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Standard Test Method for
Determination of Glycerin Assay by Titration (Sodium Meta Periodate)[1]

This standard is issued under the fixed designation D7637; 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 glycerin by the titrimetric method. It is applicable to all glycerin or glycerin/water mixtures >75 %.

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 problems associated with its use. It is the responsibility of whoever uses this standard to consult the established and 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

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 *Other Standards:*

The United States Pharmacopoeia 31 Glycerin Monograph – Assay Method[3]

AOCS Official Method EA 6-94 (Replaces AOCS EA 6-51), Determination of Crude Glycerin, Titrimetric Method[4]

BS 5711: Part 3, 1979 Sampling and Test for Glycerol - Determination of Glycerol Content[5]

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, glycerol. CAS #56-81-5.

3.1.2 *SMP*—Sodium Meta Periodate.

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

4. Significance and Use

4.1 This test method is based on the cold oxidation of the glycerol by sodium metaperiodate in a strong acidic medium. Formaldehyde and formic acid are produced in this reaction and the latter is used to measure the glycerol content by titration with standard sodium hydroxide solution, to a pH 8.1 ± 0.1. The glycerol content is expressed as a percentage (m/m).

$$CH_2OH - CHOH - CH_2OH + 2\ NaIO_4 \rightarrow \quad (1)$$

$$HCOOH + 2\ HCHO + 2\ NaIO_3 + H_2O$$

4.2 *Interferences*—The glycerin sample should be free of organic compounds with more than two hydroxyl groups on adjacent carbon atoms (for example, sugars, glycols). These types of compounds may produce formic acid which interferes with the determination of the glycerol content.

5. Apparatus

5.1 *Burette*—50 mL "Type A" unit that can deliver 30 drops per mL and calibrated to meet the NIST standards.

NOTE 1— It is critical that all glassware be "Type A" and thoroughly cleaned before use as dirty glassware will impact the analysis results.

5.2 *pH meter,* fitted with glass electrode.

NOTE 2—The pH meter should be standardized with a minimum of two

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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.

[4] Available from American Oil Chemists' Society (AOCS), 2710 S. Boulder, Urbana, IL 61802-6996, http://www.aocs.org.

[5] Available from British Standards Institute (BSI), 389 Chiswick High Rd., London W4 4AL, U.K., http://www.bsigroup.com.

buffer solutions at 10.0 and 7.0. (See 7.12.)

5.3 *Stirrer*—preference should be given to a magnetic stirrer. In this case, check that it does not influence the pH meter.

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.

NOTE 3—The presence of carbon dioxide can introduce errors; therefore it is advisable to prepare 500 mL of water by boiling for 5 min and cooling 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 Sodium Metaperiodate, $NaIO_4$, acidic solution—Dissolve 60 g of sodium metaperiodate in sufficient water containing 120 mL of 0.1 N sulfuric acid to make 1000 mL. *Do not heat to dissolve the periodate*. If the solution is not clear, pass it through a sintered-glass filter. Store the solution in a glass-stoppered, light-resistant container.

7.2 Hydrochloric Acid, aqueous solution, approximately 0.1 N.

7.3 Sodium Hydroxide, aqueous solution, approximately 0.05 N.

7.4 Sodium Hydroxide, 0.1 N, Standardized —Dissolve four grams of sodium hydroxide (NaOH) in water and dilute to one liter. Standardize accurately to ±0.0001 N. The standardized sodium hydroxide solution should be protected against evaporation and absorption of carbon dioxide (CO_2) from the air.

7.5 Ethylene glycol (1,2-ethanediol, free from glycerol) solution in water. 1:1 (v/v).

7.6 Sulfuric Acid Solution, aqueous solution, approximately 0.1 N.

7.7 Sulfuric Acid Solution, aqueous solution, approximately 0.2 N.

7.8 Sodium Thiosulfate, 0.1 N, aqueous solution.

7.9 Potassium Iodide, aqueous solution—Dissolve 16.5 g of potassium iodide in water to make 100 mL. Store tightly capped in a light-resistant container.

7.10 Starch Solution—Mix 1g of soluble starch with sufficient cold water to make a thin paste. Add 200 mL of boiling water, and boil for 1 min with continuous stirring. Cool, and use only the clear solution.

NOTE 4—It is recommended that freshly prepared starch solution be used to ensure a sharper endpoint. Commercially available, stabilized starch indicator solution may be also used in place of freshly prepared starch.

7.11 Bromothymol blue indicator solution—Dissolve 100 mg of bromothymol blue in 100 mL of water to make 100 mL of indicator solution.

7.12 pH Buffers (7.0 ± 0.01 and 10.0 ± 0.01 at 25°C) needed for pH meter standardization.

7.13 Freshly boiled water, or equivalent. (See 6.2.)

8. Precautions

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

8.2 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 prior to use.

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

9. Procedure

9.1 *Sodium Periodate Solution Suitability Test*—Pipet 10 mL of the prepared sodium periodate solution (Reagent 7.1) into a 250-mL volumetric flask, dilute with water to volume, and mix.

9.2 Weigh approximately 550 mg of glycerin into flask. Dissolve the sample in 50 mL of water and pipette 50 mL of the diluted periodate solution prepared in 9.1. Allow the solution to stand for 30 min.

9.3 Add 5 mL of hydrochloric acid solution (Reagent 7.2) and 10 mL of potassium iodide solution (Reagent 7.9), and gently swirl to mix. Allow the solution to stand for 5 min.

