



Standard Test Method for Determination of the Maximum Flocculation Ratio and Peptizing Power in Residual and Heavy Fuel Oils (Optical Detection Method)¹

This standard is issued under the fixed designation D 7060; 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 a procedure for quantifying the maximum flocculation ratio of the asphaltenes in the oil and the peptizing power of the oil medium, by an automatic instrument using an optical device.

1.2 This test method is applicable to atmospheric or vacuum distillation residues, thermally cracked residue, intermediate and finished residual fuel oils, containing at least 1 mass % asphaltenes. This test method has not been developed for asphalts.

NOTE 1—An optical probe detects the formation of flocculated asphaltenes. The start of flocculation is interpreted when a significant and sustained increase in rate-of-change of signal, as measured by the optical probe, ensures flocculation is in progress. The start of flocculation can be detected unambiguously when the sample contains at least 1 % mass asphaltenes as measured by Test Method D 6560.

NOTE 2—This test method is applicable to products typical of Specification D 396—Grades 5L, 5H, and 6, and Specification D 2880—Grades 3-GT and 4-GT.

1.3 This test method was evaluated in a within-laboratory study in the range of 16 to 57 for the maximum flocculation ratio and in the ranges of 27 to 96 for peptizing power.

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 Documents

2.1 ASTM Standards:²

D 396 Specification for Fuel Oils

D 2880 Specification for Gas Turbine Fuel Oils

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D 4870 Test Method for Determination of Total Sediment in Residual Fuels

D 6560 Test Method for Determination of Asphaltenes (Heptane Insolubles) in Crude Petroleum and Petroleum Products

D 6792 Guide for Quality System in Petroleum Products and Lubricants Testing Laboratories

3. Terminology

3.1 Definitions:

3.1.1 *asphaltene, n*—in petroleum technology, a molecule of high molecular mass, high carbon/hydrogen ratio, and containing heteroatoms.

3.1.1.1 *Discussion*—Asphaltenes are found largely in crude oils and in heavy fuel oils containing residual fractions. They are insoluble in alkanes such as *n*-heptane and cetane, but soluble in aromatic solvents such as benzene, toluene, and 1-methylnaphthalene.

3.1.2 *compatibility, n*—of crude oils or of heavy fuel oils, the ability of two or more crude oils or fuel oils to blend together within certain concentration ranges without evidence of separation, such as the formation of multiple phases.

3.1.2.1 *Discussion*—Incompatible heavy fuel oils or crude oils, when mixed or blended, result in the flocculation or precipitation of asphaltenes. Some oils may be compatible within certain concentration ranges in specific mixtures, but incompatible outside those ranges.

3.1.3 *flocculation, n*—of asphaltenes from crude oils or heavy fuel oils, the aggregation of colloiddally dispersed asphaltenes into visibly larger masses which may or may not settle.

3.1.4 *peptization, n*—of asphaltenes in crude oils or heavy fuel oils, the dispersion of asphaltenes to produce a colloidal dispersion.

3.1.5 *stability reserve, n*—in petroleum technology, the property of an oil to maintain asphaltenes in a peptized state and prevent flocculation of the asphaltenes.

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.

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

3.1.5.1 *Discussion*—An oil with a low stability reserve is likely to undergo flocculation of asphaltenes when stressed (for example, extended heated storage) or blended with a range of other oils. Two oils each with a high stability reserve are likely to maintain asphaltenes in a peptized state and not lead to flocculation when blended together.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *critical cetane dilution, n*—number of millilitres of cetane with which 1 g of undiluted sample can be diluted until it just does not flocculate the asphaltenes.

3.2.2 *flocculation ratio at critical dilution, n*—percentage by volume of 1-methylnaphthalene in a mixture of 1-methylnaphthalene and cetane at the inflection point.

3.2.3 *inflection point, n*—last step during the titration with cetane, where flocculation of asphaltenes is *not* detected by the optical probe as a significant and sustained increase in rate-of-change of signal.

3.2.4 *maximum flocculation ratio, n*—of asphaltenes, minimum required solvency power, expressed as percentage by volume of 1-methylnaphthalene in a mixture of 1-methylnaphthalene and cetane, to keep the asphaltenes in a colloidal solution.

3.2.4.1 *Discussion*—Maximum flocculation ratio is the flocculation ratio at extrapolated infinite dilution of the sample.

