



## Standard Test Method for Acidity in Aviation Turbine Fuel<sup>1</sup>

This standard is issued under the fixed designation D 3242; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the Department of Defense. This test method has been approved by the sponsoring committees and accepted by the cooperating societies in accordance with established procedures.*

### 1. Scope

1.1 This test method covers the determination of the acidity in aviation turbine fuel in the range from 0.000 to 0.100 mg KOH/g.

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *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 664 Test Method for Acid Number of Petroleum Products by Potentiometric Titration<sup>2</sup>

D 1193 Specification for Reagent Water<sup>3</sup>

### 3. Terminology

#### 3.1 Definitions:

3.1.1 *acid number, n*—the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample that is required to titrate a sample in a specific solvent to a specific end point.

3.1.1.1 *Discussion*—*in this test method*, the solvent is a toluene-water-isopropanol mixture and the end point is determined when a green/green brown color is obtained using the specified p-naphtholbenzein indicator solution.

### 4. Summary of Test Method

4.1 The sample is dissolved in a mixture of toluene and isopropyl alcohol containing a small amount of water. The

resulting single phase solution is blanketed by a stream of nitrogen bubbling through it and is titrated with standard alcoholic potassium hydroxide to the end point indicated by the color change (orange in acid and green in base) of the added p-naphtholbenzein solution.

### 5. Significance and Use

5.1 Some acids can be present in aviation turbine fuels due either to the acid treatment during the refining process or to naturally occurring organic acids. Significant acid contamination is not likely to be present because of the many check tests made during the various stages of refining. However, trace amounts of acid can be present and are undesirable because of the consequent tendencies of the fuel to corrode metals that it contacts or to impair the water separation characteristics of the aviation turbine fuel.

5.2 This test method is designed to measure the levels of acidity that can be present in aviation turbine fuel and is not suitable for determining significant acid contamination.

### 6. Apparatus

6.1 *Buret*—A 25-mL buret graduated in 0.1-mL subdivisions, or a 10-mL buret graduated in 0.05-mL subdivisions.

NOTE 1—An automated buret capable of delivering titrant amounts in 0.05 mL or smaller increments can be used, but the stated precision data were obtained using manual burets only.

### 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.<sup>4</sup> Other grades may be

<sup>1</sup> 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 August 10, 2001. Published September 2001. Originally published as D 3242 – 73 T. Last previous edition D 3242 – 98.

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>4</sup> *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.

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.

NOTE 2—Commercially available reagents may be used in place of laboratory preparations when they are certified in accordance with 7.1.

7.2 *Purity of Water*—References to water shall be understood to mean distilled water as defined by Type III water of Specification D 1193.

7.3 *p-Naphtholbenzein<sup>5</sup> Indicator Solution*—The *p*-naphtholbenzein must meet the specifications given in Annex A1. Prepare a solution of *p*-naphtholbenzein in titration solvent equal to  $10 \pm 0.01$  g/L.

7.4 *Nitrogen*, dry-type, carbon dioxide-free. (**Warning**—Compressed gas under high pressure. Gas reduces oxygen available for breathing.)

7.5 *Potassium Hydroxide Solution, Standard Alcoholic (0.01 N)*—Add 0.6 g of solid KOH (**Warning**—Highly corrosive to all body tissue both in solid form and in solution.) to approximately 1 L of anhydrous isopropyl alcohol (**Warning**—Flammable. Vapor harmful. Keep away from heat, sparks, and open flame.) (containing less than 0.9 % water) in a 2-L Erlenmeyer flask. Boil the mixture gently for 10 to 15 min, stirring to prevent the solids from forming a cake on the bottom. Add at least 0.2 g of barium hydroxide (Ba(OH)<sub>2</sub>) (**Warning**—Poisonous if ingested. Strongly alkaline, causes severe irritation producing dermatitis.) and again boil gently for 5 to 10 min. Cool to room temperature, allow to stand for several hours, and filter the supernatant liquid through a fine sintered-glass or porcelain filtering funnel; avoid unnecessary exposure to carbon dioxide (CO<sub>2</sub>) during filtration. Store the solution 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.

NOTE 3—Because of the relative large coefficient of cubic expansion of organic liquids, such as isopropyl alcohol, the standard alcoholic solutions should be standardized at temperatures close to those employed in the titration of samples.

