



Designation: D3339 – 21

Standard Test Method for Acid Number of Petroleum Products by Semi-Micro Color Indicator Titration¹

This standard is issued under the fixed designation D3339; 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 acidic constituents in new or used petroleum products and lubricants soluble or nearly soluble in mixtures of toluene, and isopropyl alcohol. The test method is especially intended for cases in which the amount of sample available to be analyzed is too small to allow accurate analysis by Test Methods D974 or D664. It is applicable for the determination of acids having dissociation constants in water larger than 10^{-9} . Extremely weak acids having dissociation constants smaller than 10^{-9} do not interfere. Salts titrate if their hydrolysis constants are larger than 10^{-9} .

1.2 This test method can be used to indicate relative changes in acid number that occur in an oil during use under oxidizing conditions. Although the titration is made under definite equilibrium conditions, the method does not measure an absolute acidic property that can be used to predict performance of an oil under service conditions. No general relationship between bearing corrosion and acid number is known.

1.3 Since this test method requires substantially less sample than Test Methods D974 or D664, it provides an advantageous means of monitoring an oxidation test by changes in acid number by (1) minimizing test sample depletion for acid number analyses and thus minimizing the disturbance of the test or (2) allowing additional acid number analyses to be made while maintaining the same test sample depletion and thus providing additional data.

NOTE 1—Some oils, such as many cutting oils, rust-proofing oils, and similar compounded oils, or excessively dark-colored oils, may be more difficult to analyze by this test method due to obscurity of the color-indicator end point. These oils can be analyzed by Test Method D664 provided sufficient sample is available. However, this situation is much less likely using Test Method D3339 than using Test Method D974 due to the use of a more highly dilute sample during the titration and due to the greater stability of the end point color change. The acid numbers obtained by Test Method D3339 may or may not be numerically the same as those

obtained by Test Method D664 but they should be of the same order of magnitude.

NOTE 2—The results obtained using this method have been found to be numerically the same as those obtained using Test Method D974, within the precision of the two methods, for new or oxidized lubricants of the type primarily intended for hydraulic or steam turbine type service. The oxidized lubricants were obtained using the Test Method D943 oxidation test. This correlation is shown by the correlation coefficient $r = 0.989$ with slope $s = +1.017$ and intercept $y = +0.029$, calculated using the acid numbers obtained using both titration methods for the samples used for the precision statement (12.2).²

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.* For specific warning statements, see Sections 7 and 9, A1.1.4, A2.3.1, and A2.10.1.

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:³

- D664 Test Method for Acid Number of Petroleum Products by Potentiometric Titration
- D943 Test Method for Oxidation Characteristics of Inhibited Mineral Oils
- D974 Test Method for Acid and Base Number by Color-Indicator Titration
- D1193 Specification for Reagent Water

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 D02.06 on Analysis of Liquid Fuels and Lubricants.

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² Use of the correlation coefficient is given in Mack, C., *Essentials of Statistics for Scientists and Technologists*, Plenum Press, New York, NY, 1967, or other publications on statistics.

³ 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

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

3. Terminology

3.1 Definitions:

3.1.1 *acid number, n*—the quantity of a specified base, expressed in milligrams of potassium hydroxide per gram of sample, required to titrate a sample in a specified solvent to a specified endpoint using a specified detection system.

3.1.1.1 *Discussion*—In this test method, acids or salts with dissociation constants greater than 10^{-9} , are titrated to a green end point with *p*-naphtholbenzein indicator.

3.1.2 *used oil, n*—any oil that has been in a piece of equipment (for example, an engine, gearbox, transformer or turbine) whether operated or not.

3.1.2.1 *Discussion*—Typically, in this test method, the acidity of oxidized hydraulic or steam turbine oils is measured.

4. Summary of Test Method

4.1 To determine the acid number a sample of the oil is dissolved in a solvent consisting of toluene, isopropyl alcohol, and a small amount of water. The resulting single-phase solution is titrated at room temperature under a nitrogen atmosphere with standardized 0.01 *M* potassium hydroxide (KOH) in isopropyl alcohol to the stable green color of the added *p*-naphtholbenzein indicator.