3.2.5 *peptizing power, n*—available solvency power, expressed as percentage by volume of 1-methylnaphthalene in a mixture of 1-methylnaphthalene and cetane, to keep asphaltenes in a colloidal solution.

3.2.6 *reciprocal dilution, n*—dilution ratio of sample in solvent mixture of 1-methylnaphthalene and cetane.

3.3 *Symbols:*

FR_{max}	= maximum flocculation ratio
FR_x	= flocculation ratio at critical dilution
Po	= peptizing power
X_{min}	= critical cetane dilution
X_c	= critical dilution

4. Summary of Test Method

4.1 Six portions of the sample are diluted in various ratios with 1-methylnaphthalene. Each solution is inserted into the automatic apparatus, and titrated with cetane until flocculation of asphaltenes is detected by the optical probe. The first two solutions are titrated with cetane in coarse determinations in which the flocculation ratio is decreased in 5 % steps. The coarse determinations help to establish suitable starting values for the fine determinations, in which the flocculation ratio is decreased in 1 % steps. The four flocculation ratios at critical dilution, measured during the fine determinations, are used to calculate the maximum flocculation ratio of the sample's asphaltenes and the peptizing power of the sample's oil medium.

5. Significance and Use

5.1 Asphaltenes are naturally occurring materials in crude petroleum and petroleum products containing residual material. The asphaltenes are usually present in colloidal suspensions, but they may agglomerate and flocculate if the suspen-

sion of asphaltene molecules is disturbed through excess stress or incompatibility. This test method provides compatibility parameters, which can be used to assess stability reserve and compatibility.

5.2 A blend is considered stable when the blend's peptizing power is higher than the blend's maximum flocculation ratio;^{3,4} both of them can be calculated using empirical blend rules. Refineries and terminal owners can prevent the flocculation of asphaltenes due to incompatibility by assessing the compatibility of fuels beforehand.

NOTE 3—See Appendix X1 for an example of prediction of compatibility.

6. Interferences

6.1 High content of insoluble inorganic matter (sediment) has some interference in this test method. In this case, the insoluble matter shall be removed by filtration according to Test Method D 4870.

6.2 The presence of wax, present in paraffinic crudes or fuels from such crudes, does not interfere.

7. Apparatus

7.1 *Integrated Automated Analytical Measurement System*—This test method uses an integrated automated analytical measurement system⁵ comprised of a PC-based computer and two titration stations (Fig. 1). See Annex A1 for detailed information.

7.2 The computer controls test sequencing, acquires and accumulates optical probe signal data, provides processing calculations, and automatically produces a report of important test parameters. The computer is capable of controlling one or two independent titration stations.

7.3 Each titration station consists of the following:

- 7.3.1 Automatic titration unit,
- 7.3.2 Heater,
- 7.3.3 Magnetic stirrer,
- 7.3.4 Optical probe, and
- 7.3.5 Reaction cell plus lid.

7.4 *Magnetic Stirrer/Hotplate*, thermostatically controlled.

7.5 *Stirring Bar*, magnetic, PTFE-coated, 25 mm in length.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where

³ Berryman, T. J., and Lewis, C. P. G., "The Stability of Residual Fuels. Theory and Practice of the Shell Concept," 16th CIMAC Conference, Oslo, 1985.

⁴ Berg van den, F. G. A., "Developments in Fuel Oil Blending," IASH 7th International Conference, Graz, Austria, 2000.

⁵ The following instrument has been found satisfactory for this purpose—Automated Stability Analyser available from Zematra, 3194 DG Hoogvliet, The Netherlands. 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 committee, which you may attend.