7.5.1 *Standardization of Potassium Hydroxide Solution*—Standardize frequently enough to detect changes of 0.0002*N*. One way to accomplish this is as follows. Weigh, to the nearest 0.1 mg, approximately 0.02 g of potassium acid phthalate, which has been dried for at least 1 h at  $110 \pm 1^\circ\text{C}$  and dissolve in  $40 \pm 1$  mL of water, free of CO<sub>2</sub>. Titrate with the potassium hydroxide alcoholic solution to either of the following end-points: (a) when the titration is electrometric, titrate to a well defined inflection point at the voltage that corresponds to the voltage of the basic buffer solution; (b) when the titration is colorimetric, add 6 drops of phenolphthalein indicator solution and titrate to the appearance of a permanent pink color. Perform the blank titration on the water used to dissolve the potassium acid phthalate. Calculate the normality using the equation:

$$\text{Normality} = \frac{W_p}{204.23} \times \frac{1000}{V - V_b} \quad (1)$$

where:

- $W_p$  = weight of the potassium acid phthalate, g,
- 204.23 = molecular weight of the potassium acid phthalate,
- $V$  = volume of titrant used to titrate the salt to the specific end-point, mL, and
- $V_b$  = volume of titrant used to titrate the blank, mL.

7.5.2 *Phenolphthalein Indicator Solution*—Dissolve 0.1 g  $\pm 0.01$  of pure solid phenolphthalein in 50 mL of water, free of CO<sub>2</sub>, and 50 mL of ethanol.

7.6 *Titration Solvent*—Add 500 mL of toluene (**Warning**—Flammable. Vapor harmful. Keep away from heat, sparks, and open flame.) and 5 mL of water to 495 mL of anhydrous isopropyl alcohol.

## 8. Procedure

8.1 Introduce  $100 \pm 5$  g of the sample weighed to the nearest 0.5 g, into a 500-mL wide-mouth Erlenmeyer flask. (One type of suitable modified flask is shown in Fig. 1.) Add 100 mL of the titration solvent and 0.1 mL of the indicator solution. Introduce nitrogen through a 6 to 8 mm outside diameter glass tube to a point within 5 mm of the flask bottom at a rate of 600 to 800 mL/min. Bubble the solution for 3 min  $\pm 30$  s with occasional mixing.

8.1.1 The vapor from this treatment contains toluene and should be removed with adequate ventilation.

8.2 Continue the nitrogen addition and titrate without delay at a temperature below 30°C. Add 0.01 *N* KOH solution in increments and swirl to disperse until a green end point is reached that persists for 15 s.

NOTE 4—The temperature can be measured by any suitable temperature measuring device.

8.3 *Blank*—Perform a blank titration on 100 mL of the titration solvent and 0.1 mL of the indicator solution, introducing the nitrogen in the same manner and titrating to the same end point as above.

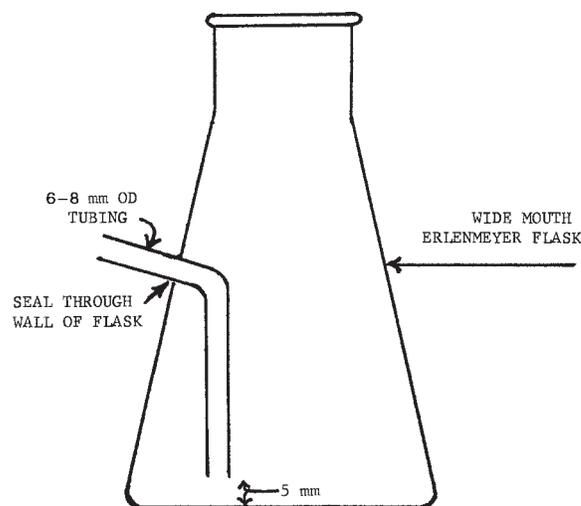


FIG. 1 Titration Flask

<sup>5</sup> In a 1992 study, only Kodak and Fisher *p*-naphtholbenzein were found to meet the specifications in Annex A1. The Fisher Reagent Solution was the only commercially available solution to meet the specifications.

## 9. Quality Control Checks

9.1 Confirm the performance of the equipment or the procedure each day it is in use, by analyzing a quality control (QC) sample. It is advisable to analyze additional QC samples as appropriate, such as at the end of a batch of samples or after a fixed number of samples to ensure the quality of the results. Analysis of result(s) from these QC samples can be carried out using control chart techniques.<sup>6</sup> When the QC sample result causes the laboratory to be in an out-of-control situation, such as exceeding the laboratory's control limits, instrument recalibration may be required. An ample supply of QC sample material shall be available for the intended period of use, and shall be homogeneous and stable under the anticipated storage conditions. If possible, the QC sample shall be representative of samples typically analyzed and the average value and control limits of the QC sample shall be determined prior to monitoring the measurement process. The QC sample precision shall be checked against the ASTM method precision to ensure data quality.

NOTE 5—Because the acid number can vary while the QC sample is in storage, when an out-of-control situation arises, the stability of the QC sample can be a source of the error.