5. Significance and Use

5.1 This test method measures the acid number of oils obtained from laboratory oxidation tests using smaller amounts of sample than Test Methods D974 or D664. It has specific application in Test Method D943 in which small aliquots of oil are periodically removed for testing by Test Method D3339. This test method, therefore, provides a means of monitoring the relative oxidation of oils, by measuring changes in acid number, at different time intervals and under the various oxidizing test conditions.

6. Apparatus (Refer to Fig. 1)

6.1 *Titration Buret*—A micro scale, automatic buret with 0.01 mL subdivisions and at least a 2 mL buret capacity.

6.2 *Titration Reservoir*—The preferred reservoir is one that is integral with the automatic buret, such as shown in Fig. 1. A titration reservoir separate from the automatic buret may be used if the line connecting the reservoir with the buret is all glass. Exposure of the titrant to light should be minimized by use of amber glass for the reservoir, by wrapping the reservoir with foil such as aluminum foil, or by other suitable means. Also, the tube in the reservoir for titrant withdrawal is adjusted so that the end of the tube is about 20 mm from the bottom of the reservoir so that any precipitate that may collect on the bottom of the reservoir will not be disturbed. To further avoid disturbing any precipitate in the reservoir, movement of the reservoir must be minimized.

6.2.1 With either type of reservoir all entrances and exits to the buret and reservoir must be connected to absorption tubes

to remove atmospheric carbon dioxide and water, for example, tubes containing 10 mesh to 20 mesh anhydrous calcium sulfate as desiccant and soda-lime as carbon dioxide absorbent. Precautions must be taken to prevent introduction of any soda-lime into the titrant reservoir or buret.

6.3 *Titration Beaker*—100 mL capacity tall-form Berzelius beaker without pouring spout. Approximate dimensions are 47 mm in inside diameter and 79 mm in height.

6.4 *Titration Beaker Purging Stopper*—A stopper to enclose the titration beaker. The stopper must be composed of an elastomeric material, such as neoprene, that is essentially unaffected by the titration solvent. Approximate stopper dimensions are 53 mm top diameter, 45 mm bottom diameter, and 25 mm height. The stopper is fitted with a 8 mm outside diameter glass inlet tube extending 15 mm \pm 2 mm beyond the bottom of the stopper and with a 7 mm \pm 1 mm inside diameter hole. The inlet tube and hole are placed on opposite sides of the stopper with a center-to-center separation distance of 30 mm \pm 1 mm.

6.5 *Purge Gas Rotameter*, capable of indicating a flow rate of 10 L/h.

6.6 *Stirrer Motor*, variable speed, magnetically linked.

NOTE 3—A propeller may also be used instead of a magnetic stirrer to mix the samples.

6.7 *Stirring Bar*, cylindrical, TFE-fluorocarbon encased, 25.4 mm long and 7.9 mm in diameter.

6.8 *Pipet*, capable of transferring 0.100 mL \pm 0.002 mL of titration indicator solution.

6.9 *Titration Solvent Buret*—A 500 mL or larger capacity buret with 5 mL subdivisions. The top of the buret is stoppered and connected with an absorption tube, as in 6.2, to remove atmospheric carbon dioxide and water. An alternative means of dispensing the titration solvent may be used provided a dispensing repeatability within \pm 1 mL for 40 mL is obtainable and the solvent in the dispenser is isolated from atmospheric carbon dioxide and water.

NOTE 4—An automated photometric device may also be used for detecting the titration end point. However, the precision estimates given in Section 13 may not apply to this mode of titration.

7. Reagents and Materials

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 such recognized standards for reagent chemicals.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