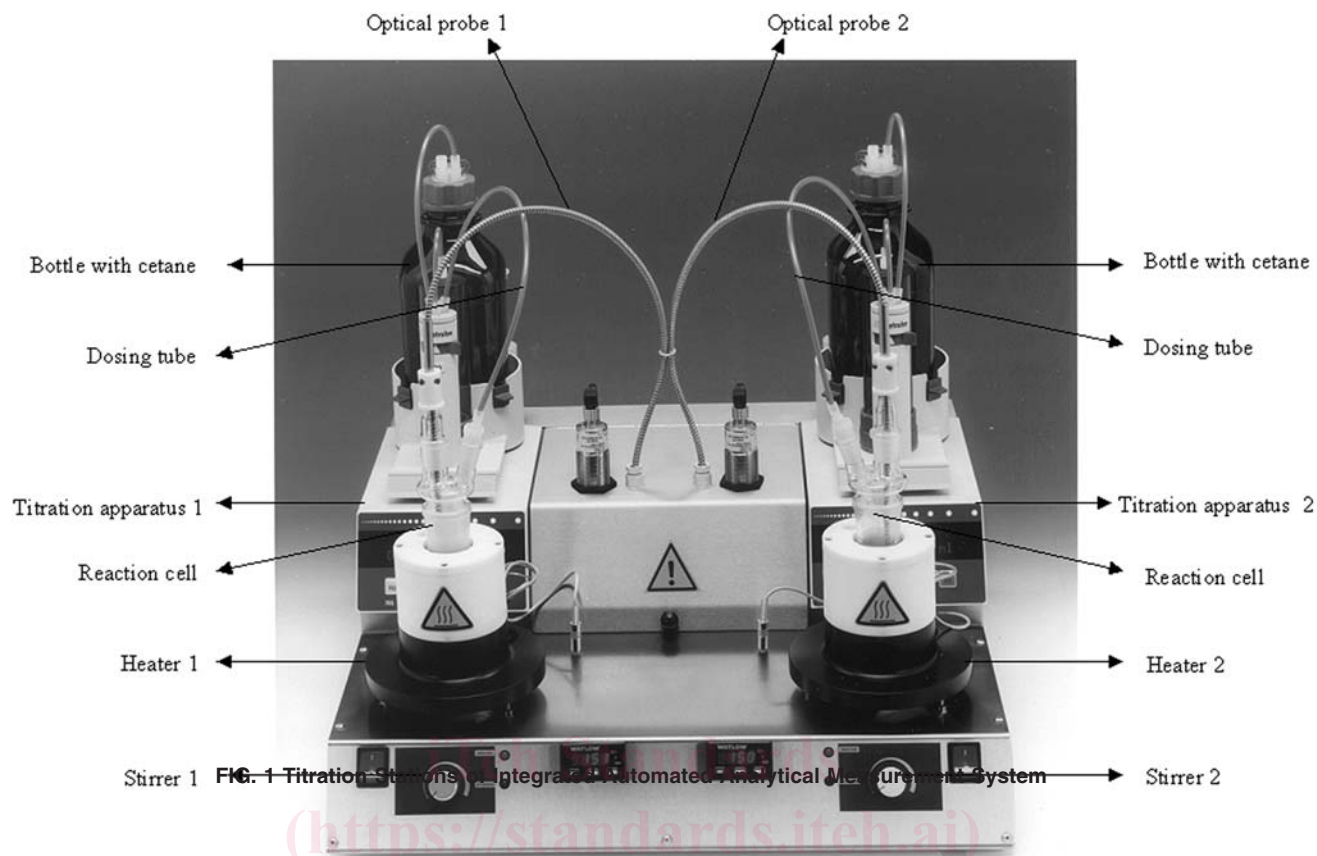


FIG. 1 Titration Stations Integrated Automated Analytical Measurement System

such

provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Asphaltene Solution* (3 g/L)—Dissolve 0.15 g of dry asphaltenes in 1-methylnaphthalene and dilute to 50 mL. A procedure to obtain asphaltenes is described in Appendix X2. Prepare fresh daily, as needed.

8.3 *Cetane (n-Hexadecane)*. (**Warning**—Irritating to respiratory system and skin.)

8.4 *Cleaning Solvent*, technical grade, 95 % purity, for cleaning. It consists of one of the following:

8.4.1 *Tetrahydrofuran*, stabilized. (**Warning**—Extremely flammable. Irritating to eyes and respiratory system.)

8.4.2 *Toluene*. (**Warning**—Flammable. Health Hazard.)

8.4.3 *Xylene*. (**Warning**—Flammable. Harmful by inhalation and in contact with skin. Irritating to skin.)

8.5 *n-Heptane*. (**Warning**—Flammable. Vapor harmful. Vapor may cause flash fire.)

8.6 *1-Methylnaphthalene*. (**Warning**—Harmful if swallowed. Irritating to skin.)

8.7 *Quality Control (QC) Sample*, a stable and homogeneous residual fuel oil. The QC sample contains at least 1

range of 180 to 380 mm²/s at 50°C.

