conditions.

3.1.3.1 *Discussion*—To many observers, the cluster of wax crystals looks like a patch of whitish or milky cloud, hence the name of the test method. The cloud appears when the temperature of the specimen is low enough to cause wax crystals to form. For many specimens, the crystals first form at the lower circumferential wall of the test jar where the temperature is lowest. The size and position of the cloud or cluster at the cloud point varies depending on the nature of the specimen. Some samples will form large, easily observable, clusters, while others are barely perceptible.

3.1.3.2 *Discussion*—Upon cooling to temperatures lower than the cloud point, clusters of crystals will grow in multiple directions; for example, around the lower circumference of the test jar, towards the center of the jar, or vertically upwards. The crystals can develop into a ring of cloud along the bottom circumference, followed by extensive crystallization across the bottom of the test jar as temperature decreases. Nevertheless, the cloud point is defined as the temperature at which the crystals first appear, not when an entire ring or full layer of wax has been formed at the bottom of the test jar.

3.1.3.3 *Discussion*—In general, it is easier to detect the cloud point of samples with large clusters that form quickly, such as paraffinic samples. The contrast between the opacity of the cluster and the liquid is also sharper. In addition, small brightly-reflective spots can sometimes be observed inside the cluster when the specimen is well illuminated. For other more difficult samples, such as naphthenic, hydrocracked, and those samples whose cold flow behavior have been chemically altered, the appearance of the first cloud can be less distinct. The rate of crystal growth is slow, the opacity contrast is weak,

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.07 on Flow Properties.

Current edition approved July 1, 2005. Published August 2005. Originally approved in 1966. Last previous edition approved in 2002 as D 2500–02¹.

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

³ Available from Energy Institute, 61 New Cavendish St., London, England W1M 8AR.

*A Summary of Changes section appears at the end of this standard.

and the boundary of the cluster is more diffuse. As the temperature of these specimens decrease below the cloud point, the diffuse cluster will increase in size and can form a general haze throughout. A slight haze throughout the entire sample, which slowly becomes more apparent as the temperature of the specimen decreases, can also be caused by traces of water in the specimen instead of crystal formation (see **Note 4**). With these difficult samples, drying the sample prior to testing can eliminate this type of interference.

3.1.3.4 *Discussion*—The purpose of the cloud point method is to detect the presence of the wax crystals in the specimen; however trace amounts of water and inorganic compounds may also be present. The intent of the cloud point method is to capture the temperature at which the liquids in the specimen begin to change from a single liquid phase to a two-phase system containing solid and liquid. It is not the intent of this test method to monitor the phase transition of the trace components, such as water.

4. Summary of Test Method

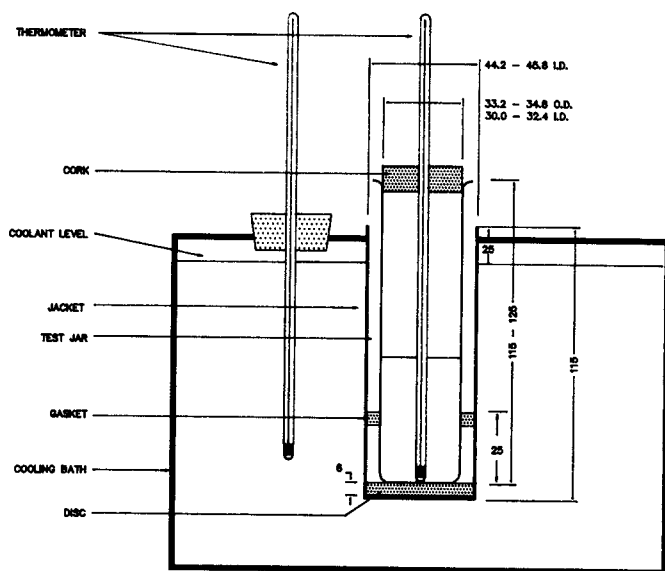
4.1 The specimen is cooled at a specified rate and examined periodically. The temperature at which a cloud is first observed at the bottom of the test jar is recorded as the cloud point.

5. Significance and Use

5.1 For petroleum products and biodiesel fuels, cloud point of a petroleum product is an index of the lowest temperature of their utility for certain applications.

6. Apparatus (see **Fig. 1**)

6.1 *Test Jar*, clear, cylindrical glass, flat bottom, 33.2 to 34.8-mm outside diameter and 115 and 125-mm height. The inside diameter of the jar may range from 30 to 32.4 mm within the constraint that the wall thickness be no greater than 1.6 mm. The jar should be marked with a line to indicate sample height 54 ± 3 mm above the inside bottom.



NOTE—All dimensions are in millimetres.
FIG. 1 Apparatus for Cloud Point Test

6.2 *Thermometers*, having ranges shown below and conforming to the requirements as prescribed in Specification **E 1** or Specifications for IP Standard Thermometers.

Thermometer	Temperature Range	Thermometer Number	
		ASTM	IP
High cloud and pour	-38 to +50°C	5C	1C
Low cloud and pour	-80 to +20°C	6C	2C

6.3 *Cork*, to fit the test jar, bored centrally for the test thermometer.

6.4 *Jacket*, metal or glass, watertight, cylindrical, flat bottom, about 115 mm in depth, with an inside diameter of 44.2 to 45.8 mm. It shall be supported free of excessive vibration and firmly in a vertical position in the cooling bath of **6.7** so that not more than 25 mm projects out of the cooling medium.

6.5 *Disk*, cork or felt, 6-mm thick to fit loosely inside the jacket.

6.6 *Gasket*, ring form, about 5 mm in thickness, to fit snugly around the outside of the test jar and loosely inside the jacket. The gasket may be made of rubber, leather, or other material that is elastic enough to cling to the test jar and hard enough to hold its shape. Its purpose is to prevent the test jar from touching the jacket.

6.7 *Bath or Baths*, maintained at prescribed temperatures with a firm support to hold the jacket vertical. The required bath temperatures may be maintained by refrigeration if available, otherwise by suitable freezing mixtures.

NOTE 2—The mixtures commonly used for temperatures down to those shown are as follows:

Ice and water	10°C
Crushed ice and sodium chloride crystals	-12°C
Crushed ice and calcium chloride crystals	-26°C
Acetone, methyl or ethyl alcohol, or petroleum naphtha chilled in a covered metal beaker with an ice-salt mixture to -12°C, then with enough solid carbon dioxide to give the desired temperature	-57°C

7. Reagents and Materials

7.1 *Acetone*—Technical grade acetone is suitable for the cooling bath, provided it does not leave a residue on drying. (**Warning**—Extremely flammable.)

7.2 *Calcium Chloride*—Commercial or technical grade calcium chloride is suitable.

7.3 *Carbon Dioxide (Solid) or Dry Ice*—A commercial grade of dry ice is suitable for use in the cooling bath.

7.4 *Ethanol or Ethyl Alcohol*—A commercial or technical grade of dry ethanol is suitable for the cooling bath. (**Warning**—Flammable. Denatured, cannot be made non-toxic.)

7.5 *Methanol or Methyl Alcohol*—A commercial or technical grade of dry methanol is suitable for the cooling bath. (**Warning**—Flammable. Vapor harmful.)

7.6 *Petroleum Naphtha*—A commercial or technical grade of petroleum naphtha is suitable for the cooling bath. (**Warning**—Combustible. Vapor harmful.)

7.7 *Sodium Chloride Crystals*—Commercial or technical grade sodium chloride is suitable.

7.8 *Sodium Sulfate*—A reagent grade of anhydrous sodium sulfate should be used when required (see **Note 4**).

8. Procedure

8.1 Bring the sample to be tested to a temperature at least 14°C above the expected cloud point. Remove any moisture present by a method such as filtration through dry lintless filter paper until the oil is perfectly clear, but make such filtration at a temperature of at least 14°C above the approximate cloud point.

8.2 Pour the sample into the test jar to the level mark.

8.3 Close the test jar tightly by the cork carrying the test thermometer. Use the high cloud and pour thermometer if the expected cloud point is above -36°C and the low cloud and pour thermometer if the expected cloud point is below -36°C. Adjust the position of the cork and the thermometer so that the cork fits tightly, the thermometer and the jar are coaxial, and the thermometer bulb is resting on the bottom of the jar.

NOTE 3—Liquid column separation of thermometers occasionally occurs and may escape detection. Thermometers should be checked periodically and used only if their ice points are $0 \pm 1^\circ\text{C}$, when the thermometer is immersed to the immersion line in an ice bath, and when the emergent column temperature does not differ significantly from 21°C. Alternatively, immerse the thermometer to a reading and correct for the resultant cooler stem temperature.

8.4 See that the disk, gasket, and the inside of the jacket are clean and dry. Place the disk in the bottom of the jacket. The disk and jacket shall have been placed in the cooling medium a minimum of 10 min before the test jar is inserted. The use of a jacket cover while the empty jacket is cooling is permitted. Place the gasket around the test jar, 25 mm from the bottom. Insert the test jar in the jacket. Never place a jar directly into the cooling medium.

NOTE 4—Failure to keep the disk, gasket, and the inside of the jacket clean and dry may lead to frost formation, which may cause erroneous results.

8.5 Maintain the temperature of the cooling bath at $0 \pm 1.5^\circ\text{C}$.

8.6 At each test thermometer reading that is a multiple of 1°C, remove the test jar from the jacket quickly but without disturbing the specimen, inspect for cloud, and replace in the jacket. This complete operation shall require not more than 3 s. If the oil does not show a cloud when it has been cooled to 9°C, transfer the test jar to a jacket in a second bath maintained at a temperature of $-18 \pm 1.5^\circ\text{C}$ (see Table 1). Do not transfer the jacket. If the specimen does not show a cloud when it has been cooled to -6°C, transfer the test jar to a jacket in a third bath maintained at a temperature of $-33 \pm 1.5^\circ\text{C}$. For the determination of very low cloud points, additional baths are required, each bath to be maintained in accordance with Table 1. In each case, transfer the jar to the next bath, if the specimen does not exhibit cloud point and the temperature of the specimen

reaches the lowest specimen temperature in the range identified for the current bath in use, based on the ranges stated in Table 1.

8.7 Report the cloud point, to the nearest 1°C, at which any cloud is observed at the bottom of the test jar, which is confirmed by continued cooling.

NOTE 5—A wax cloud or haze is always noted first at the bottom of the test jar where the temperature is lowest. A slight haze throughout the entire sample, which slowly becomes more apparent as the temperature is lowered, is usually due to traces of water in the oil. Generally this water haze will not interfere with the determination of the wax cloud point. In most cases of interference, filtration through dry lintless filter papers, such as described in 8.1, is sufficient. In the case of diesel fuels, however, if the haze is very dense, a fresh portion of the sample should be dried by shaking 100 mL with 5 g of anhydrous sodium sulfate for at least 5 min and then filtering through dry lintless filter paper. Given sufficient contact time, this procedure will remove or sufficiently reduce the water haze so that the wax cloud can be readily discerned. Drying and filtering should be done always at a temperature at least 14°C above the approximate cloud point but otherwise not in excess of 49°C.

9. Report

9.1 Report the temperature recorded in 8.7 as the cloud point, Test Method D 2500.

10. Precision and Bias

10.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

10.1.1 *Repeatability*—The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of this test method, exceed 2°C only in 1 case in 20.

10.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of this test method, exceed 4°C only in 1 case in 20.

10.1.3 The precision statements were derived from a 1990 interlaboratory cooperative test program.⁴ Participants analyzed 13 sample sets comprised of various distillate fuels and lubricating oils with temperature range from -1 to -37°C. Eight laboratories participated with the manual D 2500/IP219 test method. Information on the type of samples and their average cloud points are in the research report.

10.2 *Bias*—The procedure in this test method has no bias, because the value of cloud point can be defined only in terms of a test method.

10.3 *Precision for Biodiesel Products*⁵—The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

10.3.1 *Repeatability for Blends of Biodiesel in Diesel*—The difference between successive test results obtained by the same operator, using the same apparatus, under constant operating

TABLE 1 Bath and Sample Temperature Ranges

Bath	Bath Temperature Setting, °C	Sample Temperature Range, °C
1	0 ± 1.5	Start to 9
2	-18 ± 1.5	9 to -6
3	-33 ± 1.5	-6 to -24
4	-51 ± 1.5	-24 to -42
5	-69 ± 1.5	-42 to -60

⁴ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1444.

⁵ Supporting data (the results of the 2001 interlaboratory cooperative test program) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1524.

conditions, on identical test material would, in the long run, in the normal and correct operation of this test method, exceed 2°C only in 1 case in 20.

10.3.2 *Reproducibility for Blends of Biodiesel in Diesel*—The difference between two single and independent test results obtained by different operators, working in different laboratories, on identical test material would, in the long run, in the normal and correct operation of this test method, exceed 3°C only in 1 case in 20.

NOTE 6—The precision for blends of biodiesel in diesel samples comprised cloud points from about -2 to +10°C.

10.3.3 The precision statements were derived from a 2001 interlaboratory cooperative test program.⁵ Participants analyzed eleven sample sets comprised of different blends of two petroleum distillate fuels, diesel and kerosene, with various biodiesel fuels with temperature range from +10 to -45°C. Ten laboratories participated with the manual D 2500/IP219 test method. Information on the type of samples and their average cloud points are in the research report.

NOTE 7—One of the outcomes of the interlaboratory study was the selection of the sample types, since the ones used in the study contributed to a difficulty in determining the precision statement. Kerosene is a sufficiently different fuel type from biodiesel to cause some slight separation of phases upon cooling when in B20 blends. Also, the particular kerosene sample used was atypical, which complicated the study further. Therefore, data from the blends of kerosene in biodiesel were not used in the precision statement. In addition, the diesel fuel used in the research report was high cloud point material. Due to the cloud point of the base diesel material, this temperature range in the precision statement was limited.

NOTE 8—A future interlaboratory cloud study will be done to include a wider range of base biodiesel fuels with various distillate blend stocks.

10.4 *Bias for Biodiesel Products*⁵—The procedure in this test method has no bias, because the value of cloud point can be defined only in terms of a test method.

11. Keywords

11.1 cloud point; petroleum products; wax crystals

SUMMARY OF CHANGES

Subcommittee D02.07 has identified the location of selected changes to this standard since the last issue, D 2500-02^{e1}, that may impact the use of this standard.

(1) Added a discussion to the definition of cloud point (3.1.3).

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Standard Test Method for Cetane Number of Diesel Fuel Oil¹

This standard is issued under the fixed designation D 613; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope*

1.1 This test method determines the rating of diesel fuel oil in terms of an arbitrary scale of cetane numbers using a standard single cylinder, four-stroke cycle, variable compression ratio, indirect injected diesel engine.

1.2 The cetane number scale covers the range from zero (0) to 100 but typical testing is in the range of 30 to 65 cetane number.

1.3 The values for operating conditions are stated in SI units and are to be regarded as the standard. The values given in parentheses are the historical inch-pound units for information only. In addition, the engine measurements continue to be in inch-pound units because of the extensive and expensive tooling that has been created for these units.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For more specific warning statements, see [Annex A1](#).

2. Referenced Documents

2.1 ASTM Standards:²

- D 975** Specification for Diesel Fuel Oils
- D 1193** Specification for Reagent Water
- D 2500** Test Method for Cloud Point of Petroleum Products
- D 4057** Practice for Manual Sampling of Petroleum and Petroleum Products
- D 4175** Terminology Relating to Petroleum, Petroleum Products, and Lubricants

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

E 1 Specification for ASTM Liquid-in-Glass Thermometers

E 456 Terminology Relating to Quality and Statistics

E 542 Practice for Calibration of Laboratory Volumetric Apparatus

E 832 Specification for Laboratory Filter Papers

3. Terminology

3.1 Definitions:

3.1.1 *accepted reference value (ARV), n*—a value that serves as an agreed-upon reference for comparison, and which is derived as: (1) a theoretical or established value, based on scientific principles, or (2) an assigned or certified value, based on experimental work of some national or international organization, or (3) a consensus or certified value, based on collaborative experimental work under the auspices of a scientific or engineering group. **E 456**

3.1.1.1 *Discussion*—In the context of this test method, accepted reference value is understood to apply to the cetane number of specific reference materials determined empirically under reproducibility conditions by the National Exchange Group or another recognized exchange testing organization.

3.1.2 *cetane number, n*—a measure of the ignition performance of a diesel fuel oil obtained by comparing it to reference fuels in a standardized engine test. **D 4175**

3.1.2.1 *Discussion*—In the context of this test method, ignition performance is understood to mean the ignition delay of the fuel as determined in a standard test engine under controlled conditions of fuel flow rate, injection timing and compression ratio.

3.1.3 *compression ratio, n*—the ratio of the volume of the combustion chamber including the precombustion chamber with the piston at bottom dead center to the comparable volume with the piston at top dead center.

3.1.4 *ignition delay, n*—that period of time, expressed in degrees of crank angle rotation, between the start of fuel injection and the start of combustion.

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.01 on Combustion Characteristics.

Current edition approved May 1, 2005. Published May 2005. Originally approved in 1941. Last previous edition approved in 2003 as D 613–03b.

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

*A Summary of Changes section appears at the end of this standard.

3.1.5 *injection timing (injection advance), n*—that time in the combustion cycle, measured in degrees of crank angle, at which fuel injection into the combustion chamber is initiated.

3.1.6 *repeatability conditions, n*—conditions where independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time.

E 456

3.1.6.1 *Discussion*—In the context of this method, a short time interval between two ratings on a sample fuel is understood to be not less than the time to obtain at least one rating on another sample fuel between them but not so long as to permit any significant change in the sample fuel, test equipment, or environment.

3.1.7 *reproducibility conditions, n*—conditions where test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment.

E 456

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *cetane meter (ignition delay meter), n*—the electronic instrument which displays injection advance and ignition delay derived from input pulses of multiple transducers (pickups).

3.2.2 *Check Fuels, n*—for quality control testing, a diesel fuel oil of selected characteristics having a cetane number accepted reference value determined by round-robin testing under reproducibility conditions.

3.2.3 *combustion pickup, n*—pressure transducer exposed to cylinder pressure to indicate the start of combustion.

3.2.4 *handwheel reading, n*—an arbitrary numerical value, related to compression ratio, obtained from a micrometer scale that indicates the position of the variable compression plug in the precombustion chamber of the engine.

3.2.5 *injector opening pressure, n*—the fuel pressure that overcomes the resistance of the spring which normally holds the nozzle pintle closed, and thus forces the pintle to lift and release an injection spray from the nozzle.

3.2.6 *injector pickup, n*—transducer to detect motion of the injector pintle, thereby indicating the beginning of injection.

3.2.7 *primary reference fuels, n*— *n*-cetane, heptamethyl nonane (HMN) and volumetrically proportioned mixtures of these materials which now define the cetane number scale by the relationship:

$$\text{Cetane Number} = \% n\text{-cetane} + 0.15 (\% \text{HMN}) \quad (1)$$

3.2.7.1 *Discussion*—In the context of this test method, the arbitrary cetane number scale was originally defined as the volume percent of *n*-cetane in a blend with alpha-methylnaphthalene (AMN) where *n*-cetane had an assigned value of 100 and AMN an assigned value of zero (0). A change from alpha-methylnaphthalene to heptamethylnonane as the low cetane ingredient was made in 1962 to utilize a material of better storage stability and availability. Heptamethylnonane was determined to have a cetane number accepted reference value (CN_{ARV}) of 15 based on engine testing by the ASTM Diesel National Exchange Group, using blends of *n*-cetane and AMN as primary reference fuels.

3.2.7.2 *Discussion*—In the context of this test method, the Diesel National Exchange Group of Subcommittee D02.01³ is composed of petroleum industry, governmental, and independent laboratories. It conducts regular monthly exchange sample analyses to generate precision data for this engine test standard and determines the CN_{ARV} of reference materials used by all laboratories.

3.2.8 *reference pickups, n*—transducer(s) mounted over the flywheel of the engine, triggered by a flywheel indicator, used to establish a top-dead-center (tdc) reference and a time base for calibration of the ignition delay meter.

3.2.9 *secondary reference fuels, n*—volumetrically proportioned blends of two selected, numbered, and paired hydrocarbon mixtures designated *T Fuel* (high cetane) and *U Fuel* (low cetane) that have been rated by the ASTM Diesel National Exchange Group using primary reference fuels to determine a cetane number accepted reference value for each individually and for various combinations of the two.

4. Summary of Test Method

4.1 The cetane number of a diesel fuel oil is determined by comparing its combustion characteristics in a test engine with those for blends of reference fuels of known cetane number under standard operating conditions. This is accomplished using the bracketing handwheel procedure which varies the compression ratio (handwheel reading) for the sample and each of two bracketing reference fuels to obtain a specific ignition delay permitting interpolation of cetane number in terms of handwheel reading.

5. Significance and Use

5.1 The cetane number provides a measure of the ignition characteristics of diesel fuel oil in compression ignition engines.

5.2 This test method is used by engine manufacturers, petroleum refiners and marketers, and in commerce as a primary specification measurement related to matching of fuels and engines.

5.3 Cetane number is determined at constant speed in a precombustion chamber type compression ignition test engine. The relationship of test engine performance to full scale, variable speed, variable load engines is not completely understood.

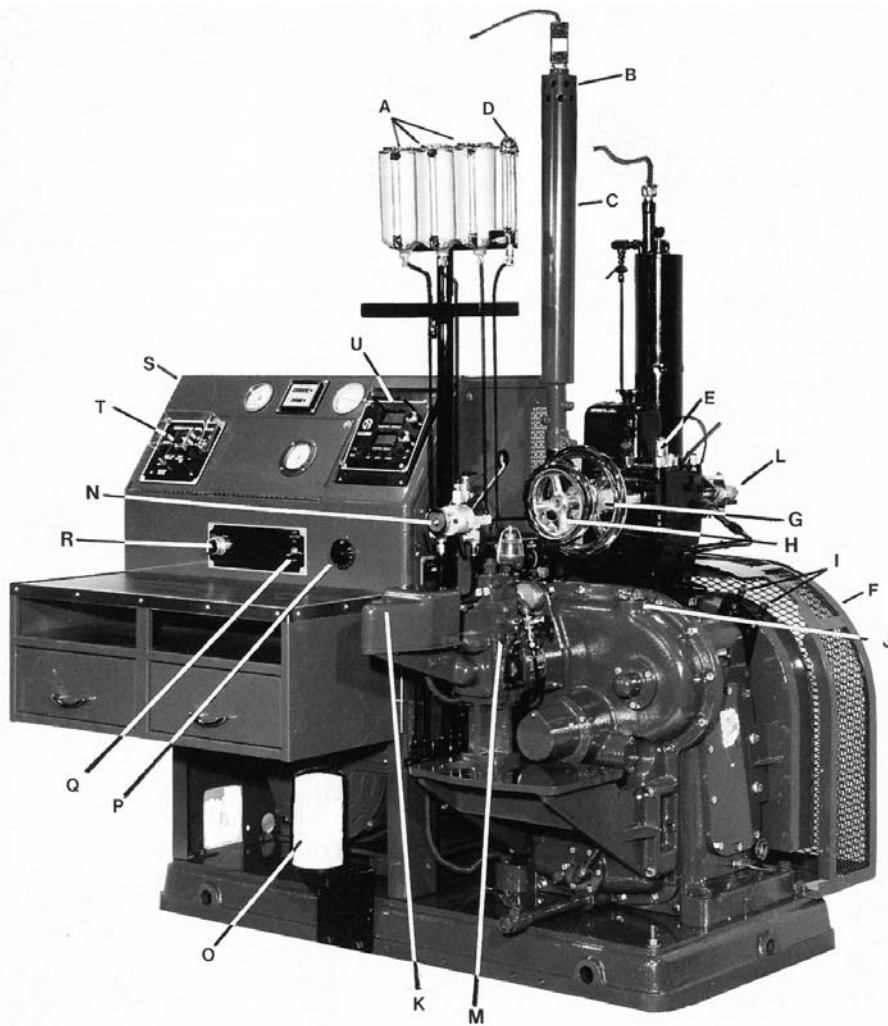
5.4 This test method may be used for unconventional fuels such as synthetics, vegetable oils, and the like. However, the relationship to the performance of such materials in full scale engines is not completely understood.

6. Interferences

6.1 (**Warning**—Avoid exposure of sample fuels and reference fuels to sunlight or fluorescent lamp UV emissions to minimize induced chemical reactions that can affect cetane number ratings.)⁴

³ Bylaws governing ASTM Subcommittee D02.01 on Combustion Characteristics are available from the subcommittee or from ASTM International.

⁴ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1502.



- A—Fuel Tanks
- B—Air Heater Housing
- C—Air Intake Silencer
- D—Fuel Flow Rate Buret
- E—Combustion Pickup
- F—Safety Guard
- G—Variable Compression Plug Handwheel
- H—V.C.P. Locking Handwheel
- I—Flywheel Pickups
- J—Oil Filler Cap
- K—Injection Pump Safety Shut-Off Solenoid
- L—Injector Assembly
- M—Fuel Injection Pump
- N—Fuel Selector-Valve
- O—Oil Filter
- P—Crankcase Oil Heater Control
- Q—Air Heater Switch
- R—Engine Start-Stop Switch
- S—Instrument Panel
- T—Intake Air Temperature Controller
- U—Dual Digital Cetane Meter

FIG. 1 Cetane Method Test Engine Assembly

6.1.1 Exposure of these fuels to UV wavelengths shorter than 550 nm for a short period of time may significantly affect cetane number ratings.

6.2 Certain gases and fumes present in the area where the cetane test engine is located may have a measurable effect on the cetane number test result.

6.3 This test method is not suitable for rating diesel fuel oils with fluid properties that interfere with unimpeded gravity flow of fuel to the fuel pump or delivery through the injector nozzle.

7. Apparatus

7.1 *Engine Equipment*^{5,6}—This test method uses a single cylinder engine which consists of a standard crankcase with

fuel pump assembly, a cylinder with separate head assembly of the precombustion type, thermal syphon recirculating jacket coolant system, multiple fuel tank system with selector valving, injector assembly with specific injector nozzle, electrical controls, and a suitable exhaust pipe. The engine is belt connected to a special electric power-absorption motor which acts as a motor driver to start the engine and as a means to absorb power at constant speed when combustion is occurring (engine firing). See Fig. 1.

7.1.1 See Annex A2 for detail and description of all critical, non-critical and equivalent engine equipment.

7.2 *Instrumentation*^{5,6}—This test method uses an electronic instrument to measure injection and ignition delay timing as well as conventional thermometry, gages and general purpose meters.

7.2.1 A *Cetane Meter*, (Ignition Delay Meter) is critical and shall be used for this test method.

7.2.2 See Annex A3 for detail and description of all critical, non-critical and equivalent instrumentation.

⁵ The sole source of supply of the engine equipment and instrumentation known to the committee at this time is Waukesha Engine, Dresser Inc., 1000 West St. Paul Avenue, Waukesha, WI 53188. Waukesha Engine also has CFR engine authorized sales and service organizations in selected geographical areas.

⁶ If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee¹, which you may attend.

7.3 Reference Fuel Dispensing Equipment—This test method requires repeated blending of two secondary reference fuel materials in volumetric proportions on an as-needed basis. Measurement shall be performed accurately because rating error is proportional to blending error.

7.3.1 Volumetric Blending of Reference Fuels—Volumetric blending has historically been employed to prepare the required blends of reference fuels. For volumetric blending, a set of two burets or accurate volumetric ware shall be used and the desired batch quantity shall be collected in an appropriate container and thoroughly mixed before being introduced to the engine fuel system.

7.3.1.1 Calibrated burets or volumetric ware having a capacity of 400 or 500 mL and a maximum volumetric tolerance of $\pm 0.2\%$ shall be used. Calibration shall be verified in accordance with Practice **E 542**.

7.3.1.2 Calibrated burets shall be outfitted with a dispensing valve and delivery tip to accurately control dispensed volume. The delivery tip shall be of such size and design that shutoff tip discharge does not exceed 0.5 mL.

7.3.1.3 The rate of delivery from the dispensing system shall not exceed 500 mL per 60 s.

7.3.1.4 The set of burets for the reference and standardization fuels shall be installed in such a manner and be supplied with fluids such that all components of each batch or blend are dispensed at the same temperature.

7.3.1.5 See **Appendix X1**, Volumetric Reference Fuel Blending Apparatus and Procedures, for typical dispensing system information.

7.3.2 Gravimetric Blending of Reference Fuels—Use of blending systems that allow preparation of the volumetrically-defined blends by gravimetric (mass) measurements based on the density of the individual components is also permitted, provided the system meets the requirement for maximum 0.2 % blending tolerance limits.

7.3.2.1 Calculate the mass equivalents of the volumetrically-defined blend components from the densities of the individual components at 15.56°C (60°F).

7.4 Auxiliary Apparatus:

7.4.1 Injector Nozzle Tester—The injector nozzle assembly shall be checked whenever the injector nozzle is removed and reassembled to ensure the initial pressure at which fuel is discharged from the nozzle is properly set. It is also important to inspect the type of spray pattern. Commercial injector nozzle testers which include a lever-operated pressure cylinder, fuel reservoir and pressure gage are available from several sources as common diesel engine maintenance equipment.

7.4.2 Special Maintenance Tools—A number of specialty tools and measuring instruments should be utilized for easy, convenient and effective maintenance of the engine and testing equipment. Lists and descriptions of these tools and instruments are available from the manufacturers of the engine equipment and those organizations offering engineering and service support for this test method.

8. Reagents and Reference Materials

8.1 Cylinder Jacket Coolant—Water shall be used in the cylinder jacket for laboratory locations where the resultant boiling temperature shall be $100 \pm 2^\circ\text{C}$ ($212 \pm 3^\circ\text{F}$). Water

with commercial glycol-based antifreeze added in sufficient quantity to meet the boiling temperature requirement shall be used when laboratory altitude dictates. A commercial multi-functional water treatment material should be used in the coolant to minimize corrosion and mineral scale that can alter heat transfer and rating results.

8.1.1 Water shall be understood to mean reagent water conforming to Type IV of Specification **D 1193**.

8.2 Engine Crankcase Lubricating Oil—An SAE 30 viscosity grade oil meeting service classification SF/CD or SG/CE shall be used. It shall contain a detergent additive and have a kinematic viscosity of 9.3 to 12.5 cSt (mm^2 per s) at 100°C (212°F) and a viscosity index of not less than 85. Oils containing viscosity index improvers shall not be used. Multi-graded oils shall not be used. (**Warning**—Lubricating oil is combustible, and its vapor is harmful. See **Annex A1**.)

8.3 Primary Reference Fuels—(**Warning**—Primary Reference Fuel—Combustible. Vapor harmful. See **Annex A1**.)^{6,7}

8.3.1 n-Cetane (n-hexadecane)—With a minimum purity of 99.0 % as determined by chromatographic analysis shall be used as the designated 100 cetane number component.

8.3.2 Heptamethylnonane (2,2,4,4,6,8,8-heptamethylnonane)—With a minimum purity of 98 % as determined by chromatographic analysis shall be used as the designated 15 cetane number component.

8.4 Secondary Reference Fuels^{6,8}—(**Warning**—Secondary Reference Fuel—Combustible. Vapor harmful. See **Annex A1**.)

8.4.1 T Fuel—Diesel fuel with a CN_{ARV} typically in the range of 73 to 75.

8.4.2 U Fuel—Diesel fuel with a CN_{ARV} typically in the range of 20 to 22.

8.4.3 Storage and use of *T Fuel* and *U Fuel* should be at temperatures above 0°C (32°F) to avoid potential solidification, particularly of *T Fuel*. Before a container that has been stored at low temperature is placed in service, it should be warmed to a temperature of at least 15°C (27°F) above its Cloud Point. (See Test Method **D 2500**.) It should be held at this temperature for a period of at least 30 min and then the container should be thoroughly remixed.

8.5 Check Fuels⁹—Diesel fuel oils typical of Specification **D 975** grade No. 2-D distillate fuel oil. (**Warning**—Check Fuel—Combustible. Vapor harmful. See **Annex A1**.)

8.5.1 Low Cetane Check Fuel—With a CN_{ARV} typically in the range of 38 to 42.

8.5.2 High Cetane Check Fuel—With a CN_{ARV} typically in the range of 50 to 55.

9. Sampling

9.1 Collect samples in accordance with Practice **D 4057** or **D 4177**.

⁷ The sole source of supply of primary reference fuels known to the committee at this time is Humphrey Chemical Co., Devine Street, North Haven, CT 06473.

⁸ The sole source of supply of the secondary reference and check fuels known to the committee at this time is Chevron Phillips Chemical Company LP, 1301 McKinney, Suite 2130, Houston, TX 77010-3030.

⁹ Blend Tables for batches of *T Fuel* and *U Fuel* can be obtained from the fuel supplier or by requesting Research Report RR: D02-1302 from ASTM International.

9.1.1 *Protection from Light*—Collect and store sample fuels in an opaque container such as a dark brown glass bottle, metal can, or a minimally reactive plastic container to minimize exposure to UV emissions from sources such as sunlight or fluorescent lamps.

9.2 *Fuel Temperature*—Samples shall be brought to room temperature typically 18 to 32°C (65 to 90°F) before engine testing.

9.3 *Filtration*—Samples may be filtered through a Type I, Class A filter paper at room temperature and pressure before engine testing. See Specification **E 832**.

10. Basic Engine and Instrument Settings and Standard Operating Conditions

10.1 *Installation of Engine Equipment and Instrumentation*—Installation of the engine and instrumentation requires placement of the engine on a suitable foundation and hookup of all utilities. Engineering and technical support for this function is required, and the user shall be responsible to comply with all local and national codes and installation requirements.

10.1.1 Proper operation of the test engine requires assembly of a number of engine components and adjustment of a series of engine variables to prescribed specifications. Some of these settings are established by component specifications, others are established at the time of engine assembly or after overhaul and still others are engine running conditions that must be observed or determined by operator adjustment, or both, during the testing process.

10.2 Conditions Based on Component Specifications:

10.2.1 *Engine Speed*—900 ± 9 rpm, when the engine is operating with combustion with a maximum variation of 9 rpm occurring during a rating. Engine speed when combustion is occurring shall not be more than 3 rpm greater than that for motoring without combustion.

10.2.2 *Valve Timing*—The engine uses a four-stroke cycle with two crankshaft revolutions for each complete combustion cycle. The two critical valve events are those that occur near top-dead-center (tdc); intake valve opening and exhaust valve closing. See **Annex A4** for Camshaft Timing and Valve Lift Measurement Procedure.

10.2.2.1 Intake valve opening shall occur 10.0 ± 2.5° after-top-dead-center (atdc) with closing at 34° after-bottom-dead-center (abdc) on one revolution of the crankshaft and flywheel.

10.2.2.2 Exhaust valve opening shall occur 40° before-bottom-dead-center (bbdc) on the second revolution of the crankshaft or flywheel with closing at 15.0 ± 2.5° after-top-dead-center on the next revolution of the crankshaft or flywheel.

10.2.3 *Valve Lift*—Intake and exhaust cam lobe contours, while different in shape, shall have a contour rise of 6.223 to 6.350 mm (0.245 to 0.250 in.) from the base circle to the top of the lobe so that the resulting valve lift shall be 6.045 ± 0.05 mm (0.238 ± 0.002 in.). See **Annex A4** for Camshaft Timing and Valve Lift Measurement Procedure.

10.2.4 *Fuel Pump Timing*—Closure of the pump plunger inlet port shall occur at a flywheel crank angle between 300 and 306° on the engine compression stroke when the fuel flow-

rate-micrometer is set to a typical operating position and the variable timing device lever is at full advance (nearest to operator). See **Annex A4** for detailed instructions on setting and checking the fuel pump timing.

10.2.5 *Fuel Pump Inlet Pressure*—A minimum fuel head established by assembly of the fuel tanks (storage reservoirs) and flow rate measuring buret so that the discharge from them is 635 ± 25 mm (25 ± 1 in.) above the centerline of the fuel injection pump inlet.

10.3 Assembly Settings and Operating Conditions:

10.3.1 *Direction of Engine Rotation*—Clockwise rotation of the crankshaft when observed from the front of the engine.

10.3.2 *Injection Timing*—13.0° before-top-dead-center (bt dc), for the sample and reference fuels.

10.3.3 *Injector Nozzle Opening Pressure*—10.3 ± 0.34 MPa (1500 ± 50 psi).

10.3.4 *Injection Flow Rate*—13.0 ± 0.2 mL/min (60 ± 1 s per 13.0 mL).

10.3.5 *Injector Coolant Passage Temperature*—38 ± 3°C (100 ± 5°F).

10.3.6 Valve Clearances:

10.3.6.1 *Engine Stopped and Cold*—Clearance between the valve stem and valve rocker half-ball set to the following approximate measurements upon assembly before the engine is operated will typically provide the controlling engine running and hot clearance:

Intake Valve	0.075 mm (0.004 in.)
Exhaust Valve	0.330 mm (0.014 in.)

These clearances should ensure that both valves have sufficient clearance to cause valve seating during engine warm-up. The adjustable-length valve push-rods shall be set so that the valve rocker adjusting screws have adequate travel to permit the final clearance setting.

10.3.6.2 *Engine Running and Hot*—The clearance for both intake and exhaust valves shall be set to 0.20 ± 0.025 mm (0.008 ± 0.001 in.), measured under standard operating conditions with the engine running at equilibrium conditions on a typical diesel fuel oil.

10.3.7 *Oil Pressure*—172 to 207 kPa (25 to 30 psi). See **Annex A4** for the Adjusting Crankcase Lubricating Oil Pressure procedure.

10.3.8 *Oil Temperature*—57 ± 8°C (135 ± 15°F).

10.3.9 *Cylinder Jacket Coolant Temperature*—100 ± 2°C (212 ± 3°F).

10.3.10 *Intake Air Temperature*—66 ± 0.5°C (150 ± 1°F).

10.3.11 *Basic Ignition Delay*—13.0° for the sample and reference fuels.

10.3.12 Cylinder Jacket Coolant Level:

10.3.12.1 *Engine Stopped and Cold*—Treated water/coolant added to the cooling condenser—cylinder jacket to a level just observable in the bottom of the condenser sight glass will typically provide the controlling engine running and hot operating level.

10.3.12.2 *Engine Running and Hot*—Coolant level in the condenser sight glass shall be within ±1 cm (0.4 in.) of the LEVEL HOT mark on the coolant condenser.

10.3.13 Engine Crankcase Lubricating Oil Level:

10.3.13.1 *Engine Stopped and Cold*—Oil added to the crankcase so that the level is near the top of the sight glass will typically provide the controlling engine running and hot operating level.

10.3.13.2 *Engine Running and Hot*—Oil level shall be approximately mid-position in the crankcase oil sight glass.

10.3.14 *Crankcase Internal Pressure*—As mentioned by a gage or manometer connected to an opening to the inside of the crankcase through a snubber orifice to minimize pulsations, the pressure shall be less than zero (a vacuum) and typically from 25 to 150 mm (1 to 6 in.) of water less than atmospheric pressure. Vacuum shall not exceed 255 mm (10 in.) of water.

10.3.15 *Exhaust Back Pressure*—As measured by a gage or manometer connected to an opening in the exhaust surge tank or main exhaust stack through a snubber orifice to minimize pulsations, the static pressure should be as low as possible, but shall not create a vacuum nor exceed 254 mm (10 in.) of water differential in excess of atmospheric pressure.

10.3.16 *Exhaust and Crankcase Breather System Resonance*—The exhaust and crankcase breather piping systems shall have internal volumes and be of such length that gas resonance does not result. See [Appendix X2](#) for a suitable procedure to determine if resonance exists.

10.3.17 *Piston Over-Travel*—Assembly of the cylinder to the crankcase shall result in the piston protruding above the top of the cylinder surface 0.381 ± 0.025 mm (0.015 ± 0.001 in.) when the piston is at top-dead-center. Proper positioning is accomplished through the use of plastic or paper gaskets, available in several thicknesses and selected by trial and error for assembly between the cylinder and crankcase deck.

10.3.18 *Belt Tension*—The belts connecting the flywheel to the absorption motor shall be tightened, after an initial break-in, so that with the engine stopped, a 2.25 kg (5 lb) weight suspended from one belt half way between the flywheel and motor pulley shall depress the belt approximately 12.5 mm (0.5 in.).

10.3.19 *Setting Injector Nozzle Assembly Pressure and Spray Pattern Check*—(Warning—Personnel shall avoid contact with the spray pattern from injector nozzles because of the high pressure which can penetrate the skin. Spray pattern performance checks shall be made in a hood or where adequate ventilation insures that inhalation of the vapors is avoided.)

10.3.19.1 *Injector Opening or Release Pressure*—The pressure adjusting screw is adjustable and shall be set to release fuel at a pressure of 10.3 ± 0.34 MPa (1500 ± 50 psi). Check this setting using an injector nozzle bench tester, each time the nozzle is reassembled and after cleaning. Use of a commercial injector nozzle bench tester is recommended. See [Annex A4](#) for procedural detail.

10.3.19.2 *Injector Spray Pattern*—Check the spray pattern for symmetry and characteristic by inspection of the impression of a single injection made on a piece of filter paper or other slightly absorbent material placed at a distance of approximately 7.6 cm (3 in.) from the nozzle. A typical spray pattern is illustrated in [Fig. 2](#).

10.3.20 *Indexing Handwheel Reading*—Handwheel readings are a simple and convenient indication of engine compression ratio which is a critical variable in the cetane method

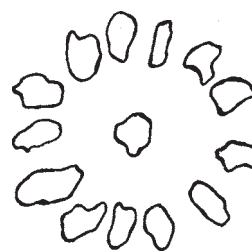


FIG. 2 Typical Injector Spray Pattern

of test. The actual compression ratio is not important but an indication of compression ratio which relates to cetane number is a useful guide for selecting reference fuels to bracket the sample of diesel fuel oil. The following procedure shall be used to index the handwheel reading when the engine is new or anytime the matched handwheel assembly/cylinder head combination is interchanged or mechanically reassembled. See [Appendix X3](#) for handwheel assembly reworking instructions.

10.3.20.1 *Handwheel Micrometer Drum and Scale Setting*—Refer to [Table 1](#) to select the appropriate handwheel reading to be used in aligning the drum and scale.

10.3.20.2 *Basic Setting of Variable Compression Plug*—Position the variable compression plug so that the flat surface is just visible and exactly in line with the edge of the threads of the combustion pickup hole, as verified with a straightedge.

10.3.20.3 *Setting Handwheel Reading*—Tighten the small locking handwheel snugly by hand to ensure that the variable compression plug is held in place in the bore. Loosen the lock nut of the large handwheel and remove the locking L-shaped key. Turn the large handwheel so that the edge of the drum is in alignment with the 1.000 graduation on the horizontal scale. Reinstall the L-shaped key in the nearest keyway slot of the large handwheel with the shorter leg in the handwheel. A slight shifting of the handwheel to achieve slot lineup will not affect the indexing. Tighten the lock nut hand-tight to hold the key in place. Remove the locating screw from the drum and rotate the drum so that the zero graduation mark is in line with the selected reading from [Table 1](#). Locate the screw hole in the drum which lines up with the handwheel hub hole and reinstall the locating screw. Wrench tighten the large handwheel lock nut and recheck that the variable compression plug is properly positioned and the handwheel reading is in accordance with the value in [Table 1](#).

10.3.21 *Basic Compression Pressure*—At a handwheel reading of 1.000, the compression pressure for an engine operated at standard barometric pressure of 760 mm Hg. (29.92 in. Hg) shall be 3275 ± 138 kPa (475 ± 20 psi) when read as quickly as possible after shutdown of the engine which had been at standard operating conditions. If the condition is not within limits, recheck the basic handwheel setting and, if

TABLE 1 Handwheel Setting for Various Cylinder Bore Diameters

Cylinder Diameter, in.	Handwheel Reading
3.250 (Standard Bore)	1.000
3.260 (Rebored 0.010 in. Oversize)	0.993
3.270 (Rebored 0.020 in. Oversize)	0.986
3.280 (Rebored 0.030 in. Oversize)	0.978

necessary, perform mechanical maintenance. See [Annex A4](#) for the Checking Compression Pressure procedure.

10.3.21.1 For engines operated at other than standard barometric pressure, the compression pressure will typically be in proportion to the ratio of the local barometric pressure divided by standard barometric pressure. As an example, an engine located where the barometric pressure is 710 mm Hg would be expected to have a compression pressure of approximately 3060 ± 138 kPa (444 ± 20 psi). (**Warning**—In addition to other precautions, compression pressure testing using a compression pressure gage should be completed in as short a period of time as possible to avoid the possibility of combustion occurrence due to the presence of any small amount of oil in the gage or combustion chamber.)

$$\begin{aligned} \text{Compression Pressure}_{(\text{LocalBaro.,mmHg})} \\ = 3275 \text{ kPa} \times \text{Local Baro./Standard Baro.} \end{aligned} \quad (2)$$

$$\begin{aligned} \text{Example: Compression Pressure}_{710\text{mmHg}} \\ = 3275 \times 710/760 = 3060 \text{ kPa} \end{aligned}$$

10.3.22 *Fuel Pump Lubricating Oil Level*—With the engine stopped, sufficient engine crankcase lubricating oil shall be added to the pump sump so that the level is at the mark on the dip stick. (**Warning**—As a result of engine operation, especially when the pump barrel/plunger assembly begins to wear, the level in the sump will increase due to fuel dilution as observed through a clear plastic side plate on the pump housing. When the level rises appreciably, the sump should be drained and a fresh charge of oil added.)