## 10. Calculations

10.1 Calculate the acid number as follows:

$$\text{Acid number, mg of KOH/g} = [(A - B)N \times 56.1]/W \quad (2)$$

where:

$A$  = KOH solution required for titration of the sample (8.2), mL,

$B$  = KOH solution required for titration of the blank (8.3), mL,

$N$  = normality of the KOH solution, and

$W$  = sample used, g.

## 11. Report

11.1 Report the result to the nearest 0.001 mg KOH/g as Acid Number (Test Method D 3242) = (Result).

<sup>6</sup> ASTM MNL 7, *Manual on Presentation of Data Control Chart Analysis*, 6th ed, Section 3: Control Charts for Individuals, available from ASTM Headquarters.

## 12. Precision and Bias<sup>7</sup>

12.1 *Precision*—The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

12.1.1 *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 only in one case in twenty (see Table 1).

12.1.2 *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 (see Table 1).

NOTE 6—The precision statements were based on the use of manual burets only. The user is cautioned that the precision statements may or may not be applicable to titrations performed with the use of automated burets, since no interlaboratory study has been conducted to date to statistically evaluate results determined by both techniques.

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

## 13. Keywords

13.1 acidity; aviation turbine fuel

<sup>7</sup> The basis for this precision data is available from the ASTM by requesting RR:D02-1010.

**TABLE 1 Precision<sup>A</sup>**  
**All values are in acid number units.**

Average Acid Number	Repeatability	Reproducibility
0.001	0.0004	0.0013
0.002	0.0006	0.0018
0.005	0.0009	0.0029
0.010	0.0013	0.0041
0.020	0.0019	0.0057
0.050	0.0030	0.0091
0.100	0.0042	0.0128

<sup>A</sup> These precision data were derived as follows:  
 Repeatability =  $0.0132 \sqrt{a}$   
 Reproducibility =  $0.0406 \sqrt{a}$

where:  $a$  = acid number

**ANNEXES**
**(Mandatory Information)**
**A1. SPECIFICATIONS FOR *p*-NAPHTHOLBENZEIN**
**A1.1 Conformity Requirements**

A1.1.1 *Appearance*—Red amorphous powder.

A1.1.2 *Chlorides*—Less than 0.5 %.

A1.1.3 *Solubility*—Ten grams shall dissolve completely in 1 L of titration solvent.

A1.1.4 *Minimum Absorbance*—Exactly 0.1000 g of the sample is dissolve in 250 mL of methanol. (**Warning**—Flammable.) Five millilitres of this solution is made up to 100 mL with pH 12 buffer. This final dilution should have a minimum absorbance of 1.20 when read at the 650-nm peak using a Beckman DU or alternative type spectrophotometer, 1-cm cells, and water as the blank.

A1.1.5 *pH Range*:

A1.1.5.1 Indicator turns to the first clear green at a relative pH of  $11 \pm 0.5$  when tested by the method for pHr range of *p*-naphtholbenzein indicator as described in Annex A2.

A1.1.5.2 Requires not more than 0.5 mL of 0.01 *N* KOH solution above that for the blank to bring the indicator solution to the first clear green.

A1.1.5.3 Requires not more than 1.0 mL of 0.01 *N* KOH solution above that for the blank to bring the indicator solution to a blue color.

A1.1.5.4 Initial pHr of the indicator solution is at least as high as that of the blank.

A1.1.5.5 Buffer is made by mixing 50 mL of 0.05 *M* dibasic sodium phosphate with 26.9 mL 0.1 *M* sodium hydroxide.

**A2. TEST METHOD FOR DETERMINING pHr RANGE OF *p*-NAPHTHOLBENZEIN INDICATOR**
**A2.1 Scope**

A2.1.1 This test method is intended for determining the acceptability of *p*-naphtholbenzein indicator for use in Test Method D 3242 with regard to color change over a pHr range.

**A2.2. Terminology**

A2.2.1 *Definitions of Terms Specific to This Standard:*

A2.2.1.1 *pHr*—an arbitrary term which expresses the relative hydrogen ion activity in the toluene-isopropyl alcohol medium in a manner similar to that in which the term pH expresses the actual hydrogen ion activity in aqueous solutions. For the purpose of this test method, the pHr acidity scale is defined by two standard buffer solutions which have been designated pHr 4 and pHr 11. The exact relation between pHr and the true pH of a toluene-isopropyl alcohol solution is not known and cannot be readily determined.

**A2.3 Summary of Test Method**

A2.3.1 A prescribed amount of indicator is titrated electrometrically through the various color changes with alcoholic potassium hydroxide and results plotted against meter readings converted to pHr units.