9. Sampling and Test Specimens

9.1 Sampling:

9.1.1 Obtain samples in accordance with Practices D 4057 or D 4177.

9.1.2 Samples of very viscous materials may be warmed until they are reasonably fluid before they are sampled.

9.1.3 Store samples prior to taking test specimens at ambient temperatures.

9.2 Test Specimen Preparation:

9.2.1 *Sample Fuel Temperature*—Warm viscous samples until they can be mixed readily before opening the storage container. For fuels with a high wax content (high pour point) the temperature shall be at least 15°C above the pour point.

9.2.2 Shake or mix the sample thoroughly. If the sample contains a high content of insoluble matter, filter the sample through a 47-mm diameter glass fiber filter medium (such as Whatman Grade GF/A) using the Test Method D 4870 filtration apparatus.

9.2.3 *Preparation of Six Specimen Blends*—Visually check the reaction cell and the lid for cleanliness. Dissolve specimen in 1-methylnaphthalene in several different ratios of solvent according to Table 1. Prepare the blends shortly before the test procedure. Generally follow the sequence: (1) prepare and test Blends A1 and B1, (2) prepare and test Blends A2 and B2, and (3) prepare and test Blends C, and D.

NOTE 4—Blends A1 and B1 can be omitted when the coarse determinations are skipped.

⁶ 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.

TABLE 1 Typical Specimen and 1-Methylnaphthalene Solutions

Blend	Determination Mode	Specimen, g	1-Methylnaphthalene, mL	Reciprocal Dilution, g/mL
A1	Coarse	5	5	1
B1	Coarse	7	3.5	2
A2	Fine	5	5	1
B2	Fine	7	3.5	2
C	Fine	7.5	2.5	3
D	Fine	9	1.5	6

9.2.3.1 Weigh, according to Table 1, specimen to the nearest 0.01 g into a clean reaction cell and add a PFTE-coated magnetic stirring bar. Place the reaction cell in the center of the preheated (approximately 150°C) magnetic stirrer/hotplate and switch on the magnetic stirrer. Allow the specimen to warm up, until its viscosity is low enough to obtain a smooth stirring performance.

9.2.3.2 Add, according to Table 1, while continuously stirring, an appropriate volume of 1-methylnaphthalene to the nearest 0.01 mL.

9.2.3.3 Put the lid in place. Initiate the test procedure (12.3) within 10 min.

NOTE 5—Never use excessive force when placing the lid in place.

10. Preparation of Apparatus

10.1 Prepare the instrument for operation in accordance with the manufacturer's instructions.⁷

10.2 Inspect the optical probe's glass surface for cleanliness and damage before use. Connect the optical probes to the respective apparatus' titration station. Place the optical probes in the holder at the back of the corresponding titration station.

10.3 *Cleaning Instructions*—Perform the following cleaning procedure after the test procedure (see 12.3).

10.3.1 Remove the dosing tube. Clean the tube with a clean, lintless cloth. Place the tube into its storage place.

10.3.2 Carefully remove the optical sensor from the reaction cell. (**Warning**—The hot sensor and reaction cell can cause severe burns.) Clean the optical sensor with a clean, lintless soft cloth using an appropriate solvent (see 8.4). Place the sensor in the holder on top of the reaction cell heater.

10.3.3 Take the reaction cell from the heater using wooden clamps, or use other protective measures to prevent burns.

10.3.4 Remove the lid. Remove the stirrer bar. Empty the reaction cell.

NOTE 6—A small silicon or rubber tube with an attached magnetic stirrer is a handy tool to remove the stirrer bar from the reaction cell. Otherwise, the liquid can be poured over a metal sieve.

10.3.5 Clean the reaction cell and stirrer with an appropriate solvent (see 8.4). Use a clean, lintless cloth to remove any deposits.

11. Performance Check and QC

11.1 The instrument manufacturer checks the performance of the apparatus prior to delivery of the instrument to the end user.

11.2 *Performance Check*—Check the instrument's performance after the installation.

11.3 *Performance Check Procedures*—Perform the maximum flocculation ratio and the peptizing power determination on the asphaltene solution (8.2) according to Sections 12 and 13. The instrument's performance is acceptable when the peptizing power is $100 \pm 10\%$ (V/V).

11.4 *QC*—Confirm the performance of the instrument or the test procedure by analyzing a QC sample.

11.4.1 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.

11.4.2 When there is no QC/QA protocol established in the testing facility, use Guide D 6792 for guidance.

12. Procedure

12.1 Analyze the blends (9.2.3) according to the following test sequence.

12.1.1 Two coarse determination using Blends A1 and B1.

NOTE 7—During the coarse determination, cetane is added to decrease FR by 5% stepwise.