10.3.23 *Fuel Pump Timing Gear Box Oil Level*—With the engine stopped, unplug the openings on the top and at the mid-height of either side of the gear box. Add sufficient engine crankcase lubricating oil through the top hole to cause the level to rise to the height of the side opening. Replug both openings. (**Warning**—The pump and timing gear box oil sumps are not connected to each other and the lubrication for the two is independent.)

10.3.24 *Instrumentation*—Positioning of the reference pickups and injector pickup is important to ensure that timing of the injection and ignition delay functions is uniform and correct.

10.3.24.1 *Setting Reference Pickups*—These two pickups are identical and interchangeable. They are installed in a bracket positioned over the flywheel so that they clear the flywheel indicator which triggers them.

10.3.24.2 Position each pickup in the bracket so that it is properly referenced to the flywheel indicator in accordance with the instructions supplied with the specific pickup.

10.3.24.3 Measurement of pickup to flywheel indicator clearance, if required, shall be made using a nonmagnetic feeler gage.

10.3.25 *Setting Injector Pickup Gap*—Set the air gap to typically 1 mm (0.040 in.) with the engine stopped.

10.3.25.1 Individual pickups may require more or less air gap to obtain steady meter operation when the engine is ultimately running but too little gap can cause the ignition delay angle display to drive off scale.

11. Calibration and Engine Qualification

11.1 *Engine Compliance*—It is assumed that the engine has been commissioned and that all settings and operating vari-

ables are at equilibrium and in compliance with basic engine and instrument settings and standard operating conditions.

11.1.1 Engine warm-up requires typically 1 h to ensure that all critical variables are stable.

11.2 *Checking Performance on Check Fuels*—This engine test does not have any satisfactory standardization fuel blend or blends to qualify the engine. The Check Fuels are the most helpful means available to permit judgement of good performance.

11.2.1 Test one or more of the Check Fuels.

11.2.2 Engine performance is judged satisfactory if the cetane rating obtained on a Check Fuel is within the Check Fuel tolerance limits calculated as follows:

$$\text{Tolerance Limits} = CN_{ARV} \pm 1.5 \times S_{ARV} \quad (3)$$

where:

CN_{ARV} = the cetane number accepted reference value of the Check Fuel,

1.5 = a selected tolerance limit factor (K) for normal distributions,

S_{ARV} = the standard deviation of the Check Fuel data used to determine CN_{ARV} .

11.2.2.1 *In the context of this test method*, the statistical tolerance limit factor (K), based on a sample size (n), permits an estimation of the percentage of engines that would be able to rate the Check Fuel within the calculated tolerance limits. Based on a data set of 17 to 20 ratings used to determine the Check Fuel CN_{ARV} , and a value of $K = 1.5$, it is estimated that in the long run, in 19 cases out of 20, at least 70 % of the engines would rate the Check Fuel within the calculated tolerance limits.

11.2.3 If the results are outside this tolerance range, the engine is not acceptable for rating samples and a check of all operating conditions is warranted followed by mechanical maintenance which may require critical parts replacement. The injector nozzle can be a very critical factor and this should be the first item checked or replaced to achieve rating compliance.

12. Procedure

12.1 *Bracketing by Handwheel Procedure*—See [Appendix X2](#) for the details of engine operation and the adjustment of each of the individual operating variables.

12.1.1 Check that all engine operating conditions are in compliance and equilibrated with the engine running on a typical diesel fuel oil. (**Warning**—In addition to other precautions, always position the ignition delay meter (Mark II and earlier models) to CALIBRATE before proceeding with fuel switching so that violent meter needle full-scale pegging does not occur. Calibration adjustment should be checked before each rating but never changed during a rating.)

12.1.2 Introduce the sample to an empty fuel tank, rinse the fuel buret, purge any air from the fuel line to the pump and position the fuel-selector valve to operate the engine on this fuel. (**Warning**—Sample and Fuel—Combustible. Vapor harmful. See [Annex A1](#).)

12.1.3 *Fuel Flow Rate*—Check the fuel flow rate and adjust the flow-rate-micrometer of the fuel pump to obtain 13 mL per min consumption. The final flow rate measurement shall be

made over a full 60 ± 1 s period. Note the flow-rate-micrometer reading for reference.

12.1.4 *Fuel Injection Timing*—After establishing the fuel flow rate, adjust the injection-timing-micrometer of the fuel pump assembly to obtain a $13.0 \pm 0.2^\circ$ injection advance reading. Note the injection-timing-micrometer reading for reference.

12.1.5 *Ignition Delay*—Adjust the handwheel to change the compression ratio and obtain a $13.0 \pm 0.2^\circ$ ignition delay reading. Make the final handwheel adjustment in the clockwise direction (viewed from front of engine) to eliminate backlash in the handwheel mechanism and a potential error.

12.1.6 *Equilibration*—It is important to achieve stable injection advance and ignition delay readings.

12.1.6.1 Stable readings should typically occur within 5 to 10 min.

12.1.6.2 The time used for the sample and each of the reference fuels should be consistent and shall not be less than 3 min.

12.1.7 *Handwheel Reading*—Observe and record the handwheel reading as the representative indication of the combustion characteristic for this fuel sample.

NOTE 1—Experience has shown that if handwheel readings are taken when the fuel tank levels of samples and reference fuels are similar, more consistent results are obtained.

12.1.8 *Reference Fuel No. 1*—Select a secondary reference fuel (*T Fuel* and *U Fuel*) blend close to the estimated cetane number of the sample.

NOTE 2—The handwheel reading versus cetane number relationship based on this procedure is engine and overhaul dependent but it can be established for each engine as testing experience is gained after each overhaul. A plot or table of handwheel readings provides a simple guide to selection of the reference fuel.

12.1.8.1 Prepare a fresh 400 or 500 mL batch of the selected reference blend.

12.1.8.2 Introduce Reference Fuel No. 1 to one of the unused fuel tanks taking care to flush the fuel lines in the same manner as noted for the sample.

12.1.8.3 Perform the same adjustment and measurement steps used for the sample and record the resulting handwheel reading.

12.1.9 *Reference Fuel No. 2*—Select another secondary reference fuel blend which can be expected to result in a handwheel reading that causes the two reference fuel handwheel readings to bracket that for the sample. The difference between the two reference fuel blends shall not exceed 5.5 cetane numbers. Typically, blends differing by 5 volume percent *T Fuel* will span about 2.7 cetane numbers and those differing by 10 volume percent *T Fuel* will span about 5.3 cetane numbers.

12.1.9.1 Prepare a fresh 400 or 500 mL batch of the selected reference fuel blend.

12.1.9.2 Introduce Reference Fuel No. 2 to the third fuel tank taking care to flush the fuel lines in the same manner as noted for the sample.

12.1.9.3 Perform the same adjustment and measurement steps used for the sample and first reference fuel and record the resulting handwheel reading.

NOTE 3—Typically, the fuel-flow-rate should be the same for both reference fuels because they are sufficiently similar in composition.

12.1.9.4 If the handwheel reading for the sample is bracketed by those of the reference fuel blends, continue the test; otherwise try an additional reference fuel blend(s) until this requirement is satisfied.

12.1.10 *Repeat Readings*—After operation on a satisfactory second reference fuel blend, perform the necessary steps to rerun Reference Fuel No. 1, then the sample and finally Reference Fuel No. 2. For each fuel, be certain to check all parameters carefully and allow operation to reach equilibrium before recording the handwheel readings. The fuel switching shall be as illustrated in Fig. 3 Sample and Reference Fuel Reading Sequence A.

12.1.10.1 If a sample is tested immediately following one for which the Reference Fuel No. 2 will be applicable, that reference fuel handwheel reading can be utilized for the new sample. The fuel switching shall thus be as illustrated in Fig. 3, Sample and Reference Fuel Reading Sequence B.

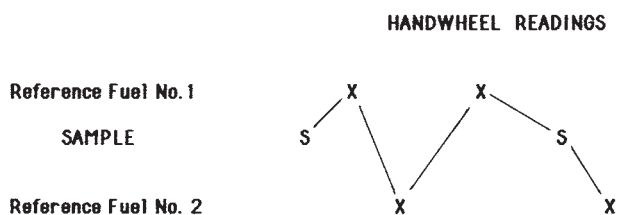
13. Calculation of Cetane Number

13.1 Calculate the average handwheel readings for the sample and each of the reference fuel blends.

13.2 Calculate the cetane number by interpolation of these average handwheel readings proportioned to the cetane numbers of the bracketing reference fuel blends in accordance with Eq 4. See Fig. 4.

13.2.1 For the Handwheel Bracketing Procedure:

SAMPLE AND REFERENCE FUEL READING SEQUENCE A



SAMPLE AND REFERENCE FUEL READING SEQUENCE B

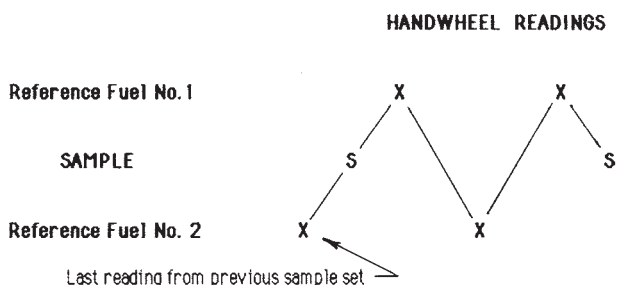
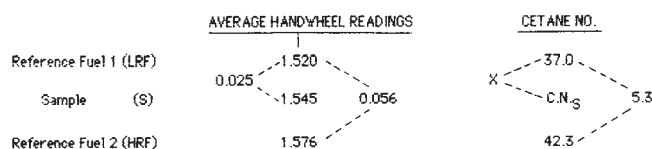


FIG. 3 Sample and Reference Fuel Reading Sequence

HANDWHEEL BRACKETING PROCEDURE



$$\begin{aligned}
 CN_S &= CN_{LRF} + \left(\frac{HW_S - HW_{LRF}}{HW_{HRF} - HW_{LRF}} \right) (CN_{HRF} - CN_{LRF}) \\
 &= 37.0 + \left(\frac{1.545 - 1.520}{1.576 - 1.520} \right) (42.3 - 37.0) \\
 &= 37.0 + (0.446)(5.3) = 39.4
 \end{aligned}$$

FIG. 4 Example of Cetane Number Calculations

$$CN_S = CN_{LRF} + \left(\frac{HW_S - HW_{LRF}}{HW_{HRF} - HW_{LRF}} \right) (CN_{HRF} - CN_{LRF}) \quad (4)$$

where:

- CN_S = cetane number of sample,
- CN_{LRF} = cetane Number of low reference fuel,
- CN_{HRF} = cetane number of high reference fuel,
- HW_S = handwheel reading of sample,
- HW_{LRF} = handwheel reading of low reference fuel, and
- HW_{HRF} = handwheel reading of high reference fuel.

13.2.2 Do not interpolate using reference fuel blend volume percent of *T Fuel* values and convert that equivalent percent to cetane number.

13.3 Round the calculated cetane number to the nearest tenth. Any cetane number ending in exactly 5 in the second decimal place shall be rounded to the nearest even tenth number; for example, round 35.55 and 35.65 to 35.6 cetane number.

14. Report

14.1 Report the calculated result as cetane number.

14.2 If the sample was filtered before testing, include this information in the report.

15. Precision and Bias

15.1 *Handwheel Bracketing Procedure Precision*—The precision of this test method and procedure based on statistical examination of interlaboratory test results is as follows:

15.1.1 *Repeatability*—The difference between two test results, obtained on identical test samples under repeatability

TABLE 2 Cetane Number Repeatability and Reproducibility Limits

Average Cetane Number Level ^A	Repeatability Limits, Cetane Number	Reproducibility Limits Cetane Number
40	0.8	2.8
44	0.9	3.3
48	0.9	3.8
52	0.9	4.3
56	1.0	4.8

^A Values for cetane numbers intermediate to those listed above, may be obtained by linear interpolation.

conditions would, in the long run, in the normal and correct operation of the test method, exceed the values in Table 2 only in 1 case in 20.

15.1.2 *Reproducibility*—The difference between two single and independent results obtained on identical test samples under reproducibility conditions would, in the long run, in the normal and correct operation of the test method, exceed the values in Table 2 only in 1 case in 20.

15.1.3 Repeatability precision limits are based on the ASTM National Exchange Group (NEG) monthly sample testing program data from mid-1978 through 1987. During this period each exchange sample was rated twice on the same day by the same operator on one engine in each of the Member laboratories.¹⁰

15.1.4 Reproducibility precision limits are based on the combined NEG monthly sample testing program data from mid-1978 through mid-1992, the Institute of Petroleum monthly sample data for 1988 through mid-1992 and the Institut Francais du Petrole monthly sample data for 1989 through early 1992.

15.1.5 The combination of the large number of sample sets and the fact that each sample is tested by 12 to 25 laboratories provides a comprehensive picture of the precision achievable using this test method. Analyzed graphically, the respective sample standard deviations were plotted versus cetane number. The variation in precision with respect to cetane number level for these data is best expressed by a linear regression of the values. The average standard deviation for each cetane number level has been multiplied by 2.772 to obtain the respective limit values.

15.2 *Bias*—The procedure in this test method for cetane number of diesel fuel oil has no bias because the value of cetane number can be defined only in terms of the test method.

16. Keywords

16.1 cetane number; diesel performance; ignition delay

¹⁰ Supporting data (a listing of the data and the analyses used to establish the precision statements) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1303.

ANNEXES
(Mandatory Information)
A1. WARNING INFORMATION
A1.1 Introduction

A1.1.1 In the performance of the standard test method there are hazards to personnel. These are indicated in the text. For more detailed information regarding the hazards, refer to the appropriate Material Safety Data Sheet (MSDS) for each of the applicable substances to establish risks, proper handling, and safety precautions.

A1.2 Warning

- A1.2.1 Combustible. Vapor harmful.
- A1.2.2 *Applicable Substances:*
 - A1.2.2.1 Diesel fuel oil.
 - A1.2.2.2 Reference material.
 - A1.2.2.3 Reference fuel.
 - A1.2.2.4 *n*-cetane.
 - A1.2.2.5 Heptamethylnonane.
 - A1.2.2.6 Alpha-methylnaphthalene.

- A1.2.2.7 Secondary reference fuels, *T Fuel* and *U Fuel*
- A1.2.2.8 Check Fuel.
- A1.2.2.9 Kerosine.
- A1.2.2.10 Warm-up fuel.
- A1.2.2.11 Engine crankcase lubricating oil.

A1.3 Warning

- A1.3.1 Flammable. Vapors harmful if inhaled. Vapors may cause flash fire.
- A1.3.2 *Applicable Substances:*
 - A1.3.2.1 Petroleum based solvent.

A1.4 Warning

- A1.4.1 Poison. May be harmful or fatal if inhaled or swallowed.
- A1.4.2 *Applicable Substances:*
 - A1.4.2.1 Ethylene glycol based antifreeze

A2. ENGINE EQUIPMENT DESCRIPTION AND SPECIFICATIONS
A2.1 Engine Equipment

A2.1.1 The single cylinder cetane test engine is manufactured as a complete unit by Waukesha Engine Division, Dresser Industries, Inc. and consists of both critical and non-critical equipment. The Waukesha Engine Division designation is Model CFR F-5 Cetane Method Diesel Fuel Rating Unit. Waukesha Engine Division Part Numbers or References are included in parenthesis after the items where applicable.

A2.1.1.1 See **Table A2.1**.

A2.2 *Critical Equipment*—Critical engine components and primary assemblies which shall be used for this test method are listed. The bearings, gears, seals, covers, special fittings or hardware and gaskets manufactured by Waukesha Engine Division and applicable to each critical assembly shall also be considered critical.

A2.2.1 *Crankcase Assembly*—Model CFR-48 (109520D) specified to include the following major items (see **Fig. A2.1**):

- A2.2.1.1 Crankshaft Assembly (A109511H).
- A2.2.1.2 Piston Assembly (0023204B).
- A2.2.1.3 Rings, Piston, Compression, Straight (106222A), 4 required.

NOTE A2.1—Ring, Piston, Compression, Straight, Chrome (106222B), Use of a chrome ring in the top groove is optional with 3 compression rings (106222A) in the other 3 compression ring grooves.

- A2.2.1.4 Ring, Piston, Oil (23505).
- A2.2.1.5 Connecting Rod Assembly (BA111666).
- A2.2.1.6 Camshaft (109583B).
- A2.2.1.7 Balancing Shaft, 2 required (109510A).

TABLE A2.1 General Engine Characteristics and Information

Item	Description
Crankcase	Model CFR-48 (Preferred), High or Low Speed Models (Optional)
Cylinder Type	Single bore cast iron with integral coolant jacket
Cylinder Head Type	Cast Iron with turbulence precombustion chamber, variable compression plug passage, integral coolant passages, and in-head valve assembly
Compression Ratio	Adjustable 8:1 to 36:1 by external handwheel assembly
Cylinder Bore (Diameter), in.	3.250 (Standard), Reboring to 0.010, 0.020, 0.030 over is acceptable
Stroke, in.	4.50
Displacement, cu in	37.33
Valve Mechanism	In-head with enclosure
Intake and Exhaust Valves	Stellite faced, plain type without shroud
Piston	Cast iron, flat top
Piston Rings:	
Compression Type	4, Ferrous, straight sided (Top may be chrome plated—Optional)
Oil Control	1, Cast iron, one piece, slotted (Type 85)
Camshaft Over lap, degree	5
Fuel System	Injection pump with variable timing device and injector
Injector	Holder with bypass pressure release valve
Spray Nozzle	Closed, differential-needle, hydraulically-operated, pintle type
Weight of Engine	Approximately 400 kg (880 lb)
Weight of Complete Test Unit	Approximately 1250 kg (2750 lb)

- A2.2.1.8 Counterweight for Balancing Shaft, (109565) 2 required.
- A2.2.1.9 Flywheel (109501H) (applicable for 50 or 60 Hz units).
- A2.2.1.10 Oil Pump Assembly (110150A).

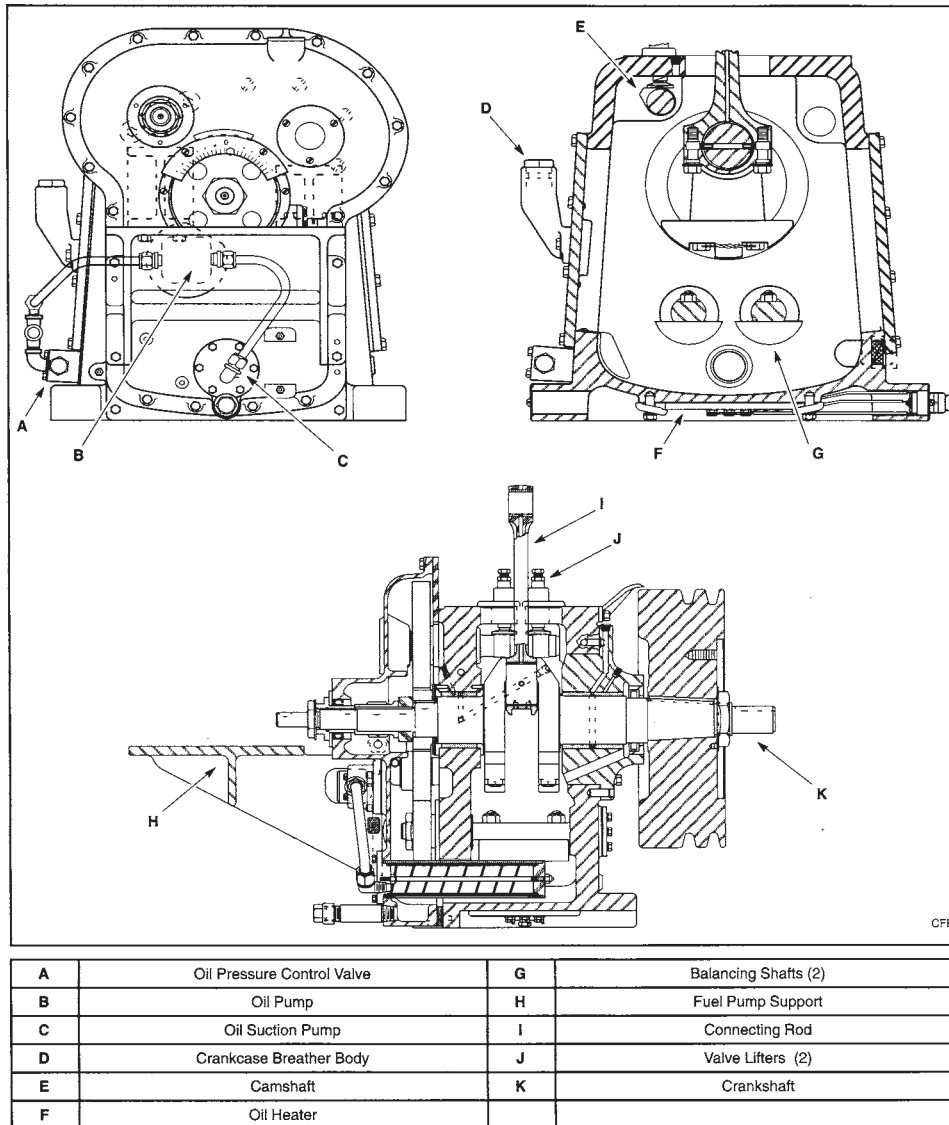


FIG. A2.1 CFR-48 Crankcase—Sectional Views

A2.2.1.11 Oil Suction Screen Assembly (0109552).

A2.2.1.12 Oil Pressure Control Valve Assembly (A109538A).

A2.2.1.13 Crankcase Breather Assembly (Group 070.00).

A2.2.1.14 Accessory Bracket, Fuel Pump (109515A).

A2.2.1.15 Stud Assembly, Crankcase to Cylinder (B839.4 required; B5764.2 required).

A2.2.1.16 Stud Nuts, Cylinder (105361, 6 required).

A2.2.2 *Cylinder Assembly*—(0105081) of cast iron with internal coolant passages and a basic bore diameter of 3.250 in., specified to include the following (see Fig. A2.2):

A2.2.2.1 Stud Assembly, Cylinder to Head (B-8200, 5 required).

A2.2.2.2 Stud Nuts, Cylinder Head (105361, 7 required).

A2.2.2.3 Crankcase to Cylinder Spacer Gasket Set—Selection of one or more gaskets must be made at the time of cylinder assembly to achieve the specified piston over travel. Available gaskets are:

Gasket, Cylinder Base—0.021 in. thick (105181)

Gasket, Cylinder Base—0.015 in. thick (105181A)

Gasket, Cylinder Base—0.010 in. thick (105181B)

Gasket, Cylinder Base—0.003 in. thick (105181C)

A2.2.3 *Cylinder Head Assembly*—(AF105082B) of cast iron with internal coolant passages, a flattop combustion chamber surface, a horizontal and cylindrical precombustion chamber to accept a matched and pinned, variable compression ratio handwheel housing on one end and including a passage for insertion of an injector assembly at the other end. An angled passage, 0.5 in. square in cross-section, connects the precombustion chamber to the main combustion chamber. The assembly is specified to include the following major items (see Fig. A2.2 and Fig. A2.3):

A2.2.3.1 Integral but replaceable, hardened, Valve Seat Inserts (105987A),

A2.2.3.2 Integral but replaceable Valve Guides (23109A),

A2.2.3.3 Intake and Exhaust Valve (106625),

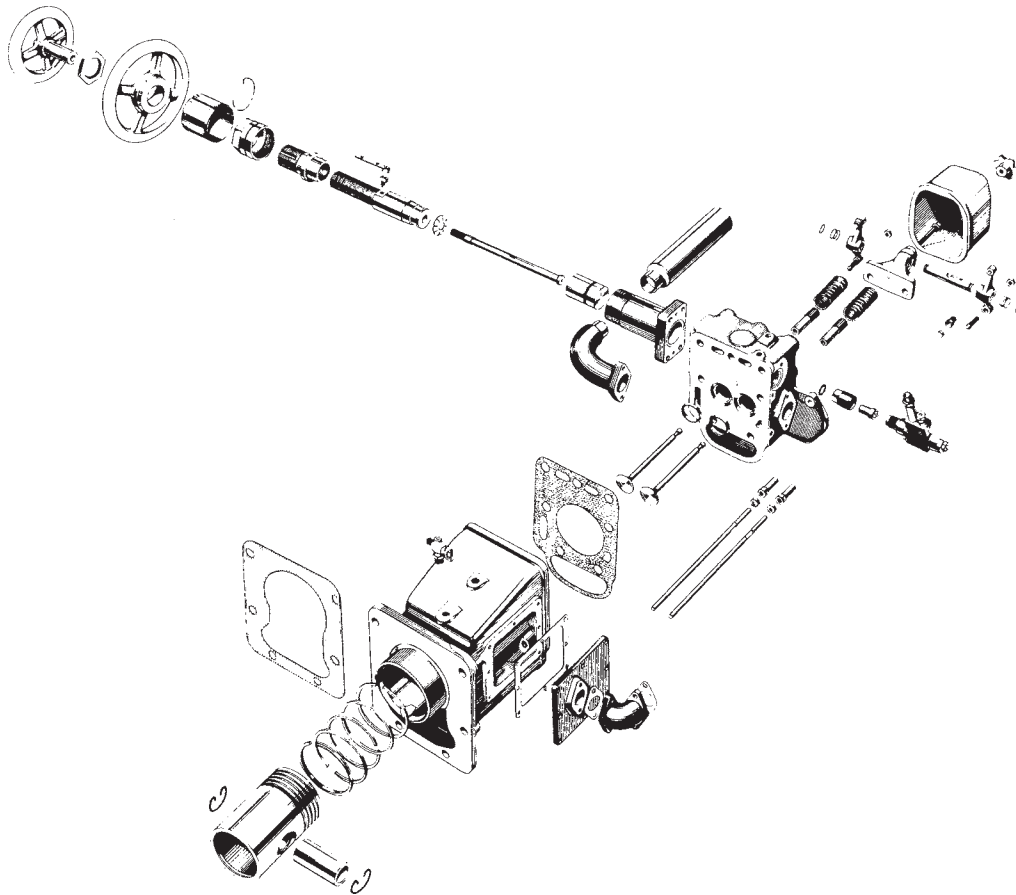


FIG. A2.2 Exploded View of Cetane Cylinder and Head Assembly

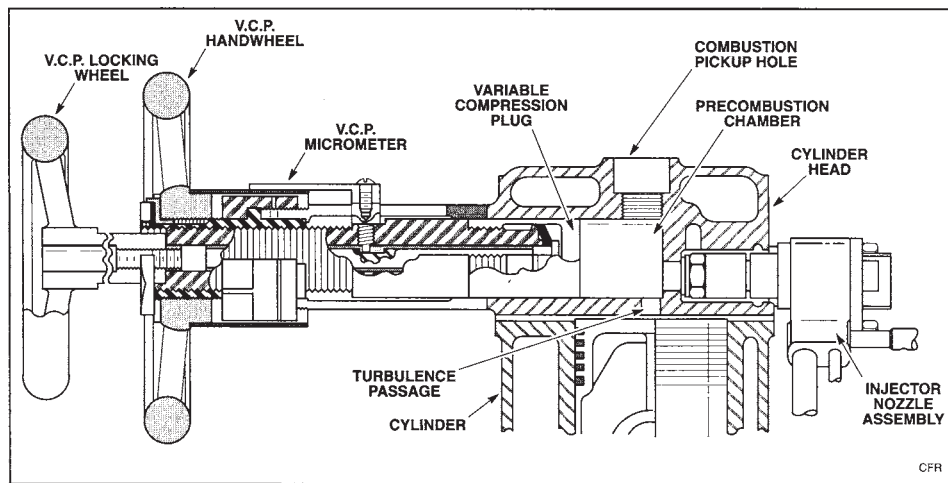


FIG. A2.3 Cylinder Head and Handwheel Assembly—Sectional View

A2.2.3.4 Valve Spring, Rotator Assembly (G-806-3) including spring (109659), spacer (110200), felt (B4680), rotator (110165B) and tapers (109658),

A2.2.3.5 Valve Rocker Arm Subassembly (Group G-002.10).

A2.2.4 Handwheel—Variable Compression Plug Assembly—(A105097) including an expandable plug that is screwed in or out of the handwheel housing, an adjusting handwheel, a micrometer scale and barrel vernier to indicate

plug position, and a locking wheel to cause a dished, split-washer to flatten and expand the variable compression plug to seal the precombustion chamber. See Fig. A2.3.

A2.2.5 Cylinder Coolant System Assembly, specified to include the following major items.

A2.2.5.1 Condenser Body Assembly (A109264A) including condenser coil subassembly, baffle tube and sight glass subassembly.

A2.2.5.2 Condenser Water Pipe Assembly (0109131B).

A2.2.5.3 Water Inlet Pipe (105083).

A2.2.6 *Inlet Air System Assembly* (Group G-841-9) specified to include the following major items:

A2.2.6.1 Air Silencer Elbow (105188), with gaskets, nuts and washers.

A2.2.6.2 Air Heater Silencer Assembly (AA110468).

A2.2.6.3 Air Inlet Heater Assembly (A106583E).

A2.2.7 *Fuel System*—Components required to permit constant pressure introduction of sample or reference fuel blends to an injection pump, the injection pump with adjustment for flow rate, an integral variable timing device, a pump gallery air trap device, a high pressure fuel delivery tubing and an injector nozzle assembly with mechanism to permit sensing of the time of injection. Critical Equipment is specified to include the following major items:

A2.2.7.1 *Fuel Injection Pump Assembly (C106941C)*—Bosch specification APE 1B-50P-5625C Injection Pump equipped with a 5 mm Barrel and Plunger Assembly (110754).

A2.2.7.2 *Fuel Selector-Valve Assembly (A111388)*—Including pump inlet fitting (105303A).

A2.2.7.3 *Fuel Line Air Trap Assembly (Group G-808-9)*—Including pump outlet fitting (105302).

A2.2.7.4 *Variable Timing Device Assembly (Group G-808-10)*—For integral mounting to the pump housing and including the Timing Device (110778) and associated Disk Coupling (B9496).

A2.2.7.5 *Shaft Coupling Assembly (Group G-808-11)*—For connection of the variable timing device shaft to the engine camshaft.

A2.2.7.6 *Fuel Injection Tube or Line (A106318E)*—For connection of the fuel pump to the injector assembly. This tube shall be 28 in. long of ¼ in. OD, ⅛ in. ID steel tubing.

A2.2.7.7 *Fuel Injector Assembly (A75067E)*—Including an O.M.T., S.p.A. specification SP8-S-1003/W Injector Nozzle (110700), a nozzle opening pressure adjustment, an extended pintle feeler pin for indication of time of injection and a fuel bypass valve to release injection pump fuel pressure from the nozzle.

A2.2.8 *Power Absorption Motor*—Reluctance-type, synchronous, single-speed, electric motor for belt drive connection to the engine and capable of both starting the engine and absorbing the power developed when combustion is in process. Waukesha Engine Division is the sole supplier of this item in order to insure meeting the following speed and load absorbing specifications. Part numbers are dependent on the three-phase electrical service voltage and frequency available at the site of unit installation.

A2.2.8.1 *Speed*—1200 rpm \pm 1 % for 60 Hz, three-phase power; 1500 rpm \pm 1 % for 50 Hz, three-phase power.

A2.3 Engine Dimensions

A2.3.1 See [Table A2.2](#).

A2.4 Equivalent Equipment

A2.4.1 *Crankcase Assembly*—Commonly known as the standard or low-speed crankcase which was the original model developed in 1933. Parts for this crankcase are no longer manufactured.

A2.4.2 *Crankcase Assembly*—Commonly known as the high-speed crankcase, this model was the standard version manufactured from about 1939 through 1954. Parts for this crankcase are no longer manufactured.

A2.4.3 *Cylinder Assembly*—(0105081) which has, through operational wear, exceeded the basic bore diameter tolerance and has been successfully rebored to 0.010, 0.020, or 0.030 in. oversize.

A2.4.4 *Piston Assembly*—for rebored cylinder assemblies as follows:

A2.4.4.1 For 0.010 in. oversize cylinders (23204B1).

A2.4.4.2 For 0.020 in. oversize cylinders (23204B2).

A2.4.4.3 For 0.030 in. oversize cylinders (23204B3).

A2.4.5 *Ring, Piston, Compression, Straight*—for rebored cylinder assemblies as follows:

A2.4.5.1 For 0.010 in. oversize pistons (106222A1) or chrome (106222B1).

A2.4.5.2 For 0.020 in. oversize pistons (106222A2) or chrome (106222B2).

A2.4.5.3 For 0.030 in. oversize pistons (106222A3) or chrome (106222B3).

A2.4.6 *Ring, Piston, Oil*—for rebored cylinder assemblies as follows:

A2.4.6.1 For 0.010 in. oversize pistons (23505-1).

A2.4.6.2 For 0.020 in. oversize pistons (23505-2).

A2.4.6.3 For 0.030 in. oversize pistons (23505-3).

A2.4.7 *Injector Nozzle*, American Bosch ADN-30S-3/1 (110700) which was the predecessor to the current SP8-S-1003/W but which is no longer manufactured.

A2.5 *Non-Critical Equipment and Specifications*—A number of components and devices are required to integrate the critical equipment items into a complete working system or unit. Many of these are common hardware, tubing, fasteners and electrical items potentially available from multiple sources. In some cases, however, selection of specific sizes or specification criteria are important to achieve the proper conditions for the cetane testing equipment unit. Important criteria for a component are included when applicable.

A2.5.1 *Foundation and Bedplate*:

A2.5.1.1 *Foundation*—Typically, in the form of a reinforced concrete block, site poured, the foundation should be approximately 700 mm wide, 1320 mm long and a minimum of 280 mm high (28 in. wide, 52 in. long and a minimum of 11 in. high). Height of the foundation should be minimized so that the fuel sample reservoirs are at an elevation for safe pouring of fuel oil by operators of average height without the use of a raised platform or step in front of the engine. If the unit is placed on an industrial building floor of reinforced concrete approximately 200 mm or 8 in. thick, no special support for the foundation is required.

A2.5.1.2 *Bedplate (27671H)*, of cast iron, 24 in. wide, 48 in. long and 4 in. high such that the engine and power absorption motor can be solidly mounted and aligned as well as providing a platform for assembly of accessory electrical equipment, controls, instrumentation and utility connections.

A2.5.2 *Heater for Crankcase (B3109A)*, dual element, 300 watt maximum, surface mounting, flat, circular electrical heater.



TABLE A2.2 Engine Dimensions, Manufacturing Tolerances and Replacement Limits

Item	Basic Dimension	Manufacturing Tolerances	Replacement Limits
Crankcase:			
Oil Passages in Crankcase	Pass ¼ in. rod		
Crankshaft Bearings:			
Front Main:			
Journal Diameter	3.00		
Journal to Bearing Clearance		0.0035 to 0.0049	0.006 max
Rear Main:			
Journal Diameter	3.00		
Journal to Bearing Clearance	...	0.0035 to 0.0049	0.006 max
Main Bearing to Case Clearance (Both)		0.0005 to 0.002	...
Crankshaft End-play	...	0.006 to 0.008	0.010 max
Connecting Rod Bearing (Big-End):			
Crankshaft Journal Diameter	2.50		
Journal to Bearing Clearance	...	0.0011 to 0.0036	0.005 max
End-play	...	0.008 to 0.014	0.016 max
Connecting Rod Bearing (Piston Pin End):			
Rod End to Piston Boss Clearance	1/16 min
Piston Pin to Bushing Clearance	...	0.0005 to 0.0010	0.015 max
Connecting Rod Alignment:			
(1)	Piston wall perpendicular to axis of journal within 0.003		
(2)	Piston pin twist in length of big-end bearing within 0.002		
(3)	Centerline of rod perpendicular to axis of bearings within 0.003		
Camshaft Bearings:			
Camshaft Journal Diameter:			
Front		1.7795 to 1.7805	
Rear		1.2485 to 1.2495	
Front Journal to Bearing Clearance	...	0.0015 to 0.003	0.004 max
Rear Journal to Bearing Clearance	...	0.002 to 0.0035	0.004 max
Bearing to Case Clearance (Both)	...	0.0005 to 0.002	...
End-play	...	0.002 to 0.005	0.007 max
Balancing Shaft Bearings:			
Balancing Shaft Journal Diameter		1.748 to 1.749	
Shaft to Bearing Clearance (Both)	...	0.0015 to 0.003	0.004 max
Bearing to Case Clearance (Both)	...	0.0005 to 0.002	...
End-play	...	0.002 to 0.006	0.010 max
Idle Gear:			
Stub Shaft Diameter		0.9980 to 0.9985	
Stub Shaft to Bearing Clearance	...	0.0015 to 0.003	0.004 max
End-play	...	0.002 to 0.004	0.008 max
Gear Tooth Backlash	...	0.002 to 0.004	0.006 max
Tappet Guide Clearance	...	0.0005 to 0.002	0.003 max
Valve Timing (Based on 0.008 ± 0.001 valve clearance):			
Inlet Valve Opens	10° atdc ± 2.5°		
Inlet Valve Closes	34° abdc		
Exhaust Valve Opens	40° bbdc		
Exhaust Valve Closes	15° atdc ± 2.5°		
Flywheel:			
Side Face Runout	...	0.005 max	0.007 max
Rim Surface Eccentricity	...	0.003 max	0.005 max
Piston:			
Piston Diameters:			
Top Land	3.235 to 3.237	NOTE: oversize piston diameter dimensions increase 0.010, 0.020 and 0.030 in respectively	
Second/Fifth Lands	3.242 to 3.244		
Skirt Diameter	3.2465 to 3.2475		
Piston to Cylinder Clearance			
Top Land	...	0.013 to 0.015	
Second/Fifth Lands	...	0.006 to 0.008	
Skirt	...	0.0025 to 0.0035	0.0045
Ring to Land Side Clearances:			
Top		0.001 to 0.003	0.004
All Others	...	0.001 to 0.0025	0.0035
Ring Gap Clearances:			
Compression Rings	...	0.007 to 0.017	0.030
Oil Ring	...	0.010 to 0.018	0.030
Piston Pin Diameter			
Pin to Piston Clearance		1.2495 to 1.2498	
		0.0002 to 0.0004	0.002
Piston Pin Retainers (Truarc):			
Free Diameter after Compression	1.340 min		
Piston Pin Hole Alignment			
		0.001 max.	0.0015
Piston Over-Travel:			
Piston top above top of cylinder	0.014 to 0.016		
Standard Cylinder:			
Internal Diameter	3.250	3.250 to 3.2515	0.006 over original bore

NOTE A2.2—Reboring of cylinders to + 0.010, + 0.020, or + 0.030 inch oversize is permitted with a tolerance of 0.0000 to + 0.0015 inch.

TABLE A2.2 *Continued*

Item	Basic Dimension	Manufacturing Tolerances	Replacement Limits
Bore Out of Round	...	0.0005 max.	0.0025
Bore Surface Quality	...	10 to 20 microinches	Scored and/or pitted
Hardness, Bore Surface		200 to 235 Brinell	...
Wall Thickness		0.312 to 0.375	...
Cylinder Head:			
Hardness, Combustion Chamber Surface		180 to 220 Brinell	...
Combustion Pick-up Hole Depth (Top face to bottom of variable compression plug hole)		2.2812 to 2.3125	...
Variable Compression Plug Hole Diameter	1.6250	1.6245 to 1.6250	1.630 max.
Nozzle Hole Diameter		0.554 to 0.557	
Nozzle Seat Counter Bore (O.D.)		0.4062 to 0.4375	
Nozzle Sealing Ring Groove:			
Diameter		1.333 to 1.343	...
Width		0.187 to 0.192	...
Hole Diameter for Guide		0.6250 to 0.6255	
Valve Port			
Concentricity to Valve Axis		±0.031	...
Rocker Arms:			
Bearing Clearance, plain		0.001 to 0.002	...
Bearing Shaft Diameter		0.6230 to 0.6235	
Ball Seats		Smooth and fit ball	
Valves, Intake and Exhaust:			
Stem Diameter	0.3725	0.3725 to 0.3720	0.3705 min.
Face Angle, degrees	45
Concentricity, Stem to Face (Run-out)	...		0.0015 max.
Valve Guides, Intake and Exhaust:			
Internal Diameter	0.3750	0.3750 to 0.3765	0.3785 max.
Valve Guide to Valve Stem Clearance:		0.003 to 0.004	0.005 max.
Valve Seat Inserts, Intake and Exhaust:			
Concentricity, Seat to Guide	...	0.0010 max.	...
Seat Width	...	0.050 to 0.060	0.070 max.
Face Angle, degrees	...	45°	...
NOTE—For interference angle approach, use face angle of 46 to 47° on seats.			
Valve Head Recess from Cylinder Head Surface	0.020 min.	0.020 to 0.025	0.060 max.
Valve Springs:			
Free Length (rotator type)		2.125 min.	2.125 min.
Handwheel Assembly:			
Variable Compression Plug:			
External Diameter		1.6230 to 1.6235	
Internal Diameter (At Head)		1.4585 to 1.4590	
Split Locking Washer Diameter (Ground)		1.457 to 1.458	
Housing Nut to Sleeve Clearance		0.010 max.	0.010 max.
Fuel Injection Pump:			
Plunger Diameter	5 mm		
Plunger Lift at Port Closure		0.075 to 0.091	
Fuel Injector Nozzle:			
Pintle Lift		0.004 to 0.006	0.006 max.
Fuel Injection Tube or Line (High Pressure):			
Bore	1/16		
Length	28		

A2.5.3 *Exhaust Discharge System Assembly (023242A and A109887E)*—Piping, with or without water cooling, suitable to discharge exhaust fumes from the combustion chamber to atmosphere and having adequate volume and length to comply with the specified operating conditions for exhaust back pressure without resonance.

A2.5.4 *Filter Assembly for Crankcase Oil (AA111345)*.

A2.5.5 *Fuel Oil Sample and Reference Fuel Reservoir Assembly (Groups 216 and 400)*—Minimum of three (3) fuel tanks each of 300 mL minimum capacity with a sight glass assembly to indicate fuel level and including discharge tubing of stainless steel or other material impervious to diesel fuel oil. Discharge tubing diameter shall be as small as practical to

minimize system holdup but shall not be smaller than that of either 10 mm OD or 5/16 in. OD standard tubing.

A2.5.6 *Belting, Engine Flywheel to Power Absorption Motor*—Set of two “C” section, typically of 2160 mm or 85 in. length (027970 for 60 Hz power; OB5500 for 50 Hz power).

A2.5.7 *Electrical Switchgear*, including input connections and circuit protection for three phase power to operate the power absorption motor and single phase power to operate start-stop circuitry, controls, heaters, safety devices and instrumentation. Circuit design shall ensure that failure of either the single or three phase power source will disconnect the other source.

A3. INSTRUMENTATION DESCRIPTION AND SPECIFICATIONS

A3.1 Instrumentation

A3.1.1 The single cylinder cetane test engine is manufactured by Waukesha Engine Division, Dresser Industries and includes both critical and non-critical instrumentation. Waukesha Engine Division Part Numbers are included in parenthesis after the items where appropriate.

A3.2 *Critical Instrumentation*—Critical instrumentation components or specifications for instrumentation which shall be used for this test method are listed.

A3.2.1 *Cetane Meter Specification*—The instrumentation shall be capable of sensing diesel engine combustion cycle events. The parameters which shall be indicated are as follows:

A3.2.1.1 *Injection Advance*, in terms of the crank angle degrees before top-dead-center at which fuel injection is initiated.

A3.2.1.2 *Ignition Delay*, in terms of the crank angle degrees from the time of fuel injection to the first indication of combustion.

A3.2.1.3 The crank angle degree values shall be stable average measurements of the results of multiple combustion cycles presented in either analog or digital form. The range shall be 0 to 18°. The readability shall be at least 0.1°.

A3.2.2 *Cetane Meter*, Waukesha Dual Digital Cetane Meter (A111462B).

A3.2.3 *Cetane Meter Transducers*—Pickups required to provide input pulses to the dual digital cetane meter to indicate critical engine cycle events.

A3.2.3.1 *Reference Pickups (111464A)*—Two are required to establish a crank angle degree time base for calibration of the dual digital cetane meter.

A3.2.3.2 *Injection Pickup (111465A)*—To sense the beginning of fuel injection.

A3.2.3.3 *Combustion Pickup (111463A)*—To sense the beginning of combustion as evidenced by a significant increase in the rate-of-change of pressure in the combustion chamber.

A3.3 Equivalent Instrumentation

A3.3.1 *Ignition Delay Meter, Model Mark I*, which is no longer manufactured or serviced but which, as the predecessor to the Mark II, meets the requirements of the specifications with the exception that it is only readable to 0.25°.

A3.3.2 *Ignition Delay Meter, Model Mark II (A111462)*, which is no longer manufactured but meets the requirements of the specifications with the exception that it is only readable to 0.25°.

A3.3.3 *Expanded Scale Meter Kit with Ignition Delay Meter, Mark II*—The Expanded Scale Meter Kit (made in limited quantity and no longer manufactured or serviced) upgrades the Mark II instrument so that crank angle events can be read to 0.1°.