⁴ *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

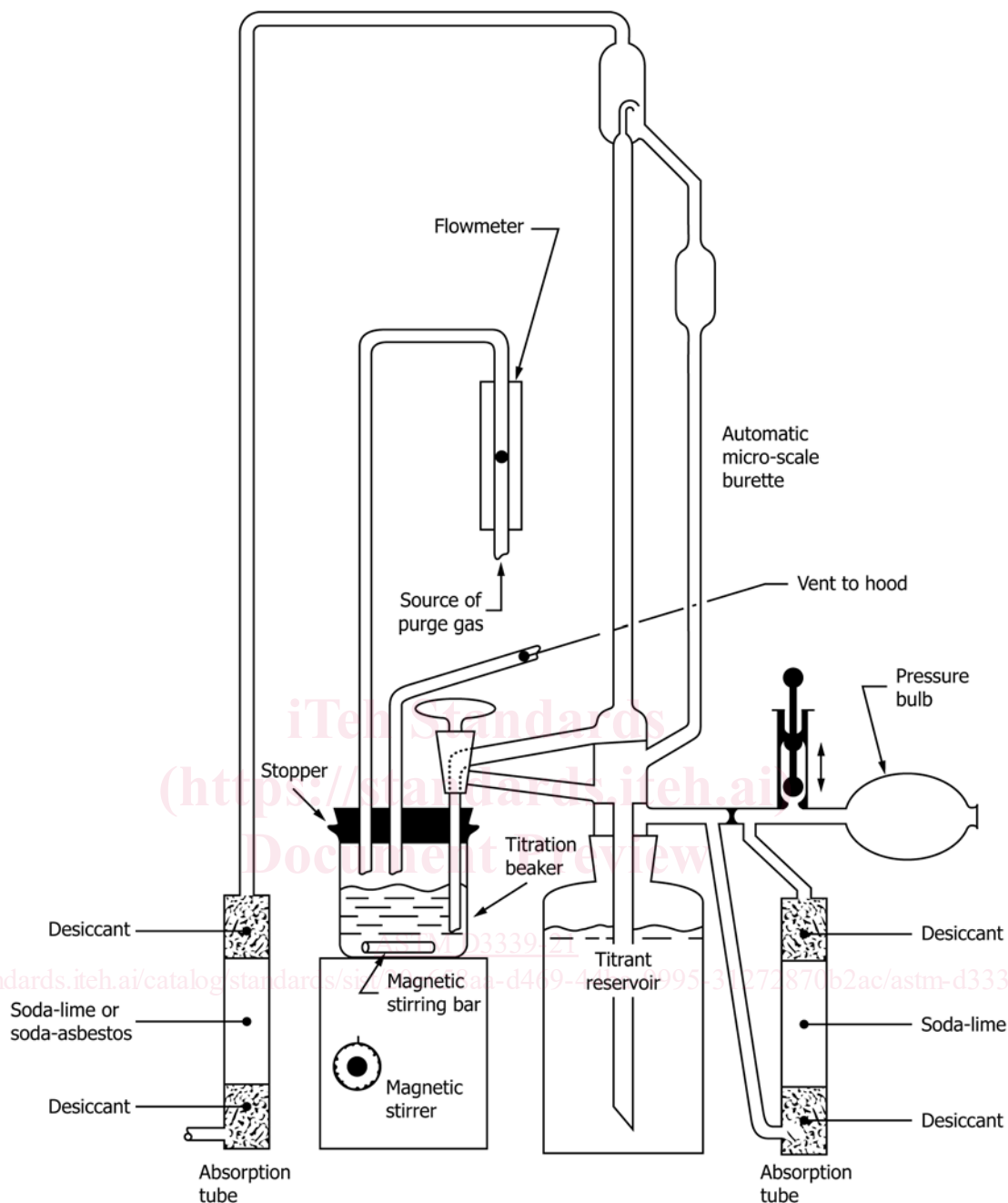


FIG. 1 Schematic Drawing of Typical Apparatus

7.2 *Purity of Water*—All references to water shall be understood to mean freshly distilled (carbon dioxide-free) water conforming to Specification D1193, Type II or III.

7.3 *Ethyl Alcohol*—(Warning—Flammable. Denatured—Cannot be made nontoxic.) USP 200 proof or denatured alcohol according to Formula 30 of the U. S. Bureau of Internal Revenue.

7.4 *Propanol-2-ol, (Isopropyl Alcohol) Anhydrous*, (Warning—Flammable, see also Note 5.) containing less than 0.9 % water.

NOTE 5—It has been reported that, if not inhibited against it, propanol-2-ol can contain peroxides. When this occurs, an explosive mixture is

possible when the storage vessel or other equipment such as a dispensing bottle, are near empty and approaching dryness.

7.5 *p-Naphtholbenzein Indicator*^{5,6} Solution—The *p*-naphtholbenzein must meet the specifications given in Annex A1. Prepare a solution containing 10 g of *p*-naphtholbenzein per litre of titration solvent.

⁵ In a 2006 study, only Kodak, Baker (Mallinkrodt), Fluka, and Aldrich were found to meet the specifications in Annex A1. However, Kodak brand is no longer available.