NOTE 8—The coarse determinations are used to estimate suitable starting values of FR for the fine determinations. The coarse determinations may be skipped when the operator has a good approximation of the sample's P_o and FR_{max} parameters.

NOTE 9—Appendix X3 shows an example of coarse dilution steps with cetane for Blend A1.

12.1.2 Four fine determinations using Blends A2, B2, C, and D.

NOTE 10—During the fine determination, cetane is added to decrease FR by 1% stepwise.

NOTE 11—Appendix X3 shows an example of fine dilution steps with cetane for Blend A2.

12.2 Initiate an automatic test sequence on the computer according to the manufacturer's instruction manual.⁷

12.3 *Test Procedure:*

12.3.1 Place the reaction cell into the appropriate heater position. Place the reaction cells from left (Heater 1) to right (Heater 2). The left position always contains the blend with the letter that is alphabetically first; that is, A before B before C before D. Single blend determinations must always be in left (1) position.

12.3.2 Position the clean optical probe in the reaction cell. Allow the blend to warm up, until its viscosity is low enough to obtain a smooth stirring performance.

12.3.3 Place the dosing tube of the titration apparatus into the reaction cell. Make sure that the end of the tube does not touch the glass sleeve of the optical probe inside the cell to prevent titrant running down the glass sleeve. The position of the tube is such that droplets fall directly into the sample vortex so that mixing is optimal.

12.3.4 Switch on the magnetic stirrer and adjust the speed so that agitation is just visible on the surface of the sample. Higher viscosity samples may require a higher speed.

12.3.5 Initiate the automatic test procedure according to the manufacturer's instruction manual.⁷

NOTE 12—See Appendix X4 for detailed automatic test program.

⁷ Automated Stability Analyser User Manual, Version 2, available from Zematra, 3194 DG Hoogvliet, The Netherlands.

13. Calculation of Results

13.1 The following calculations can be completed manually, but they are also performed automatically by the computer system.

13.2 Calculate the flocculation ratio at the critical dilution and the reciprocal critical dilution for the Blends A2, B2, C, and D.

13.2.1 Calculation of flocculation ratio at critical dilution, FR_x :

$$FR_x, \% = \frac{V_s}{V_s + V_c} \times 100 \tag{1}$$

where:

V_s = millilitres of 1-methylnaphthalene (9.2.3.2), and
 V_c = millilitres of cetane at inflection point as measured in 12.3.

13.2.2 Calculation of reciprocal critical dilution, $1/X_c$:

$$\frac{1}{X_c} = \frac{Ma}{V_s + V_c} \tag{2}$$

where:

V_s = millilitres of 1-methylnaphthalene (9.2.3.2),
 V_c = millilitres of cetane at inflection point as measured in 12.3, and
 Ma = grams of sample (9.2.3.1).

13.3 Plot the flocculation ratio at critical dilution values against the reciprocal critical dilution values for each of the four blends. Draw a straight line through the four points using the quadratic least-squares fit equation. Extrapolate the line to the x - and y -axes to determine the reciprocal critical cetane dilution ($1/X_{min}$) and the maximum flocculation ratio (FR_{max}). The value of $1/X_{min}$ is the point at which the line intercepts the x -axis, the y intercept is FR_{max} (see Fig. 2).

13.4 Calculate the peptizing power using Eq 3:

$$Po = FR_{max} \left[\left(\frac{1}{1/X_{min}} \right) + 1 \right] \tag{3}$$

14. Report

14.1 Report the following information:

14.1.1 A reference to this test method,

14.1.2 The sample identification,

14.1.3 The date of the test,

14.1.4 The calculated maximum flocculation ratio (FR_{max}) to the nearest 1 volume %, and

14.1.5 The calculated peptizing power (Po) to the nearest 1 volume %, and

14.1.6 Any deviation, by agreement or otherwise, from the specified procedures.

15. Precision and Bias

15.1 The precision statements for maximum flocculation ratio and peptizing power are based on results from a within-laboratory study. The study involved nine samples and covered the maximum flocculation ratio range from 16 to 57 and the peptizing power range from 27 to 96.

15.1.1 *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 values only in one case in twenty:

maximum flocculation ratio (FR_{max}): $r = 3$

peptizing power (Po): $r = 6$

NOTE 13—An interlaboratory round robin will be run. The repeatability data in 15.1.1 will be updated accordingly.