**A2.4 Apparatus**

A2.4.1 *Meter, Glass Electrode, Calomel Electrode, Stirrer, Beaker and Stand*, as specified in the Appendix to Test Method D 664 – IP 177.

**A2.5 Reagents**

A2.5.1 *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.<sup>4</sup> 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.

A2.5.2 *Purity of Water*—References to water shall be understood to mean distilled water.

A2.5.3 *Acidic Buffer Solution* (pHr = 4.0)—Prepare a stock solution in accordance with Test Method D 664 – IP 177. Add 10 mL of buffer stock solution to 100 mL of titration solvent. Use the diluted solution within 1 h.

A2.5.4 *Alkaline Buffer Solution* (pHr = 11.0)—Prepare a stock solution in accordance with Test Method D 664 – IP 177. Add 10 mL of buffer stock solution to 100 mL of titration solvent. Use the diluted solution within 1 h.

A2.5.5 *Hydrochloric Acid, Standard Alcoholic Solution* (0.2 *N*)—Prepare and standardize in accordance with Test Method D 664 – IP 177.

A2.5.6 *p-Naphtholbenzein Indicator Solution*—Prepare as described in 7.3.

A2.5.7 *Potassium Chloride Electrolyte*—Prepare a saturated solution of potassium chloride (KCl) in water.

A2.5.8 *Potassium Hydroxide, Standard Alcoholic Solution*—(0.2 *N*)—Prepare, store, and standardize in accordance with Test Method D 664 – IP 177.

A2.5.9 *Titration Solvent*—Add 500 mL of toluene and 5 mL of water to 495 mL of anhydrous isopropyl alcohol. The titration solvent should be made up in large quantities.

**A2.6 Preparation of Electrode System**

A2.6.1 Prepare the electrode system in accordance with 7.1 and 7.2 of Test Method D 664 – IP 177.

**A2.7 Standardization of Apparatus**

A2.7.1 Prior to each test or series of tests, set the meter to read on the pH scale, insert the electrodes into a beaker containing the acidic nonaqueous buffer solution at a temperature of  $25 \pm 2^\circ\text{C}$  and stir the solution vigorously. When the pH

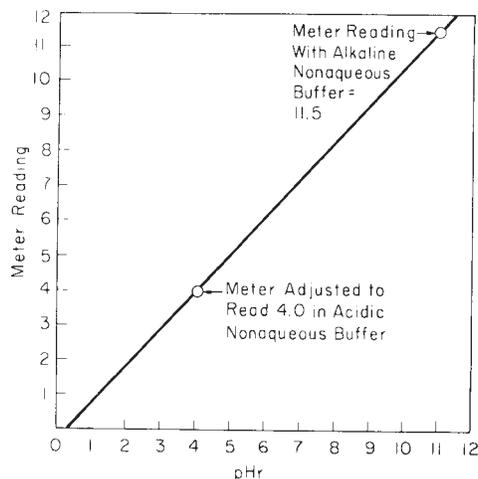


FIG. A2.1 Calibration Curve for Conversion of pH Meter Readings to pHr

meter reading becomes constant adjust the asymmetry potential dial of the instrument so that the meter reads 4.0.

A2.7.2 Remove the acidic buffer, clean the electrodes, and immerse them in water for several minutes. Dry the electrodes and insert them in a beaker containing alkaline nonaqueous buffer solution at  $25 \pm 2^\circ\text{C}$ . When the pH meter reading has become steady, record the exact value. If the reading is within 0.2 pH units of 11.0, the initial acidity, pHr, of unknown solutions may be read directly from the dial of the meter. If the reading is not within 0.2 units of 11.0 prepare a correction graph as shown in Fig. A2.1. Use this graph to convert pH meter readings to initial acidity, pHr.

### A2.8 Procedure

A2.8.1 Titrate 100 mL of titration solvent with 0.01 N KOH solution until the meter indicates a pHr between 13 and 14.

A2.8.2 Add 0.5 mL of indicator solution to a fresh portion of titration solvent and after cleaning the electrodes titrate with 0.01 N KOH solution until the meter indicates a pHr between 13 and 14.

A2.8.3 During the titration, plot the volume of titrant against the pHr or meter reading and note on the curve the various color changes at the corresponding pHr values.

NOTE A2.1—The following color changes, in order, are intended as a guide:

- Amber to olive green
- Olive green to clear green
- Clear green to bluish green
- Bluish green to blue

A2.8.4 Plot the blank titration on the same paper used for the indicator.

### A2.9 Calculation

A2.9.1 Subtract the volume of titrant used in the blank titration from that used for the indicator solution titration at the same pHr corresponding to the definite color changes between 10 to 12 pHr.

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