A3.3.4 *Cetane Meter Transducers*—pickups required to provide input pulses to the Cetane Meter to indicate critical engine cycle events.

A3.3.4.1 Reference Pickups (111464) 2 required to establish a crank angle degree time base for calibration of the Mark I and Mark II Ignition Delay Meters.

A3.4 Non-Critical Instrumentation

A3.4.1 *Temperature Measurement:*

A3.4.1.1 *Intake Air Thermometer Assembly (0106317A)*, using Thermometer (106317A) having a range from 15 to 70°C graduated in 1°C divisions (60 to 160°F graduated in 1°F divisions) and conforming to the requirements for Thermometer 83C (83F) in Specification E 1.

A3.4.1.2 *Intake Air Temperature Controller*, with associated thermal sensor, for on/off (AA111412B) or proportional temperature control to within the specified limits as measured by the Intake Air Thermometer.

A3.4.1.3 *Cylinder Jacket Coolant Thermometer Assembly (0105180)*, using Thermometer (105180) having a range from –15 to 105°C graduated in 1°C divisions (0 to 220°F graduated in 2°F divisions) and conforming to the requirements for Thermometer 82C (82F) in Specification E 1.

A3.4.1.4 *Injector Coolant Passage Thermometer Assembly (0105180)*, using Thermometer (105180) having a range from –15 to 105°C graduated in 1°C divisions (0 to 220°F graduated in 2°F divisions) and conforming to the requirements for Thermometer 82°C (82°F) in Specification E 1.

A3.4.1.5 *Engine Crankcase Lubricating Oil Temperature Indicator (105321D)*, having a range of 15 to 85°C readable to 3°C (60 to 180°F readable to 5°F).

A3.4.2 *Pressure Measurement:*

A3.4.2.1 *Crankcase Internal Pressure Gage (pressure/vacuum gage) (109929)*, with a range that includes –500 to 500 mm (–20 to 20 in.) of water. A water manometer may be substituted.

A3.4.2.2 *Exhaust Back Pressure Gage*—with a range that includes 0 to 500 mm (0 to 20 in.) of water. A water manometer is a satisfactory alternative.

A3.4.3 *Flow Rate Measurement:*

A3.4.3.1 *Fuel Buret (106334)*, 16 mm I.D. glass buret, 176 mm long with 1 mL graduations.

A3.4.3.2 *Fuel Flow Rate Micrometer Assembly (0109427)*, readable to 0.025 mm (0.001 in.).

A3.4.4 *Time Measurement:*

A3.4.4.1 *Fuel Flow Rate Timer*—Any commercial stop watch or electrical timer having a range in excess of 60 s and graduated in tenths of 1 s.

A3.4.4.2 *Fuel Injection Timing Micrometer Assembly (0109427)*—Readable to 0.025 mm (0.001 in.).

A4. APPARATUS ASSEMBLY AND SETTING INSTRUCTIONS

A4.1 *Camshaft Timing & Valve Lift Measurement*—The camshaft for the Model CFR-48 crankcase used for the cetane method has intake and exhaust cam lobes both ground to produce a valve lift of 0.238 in. Each lobe is designed to include a quieting ramp at the beginning and end of the contour change from the base circle diameter. These quieting ramps are flat spots in the contour which occur at 0.008 to 0.010 in. rise from the base circle of the lobe and which extend for typically 4 to 6° of crank angle rotation. Actual valve lift does not take place until valve clearance is overcome and this is essentially coincident with the flat spot of the quieting ramp. The maximum height of the lobe from the base circle is typically 0.248 in.

A4.1.1 *Measurement Principle*—It is difficult to define the actual point at which a valve should open or close because the event takes place on the quieting ramp where the rate-of-change of the cam profile is minimal. The following procedure uses a point higher up on the contour of the lobes where maximum lift velocity occurs. Thus, all timing events are referenced to the flywheel crank angle degree readings which occur at a rise of 0.054 in. off the cam lobe base circle. Timing of the camshaft can be judged by measurement of the intake valve opening event which along with the exhaust valve closing event are the so-called “top end1” events that are most critical. Fig. A4.1 illustrates both the intake and exhaust lobe profiles and their relationship in the 720° of rotation of the flywheel during one combustion cycle.

A4.1.2 *Timing Check Procedure:*

A4.1.2.1 Measurement is best made when the cylinder assembly is removed from the crankcase although it is possible with the cylinder, head and valve mechanism in place.

A4.1.2.2 Assemble a dial indicator on the deck of the crankcase so that it can be positioned to indicate the lift of the intake valve tappet.

A4.1.2.3 The dial indicator must have a minimum travel of 0.250 in. and read to 0.001 in.

A4.1.2.4 Position the flywheel to top dead center (tdc) on the compression stroke and zero the dial indicator to zero.

A4.1.2.5 Rotate the flywheel in the normal direction until the valve tappet rises causing movement of the dial indicator.

A4.1.2.6 Continue flywheel rotation until the dial indicator reading is 0.054 in.

A4.1.2.7 Read the flywheel crank angle and compare it to the specification which is 30°.

A4.1.2.8 If the observed crank angle is within $30 \pm 2^\circ$, the timing is satisfactory. Otherwise, the camshaft needs retiming either by shifting the cam gear with respect to the crankshaft or by locating the cam gear on its shaft by using one of the other three keyways. Changing the point of mesh of the cam gear with respect to the crankshaft gear by one full gear tooth makes a 9.5° change on the flywheel for a given mark. Four keyways in the cam gear permit shifts of timing in 1°, 11 min increments for a given mark. Cam gears are supplied with an X mark at the tooth to be aligned with the corresponding X mark on the crankshaft gear. If another keyway is used, the gear X mark is

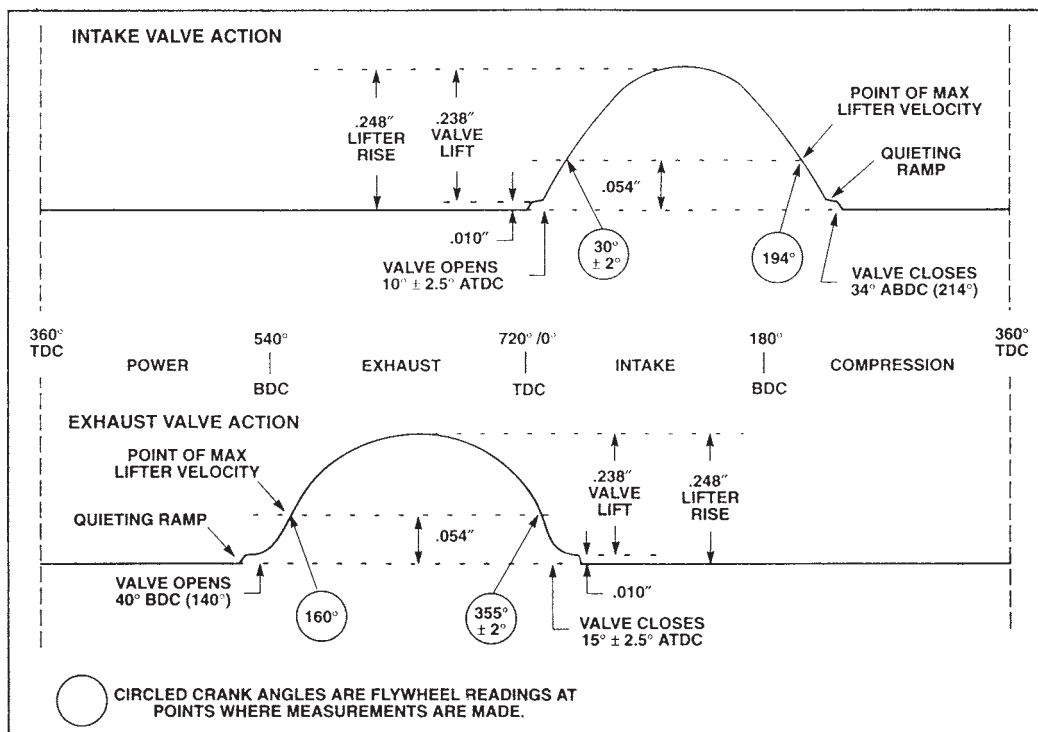


FIG. A4.1 Camshaft Timing Diagram

irrelevant and the proper tooth for the unmarked keyway must be determined. Greater detail is available from the engine manufacturer.

NOTE A4.1—The other valve opening and closing events may also be checked but the single measurement based on the intake valve opening event is sufficient to make the judgement as to proper camshaft timing.

A4.1.3 Valve Lift Check Procedure:

A4.1.3.1 With the dial indicator still positioned over the intake valve tappet, continue rotation of the flywheel until a maximum reading is obtained on the dial indicator.

A4.1.3.2 Read the dial indicator and compare it to the specification which is 0.246 to 0.250 in. If the rise is less than 0.246 from the base circle of the cam, wear of the lobe has occurred and camshaft replacement is indicated.

A4.1.3.3 Valve lift for the exhaust cam lobe should also be checked by repeating the procedure with the dial indicator

positioned over that valve tappet. The lift specification is the same as for the intake valve.

A4.2 Fuel Pump Timing—Pump timing involves coupling the drive shaft of the variable timing device of the pump assembly to the engine camshaft so that the time of fuel injection occurs at the proper point in the combustion cycle. With the pump shaft rotated to cause the pump plunger to just close the fuel inlet ports, the engine flywheel shall be positioned between 300 and 306° on the compression stroke.

A4.2.1 Fuel pump timing is required whenever the pump is disassembled or when critical pump parts are replaced. Fig. A4.2 illustrates the important parts related to the timing procedure.

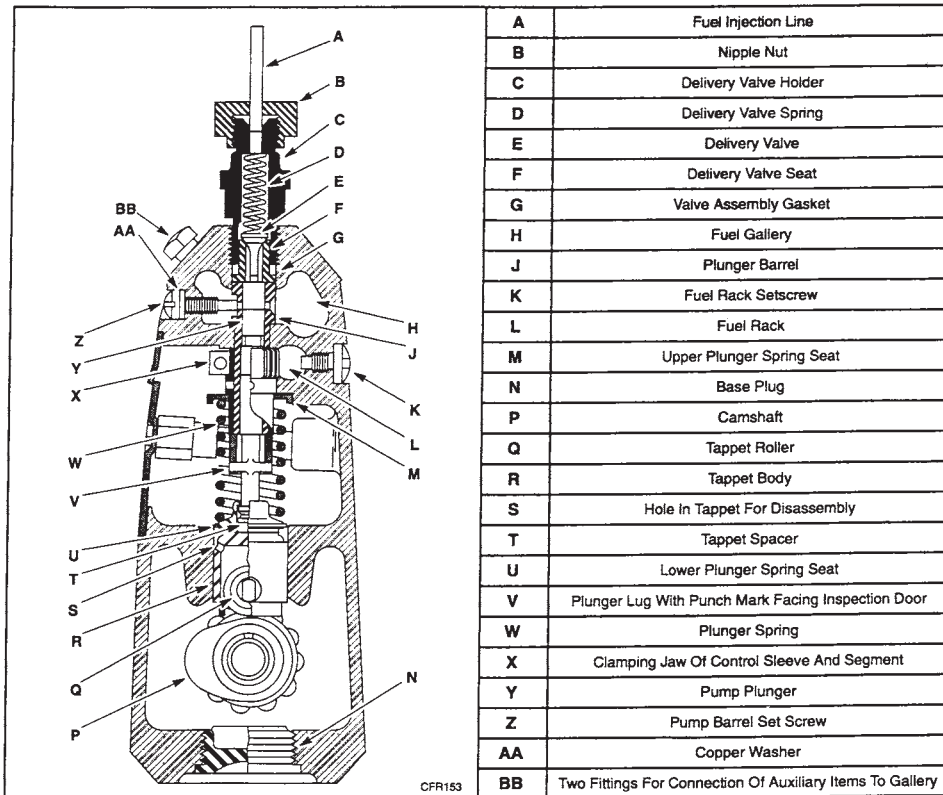


FIG. A4.2 Fuel Injection Pump—Sectional View

A4.2.2 Disconnect the fuel injection tube from the fuel pump outlet and remove delivery valve holder C, spring D and delivery valve E from the pump as shown in Fig. A4.2. (**Warning**—Wear gloves to protect lapped or polished surfaces that could be etched by body acid if handled with bare fingers.) (**Warning**—Immerse all disassembled parts in a container of diesel fuel oil such as secondary reference fuel. Any mated parts, such as delivery valve and seat or barrel and plunger assembly, must be kept together. When making replacements always use a complete mated assembly. Wash each part in a clean diesel fuel oil and wipe it with a clean, lint-free cloth. Check replacement parts by number and visual inspection. Lubricate moving parts with SAE 30 engine crankcase lubricating oil before assembly.)

A4.2.3 Reinstall delivery valve holder C without the spring and delivery valve.

A4.2.4 Provide and install suitable items to use a rubber bulb to blow air into the delivery valve holder C when instructed.

A4.2.5 Disconnect the tube that is between buret D, Fig. 1 and the glass fuel line air trap on the injection pump. Connect a piece of plastic tubing to the fuel line air trap connection and submerge the other end of this tube in a small container of diesel fuel oil such that bubbling in the container may be observed when appropriate.

A4.2.6 Set the fuel selector-valve between, rather than on, the numbered mark for a specific fuel tank. Set the flywheel to a position at any point on the intake stroke. Remove the machine bolt which connects the fuel rack to the safety shutoff solenoid and check that the rack is forced forward against the fuel flow-rate micrometer which should be in a typical operating position. Rotate the fuel injection timing micrometer so that the advance lever is at full advance (nearest to operator).

A4.2.7 While slowly rotating the flywheel in the clockwise direction (as seen from the front of the engine), use the rubber bulb to blow air steadily into the delivery valve holder C, Fig. A4.3, and observe air bubbles at the end of the tube submerged

in the container of diesel fuel oil. When the bubbles stop, the port has just been closed by the plunger on its upward stroke. Determine this point by several trials noting the flywheel crank angle for each to establish an average point.

A4.2.8 For reference purposes, use this average flywheel position and observe the scribed line on the edge of the variable timing device drive hub and scribe a matching line on the housing if one is not already present. This reference mark may change if new components are installed in the injection pump.

A4.2.9 For proper timing, the closure of the plunger should occur at a flywheel crank angle of between 300 and 306° on the compression stroke. If not, remove the two cap screws which fasten the pump to camshaft vernier coupling disks together. Hold the pump disk at the port closing mark, rotate the flywheel to a 300° to 306° position and reinstall the two coupling cap screws using the best matching holes.

A4.2.10 Reinstall the delivery valve, spring, fuel injection tube and the tube between the fuel line air trap and the buret. Also reconnect the fuel rack safety shutoff solenoid linkage.

A4.3 *Fuel Pump Plunger Lift*—The port of the pump plunger should close when the plunger has moved up 0.076 in. from the base circle of the pump can. This setting is made at the factory and there is no provision for field adjustment.

A4.4 *Fuel Pump Safety Shutoff Solenoid Linkage Setting*—This safety solenoid is utilized to stop fuel delivery to the engine and thus prevent uncontrolled engine overspeed in the event of electrical power failure. In the power off condition, a heavy spring pulls the solenoid shaft, the connecting linkage and the fuel control rack to a zero delivery position. When the engine is running, the solenoid overcomes the force of the spring and allows the rack to move into contact with the fuel flow rate micrometer. At no time should the linkage setting permit the linkage to force movement of the solenoid core piece which typically causes loud humming or buzzing and ultimately leads to overheating of the winding. A slot in the solenoid connecting linkage permits an adequate range of freedom of micrometer adjustment to provide the proper fuel flow rate for typical fuels. The connecting linkage includes an adjustable shaft which should be set so that the slotted control yoke permits play relative to the solenoid core piece when the solenoid is energized and the fuel flow-rate micrometer is at a typical operating position. To adjust, loosen the locknut and change the length of the connecting screw appropriately and then relock the nut.

A4.5 *Fuel Injector Nozzle Assembly Opening Pressure Setting*—Fuel injection occurs when the pressure in the nozzle assembly passages forces the nozzle pintle to lift against the force of an adjustable spring in the nozzle assembly. The setting should be checked each time the nozzle is disassembled and cleaned.

A4.5.1 To adjust the injection opening pressure, assemble the injector nozzle assembly in a suitable injector nozzle tester in a ventilated hood.

A4.5.2 Loosen the locknut B, Fig. A4.4 on the pressure adjusting screw A and turn the adjusting screw as required to obtain the specified 10.3 ± 0.34 MPa (1500 ± 50 psi) injection

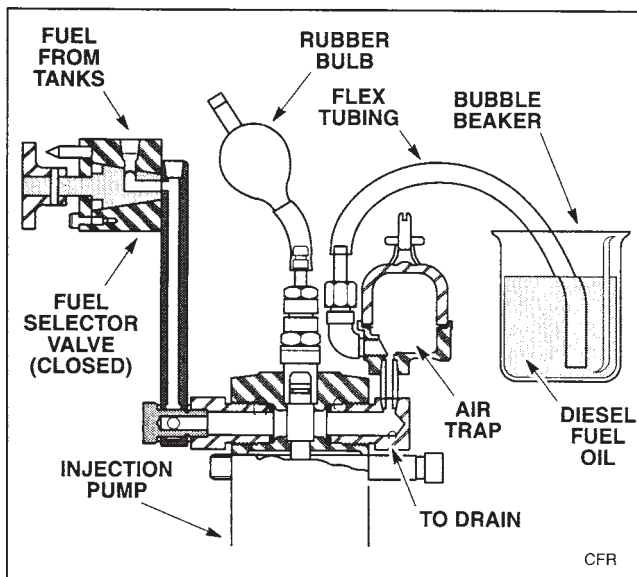


FIG. A4.3 Fuel Pump Timing Test Fittings

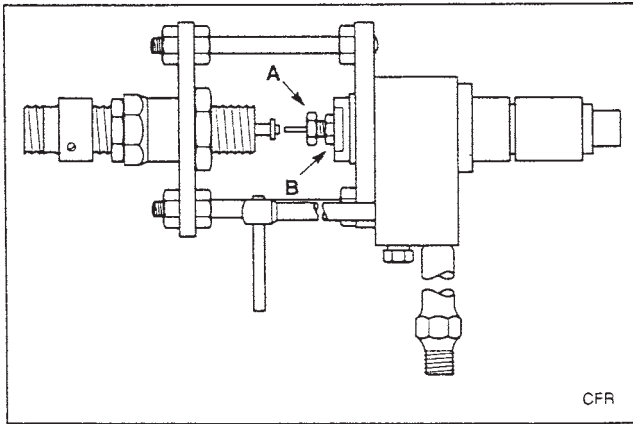


FIG. A4.4 Injector Assembly Showing Pickup Mounted

pressure. This is a trial and error procedure whereby the pressure is checked by use of the injector tester after each screw adjustment accompanied by relocking of the locknut B. Inspection for possible nozzle pintle drip as well as spray pattern should be observed when making this setting.

A4.5.3 After setting injection opening pressure, check that the injector pickup gap is typically 1 mm (0.040 in.) before reinstalling the injector assembly in the engine.

A4.6 *Checking Compression Pressure*—Determination of the compression pressure requires use of a compression pressure gage assembly such as that illustrated in Fig. A4.5, (Waukesha Part Number A110376), readable to 2.5 psi and equipped with a suitable check valve and deflator or pressure release valve.

A4.6.1 Compression pressure is measured after the engine has been thoroughly warmed up on a typical diesel fuel oil under standard operating conditions for that fuel. The follow-

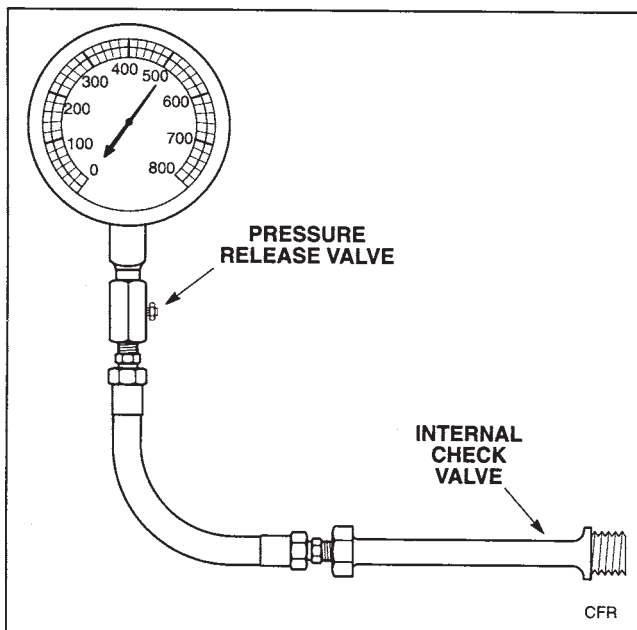


FIG. A4.5 Compression Pressure Gage Assembly

ing steps should be performed as quickly as possible to ensure that the pressure readings represent hot engine conditions.

A4.6.2 Collect and have ready a calibrated compression pressure gage assembly and the tools required to remove the combustion pickup and install the gage assembly in the combustion chamber pickup hole.

A4.6.3 Shut the engine down by opening the injector assembly fuel bypass valve and then turning off the engine power switch. The bypass valve must remain open for the remainder of the compression pressure check procedure.

A4.6.4 The fuel selector valve must be positioned so that fuel will continue to be delivered to the fuel pump to maintain proper pump barrel and plunger lubrication.

A4.6.5 Remove the combustion pickup from the cylinder head and install the compression pressure gage assembly. (**Warning**—Personnel shall avoid contact with the combustion pickup because it is extremely hot and can cause serious burns.)

A4.6.6 Set the handwheel to 1.000, regardless of the bore diameter of the cylinder in use.

A4.6.7 Restart the engine and operate in a motoring mode without any fuel being injected into the cylinder.

A4.6.8 Observe the compression pressure gage reading, release the pressure once or twice using the deflator valve and record the equilibrium pressure which results. (**Warning**—In addition to other precautions, read the compression pressure gage in whatever position it faces without twisting the gage and hose which can distort the readings.)

A4.6.9 Satisfactory basic handwheel indexing is indicated if the compression pressure is 3275 ± 138 kPa (475 ± 20 psi).

NOTE A4.2—Compression pressure values for engines operating at barometric pressures below 27 in. Hg have not been established.

A4.6.10 Shut the engine down, remove the compression pressure gage assembly, reinstall the combustion pickup with a new gasket and tighten the pickup to the specified torque setting (30 lbf-ft).

A4.7 *Adjusting Crankcase Lubricating Oil Pressure*—The oil pressure of the lubricating oil in the engine crankcase gallery is dependent on the setting of the pressure control valve located at the lower left side of the engine crankcase when viewed from in front of the engine. (See Fig. A4.6.)

A4.7.1 The oil pressure should be adjusted with the engine hot and running.

A4.7.2 Remove the acorn nut and gasket from the oil pressure control valve assembly.

A4.7.3 Loosen the gasketed locknut so that the adjusting screw is free.

A4.7.4 While observing the engine oil pressure gauge, set the adjusting screw to obtain the specified 0.17 to 0.20 MPa (25 to 30 psi) pressure.

A4.7.5 Tighten the gasketed locknut while observing that the pressure remains within limits.

A4.7.6 Reinstall the gasket and acorn nut.

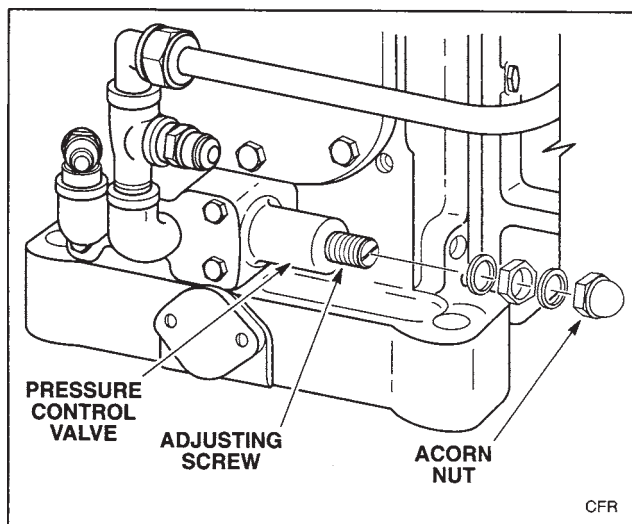


FIG. A4.6 Oil Pressure Control Valve Assembly

APPENDICES

(Nonmandatory Information)

X1. VOLUMETRIC REFERENCE FUEL BLENDING APPARATUS AND PROCEDURES

X1.1 *Background*—Primary reference fuels which are used infrequently are usually packaged in relatively small containers and storage and dispensing is handled in the manner used for general chemicals. Secondary reference fuels are supplied in bulk containers of 5 or 55 U.S. gal capacity (0.019 or 0.208 m³) and for laboratory safety reasons these bulk quantities are typically stored in a special fuel storage room or outside of the engine laboratory.

X1.2 *Delivery from Storage*—Delivery of reference fuel material from the bulk storage container to a dispensing apparatus in the engine laboratory may be handled in any of several ways. The equipment and procedures required for delivery of the reference fuel material are the responsibility of the user of this standard.

X1.3 *Dispensing Equipment*—A common means of accurately measuring reference fuel blend volumes applies a matched pair of calibrated glass burets, one for each of the two secondary reference fuels. Fuel is dispensed either through an integral glass stopcock or a separate valve.

X1.3.1 Burets of glass with an automatic zero top fitting provide accurate, efficient and convenient measurement. A typical buret is illustrated in Fig. X1.1. Specifications for a typical buret are given in Table X1.1.

X1.3.2 *Separate Dispensing Valves*—It is common practice to utilize burets that do not have a dispensing stopcock. Bottom delivery from the buret is from a straight tubing bib which is connected by plastic tubing to a three-way valve similar to that shown in Fig. X1.2. The most important feature of such a valve assembly is the dispensing fitting which is formed so that only a very minimum of drip can occur if the collection container is

inadvertently touched against the orifice tip. These valves can also be the means for controlling discharge flow rate to specification by use of the 6 mm (³/₁₆ in. O.D.) tubing for the formed tip.

X1.4 *System Installation and Operation*—User experience with reference fuel systems has pointed out a number of important aspects that support the following recommendations:

X1.4.1 Use amber glass burets for dispensing reference fuels or provide opaque shielding around all but the calibration mark area of clear glass burets.

X1.4.2 Mount burets vertically at an elevation that permits horizontal sighting of all calibration marks.

X1.4.3 Install a separate buret for each of the reference fuels.

X1.4.4 Mount burets in a manner that ensures freedom from vibration.

X1.4.5 Store bulk reference fuel containers and provide appropriate tubing for delivery of the fuels to the dispensing burets in accordance with the instructions of the manufacturer and in compliance with all local codes and regulations.

X1.4.5.1 Avoid the use of gravity flow delivery of reference fuel to burets.

X1.4.6 Thoroughly clean reference fuel burets on a regular basis to minimize hangup or clinging on the inner surface of the buret that can lead to blending errors.

X1.4.7 Burets should not be filled until a blend is required in order to minimize any tendency for deterioration of the fuel by exposure to light.

X1.4.8 Use stainless steel tubing, or other opaque tubing that does not react with reference fuel, to connect between the bulk reference fuel container and the dispensing buret.

X1.5 Procedure for Use of Buret System

X1.5.1 To fill the buret, set the valve or stopcock to “fill” position, so that fuel rises in the buret until it overflows at the automatic zero. Stop filling by setting the valve to “off” position. Check that any bubbles are purged at the zero tip and refill the tip, if necessary.

X1.5.2 To dispense fuel, set the valve to “dispense” position, so that fuel is delivered to the collection container. Stop dispensing by setting the valve to “off” position while carefully noting the level of the fuel in the calibrated section of the buret and locating the bottom of the liquid meniscus at the desired volume percent mark.

X1.5.3 Before drawing a measured volume, make certain that the tip of the dispensing tube is full. When the measured volume has been collected, be certain not to drain any fuel from the tip of the dispensing tube as this will cause an error.

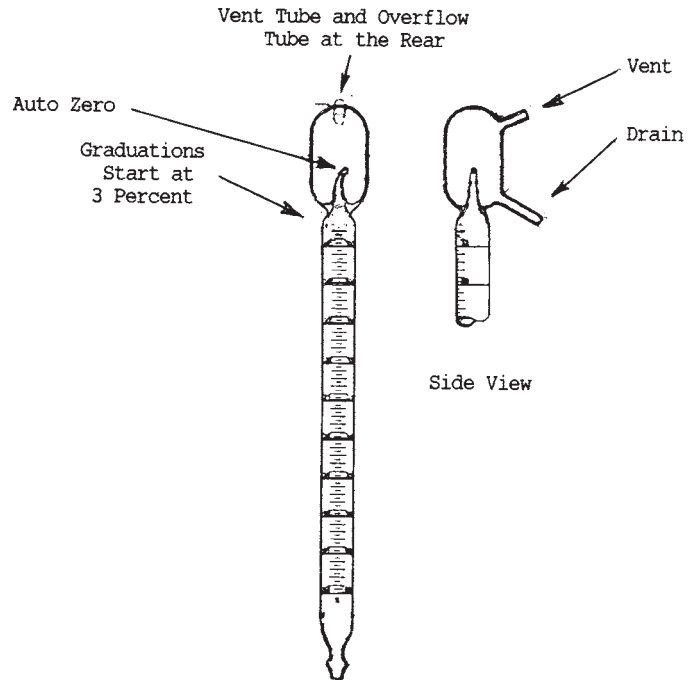


FIG. X1.1 Typical Reference Fuel Dispensing Buret

TABLE X1.1 Typical Buret Specifications

Buret Capacity	mL	500
Automatic Zero		YES
Graduations:		
Major Marks	%	5
Minor Marks	%	1
Internal Diameter of Graduated Tube:		
Minimum	mm	32
Maximum	mm	34
Scale Length, 5 to 100 %:		
Minimum	mm	523
Maximum	mm	591
Top of Overflow Bulb to 5 %	mm	100/120
Mark Length (nominal)		
Overall Length (including tip):		
Minimum	mm	650
Scale Error (Maximum)	%	0.1

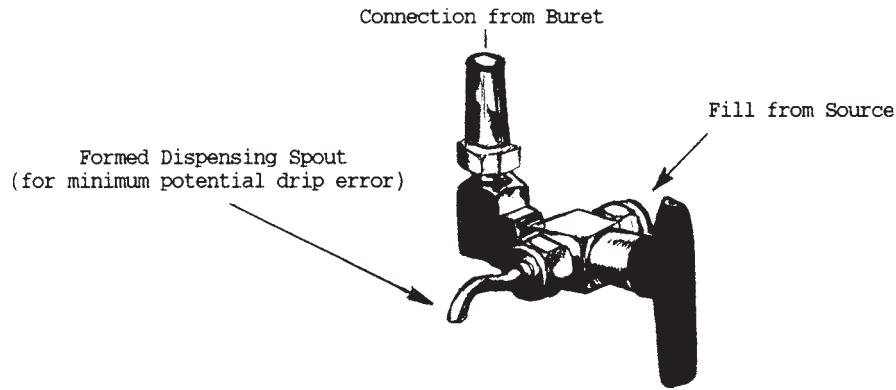


FIG. X1.2 Typical Fill/Dispense Valve

X2. OPERATING TECHNIQUES—ADJUSTMENT OF VARIABLES

X2.1 *Compression Ratio versus Handwheel Reading*—The compression ratio of the cetane engine is variable and depends upon the position of the variable compression plug in the precombustion chamber of the cylinder head. The variable compression plug is positioned by the screw action of the handwheel and the relative location of the plug is indicated by an indexed vernier scale. This handwheel reading scale extends from 0.500 to 3.000 and is inversely related to compression ratio. Low handwheel readings correspond to high compression ratio conditions while high handwheel readings reflect low compression ratio conditions.

X2.1.1 If the handwheel has been carefully indexed, the compression ratio of the cetane engine for any position of the variable compression plug can be calculated using the following equation:

$$C.R. = \frac{V_S + (V_{CC} + V_{TP} + V_{PU}) + V_{PC}}{(V_{CC} + V_{TP} + V_{PU}) + V_{PC}} \quad (X2.1)$$

where:

- C.R. = compression ratio,
- V_S = volume swept by piston in cylinder,
- V_{CC} = volume in main combustion chamber above piston at tdc including the valve recesses and piston top-land clearance,
- V_{TP} = volume of turbulence passage between combustion and pre-combustion chambers,
- V_{PU} = volume of threaded pickup hole with a pickup installed, and
- V_{PC} = volume of pre-combustion chamber.

X2.1.2 Volumes V_{CC} , V_{TP} , and V_{PU} are independent of cylinder bore diameter and are based on the physical dimensions of the cylinder head. The sum of these volumes is 0.659 cu. in. (10.8 cc) as determined by both calculation and measurement. The equation for compression ratio, when calculated using cu. in. units is thus:

$$C.R. = \frac{V_S + V_{PC} + 0.659}{V_{PC} + 0.659} \quad (X2.2)$$

X2.2 Adjusting Compression Ratio Using the Handwheel

X2.2.1 Cetane method testing requires adjustment of compression ratio (C.R.) to attain the proper ignition delay condi-

tions for each specific diesel fuel oil or reference fuel. Changing handwheel setting changes the ignition delay period. Low cetane number fuels have inherently longer ignition delay characteristics than high cetane number fuels. The cetane method test procedure requires that all fuels operate at a specified ignition delay period and therefore changes in handwheel setting are necessary.

X2.2.2 Handwheel Adjustment Procedure:

X2.2.2.1 Loosen the small locking wheel of the handwheel assembly by counterclockwise rotation as viewed from the front of the engine. This releases the mechanism and permits the larger handwheel to be turned so that the variable compression plug can be properly moved in or out of the precombustion chamber.

X2.2.2.2 Set the larger handwheel to establish the required ignition delay period as indicated on the ignition delay meter. Clockwise rotation of the handwheel (viewed from in front of the engine) increases C.R. and decreases the ignition delay crank angle degree reading.

X2.2.2.3 Always make the final adjustment of the handwheel in the clockwise direction to minimize scale reading errors by eliminating the unavoidable play in the handwheel mechanism.

X2.2.2.4 Lock the mechanism by turning the small locking wheel clockwise until tight. (**Warning**—Hand tightening of the locking wheel should be adequate if the handwheel mechanism is in proper working order. The need to use additional leverage to achieve a locked condition indicates a need for handwheel assembly maintenance.)

X2.3 *Fuel System Operation*—As illustrated in Fig. X2.1 the fuel system incorporates three fuel tanks each with a drain valve ahead of a selector valve. The selector valve is positioned to deliver fuel from a specific fuel tank by rotation of the valve to the mark for that tank. The selected fuel is delivered to the fuel pump inlet and fills the fuel sump or gallery. The pump gallery also connects to the flow-rate buret through an air trap which is fitted with a drain valve. The fuel level in the buret will be the same as that in the fuel tank. When the selector valve is positioned so that the pointer is indexed between the fuel tank marks, fuel delivery from the tank is blocked. In this

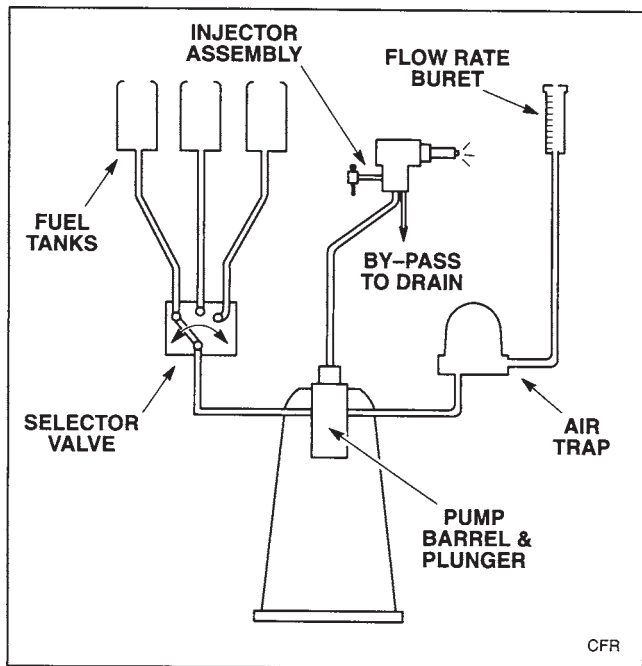


FIG. X2.1 Fuel System Schematic

mode, the engine will continue to operate on the fuel which is in the gallery and the line from the flow rate buret. Fuel flow rate measurement can thus be performed by first filling the flow rate buret from the tank with the selector valve positioned on the tank mark and then positioning the valve between tank marks so that fuel from the buret leg alone supplies the fuel pump.

X2.3.1 The fuel flow-rate-buret is mounted so that the vent hole at the top of the buret is slightly above the level of the top of the fuel tanks thus preventing fuel overflow from the buret when the tank is full. The calibration marks on the buret are in 1 mL increments so that fuel flow rate is easily measured by noting the time required for engine consumption to lower the buret fuel level by a specific number of mL.

X2.3.2 *Changing to a New Fuel*—Introduction of a diesel fuel oil involves filling a fuel tank, purging the flow-rate-buret and air trap leg and displacement of the fuel in the fuel line from the pump to the injector assembly. (**Warning**—Diesel Fuel Oil—Combustible. Vapor harmful. See Annex A1.) The typical sequence for this process is as follows:

X2.3.2.1 Check that there is sufficient fuel in the buret leg to operate the engine while filling a tank with a new fuel. (**Warning**—Do not allow the fuel pump to run dry, except during the momentary periods required to switch from one fuel to another, because the fuel pump is partly dependent on fuel for lubrication.)

X2.3.2.2 Position the selector-valve so that it is between marks but adjacent to the mark for the fuel tank into which the new fuel is to be introduced.

X2.3.2.3 Check that the selected fuel tank is empty by opening the tank drain valve.

X2.3.2.4 Introduce the fuel to the fuel tank while leaving the associated drain valve open for an instant; then alternately

close and open the valve a few times to remove any entrained air from the passages before finally closing the drain valve.

X2.3.2.5 In a series of quick steps, drain the buret leg, position the selector-valve to introduce the new fuel and when fuel begins to appear in the buret, position the selector-valve to between marks so the engine operates from the buret alone. This step purges the fuel system with the exception of the line from the pump to the injector. When the engine runs out of fuel, repeat the purging sequence. Engine operation on the purge sequences will afford sufficient time to completely displace the fuel in the line from the injection pump to the injector.

NOTE X2.1—Diesel fuel oils which are highly viscous or cause discoloring of the flow-rate-buret, may require more drastic flushing action for adequate purging.

X2.3.3 *Measuring Fuel Flow Rate:*

X2.3.3.1 Fill the flow-rate-buret and turn the selector-valve to between the marks.

X2.3.3.2 Using an electric stop clock (or stop watch), measure the fuel consumption by starting the clock as the meniscus passes a millilitre graduation on the buret and stopping the clock as the meniscus passes the mark selected for the amount of fuel to be consumed (typically 13 mL below the starting mark). Turn the fuel-selector-valve back to the mark to again draw fuel from the appropriate tank.

X2.3.3.3 If the time registered by the clock is not correct (60 ± 1 s for 13 mL), readjust the fuel flow-rate-micrometer to change the pump rack position and thereby the amount of fuel being injected to the engine (see Fig. X2.2). Turn the flow rate micrometer clockwise (as viewed from in front of the engine) to increase fuel flow (shorten the clock time per unit volume). Typically, 0.005 micrometer divisions will cause a change of 1 s for 13 mL of fuel consumption.

X2.3.3.4 Repeat the flow rate measurement procedure until the specified fuel flow rate is achieved.

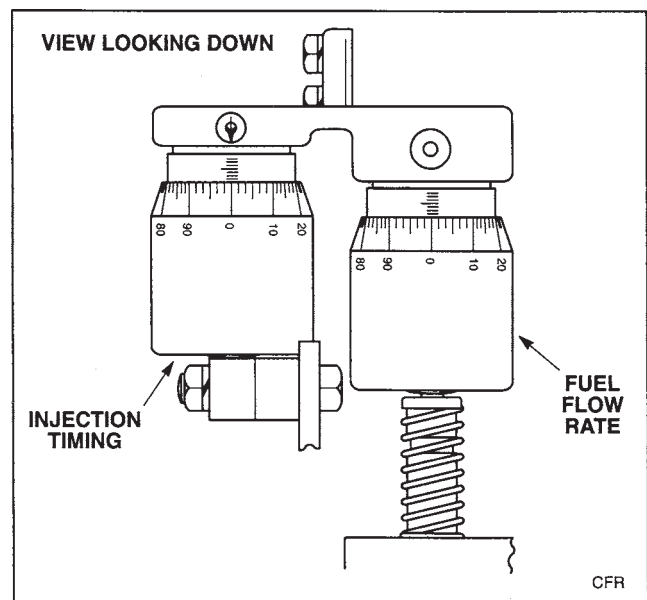


FIG. X2.2 Fuel Pump Flow Rate and Injection Timing Micrometers

X2.3.3.5 When the fuel level in the fuel tank lowers, the level in the flow-rate-buret may not be adequate to permit good flow rate measurement. In this case, use a suction bulb applied to the top vent hole of the buret and with the selector-valve positioned on the tank mark, pull fuel up from the pump gallery to the desired level. Before removing the suction bulb, quickly move the selector-valve to a position between the tank marks. Flow rate measurement must then be started almost immediately because the engine will be drawing fuel from the buret and the level in the buret will be falling.

X2.3.3.6 Determination of the proper flow rate is a trial and error procedure. Initial checks may be made using a 10 s time interval which should result in consumption of approximately 2 mL of fuel. The final flow rate measurement shall be made over a full 60 ± 1 s period.

X2.3.4 *Adjusting Fuel Injection Timing*—While operating the engine at the proper fuel flow rate and with the fuel-selector-valve positioned on the mark for the fuel being evaluated, observe the indicated injection timing (injection advance) value. Adjust the fuel injection timing micrometer to achieve the specified injection advance degrees (see Fig. X2.2). Turn the injection timing micrometer clockwise (as viewed from in front of the engine) to decrease the indicated number of degrees of advance.

X2.4 Preparations Before Starting Engine

X2.4.1 Check the jacket coolant level in the condenser sight glass.

X2.4.2 Check the engine crankcase lubricating oil level in the crankcase oil sight glass.

X2.4.2.1 Check the crankcase breather assembly to insure that it is clean and operable.

X2.4.2.2 Turn on the crankcase oil heater or oil heat temperature controller.

X2.4.3 Check the fuel pump lubricating oil level using either the dip stick or by sighting through the plastic sump cover located on the side of the pump.

X2.4.4 Fill one of the fuel tanks with a diesel fuel oil suitable for engine warm-up taking care to purge the tank line of any trapped air.

X2.4.4.1 Set the fuel-selector valve to the mark for the specific fuel tank so that fuel will flow to the fuel pump gallery and flow rate buret leg.

X2.4.4.2 Purge the fuel pump gallery of any entrained air by opening and closing the drain valve from the glass air trap three times.

X2.4.5 Open the cooling water valve or check that cooling water will be available for both the condenser and the injector coolant chamber when the engine is started.

X2.4.6 Using the hand crank, manually rotate the engine crankshaft three or four complete revolutions to ensure that all parts move freely. Complete the cranking so that the flywheel is positioned at top-dead-center on the compression stroke to minimize the load on the absorption motor when the engine is started.

X2.5 *Starting the Engine*—It is assumed that the engine has been commissioned and is in operable condition and that electrical circuits and cooling water are available on demand.

X2.5.1 Check that the injector bypass valve (see Fig. X2.3) is open and the handwheel is set to about 1.000.

X2.5.2 Position the off-run-start switch to start and hold it in the start position for a few seconds to allow oil pressure to rise sufficiently to actuate the engine run circuitry so that the engine continues to operate when the start switch is released to the run position.

X2.5.3 Turn on the intake air heater.

X2.5.4 Allow the engine to motor (operate under non-firing conditions) for an additional few seconds to purge the fuel lines and injector.

X2.5.5 Initiate engine combustion by closing the injector bypass valve and if necessary, by increasing the C.R. through clockwise rotation (as viewed from in front of the engine) of the unlocked handwheel. After firing commences, back off the handwheel toward the higher reading direction (counterclockwise) until the engine operates smoothly. (**Warning**—Sharp knocking sounds may occur and blowby smoke may appear from the mechanism as the handwheel is rotated in the counterclockwise direction which increases the handwheel reading. These are normal.)

X2.5.6 Energize the cetane or ignition delay meter instrumentation in accordance with manufacturer instructions.

X2.5.7 Set the fuel flow rate to approximately the specified value.

X2.5.8 Set the injection timing to approximately the specified value.

X2.5.9 Check that the ignition delay period is nominally at the specified value.