⁶ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1626. Contact ASTM Customer Service at service@astm.org.

TABLE 1 Size of Sample^A

Total Acid Number Range, mg KOH/g Sample	Sample Weight Range, g
< 0.01	5.0 to 2.0
0.01 < 0.1	2.0 to 1.5
0.1 < 0.5	1.5 to 1.0
0.5 < 3.0	1.0 to 0.2
> 3.0	0.2 to 0.1

^A Dark colored samples with total acid numbers of 0.1 or less may require use of smaller size samples to minimize interference of the sample color with the indicator colors.

7.6 *Nitrogen*, dry and carbon dioxide-free.

7.6.1 In order to obtain repeatable results and a stable end point color change, it is especially important that the nitrogen purge gas be free of carbon dioxide. Prepurified grade nitrogen has been found to be satisfactory.

7.7 *Phenolphthalein Indicator Solution*—Dissolve 0.10 g of solid pure phenolphthalein in 50 mL of water and 50 mL of ethyl alcohol.

7.8 *Titration Solvent*—Consisting of 5.0 mL \pm 0.1 mL of water, 495 mL \pm 1 mL of anhydrous propanol-2-ol, and 500 mL \pm 1 mL of toluene.

7.9 *Potassium Hydroxide Solution, Standard Alcoholic (0.01 M)*, (**Warning**—Corrosive.)

NOTE 6—Commercially available reagents may be used in place of laboratory preparations.

7.9.1 *Preparation*, Add 3 g of solid KOH to approximately 1 L of anhydrous propanol-2-ol (isopropyl alcohol) (containing less than 0.9 % water) in a 2 L Erlenmeyer flask. Boil the mixture gently on a steam bath for 10 min to 15 min while stirring to prevent caking of solids on the bottom of the flask. Add about 1 g of barium hydroxide and again boil gently for about 10 min. Cool to room temperature, stopper to prevent contact with the room atmosphere and allow to stand overnight (about 16 h). Filter the supernatant liquid through a 10 μ m TFE-fluorocarbon membrane filter while avoiding unnecessary exposure to the atmosphere and then dilute the solution (approximately 0.05 M) with anhydrous isopropyl alcohol to a total volume of about 5 L (Note 7). Store the titrant in a chemically resistant dispensing bottle out of contact with cork, rubber, or saponifiable stopcock lubricant and protected by a guard tube containing soda-lime. Minimize exposure of the titrant to light by storing in the dark or in an amber bottle or by wrapping the bottle with aluminum foil.

NOTE 7—Care should be taken to ensure a final normality of 0.011 \pm 0.002.

NOTE 8—Because of the relatively large coefficient of cubic expansion of organic liquids, such as propanol-2-ol, the standard alcoholic solutions should be standardized at temperatures close to those employed in the titrations of samples.

7.9.2 *Standardization*—The titrant is standardized (Note 8) against dried (at least 1 h at 110 °C), pure potassium hydrogen phthalate using the method described in 9.1 for the acid number analysis, with the exception that water (40 mL \pm 1 mL) is used as the solvent and 6 drops of phenolphthalein solution is used as the indicator. The blank is obtained in the same manner except that the potassium hydrogen phthalate is excluded. Standardize the titrant frequently enough to detect changes of 0.0003 M. The mean molarity determined by at least duplicate analyses is used as the titrant molarity for the acid number calculations.

7.10 *Toluene* (**Warning**—Flammable. Vapor harmful.) Nitration-grade, or equivalent.

8. Preparation of Used Oil Samples

8.1 When applicable, refer to Practice D4057 (Manual Sampling) or Practice D4177 (Automatic Sampling) for proper sampling techniques.

8.1.1 When sampling used lubricants, the specimen shall be representative of the system sampled and shall be free of contamination from external sources.

8.1.2 Agitate used oil samples thoroughly to ensure that any sediment present is homogeneously suspended before analysis, as the sediment can be acidic or basic or have adsorbed acidic or basic material from the sample. When necessary, samples are warmed to aid mixing.

NOTE 9—As used oils can change appreciably in storage, samples should be tested as soon as possible after removal from the lubricating system and the dates of sampling and testing, if known, should be noted.