9.4 Add 100 mL of water and 3 mL of starch solution (Reagent 7.10). Titrate *slowly* with 0.1 N sodium thiosulfate (Reagent 7.8) to the starch endpoint, *mixing continuously* to ensure the solution has stabilized after each addition.

9.5 **Blank Test for Sodium Periodate Solution Suitability Test**—For the blank, pipet 50 mL of the diluted periodate solution into a flask containing 50 mL of water. Carry out, at the same time as the determination and under the same conditions, a blank test without the glycerin test portion using the same quantities of reagents and diluting water for the determinations as outlined in 9.1 through 9.4.

9.6 The ratio of the volume of 0.1 N sodium thiosulfate (Reagent 7.8) required for the glycerin-periodate mixture to that required for the blank should be between 0.750 and 0.765.

9.7 **Glycerol Assay Determination**—Transfer about 400 mg of glycerin, accurately weighed on an analytical balance, into a 600 mL beaker.

9.8 Dilute the sample in the beaker with 50 mL of water and add approximately 3 mL of bromothymol blue indicator (Reagent 7.11). Carefully acidify with 0.2 N sulfuric acid (Reagent 7.7) to a definite green or greenish yellow color. Neutralize with 0.05 N sodium hydroxide (Reagent 7.3) to a definite blue endpoint, free from green color.

9.9 Pipette 50 mL of sodium metaperiodate solution (Reagent 7.1) into the beaker. Mix using moderate agitation and cover the beaker with a watch glass. Allow the beaker to stand for 30 min at room temperature (not exceeding 35°C) in the dark or in subdued light.

NOTE 5—The presence of carbon dioxide can introduce errors; therefore it is advisable to cover the beaker containing the test solution with a watch glass during all standing periods.

9.10 Add 10 mL of the ethylene glycol solution (Reagent 7.5) into the beaker. Mix using moderate agitation and cover the beaker with a watch glass. Allow the beaker to stand for 20 min at room temperature (not exceeding 35°C) in the dark or in subdued light.

9.11 Dilute the solution with water to about 300 mL.

9.12 Insert the glass electrode and using moderate stirring, titrate *slowly* as the endpoint is approached with 0.1 N sodium hydroxide (Reagent 7.4) to a pH of 8.1 ± 0.1 for the specimen under assay.

NOTE 6—When approaching the endpoint, it is critical that the titration is conducted slowly and the solution is well mixed after each addition to ensure a stable pH reading for the endpoint determination.

9.13 **Blank Determination for Glycerine Assay Determination**—Carry out, at the same time as the assay determination and under the same conditions, a blank test without the test portion using the same quantities of reagents and diluting water for the determinations as outlined in 9.5 through 9.12. Titrate with 0.1 N sodium hydroxide to a pH of 6.5 ± 0.1 for the blank.

9.14 Each mL of 0.1 N sodium hydroxide, after correction for the blank, is equivalent to 9.210 mg of glycerol ($C_3H_8O_3$).

10. Calculation

10.1 The glycerol content, expressed as a percentage, is given by the formula:

$$Glycerol\,(\%) = \frac{(V_1 - V_B) \times F \times N}{W} \tag{2}$$

where:

V_1 = number of mL of 0.1 N sodium hydroxide solution used for the sample titration,

V_B = number of mL of 0.1 N sodium hydroxide solution used for the blank titration,

F = Factor = 9.210,

N = exact normality of sodium hydroxide that was used for the titration, and

W = mass, in g, of glycerin subjected to the reaction with sodium metaperiodate solution.

11. Report

11.1 Report the glycerin content of the sample to the nearest 0.1 %.

12. Precision and Bias

12.1 The precision of this test method is based on an interlaboratory study conducted in 2009. Each of eight laboratories tested two different materials. Every "test result" represents an individual determination, and every laboratory reported two replicate test results for each of the materials. Except for the use of only two test materials, Practice E691 was followed for the design and analysis of the data; the details are given in an ASTM Research Report.[6]

12.1.1 *Repeatability Limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "*r*" value for that material; "*r*" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

12.1.1.1 Repeatability limits are listed in Table 1.

12.1.2 *Reproducibility Limit (R)*—Two test results shall be judged not equivalent if they differ by more than the "*R*" value for that material; "*R*" is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

12.1.2.1 Reproducibility limits are listed in Table 1.

12.1.3 The terms (*repeatability limit* and *reproducibility limit*) are used as specified in Practice E177.

12.1.4 Any judgment in accordance with statements 12.1.1 and 12.1.2 would have an approximate 95 % probability of being correct.

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.

12.3 The precision statement was determined through statistical examination of 26 results, from eight laboratories, on two materials. These two materials were described as the following:

Glycerin A: a 99.5 % pure glycerine (data from seven laboratories included)

Glycerin B: a 97.5 % solution of glycerine (data from six laboratories included)

TABLE 1 Glycerin (%)

Material	Average[A]		Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	$S_{\bar{x}}$	S_r	S_R	r	R
A	99.48	0.14	0.29	0.29	0.81	0.81
B	97.48	0.36	0.17	0.38	0.48	1.05

[A] The average of the laboratories' calculated averages.

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D15-1025.

12.4 To judge the equivalency of two test results, it is recommended to choose the type of glycerin closest in characteristics to the test fluid.

13. Keywords

13.1 antifreeze; engine coolant; ethylene; glycerin; glycerine; glycerol; titrimetric

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