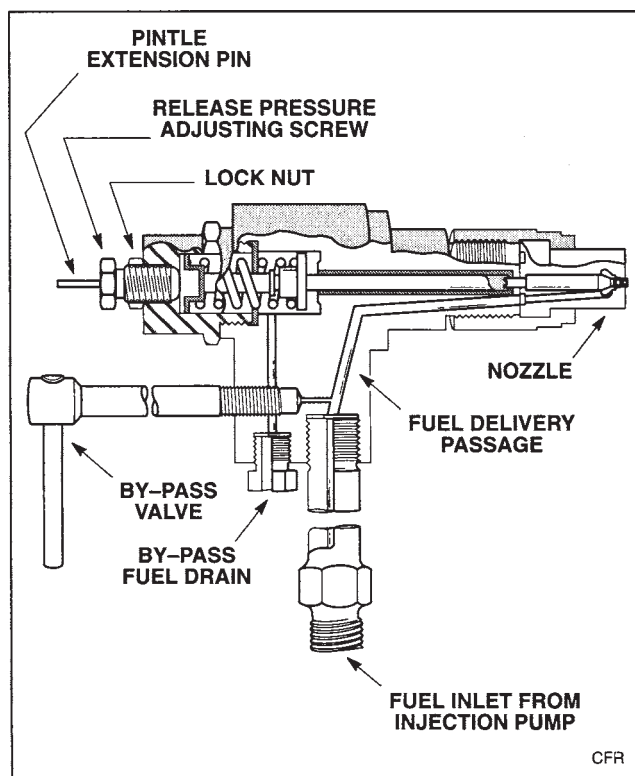


FIG. X2.3 Fuel Injector Assembly

X2.5.10 Continue engine warm-up for approximately 1 h taking care to periodically observe and if necessary, readjust all critical operating conditions.

X2.6 Stopping the Engine

X2.6.1 Turn off the cetane or ignition delay meter and the intake air heat switches.

X2.6.2 Open the injector bypass valve to prevent further injection of fuel to the combustion chamber.

X2.6.3 Stop the engine by positioning the stop-run-start switch to the off position.

X2.6.4 Using the hand crank, manually rotate the engine to set it on top-dead-center on the compression stroke so that the intake and exhaust valves are closed. This will minimize possible valve warping or corrosion in the combustion chamber between operating periods.

X2.6.5 Drain all fuel tanks and fuel lines.

X2.6.6 Turn off the cooling water.

NOTE X2.2—Cooling water flow may be continued for a period of 20 to 30 min after engine shut down, especially to the injector coolant passage, to minimize the buildup of a hard coke deposit on the tip of the injector nozzle due to potential pintle drip.

X2.7 *Checking Ignition Delay versus Cetane Number Sensitivity*—The sensitivity characteristic illustrated in Fig. X2.4 can provide a measure of confidence that the injector assembly and particularly the injector nozzle are performing in a satisfactory manner. It is a test that requires approximately 1 h to perform but it is useful to judge nozzle acceptance when engine instability has been experienced after cleaning and resetting.

X2.7.1 Using a secondary reference fuel blend of approximately 35 cetane number, adjust all engine variables to

standard operating conditions with the ignition delay period carefully set to 13.0°.

X2.7.2 Prepare a series of at least four more reference fuel blends of higher cetane number so that there is a difference of about 4 cetane numbers between each successive pair of blends.

X2.7.3 Operate the engine on each successive blend without changing the handwheel reading established for the 35 cetane number blend but adjusting the fuel flow rate to 13 mL/min and the injection timing to 13°. Record the resulting ignition delay values for each of the reference fuel blends.

X2.7.4 Plot the data on a graph similar to that in Fig. X2.4 so that the sensitivity characteristic can be observed. If the points do not fit an easily defined smooth curve, the injector nozzle is probably suspect and may require further cleaning maintenance or replacement. If a nozzle is faulty, it is often easily noted by the erratic operation and data scatter of the results obtained during the early stages of this procedure.

X2.8 Checking Exhaust and Crankcase Breather Systems for Resonance

X2.8.1 Resonance in the piping systems can occur when the configuration creates a critical length/volume relationship. A resonant condition affects the primary pressure within the system and can affect critical operating conditions.

X2.8.2 Exhaust system resonance may be checked by providing either a 3/4 inch or larger gate or ball valve at the surge tank or close to the engine exhaust port. Opening the valve should drastically change the exhaust discharge configuration while the engine is operating at standard conditions to determine if there is an effect.

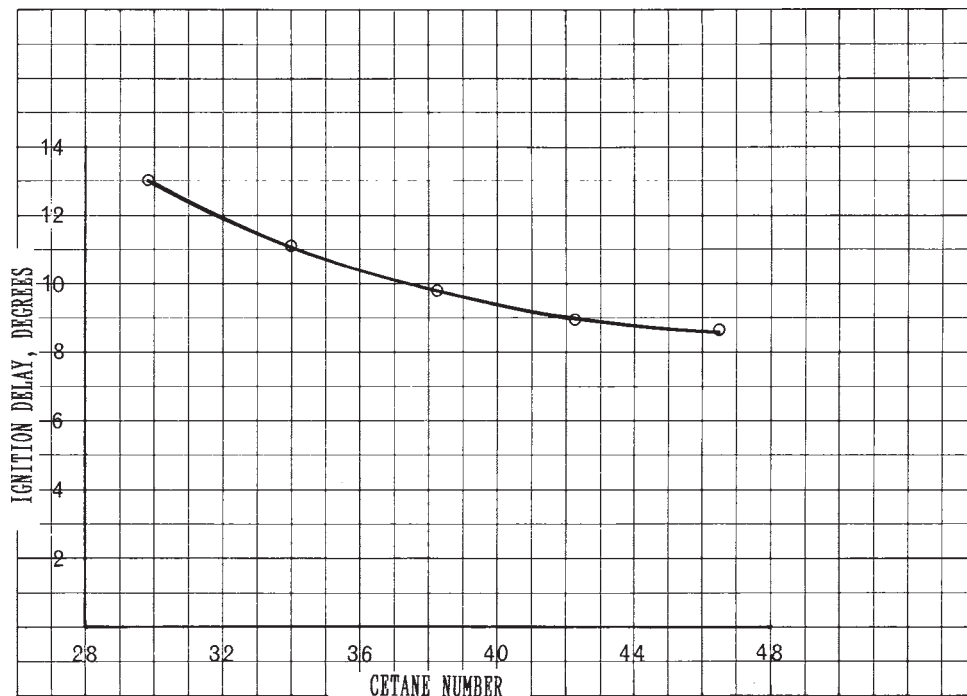


FIG. X2.4 Ignition Delay versus Cetane Number Characteristic

X2.8.2.1 Operate the engine at standard operating conditions on a typical diesel fuel oil and allow sufficient time for the ignition delay period to stabilize.

X2.8.2.2 Open the valve or effect the change in exhaust piping with the engine running.

X2.8.2.3 If the ignition delay is not affected, resonance does not occur and the piping system is satisfactory.

X2.8.2.4 If ignition delay is affected when the valve is opened, resonance may be a factor and typically a change in the length of the exhaust discharge pipe will correct the condition.

X2.8.3 Crankcase breather system resonance typically causes the crankcase pressure to be positive. Resonance in the discharge piping is not a problem as long as the operating engine creates a crankcase vacuum.

X3. MAINTENANCE TECHNIQUES

X3.1 *Importance of Maintenance*—The need for proper maintenance of the cetane engine unit cannot be overemphasized if reliable cetane number ratings of diesel fuel oils are to be obtained. The care used in the inspection, adjustment, and especially the overhaul of the combustion chamber components is a major factor in achieving these aims.

X3.2 Types of Maintenance

X3.2.1 *Daily Checks*—Those checks associated with the preparations before starting the engine as detailed in [Appendix X2](#).

X3.2.2 *Top Overhaul*—The generally accepted term used to describe valve reconditioning, the cleaning of the combustion chamber, piston, piston rings, variable expansion plug or handwheel assembly and the cleaning of the coolant jacket passages and the coolant condenser. Some other parts may also be given attention during a top overhaul, depending on need.

X3.2.2.1 Typically, a top overhaul is necessary every 100 to 300 h and the need is usually indicated by unstable or non-repeatable performance of the engine. The interval between top overhauls varies and depends primarily upon the severity of the conditions under which the unit is operated.

X3.2.3 *Injector Assembly Inspection*—The disassembly and cleaning of the nozzle, checking nozzle opening pressure and spray pattern.

X3.2.3.1 It is recommended that injector inspection and checking be performed at every top overhaul. However, depending on the severity of testing, the process may need to be performed more frequently and some testing facilities make it a practice to install a cleaned and checked injector prior to each unit startup.

X3.2.4 *Crankcase/Unit Inspection*—Encompasses crankcase cleaning, mechanical component wear checks, alarm function checks, power absorption motor inspection, belt tension adjustment, instrumentation checks, etc.

X3.2.4.1 The recommended interval between crankcase/unit inspections is every 2000 h of operation or biannually, whichever comes first. Model CFR-48 crankcases, which can be completely restored by the manufacturer, have been found to perform acceptably for periods of 40 000 h or more before such restoration is required. (**Warning**—Deactivate the engine unit before performing any maintenance. Shut off electrical power at the main disconnect, lock out, if possible. Place a WARN-

ING notice on the unit panel indicating repairs are in process and that no attempt is to be made to start the engine. Shut off coolant water to the unit.)

X3.2.5 *Auxiliary Equipment Maintenance*—Volumetric glassware such as the engine fuel flow rate buret and the reference fuel blending burets should be chemically cleaned on a regular basis to insure accurate volumetric measurement.

X3.2.5.1 Quarterly cleaning of volumetric ware is recommended.

X3.3 Top Overhaul Procedures

X3.3.1 Disassemble the complete combustion chamber and associated assemblies from the engine crankcase. Components to be removed include:

X3.3.1.1 Combustion and injector pickups.

X3.3.1.2 Thermometers and any temperature sensors.

X3.3.1.3 Intake air elbow, silencer and heater assemblies.

X3.3.1.4 Fuel injector tubing and injector assembly.

X3.3.1.5 Circulating cooling water piping at the coolant condenser, the condenser/water pipe assembly and the water inlet pipe to the cylinder.

X3.3.1.6 Exhaust pipe assembly.

X3.3.1.7 Handwheel assembly from the cylinder head using detailed instructions available from the manufacturer.

X3.3.1.8 Valve cover, rocker arm bracket assembly, rocker half-balls and push rods.

NOTE X3.1—Marking of push rods as intake and exhaust ensures they will be reassembled in the same positions.

X3.3.1.9 Cylinder head.

X3.3.1.10 Valve rotators, valve springs, and valves.

X3.3.1.11 Cylinder.

X3.3.1.12 Piston pin retainers, piston pin, and piston.

X3.3.2 *Component Cleaning*—All combustion deposits, gasket material, rust, etc. should be removed from components.

X3.3.2.1 Commercial chemical cleaning solutions may be used in accordance with the manufacturers instructions as long as they do not etch or affect the surface finish of the machined surfaces. Except for electromechanical pickups, use of ultrasonic bath equipment has been demonstrated to be effective and heating of some cleaning solutions can also be beneficial. (**Warning**—Chemical Cleaning Solutions—Poison. May be harmful or fatal if inhaled or swallowed. See [Annex A1](#).)

X3.3.2.2 Scraping, brass wire brushes (manually or power driven), and fine steel wool have been found to be effective cleaning aids.

X3.3.2.3 Complete any cleaning sequence by rinsing of all parts with a solvent, such as kerosine. (**Warning**—Kerosine—Combustible. Vapor harmful. See [Annex A1](#).)

X3.3.3 *Cylinder Head:*

X3.3.3.1 *Combustion Chamber Surface*—Discard head if badly pitted or corroded.

X3.3.3.2 *Precombustion Chamber*—Discard head and hand-wheel housing if internal diameter of chamber exceeds 1.630 in.

X3.3.3.3 *Valve Guides*—Replace a guide when the internal diameter exceeds 0.3785 in. Replacement requires special tools.

X3.3.3.4 *Valves*—Discard if stem is badly scuffed or diameter is less than 0.3705 in. Reface to 45° using a valve refacing (grinding) machine so that face runout is within less than 0.0015 in. Discard valve if grinding has created a sharp edge at the outer diameter of the head indicating stellite coating has been removed.

X3.3.3.5 *Valve Seats*—Reface seats using a valve seat grinding machine or a valve seat cutter kit. Use a 45° seat angle and subsequently lap the valve to the seat. Alternatively, an interference angle approach may be utilized by refacing the seat at both 46° and 15° so that the intersecting line becomes the contact surface with a 45° faced valve. When an interference angle approach is utilized, lapping may be performed but extreme care must be taken to exert very light pressure to prevent creating a groove in the valve face.

X3.3.3.6 *Valve to Valve Seat Matchup*—Check the valve to seat contact. Lapped valve seat width must not exceed 0.070 in. as viewed on the valve. The top edge of the contact line or area shall be at least 0.030 in. from the top edge of the faced portion of the valve. The valve head shall be recessed at least 0.020 in. below the surface of the cylinder head, however, the recess shall not exceed 0.060 in.

X3.3.3.7 *Face of Nozzle Hole in Head*—Check that surface against which the nozzle seats is flat and not excessively corroded.

X3.3.3.8 *Valve Rotators*—Inspect the races which should rotate freely so that, when the engine is operating, the valve will rotate at approximately 1 to 2 rpm.

X3.3.3.9 Reassemble valves, felt lubrication washers, springs, spacers and rotators. Install valve springs with closely wound coils next to the cylinder head.

X3.3.4 *Cylinder:*

X3.3.4.1 Check the cylinder bore diameter at the top, middle, and bottom areas of ring travel in two planes which are 90° apart. Replace the cylinder if the internal diameter at the area of maximum wear is more than 0.006 in. larger than the unworn skirt internal diameter. Replace the cylinder if the bore is out of round in excess of 0.0025 in.

X3.3.4.2 Cylinders rebored to 0.010, 0.020, and 0.030 in. larger than the original 3.250 in. diameter are permitted and the same wear limits apply based on the unworn skirt diameter of the rebore.

X3.3.5 *Piston and Rings:*

X3.3.5.1 Replace the piston if there is evidence of scoring or a wear pattern.

X3.3.5.2 Replacement of all rings at the time of every overhaul is typical. If a chrome plated top compression ring is used, it may be reused for several overhaul periods.

X3.3.5.3 The ring gaps should be checked by feeler gauge with the ring inserted in the skirt end of the cylinder. The piston should be used to square the ring in the bore about 1 in. beyond the chamfer. Rings should be rejected if the gap is not within 0.007 to 0.030 in. for compression rings and 0.010 to 0.030 in. for oil rings.

X3.3.5.4 After assembly of the rings on the piston, the ring to land clearances, as measured using a feeler gage, should not exceed 0.004 in. for top compression ring or 0.0035 in. for all other rings.

X3.3.5.5 Piston pin replacement should be made when scoring or wear marks are observed.

X3.3.6 *Handwheel Assembly*—The handwheel assembly is an integral part of the cylinder head assembly and includes a variable compression plug that is a close fit in the precombustion chamber bore. It is screwed in and out of the head by the handwheel to effect changes in compression ratio. To prevent leakage of combustion gases, this plug, which has no seals or rings, is expanded by action of the locking wheel which is connected to a drawbolt that exerts pressure on a dished and split washer inserted in the plug causing it to expand and clamp the plug in the bore. The variable compression plug mechanism should be kept free-working, and easily adjusted. The locking wheel should be easily released and locked by hand without the use of an auxiliary wrench.

X3.3.6.1 Detailed instructions, available from the manufacturer, include specific inspection criteria, proper parts selection, as well as the proper order of reassembly and lubrication instructions.

X3.3.7 *Rocker-Arm Assembly:*

X3.3.7.1 Inspect each rocker for excessive bearing wear or wobble on the rocker shaft.

X3.3.7.2 Inspect the rocker adjusting screws for galled ball ends and also for damaged Phillips screwdriver slots.

X3.3.7.3 Inspect the rocker ball sockets for wear or galling.

X3.3.7.4 Replace any worn or out of specification parts.

NOTE X3.2—When installing the rocker arm shaft, the pipe plug end should face the intake side and the center feed hole should point downward to receive oil. The exhaust rocker bushing must have a hole to permit pressurized oil to reach the distribution channel on the top rocker surface.

X3.3.8 *Condenser and Cooling System:*

X3.3.8.1 Inspect the inner surfaces of the condenser and the baffle tube for rust or scale deposits, wipe out the cavity, and rinse with hot water prior to reassembly.

X3.3.8.2 Inspect the cooling coil, clean surface deposits, and observe that the coils are slightly separated from each other to maximize the cooling surface exposed to coolant steam.

X3.3.8.3 Chemical cleaning of coolant system surfaces should take place whenever significant deposits are observed or at least at every third top overhaul. One approach is to introduce a commercial cooling system cleaner in the cooling system after reassembly of the engine. By running the engine

for intermittent periods, the solution can be heated to 80 to 90°C (180 to 200°F). The solution should be kept at this temperature for approximately 30 min and drained. The system should then be flushed with clean hot water before recharging with rust inhibited coolant water. (**Warning**—Chemical cleaning solutions are poisonous and may be harmful or fatal if inhaled or swallowed. See [Annex A1](#).)

X3.3.9 Reassembly Procedures:

X3.3.9.1 Install the piston, piston pin and pin retainers on the connecting rod. Lubricate the rings with SAE 30 engine crankcase oil.

X3.3.9.2 Place a selection of cylinder base gaskets on the crankcase surface. Cylinder base gaskets of several thicknesses are available and the number and thicknesses must be selected by trial and error to obtain the proper piston overtravel of 0.014 to 0.016 in.

X3.3.9.3 Rigidly support the piston above the crankcase surface. Install the cylinder over the piston so that it is seated on the cylinder base gaskets. Care should be taken not to break any of the rings as they enter the chamfered bore. (Use of a ring compressor tool over the piston rings is advisable despite the cylinder chamfer). Manually rotate the crankshaft through several revolutions so that the cylinder is centered. Tighten and torque the cylinder stud nuts to 75 lbf-ft.

X3.3.9.4 Manually rotate the crankshaft so that the piston is at top-dead-center as indicated by the flywheel pointer.

X3.3.9.5 Place a true piece of metal flat stock on the piston so that it projects over the top cylinder surface. Using a feeler gage, measure the piston overtravel or separation of the flat stock above the cylinder surface. Make the same measurement in two directions, parallel to and at 90° to the crankshaft center line. The overtravel should be 0.014 to 0.016 in. or the cylinder must be removed and the number and thickness of the cylinder base gaskets changed to bring the overtravel within specification.

X3.3.9.6 Place the cylinder head gasket on the cylinder surface.

NOTE X3.3—Current cylinder head gaskets have a special non-stick/sealer coating and do not require additional sealer/lubricant.

X3.3.9.7 Install the cylinder head.

X3.3.9.8 Install the marked push rods, and manually rotate the crankshaft so that both rods are at their lowest point of travel (flywheel at top-dead-center, compression stroke).

X3.3.9.9 Install the rocker-arm assembly with the half-balls properly inserted.

X3.3.9.10 Install, tighten and torque the head nuts to 75 lbf-ft.

X3.3.9.11 Set the valve clearances to 0.004 in. for the intake valve and 0.014 in. for the exhaust valve.

X3.3.9.12 Install the handwheel assembly.

X3.3.9.13 Reassemble the condenser, the intake air elbow and silencer, the exhaust pipe, the cooling water lines to the condenser and injector cooling passage.

X3.3.9.14 Introduce coolant water through the condenser cover fill hole until coolant just appears in the condenser sight glass.

X3.3.9.15 Install a cleaned and inspected injector assembly using a new solid copper gasket. Install the associated fuel lines.

X3.3.9.16 Install the injector pickup and set the pickup gap to 0.040 in. using a nonmagnetic feeler gage.

X3.3.9.17 Turn on the main cooling water and establish flow through the injector cooling passage. Observe the face of the injector nozzle through the pickup hole to be certain the injector assembly is tightened evenly and coolant is not leaking past the nozzle into the precombustion chamber.

X3.3.9.18 Index the handwheel assembly.

X3.3.10 Crankcase Breather:

X3.3.10.1 Disconnect the breather pipe and remove the breather assembly from the engine crankcase.

X3.3.10.2 Unscrew the cap from the body, remove the plastic cup, and clean the emulsion deposits from all of the pieces.

X3.3.10.3 Inspect the cup and if the surface of the open edge is rounded rather than square, replace the cup.

X3.3.10.4 Rinse the components using a petroleum based solvent or kerosine and reassemble them on the engine. (**Warning**—Petroleum Based Solvent—Flammable. Vapors harmful if inhaled. Vapors may cause flash fire. See [Appendix X1](#).) (**Warning**—Kerosine—Combustible. Vapor harmful. See [Annex A1](#).)

X3.3.11 Crankcase Oil Change:

X3.3.11.1 Drain the used oil and add new SAE 30 Grade engine crankcase lubricating oil.

X3.3.11.2 It is recommended that the crankcase lubricating oil be changed at intervals of approximately 50 h of engine operation and at the time of each top overhaul.

X3.3.11.3 It is recommended that the oil filter cartridge be changed at the time of every other oil change.

X3.3.12 Fuel Injection Pump:

X3.3.12.1 Drain the used oil and add new SAE 30 Grade engine crankcase lubricating oil.

X3.3.12.2 The fuel pump assembly seldom needs maintenance or basic adjustment other than attention to regular and proper lubrication. If any disassembly is attempted in the field, it should be performed by a qualified fuel injection equipment specialist.

X3.3.12.3 If diesel fuel oils having high sulfur content are being tested on a fairly regular basis, inspection of the fuel pump delivery valve holder and delivery valve is recommended at approximately 500 h periods of operation. Typically this inspection could be part of a top overhaul. If pitting or corrosion of these components is observed, the parts should be replaced.

X3.3.13 *Engine Starting Preparations*—See [Appendix X2](#).

X3.4 Injector Assembly Inspection:

X3.4.1 Disassembly.

X3.4.1.1 With the engine shut down, close the coolant water valves (supply and return) to the injector cooling passage, and drain the coolant from the injector cooling passage.

X3.4.1.2 Disconnect the fuel lines at the injector assembly.

X3.4.1.3 Remove the injector pickup and associated bracket.

X3.4.1.4 Remove the injector assembly.

X3.4.2 *Nozzle Cleaning*—(**Warning**—Injector nozzles are precision devices which have finely finished fits and meticulously polished surfaces. Scrupulous cleanliness must be observed to prevent dirt or moisture from causing damage. As parts are removed, they should be placed in a clean container and submerged in diesel fuel oil or kerosine. Do not touch the critical lapped surfaces with bare fingers because body acids can cause undesirable etching.)

X3.4.2.1 Clamp the injector assembly in a vise so that the nozzle cap nut can be loosened and removed. Separate the nozzle from the cap nut.

X3.4.2.2 Clean the carbon from the nozzle, pintle and cap nut by immersion in a suitable cleaner for as long as necessary. Placing the parts container of cleaner solution in an ultrasonic bath hastens the cleaning process.

X3.4.2.3 Reassemble the nozzle components on the injector assembly and tighten the nozzle cap nut to a torque of 50 lbf-ft.

X3.4.2.4 Check the injector nozzle opening pressure and spray pattern.

X3.4.2.5 Reinstall the injector assembly with injector pickup on the engine and check for cooling water leakage past the nozzle into the precombustion chamber.

X3.4.2.6 Before installing the combustion pickup, motor the engine for a short time to blow out any water which may have entered the combustion chamber during the maintenance process. Restricting the pickup hole by pressing a cloth (not paper) wiper against the opening will aid in removing any entrained water.

X3.5 *Crankcase/Unit Inspection:*

X3.5.1 *Crankcase*—Inspect the crankcase annually as follows.

X3.5.1.1 Turn off the electrical power circuits to the engine and unit.

X3.5.1.2 Drain the crankcase lubricating oil and clean the crankcase sump using a petroleum based solvent.

X3.5.1.3 Disassemble the oil suction screen assembly and clean the components.

X3.5.1.4 Disassemble the crankcase breather body from the crankcase side door and clean the internal passage and baffles.

X3.5.1.5 Disassemble the connecting rod from the crankshaft. Inspect the big end bearing shells and replace if wear is indicated. Reassemble the connecting rod and torque the bearing cap bolts to 104 lbf-ft.

X3.5.1.6 Disassemble the valve lifters from the top of the crankcase, clean, inspect and, if necessary, replace worn assembly components.

X3.5.1.7 Approximate the rear main bearing clearance by dial indicator measurement of the movement of the crankcase edge of the flywheel outer surface. Measure with the flywheel at rest and then with the flywheel lifted using an appropriate lever, if the difference in the measurements exceeds 0.006 in., crankcase rebuilding is recommended.

X3.5.1.8 Disassemble the oil pressure control valve assembly, solvent clean, inspect for worn components and replace as required. (**Warning**—In addition to other precautions, avoid over tightening the four relief valve body fastening bolts to prevent valve body distortion and restriction of the plunger movement.)

X3.5.1.9 Inspect the outer crankcase surfaces for indications of oil seal leakage which may require extensive maintenance or crankcase rebuilding.

X3.5.2 *Power Absorption Motor*—Inspect the power absorption motor annually as follows:

X3.5.2.1 Turn off all the electrical power circuits to the engine and unit.

X3.5.2.2 Check the condition and tension of the drive belts. Replace belts as required and adjust the motor position to achieve proper belt tension.

X3.5.2.3 Inspect the motor bearing housings for evidence of wear or loss of lubricant. Flush lubricate the bearings if the unit is equipped with field lubrication fittings.

X3.5.2.4 Remove dust and dirt from the motor end bell openings using low pressure compressed air.

X3.5.3 *Safety Cutoff Checks:*

X3.5.3.1 *High Coolant Temperature Switch*—After shutting off the cooling water to the condenser coil, the engine should stop within one minute. Check and adjust the thermal switch set point as required.

X3.5.3.2 *Low Oil Pressure Switch*—When starting the engine, release of the momentary start switch before the oil pressure reaches approximately 20 psi (138 kPa), should result in unit shut down.

X3.5.3.3 *Electrical Interlock*—Disconnecting either the single phase or the three phase power at the appropriate supply switch should cause unit shut down.

X3.5.3.4 *Fuel Pump Safety Solenoid*—Disconnecting the single phase power should cause release of the fuel pump safety solenoid, closing of the fuel pump rack with the result that combustion ceases.

X3.6 *Engine Torque Tightening Recommendations*—Recommended torque values are given in **Table X3.1**.

TABLE X3.1 Recommended Torque Values

Item	Torque, lbf-ft	Torque, N-m
Cylinder head stud nuts	75	101.7
Cylinder stud nuts	75	101.7
Crankshaft balancing weight bolts	100	135.6
Balancing shaft weight bolts	100	135.6
Balancing shaft weight bolt locknuts	75	101.7
Connecting rod big end bolts	104	141.0
Combustion pickup	30	40.7
Injector Cap Nut	50	67.8

SUMMARY OF CHANGES

Subcommittee D02.01 has identified the location of selected changes to this standard since the last issue (D 613–03b) that may impact the use of this standard.

(1) Added **Note 1**.

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Designation: D 445 – 06

An American National Standard
British Standard 2000: Part 71:1990



Designation: 71/1/97

Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)¹

This standard is issued under the fixed designation D 445; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope*

1.1 This test method specifies a procedure for the determination of the kinematic viscosity, ν , of liquid petroleum products, both transparent and opaque, by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. The dynamic viscosity, η , can be obtained by multiplying the kinematic viscosity, ν , by the density, ρ , of the liquid.

NOTE 1—For the measurement of the kinematic viscosity and viscosity of bitumens, see also Test Methods D 2170 and D 2171.

NOTE 2—ISO 3104 corresponds to Test Method D 445.

1.2 The result obtained from this test method is dependent upon the behavior of the sample and is intended for application to liquids for which primarily the shear stress and shear rates are proportional (Newtonian flow behavior). If, however, the viscosity varies significantly with the rate of shear, different results may be obtained from viscometers of different capillary diameters. The procedure and precision values for residual fuel oils, which under some conditions exhibit non-Newtonian behavior, have been included.

1.3 The range of kinematic viscosities covered by this test method is from 0.2 to 300 000 mm²/s (see Table A1.1) at all temperatures (see 6.3 and 6.4). The precision has only been determined for those materials, kinematic viscosity ranges and temperatures as shown in the footnotes to the precision section.

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

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appro-*

priate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 ASTM Standards:²

- D 446 Specifications and Operating Instructions for Glass Capillary Kinematic Viscometers
- D 1193 Specification for Reagent Water
- D 1217 Test Method for Density and Relative Density (Specific Gravity) of Liquids by Bingham Pycnometer
- D 1480 Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Bingham Pycnometer
- D 1481 Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Lipkin Bicapillary Pycnometer
- D 2162 Practice for Basic Calibration of Master Viscometers and Viscosity Oil Standards
- D 2170 Test Method for Kinematic Viscosity of Asphalts (Bitumens)
- D 2171 Test Method for Viscosity of Asphalts by Vacuum Capillary Viscometer
- D 6071 Test Method for Low Level Sodium in High Purity Water by Graphite Furnace Atomic Absorption Spectroscopy
- D 6074 Guide for Characterizing Hydrocarbon Lubricant Base Oils
- D 6617 Practice for Laboratory Bias Detection Using Single Test Result from Standard Material
- E 1 Specification for ASTM Liquid-in-Glass Thermometers
- E 77 Test Method for Inspection and Verification of Thermometers

2.2 ISO Standards:³

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.07 on Flow Properties.

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In the IP, this test method is under the jurisdiction of the Standardization Committee.

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

³ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

*A Summary of Changes section appears at the end of this standard.

ISO 3104 Petroleum Products—Transparent and Opaque Liquids—Determination of Kinematic Viscosity and Calculation of Dynamic Viscosity

ISO 3105 Glass Capillary Kinematic Viscometers—Specification and Operating Instructions

ISO 3696 Water for Analytical Laboratory Use—Specification and Test Methods

ISO 5725 Accuracy (trueness and precision) of measurement methods and results.

ISO 9000 Quality Management and Quality Assurance Standards—Guidelines for Selection and Use

ISO 17025 General Requirements for the Competence of Testing and Calibration Laboratories

2.3 *NIST Standards*:⁴

NIST Technical Note 1297, Guideline for Evaluating and Expressing the Uncertainty of NIST Measurement Results

NIST GMP 11

NIST Special Publication 819

3. Terminology

3.1 *Definitions of Terms Specific to This Standard*:

3.1.1 *automated viscometer, n*—apparatus which, in part or in whole, has mechanized one or more of the procedural steps indicated in Section 11 or 12 without changing the principle or technique of the basic manual apparatus. The essential elements of the apparatus in respect to dimensions, design, and operational characteristics are the same as those of the manual method.

3.1.1.1 *Discussion*—Automated viscometers have the capability to mimic some operation of the test method while reducing or removing the need for manual intervention or interpretation. Apparatus which determine kinematic viscosity by physical techniques that are different than those used in this test method are not considered to be Automated Viscometers.

3.1.2 *density, n*—the mass per unit volume of a substance at a given temperature.

3.1.3 *dynamic viscosity, n*—the ratio between the applied shear stress and rate of shear of a liquid.

3.1.3.1 *Discussion*—It is sometimes called the coefficient of dynamic viscosity or, simply, viscosity. Thus dynamic viscosity is a measure of the resistance to flow or deformation of a liquid.

3.1.3.2 *Discussion*—The term dynamic viscosity can also be used in a different context to denote a frequency-dependent quantity in which shear stress and shear rate have a sinusoidal time dependence.

3.1.4 *kinematic viscosity, n*—the resistance to flow of a fluid under gravity.

3.1.4.1 *Discussion*—For gravity flow under a given hydrostatic head, the pressure head of a liquid is proportional to its density, ρ . For any particular viscometer, the time of flow of a fixed volume of fluid is directly proportional to its kinematic viscosity, ν , where $\nu = \eta/\rho$, and η is the dynamic viscosity coefficient.

4. Summary of Test Method

4.1 The time is measured for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled and known temperature. The kinematic viscosity (determined value) is the product of the measured flow time and the calibration constant of the viscometer. Two such determinations are needed from which to calculate a kinematic viscosity result that is the average of two acceptable determined values.

5. Significance and Use

5.1 Many petroleum products, and some non-petroleum materials, are used as lubricants, and the correct operation of the equipment depends upon the appropriate viscosity of the liquid being used. In addition, the viscosity of many petroleum fuels is important for the estimation of optimum storage, handling, and operational conditions. Thus, the accurate determination of viscosity is essential to many product specifications.

6. Apparatus

6.1 *Viscometers*—Use only calibrated viscometers of the glass capillary type, capable of being used to determine kinematic viscosity within the limits of the precision given in the precision section.

6.1.1 Viscometers listed in **Table A1.1**, whose specifications meet those given in Specifications **D 446** and in **ISO 3105** meet these requirements. It is not intended to restrict this test method to the use of only those viscometers listed in **Table A1.1**. **Annex A1** gives further guidance.

6.1.2 *Automated Viscometers*—Automated apparatus may be used as long as they mimic the physical conditions, operations or processes of the manual apparatus. Any viscometer, temperature measuring device, temperature control, temperature controlled bath or timing device incorporated in the automated apparatus shall conform to the specification for these components as stated in Section 6 of this test method. Flow times of less than 200 s are permitted, however, a kinetic energy correction shall be applied in accordance with Section 7 on Kinematic Viscosity Calculation of Specifications **D 446**. The kinetic energy correction shall not exceed 3.0 % of the measured viscosity. The automated apparatus shall be capable of determining kinematic viscosity of a certified viscosity reference standard within the limits stated in **9.2.1** and Section **17**. The precision shall be of statistical equivalence to, or better (has less variability) than the manual apparatus.

NOTE 3—Precision and bias of kinematic viscosity measurements for flow times of less than 200 s has not been determined. The precision stated in Section 17 is not known to be valid for kinematic viscosity measurements with flow times less than 200 s.

6.2 *Viscometer Holders*—Use viscometer holders to enable all viscometers which have the upper meniscus directly above the lower meniscus to be suspended vertically within 1° in all directions. Those viscometers whose upper meniscus is offset from directly above the lower meniscus shall be suspended vertically within 0.3° in all directions (see Specifications **D 446** and **ISO 3105**).

⁴ Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 3460, Gaithersburg, MD 20899-3460.

6.2.1 Viscometers shall be mounted in the constant temperature bath in the same manner as when calibrated and stated on the certificate of calibration. See Specifications D 446, see Operating Instructions in Annexes A1–A3. For those viscometers which have Tube L (see Specifications D 446) held vertical, vertical alignment shall be confirmed by using (1) a holder ensured to hold Tube L vertical, or (2) a bubble level mounted on a rod designed to fit into Tube L, or (3) a plumb line suspended from the center of Tube L, or (4) other internal means of support provided in the constant temperature bath.

6.3 *Temperature-Controlled Bath*—Use a transparent liquid bath of sufficient depth such, that at no time during the measurement of flow time, any portion of the sample in the viscometer is less than 20 mm below the surface of the bath liquid or less than 20 mm above the bottom of the bath.

6.3.1 *Temperature Control*—For each series of flow time measurements, the temperature control of the bath liquid shall be such that within the range from 15 to 100°C, the temperature of the bath medium does not vary by more than $\pm 0.02^\circ\text{C}$ of the selected temperature over the length of the viscometer, or between the position of each viscometer, or at the location of the thermometer. For temperatures outside this range, the deviation from the desired temperature must not exceed $\pm 0.05^\circ\text{C}$.

6.4 *Temperature Measuring Device in the Range from 0 to 100°C*—Use either calibrated liquid-in-glass thermometers (Annex A2) of an accuracy after correction of $\pm 0.02^\circ\text{C}$ or better, or any other thermometric device of equal or better accuracy.

6.4.1 If calibrated liquid-in-glass thermometers are used, the use of two thermometers is recommended. The two thermometers shall agree within 0.04°C .

6.4.2 Outside the range from 0 to 100°C, use either calibrated liquid-in-glass thermometers of an accuracy after correction of $\pm 0.05^\circ\text{C}$ or better, or any other thermometric device of equal or better accuracy. When two temperature measuring devices are used in the same bath, they shall agree within $\pm 0.1^\circ\text{C}$.

6.4.3 When using liquid-in-glass thermometers, such as those in Table A2.1, use a magnifying device to read the thermometer to the nearest $\frac{1}{5}$ division (for example, 0.01°C or 0.02°F) to ensure that the required test temperature and temperature control capabilities are met (see 10.1). It is recommended that thermometer readings (and any corrections supplied on the certificates of calibrations for the thermometers) be recorded on a periodic basis to demonstrate compliance with the test method requirements. This information can be quite useful, especially when investigating issues or causes relating to testing accuracy and precision.

6.5 *Timing Device*—Use any timing device that is capable of taking readings with a discrimination of 0.1 s or better and has an accuracy within $\pm 0.07\%$ (see Annex A3) of the reading when tested over the minimum and maximum intervals of expected flow times.

6.5.1 Electrical timing devices may be used if the current frequency is controlled to an accuracy of 0.05% or better. Alternating currents, as provided by some public power systems, are intermittently rather than continuously controlled.

When used to actuate electrical timing devices, such control can cause large errors in kinematic viscosity flow time measurements.

7. Reagents and Materials

7.1 *Chromic Acid Cleaning Solution*, or a nonchromium-containing, strongly oxidizing acid cleaning solution. (**Warning**—Chromic acid is a health hazard. It is toxic, a recognized carcinogen, highly corrosive, and potentially hazardous in contact with organic materials. If used, wear a full face-shield and full-length protective clothing including suitable gloves. Avoid breathing vapor. Dispose of used chromic acid carefully as it remains hazardous. Nonchromium-containing, strongly oxidizing acid cleaning solutions are also highly corrosive and potentially hazardous in contact with organic materials, but do not contain chromium which has special disposal problems.)

7.2 *Sample Solvent*, completely miscible with the sample. Filter before use.

7.2.1 For most samples a volatile petroleum spirit or naphtha is suitable. For residual fuels, a prewash with an aromatic solvent such as toluene or xylene may be necessary to remove asphaltenic material.

7.3 *Drying Solvent*, a volatile solvent miscible with the sample solvent (see 7.2) and water (see 7.4). Filter before use.

7.3.1 Acetone is suitable. (**Warning**—Extremely flammable.)

7.4 *Water*, deionized or distilled and conforming to Specification D 1193 or Grade 3 of ISO 3696. Filter before use.

8. Certified Viscosity Reference Standards

8.1 Certified viscosity reference standards shall be certified by a laboratory that has been shown to meet the requirements of ISO 17025 by independent assessment. Viscosity standards shall be traceable to master viscometer procedures described in Test Method D 2162.

8.2 The uncertainty of the certified viscosity reference standard shall be stated for each certified value ($k = 2$, 95% confidence). See ISO 5725 or NIST 1297.

9. Calibration and Verification

9.1 *Viscometers*—Use only calibrated viscometers, thermometers, and timers as described in Section 6.

9.2 *Certified Viscosity Reference Standards* (Table A1.2)—These are for use as confirmatory checks on the procedure in the laboratory.

9.2.1 If the determined kinematic viscosity does not agree within the acceptable tolerance band, as calculated from Annex A4, of the certified value, recheck each step in the procedure, including thermometer and viscometer calibration, to locate the source of error. Annex A1 gives details of standards available.

NOTE 4—In previous issues of Test Method D 445, limits of $\pm 0.35\%$ of the certified value have been used. The data to support the limit of $\pm 0.35\%$ cannot be verified. Annex A4 provides instructions on how to determine the tolerance band. The tolerance band combines both the uncertainty of the certified viscosity reference standard as well as the uncertainty of the laboratory using the certified viscosity reference standard.

9.2.1.1 As an alternative to the calculation in [Annex A4](#), the approximate tolerance bands in [Table 1](#) may be used.

9.2.2 The most common sources of error are caused by particles of dust lodged in the capillary bore and temperature measurement errors. It must be appreciated that a correct result obtained on a standard oil does not preclude the possibility of a counterbalancing combination of the possible sources of error.

9.3 The calibration constant, C , is dependent upon the gravitational acceleration at the place of calibration and this must, therefore, be supplied by the standardization laboratory together with the instrument constant. Where the acceleration of gravity, g , differs by more than 0.1 %, correct the calibration constant as follows:

$$C_2 = (g_2/g_1) \times C_1 \quad (1)$$

where the subscripts 1 and 2 indicate, respectively, the standardization laboratory and the testing laboratory.

10. General Procedure for Kinematic Viscosity

10.1 Adjust and maintain the viscometer bath at the required test temperature within the limits given in [6.3.1](#) taking account of the conditions given in [Annex A2](#) and of the corrections supplied on the certificates of calibration for the thermometers.

10.1.1 Thermometers shall be held in an upright position under the same conditions of immersion as when calibrated.

10.1.2 In order to obtain the most reliable temperature measurement, it is recommended that two thermometers with valid calibration certificates be used (see [6.4](#)).

10.1.3 They should be viewed with a lens assembly giving approximately five times magnification and be arranged to eliminate parallax errors.

10.2 Select a clean, dry, calibrated viscometer having a range covering the estimated kinematic viscosity (that is, a wide capillary for a very viscous liquid and a narrower capillary for a more fluid liquid). The flow time for manual viscometers shall not be less than 200 s or the longer time noted in [Specifications D 446](#). Flow times of less than 200 s are permitted for automated viscometers, provided they meet the requirements of [6.1.2](#).

10.2.1 The specific details of operation vary for the different types of viscometers listed in [Table A1.1](#). The operating instructions for the different types of viscometers are given in [Specifications D 446](#).

10.2.2 When the test temperature is below the dew point, fill the viscometer in the normal manner as required in [11.1](#). To ensure that moisture does not condense or freeze on the walls

of the capillary, draw the test portion into the working capillary and timing bulb, place rubber stoppers into the tubes to hold the test portion in place, and insert the viscometer into the bath. After insertion, allow the viscometer to reach bath temperature, and then remove the stoppers. When performing manual viscosity determinations, do not use those viscometers which cannot be removed from the constant temperature bath for charging the sample portion.

10.2.2.1 The use of loosely packed drying tubes affixed to the open ends of the viscometer is permitted, but not required. If used, the drying tubes shall fit the design of the viscometer and not restrict the flow of the sample by pressures created in the instrument.

10.2.3 Viscometers used for silicone fluids, fluorocarbons, and other liquids which are difficult to remove by the use of a cleaning agent, shall be reserved for the exclusive use of those fluids except during their calibration. Subject such viscometers to calibration checks at frequent intervals. The solvent washings from these viscometers shall not be used for the cleaning of other viscometers.

11. Procedure for Transparent Liquids

11.1 Charge the viscometer in the manner dictated by the design of the instrument, this operation being in conformity with that employed when the instrument was calibrated. If the sample is thought or known to contain fibers or solid particles, filter through a 75 μm screen, either prior to or during charging (see [Specifications D 446](#)).

NOTE 5—To minimize the potential of particles passing through the filter from aggregating, it is recommended that the time lapse between filtering and charging be kept to a minimum.

11.1.1 In general, the viscometers used for transparent liquids are of the type listed in [Table A1.1](#), A and B.

11.1.2 With certain products which exhibit *gel-like* behavior, exercise care that flow time measurements are made at sufficiently high temperatures for such materials to flow freely, so that similar kinematic viscosity results are obtained in viscometers of different capillary diameters.

11.1.3 Allow the charged viscometer to remain in the bath long enough to reach the test temperature. Where one bath is used to accommodate several viscometers, never add or withdraw, or clean a viscometer while any other viscometer is in use for measuring a flow time.

11.1.4 Because this time will vary for different instruments, for different temperatures, and for different kinematic viscosities, establish a safe equilibrium time by trial.

11.1.4.1 Thirty minutes should be sufficient except for the highest kinematic viscosities.

11.1.5 Where the design of the viscometer requires it, adjust the volume of the sample to the mark after the sample has reached temperature equilibrium.

11.2 Use suction (if the sample contains no volatile constituents) or pressure to adjust the head level of the test sample to a position in the capillary arm of the instrument about 7 mm above the first timing mark, unless any other value is stated in the operating instructions for the viscometer. With the sample flowing freely, measure, in seconds to within 0.1 s, the time required for the meniscus to pass from the first to the second

TABLE 1 Approximate Tolerance Bands

NOTE—The tolerance bands were determined using [Practice D 6617](#). The calculation is documented in Research Report RR: D02-1498.^A

Viscosity of Reference Material, mm ² /s	Tolerance Band
< 10	±0.30%
10 to 100	±0.32%
100 to 1000	±0.36%
1000 to 10 000	±0.42%
10 000 to 100 000	±0.54%
> 100 000	±0.73%

^ASupporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1498.

timing mark. If this flow time is less than the specified minimum (see 10.2), select a viscometer with a capillary of smaller diameter and repeat the operation.

11.2.1 Repeat the procedure described in 11.2 to make a second measurement of flow time. Record both measurements.

11.2.2 From the two measurements of flow time, calculate two determined values of kinematic viscosity.

11.2.3 If the two determined values of kinematic viscosity calculated from the flow time measurements agree within the stated determinability figure (see 17.1.1) for the product, use the average of these determined values to calculate the kinematic viscosity result to be reported. Record the result. If not, repeat the measurements of flow times after a thorough cleaning and drying of the viscometers and filtering (where required, see 11.1) of the sample until the calculated kinematic viscosity determinations agree with the stated determinability.

11.2.4 If the material or temperature, or both, is not listed in 17.1.1, for temperatures between 15 and 100°C, use as an estimate of the determinability 0.20% and 0.35% for temperatures outside this range.

