Standard Test Method for Determination of Fatty Acids and Esters in Glycerin[1]

This standard is issued under the fixed designation D7638; 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 provides the quantitative determination of the fatty acid and ester content in purified glycerin by the titrimetric method.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard may involve hazardous materials, operations and equipment. 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.* Specific precautions are listed in Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D4725 Terminology for Engine Coolants and Related Fluids

2.2 *Other Standard:*

The United States Pharmacopeia 31 Glycerin Monograph – Fatty Acids and Esters[3]

3. Terminology

3.1 *Definitions:*

3.1.1 *glycerin*—propane-1,2,3-Triol, $C_3H_5(OH)_3$ (also known as glycerine), 1,2,3-propanetriol, 1,2,3-trihydroxypropane, glyceritol, glycyl alcohol. CAS #56-81-5

3.1.2 *FA&E*—Fatty acid and Esters

3.1.3 For other definitions of terms used in this specification, refer to Terminology D4725.

4. Significance and Use

4.1 Any residual fatty acid and esters (FA&E) should be present only at very low levels in purified glycerine.

4.2 This procedure requires the addition of a measured volume of sodium hydroxide, in excess of the amount actually needed to react with FA&E in the glycerine sample. After boiling, the excess sodium hydroxide is back titrated with standardized hydrochloric acid. The quantity of the substance being titrated is calculated as the difference between the volumes of the sodium hydroxide solution originally added, corrected by means of a blank titration, and that was consumed by the titrant in the back titration.

NOTE 1—The standardized solutions for sodium hydroxide and hydrochloric acid are commercially available.

5. Apparatus

5.1 *Standard Type A Glassware.*

5.2 *Erlenmeyer flask*, 200 to 250 mL, alkali-resistant with a standard tapered 24/40 ground glass neck joint, or equivalent.

5.3 *Microburette* having a capacity of 5 mL, graduated to 0.02 mL and calibrated to meet the NIST specification. An automatic titrator with a minimum capacity of 5 mL can also be used.

5.4 *Pipette*, standard or automatic that can accurately deliver 5 ± 0.01 mL.

5.5 *Air reflux condenser* with standard taper ground glass joint which fits the Erlenmeyer flask in 5.1. Minimum length, 550 mm.

6. Purity of Reagents and Water

6.1 *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 such specifications are available. 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 *Purity of Water*—Unless indicated otherwise, references to water shall be understood to mean Type II reagent water as defined in Specification D1193.

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[1] This test method is under the jurisdiction of ASTM Committee D15 on Engine Coolants and Related Fluids and is the direct responsibility of Subcommittee D15.93 on Research and Long Range Planning.

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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] Available from U.S. Pharmacopeia (USP), 12601 Twinbrook Parkway, Rockville, MD 20852-1790, http://www.usp.org.

NOTE 2—The presence of carbon dioxide can introduce errors; therefore it is advisable to prepare 500 mL of water by boiling for 5 min. Cool to room temperature. Check the pH of the distilled water before use. The pH should be 7.0 ± 0.1. If not, adjust the pH with 0.1 N sodium hydroxide (NaOH) or 0.1 N hydrogen chloride (HCl), whichever is appropriate. Store the freshly boiled and neutralized water in a *tightly closed container*.

7. Reagents

7.1 *Phenolphthalein Solution*—(See Note 2.) Dissolve 1 g of phenolphthalein in 100 mL of ethanol (95 %), methanol or isopropanol. This solution can be purchased.

7.2 *Hydrochloric Acid, 0.5 N, aqueous solution*—(See Note 1 and Note 2.) To a 1000-mL volumetric flask containing 40 mL of water, slowly add 43 mL of concentrated hydrochloric acid. Cool, and add water to volume. Standardize the solution to an accuracy of ±0.001 N.

7.3 *Sodium Hydroxide, 0.5 N, aqueous solution*—(See Note 1 and Note 2.) Dissolve 22.0 g of NaOH in water and dilute to 1 L. Allow to stand overnight. Siphon the liquid into a clean bottle. Standardize accurately to ±0.001 N with potassium acid phthalate. The standardized sodium hydroxide solution should be protected against evaporation and absorption of carbon dioxide (CO_2) from the air.

NOTE 3—The normality of the hydrochloric acid and sodium hydroxide solutions may be in the range of 0.5 ± 0.05 N.