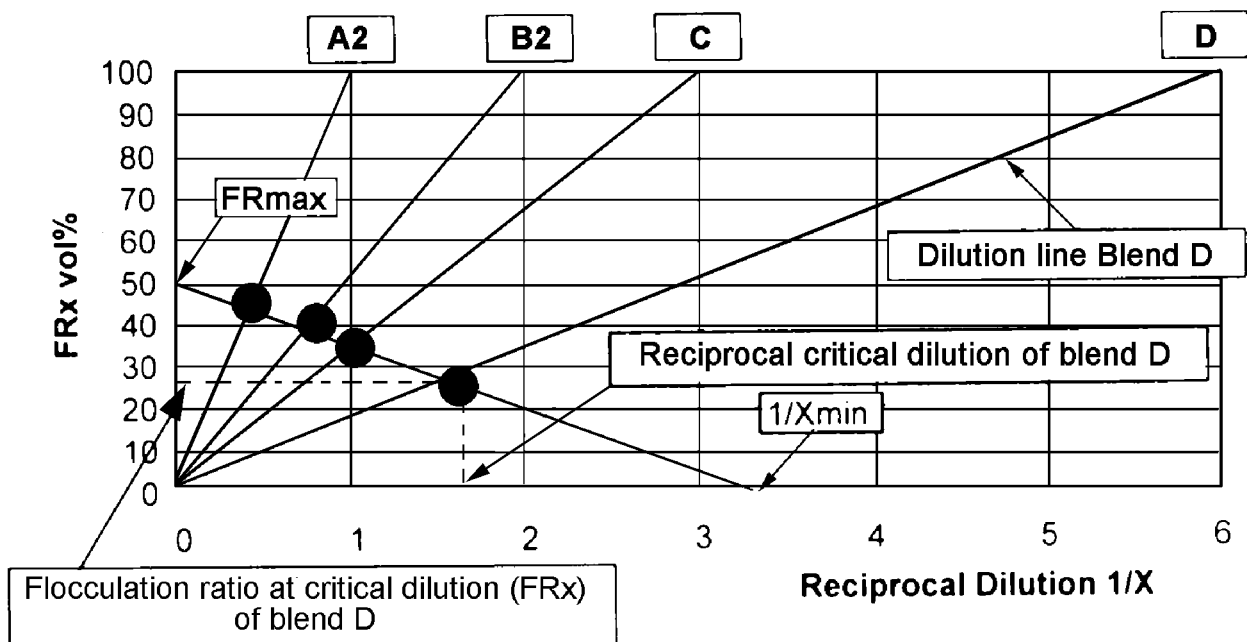


FIG. 2 Derivation of Maximum Flocculation Ratio (FR_{max}) and Reciprocal Critical Cetane Dilution ($1/X_{min}$)

15.1.2 *Reproducibility*—The reproducibility of this test method is being determined and will be available on or before 2009.

15.2 *Bias*—This test method has no bias because the results of the test are defined only in terms of this test method.

16. Keywords

16.1 compatibility; heavy fuel oil; maximum flocculation ratio; peptizing power; *P*-ratio; residual fuel oil

ANNEX

(Mandatory Information)

A1. INTEGRATED AUTOMATED ANALYTICAL MEASUREMENT SYSTEM

A1.1 *General*—(See Fig. A1.1). The integrated automated analytical measurement system consists of a PC based computer and two titration stations. The computer controls test sequencing, acquires and accumulates optical probe signal data, provides processing calculations, and automatically produces a report of important test parameters. The computer is capable of controlling one or two independent titration stations. Each titration station consists of the following:

A1.2 *Automatic Titration Unit*, computer controlled, motor-driven, with a volume dispensing accuracy of ± 0.01 mL.

A1.3 *Heater*, capable of heating the reaction cell to $150 \pm 1^\circ\text{C}$.

A1.4 *Magnetic Stirrer*, adjustable from 200 to 400 rpm.

A1.5 *Optical Probe*, consists of several glass fibers. There are two types of fibers, which are evenly distributed: (1) light emitting (880 nm) fibers and (2) light receiving fibers. The fibers are fitted in a glass sleeve (see Fig. A1.2).

A1.6 *Reaction Cell plus Lid*, of borosilicate glass (see Figs. A1.3 and A1.4). The lid has two upper joints: one joint is for connecting the glass sleeve and the other joint is for connecting the dosing tube. The assembly of reaction cell, lid, and glass sleeve is shown in Fig. A1.5.

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