12. Procedure for Opaque Liquids

12.1 For steam-refined cylinder oils and black lubricating oils, proceed to 12.3 ensuring a thoroughly representative sample is used. The kinematic viscosity of residual fuel oils and similar waxy products can be affected by the previous thermal history and the following procedure described in 12.1.1-12.2.2 shall be followed to minimize this.

12.1.1 In general, the viscometers used for opaque liquids are of the reverse-flow type listed in Table A1.1, C.

12.1.2 Heat in the original container, in an oven, at 60 ± 2°C for 1 h.

12.1.3 Thoroughly stir the sample with a suitable rod of sufficient length to reach the bottom of the container. Continue stirring until there is no sludge or wax adhering to the rod.

12.1.4 Recap the container tightly and shake vigorously for 1 min to complete the mixing.

12.1.4.1 With samples of a very waxy nature or oils of high kinematic viscosity, it may be necessary to increase the heating temperature above 60°C to achieve proper mixing. The sample should be sufficiently fluid for ease of stirring and shaking.

12.2 Immediately after completing 12.1.4, pour sufficient sample to fill two viscometers into a 100-mL glass flask and loosely stopper.

12.2.1 Immerse the flask in a bath of boiling water for 30 min. (**Warning**—Exercise care as vigorous boil-over can occur when opaque liquids which contain high levels of water are heated to high temperatures.)

12.2.2 Remove the flask from the bath, stopper tightly, and shake for 60 s.

12.3 Two determinations of the kinematic viscosity of the test material are required. For those viscometers that require a complete cleaning after each flow time measurement, two viscometers may be used. A single viscometer in which an immediate, repeat flow time measurement can be made without cleaning may also be used for the two measurements of flow time and calculation of kinematic viscosity. Charge two viscometers in the manner dictated by the design of the instrument. For example, for the cross-arm or the BS U-tube

viscometers for opaque liquids, filter the sample through a 75- μ m filter into two viscometers previously placed in the bath. For samples subjected to heat treatment, use a preheated filter to prevent the sample coagulating during the filtration.

12.3.1 Viscometers which are charged before being inserted into the bath may need to be preheated in an oven prior to charging the sample. This is to ensure that the sample will not be cooled below test temperature.

12.3.2 After 10 min, adjust the volume of the sample (where the design of the viscometer requires) to coincide with the filling marks as in the viscometer specifications (see Specifications D 446).

12.3.3 Allow the charged viscometers enough time to reach the test temperature (see 12.3.1). Where one bath is used to accommodate several viscometers, never add or withdraw, or clean a viscometer while any other viscometer is in use for measuring flow time.

12.4 With the sample flowing freely, measure in seconds to within 0.1 s, the time required for the advancing ring of contact to pass from the first timing mark to the second. Record the measurement.

12.4.1 In the case of samples requiring heat treatment described in 12.1 through 12.2.1, complete the measurements of flow time within 1 h of completing 12.2.2. Record the measured flow times.

12.5 Calculate kinematic viscosity, ν , in mm²/s, from each measured flow time. Regard these as two determined values of kinematic viscosity.

12.5.1 For residual fuel oils, if the two determined values of kinematic viscosity agree within the stated determinability figure (see 17.1.1), use the average of these determined values to calculate the kinematic viscosity result to be reported. Record the result. If the calculated kinematic viscosities do not agree, repeat the measurements of flow times after thorough cleaning and drying of the viscometers and filtering of the sample. If the material or temperature, or both, is not listed in 17.1.1, for temperatures between 15 and 100°C use as an estimate of the determinability 1.0 %, and 1.5 % for temperatures outside this range; it must be realized that these materials can be non-Newtonian, and can contain solids which can come out of solution as the flow time is being measured.

13. Cleaning of Viscometer

13.1 Between successive determinations of kinematic viscosity, clean the viscometer thoroughly by several rinsings with the sample solvent, followed by the drying solvent (see 7.3). Dry the tube by passing a slow stream of filtered dry air through the viscometer for 2 min or until the last trace of solvent is removed.

13.2 Periodically clean the viscometer with the cleaning solution (**Warning**—see 7.1), for several hours to remove residual traces of organic deposits, rinse thoroughly with water (7.4) and drying solvent (see 7.3), and dry with filtered dry air or a vacuum line. Remove any inorganic deposits by hydrochloric acid treatment before the use of cleaning acid, particularly if the presence of barium salts is suspected. (**Warning**—It is essential that alkaline cleaning solutions are not used as changes in the viscometer calibration can occur.)

14. Calculation

14.1 Calculate each of the determined kinematic viscosity values, ν_1 and ν_2 , from the measured flow times, t_1 and t_2 , and the viscometer constant, C , by means of the following equation:

$$\nu_{1,2} = C \cdot t_{1,2} \quad (2)$$

where:

$\nu_{1,2}$ = determined kinematic viscosity values for ν_1 and ν_2 , respectively, mm^2/s ,

C = calibration constant of the viscometer, mm^2/s^2 , and

$t_{1,2}$ = measured flow times for t_1 and t_2 , respectively, s.

Calculate the kinematic viscosity result, ν , as an average of ν_1 and ν_2 (see 11.2.3 and 12.5.1).

14.2 Calculate the dynamic viscosity, η , from the calculated kinematic viscosity, ν , and the density, ρ , by means of the following equation:

$$\eta = \nu \times \rho \times 10^{-3} \quad (3)$$

where:

η = dynamic viscosity, $\text{mPa}\cdot\text{s}$,

ρ = density, kg/m^3 , at the same temperature used for the determination of the kinematic viscosity, and

ν = kinematic viscosity, mm^2/s .

14.2.1 The density of the sample can be determined at the test temperature of the kinematic viscosity determination by an appropriate method such as Test Methods D 1217, D 1480, or D 1481.

15. Expression of Results

15.1 Report the test results for the kinematic or dynamic viscosity, or both, to four significant figures, together with the test temperature.

16. Report

16.1 Report the following information:

16.1.1 Type and identification of the product tested,

16.1.2 Reference to this test method or a corresponding international standard,

16.1.3 Result of the test (see Section 15),

16.1.4 Any deviation, by agreement or otherwise, from the procedure specified,

16.1.5 Date of the test, and

16.1.6 Name and address of the test laboratory.

17. Precision

17.1 *Comparison of Determined Values:*

17.1.1 *Determinability (d)*—The difference between successive determined values obtained by the same operator in the same laboratory using the same apparatus for a series of operations leading to a single result, would in the long run, in the normal and correct operation of this test method, exceed the values indicated only in one case in twenty:

Base oils at 40 and 100°C ⁵	0.0020 y	(0.20 %)
Formulated oils at 40 and 100°C ⁶	0.0013 y	(0.13 %)
Formulated oils at 150°C ⁷	0.015 y	(1.5 %)
Petroleum wax at 100°C ⁸	0.0080 y	(0.80 %)
Residual fuel oils at 80 and 100°C ⁹	0.011 (y + 8)	
Residual fuel oils at 50°C ⁹	0.017 y	(1.7 %)
Additives at 100°C ¹⁰	0.00106 y ^{1.1}	

Gas oils at 40°C ¹¹	0.0013 (y+1)	
Jet fuels at -20°C ¹²	0.0018 y	(0.18 %)

where: y is the average of determined values being compared.

17.2 *Comparison of Results:*

17.2.1 *Repeatability (r)*—The difference between successive results obtained by the same operator in the same laboratory with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of this test method, exceed the values indicated only in one case in twenty:

Base oils at 40 and 100°C ⁵	0.0011 x	(0.11 %)
Formulated oils at 40 and 100°C ⁶	0.0026 x	(0.26 %)
Formulated oils at 150°C ⁷	0.0056 x	(0.56 %)
Petroleum wax at 100°C ⁸	0.0141 x ^{1.2}	
Residual fuel oils at 80 and 100°C ⁹	0.013 (x + 8)	
Residual oils at 50°C ⁹	0.015 x	(1.5 %)
Additives at 100°C ¹⁰	0.00192 x ^{1.1}	
Gas oils at 40°C ¹¹	0.0043 (x+1)	
Jet fuels at -20°C ¹²	0.007 x	(0.7 %)

where: x is the average of results being compared.

17.2.2 *Reproducibility (R)*—The difference between two single and independent results obtained by different operators working in different laboratories on nominally identical test material would, in the long run, in the normal and correct operation of this test method, exceed the values indicated below only in one case in twenty.

⁵ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Reports RR:D02-1331 and RR:D02-1132. These precision values were obtained by statistical examination of interlaboratory results from six mineral oils (base oils without additive package) in the range from 8 to 1005 mm^2/s at 40°C and from 2 to 43 mm^2/s at 100°C, and were first published in 1989. Request See Guide D 6074.

⁶ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1332. These precision values were obtained by statistical examination of interlaboratory results from seven fully formulated engine oils in the range from 36 to 340 mm^2/s at 40°C and from 6 to 25 mm^2/s at 100°C, and were first published in 1991. See Guide D 6071.

⁷ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1333. These precision values were obtained by statistical examination of interlaboratory results for eight fully formulated engine oils in the range from 7 to 19 mm^2/s at 150°C, and first published in 1991. See Guide D 6074.

⁸ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1334. These precision values were obtained by statistical examination of interlaboratory results from five petroleum waxes in the range from 3 to 16 mm^2/s at 100°C, and were first published in 1988.

⁹ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1198. These precision values were obtained by statistical examination of interlaboratory results from fourteen residual fuel oils in the range from 30 to 1300 mm^2/s at 50°C and from 5 to 170 mm^2/s at 80 and 100°C, and were first published in 1984.

¹⁰ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1421. These precision values were obtained by statistical examination of interlaboratory results from eight additives in the range from 145 to 1500 mm^2/s at 100°C and were first available in 1997.

¹¹ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1422. These precision values were obtained by statistical examination of interlaboratory results from eight gas oils in the range from 1 to 13 mm^2/s at 40°C and were first available in 1997.

¹² Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1420. These precision values were obtained by statistical examination of interlaboratory results from nine jet fuels in the range from 4.3 to 5.6 mm^2/s at -20°C and were first available in 1997.

Base oils at 40 and 100°C ⁵	0.0065 x	(0.65 %)
Formulated oils at 40 and 100°C ⁶	0.0076 x	(0.76 %)
Formulated oils at 150°C ⁷	0.018 x	(1.8 %)
Petroleum wax at 100°C ⁸	0.0366 x ^{1,2}	
Residual fuel oils at 80 and 100°C ⁹	0.04 (x + 8)	
Residual oils at 50°C ⁹	0.074 x	(7.4 %)
Additives at 100°C ¹⁰	0.00862 x ^{1,-1}	
Gas oils at 40°C ¹¹	0.0082 (x+1)	
Jet fuels at -20°C ¹²	0.019 x	(1.9 %)

where: x is the average of results being compared.

17.3 The precision for used oils has not been determined but is expected to be poorer than that for formulated oils. Because of the extreme variability of such used oils, it is not anticipated that the precision of used oils will be determined.

17.4 The precision for specific automated viscometers has not been determined. However, an analysis has been made of a

large data set including both automated and manual viscometers over the temperature range of 40 to 100°C. The reproducibility of automated viscometer data is not statistically significantly different than the reproducibility of manual viscometer data. It is also shown that there is no bias of the automated data in comparison to the manual data.¹³

18. Keywords

18.1 dynamic viscosity; kinematic viscosity; viscometer; viscosity

¹³ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1498.

ANNEXES

(Mandatory Information)

A1. VISCOMETER TYPES AND CERTIFIED VISCOSITY REFERENCE STANDARDS

A1.1 Viscometer Types

A1.1.1 **Table A1.1** lists capillary viscometers commonly in use for viscosity determinations on petroleum products. For specifications, operating instructions, and calibration, refer to specifications in Specifications **D 446**.

A1.1.2 **Table A1.2** lists certified viscosity reference standards.

TABLE A1.1 Viscometer Types

Viscometer Identification	Kinematic Viscosity Range, ^A mm ² /s
A. Ostwald Types for Transparent Liquids	
Cannon-Fenske routine ^B	0.5 to 20 000
Zeitfuchs	0.6 to 3 000
BS/U-tube ^B	0.9 to 10 000
BS/U/M miniature	0.2 to 100
SIL ^B	0.6 to 10 000
Cannon-Manning semi-micro	0.4 to 20 000
Pinkevitch ^B	0.6 to 17 000
B. Suspended-level Types for Transparent Liquids	
BS/IP/SL ^B	3.5 to 100 000
BS/IP/SL(S) ^B	1.05 to 10 000
BS/IP/MSL	0.6 to 3 000
Ubbelohde ^B	0.3 to 100 000
FitzSimons	0.6 to 1 200
Atlantic ^B	0.75 to 5 000
Cannon-Ubbelohde(A), Cannon Ubbelohde dilution ^B (B)	0.5 to 100 000
Cannon-Ubbelohde semi-micro	0.4 to 20 000
C. Reverse-flow Types for Transparent and Opaque Liquids	
Cannon-Fenske opaque	0.4 to 20 000
Zeitfuchs cross-arm	0.6 to 100 000
BS/IP/RF U-tube reverse-flow	0.6 to 300 000
Lantz-Zeitfuchs type reverse-flow	60 to 100 000

^A Each range quoted requires a series of viscometers. To avoid the necessity of making a kinetic energy correction, these viscometers are designed for a flow time in excess of 200 s except where noted in Specifications **D 446**.

^B In each of these series, the minimum flow time for the viscometers with lowest constants exceeds 200 s.

TABLE A1.2 Certified Viscosity Reference Standards

Designation	Approximate Kinematic Viscosity, mm ² /s					
	20°C	25°C	40°C	50°C	80 °C	100°C
S3	4.6	4.0	2.9	1.2
S6	11	8.9	5.7	1.8
S20	44	34	18	3.9
S60	170	120	54	7.2
S200	640	450	180	17
S600	2400	1600	520	280	67	32
S2000	8700	5600	1700	75
S8000	37 000	23 000	6700
S30 000	...	81 000	23 000	11 000

A2. KINEMATIC VISCOSITY TEST THERMOMETERS

A2.1 Short-Range Specialized Thermometer

A2.1.1 Use a short-range specialized thermometer conforming to the generic specification given in [Table A2.1](#) and [Table A2.2](#) and to one of the designs shown in [Fig. A2.1](#).

A2.1.2 The difference in the designs rests mainly in the position of the ice point scale. In Design A, the ice point is within the scale range, in Design B, the ice point is below the scale range, and in Design C, the ice point is above the scale range.

A2.2 Calibration

A2.2.1 Use liquid-in-glass thermometers with an accuracy after correction of 0.02°C or better, calibrated by a laboratory meeting the requirements of [ISO 9000](#) or [ISO 17025](#), and carrying certificates confirming that the calibration is traceable to a national standard. As an alternative, use thermometric devices such as platinum resistance thermometers, of equal or better accuracy, with the same certification requirements.

A2.2.2 The scale correction of liquid-in-glass thermometers can change during storage and use, and therefore regular re-calibration is required. This is most conveniently achieved in a working laboratory by means of a re-calibration of the ice point, and all of the main scale corrections altered for the change seen in the ice point.

TABLE A2.1 General Specification for Thermometers

NOTE—[Table A2.2](#) gives a range of ASTM, IP, and ASTM/IP thermometers that comply with the specification in [Table A2.1](#), together with their designated test temperatures. See Specification [E 1](#) and Test Method [E 77](#).

Immersion		Total
Scale marks:		
Subdivisions	°C	0.05
Long lines at each	°C	0.1 and 0.5
Numbers at each	°C	1
Maximum line width	mm	0.10
Scale error at test temperature, max	°C	0.1
Expansion chamber:		
Permit heating to	°C	105 up to 90, 120 between 90 and 95 130 between 95 and 105, 170 above 105
Total length	mm	300 to 310
Stem outside diameter	mm	6.0 to 8.0
Bulb length	mm	45 to 55
Bulb outside diameter	mm	no greater than stem
Length of scale range	mm	40 to 90

TABLE A2.2 Complying Thermometers

Thermometer No.	Test Temperature		Thermometer No.	Test Temperature	
	°C	°F		°C	°F
	ASTM 132C, IP 102C	150			ASTM 128C, F/IP 33C
ASTM 110C, F/IP 93C	135	275	ASTM 72C, F/IP 67C	-17.8	0
ASTM 121C/IP 32C	98.9,	210,	ASTM 127C/IP 99C	-20	-4
	100	212	ASTM 126C, F/IP 71C	-26.1	-20
ASTM 129C, F/IP 36C	93.3	200	ASTM 73C, F/IP 68C	-40	-40
ASTM 48C, F/IP 90C	82.2	180	ASTM 74C, F/IP 69C	-53.9	-65
IP 100C	80				
ASTM 47C, F/IP 35C	60	140			
ASTM 29C, F/IP 34C	54.4	130			
ASTM 46C F/IP 66C	50	122			
ASTM 120C/IP 92C	40				
ASTM 28C, F/IP 31C	37.8	100			
ASTM 118C, F	30	86			
ASTM 45C, F/IP 30C	25	77			
ASTM 44C, F/IP 29C	20	68			

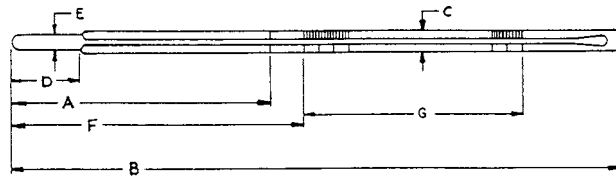
A2.2.2.1 The interval for ice-point recalibration shall be no longer than six months (see [NIST GMP 11](#)). For new thermometers, monthly checking for the first six months is recommended. A change of one or more scale divisions in the ice point means that the thermometer may have been overheated or damaged, and it may be out of calibration. Such thermometers shall be removed from service until inspected, or recalibrated, or both. A complete recalibration of the thermometer, while permitted, is not necessary in order to meet the accuracy ascribed to this design thermometer (see [NIST Special Publication 819](#)). Any change in ice-point correction shall be added to the other corrections of the original Report of Calibration.

A2.2.2.2 Other thermometric devices, if used, will also require periodic recalibration. Keep records of all recalibration.

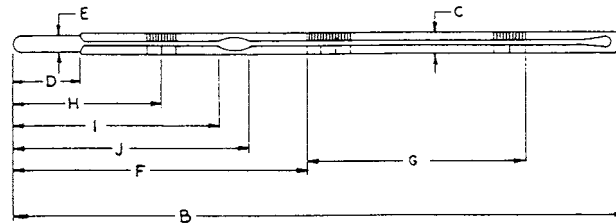
A2.2.3 *Procedure for Ice-point Recalibration of Liquid-in-glass Thermometers.*

A2.2.3.1 Unless otherwise listed on the certificate of calibration, the recalibration of calibrated kinematic viscosity thermometers requires that the ice-point reading shall be taken within 60 min after being at test temperature for not less than 3 min.

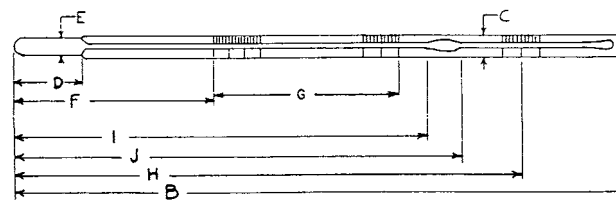
A2.2.3.2 Select clear pieces of ice, preferably made from distilled or pure water. Discard any cloudy or unsound portions. Rinse the ice with distilled water and shave or crush into small pieces, avoiding direct contact with the hands or any chemically unclean objects. Fill the Dewar vessel with the



(a)



(b)



(c)

FIG. A2.1 Thermometer Designs

crushed ice and add sufficient water to form a slush, but not enough to float the ice. As the ice melts, drain off some of the water and add more crushed ice. Insert the thermometer, and pack the ice gently about the stem, to a depth approximately one scale division below the 0°C graduation.

A2.2.3.3 After at least 3 min have elapsed, tap the thermometer gently and repeatedly at right angles to its axis while making observations. Successive readings taken at least 1 min apart shall agree within 0.005°C.

A2.2.3.4 Record the ice-point readings and determine the thermometer correction at this temperature from the mean reading. If the correction is found to be higher or lower than that corresponding to a previous calibration, change the correction at all other temperatures by the same value.

A2.2.3.5 During the procedure, apply the following conditions:

(1) The thermometer shall be supported vertically.

(2) View the thermometer with an optical aid that gives a magnification of approximately five and also eliminates parallax.

(3) Express the ice-point reading to the nearest 0.005°C.

A2.2.4 When in use, immerse the thermometric device to the same depth as when it was fully calibrated. For example, if a liquid-in-glass thermometer was calibrated at the normal total immersion condition, it shall be immersed to the top of the mercury column with the remainder of the stem and the expansion volume at the uppermost end exposed to room temperature and pressure. In practice, this means that the top of the mercury column shall be within a length equivalent to four scale divisions of the surface of the medium whose temperature is being measured.

A2.2.4.1 If this condition cannot be met, then an extra correction may be necessary.

A3. TIMER ACCURACY

A3.1 Regularly check timers for accuracy and maintain records of such checks.

WWVH	Kauai, HI	2.5, 5, 10, 15, MHz
CHU	Ottawa, Canada	3.33, 7.335, 14.67 MHz

A3.1.1 Time signals as broadcast by the National Institute of Standards and Technology are a convenient and primary standard reference for calibrating timing devices. The following can be used to an accuracy of 0.1 s:

A3.1.2 Radio broadcast of voice and audio on a telephone line at phone 303-499-7111. Additional time services are available from the National Institute of Standards and Technology.

WWV	Fort Collins, CO	2.5, 5, 10, 15, 20 MHz
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A4. CALCULATION OF ACCEPTABLE TOLERANCE ZONE (BAND) TO DETERMINE CONFORMANCE WITH A CERTIFIED REFERENCE MATERIAL

A4.1 Determine the standard deviation for site uncertainty, σ_{site} , from a laboratory quality control program.

A4.3 Calculate the standard error of the accepted reference value (SEARV) by dividing the CEU by the coverage factor, k , listed on the supplier's label or included documentation.

A4.1.1 If the standard deviation for site uncertainty, σ_{site} , is not known, use the value 0.19%.

A4.3.1 If the coverage factor, k , is not known, use the value 2.

A4.2 Determine the combined extended uncertainty (CEU) of the accepted reference value (ARV) of the certified reference material (CRM) from the supplier's label or included documentation.

A4.4 Construct the acceptable tolerance zone:

$$TZ = \pm 1.44 \sqrt{\sigma_{\text{site}}^2 + SE_{\text{ARV}}^2}$$

SUMMARY OF CHANGES

Subcommittee D02.07 has identified the location of selected changes to this standard since the last issue (D 445–04^{e2}) that may impact the use of this standard.

- | | |
|--|---------------------------|
| (1) Revised 3.1.1 . | (3) Revised 10.2 . |
| (2) Revised 6.1.2 and added Note 3 . | (4) Added Note 2 . |

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Standard Test Method for Determination of Carbon Residue (Micro Method)¹

This standard is issued under the fixed designation D 4530; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last approval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope*

1.1 This test method covers the determination of the amount of carbon residue (see **Note 1**) formed after evaporation and pyrolysis of petroleum materials under certain conditions and is intended to provide some indication of the relative coke forming tendency of such materials.

1.2 The test results are equivalent to the Conradson Carbon Residue test (see Test Method **D 189**).

NOTE 1—This procedure is a modification of the original method and apparatus for carbon residue of petroleum materials, where it has been demonstrated that thermogravimetry is another applicable technique.² However, it is the responsibility of the operator to establish operating conditions to obtain equivalent results when using thermogravimetry.

1.3 This test method is applicable to petroleum products that partially decompose on distillation at atmospheric pressure and was tested for carbon residue values of 0.10 to 30 % (m/m). Samples expected to be below 0.10 weight % (m/m) residue should be distilled to remove 90 % (V/V) of the flask charge (see Section 9). The 10 % bottoms remaining is then tested for carbon residue by this test method.

1.4 Ash-forming constituents, as defined by Test Method **D 482**, or non-volatile additives present in the sample will add to the carbon residue value and be included as part of the total carbon residue value reported.

1.5 Also in diesel fuel, the presence of alkyl nitrates, such as amyl nitrate, hexyl nitrate, or octyl nitrate, causes a higher carbon residue value than observed in untreated fuel, which may lead to erroneous conclusions as to the coke-forming propensity of the fuel. The presence of alkyl nitrate in the fuel may be detected by Test Method **D 4046**.

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

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appro-*

priate safety practices and to determine the applicability of regulatory limitations prior to use. For specific warning statements, see 8.2.3 and 8.4.

2. Referenced Documents

2.1 ASTM Standards:

D 189 Test Method for Conradson Carbon Residue of Petroleum Products³

D 482 Test Method for Ash from Petroleum Products³

D 4046 Test Method for Alkyl Nitrate in Diesel Fuels by Spectrophotometry⁴

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products⁴

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products⁴

E 1 Specification for ASTM Thermometers⁵

E 133 Specification for Distillation Equipment⁶

2.2 IP Standard:

Specification for IP Standard Thermometers⁷

3. Terminology

3.1 Definitions:

3.1.1 *carbon residue, n*—in petroleum products, the part remaining after a sample has been subjected to thermal decomposition.

3.1.1.1 *Discussion*—The amount of residue is dependent on the test conditions of evaporation and pyrolysis. The term may be misleading here in that the residue may contain other than carbon decomposition products. However, the term is retained due to its wide common usage.

4. Summary of Test Method

4.1 A weighed quantity of sample is placed in a glass vial and heated to 500°C under an inert (nitrogen) atmosphere in a controlled manner for a specific time. The sample undergoes coking reactions, and volatiles formed are swept away by the

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.06 on Analysis of Lubricants.

Current edition approved May 10, 2003. Published June 2003. Originally approved in 1985. Last previous edition approved in 2000 as D 4530-00.

² See *Fuel*, Vol 63, July 1984, pp. 931-934.

³ *Annual Book of ASTM Standards*, Vol 05.01.

⁴ *Annual Book of ASTM Standards*, Vol 05.02.

⁵ *Annual Book of ASTM Standards*, Vol 14.03.

⁶ *Annual Book of ASTM Standards*, Vol 14.04.

⁷ *Methods for Analysis and Testing*, Institute of Petroleum Standard Methods for Petroleum and Its Products, Part I, Vol 2. Available from Institute of Petroleum, 61 New Cavendish St., London, W1M 8AR, UK.

*A Summary of Changes section appears at the end of this standard.

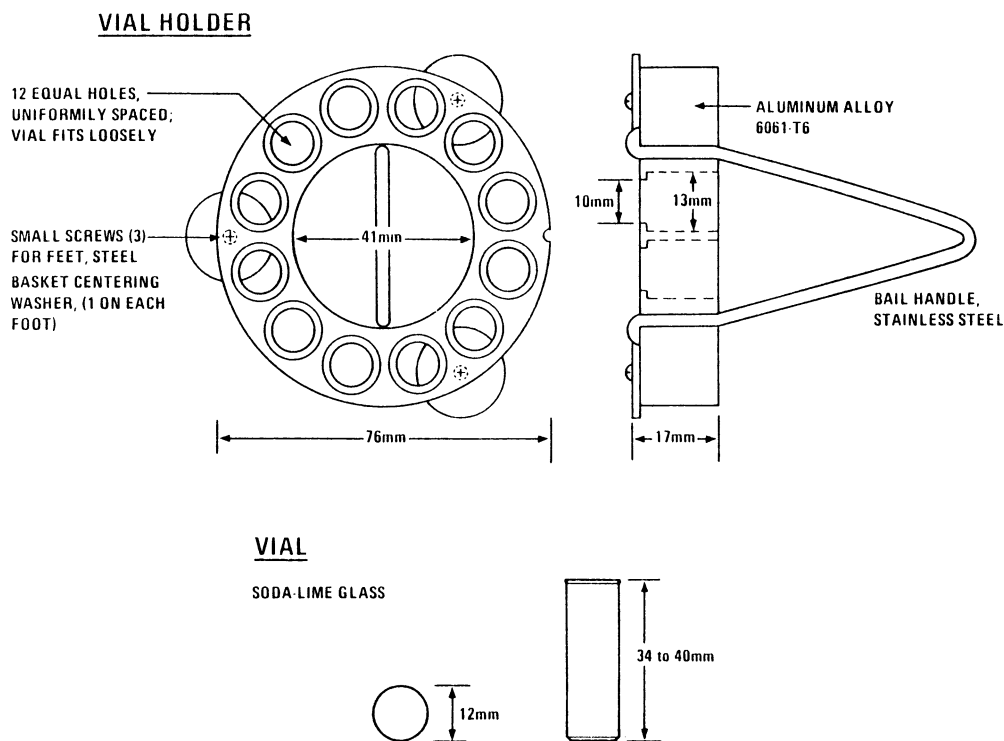


FIG. 1 Sample Vial Holder and Vial

nitrogen. The carbonaceous-type residue remaining is reported as a percent of the original sample as “carbon residue (micro).”

4.1.1 When the test result is expected to be below 0.10 % (m/m), the sample can be distilled to produce a 10 % (V/V) bottoms, prior to performing the test.

5. Significance and Use

5.1 The carbon residue value of the various petroleum materials serves as an approximation of the tendency of the material to form carbonaceous type deposits under degradation conditions similar to those used in the test method, and can be useful as a guide in manufacture of certain stocks. However, care needs to be exercised in interpreting the results.

5.2 This test method offers advantages of better control of test conditions, smaller samples, and less operator attention compared to Test Method D 189, to which it is equivalent.

5.3 Up to twelve samples may be run simultaneously, including a control sample when the vial holder shown in Fig. 1 is used exclusively for sample analysis.

6. Apparatus

6.1 *Glass Sample Vials*, 2-mL capacity, 12-mm outside diameter by approximately 35-mm high.

6.2 *Larger 4 dram Glass Sample Vials*, 15-mL capacity (20.5 to 21-mm outside diameter by 70 ± 1 -mm high), may be used for samples that are expected to yield residues <0.10 % (m/m) so that a more appreciable mass difference can be determined. It should be noted the precision statements for the test method were determined using the 2-mL capacity vials only (with sample residues between 0.3 and 26 % (m/m) and that the precision associated with using the larger sample vials has not been determined.

6.3 *Eyedropper, Syringe, or Small Rod*, for sample transfer.

6.4 *Coking Oven*⁸ with circular heating chamber approximately 85 mm (3 $\frac{3}{8}$ in.) in diameter by 100-mm (4-in.) deep, for top loading, with heating capability from 10 to 40°C/min rate to 500°C, with exhaust port 13-mm (1/2-in.) inside diameter for nitrogen purge of oven chamber (inlet near top, exhaust at bottom center) with thermocouple sensor located in oven chamber next to but not touching sample vials, with lid capable of sealing out air, and with removable condensate trap located at the oven chamber base. A schematic diagram is given in Fig. 2.

6.5 *Sample Vial Holder*—Cylindrical aluminum block, approximately 76 mm (3 in.) in diameter by 16-mm (5/8-in.) thick, with twelve evenly spaced holes (for vials) each 13 mm (1/2 in.) in diameter by 13-mm (1/2-in.) deep. The holes are arranged in a circular pattern approximately 3 mm (1/8 in.) from the perimeter. The holder has legs 6-mm (1/4-in.) long, with guides to center in oven chamber, and an index mark on the side to use as position reference. The sample vial holder is shown in Fig. 1.

6.6 A modified version of the standard sample vial holder (see Fig. 1) is required when larger glass sample vials (see 6.2) are used. The modified sample vial holder is similar in nature to the twelve hole vial holder, except that there are six evenly

⁸ The sole source of supply of a satisfactory oven with associated automatic controls that performs this carbon residue test known to the committee at this time is ALCOR-PAC, Inc., 3234 East Pasadena Freeway, Pasadena, TX 77503. This commercial unit is known as the MCRT. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee¹, which you may attend.

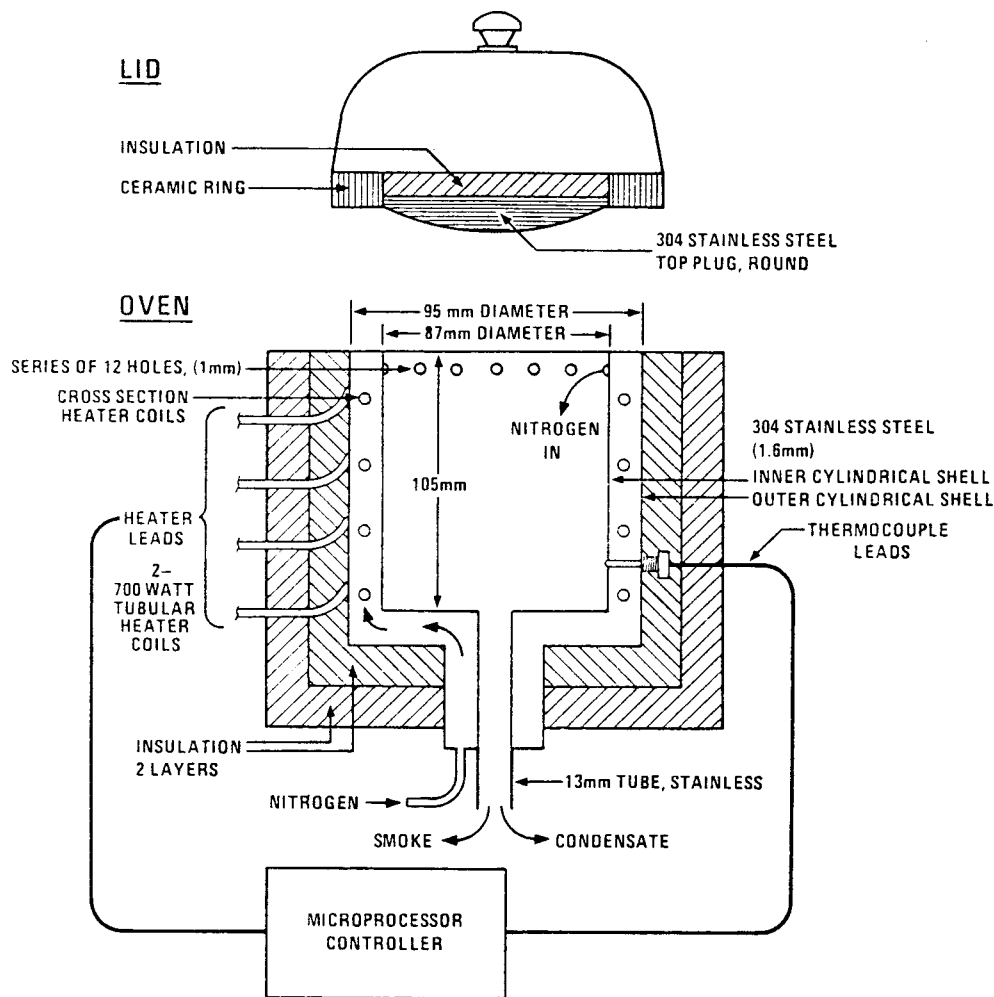


FIG. 2 Coking Oven and Lid

spaced holes (for vials) each 21.2 ± 0.1 mm in diameter by approximately 16-mm deep, arranged in a circular pattern.

6.7 *Thermocouple*, suitable for controller and temperature range of interest, with exterior temperature readout, degrees Celsius.

6.8 *Analytical Balance*, with ± 0.1 mg sensitivity to 20 g minimum weighing capacity.

6.9 *Nitrogen*, minimum 99.998 % purity with suitable means of delivering a pressure of 0 to 200 kPa (0 to 30 psig). Cylinders of zero grade nitrogen have been found suitable to use.

7. Sampling

7.1 Using the practices outlined in Practice D 4057 (manual sampling) or Practice D 4177 (automatic sampling), ensure that a representative sample of material to be tested is obtained.

8. Procedure

8.1 Sample Preparation:

8.1.1 Determine the mass of each clean sample vial being used in the sample analysis, and record the mass to nearest 0.1 mg.

8.1.2 During weighing and filling, handle vials with forceps to help minimize weighing errors. Discard the sample vials after use.

8.1.3 It is assumed that a representative sample of the stock or process has been obtained for laboratory use following Practice D 4057 or similar standard. Stir the sample to be tested, first warming if necessary to reduce its viscosity. Samples that are homogeneous liquids can be transferred directly to vials using a rod, syringe, or eyedropper. Solid materials may also be heated; or frozen with liquid nitrogen, and then shattered to provide manageable pieces.

8.1.4 Transfer an appropriate mass of the sample (see Table 1) into a tared-sample vial, reweigh to nearest 0.1 mg, and record. Place the loaded sample vials into vial holder (up to twelve), noting position of each sample with respect to index mark.

NOTE 2—A control sample can be included in each batch of samples being tested. This control sample should be a typical sample that has been tested at least 20 times in the same equipment in order to define an average percent carbon residue and standard deviation. Results for each batch are deemed acceptable when results for the control sample fall within the average percent carbon residue \pm three standard deviations. Control

TABLE 1 Guide for Sample Size

Sample Description	Expected Carbon Residue, (m/m) %	Recommended Sample Size, g
Black, viscous or solid	>5	0.15 ± 0.05
Brown, viscous	1–5	0.5 ± 0.1
Lube oil consistency and appearance, 10 % bottoms on distillate material	0.1–<1	1.5 ± 0.5
Large vials only	<0.1	5.0 ± 1.0
Small vials only	<0.1	1.5 ± 0.5

results that are outside these limits indicate problems with the procedure or the equipment.

8.2 Processing of Samples:

8.2.1 With the oven at less than 100°C, place the vial holder into the oven chamber and secure lid. Purge with nitrogen for at least 10 min at 600 mL/min. Then decrease the purge to 150 mL/min and heat the oven slowly to 500°C at 10°–15°C/min.

8.2.2 If the sample foams or spatters, causing loss of sample, discard and repeat the test.

NOTE 3—Spattering may be due to water that can be removed by prior gentle heating in a vacuum, followed by a nitrogen sweep. Alternatively, a smaller sample size can be used.

8.2.3 Hold oven at 500 ± 2°C for 15 min. Then shut off furnace power and allow oven to cool freely while under nitrogen purge of 600 mL/min. When oven temperature is less than 250°C, remove the vial holder for further cooling in desiccator. After the samples are removed from the oven, the nitrogen purge may be shut off. (**Warning**—Do not open oven to air at any time during the heating cycle. The introduction of air (oxygen) will likely cause the sample to ignite and spoil the test. (Because of the oven design and materials, such an ignition is normally not a hazard to the operator.) Open the oven only after oven temperature falls below 250°C during the cooling step. Maintain nitrogen flow until after the vial holder has been removed from the oven.) (**Warning**—Locate the coking oven in laboratory exhaust hood for safe venting of smoke and fumes. Alternatively, install vent line from MCRT oven exhaust to laboratory exhaust system.) (**Warning**—If a vent line is used, do not connect directly to exhaust chimney to avoid creating negative pressure in the line.)

NOTE 4—To reduce oven temperature for the next run, remove the oven lid to allow faster cooling. As required by the procedure, the subsequent test can be started when the oven has been cooled to below 100°C.

8.3 *Final Weighing*—Transfer sample vials (maintained in place in the vial holder) to desiccator and allow vials to cool to room temperature. Weigh the cooled vials to the nearest 0.1 mg and record. Handle the vials with forceps. Discard the used glass sample vials.

8.4 Occasionally examine the condensate trap at the bottom of the oven chamber; empty if necessary and replace. (**Warning**—The condensate trap residue may have some carcinogenic materials present. Avoid contact with the trap residue; dispose of it in accordance with local laboratory practice.)

9. Procedure for Carbon Residue on 10 % (V/V) Distillation Residue

9.1 This procedure is applicable to light distillate materials, such as ASTM No. 1 and No. 2 fuel oil or materials expected to have less than 0.1 % (m/m) carbon residue.

9.2 A distillation analysis using either a 100 or 200-mL starting volume is required in order to collect a sufficient amount of the 10 % (V/V) residue needed in this analysis. For a 100-mL distillation, assemble the distillation apparatus described in Specification E 133, using flask B (125-mL bulb volume), flask support board with 50-mm diameter opening, and graduated cylinder B (100-mL capacity). For a 200-mL distillation, assemble the distillation apparatus described in Specification E 133, using flask D (250-mL bulb volume), flask support board with 50-mm diameter opening, and graduated cylinder C (200-mL capacity). A thermometer is not required, but the use of the ASTM High Distillation Thermometer 8F or 8C, as prescribed in Specification E 1, or the IP High Distillation Thermometer 6C, as prescribed in the **Specification for IP Thermometers**, is recommended.

9.3 Depending upon which distillation flask is used, place either 100 or 200 mL of sample (as measured at ambient temperature) into a tared distillation flask that is held at a temperature between 13°C and ambient, and record the mass of sample transferred (E_1). Maintain the condenser bath temperature between 0 and 60°C so as to provide a sufficient temperature differential for sample condensation, while avoiding any solidification of waxy material in the condenser tube. Use, without cleaning, the cylinder from which the sample was measured as the receiver, and place it so that the tip of the condenser does not touch the wall of the cylinder. The receiver temperature is required to be maintained at the same temperature (within ±3°C) as the sample taken at the start of the test in order to obtain an accurate volume measurement in the receiving flask.

9.4 Apply the heat to the flask at a uniform rate so regulated that the first drop of condensate exits from the condenser between 10 and 15 min (for 200-mL samples) or between 5 and 15 min (for 100-mL samples) after initial application of heat. After the first drop falls, move the receiving cylinder so that the tip of the condenser tube touches the wall of the cylinder. Then regulate the heat so that the distillation proceeds at a uniform rate of 8 to 10 mL/min (for 200-mL samples) or 4 to 5 mL/min (for 100-mL samples). For 200-mL samples, continue the distillation until approximately 178 mL of distillate has been collected, and then discontinue heating and allow the condenser to drain until 180 mL (90 % (V/V) of the charge to the flask) has been collected in the cylinder. For 100-mL samples, continue the distillation until approximately 88 mL of distillate has been collected, and then discontinue heating and allow the condenser to drain until 90 mL (90 % (V/V) of the charge to the flask) has been collected in the cylinder.

9.5 Catch final drainage, if any, by immediately replacing the cylinder with a suitably tared container, such as a small Erlenmeyer flask. Add to this container, while still warm, the distillation residue left in the distilling flask, and mix well. The contents of the container then represents a 10 % (V/V) distillation residue from the original product. Allow the contents of

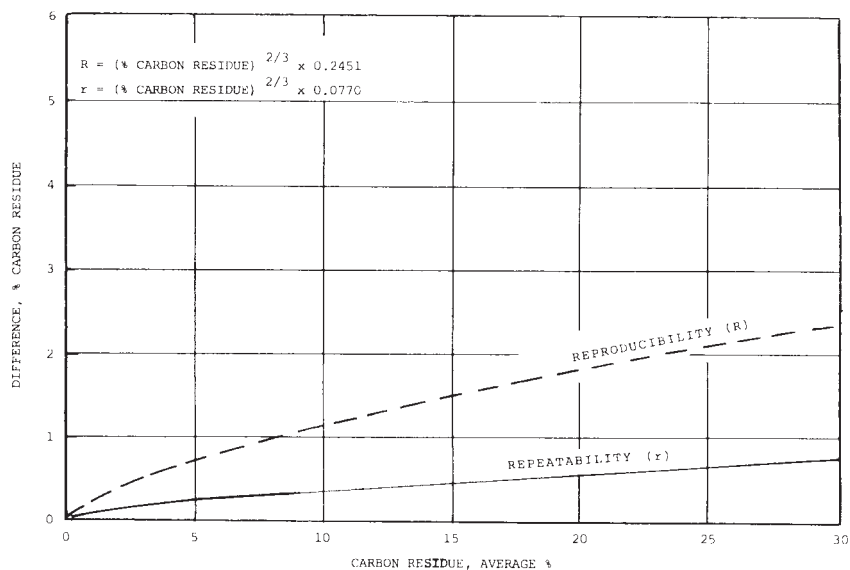


FIG. 3 Carbon Residue (Micro) Precision Data

the container to cool to ambient temperature before weighing the container and its contents in order to obtain an accurate measurement.

9.6 If the distillation residue is too viscous to flow freely at ambient temperature, it is necessary to warm the distillation residue to a sufficient temperature that will allow a portion of the material to be transferred into a previously weighted vial for analysis (see Table 1). After allowing the material in the vial to cool to ambient temperature, determine the mass of the test specimen to the nearest 0.1 mg and carry out the carbon residue test in accordance with the procedure described in Section 8.

10. Calculation

10.1 Calculate the mass % carbon residue in the original sample, or in the 10 % distillation bottoms as follows:

10.1.1 Calculate percent residue as follows:

$$\% \text{ carbon residue} = \frac{(A \times 100)}{W} \quad (1)$$

where:

- A = carbon residue, g, and
- W = sample used, g.

11. Report

11.1 Report the value obtained as Micro Method carbon residue, percent or as Micro Method carbon residue on 10 % distillation residue, percent to the nearest 0.1 % (m/m).

12. Precision and Bias ⁹

12.1 The precision of this test method as determined by (see Note 5) statistical examination of interlaboratory results is as follows:

NOTE 5—Precision data and Conradson carbon residue/micro carbon residue correlation data were generated by a task force in 1983. The round robin involved 18 laboratories, six petroleum materials in duplicate analysis for both micro method and Test Method D 189 tests. The range of values for samples was from 0.3 % to 26 % (m/m). No precision data or correlation data exists for results obtained using 10 % bottoms or 15-mL vials, or both.