7.4 *Freshly boiled water,* or equivalent. (See 6.2.)

8. Precautions

8.1 Hydrochloric acid and sodium hydroxide solutions are corrosive. Avoid eye and skin contact.

8.2 Prior to use, please study and be aware of the Material Safety Data Sheet and correct laboratory performance for the appropriate health and safety precautions that may apply to any of the chemicals and equipment that are used in this procedure.

8.3 It is the responsibility of each organization to conduct a job hazard analysis to assess all the safety risks and PPE needed for performance of this test method.

9. Procedure

9.1 Weigh 50 ± 0.1 g of a well-mixed glycerine sample into a 200 to 250 mL Erlenmeyer flask.

9.2 Dilute the sample with 50 mL of freshly boiled and cooled water.

9.3 Add 5.00 ± 0.1 mL of 0.5 N sodium hydroxide solution to the flask using a pipette or automatic titrator. Gently swirl the flask to ensure mixing.

NOTE 4—Ensure the glycerine sample, the water and the sodium hydroxide solution are well mixed before refluxing, otherwise, bumping and erratic boiling can occur.

9.4 Add three to five boiling chips into the flask and securely place the fitted air condenser into the neck of the flask. Using a polytetrafluoroethylene (PTFE)[4] sleeve between the glass joint is suggested.

NOTE 5—When testing samples with expected high FA&E values (>0.4), the sample is inclined to foam up the condenser. The addition of boiling chips helps control this problem.

9.5 Place the flask on the heat source and clamp the condenser and flask securely in place. Reflux the solution for a minimum of 5 min after refluxing has begun.

9.6 Carefully remove the flask and condenser assembly from the heating device and cool to room temperature. Once cooled, carefully remove the air condenser.

9.7 Add approximately 1 mL of phenolphthalein indicator solution to the flask.

9.8 Titrate the excess alkali with the standardized 0.5 N hydrochloric acid solution until the pink color of the indicator disappears. Record the volume of the hydrochloric acid in mL (S) required to titrate the sample.

9.9 In the event that the glycerin sample has a very high fatty acid and ester content and consumes all of the sodium hydroxide solution as indicated by the absence of a color change when phenolphthalein indicator is added in 9.7, the test is invalid and must be repeated. In this case, use a 25 ± 0.1 g sample weight and repeat steps 9.1 to 9.8. The analysis results must be corrected to a sample weight of 50 g.

9.10 Conduct a blank test following the procedure as described in 9.2 through 9.8, using only 50 mL of freshly boiled water. Record the titration volume for the blank determination (B) in mL.

10. Calculation

10.1 Calculation of the fatty acid and ester equivalent expressed as millilitres of 0.5 N NaOH consumed per 50 g of sample is expressed by the following equation:

$$\frac{(B - S) \times N}{0.5} = \text{FA\&E as mL of 0.5 N NaOH per 50 g sample} \quad (1)$$

where:

B = the volume of 0.5 N hydrochloric acid solution, in mL (±0.01 mL) used to titrate the blank,
S = the volume of 0.5 N hydrochloric acid solution, in mL (±0.01 mL) required to titrate the sample, and
N = Normality of the HCl solution reported to ±0.001 mL.

Example:

B = 4.95 mL HCl titrated for the blank,
S = 4.65 mL HCl titrated for the sample, and
N = HCl normality of 0.525 N.

$$\text{FA\&E} = \frac{(4.95\text{ mL} - 4.65\text{ mL}) \times 0.525}{0.5}$$

$$= 0.32 \text{ mL of 0.5 N NaOH per 50 g sample} \quad (2)$$

11. Report

11.1 Report the Fatty Acid and Ester content of the sample to the nearest 0.01 mL of NaOH consumed per 50 g of sample.

12. Precision and Bias[5]

12.1 *Precision*—See Table 1.

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[4] Brand name Teflon is a trademark of Dupont.

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D15-1026.

TABLE 1 Fatty Acids and Esters in Glycerin (%)

Material	Average	Std Dev	Repeatability Std Dev	Reproducibility Std Dev	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	$S\bar{x}$	S_r	S_R	r	R
A	0.30	0.07	0.004	0.068	0.012	0.189
B	0.54	0.05	0.009	0.047	0.025	0.131

12.2 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

13. Keywords

13.1 antifreeze; engine coolant; esters; ethylene; fatty acids; glycerin; glycerine; glycerol; titrimetric

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