9. Procedure

9.1 *Sample Titration*—Weigh to the nearest 0.1 mg the required amount of sample into a clean, tared titration beaker. Guidelines for determining the amount of sample required are given in Table 1. Place the magnetic stirring bar into the beaker taking care not to splash the sample. Pour 40 mL of titration solvent into the titration beaker, using part of this volume of solvent to wash down any sample that may have splashed onto the sides of the beaker above the solvent-sample solution level. Add 0.100 mL \pm 0.002 mL of *p*-naphtholbenzein indicator solution to the solvent-sample solution. Immediately assemble the titration beaker with the purging stopper, previously connected with the rotameter and nitrogen purge gas. Insert the buret tip into the beaker through the hole in the stopper. Adjust the position of the buret tip so that the purge gas can freely exit through the hole (**Warning**—The purge gas must be able to exit freely or otherwise dangerous pressures could develop. Also, the vapor from this treatment contains toluene and should be removed with adequate ventilation.) and the bottom of the buret tip is approximately 10 mm above the surface of the solution. Immediately start the purge gas flow through the beaker at a relatively fast rate, for example, about 30 L/h to 40 L/h, to purge the atmosphere in the beaker rapidly, and then start mixing the solution using the magnetic stirrer. Adjust the purge gas flow rate to 10 L/h \pm 1 L/h after purging at the faster flow rate for 15 s to 30 s. Adjust the stirring rate to mix the solution efficiently but without splashing the solution or mixing purge gas into the solution.

NOTE 10—In routine analysis, the indicator may be pre-mixed with the titration solvent before adding to the sample.

9.1.1 Titrate the sample at a temperature below 30 °C with the standardized 0.01 M KOH titrant. The indicator color changes are from the starting orange to a bright yellow and then to green. When the solution first turns green, reduce the

increment size to dropwise (manual buret) or between 0.01 mL and 0.05 mL (automated buret). Continue until a persistent green end point is reached and held for a minimum of 15 s after the addition of the last increment. This end point can be anticipated by the initial change to yellow, which occurs very close to the end point. Record the quantity of titrant required to obtain the stable end point.

10. Calculation

10.1 Calculate the acid number of the sample as follows:

$$\text{Acid number, mg KOH/g} = 56.10 M (A - B)/W \quad (1)$$

where:

- A = millilitres of titrant required for titration of the sample (9.1),
 B = millilitres of titrant required for titration of the blank,
 M = molarity of the titrant (7.9.2), and
 W = grams of sample used (9.1).

11. Report

11.1 Report the result as follows:

$$\text{Acid Number, (Test Method D 3339)} = (\text{Result}) \quad (2)$$

11.2 Report the acid number values as follows:

Acid Number	Report Results
< 0.01	< 0.01
0.01 to < 1.0	Report to the nearest 0.01
1.0 to < 10	Report to the nearest 0.1
10.0 to 20	Report to the nearest 1.0

12. Quality Control Checks

12.1 Confirm the performance of the test procedure by analyzing a quality control (QC) sample that is, if possible, representative of the samples typically analyzed.

12.2 Prior to monitoring the measurement process, the user of the method needs to determine the average value and control limits of the QC sample.⁷

12.3 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.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 recalibration.

12.4 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.

12.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the sample 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 acid number can vary while an out-of-control situation arises, the stability of the QC sample can be a source of the error.

13. Precision and Bias

13.1 This precision section applies only to new and used petroleum-based, inhibited steam turbine and hydraulic oils. Insufficient data are available on other oils coming within the scope of this test method so no precision is given for such oils.

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

13.2.1 *Repeatability*—The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of this test method, exceed the following values only in one case in twenty:

Acid Number	Repeatability
0.05 to 20.0	0.08 (X) ^{1/2}

where:

X = mean acid number of sample.

13.2.2 *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 this test method, exceed the following values only in one case in twenty:

Acid Number	Reproducibility
0.05 to 20.0	0.27 (X) ^{1/2}

where:

X = mean acid number of sample.

13.3 *Bias*—The procedure in this test method has no bias because the value of the acid number can be defined only in terms of this test method.

14. Keywords

14.1 acid number; petroleum products; semi-micro color indicator titration

⁷ MNL7, *Manual on Presentation of Data and Control Chart Analysis*, 6th ed., ASTM International, W. Conshohocken, PA, 1990.