12.2 Repeatability—The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would, in the long run, in the normal and correct operation of the test method, exceed the values shown in Fig. 3 in only one case in twenty.

12.3 Reproducibility—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, would, in the long run, in the normal and correct operation of the test method, exceed the values shown in Fig. 3 in only one case in twenty.

12.4 Bias—The procedure in Test Method D 4530 for measuring carbon residue of petroleum by the carbon residue method has no bias because the mass % of carbon residue can be defined only in terms of the test method.

13. Keywords

13.1 carbon residue; carbon residue (micro method); diesel fuel; lubricating oil; petroleum products

⁹ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1192.

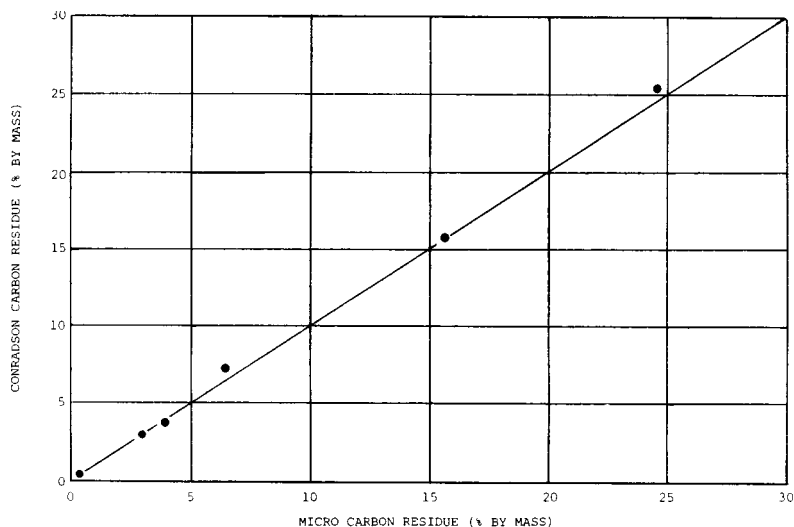


FIG. X1.1 Correlation of Conradson and Carbon Residue (Micro) Tests

APPENDIXES

(Nonmandatory Information)

X1. CORRELATION TO OTHER METHODS

X1.1 A correlation (see Fig. X1.1) has been derived between the carbon residue test by the micro method and the Conradson carbon residue test (see Test Method D 189) in a cooperative program involving 18 laboratories and six petroleum materials.

X1.2 Statistical analysis using modified Student's *t* tests

and nonparametric analysis show that, considering the precisions of both tests, there is no difference between the two methods. The data generated by the carbon residue test by the micro method are statistically equivalent to the Conradson carbon residue test, except for better precision in the micro method residue test.

X2. HELPFUL HINTS FOR THE ANALYST

X2.1 An exhaust system should be provided that will remove the small amount of smoke produced during carbon residue testing. Any suction line used to draw the smoke away should not be connected directly to the MCRT chimney. Allow a small space between the chimney and the suction line. This prevents a negative pressure from being created within the apparatus.

X2.2 The sample vials should be handled only with gloved hands or forceps.

X2.3 The large 4 dram vials should be used only for light oils and the samples that are expected to yield residues less than 0.10 m/m %.

X2.4 The final residue should be less than about 50 mg and preferably around 25 mg. If too much sample is taken, the material may boil over during heating, especially with high residue oils. Use the equation and the table given in this test method as a guide for recommended sample masses to be taken.

X2.5 If there is spattering or foaming of samples during the initial heating stage, this may be due to the presence of water in the sample. A smaller sample size can be used, or the water can be removed by gentle heating in vacuum, followed by a nitrogen sweep.

SUMMARY OF CHANGES

Subcommittee D02.06 has identified the location of selected changes to this standard since the last issue (D 4530–00) that may impact the use of this standard.

- | | |
|--|---|
| (1) Updated 6.2. | (7) Deleted 10.1.2. |
| (2) Updated 6.3. | (8) Updated 11.1 to allow reporting of 10 % distillation residue results. |
| (3) Updated address of the vendor in Footnote 8. | (9) Changed Appendix X1 title. |
| (4) Deleted use of only cylinders as a source of nitrogen in 6.9. | (10) Added new Appendix X2 to provide helpful hints to the analyst for running this test. |
| (5) Simplified sample requirements in 8.1.3. | |
| (6) Added 9.6 for guidance on handling viscous distillation residue. | |

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Standard Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method¹

This standard is issued under the fixed designation D 1298; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the laboratory determination using a glass hydrometer, of the density, relative density (specific gravity), or API gravity of crude petroleum, petroleum products, or mixtures of petroleum and nonpetroleum products normally handled as liquids, and having a Reid vapor pressure of 101.325 kPa (14.696 psi) or less.

1.2 Values are measured on a hydrometer at either the reference temperature or at another convenient temperature, and readings corrected to the reference temperature by means of the Petroleum Measurement Tables; values obtained at other than the reference temperature being hydrometer readings and not density measurements.

1.3 Values determined as density, relative density, or API gravity can be converted to equivalent values in the other units at alternate reference temperatures by means of the Petroleum Measurement Tables.

1.4 Annex A1 contains a procedure for verifying or certifying the equipment for this test method.

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

2. Referenced Documents

2.1 ASTM Standards:

- D 97 Test Method for Pour Point of Petroleum Products²
- D 323 Test Method for Vapor Pressure of Petroleum Products (Reid Method)²

¹ This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.02 on Static Petroleum Measurement.

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² *Annual Book of ASTM Standards*, Vol 05.01.

- D 1250 Guide for Petroleum Measurement Tables²
- D 2500 Test Method for Cloud Point of Petroleum Oils²
- D 3117 Test Method for Wax Appearance Point of Distillate Fuels³
- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products³
- D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products³
- D 5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products⁴
- E 1 Specification for ASTM Thermometers⁵
- E 100 Specification for ASTM Hydrometers⁵
- 2.2 *Institute of Petroleum Standards*⁶
- IP 389 Determination of wax appearance temperature (WAT) of middle distillate fuels by differential thermal analysis (DTA) or differential scanning calorimetry (DSC)
- IP Standard Methods Book, Appendix A, Specifications – IP Standard Thermometers
- 2.3 *ISO Standards*⁷
- ISO 649-1 Laboratory glassware – Density hydrometers for general purpose – Part 1: Specification

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *density, n*—the mass of liquid per unit volume at 15°C and 101.325 kPa with the standard unit of measurement being kilograms per cubic metre.

3.1.1.1 *Discussion*—Other reference temperatures, such as 20°C may be used for some products or in some locations. Less

³ *Annual Book of ASTM Standards*, Vol 05.02.

⁴ *Annual Book of ASTM Standards*, Vol 05.03.

⁵ *Annual Book of ASTM Standards*, Vol 14.03.

⁶ Available from Institute of Petroleum, 61 New Cavendish St., London, W1M 8AR, UK.

⁷ Available from American National Standards Institute, 11 W 42nd St., 13th floor, New York, NY 10036.

preferred units of measurement; for example, kg/L or g/mL are still in use.

3.1.2 *relative density (specific gravity), n*—the ratio of the mass of a given volume of liquid at a specific temperature to the mass of an equal volume of pure water at the same or different temperature. Both reference temperatures shall be explicitly stated.

3.1.2.1 *Discussion*—Common reference temperatures include 60/60°F, 20/20°C, 20/4°C. The historic deprecated term specific gravity may still be found.

3.1.3 *API gravity, n*—a special function of relative density (specific gravity) 60/60°F, represented by:

$$^{\circ} \text{API} = 141.5/(\text{sp gr } 60/60^{\circ}\text{F}) - 131.5 \quad (1)$$

3.1.3.1 *Discussion*—No statement of reference temperature is required, as 60°F is included in the definition.

3.1.4 *observed values, n*—values observed at temperatures other than the specified reference temperature. These values are only hydrometer readings and not density, relative density (specific gravity), or API gravity at that other temperature.

3.1.5 *cloud point, n*—temperature at which a cloud of wax crystals first appears in a liquid when it is cooled under specific conditions.

3.1.6 *pour point, n*—lowest temperature at which a test portion of crude petroleum or petroleum product will continue to flow when it is cooled under specified conditions.

3.1.7 *wax appearance temperature (WAT), n*—temperature at which waxy solids form when a crude petroleum or petroleum product is cooled under specified conditions.

4. Summary of Test Method

4.1 The sample is brought to a specified temperature and a test portion is transferred to a hydrometer cylinder that has been brought to approximately the same temperature. The appropriate hydrometer, also at a similar temperature, is lowered into the test portion and allowed to settle. After temperature equilibrium has been reached, the hydrometer scale is read, and the temperature of the test portion is taken. The observed hydrometer reading is reduced to the reference temperature by means of the Petroleum Measurement Tables. If necessary, the hydrometer cylinder and its contents are placed in a constant temperature bath to avoid excessive temperature variation during the test.

5. Significance and Use

5.1 Accurate determination of the density, relative density (specific gravity), or API gravity of petroleum and its products is necessary for the conversion of measured volumes to volumes or masses, or both, at the standard reference temperatures during custody transfer.

5.2 This test method is most suitable for determining the density, relative density (specific gravity), or API gravity of low viscosity transparent liquids. This test method can also be used for viscous liquids by allowing sufficient time for the hydrometer to reach equilibrium, and for opaque liquids by employing a suitable meniscus correction.

5.3 When used in connection with bulk oil measurements, volume correction errors are minimized by observing the hydrometer reading at a temperature close to that of the bulk oil temperature.

5.4 Density, relative density (specific gravity), or API gravity is a factor governing the quality and pricing of crude petroleum. However, this property of petroleum is an uncertain indication of its quality unless correlated with other properties.

5.5 Density is an important quality indicator for automotive, aviation and marine fuels, where it affects storage, handling and combustion.

6. Apparatus

6.1 *Hydrometers*, of glass, graduated in units of density, relative density, or API gravity as required, conforming to Specification E 100 or ISO 649-1, and the requirements given in Table 1.

6.1.1 The user should ascertain that the instruments used for this test conform to the requirements set out above with respect to materials, dimensions, and scale errors. In cases where the instrument is provided with a calibration certificate issued by a recognized standardizing body, the instrument is classed as certified and the appropriate corrections listed shall be applied to the observed readings. Instruments that satisfy the requirements of this test method, but are not provided with a recognized calibration certificate, are classed as uncertified.

6.2 *Thermometers*, having range, graduation intervals and maximum permitted scale error shown in Table 2 and conforming to Specification E 1 or IP Appendix A.

6.2.1 Alternate measuring devices or systems may be used, provided that the total uncertainty of the calibrated system is no greater than when using liquid-in-glass thermometers.

6.3 *Hydrometer Cylinder*, clear glass, plastic (see 6.3.1), or metal. The inside diameter of the cylinder shall be at least 25 mm greater than the outside diameter of the hydrometer and the height shall be such that the appropriate hydrometer floats in the test portion with at least 25 mm clearance between the bottom of the hydrometer and the bottom of the cylinder.

6.3.1 Hydrometer cylinders constructed of plastic materials shall be resistant to discoloration or attack by oil samples and shall not affect the material being tested. They shall not become opaque under prolonged exposure to sunlight.

6.4 *Constant-Temperature Bath*, if required, of dimensions such that it can accommodate the hydrometer cylinder with the test portion fully immersed below the test portion liquid surface, and a temperature control system capable of maintaining the bath temperature within 0.25°C of the test temperature throughout the duration of the test.

6.5 *Stirring Rod*, optional, of glass or plastic, approximately 400 mm in length.

TABLE 1 Recommended Hydrometers

Units	Range		Scale		Meniscus Correction
	Total	Each Unit	Interval	Error	
Density, kg/m ³ at 15°C	600 - 1100	20	0.2	± 0.2	+0.3 ¹
	600 - 1100	50	0.5	± 0.3	+0.7
	600 - 1100	50	1.0	± 0.6	+1.4
Relative density (specific gravity) 60/60°F	0.600 - 1.100	0.020	0.0002	± 0.0002	+0.0003
	0.600 - 1.100	0.050	0.0005	± 0.0003	+0.0007
	0.600 - 1.100	0.050	0.001	± 0.0006	+0.0014
Relative density (specific gravity), 60/60°F	0.650 - 1.100	0.050	0.0005	± 0.0005	
	API	-1 - +101	12	0.1	± 0.1

TABLE 2 Recommended Thermometers

Scale	Range	Graduation Interval	Scale Error
°C	-1 - +38	0.1	± 0.1
°C	-20 - +102	0.2	± 0.15
°F	-5 - +215	0.5	± 0.25

7. Sampling

7.1 Unless otherwise specified, samples of non-volatile petroleum and petroleum products shall be taken by the procedures described in Practices D 4057 and D 4177.

7.2 Samples of volatile crude petroleum or petroleum products are preferably taken by Practice D 4177, using a variable volume (floating piston) sample receiver to minimize any loss of light components which may affect the accuracy of the density measurement. In the absence of this facility, extreme care shall be taken to minimize these losses, including the transfer of the sample to a chilled container immediately after sampling.

7.3 *Sample Mixing*—may be necessary to obtain a test portion representative of the bulk sample to be tested, but precautions shall be taken to maintain the integrity of the sample during this operation. Mixing of volatile crude petroleum or petroleum products containing water or sediments, or both, or the heating of waxy volatile crude petroleum or petroleum products may result in the loss of light components. The following sections (7.3.1 to 7.3.4) will give some guidance on sample integrity maintenance.

7.3.1 *Volatile Crude Petroleum and Petroleum Products Having an RVP Greater than 50 kPa*—Mix the sample in its original closed container in order to minimize the loss of light components.

NOTE 1—Mixing volatile samples in open containers will lead to loss of light components and consequently affect the value of the density obtained.

7.3.2 *Waxy Crude Petroleum*—If the petroleum has a pour point above 10°C, or a cloud point or WAT above 15°C, warm the sample to 9°C above the pour point, or 3°C above the cloud point or WAT, prior to mixing. Whenever possible, mix the sample in its original closed container in order to minimize the loss of light components.

7.3.3 *Waxy Distillate*—Warm the sample to 3°C above its cloud point or WAT prior to mixing.

7.3.4 *Residual Fuel Oils*—Heat the sample to the test temperature prior to mixing (see 8.1.1 and Note 4).

7.4 Additional information on the mixing and handling of liquid samples will be found in Practice D 5854.

8. Procedure

8.1 Temperature of Test:

8.1.1 Bring the sample to the test temperature which shall be such that the sample is sufficiently fluid but not so high as to cause the loss of light components, nor so low as to result in the appearance of wax in the test portion.

NOTE 2—The density, relative density or API gravity determined by the hydrometer is most accurate at or near the reference temperature.

NOTE 3—The volume and density, the relative density, and the API corrections in the Petroleum Measurement Tables are based on the average

expansions of a number of typical materials. Since the same coefficients were used in compiling each set of tables, corrections made over the same temperature interval minimize errors arising from possible differences between the coefficient of the material under test and the standard coefficients. This effect becomes more important as temperatures diverge from the reference temperature.

NOTE 4—The hydrometer reading is obtained at a temperature appropriate to the physico-chemical characteristics of the material under test. This temperature is preferably close to the reference temperature; or when the value is used in conjunction with bulk oil measurements, within 3°C of the bulk temperature (see 5.3).

8.1.2 For crude petroleum, bring the sample close to the reference temperature or, if wax is present, to 9°C above its pour point or 3°C above its cloud point or WAT, whichever is higher.

NOTE 5—For crude petroleum an indication of the WAT can be found using IP 389, with the modification of using 50 µL ± 5 µL of sample. The precision of WAT for crude petroleum using this technique has not been determined.

9. Apparatus Verification or Certification

9.1 Hydrometers and thermometers shall be verified in accordance with the procedures in Annex A1.

10. Procedure

10.1 Bring the hydrometer cylinder and thermometer to within approximately 5°C of the test temperature.

10.2 Transfer the sample to the clean, temperature-stabilized hydrometer cylinder without splashing, to avoid the formation of air bubbles, and minimize evaporation of the lower boiling constituents of more volatile samples.

NOTE 6—Warning: Extremely flammable. Vapors may cause flash fire!

10.3 Transfer highly volatile samples by siphoning or water displacement.

NOTE 7—Warning: Siphoning by mouth could result in ingestion of sample!

10.3.1 Samples containing alcohol or other water-soluble materials should be placed into the cylinder by siphoning.

10.4 Remove any air bubbles formed after they have collected on the surface of the test portion, by touching them with a piece of clean filter paper before inserting the hydrometer.

10.5 Place the cylinder containing the test portion in a vertical position in a location free from air currents and where the temperature of the surrounding medium does not change more than 2°C during the time taken to complete the test. When the temperature of the test portion differs by more than 2°C from ambient, use a constant temperature bath to maintain an even temperature throughout the test duration.

10.6 Insert the appropriate thermometer or temperature measurement device and stir the test portion with a stirring rod, using a combination of vertical and rotational motions to ensure uniform temperature and density throughout the hydrometer cylinder. Record the temperature of the sample to the nearest 0.1°C and remove the thermometer/temperature measuring device and stirring rod from the hydrometer cylinder.

NOTE 8—If a liquid-in-glass thermometer is used, this is commonly used as the stirring rod.

10.7 Lower the appropriate hydrometer into the liquid and release when in a position of equilibrium, taking care to avoid

wetting the stem above the level at which it floats freely. For low viscosity transparent or translucent liquids observe the meniscus shape when the hydrometer is pressed below the point of equilibrium about 1 to 2 mm and allowed to return to equilibrium. If the meniscus changes, clean the hydrometer stem and repeat until the meniscus shape remains constant.

10.8 For opaque viscous liquids, allow the hydrometer to settle slowly into the liquid.

10.9 For low viscosity transparent or translucent liquids depress the hydrometer about two scale divisions into the liquid, and then release it, imparting a slight spin to the hydrometer on release to assist in bringing it to rest floating freely from the walls of the hydrometer cylinder. Ensure that the remainder of the hydrometer stem, which is above the liquid level, is not wetted as liquid on the stem affects the reading obtained.

10.10 Allow sufficient time for the hydrometer to come to rest, and for all air bubbles to come to the surface. Remove any air bubbles before taking a reading (see 10.4).

10.11 If the hydrometer cylinder is made of plastic, dissipate any static charges by wiping the outside with a damp cloth.

NOTE 9—**Caution:** Static charges often build up on plastic cylinders and may prevent the hydrometer from floating freely.

10.12 When the hydrometer has come to rest floating freely away from the walls of the cylinder, read the hydrometer scale reading to the nearest one-fifth of a full scale division in accordance with 10.12.1 or 10.12.2.

10.12.1 For transparent liquids, record the hydrometer reading as the point on the hydrometer scale at which the principal surface of the liquid cuts the scale by placing the eye slightly below the level of the liquid and slowly raising it until the surface, first seen as a distorted ellipse, appears to become a straight line cutting the hydrometer scale (see Fig. 1).

10.12.2 For opaque liquids record the hydrometer reading at the point on the hydrometer scale to which the sample rises, by observing with the eye slightly above the plane of the surface of the liquid (see Fig. 2).

NOTE 10—When testing opaque liquids using a metal hydrometer cylinder, accurate readings of the hydrometer scale can only be ensured if the liquid surface is within 5 mm of the top of the cylinder.

10.13 Immediately after recording the hydrometer scale reading, carefully lift the hydrometer out of the liquid, insert the thermometer or temperature measurement device and stir the test portion vertically with the stirring rod. Record the temperature of the test portion to the nearest 0.1°C. If this temperature differs from the previous reading (10.6) by more than 0.5°C, repeat the hydrometer observations and thermometer observations until the temperature becomes stable within 0.5°C. If a stable temperature cannot be obtained, place the hydrometer cylinder in a constant temperature bath and repeat the procedure from 10.5.

10.14 If the test temperature is higher than 38°C, allow all hydrometers of the lead shot-in-wax type to drain and cool in a vertical position.

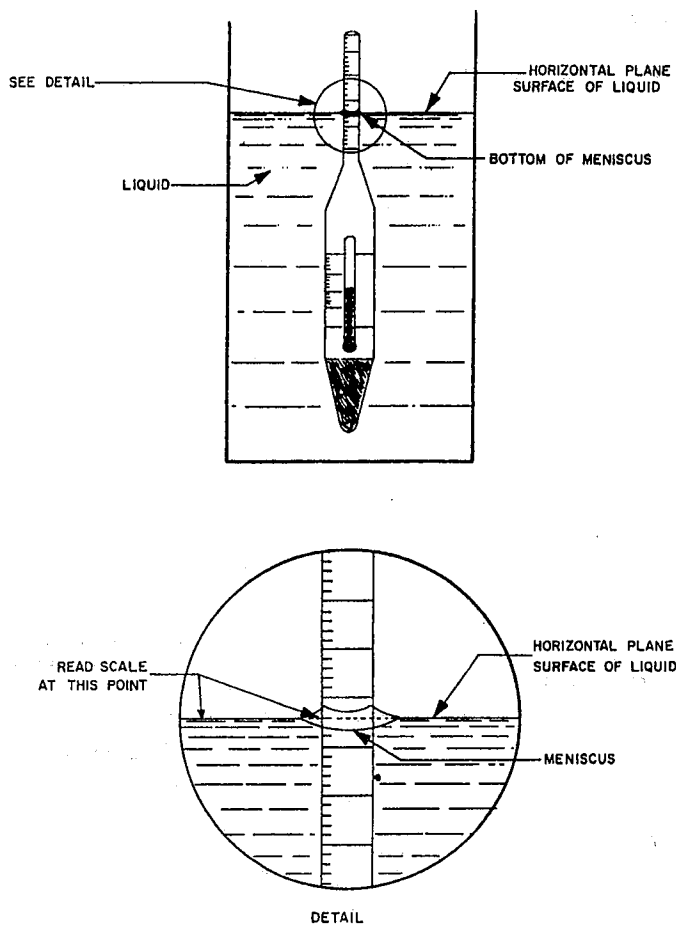


FIG. 1 Hydrometer Scale Reading for Transparent Liquids

11. Calculation

11.1 Apply any relevant thermometer corrections to the temperature reading observed in 10.6 and 10.13 and record the average of those two temperatures to the nearest 0.1°C.

11.2 For opaque samples, apply the relevant meniscus correction given in Table 1 to the observed hydrometer reading (10.12.2) as hydrometers are calibrated to be read at the principal surface of the liquid.

NOTE 11—The meniscus correction for a particular hydrometer in use is determined by observing the maximum height above the principal surface of the liquid to which liquid rises on the hydrometer scale when the hydrometer in question is immersed in a transparent liquid having a surface tension similar to that of the sample under test. For hydrometers specified in this test method, the corrections in Table 1 are approximate.

11.3 Apply any hydrometer correction to the observed reading and record the corrected hydrometer scale reading to the nearest 0.1 kg/m³ in density, 0.0001 g/mL, kg/L or relative density, or 0.1° API.

11.4 If the hydrometer has been calibrated at a temperature other than the reference temperature, use the equation below to correct the hydrometer scale reading:

$$\rho_t = \frac{\rho_r}{1 - [23 \times 10^{-6} (t-r) - 2 \times 10^{-8} (t-r)^2]} \quad (2)$$

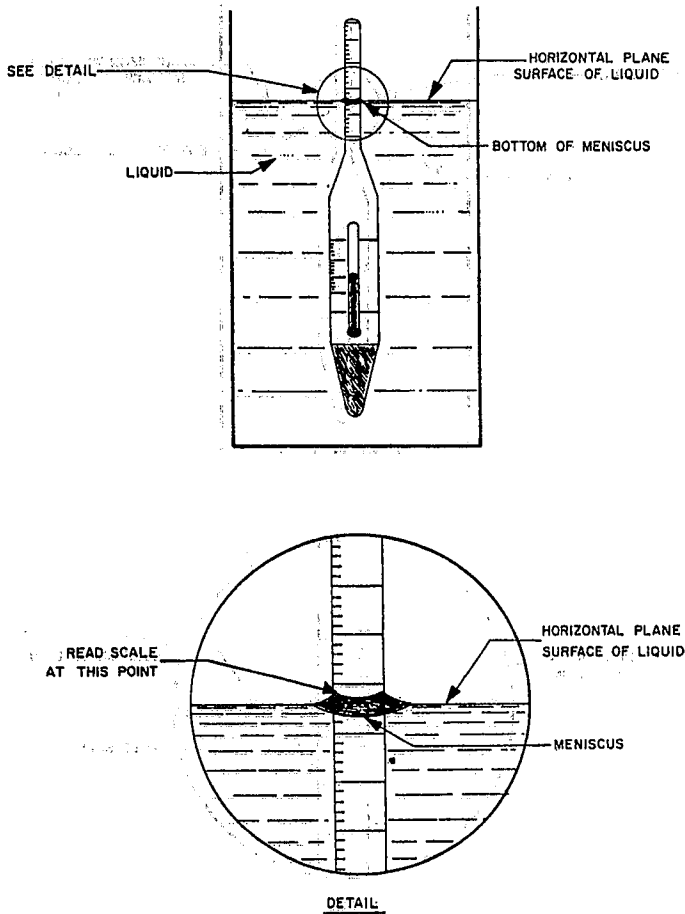


FIG. 2 Hydrometer Scale Reading for Opaque Fluids

where:

ρ_r = hydrometer reading at the reference temperature, r °C, and

ρ_t = hydrometer reading on the hydrometer scale whose reference temperature is t °C.

11.5 Convert the corrected hydrometer scale reading to density, relative density or API gravity using the appropriate parts of the Petroleum Measurement Tables in Guide D 1250 according to the nature of the materials under test. Table 3 gives some examples of relevant table numbers in the Petroleum Measurement Tables.

11.5.1 The strictly correct procedure for the conversion is to use the computer implementation procedures contained in the Petroleum Measurement Tables and not the printed tables. If the printed tables are used, ensure that all errata discovered since original publication have been included in the version used. The tables include corrections for soda-lime glass expansion and contraction of the hydrometer over the temperature

TABLE 3 Example PMT Table Numbers

Material	Density at 15°C kg/m ³	Density at 20°C kg/m ³	Relative Density at 60/60°F	°API
Crude petroleum	53A	59A	23A	5A
Petroleum products	53B	59B	23B	5B
Lubricating oils	53D	59D	-	5D

range, and thus the observed hydrometer reading is added directly after correction (11.2-11.4) as necessary.

11.5.2 To convert densities expressed in kg/m³ to densities expressed in g/mL or kg/L, divide by 10³.

11.5.3 To convert hydrometer readings from one unit to another, Tables 51 (density at 15°C), 21 (relative density at 60/60°F) or 3 (API gravity), contained in Guide D 1250, are appropriate.

12. Report

12.1 Report the final value as density, in kilograms per cubic metre, at the reference temperature, to the nearest 0.1 kg/m³.

12.2 Report the final value as density, in kilograms per litre or grams per millilitre at the reference temperature, to the nearest 0.0001.

12.3 Report the final value as relative density, with no dimensions, at the two reference temperatures, to the nearest 0.0001.

12.4 Report the final value as API gravity to the nearest 0.1° API.

13. Precision and Bias

13.1 Precision—The precision of the method as determined by statistical examination of interlaboratory results is as follows:

13.1.1 Repeatability—The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values in Table 4 only in one case in twenty.

13.1.2 Reproducibility—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty.

13.2 Bias—Bias for this test method has not been determined. However, there should be no bias from absolute measurements, if the calibration of the hydrometer and the thermometer is traceable to International Standards, such as supplied by the National Institute of Standards and Technology.

14. Keywords

14.1 API gravity; crude petroleum; density; hydrometer; Petroleum Measurement Tables; petroleum products; relative density; specific gravity

TABLE 4 Precision Values

Product	Parameter	Temperature Range, °C (°F)	Units	Repeat- ability	Repro- ducibility
Transparent Low-viscosity Liquids	Density	-2 - 24.5 (29 - 76)	kg/m ³ kg/L or g/mL	0.5 0.0005	1.2 0.0012
	Relative density		none	0.0005	0.0012
	API gravity	(42 - 78)	°API	0.1	0.3
Opaque liquids	Density	-2 - 24.5 (29 - 76)	kg/m ³ kg/L or g/mL	0.6 0.0006	1.5 0.0015
	Relative density		none	0.0006	0.0015
	API gravity	(42 - 78)	°API	0.2	0.5

ANNEX

(Mandatory Information)

A1. APPARATUS

A1.1 Apparatus Verification and Certification

A1.1.1 *Hydrometers*, shall either be certified or verified. Verification shall be either by comparison with a certified hydrometer (see 6.1.1) or by the use of a certified reference material (CRM) specific to the reference temperature used.

A1.1.1.1 The hydrometer scale shall be correctly located within the hydrometer stem by reference to the datum mark. If the scale has moved, reject the hydrometer.

A1.1.2 *Thermometers*, shall be verified at intervals of no more than six months for conformance with specifications. Either comparison with a referenced temperature measurement system traceable to an international standard, or a determination of ice point, is suitable.

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Standard Test Method for Water and Sediment in Middle Distillate Fuels by Centrifuge¹

This standard is issued under the fixed designation D 2709; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

^{e1} NOTE—Warning notes were placed in the text editorially in June 2001.

1. Scope

1.1 This test method covers the determination of the volume of free water and sediment in middle distillate fuels having viscosities at 40°C (104°F) in the range of 1.0 to 4.1 mm²/s (1.0 to 4.1 cSt) and densities in the range of 770 to 900 kg/m³.

NOTE 1—Fuels corresponding to Specification D 975 Grades 1D and 2D, Specification D 2880 Grades 0-GT, 1-GT and 2-GT, and Specification D 3699 Grades 1-K and 2-K will usually fall in this viscosity and density range. Test Method D 1796 is intended for higher viscosity fuel oils.

1.2 The values stated in inch-pound units are to be regarded as the standard. The values given in parenthesis are for information only.

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

2. Referenced Documents

2.1 ASTM Standards:

D 396 Specification for Fuel Oils²

D 975 Specification for Diesel Fuel Oils²

D 1796 Test Method for Water and Sediment in Fuel Oils by the Centrifuge Method (Laboratory Procedure)²

D 2880 Specification for Gas Turbine Fuel Oils²

D 3699 Specification for Kerosine³

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products³

3. Terminology

3.1 Description of Terms Specific to This Standard:

3.1.1 *distillate fuel*—a virgin or cracked or blend of virgin and cracked distillate having a flash point greater than 38°C.

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.14 on Stability and Cleanliness of Liquid Fuels.

Current edition approved January 10, 1996. Published March 1996. Originally published as D 2709 – 68. Last previous edition D 2709 – 93.

² Annual Book of ASTM Standards, Vol 05.01.

³ Annual Book of ASTM Standards, Vol 05.02.

4. Summary of Test Method

4.1 A 100-mL sample of the undiluted fuel is centrifuged at a relative centrifugal force of 800 for 10 min. at 21 to 32°C (70 to 90°F) in a centrifuge tube readable to 0.005 mL and measurable to 0.01 mL. After centrifugation, the volume of water and sediment which has settled into the tip of the centrifuge tube is read to the nearest 0.005 mL and reported as the volumetric percent water and sediment by centrifuge.

5. Significance and Use

5.1 This test method is used as an indication of water and sediment in middle distillate fuels such as Grades Nos. 1 and 2 fuel oil, (Specification D 396) Nos. 1-D and 2-D diesel fuel, (Specification D 975) and Nos. 0-GT, 1-GT, and 2-GT gas turbine fuels (Specification D 2880).

5.2 Appreciable amounts of water and sediment in a fuel oil tend to cause fouling of the fuel-handling facilities and to give trouble in the fuel system of a burner or engine. An accumulation of sediment in storage tanks and on filter screens can obstruct the flow of oil from the tank to the combustor. Water in middle distillate fuels can cause corrosion of tanks and equipment, and if detergent is present, the water can cause emulsions or a hazy appearance. Water is necessary to support microbiological growth at fuel water-interfaces in fuel systems.

6. Apparatus

6.1 *Centrifuge*, capable of whirling two or more filled centrifuge tubes at a speed which can be controlled to give a relative centrifugal force (rcf) of 800 ± 60 at the tip of the tubes. The revolving head, trunnion rings, and trunnion cups, including the cushions, are to be soundly constructed to withstand the maximum centrifugal force capable of being delivered by the power source. The trunnion cups and cushions shall support the tubes when the centrifuge is in motion. The centrifuge shall be enclosed by a metal shield or case strong enough to eliminate danger if any breakage occurs.

6.2 The data in Table 1 can be used to determine the centrifuge speed setting required for the centrifuge to meet relative centrifugal force requirements for this method and was developed using the following equations:

TABLE 1 Rotation Speeds Applicable for Centrifuges of Various Diameters of Swing

Diameters of Swing ^A		Rpm at 500 rcf	Rpm at 800 rcf
in.	cm		
12	30.5	1710	2160
13	33.0	1650	2080
14	35.6	1590	2000
15	38.1	1530	1930
16	40.6	1480	1870
17	43.2	1440	1820
18	45.7	1400	1770
19	48.3	1360	1720
20	50.8	1330	1680
21	53.3	1300	1640
22	55.9	1270	1600
23	58.4	1240	1560
24	61.0	1210	1530

^A Measured between tips of opposite tubes when in rotating position.

$$\text{rpm} = 265 \sqrt{\text{rcf}/d} \quad (1)$$

where:

rcf = relative centrifugal force, and

d = diameter of swing, in inches, measured between tips of opposite tubes when in rotating position or

$$\text{rpm} = 422 \sqrt{\text{rcf}/d} \quad (2)$$

where:

rcf = relative centrifugal force, and

d = diameter of swing, in centimetres, measured between tips of opposite tubes when in rotating position.

6.3 *Centrifuge Tube*, cone-shaped, 100-mL with capillary tip capable of measuring 0.01 mL⁴ and readable by estimation to 0.005 %.

6.4 *Centrifuge Tube*, pear-shaped,⁵ 100-mL, with tube tip having graduations of 0.01 mL⁵ over the range 0 to 0.2 mL.

7. Sampling

7.1 Sampling shall be consistent with the procedures of Practice D 4057.

7.2 The sample for a laboratory test will normally be an aliquot of a much larger sample taken for full or partial specification testing. The full sample should have been taken by a procedure consistent with Practice D 4057. Allow the sample container and its content to equilibrate between 21 to 32°C (70 to 90°F). In general, the chosen laboratory test temperature should not be lower than that at which the fuel is stored or used as too low a temperature may cause free water haze to form from additional free water formation.

⁴ Satisfactory tubes readable to 0.05 mL and capable of measuring to the nearest 0.01 mL are available from Stanhope-Seta, Park Close, Englefield Green, Egham, Surrey, TW 20 0Y0, England or their U.S. distributors and Kimble, 537 Crystal Ave., Vineland, NJ 08360. Other sources may be available but are not known at this time.

⁵ Precision data for this test used pearshaped tubes. Satisfactory tubes readable to 0.005 mL by interpolation and measurable markings at the nearest 0.01 mL over the range 0 to 0.2 mL are available from Fisher Scientific, 711 Forbes Ave. Pittsburgh, PA 15219-4785, and Reliance Glass Texas, 1605 Community Drive, Pasadena, TX 77501.

8. Procedure

8.1 *Temperature Control*—After the sample container and its contents have equilibrated to laboratory temperature, between 70 to 90°F (21 to 32°C), agitate the full sample by hand or preferably by a mechanical shaker for 10 min to ensure homogeneity. (**Warning**—Flammable).

8.2 As soon as possible, to prevent losing any water or sediment, fill the centrifuge tube to the 100-mL mark directly from the sample container. Stopper and place in a trunnion cup opposite another filled tube to establish a balanced condition, and whirl 10 min at a speed sufficient to produce a relative centrifugal force (rcf) of 800 ± 60 at the tip of the whirling tubes. (For the relationship between diameter of swings, rcf, and rpm, see Table 1.) Record the combined water and sediment at the bottom of the tube to the nearest 0.005 mL.

9. Report

9.1 Report the volume of the combined water and sediment read from the tube as the percentage of the total sample, since a 100-mL sample was used. Report results lower than 0.005 % as either 0 or 0.005 volume % .

10. Precision and Bias⁵

10.1 *Precision*⁶—The precision of the procedure in this test method, for measuring the volume percent amount of combined water and sediment in middle distillate fuels by centrifuge was determined by a round robin test program performed by six individuals using 13 samples at a common site.

10.1.1 *Repeatability*—The difference between successive measured volume percent amounts of combined water and sediment obtained by the same operator using the same centrifuge and type of pear shaped tube under constant operating conditions on identical distillate fuel samples at the same site would, in the long run and in the normal and correct operation of the test method, exceed 0.014 volume percent in one case in twenty.

10.1.2 *Reproducibility*—The difference between two single independent measurements of volume percent amounts of combined water and sediment obtained by different operator/centrifuge pairs using the same type of pear shaped tube on identical distillate fuel samples at the same site would, in the long run, in the normal and correct operation of the test method, exceed 0.041 volume percent in one case in twenty.

10.2 *Bias*⁶—Since there is no accepted reference material suitable for determining the bias for this procedure for measuring water, the bias is not available for this test method.

11. Keywords

11.1 centrifuge; centrifuge tube; distillate fuel; water and sediment

⁶ Supporting data is on file at ASTM Headquarters. Request RR: D02-1308.

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Standard Test Method for Sulfated Ash from Lubricating Oils and Additives¹

This standard is issued under the fixed designation D874; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 This test method covers the determination of the sulfated ash from unused lubricating oils containing additives and from additive concentrates used in compounding. These additives usually contain one or more of the following metals: barium, calcium, magnesium, zinc, potassium, sodium, and tin. The elements sulfur, phosphorus, and chlorine can also be present in combined form.

1.2 Application of this test method to sulfated ash levels below 0.02 % by mass is restricted to oils containing ashless additives. The lower limit of the test method is 0.005 % by mass sulfated ash.

NOTE 1—This test method is not intended for the analysis of used engine oils or oils containing lead. Neither is it recommended for the analysis of nonadditive lubricating oils, for which Test Method D482 can be used.

NOTE 2—There is evidence that magnesium does not react the same as other alkali metals in this test. If magnesium additives are present, the data is interpreted with caution.

NOTE 3—There is evidence that samples containing molybdenum can give low results because molybdenum compounds are not fully recovered at the temperature of ashing.

1.3 Fatty acid methyl ester (FAME) conforming to EN 14213 and EN 14214, when tested using this test method, were shown to meet its precision.

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

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

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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In the IP, this test method is under the jurisdiction of the Standardization Committee. This test method has been approved by the sponsoring committees and accepted by the cooperating societies in accordance with established procedures.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:²

- D482 Test Method for Ash from Petroleum Products
- D1193 Specification for Reagent Water
- D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
- D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
- D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

2.2 CEN Standards:³

- EN 14213 Heating Fuels—Fatty Acid Methyl Esters (FAME)—Requirements and Test Methods
- EN 14214 Automotive Fuels—Fatty Acid Methyl Esters (FAME) for Diesel Engines—Requirements and Test Methods

3. Terminology

3.1 Definitions:

3.1.1 *sulfated ash, n*—the residue remaining after the sample has been carbonized, and the residue subsequently treated with sulfuric acid and heated to constant weight.

4. Summary of Test Method

4.1 The sample is ignited and burned until only ash and carbon remain. After cooling, the residue is treated with sulfuric acid and heated at 775 °C until oxidation of carbon is

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

³ Available from European Committee for Standardization (CEN), Avenue Marnix 17, B-1000, Brussels, Belgium, <http://www.cen.eu>.

complete. The ash is then cooled, re-treated with sulfuric acid, and heated at 775 °C to constant weight.

5. Significance and Use

5.1 The sulfated ash can be used to indicate the concentration of known metal-containing additives in new oils. When phosphorus is absent, barium, calcium, magnesium, sodium and potassium are converted to their sulfates and tin (stannic) and zinc to their oxides (**Note 4**). Sulfur and chlorine do not interfere, but when phosphorus is present with metals, it remains partially or wholly in the sulfated ash as metal phosphates.

NOTE 4—Since zinc sulfate slowly decomposes to its oxide at the ignition temperature specified in the test method, samples containing zinc can give variable results unless the zinc sulfate is completely converted to the oxide.

5.2 Because of above inter-element interferences, experimentally obtained sulfated ash values may differ from sulfated ash values calculated from elemental analysis. The formation of such non-sulfated species is dependent on the temperature of ashing, time ashed, and the composition of metal compounds present in oils. Hence, sulfated ash requirement generally should not be used in product specifications without a clear understanding between a buyer and a seller of the unreliability of an ash value as an indicator of the total metallic compound content.⁴

6. Apparatus

6.1 *Evaporating Dish or Crucible*; 50 mL to 100 mL for samples containing more than 0.02 % by mass sulfated ash, or 120 mL to 150 mL for samples containing less than 0.02 % by mass sulfated ash, and made of porcelain, fused silica, or platinum. (**Warning**—Do not use platinum when the sample is likely to contain elements such as phosphorus, which attack platinum under the conditions of the test.)

NOTE 5—For best results on samples containing less than 0.1 % by mass sulfated ash, platinum dishes are used. The precision values shown in Section 13 for this type of sample were so obtained.

6.2 *Electric Muffle Furnace*—The furnace shall be capable of maintaining a temperature of 775 °C ± 25 °C and preferably have apertures at the front and rear to allow a slow natural draft of air to pass through the furnace.

6.3 *Balance*, capable of weighing to 0.1 mg.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available, or to other recognized

standards for reagent chemicals.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water defined by Types II or III of Specification **D1193**.

7.3 *Low-Ash Mineral Oil*—White oil having a sulfated ash lower than the limit capable of being determined by this test method.

NOTE 6—Determine the sulfated ash of this oil by the procedure given in 9.1 – 9.11 below using 100 g of white oil weighed to the nearest 0.5 g in a 120 mL to 150 mL platinum dish. Deduct the sulfuric acid blank as described in 9.11.

7.4 *Sulfuric Acid (relative density 1.84)*—Concentrated sulfuric acid (H₂SO₄). (**Warning**—Poison. Corrosive. Strong oxidizer.)

7.5 *Sulfuric Acid (1 + 1)*—Prepare by slowly adding 1 volume of concentrated sulfuric acid (relative density 1.84) to 1 volume of water with vigorous stirring. (**Warning**—Mixing this acid into water generates considerable heat. When necessary, cool the solution before adding more acid. Do not allow the solution to boil.)

7.6 *Propan-2-ol*, (**Warning**—Flammable, can be explosive when evaporated to or near dryness.) 99 % minimum purity.

7.7 *Toluene*, (**Warning**—Flammable, toxic.) 99 % minimum purity.

7.8 *Quality Control (QC) Samples*, preferably are portions of one or more liquid petroleum materials that are stable and representative of the samples of interest. These QC samples can be used to check the validity of the testing process as described in Section 12.

8. Sampling

8.1 Obtain samples in accordance with the instructions in Practice **D4057** or **D4177**. The sample shall be thoroughly mixed before removal of the laboratory test portion.

9. Procedure

9.1 Select the size of the evaporating dish or crucible according to the quantity of sample necessary (see 9.3).

9.2 Heat the evaporating dish or crucible that is used for the test at 775 °C ± 25 °C for a minimum of 10 min. Cool to room temperature in a suitable container and weigh to the nearest 0.1 mg.

NOTE 7—The container in which the dish is cooled does not contain a desiccating agent.

9.3 Weigh into the dish a quantity of sample given as follows:

⁴ Further discussion of these interferences can be found in Nadkarni, R. A., Ledesma, R. R., and Via, G. H., "Sulfated Ash TM: Limitations of Reliability and Reproducibility," SAE Technical Paper No. 952548, available from SAE, 400 Commonwealth Drive, Warrendale, PA 15096-0001, U.S.A.

⁵ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

$$W = 10/a \quad (1)$$

where:

W = mass of test specimen, g, and
 a = expected sulfated ash, mass %.

However, do not take a quantity in excess of 80 g. In the case of lubricating oil additives yielding a sulfated ash of 2 % by mass or more, dilute the weighed sample in the dish with approximately 10 times its weight of low-ash mineral oil. If the amount of sulfated ash found differs from the expected amount by more than a factor of two, repeat the analysis with a different weight of sample calculated from the first analysis unless the calculated sample size >80 g.

9.4 Heat the dish or crucible and sample carefully until the contents can be ignited with a flame. Maintain at such a temperature that the sample continues to burn at a uniform and moderate rate. When burning ceases, continue to heat gently until no further smoke or fumes are evolved.

9.4.1 If the sample contains sufficient moisture to cause foaming and loss of material from the dish, discard the sample and to an additional sample add 1 mL to 2 mL of 99 % propan-2-ol (**Warning**—Flammable) before heating. If this is not satisfactory, add 10 mL of a mixture of equal volumes of toluene (**Warning**—Flammable, Vapor harmful.) and propan-2-ol and mix thoroughly. Place several strips of ashless filter paper in the mixture and heat; when the paper begins to burn, the greater part of the water will have been removed.

9.5 Allow the dish to cool to room temperature, then completely moisten the residue by the dropwise addition of sulfuric acid (relative density 1.84). Carefully heat the dish at a low temperature on a hot plate or over a gas burner, avoiding spattering, and continue heating until fumes are no longer evolved.

9.6 Place the dish in the furnace at $775\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$ for 30 min ± 5 min until oxidation of the carbon is complete or almost complete.

9.7 Allow the dish to cool to room temperature. Add 3 drops of water and 10 drops of sulfuric acid (1 + 1). Move the dish so as to moisten the entire residue. Again heat the dish in accordance with 9.5.

9.8 Again place the dish in the furnace at $775\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$ and maintain at that temperature for 30 min ± 5 min (see **Note 8**). Cool the dish to room temperature in a suitable container (see **Note 7**). Zinc dialkyl or alkaryl dithiophosphates and blends containing these additives can give a residue that is partially black at this stage. In this case, repeat 9.7 and 9.8 until a white residue is obtained.

NOTE 8—A study conducted by two separate laboratories investigating whether heating sulfated ash residues for extended periods of time (for example, overnight) in a furnace at $775\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$ as opposed to 30 min as required in 9.8 revealed that a significant difference in sulfated ash results can exist. The study indicated that lower sulfated ash results were obtained on the samples left in the furnace overnight versus those that were heated in 30 min cycles. A thermogravimetric analysis also confirmed that the samples evaluated continued to lose weight at $775\text{ }^{\circ}\text{C}$ as a function of time. As such, it is essential that the 30 min heating time requirement be adhered to in performing the test method. Details

concerning the study can be found in ASTM Research Report RR:D02-1597.⁶

9.9 Weigh the dish and residue to the nearest 0.1 mg.

9.10 Repeat 9.8 and 9.9 until two successive weighings differ by no more than 1.0 mg.

NOTE 9—Normally one repeat will suffice, unless a high proportion of zinc is present, when three or four heating periods can be required.

9.11 For samples expected to contain 0.02 % mass or less of sulfated ash, determine a sulfuric acid blank by adding 1 mL of the concentrated sulfuric acid to a tared platinum dish or crucible, heating until fumes are no longer evolved and then heating in the furnace at $775\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$ for 30 min ± 5 min. Cool the dish or crucible to room temperature in a suitable container (see **Note 7**) and weigh to the nearest 0.1 mg. If any ash is found in the sulfuric acid, make an adjustment to the weight of sulfated ash obtained by subtracting the weight of ash contributed by the sulfuric acid, determined from the total volume of sulfuric acid used and the weight of ash found for the 1 mL blank, from the total grams of sulfated ash for the sample. Use this corrected weight, w , in calculating the percent sulfated ash.

10. Calculation

10.1 Calculate the sulfated ash as a percentage of the original sample as follows:

$$\text{Sulfated ash, mass \%} = (w/W) \times 100 \quad (2)$$

where:

w = grams of sulfated ash, and
 W = grams of sample used.

11. Report

11.1 Report the result to the nearest 0.001 % by mass for samples below 0.02 % by mass and to the nearest 0.01 % by mass for higher levels as the sulfated ash, Test Method D874.

12. Quality Control

12.1 Confirm the performance of the instrument or the test procedure by analyzing a QC sample (see 7.8).

12.1.1 When QC/Quality Assurance (QA) protocols are already established in the testing facility, these may be used to confirm the reliability of the test result.

12.1.2 When there is no QC/QA protocol established in the testing facility, **Appendix X1** can be used as the QC/QA system.

13. Precision and Bias⁶

13.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

13.1.1 For sulfated ash levels between 0.005 % and 0.10 % by mass.

13.1.1.1 *Repeatability*—The difference between two test results obtained by the same operator with the same apparatus

⁶ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1597. Contact ASTM Customer Service at service@astm.org.

TABLE 1 Precision at Levels Below 0.10 %

Sulfated Ash, mass %	Repeatability	Reproducibility
0.005	0.0005	0.0021
0.010	0.0009	0.0038
0.05	0.0037	0.0148
0.10	0.0066	0.0267

under constant operating conditions on identical test materials would, in the long run in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

$$r = 0.047 X^{0.85} \quad (3)$$

where X = average of two results.

13.1.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run in the normal and correct operation of the test method, exceed the following values in only one case in twenty:

$$R = 0.189 X^{0.85} \quad (4)$$

where X = average of two results.

13.1.1.3 Specimen data are shown in **Table 1**.

NOTE 10—The precision values in the range from 0.005 % to 0.10 % by mass sulfated ash were obtained by statistical examination of interlaboratory test results obtained in a joint ASTM-IP cooperative program conducted in 1975. Only platinum dishes were used.

13.1.2 For sulfated ash levels between 0.11 % and 25 % by mass:

13.1.2.1 *Repeatability*—The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run in the normal and correct operation of the test method, exceed the following values in only one case in twenty:

$$r = 0.060 X^{0.75} \quad (5)$$

where X = average of two results.

13.1.2.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run in the normal and correct operation of the test method, exceed the following values in only one case in twenty:

$$R = 0.142 X^{0.75} \quad (6)$$

TABLE 2 Precision at Levels Above 0.10 %

Sulfated Ash, mass %	Repeatability	Reproducibility
0.5	0.036	0.084
1.0	0.060	0.142
5.0	0.201	0.475
10.0	0.337	0.799
20.0	0.567	1.343
25.0	0.671	1.588

where X = average of two results.

13.1.2.3 Specimen data are shown in **Table 2**.

NOTE 11—The precision values in the range from 0.10 % to 25 % by mass sulfated ash were obtained by statistical examination of interlaboratory test results obtained in a joint ASTM-IP cooperative program conducted in 1981.

13.1.3 Based on an interlaboratory study conducted in 2006 that included nine laboratories and six heavy duty engine oils meeting the API PC 10 specifications,⁷ the following precision was obtained:⁸

Sulfated ash concentration level: 0.8 % to 1.6 % by mass

Repeatability: $0.08068 X^{1.40}$

Reproducibility: $0.1563 X^{1.40}$

13.1.4 Examples of analysis precision are shown in **Table 3**.

TABLE 3 Precision for API PC 10 Type Oils

Sulfated Ash Concentration, mass %	Repeatability	Reproducibility
0.80	0.06	0.11
0.90	0.07	0.13
1.10	0.09	0.18
1.60	0.16	0.30

13.2 *Bias*—There is no accepted reference material suitable for determining the bias of the procedures in this test method for measuring ash.

14. Keywords

14.1 additives; ash; lubricating oils

⁷ Available from American Petroleum Institute (API), 1220 L. St., NW, Washington, DC 20005-4070, <http://www.api.org>.

⁸ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1625. Contact ASTM Customer Service at service@astm.org.

APPENDIX

(Nonmandatory Information)

X1. QUALITY CONTROL

X1.1 Confirm the performance of the instrument or the test procedure by analyzing a QC sample.

X1.2 Prior to monitoring the measurement process, the user of the test method needs to determine the average value and control limits of the QC sample (see Practice **D6299** and MNL 7).⁹

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process (see Practice **D6299** and MNL 7). Any out-of-control data should trigger investigation for root cause(s).

X1.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the

criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample is analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be checked against the ASTM test method precision to ensure data quality.

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions. See Practice **D6299** and MNL 7 for further guidance on QC and control charting techniques.

⁹ MNL 7, *Manual on Presentation of Data Control Chart Analysis*, 6th Ed., ASTM International, W. Conshohocken, PA.

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Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels and Motor Oils by Ultraviolet Fluorescence¹

This standard is issued under the fixed designation D 5453; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers the determination of total sulfur in liquid hydrocarbons, boiling in the range from approximately 25 to 400°C, with viscosities between approximately 0.2 and 20 cSt (mm^2/S) at room temperature.

1.2 Three separate interlaboratory studies (ILS) on precision, and two other investigations that resulted in an ASTM research report, have determined that this test method is applicable to naphthas, distillates, oils, ethanol, Fatty Acid Methyl Ester (FAME), and motor fuels; such as gasoline, oxygen enriched gasoline (M-85, RFG), diesel, biodiesel and jet fuel. Samples containing 1.0 to 8000 mg/kg total sulfur can be analyzed (Note 1).

NOTE 1—Estimates of the pooled limit of quantification (PLOQ) for each of the five precision studies were calculated. Values ranged between less than 1.0 and less than 5.0 mg/kg (see Section 8 and 15.1).

1.3 This test method is applicable for total sulfur determination in liquid hydrocarbons containing less than 0.35 % (m/m) halogen(s).

1.4 The values stated in SI units are to be regarded as standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. See 3.1, 6.3, 6.4, Section 7, and 8.1.*

2. Referenced Documents

2.1 ASTM Standards:

D 1298 Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method²

D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter³

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products³

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products³

D 6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance⁴

3. Summary of Test Method

3.1 A hydrocarbon sample is either directly injected or placed in a sample boat. The sample or boat, or both, is inserted into a high temperature combustion tube where the sulfur is oxidized to sulfur dioxide (SO_2) in an oxygen rich atmosphere. Water produced during the sample combustion is removed and the sample combustion gases are next exposed to ultraviolet (UV) light. The SO_2 absorbs the energy from the UV light and is converted to excited sulfur dioxide (SO_2^*). The fluorescence emitted from the excited SO_2^* as it returns to a stable state, SO_2 , is detected by a photomultiplier tube and the resulting signal is a measure of the sulfur contained in the sample. (**Warning**—Exposure to excessive quantities of ultraviolet (UV) light is injurious to health. The operator must avoid exposing any part of their person, especially their eyes, not only to direct UV light but also to secondary or scattered radiation that is present.)

4. Significance and Use

4.1 Some process catalysts used in petroleum and chemical refining can be poisoned when trace amounts of sulfur bearing materials are contained in the feedstocks. This test method can be used to determine sulfur in process feeds sulfur in finished products, and can also be used for purposes of regulatory control.

5. Apparatus

5.1 *Furnace*—An electric furnace held at a temperature ($1075 \pm 25^\circ\text{C}$) sufficient to pyrolyze all of the sample and oxidize sulfur to SO_2 .

5.2 *Combustion Tube*—A quartz combustion tube constructed to allow the direct injection of the sample into the heated oxidation zone of the furnace or constructed so that the

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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² *Annual Book of ASTM Standards*, Vol 05.01.

³ *Annual Book of ASTM Standards*, Vol 05.02.

⁴ *Annual Book of ASTM Standards*, Vol 05.03.

*A Summary of Changes section appears at the end of this standard.

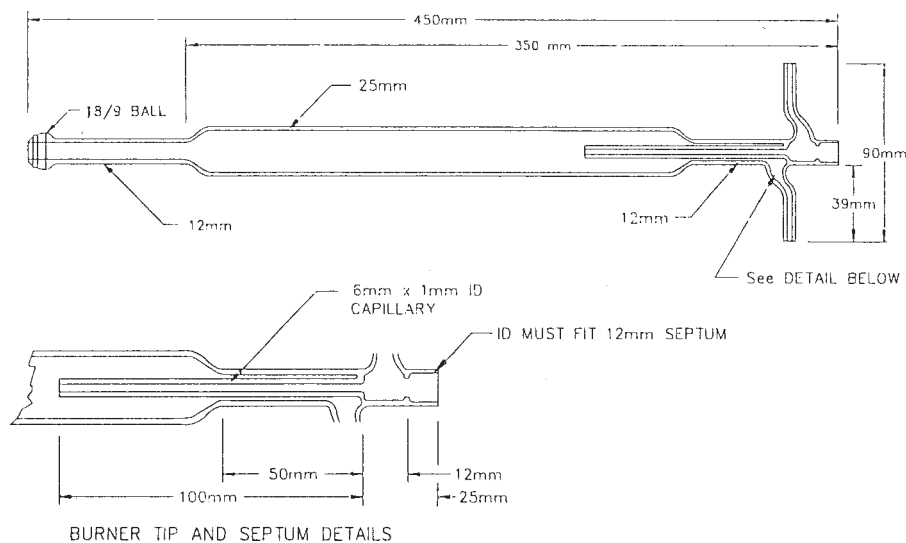


FIG. 1 Direct Inject Quartz Pyrolysis Tube

inlet end of the tube is large enough to accommodate a quartz sample boat. The combustion tube must have side arms for the introduction of oxygen and carrier gas. The oxidation section shall be large enough (see Figs. 1 and 2) to ensure complete combustion of the sample. Figs. 1 and 2 depict conventional combustion tubes. Other configurations are acceptable if precision is not degraded.

5.3 *Flow Control*—The apparatus must be equipped with flow controllers capable of maintaining a constant supply of oxygen and carrier gas.

5.4 *Drier Tube*—The apparatus must be equipped with a mechanism for the removal of water vapor. The oxidation reaction produces water vapor which must be eliminated prior to measurement by the detector. This can be accomplished with a membrane drying tube, or a *permeation dryer*, that utilizes a selective capillary action for water removal.

5.5 *UV Fluorescence Detector*—A qualitative and quantitative detector capable of measuring light emitted from the fluorescence of sulfur dioxide by UV light.

5.6 *Microlitre Syringe*—A microlitre syringe capable of accurately delivering 5 to 20- μ L quantities. The needle shall be 50 mm (± 5 mm) long.

5.7 *Sample Inlet System*—Either of two types of sample inlet systems can be used.

5.7.1 *Direct Injection*—A direct injection inlet system must be capable of allowing the quantitative delivery of the material to be analyzed into an inlet carrier stream which directs the sample into the oxidation zone at a controlled and repeatable rate. A syringe drive mechanism which discharges the sample from the microlitre syringe at a rate of approximately 1 μ L/s is required. See example, Fig. 3.

5.7.2 *Boat Inlet System*—An extended combustion tube provides a seal to the inlet of the oxidation area and is swept by a carrier gas. The system provides an area to position the sample carrying mechanism (boat) at a retracted position removed from the furnace. The boat drive mechanism will fully insert the boat into the hottest section of the furnace inlet. The sample boats and combustion tube are constructed of quartz. The combustion tube provides a cooling jacket for the

area in which the retracted boat rests awaiting sample introduction from a microlitre syringe. A drive mechanism which advances and withdraws the sample boat into and out of the furnace at a controlled and repeatable rate is required. See example, Fig. 4.

5.8 *Refrigerated Circulator*—An adjustable apparatus capable of delivering a coolant material at a constant temperature as low as 4°C could be required when using the boat inlet injection method (optional).

5.9 *Strip Chart Recorder*, (optional).

5.10 *Balance*, with a precision of ± 0.01 mg (optional).

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Inert Gas*—Argon or helium only, high purity grade (that is, chromatography or zero grade), 99.998 % minimum purity, moisture 5 ppm w/w maximum.

6.3 *Oxygen*—High purity (that is, chromatography or zero grade), 99.75 % minimum purity, moisture 5 ppm w/w maximum, dried over molecular sieves. (**Warning**—Vigorously accelerates combustion.)

6.4 *Toluene, Xylenes, Isooctane*, reagent grade (other solvents similar to those occurring in samples to be analyzed are also acceptable). Correction for sulfur contribution from solvents (solvent blank) used in standard preparation and sample

⁵ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

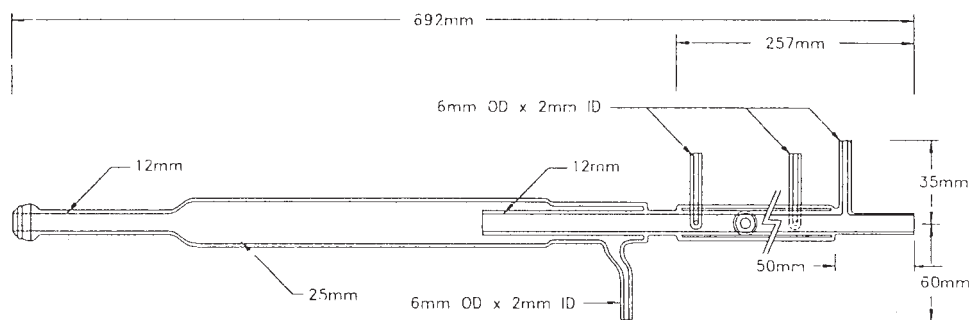


FIG. 2 Boat Inlet

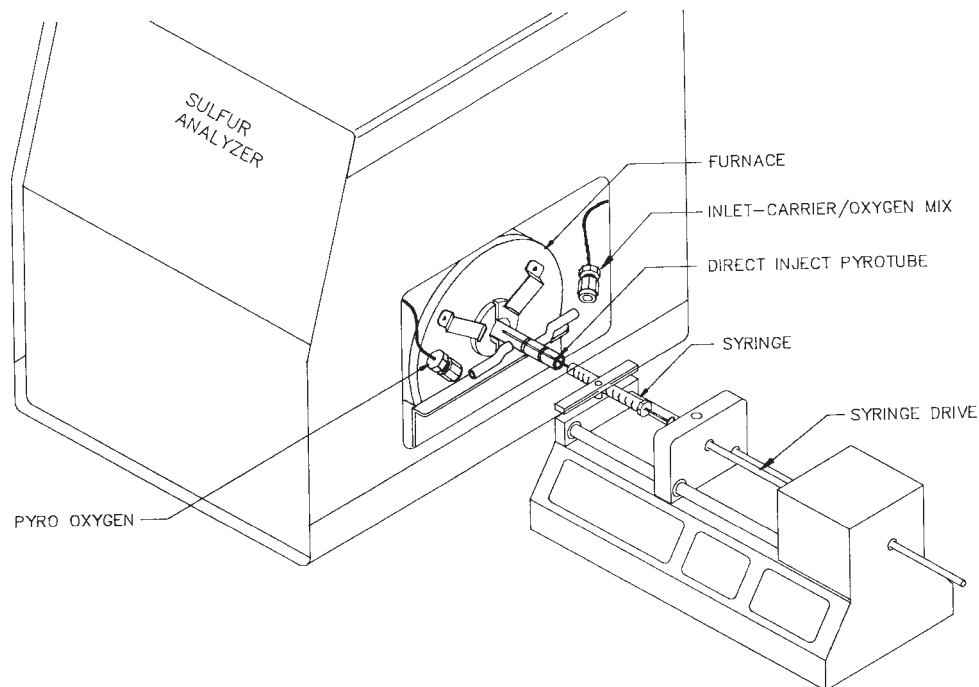


FIG. 3 Direct Inject Syringe Drive

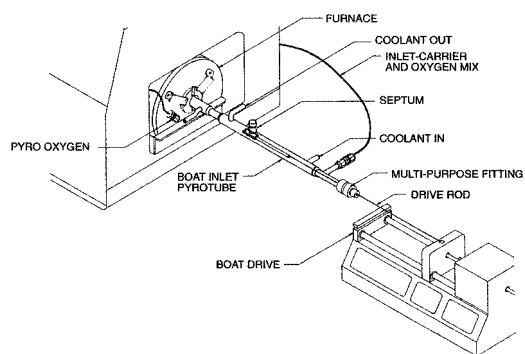


FIG. 4 Boat Inlet System

specimen dilution is required. Alternatively, use of a solvent with nondetectable level of sulfur contamination relative to the sulphur content in the sample unknown makes the blank correction unnecessary. (**Warning**—Flammable solvents.)

6.5 *Dibenzothiophene*, FW184.26, 17.399 % (m/m) S (Note 2).

6.6 *Butyl Sulfide*, FW146.29, 21.92 % (m/m) S (Note 2).

6.7 *Thionaphthene (Benzothiophene)*, FW134.20, 23.90 % (m/m) S (Note 2).

NOTE 2—A correction for chemical impurity can be required.

6.8 *Quartz Wool*:

6.9 *Sulfur Stock Solution*, 1000 µg S/mL—Prepare a stock solution by accurately weighing approximately 0.5748 g of dibenzothiophene or 0.4652 g of butyl sulfide or 0.4184 g of thionaphthene into a tared 100 mL volumetric flask. Dilute to volume with selected solvent. This stock can be further diluted to desired sulfur concentration (Notes 3-5).

NOTE 3—Working standards should be remixed on a regular basis depending upon frequency of use and age. Typically, stock solutions have a useful life of about 3 months.

NOTE 4—Calibration standards can be prepared and diluted on a mass/mass basis when result calculations are adjusted to accommodate them.

NOTE 5—Calibration standards from commercial sources can be used if checked for accuracy and if precision is not degraded.

6.10 *Quality Control (QC) Samples*, preferably are portions of one or more liquid petroleum materials that are stable and representative of the samples of interest. These QC samples

TABLE 1 Typical Operating Conditions

Syringe drive (direct inject) drive rate (700–750)	1 $\mu\text{L/s}$
Boat drive (boat inlet) drive rate (700–750)	140–160 mm/min
Furnace temperature	1075 \pm 25°C
Furnace oxygen flowmeter setting (3.8–4.1)	450–500 mL/min
Inlet oxygen flowmeter setting (0.4–0.8)	10–30 mL/min
Inlet carrier flowmeter setting (3.4–3.6)	130–160 mL/min

can be used to check the validity of the testing process as described in Section 14.

7. Hazards

7.1 High temperature is employed in this test method. Extra care must be exercised when using flammable materials near the oxidative pyrolysis furnace.

8. Sampling

8.1 Obtain a test unit in accordance with Practice D 4057 or Practice D 4177. To preserve volatile components which are in some samples, do not uncover samples any longer than necessary. Samples shall be analyzed as soon as possible after taking from bulk supplies to prevent loss of sulfur or contamination due to exposure or contact with sample container. (**Warning**—Samples that are collected at temperatures below room temperature can undergo expansion and rupture the container. For such samples, do not fill the container to the top; leave sufficient air space above the sample to allow room for expansion.)

8.2 If the test unit is not used immediately, then thoroughly mix in its container prior to taking a test specimen.

9. Preparation of Apparatus

9.1 Assemble and leak check apparatus according to manufacturer's instructions.

9.2 Adjust the apparatus, depending upon the method of sample introduction, to meet conditions described in Table 1.

9.3 Adjust the instrument sensitivity and baseline stability and perform instrument blanking procedures following manufacturer's guidelines.

10. Calibration and Standardization

10.1 Based on anticipated sulfur concentration, select one of the suggested curves outlined in Table 2. Carefully prepare a series of calibration standards accordingly. Make other volumetric dilutions of the stock solution to cover the various ranges of operation within these calibration curve guidelines. The number of standards used per curve can vary, if equivalent results are obtained.

10.2 Flush the microlitre syringe several times with the sample prior to analysis. If bubbles are present in the liquid column, flush the syringe and withdraw a new sample.

10.3 A sample size recommended for the curve selected from Table 2 must be quantitatively measured prior to injection into the combustion tube or delivery into the sample boat for analysis (Note 6 and Note 7). There are two alternative techniques available.

NOTE 6—Injection of a constant or similar sample size for all materials analyzed in a selected operating range promotes consistent combustion conditions.

TABLE 2 Sulfur Standards

Curve I Sulfur, ng/ μL	Curve II Sulfur, ng/ μL	Curve III Sulfur, ng/ μL
0.50	5.00	100.00
1.00	25.00	500.00
2.50	50.00	1000.00
5.00	100.00	
10.00		
Injection Size 10–20 μL	Injection Size 5–10 μL	Injection Size 5 μL

NOTE 7—Injection of 10 μL of the 100 ng/ μL standard would establish a calibration point equal to 1000 ng or 1.0 μg .

10.3.1 The volumetric measurement of the injected material can be obtained by filling the syringe to the selected level. Retract the plunger so that air is aspirated and the lower liquid meniscus falls on the 10 % scale mark and record the volume of liquid in the syringe. After injection, again retract the plunger so that the lower liquid meniscus falls on the 10 % scale mark and record the volume of liquid in the syringe. The difference between the two volume readings is the volume of sample injected (Note 8).

NOTE 8—An automatic sampling and injection device can be used in place of the described manual injection procedure.

10.3.2 Fill the syringe as described in 10.3.1. Weigh the device before and after injection to determine the amount of sample injected. This procedure can provide greater accuracy than the volume delivery method, provided a balance with a precision of ± 0.01 mg is used.

10.4 Once the appropriate sample size has been measured into the microlitre syringe, promptly and quantitatively deliver the sample into the apparatus. Again, there are two alternative techniques available.

10.4.1 For direct injection, carefully insert the syringe into the inlet of the combustion tube and the syringe drive. Allow time for sample residues to be burned from the needle (Needle Blank). Once a stable baseline has reestablished, promptly start the analysis. Remove syringe once the apparatus has returned to a stable baseline.

10.4.2 For the boat inlet, quantitatively discharge the contents of the syringe into the boat containing quartz wool at a slow rate being careful to displace the last drop from the syringe needle. Remove the syringe and promptly start the analysis. The instrument baseline shall remain stable until the boat approaches the furnace and vaporization of the sample begins. Instrument baseline is to be reestablished before the boat has been completely withdrawn from the furnace (Note 9). Once the boat has reached its fully retracted position, allow at least 1 min for cooling before the next sample injection (Note 9).

NOTE 9—Slowing boat speed or briefly pausing the boat in the furnace can be necessary to ensure complete sample combustion. Direct injection can ease sample handling and improve sample combustion characteristics for materials containing very volatile sulfur compounds.

10.4.3 The level of boat cooling required and the onset of sulfur detection following sample injection are directly related to the volatility of the materials analyzed. For volatile materials, effective cooling of the sample boat prior to sample

injection is essential. The use of a refrigerated circulator to minimize the vaporization of the sample until the boat begins approaching the furnace or an increased time for boat cooling can be required.

10.5 Calibrate the instrument using one of the following two techniques.

10.5.1 Perform measurements for the calibration standards and blank using one of the procedures described in 10.2-10.4. Measure the calibration standards and blank three times. Subtract the average response of the blank injections from each calibration standard response. Then determine the average integrated response of each concentration (see 6.4). Construct a curve plotting of the average integrated detector response (*y*-axis) versus micrograms of sulfur injected (*x*-axis) (Note 10). This curve shall be linear and system performance must be checked each day of use. See Section 14.

NOTE 10—Other calibration curve techniques can be used when accuracy and precision are not degraded.

10.5.2 If the apparatus features self calibration routine, measure the calibration standards and blank three times using one of the procedures described in 10.2-10.4. If blank correction is required and is not an available instrument option (see 6.4 or 10.5.1), calibrate the analyzer in accordance with manufacturer's instructions to yield results expressed as nanograms of sulfur (Note 10). This curve shall be linear and system performance must be checked with each day of use (see Section 14).

10.6 If analyzer calibration is performed using a different calibration curve than listed in Table 2, select an injection size based on the curve closest in concentration to the measured solution(s). Construct the calibration curve to yield values that can be used to report sulfur content on a mass/mass basis.

11. Procedure

11.1 Obtain a test specimen using the procedure described in Section 8. The sulfur concentration in the test specimen must be less than the concentration of the highest standard and greater than the concentration of the lowest standard used in the calibration. If required, a dilution can be performed on either a weight or volume basis.

11.1.1 *Gravimetric Dilution (mass/mass)*—Record the mass of the test specimen and the total mass of the test specimen and solvent.

11.1.2 *Volumetric Dilution (mass/volume)*—Record the mass of the test specimen and the total volume of the test specimen and solvent.

11.2 Measure the response for the test specimen solution using one of the procedures described in 10.2-10.4.

11.3 Inspect the combustion tube and other flow path components to verify complete oxidation of the test specimen.

11.3.1 *Direct Inject Systems*—Reduce the sample size or the rate of injection, or both, of the specimen into the furnace if coke or sooting is observed.

11.3.2 *Boat Inlet Systems*—Increase the residence time for the boat in the furnace if coke or soot is observed on the boat. Decrease the boat drive introduction rate or specimen sample size, or both, if coke or soot is observed on the exit end of the combustion tube.

11.3.3 *Cleaning and Recalibration*—Clean any coked or sooted parts per manufacturer's instructions. After any cleaning or adjustment, assemble and leak check the apparatus. Repeat instrument calibration prior to reanalysis of the test specimen.

11.4 To obtain one result, measure each test specimen solution three times and calculate the average detector responses.

11.5 Density values needed for calculations are to be measured using Test Methods D 1298, D 4052, or equivalent, at the temperature at which the sample was tested.

12. Calculation

12.1 For analyzers calibrated using a standard curve, calculate the sulfur content of the test specimen in parts per million (ppm) as follows:

$$\text{Sulfur, ppm } (\mu\text{g/g}) = \frac{(I - Y)}{S \times M \times K_g} \quad (1)$$

or,

$$\text{Sulfur, ppm } (\mu\text{g/g}) = \frac{(I - Y(1000))}{S \times V \times K_v} \quad (2)$$

where:

- D* = density of test specimen solution, g/mL,
- I* = average of integrated detector response for test specimen solution, counts,
- K_g* = gravimetric dilution factor, mass of test specimen/mass of test specimen and solvent, g/g,
- K_v* = volumetric dilution factor, mass of test specimen/volume of test specimen and solvent, g/mL,
- M* = mass of test specimen solution injected, either measured directly or calculated from measured volume injected and density, $V \times D$, g,
- S* = slope of standard curve, counts/ $\mu\text{g S}$,
- V* = volume of test specimen solution injected, either measured directly or calculated from measured mass injected and density, M/D , μL , and
- Y* = *y*-intercept of standard curve, counts,
- 1000 = factor to convert μL to mL.

12.2 For analyzers calibrated using self calibration routine with blank correction, calculate the sulfur in the test specimen in parts per million (ppm) as follows:

$$\text{Sulfur, ppm } (\mu\text{g/g}) = \frac{G \times 1000}{M \times K_g} \quad (3)$$

or,

$$\text{Sulfur, ppm } (\mu\text{g/g}) = \frac{G \times 1000}{V \times D} \quad (4)$$

where:

- D* = density of test specimen solution, mg/ μL (neat injection), or concentration of solution, mg/ μL (volumetric dilute injection),
- K_g* = gravimetric dilution factor, mass of test specimen/mass of test specimen and solvent, g/g,
- M* = mass of test specimen solution injected, either measured directly or calculated from measured volume injected and density, $V \times D$, mg,

- V = volume of test specimen solution injected, either measured directly or calculated from measured mass injected and density, M/D , μL ,
 G = sulfur found in test specimen, μg , and
 1000 = factor to convert $\mu\text{g}/\text{mg}$ to $\mu\text{g}/\text{g}$.

13. Report

13.1 For results equal to or greater than 10 mg/kg, report the sulfur result to the nearest mg/kg. For results less than 10 mg/kg, report the sulfur result to the nearest tenth of a mg/kg. State that the results were obtained according to Test Method D 5453.

14. Quality Control

14.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample (6.10) after each calibration and at least each day of use thereafter (see 10.5).

14.1.1 When QC/Quality Assurance (QA) protocols are already established in the testing facility, these can be used when they confirm the reliability of the test result.

14.1.2 When there is no QC/QA protocol established in the testing facility, Appendix X1 can be used as the QC/QA system.

15. Precision and Bias

15.1 The test method was examined in five separate inter-laboratory studies.^{6,7} The precision of the test method, as obtained by statistical analysis of test results, is as follows (Note 11).

NOTE 11—Volatile materials can cause a deterioration in precision when not handled with care (see Section 8 and 10.4).

15.1.1 *Repeatability*—The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in only 1 case in 20, where x = the average of the two test results.

⁶ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Reports RR:D02-1307 (1992) original with multiple matrices; RR:D02-1456 (1999) UVF/X-ray equivalence study; RR:D02-1465 (1997) gasoline and RFG only; and RR:D02-1475 (1998) low level gasoline, diesel, and biodiesel.

⁷ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1547 (2000-2001) involving 39 labs and 16 samples each of low level gasoline (1–100 $\mu\text{g}/\text{g}$ S) and diesel (5–40 $\mu\text{g}/\text{g}$ S) based on practical limits of quantitation (PLOQ) determined in the study.

TABLE 3 Repeatability (r) and Reproducibility (R)

Concentration (mg/kg S)	r	R
1	0.2	0.6
5	0.6	1.9
10	1.0	3.3
50	3.4	10.9
100	5.7	18.3
400	16.0	51.9

$$\text{Less than 400 mg/kg: } r = 0.1788 X^{(0.75)} \quad (5)$$

$$\text{Greater than 400 mg/kg: } r = 0.02902 X \quad (6)$$

15.1.1.1 Research Report RR:D02-1547 (2000-2001) results:⁷

$$\text{Gasoline: } r = 0.04356 (X + 14.844) \quad (7)$$

$$\text{Diesel: } r = 0.02777 (X + 28.158) \quad (8)$$

15.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in only 1 case in 20, where x = the average of the two test results.

$$\text{Less than 400 mg/kg: } R = 0.5797 X^{(0.75)} \quad (9)$$

$$\text{Greater than 400 mg/kg: } R = 0.1267 X \quad (10)$$

15.1.2.1 Research Report RR:D02-1547 (2000-2001) results:⁷

$$\text{Gasoline: } R = 0.3170 (X + 6.8847) \quad (11)$$

$$\text{Diesel: } R = 0.3659 (X + 2.1101) \quad (12)$$

15.2 *Bias*—The bias of this test method was determined in a 1992 research report,⁶ by analysis of standard reference materials (SRMs) containing known levels of sulfur in hydrocarbon. This report indicated that the results obtained on the SRMs were within the repeatability of the test method.

15.2.1 Three National Institute of Standards and Technology (NIST) Standard Reference Materials (SRM) were analyzed to determine the bias. These samples were gasoline SRMs 2298 (4.6 $\mu\text{g}/\text{g}$ S) and 2299 (13.6 $\mu\text{g}/\text{g}$ S), and diesel SRM 2723a (10 $\mu\text{g}/\text{g}$ S). There was no significant bias for the diesel SRM, but there was a bias of -0.97 and -2.00 for gasoline SRMs 2298 and 2299, respectively.⁷

15.3 Examples of the above precision estimates for samples containing less than 400 mg/kg are shown in Table 3.

16. Keywords

16.1 analysis; diesel; fluorescence; gasoline; jet fuel; kerosene; M-85; RFG; sulfur; ultraviolet

APPENDIXES
(Nonmandatory Information)
X1. QUALITY CONTROL

X1.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample.

X1.2 Prior to monitoring the measurement process, the user of the test method needs to determine the average value and control limits of the QC sample (see Test Method D 6299 and MNL 7).⁸

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process (see Test Method D 6299 and MNL 7). Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument re-calibration.

X1.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample is analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be checked against the ASTM test method precision to ensure data quality.

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogeneous and stable under the anticipated storage conditions. See Test Method D 6299 and MNL 7 for further guidance on QC and control charting techniques.

⁸ ASTM MNL 7, Manual on Presentation of Data Control Chart Analysis, 6th ed., available from ASTM Headquarters.

X2. IMPORTANT FACTORS IN DIRECT INJECTION ANALYSIS OF HYDROCARBONS USING TEST METHOD D 5453 (SULFUR)

X2.1 *Furnace Temperature*—A temperature of 1075 ± 25°C is required for sulfur. The use of quartz chips in the combustion zone of the pyrotube is required.

X2.2 *Needle Tip Position during Injection*—The needle tip should be presented fully into the hottest part of the inlet area of the furnace. Assembly of apparatus to manufacturer's specification and full insertion of the needle will ensure this.

X2.3 *Injection Peak/Needle Blank*—Avoid integration of any baseline upset caused by the needle penetration of the septum. After the sample specimen has been measured into the syringe, retract the plunger to form an air gap up to approximately the 10 % scale mark of the syringe barrel. Insert the syringe needle into the injection inlet and allow the needle/septum blank to dissipate. Reset the instrument baseline or enable integration, if required, prior to the injection of the syringe contents.

X2.4 *Residence Time of Needle in Furnace*—Residence time of the needle in the furnace must be consistent following the injection of the sample. For direct injections it is recommended that the needle remain in the furnace until the instrument returns to baseline and the analysis of the injected material is complete.

X2.5 *Injection Size*—As a general rule, larger sample sizes are required for measurement of lower levels of sulfur. While determining the best sample size, frequently check for evidence of incomplete combustion (sooting) that may be present

in the sample path. Control sooting by slowing the injection rate of the sample from the syringe, or increasing the pyro-oxygen or inlet oxygen supply, or a combination thereof. Suggested sample sizes are as follows:

Trace to 5 mg/kg	10 to 20 µL
5 ppm to 100 mg/kg	5 to 10 µL
100 mg/kg to %	5 µL

X2.6 *Injection Rate and Frequency*—Discharge contents of the syringe into the furnace at a slow rate, approximately one µL/s (Model 735 Sample Drive rate of 700 to 750). Frequency of injection can vary depending upon sample and syringe handling techniques, rate of injection and needle in furnace residence time. Typical injection frequency allows at least 3.5 min between injections.

X2.7 *Flow Path, Leak Check, and Back Pressure*—The sample flow path must be leak free when pressure tested in accordance with the manufacturers recommended procedure (2-3 psi). Flow path back pressure during normal operation can range from 0.75 to 2.00 psi.

X2.8 *Gas Flow Settings*—Gas supplies to various points in the sample path must be consistently controlled to allow for smooth, complete combustion of the sample. See Table X2.1.

X2.9 *Membrane Dryer Purge*—Water produced during the combustion of the sample is removed by the membrane dryer. This water must then be purged from the membrane dryer. For an apparatus that utilizes a desiccant scrubber (flow recycle) to

TABLE X2.1 Gas Flow Settings—Direct Injection Analysis

Typical Gas Flows	Flowmeter Ball	MFC
Inlet carrier flowmeter settings ^A	3.4-3.6	140-160 mL/min
Inlet oxygen flowmeter setting	0.4-0.6	10-20 mL/min
Furnace oxygen flowmeter setting	3.8-4.1	450-500 mL/min
Ozone generator flowmeter setting ^B	1.5-1.7	35-45 mL/min

^A Helium or argon may be used as a carrier gas.

^B Flow to ozone generator (optional).

provide the membrane dryer purge gas, replace the drying agent when color change (blue to pink) indicates. When an auxiliary gas flow is used, set membrane dryer purge flow at 200 to 250 mL/min.

X2.10 Sample Homogeneity/Calibration Response—Prior to analysis, mix samples and calibration materials well. Minimum detector response; (Model 7000) should be no less than 2000 to 3000 counts, (Model 9000) should be no less than 200 to 300 counts or three times baseline noise, for the lowest point on the calibration curve. The highest point on the curve is below the saturation point of the detector; use a maximum response of 350 000 to 450 000 counts (Model 7000) as a guideline. The Model 9000 should not have flat-top peaks. Adjust Gain Factor, PMT voltage or sample size, or both, accordingly.

X3. IMPORTANT FACTORS IN BOAT-INLET ANALYSIS OF HYDROCARBONS USING TEST METHOD D 5453 (SULFUR)

X3.1 Furnace Temperature—A temperature of 1075 ± 25°C is required for sulfur. The use of quartz chips in the combustion zone of the pyrotube is required.

X3.2 Boat Path—The boat should be presented fully into the inlet area of the furnace. Assembly of the apparatus to the manufacturer’s specification ensures this.

X3.3 Boat Entry Rate and Residence Time of Sample in Furnace—Insert the boat into the furnace using a drive rate of 140 to 160 mm/min (Model 735 setting of 700-750). Additional slowing of boat speed or a brief pause of the boat in the furnace may be necessary to ensure complete sample combustion. The boat should emerge from the furnace soon after detection is complete. Boat in furnace residence times can vary depending on sample volatility and levels of element measured. Typical boat in furnace residence times range between 15 to 60 s.

X3.4 Injection Size—As a general rule larger sample sizes may be required for measurement of lower concentration levels. While determining the best sample size, frequently check for evidence of incomplete combustion (sooting) that may be present in the sample path. Control sooting by slowing boat speed into the furnace, increasing the length of time the boat is in the furnace or increasing the pyro-oxygen supply, or both. Suggested sample sizes are as follows:

Trace to 5 mg/kg	10 to 20 µL
5 ppm to 100 mg/kg	5 to 10 µL
100 mg/kg to %	5 µL

X3.5 Injection Rate and Frequency—Discharge contents of

X2.11 Baseline Stability—Prior to analysis, especially when analyzing low levels, be certain that the detector baselines are stable and noise free. For a given gain factor, photomultiplier tube voltage may be adjusted to ensure maximum sensitivity while maintaining a stable, noise-free baseline. Model 9000 users can utilize the baseline evaluate and peak threshold functions to reduce baseline noise.

X2.12 Calibration Materials/ Standard Curve Construction—Prepare calibration standards with solvent materials that have minimum or no sulfur contamination relative to the concentration anticipated in the sample unknown. Correct for sulfur contribution from solvent materials and impurity of source material. Use calibration curves that bracket the expected levels in the sample unknown. Do not force the calibration curve through the 0,0 axis, unnecessarily. Construct standard concentrations that will yield a calibration curve that is linear and that does not exceed the dynamic range of the detector [use a correlation coefficient of .999 and 1 to 2 orders of magnitude (example: 5 to 100 mg/kg) as a guideline]. The curve should yield an estimated value that can be used to calculate content in the sample on a mass/mass basis.

the syringe into the boat at a slow rate (approximately 1 µL/s) being careful to discharge the last drop. Use of quartz wool in the sample boat to aid quantitative delivery is advised. Frequency of injection can vary depending upon boat speed, level of sulfur being determined, furnace residence time, and cooling capacity of the boat loading area. Typical injection frequency allows at least 2.5 min between injections.

X3.6 Boat Temperature at Time of Sample Introduction—Sample volatility must be addressed; ensure boat temperature has returned to ambient or sub-ambient temperatures prior to introduction of sample into boat. Let boat rest at least 60 s in coolant jacket or cooling area between injections. Some sulfur may be measured as the sample evaporates when the boat approaches the furnace. Sub-ambient temperature can reduce this evaporation.

X3.7 Sample Flow Path: Leak Check and Back Pressure—The sample flow path must be leak free when pressure tested in accordance with the manufacturer’s recommended procedure (2 to 3 psi). Flow path back pressure during normal operation can range from 0.75 to 2.00 PSI, for non-atmospheric-vent systems.

X3.8 Gas Flow Settings—Gas supplies to various points in the sample path must be consistently controlled to allow for smooth, complete combustion of the sample.

X3.9 Membrane Dryer Purge—Water produced during the combustion of the sample is removed by the membrane dryer. This water must then be purged. For an apparatus that utilizes



TABLE X3.1 Gas Flow Settings—Boat Inlet Analysis

Typical Gas Flows	Flowmeter Ball	MFC
Inlet carrier flowmeter settings ^A	3.4-3.6	130-160 mL/min
Inlet oxygen flowmeter setting	0.4-0.6	10-20 mL/min
Furnace oxygen flowmeter setting	3.8-4.1	450-500 mL/min
Ozone generator flowmeter setting ^B	1.5-1.7	35-45 mL/min

^A Helium or argon may be used as a carrier gas.

^B Flow to ozone generator (optional).

a desiccant scrubber (flow recycle) to provide the membrane dryer purge gas, replace the drying agent when color change (blue to pink) indicates. When an auxiliary gas flow is used, set membrane dryer purge flow at 200 to 250 mL/min.

X3.10 *Sample Homogeneity/Calibration Response*—Prior to analysis, mix samples and calibration materials well. Minimum detector response; (Model 7000) should be no less than 2000 to 3000 counts, (Model 9000) should be no less than 200 to 300 counts or three times baseline noise, for the lowest point on the calibration curve. The highest point on the curve is below the saturation point of the (Model 9000) detector; use a maximum response of 350 000 to 450 000 counts (Model 7000) as a guideline. Adjust Gain Factor, PMT Voltage and/or sample size accordingly.

X3.11 *Boat Blank/Baseline Stability*—Prior to analysis, especially when analyzing low levels, advance the empty boat

into furnace to ensure that no contamination is present in the boat or on the inside areas of the pyrotube near the injection area. Heat empty boat in the furnace to ensure that boat is clean, then rapidly move boat out to injection area.

NOTE X3.1—If the hot boat being returned to the injection area causes baseline upset, repeat the boat in and out cycle, until no sulfur is measured. For a given gain factor, photomultiplier tube voltage, can be adjusted to ensure maximum sensitivity while maintaining a stable, noise-free baseline. Model 9000 users can utilize the baseline evaluate and peak threshold functions to reduce baseline noise.

X3.12 *Calibration Materials/ Standard Curve Construction*—Prepare calibration standards with solvent materials that have minimum or no sulfur contamination relative to the concentration anticipated in the sample unknown. Correct for sulfur contribution from solvent materials and impurity of sulfur source material. Use calibration curves that bracket the expected levels in the sample unknown. Do not force the calibration curve through the 0,0 axis, unnecessarily. Construct standard concentrations that will yield a calibration curve that is linear and that does not exceed the dynamic range of the detector (use a correlation coefficient of 0.999 and 1 to 2 orders of magnitude (example: 5 to 100 mg/kg) as a guideline). The curve should yield an estimated value that can be used to calculate content in the sample on a mass/mass basis.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D 5453–03) that may impact the use of this standard.

(1) Updated Section 15, Precision and Bias, to incorporate results obtained in a low level sulfur interlaboratory study.

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D 5453–00^{e1}) that may impact the use of this standard.

(1) Changed the test method title to state motor oil.

(3) Added Section 13, Report.

(2) Updated and expanded applicable materials described in Section 1, Scope.

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Designation: D 664 – 04

An American National Standard
British Standard 4457



Designation 177/96

Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration¹

This standard is issued under the fixed designation D 664; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope*

1.1 This test method covers procedures for the determination of acidic constituents in petroleum products and lubricants soluble or nearly soluble in mixtures of toluene and propan-2-ol. It is applicable for the determination of acids whose dissociation constants in water are larger than 10^{-9} ; extremely weak acids whose dissociation constants are smaller than 10^{-9} do not interfere. Salts react if their hydrolysis constants are larger than 10^{-9} . The range of acid numbers included in the precision statement is 0.1 mg/g KOH to 150 mg/g KOH.

NOTE 1—In new and used oils, the constituents that may be considered to have acidic characteristics include organic and inorganic acids, esters, phenolic compounds, lactones, resins, salts of heavy metals, salts of ammonia and other weak bases, acid salts of polybasic acids, and addition agents such as inhibitors and detergents.

1.2 The test method may be used to indicate relative changes that occur in oil during use under oxidizing conditions regardless of the color or other properties of the resulting oil. Although the titration is made under definite equilibrium conditions, the test method is not intended to measure an absolute acidic property that can be used to predict performance of oil under service conditions. No general relationship between bearing corrosion and acid number is known.

NOTE 2—The acid number obtained by this standard may or may not be numerically the same as that obtained in accordance with Test Methods D 974 and D 3339. There has not been any attempt to correlate this method with other non-titration methods.

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

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

2. Referenced Documents²

2.1 ASTM Standards:

- D 974 Test Method for Acid and Base Number by Color-Indicator Titration
- D 1193 Specification for Reagent Water
- D 3339 Test Method for Acid Number of Petroleum Products by Semi-Micro Color Indicator Titration
- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products
- D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

3. Terminology

3.1 Definitions:

3.1.1 *acid number, n*—the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample in a specified solvent to a specified end point.

3.1.1.1 *Discussion*—This test method expresses the quantity of base as milligrams of potassium hydroxide per gram of sample, that is required to titrate a sample in a mixture of toluene and propan-2-ol to which a small amount of water has been added from its initial meter reading in millivolts to a meter reading in millivolts corresponding to an aqueous basic buffer solution or a well-defined inflection point as specified in the test method.

3.1.1.2 *Discussion*—This test method provides additional information. The quantity of base, expressed as milligrams of

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.06 on Analysis of Lubricants.

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This test method was adopted as a joint ASTM-IP standard in 1964. ASTM Test Method D 4739 has been developed as an alternative to the base number portion of D 664.

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

*A Summary of Changes section appears at the end of this standard.

potassium hydroxide per gram of sample, required to titrate a sample in the solvent from its initial meter reading in millivolts to a meter reading in millivolts corresponding to a freshly prepared aqueous acidic buffer solution or a well-defined inflection point as specified in the test method shall be reported as the *strong acid number*.

3.1.1.3 *Discussion*—The causes and effects of the so-called strong acids and the causes and effects of the other acids can be very significantly different. Therefore, the user of this test method shall differentiate and report the two, when they are found.

4. Summary of Test Method

4.1 The sample is dissolved in a mixture of toluene and propan-2-ol containing a small amount of water and titrated potentiometrically with alcoholic potassium hydroxide using a glass indicating electrode and a reference electrode or a combination electrode. The meter readings are plotted manually or automatically against the respective volumes of titrating solution and the end points are taken only at well-defined inflections in the resulting curve. When no definite inflections are obtained and for used oils, end points are taken at meter readings corresponding to those found for aqueous acidic and basic buffer solutions.

5. Significance and Use

5.1 New and used petroleum products may contain acidic constituents that are present as additives or as degradation products formed during service, such as oxidation products. The relative amount of these materials can be determined by titrating with bases. The acid number is a measure of this amount of acidic substance in the oil, always under the conditions of the test. The acid number is used as a guide in the quality control of lubricating oil formulations. It is also sometimes used as a measure of lubricant degradation in service. Any condemning limits must be empirically established.

5.2 Since a variety of oxidation products contribute to the acid number and the organic acids vary widely in corrosion properties, the test method cannot be used to predict corrosiveness of oil under service conditions. No general correlation is known between acid number and the corrosive tendency of oils toward metals.

6. Apparatus

6.1 *Manual Titration Apparatus:*

6.1.1 *Meter*, a voltmeter or a potentiometer that will operate with an accuracy of ± 0.005 V and a sensitivity of ± 0.002 V over a range of at least ± 0.5 V when the meter is used with the electrodes specified in 6.1.2 and 6.1.3 and when the resistance between the electrodes falls within the range from 0.2 to 20 M Ω . The meter shall be protected from stray electrostatic fields so that no permanent change in the meter readings over the entire operating range is produced by touching, with a grounded lead, any part of the exposed surface of the glass electrode, the glass electrode lead, the titration stand, or the meter.

NOTE 3—A suitable apparatus could consist of a continuous-reading

electronic voltmeter designed to operate on an input of less than 5×10^{-12} A, when an electrode system having 1000-M Ω resistance is connected across the meter terminals and provided with a metal shield connected to the ground, as well as a satisfactory terminal to connect the shielded connection wire from the glass electrode to the meter without interference from any external electrostatic field.

6.1.2 *Sensing Electrode*, Standard pH, suitable for non-aqueous titrations.

6.1.3 *Reference Electrode*, Silver/Silver Chloride (Ag/AgCl) Reference Electrode, filled with 1M–3M LiCl in ethanol.

6.1.3.1 *Combination Electrodes*—Sensing electrodes may have the Ag/AgCl reference electrode built into the same electrode body, which offers the convenience of working with and maintaining only one electrode. The combination electrode shall have a sleeve junction on the reference compartment and shall use an inert ethanol electrolyte, for example, 1M–3M LiCl in ethanol. These combination electrodes shall have the same response or better response than a dual electrode system. They shall have removable sleeves for easy rinsing and addition of electrolyte.

NOTE 4—A third electrode, such as a platinum electrode, may be used to increase the electrode stability in certain systems.

6.1.4 *Variable-Speed Mechanical Stirrer*, a suitable type, equipped with a propeller-type stirring paddle. The rate of stirring shall be sufficient to produce vigorous agitation without spattering and without stirring air into the solution. A propeller with blades 6 mm in radius and set at a pitch of 30 to 45° is satisfactory. A magnetic stirrer is also satisfactory.

6.1.4.1 If an electrical stirring apparatus is used, it shall be electrically correct and grounded so that connecting or disconnecting the power to the motor will not produce a permanent change in the meter reading during the course of the titration.

6.1.5 *Burette*, 10-mL capacity, graduated in 0.05-mL divisions and calibrated with an accuracy of ± 0.02 mL. The burette shall have a tip that extends 100 to 130 mm beyond the stopcock and shall be able to deliver titrant directly into the titration vessel without exposure to the surrounding air or vapors. The burette for KOH shall have a guard tube containing soda lime or other CO₂-absorbing substance.

6.1.6 *Titration Beaker*, 250 mL capacity, made of borosilicate glass or other suitable material.

6.1.7 *Titration Stand*, suitable for supporting the electrodes, stirrer, and burette.

NOTE 5—An arrangement that allows the removal of the beaker without disturbing the electrodes and stirrer is desirable.

6.2 *Automatic Titration Apparatus:*

6.2.1 Automatic titration systems shall be able to carry out the necessary analyses as prescribed in the method. As a minimum, the automatic titration system shall meet the performance and specification requirements listed in 6.1 as warranted.

6.2.2 A dynamic mode of titrant addition shall be used. During the titration, the speed and volume of the addition shall vary depending on the rate of change of the system. The recommended maximum volume increment is 0.5 mL and the recommended minimum volume increment is 0.05 mL.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available.³ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.1.1 Commercially available solutions may be used in place of laboratory preparations provided the solutions have been certified as being equivalent.

7.1.2 Alternate volumes of the solutions may be prepared, provided the final solution concentration is equivalent.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water at least at the level of Type III of Specification D 1193.

7.3 *Ethanol*, (**Warning**—Flammable and toxic, especially when denatured.)

7.4 *Hydrochloric Acid (HCl)*—Relative density 1.19. (**Warning**—Corrosive, causes burns.)

7.5 *Lithium Chloride, LiCl*.

7.6 *Lithium Chloride Electrolyte*, Prepare a 1M–3M solution of lithium chloride (LiCl) in ethanol.

7.7 *Methanol*, (**Warning**—Flammable. Toxic if swallowed.)

7.8 *Potassium Hydroxide*, (**Warning**—Causes severe burns.)

7.9 *Propan-2-ol, Anhydrous*, (less than 0.1 % H₂O). (**Warning**—Flammable.) If adequately dry reagent cannot be procured, it can be dried by distillation through a multiple plate column, discarding the first 5 % of material distilling overhead and using the 95 % remaining. Drying can also be accomplished using molecular sieves such as Linde Type 4A, by passing the solvent upward through a molecular sieve column using one part of molecular sieve per ten parts of solvent.

NOTE 6—It has been reported that, if not originally inhibited against it, propan-2-ol can contain peroxides. When this occurs, an explosion is possible when the storage of the vessel or other equipment such as a dispensing bottle, is near empty and approaching dryness.

7.10 *Toluene*, (**Warning**—Flammable.)

7.11 *Hydrochloric Acid Solution, Standard Alcoholic*, (0.1 mol/L). (**Warning**—See 7.4 and 7.9.) Mix 9 mL of hydrochloric (HCl, relative density 1.19) acid with 1 L of anhydrous propan-2-ol. Standardize frequently enough to detect concentration changes of 0.0005 by potentiometric titration of approximately 8 mL (accurately measured) of the 0.1-mol/L alcoholic KOH solution diluted with 125 mL of CO₂-free water.

7.12 *Commercial Aqueous pH 4, pH 7 and pH 11 Buffer Solutions*—These solutions shall be replaced at regular inter-

vals consistent with their stability or when contamination is suspected. Information relating to their stability should be obtained from the manufacturer.

7.13 *Potassium Hydroxide Solution, Standard Alcoholic*, (0.1 mol/L). (**Warning**—See 7.8 and 7.9.) Add 6 g of potassium hydroxide (KOH) to approximately 1 L of propan-2-ol. Boil gently for 10 min to effect solution. Allow the solution to stand for two days and then filter the supernatant liquid through a fine sintered-glass funnel. Store the solution in a chemically resistant bottle. Dispense in a manner such that the solution is protected from atmospheric carbon dioxide (CO₂) by means of a guard tube containing soda lime or soda non-fibrous silicate absorbents and such that it does not come into contact with cork, rubber, or saponifiable stopcock grease. Standardize frequently enough to detect concentration changes of 0.0005 by potentiometric titration of weighed quantities of potassium acid phthalate dissolved in CO₂-free water.

7.14 *Titration Solvent*—Add 5 ± 0.2 mL of water to 495 ± 5 mL of anhydrous propan-2-ol and mix well. Add 500 ± 5 mL of toluene. (**Warning**—Flammable.) The titration solvent should be made up in large quantities, and its blank value determined daily by titration prior to use.

7.15 *Chloroform*, (**Warning**—Flammable. Hazardous material.)

8. Electrode System

8.1 Preparation of Electrodes:

8.1.1 When a Ag/AgCl reference electrode is used for the titration and it contains an electrolyte which is not 1M–3M LiCl in ethanol, replace the electrolyte. Drain the electrolyte from the electrode, wash away all the salt (if present) with water and then rinse with ethanol. Rinse several times with the LiCl electrolyte solution. Finally, replace the sleeve and fill the electrode with the LiCl electrolyte to the filling hole. When refitting the sleeve ensure that there will be a free flow of electrolyte into the system. A combination electrode shall be prepared in the same manner. The electrolyte in a combination electrode can be removed with the aid of a vacuum suction.

8.2 *Testing of Electrodes*—Test the meter-electrode combination when first put into use, or when new electrodes are installed, and retest at intervals thereafter. Rinse the electrodes with solvent then with water. Dip them into a pH 4 aqueous buffer solution. Read the mV value after stirring one minute. Remove the electrodes and rinse with water. Dip the electrodes into a pH 7 aqueous buffer. Read the mV value after stirring one minute. Calculate the mV difference. A good electrode system will have a difference of at least 158 mV (20 to 25°C). If the difference is less than 158 mV, lift the sleeve of the electrode and insure electrolyte flow. Repeat the measurements. If the difference is still less than 158 mV, clean or replace the electrode(s).

8.2.1 When the sensing electrode and the reference electrode are separate, one pair of electrodes shall be considered as one unit. If one or the other is changed, it shall be considered as different pair and shall be re-tested.

8.3 *Maintenance and Storage of Electrodes*—Cleaning the electrodes thoroughly, keeping the ground-glass joint free of foreign materials, and regular testing of the electrodes are very

³ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

important in obtaining repeatable potentials, since contamination may introduce uncertain erratic and unnoticeable liquid contact potentials. While this is of secondary importance when end points are chosen from inflection points in the titration curve, it may be quite serious when end points are chosen at arbitrarily fixed cell potentials.

8.3.1 Clean the glass electrode at frequent intervals based on use and type of samples being analyzed (not less than once every week during continual use) by immersing in non-chromium containing, strongly oxidizing cleaning solution. The reference electrode shall be cleaned periodically when in use or when a new electrode is installed. Drain the reference electrode at least once each week and refill with the fresh LiCl electrolyte as far as the filling hole. Ensure that there are no air bubbles in the electrode liquid. If air bubbles are observed, hold the electrode in a vertical position and gently tap it to release the bubbles. Maintain the electrolyte level in the reference electrode above that of the liquid in the titration beaker or vessel at all times.

8.3.2 Prior to each titration soak the prepared electrodes in water (pH 4.5 to 5.5) for at least 5 minutes. Rinse the electrodes with propan-2-ol immediately before use, and then with the titration solvent.

8.3.3 When not in use, immerse the lower half of the reference electrode in LiCl electrolyte. When the glass electrode is used, store it in water that has been acidified with HCl to a pH of 4.5 to 5.5. Do not allow electrodes to remain immersed in titration solvent for any appreciable period of time between titrations. While the electrodes are not extremely fragile, handle them carefully at all times.

NOTE 7—*Electrode Life*—Typically, electrode usage is limited to 3 to 6 months depending, upon usage. Electrodes have a limited shelf life and shall be tested before use (see 8.2).

9. Standardization of Apparatus

9.1 *Determination of Meter Readings for the Aqueous Buffer Solutions*—To ensure comparable selection of end points when definite inflection points are not obtained in the titration curve, determine daily, for each electrode pair, the meter readings obtained with aqueous acidic and basic buffer solutions.

NOTE 8—The response of different glass electrodes to hydrogen ion activity is not the same. Therefore, it is necessary to establish regularly for each electrode system the meter readings corresponding to the buffer solutions arbitrarily selected to represent acidic or basic end points.

9.2 Immerse the electrodes in the pH 4 and the pH 11 aqueous buffers and stir each of them for approximately 5 min, maintaining the temperature of the buffer solution at a temperature within 2°C of that at which the titrations are to be made. Read the cell voltage for each of them. The readings so obtained are taken as the end points in titration curves having no inflection points.

10. Preparation of Sample of Used Oil

10.1 Strict observance of the sampling procedure is necessary since the sediment itself is acidic or basic or has absorbed acidic or basic material from the sample. Failure to obtain a representative sample causes serious errors.

10.1.1 When applicable, refer to Practice D 4057 (Manual Sampling) or Practice D 4177 (Automatic Sampling) for proper sampling techniques.

10.1.2 When sampling used lubricants, the specimen shall be representative of the system sampled and shall be free of contamination from external sources.

NOTE 9—As used oil can change appreciably in storage, test samples as soon as possible after removal from the lubricating system; and note the dates of sampling and testing.

10.2 Heat the sample (see Note 10) of used oil to $60 \pm 5^\circ\text{C}$ in the original container and agitate until all of the sediment is homogeneously suspended in the oil. If the original container is a can or if it is glass and more than three-fourths full, transfer the entire sample to a clear-glass bottle having a capacity at least one third greater than the volume of the sample. Transfer all traces of sediment from the original container to the bottle by vigorous agitation of portions of the sample in the original container.

NOTE 10—When samples are visibly free of sediment, the heating procedure described can be omitted.

10.3 After complete suspension of all sediment, strain the sample or a convenient aliquot through a 100-mesh screen for removal of large contaminating particles.

NOTE 11—When samples are visibly free of sediment, the straining procedure described can be omitted.

11. Procedure for Acid Number and Strong Acid Number

11.1 Into a 250-mL beaker or a suitable titration vessel, introduce a weighed quantity of sample as recommended in Table 1 (see Note 12) and add 125 mL of titration solvent (see Note 13). Prepare the electrodes as directed in 8.2. Place the beaker or titration vessel on the titration stand and adjust its position so that the electrodes are about half immersed. Start the stirrer, and stir throughout the determination at a rate sufficient to produce vigorous agitation without spattering and without stirring air into the solution.

NOTE 12—If it suspected that the recommended sample size will foul the electrodes, a smaller sample size can be taken. Results using smaller sample size may not be equivalent to results obtained with the recommended sample size. The precision statement does not include results when using a smaller sample size.

NOTE 13—A titration solvent that contains chloroform (**Warning**—May be fatal if swallowed. Harmful if inhaled. May produce toxic vapors if burned) can be used in place of toluene to completely dissolve certain heavy residues of asphaltic materials. Results using chloroform may not be equivalent to results obtained using toluene. The precision statement does not include results when using chloroform.

11.2 Select the right burette, fill with the 0.1-mol/L alcoholic KOH solution, and place the burette in position on the

TABLE 1 Recommended Size of Test Portion

Acid Number	Mass of Test Portion, g	Accuracy of Weighing, g
0.05 – < 1.0	20.0 ± 2.0	0.10
1.0 – < 5.0	5.0 ± 0.5	0.02
5 – < 20	1.0 ± 0.1	0.005
20 – < 100	0.25 ± 0.02	0.001
100 – < 260	0.1 ± 0.01	0.0005

titration assembly, ensuring that the tip is immersed about 25 mm in titration vessel liquid. Record the initial burette and meter (cell potential) readings.

11.3 Manual Titration Method:

11.3.1 Add suitable small portions of 0.1-mol/L alcoholic KOH solution and wait until a constant potential has been established, record the burette and meter readings.

11.3.2 At the start of the titration and in any subsequent regions (inflections) where 0.1 mL of the 0.1-mol/L KOH solution consistently produces a total change of more than 30 mV in the cell potential, add 0.05-mL portions.

11.3.3 In the intermediate regions (plateau) where 0.1 mL of 0.1-mol/L alcoholic KOH changes the cell potential less than 30 mV, add larger portions sufficient to produce a total potential change approximately equal to, but not greater than 30 mV.

11.3.4 Titrate in this manner until the potential changes less than 5 mV/0.1 mL of KOH and the cell potential indicates that the solution is more basic than the aqueous basic buffer.

11.3.5 Remove the titration solution, rinse the electrodes and burette tip with the titration solvent, then with propan-2-ol and finally with reagent grade water. Immerse the electrodes in water for at least 5 min before starting another titration to restore the aqueous gel layer of the glass electrode. After 5 min in the water, rinse the electrodes with propan-2-ol then the titration solvent before proceeding to the next titration. If the electrodes are found to be dirty and contaminated, proceed as in 8.1. Store electrodes according to 8.3.3.

11.4 Automatic Titration Method:

11.4.1 Adjust the apparatus in accordance with the manufacturer's instructions to provide a dynamic mode of titrant addition.

11.4.2 Verify that the instrument will determine the amount of strong acid when the initial mV of the test sample, relative to the mV reading of the aqueous acidic buffer, indicates the presence of such acids. Record the volume of KOH added to reach the mV of the pH 4 aqueous buffer. This value is used to calculate the strong acid number. Proceed with the automatic titration and record potentiometric curves or derivative curves as the case may be.

11.4.3 Titrate with the 0.1-mol/L alcoholic KOH solution. The apparatus shall be adjusted or programmed such that, when an inflection point, suitable for use in the calculation is approached, the rate of addition of titrant and volume of titrant added are based on the change in slope of the titration curve. The titrant shall be added in increments of a suitable size to achieve a potential difference of 5 to 15 mV per increment. Increment volume shall vary between 0.05 and 0.5 mL. The next increment shall be added if the signal does not change more than 10 mV in 10 seconds. The maximum waiting time in between increments shall not exceed 60 seconds.

11.4.4 The titration can be terminated when the signal reaches the pH 11 buffer potential past 200 mV. An equivalence point is recognizable if the first derivative of the titration curve produces a maximum, which is significantly higher than the noise produced by electrostatic effects. See also 12.1.1.

11.4.5 On completion of the titration, rinse the electrodes and burette tip with the titration solvent, then with propan-2-ol,

and finally with reagent grade water. Immerse the electrodes in water for at least 5 min before starting another titration to restore the aqueous gel layer of the glass electrode. Rinse the electrodes with propan-2-ol and finally with the titration solvent prior to running the next sample. If electrodes are found dirty and contaminated, proceed as in 8.1. Store electrodes according to 8.3.3.

NOTE 14—When acid numbers about or below 0.1 are expected, better precision can be obtained by modifying the method in one or more ways, such as by substituting a 0.01 or 0.05 M alcoholic KOH solution; increasing the sample size above 20 g; or switching from a manual operated burette (that is, graduated in 0.05 mL divisions) to an automated burette that can dispense smaller increments of the KOH solution, if samples are being analyzed by manual titration.

11.5 Blanks:

11.5.1 For each set of samples and for every new batch of titration solvent, perform a blank titration of 125 mL of the solvent. For manual titration, add 0.1-mol/L alcoholic KOH solution in 0.01 to 0.05-mL increments, waiting between each addition until a constant cell potential is reached. Record the meter and readings when the former becomes constant after each increment. For automatic titration, use the same mode of titration as for the determination of the acidic property of the sample but use smaller increments of titrant addition, 0.01 to 0.05-mL. Recheck the blank periodically based on the sample load.

11.5.2 When strong acids are present and a strong acid number is to be determined, perform a blank titration of 125 mL of the titration solvent, adding 0.1 mol/L alcoholic HCl solution in 0.01 to 0.05-mL increments in a manner comparable to that specified in 11.5.1.

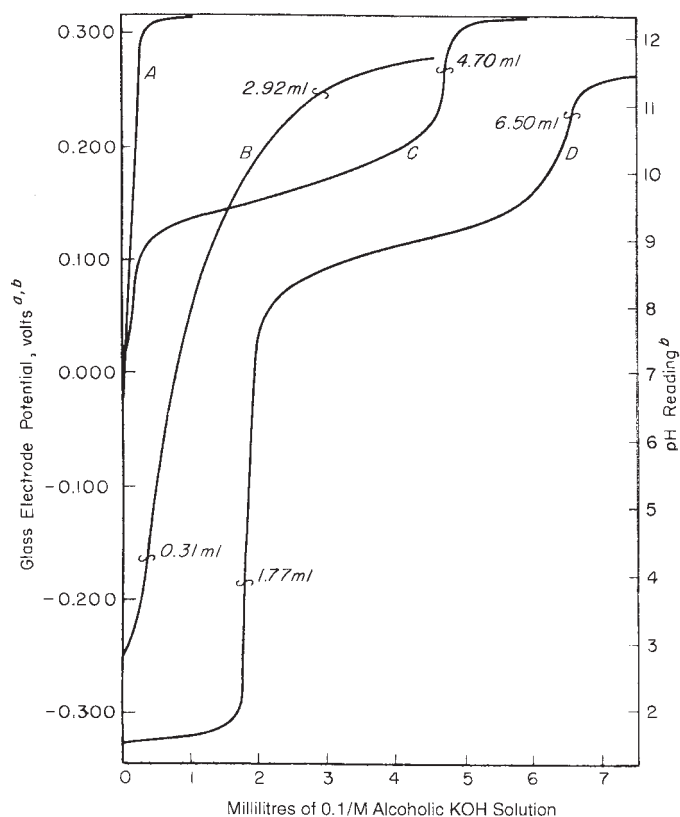
12. Calculation

12.1 *Manual Titration*—Plot the volumes of the 0.1-mol/L alcoholic KOH solution added against the corresponding meter readings (see Fig. 1). Mark as an end point only a well-defined inflection point (see Note 15) that is closest to the cell voltage corresponding to that obtained with the aqueous acidic or basic buffer. If inflections are ill defined or no inflection appears (see Fig. 1, Curve B), mark the end point at the meter reading corresponding to that obtained with the appropriate aqueous buffer.

NOTE 15—One inflection point is generally recognizable by inspection whenever several successive 0.05-mL increments each produce a cell potential change greater than 15 mV at least 30 % greater than those produced by previous or subsequent increments of the same size. Generally, definite inflection points may be discerned only in regions where increments of the same size are used.

12.1.1 Some additive chemistry may produce an inflection point beyond the buffer endpoint. For additives, take the last inflection point for calculation. **Precaution**—If using an automatic titrator, a change in the instrument parameters may be required to detect this type of endpoint.

12.1.2 For all acid titrations on used oils, mark as an end point, the point on the curve that corresponds to the meter reading for an aqueous basic buffer (pH 11) and the meter reading for the aqueous acid buffer (pH 4) when strong acids are indicated.



Key:
 Curve A—Blank on 125 mL of titration solvent.
 Curve B—10.00 g of used crankcase oil plus 125 mL of titration solvent. Since no sharp inflections are apparent, the end points are chosen at the meter readings obtained with the two aqueous buffer solutions.
 Curve C—10.00 g of oil containing a weak acid plus 125 mL of titration solvent. The end point is chosen as the point at which the curve is most nearly vertical.
 Curve D—10.00 g of oil containing weak and strong acids plus 125 mL of titration solvent. The end points are chosen as the points at which the curve is most nearly vertical.

FIG. 1 Illustrative Titration Curves

NOTE 16—The cooperative work done on acid number determinations on fresh oils, additive concentrates, and used oils indicated well-defined inflection points for fresh oils and additive concentrates, and generally ill-defined inflections, or no inflection points at all, for used oils.

12.2 Automatic Titration Method—Mark the end points on the curves obtained in 11.4, in the same way as for the manual titration method.

12.3 Method of Calculation—The method of calculation in 12.3.1 is applicable to both manual and automatic methods.

12.3.1 Calculate the acid number and strong acid number as follows:

$$\text{Acid number, mg KOH/g} = (A - B) \times M \times 56.1/W \quad (1)$$

$$\text{Strong acid number, mg KOH/g} = (CM - Dm) \times 56.1/W \quad (2)$$

where:

- A = volume of alcoholic KOH solution used to titrate sample to end point that occurs at the meter reading of the inflection point closest to the meter reading corresponding to the pH 11 aqueous buffer, or in case of ill-defined or no inflection point, to the meter reading corresponding to the pH 11 aqueous buffer, mL. For additives, A is the volume of alcoholic KOH at the last inflection point,
- B = volume corresponding to A for blank titration, mL,
- M = concentration of alcoholic KOH solution, mol/L,
- m = concentration of alcoholic HCl solution, mol/L,
- W = sample, mass, g,
- C = alcoholic KOH solution used to titrate the sample to end point that occurs at a meter reading corresponding to acid nonaqueous buffer, mL, and
- D = alcoholic HCl solution used to titrate solvent blank to end point corresponding to C, mL.

13. Quality Control Checks

13.1 Confirm the performance of the test procedure by analyzing a quality control (QC) sample that is, if possible, representative of the samples typically analyzed.

NOTE 17—Because used oils, particularly used engine oils, are known to change during storage, such samples may not be suitable for this purpose.

13.2 Prior to monitoring the measurement process, the user of the method needs to determine the average value and control limits of the QC sample.⁴

13.3 Record the QC results and analyze by control charts or other statistically equivalent technique to ascertain the statistical control status of the total testing process.⁴ Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

13.4 The frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample should be analyzed each testing day. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC precision should be periodically checked against the precision listed in the Precision and Bias Section of this method to ensure data quality.

13.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the samples routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogeneous and stable under the anticipated storage conditions. Because the base number can vary while the QC sample

⁴ See ASTM MNL 7, *Manual on Presentation of Data Control Chart Analysis*, 6th edition, ASTM International, W. Conshohocken, PA.

is in storage, when an out-of-control situation arises, the stability of the QC sample can be a source of the error.

14. Report

14.1 Given there are two different ways to determine the endpoint, report the type of endpoint used: inflection point or buffer endpoint. Report sample size used if differs from the recommended sample size. Also, report if chloroform was used as solvent. Report the results as acid number or strong acid number as follows:

$$\text{Acid number (Test Method D 664)} = (\text{result}) \quad (3)$$

$$\text{Strong acid number (Test Method D 664)} = (\text{result}) \quad (4)$$

14.2 For used oil samples report also the date of testing and, when available, the date the sample was taken (see 10.2).

15. Precision and Bias

15.1 Acid Number:

15.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty.

$$\text{Fresh Oils} = 0.044(X + 1) \quad (5)$$

$$\text{Used Oils Buffer end point} = 0.117 X \quad (6)$$

where:

X = the average of the two test results.

15.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty.

$$\text{Fresh Oils} = 0.141(X + 1) \quad (7)$$

$$\text{Used Oils Buffer end point} = 0.44X \quad (8)$$

where:

X = the average of the two test results.

15.2 Strong Acid Number:

15.2.1 Precision data have not been developed for strong acid number because of its rare occurrence in sample analysis.

15.3 *Bias*—The procedures in this test method have no bias because the acid values can be defined only in terms of the test method.

16. Keywords

16.1 acid number; lubricants; petroleum products; potentiometric; strong acid number; titration

SUMMARY OF CHANGES

Subcommittee D02.06 has identified the location of selected changes to this standard since the last issue (D 664–01) that may impact the use of this standard.

- | | |
|---|--|
| <p>(1) The majority of this standard was rewritten and differs significantly from previous versions.</p> <p>(2) Added information on the use of Ag/AgCl reference electrodes.</p> <p>(3) Added more specifications for using automatic titration equipment.</p> | <p>(4) Replaced non-aqueous buffers with aqueous buffers throughout.</p> <p>(5) Removed calomel electrodes, which are difficult to obtain.</p> <p>(6) Added a Quality Control section.</p> |
|---|--|

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Test Method ASTM D 6584 / EN 14105 for Determination of Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography

DCG has available NIST traceable by weight, gravimetrically prepared stock solutions and standard solutions for ASTM D6584 / EN 14105. All standards in addition to being gravimetrically prepared and NIST traceable by weight, have been verified by one or more analytical methods. Custom Standards are available. DCG offers several purchasing options:

Option 1: Stock Solutions and internal standards can be purchased as a complete kit or individually.

Complete Kit for Option 1 Part #: D6584 STKSOL Kit: \$375.00: Contains one each of the following:

Glycerin 25 mg / 50 mL pyridine. 1 mL pre-scored ampoule.
 Monoolein 50 mg / 10 mL pyridine. 2 mL pre-scored ampoule.
 Diolein 50 mg / 10 mL pyridine. 1 mL pre-scored ampoule.
 Triolein 50 mg / 10 mL pyridine. 1 mL pre-scored ampoule.
 Internal Standard # 1: 1, 2, 4 Butanetriol 25 mg / 25 mL pyridine. 5 mL pre-scored ampoule.
 Internal Standard # 2: Tricaprin 80 mg / 10 mL pyridine. 5 mL pre-scored ampoule.

Individual Part Numbers for Option 1:

Part #: D6584 Glycerin STKSOL: \$24.00: Glycerin 25 mg / 50 mL pyridine. 1 mL pre-scored ampoule.
Part #: D6584 Monoolein STKSOL: \$24.00: Monoolein 50 mg / 10 mL pyridine. 2 mL pre-scored ampoule.
Part #: D6584 Diolein STKSOL: \$24.00: Diolein 50 mg / 10 mL pyridine. 1 mL pre-scored ampoule.
Part #: D6584 Triolein STKSOL: \$24.00: Triolein 50 mg / 10 mL pyridine. 1 mL pre-scored ampoule.
Part #: D6584 Butanetriol STKSOL (Internal Standard # 1): \$148.00: 1,2,4 Butanetriol 25 mg / 25 mL pyridine. 5 mL pre-scored ampoule.
Part #: D6584 Tricaprin STKSOL (Internal Standard # 2): \$148.00: Tricaprin 80 mg / 10 mL pyridine. 5 mL pre-scored ampoule.

Option 2

The following Standard Solutions from D6584 Table 2 are purchased as a complete kit. The Internal Standards are premixed into the standard solutions.

Complete Kit Part #: D6584 Table 2 Kit with Internal Standards Added: \$140.00: Contains one each of standard Solution #'s 1, 2, 3, 4 & 5 with Internal Standards # 1 & 2 premixed into the Standard Solutions. Packaged in 1 mL pre-scored ampoules.

Table 2

Standard Solution with Internal Standards	# 1	# 2	# 3	# 4	# 5
µL of Glycerin Stock Solution	10	30	50	70	100
µL of Monoolein Stock Solution	20	50	100	150	200
µL of Diolein Stock Solution	10	20	40	70	100
µL of Triolein Stock Solution	10	20	40	70	100
µL of Butanetriol Stock Solution, Internal Standard # 1	100	100	100	100	100
µL of Tricaprin Stock Solution, Internal Standard # 2	100	100	100	100	100

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Chromatographic Reference Materials



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Additional Products Required For ASTM D 6584 / EN 14105

Internal Standards for Samples:

Part #: D6584 Butanetriol STKSOL (Internal Standard # 1): \$148.00. 5 mL pre-scored ampoule.

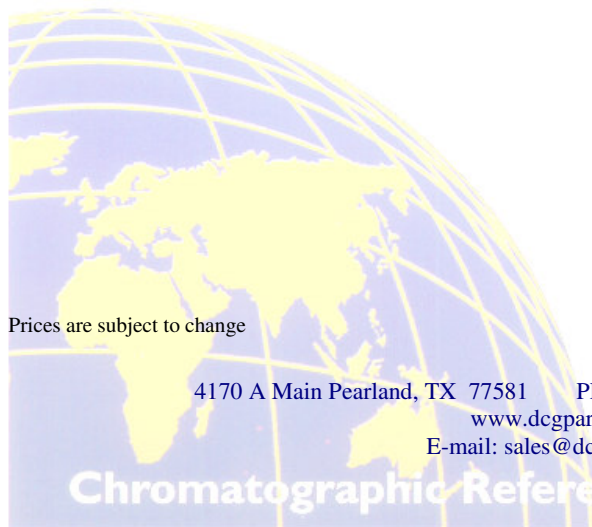
Part #: D6584 Tricaprin STKSOL (Internal Standard # 2): \$148.00. 5 mL pre-scored ampoule.

Silyating Agent, N-Methyl-N-trimethylsilyltrifluoroacetamide (MSTFA)

Part #: D6584 MSTFA 5 mL: \$145.00: N-Methyl-N-trimethylsilyltrifluoroacetamide (MSTFA), Packaged in 5 mL pre-scored ampoule.

Part #: D6584 n-Heptane: \$75.00: Reagent Grade n-Heptane, 100 mL

Part #: D6584 vial, cap & Septa: \$220.00: 200 each 12 mL amber glass screw thread vial with cap and PTFE/silicone septa.



Prices are subject to change

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Standard Test Method for Undissolved Water In Aviation Turbine Fuels¹

This standard is issued under the fixed designation D 3240; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This test method covers the measurement of undissolved water in aviation turbine fuels in flowing fuel streams without exposing the fuel sample to the atmosphere or to a sample container. The usual range of test readings covers from 1 to 60 ppm of free water. This test method does not detect water dissolved in the fuel, and thus test results for comparable fuel streams can vary with fuel temperature and the degree of water solubility in the fuel.

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

2. Terminology

2.1 *Definition of a Term Specific to This Standard:*

2.1.1 *free water*—water not dissolved in the fuel.

3. Summary of Test Method

3.1 A measured sample of fuel is passed through an uranine dye-treated filter pad. Undissolved (free) water in the fuel will react with the uranine dye. When the pad is subsequently illuminated by ultra violet (UV) light, the dye previously contacted by free water will fluoresce a bright yellow with the brightness increasing for increasing amounts of free water in the fuel. The UV light-illuminated pad is compared to a known standard using a photocell comparator, and the free water in the fuel sample is read out in parts per million by volume. By varying the fuel sample size, the range of the test method can be increased.

4. Significance and Use

4.1 Undissolved (free) water in aviation fuel can encourage the growth of microorganisms and subsequent corrosion in the tanks of aircraft and can also lead to icing of filters in the fuel system. Control of free water is exercised in ground fueling equipment by use of filter-coalescers and water separators.

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.J0 on Aviation Fuels.

Current edition approved May 15, 1991. Published July 1991. Originally published as D 3240–73T. Last previous edition D 3240–86a.

5. Apparatus

5.1 *Test Pad Rater*—A device² for comparing the fluorescence of the test pad to a known standard, while both are illuminated by the same source of UV light, shall be used. The amount of UV light striking the standard shall be modulated until the total fluorescence of the test pad and the standard are equal; this shall be determined using a photocell bridge circuit null indicator. The light modulating device for controlling the UV light striking the standard shall provide a direct reading in parts per million by volume of free water.

5.2 *Test Pads*—Absorbent filter disks of 25-mm diameter shall be coated on one side with uranine (sodium fluorescein) dye at a concentration of 0.23 to 0.29 mg per 25 mm pad. The test pads³ shall be individually packaged in hermetically sealed envelopes or other suitable containers. Fresh, unused test pads shall have an orange color over the dyed surface. Any discoloration, unevenness in dye content, or faded (to a yellow color) appearance shall be cause for rejection.

5.3 *Test Pad Holder⁴ and Sampling Line*—A test pad holder and sampling line shall be used to draw the fuel sample through the test pad at a rate of 600 to 800 mL/min. Means shall be provided to flush the test pad sampling line and holder immediately prior to use. The test pad holder shall include an orifice of 1-mm (0.040-in.) diameter upstream of the pad to disperse water droplets in the fuel.

5.4 *Tweezers*—Suitable clean, dry tweezers shall be used at all times when handling the test pad.

5.5 *Blotting Paper*—Clean, dry, absorbent paper towels, blotters, etc., shall be provided for blotting the test pad prior to rating to remove excess fuel. The blotter paper shall neither impart color or stain nor leave any residue on the test pads.

5.6 *Sampling Valve Connection*, designed to meet the following requirements: (1) It shall be mounted in the sampling

² The Aqua-Glo Series II instrument manufactured by Gammon Technical Products, Inc., P.O. Box 400, Manasquan, NJ 08736-0400 was used in the precision test program. The unit is currently available in a Series III configuration which is changed only in the power supply. All water content measuring components remain of the same configuration as the Series II instrument. Manufacturers who wish to offer similar products are referred to Committee D02 Equipment Replacement Guidelines.

³ Aqua-Glo test pads used in the Precision Test Program are available from Gammon Technical Products Inc., P.O. Box 400, Manasquan, NJ 08736-0400.

⁴ A test pad holder used in the Precision Test Program is available from Gammon Technical Products Inc., P.O. Box 400, Manasquan, NJ 08736-0400.

point and must incorporate a self-sealing quick action coupling designed to mate with a suitable connection leading to the selector valve of the sampling assembly. (2) It must be completely resistant to fuel and be leak proof up to the maximum working pressures to be encountered. (3) It must have a minimum of internal recesses which could cause the holdup of contaminant. (4) It must be provided with a dust cap.

5.7 *Calibrating Standard*, Calibration of the instrument should be performed using a calibrating standard of known values.

6. Sampling

6.1 The following procedure is applicable for dynamic line samples only; that is, taking the fuel sample directly from the test system and through the test pad without exposing the sample to the atmosphere or to a sample container. The use of sample containers such as bottles or cans for the temporary storage of the sample will result in large errors and is not recommended.

NOTE 1—The amount of free water in a sample is very sensitive to the temperature of the sample. The use of sample containers such as bottles or cans can result in large errors due to changes in sample temperature, adsorption of water on container walls, etc.

6.2 Attach the test pad holder assembly to the sampling port on the system.

6.3 Flush the test pad holder assembly immediately prior to sampling, displacing the sampling line with at least two volumes of test fuel.

6.4 Remove the sampling assembly, open the pad holder, and insert the new test pad using tweezers making sure that the treated side of the test pad is facing upstream. Installation of a three-way valve immediately upstream of the test pad holder will permit flushing with the test pad in place.

NOTE 2—Do not remove the test pad from the hermetically sealed package until ready for use. Do not allow any discrete water droplets to come into contact with the pad (from rain, sneezing, coughing, etc.). Exposure of the test pad to the atmosphere, especially on humid days, will also ruin the pad in a matter of minutes.

6.5 Pass 500 mL of fuel through the pad, accurately measuring the test sample quantity. Normal sample volume is 500 mL of test fuel, but if the reading is off scale (on high side), sample volumes down to 100 mL in volume may be used. In the latter case, a small graduated cylinder should be used to measure the sample volume.

7. Calibration

7.1 The calibrating standard⁵ corresponding to a given undissolved water content is placed in the test pad window. Turn on the lamp and press the photocell comparator button. Zero the photocell comparator by adjusting the light modulating lever until there is a steady reading for 10 to 15 s. This may take a minute or longer. Always move the light modulating lever in the same direction when zeroing the photocell comparator in calibration or testing to eliminate errors caused by

play in the lever. If the reading obtained does not agree with the calibration pad rating, adjust the photocell comparator by removing the plug screw on the side of the photocell comparator at the 45° bend. Insert a small screwdriver, and adjust as necessary. Repeat the above procedure until the rating obtained agrees with the calibration pad rating. The instrument should be calibrated prior to use each day, after each hour of use, and when the ultra violet light battery is replaced or recharged.

8. Rating Procedure

8.1 Remove the test pad from the sampling holder using tweezers and press between dry paper blotters or absorbent towels to remove excess fuel. To blot, press firmly (about 5 lb force) 3 or 4 times with heel of hand, moving the pad with tweezers each time.

8.1.1 For maximum accuracy the test pad should be read within 3 min after sampling is initiated. If the test pad is not read immediately after sampling, it must be placed in a desiccator to prevent moisture pickup from the air. However, ratings made on dried test pads, that is, not damp with fuel, should be avoided if possible since they will give high and erroneous results. Conversely, rating a pad which has not been well blotted will give a low reading as the excess fuel will absorb part of the UV light and decrease fluorescence.

8.2 Using tweezers, put the pad into the pad rating device. Turn on the lamp and press the photocell button. Continuously zero the photo-cell comparator by adjusting the light modulating lever until there is a steady reading for 10 to 15 s. Always move the light modulating lever in the same direction when zeroing the photocell comparator to eliminate errors caused by backlash. This may take a minute or longer. Turn off the instrument light immediately after use to conserve battery power.

8.2.1 The ultraviolet light must be on to get a reading. This can be checked by moving the light modulating lever from one extreme to another. The photo-cell comparator meter needle should swing violently when this is done.

8.3 Record the instrument reading (estimated to the nearest tenth) and the sample volume. Record the temperature of the fuel.

8.4 Visual observation of the used test pad is often of value. This is easily accomplished by removing the photocell comparator assembly and viewing the test pad. Free water in fuel is normally well dispersed and will form an even distribution of many, small points of yellow fluorescence on the test pad when illuminated by ultra violet light. Large water drops, however, will form a few, large spots of yellow fluorescence on the pad. These large spots may give erroneous readings; the result should be disregarded and a new sample tested.

9. Calculation

9.1 The instrument reads directly if the sample volume is 500 mL. Correct the readings for other sample volume by multiplying reading by 500/sample size in millilitres:

$$\text{Free water, ppm} = (\text{meterreading, ppm})(500)/(\text{sample volume, mL}) \quad (1)$$

⁵ Replacement calibrating standards are available from Gammon Technical Products Inc., P.O. Box 400, Manasquan, NJ 08736-0400, but only if the fluorescing standard for the instrument is returned for comparison rating.

10. Report

10.1 Report the result to the nearest whole number as ppm by volume of undissolved water in fuel, and also the sample volume used in the test. Report the temperature of the sample if available.

11. Precision and Bias ⁶

11.1 The precision (Note 3, Note 4) of this test method as determined by statistical examination of test results obtained by operator-instrument pairs at a common test site is as given in this section. Each operator used a separate instrument.

11.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method exceed the following values only in one case in twenty.

$$\text{Repeatability} = 0.32x \quad (2)$$

where x = average of two results in parts per million volume over the range from 1 through 60 ppm V (Note 5).

⁶ The results of the cooperative test program from which these values have been derived, are filed at ASTM Headquarters. Request RR:D02-1195.

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11.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working at a common test site on identical test material would, in the long run, exceed the following values only in one case in twenty.

$$\text{Reproducibility} = 0.47x \quad (3)$$

NOTE 3—The reproducibility values above were estimates from results obtained at the same location and on the same day by seven operator/instruments testing identical samples. In the case of this test method it is not possible to obtain meaningful results when fuels are shipped to different locations since water would separate during shipment.

NOTE 4—The presence of fuel additives such as corrosion inhibitors, fuel system icing inhibitors, and antistatic materials may affect the calibration of the test.

NOTE 5—Sample size was not found to be a significant factor in precision. Data were analyzed using a log transformation but the repeatability results are expressed in untransformed units.

11.1.3 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in Test Method D 3240 for measuring the undissolved water in aviation turbine fuels, bias has not been determined.

12. Keywords

12.1 calibrating standard; fluorescence; fluorescing standard; free water; sodium fluorescein; undissolved water; uranine