Designation: D7736 – 12

Standard Test Method for Determination of Acids and Glycol Esters in Ethylene Glycol[1]

This standard is issued under the fixed designation D7736; 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 free acids and glycol esters in ethylene glycol by titration.

1.2 This test method is for used on ethylene glycol used for the manufacture of engine coolant. It can not be used on formulated engine coolant. The inhibitors will interfere with the determination.

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

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]

D1176 Practice for Sampling and Preparing Aqueous Solutions of Engine Coolants or Antirusts for Testing Purposes
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

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology D4725.

4. Summary of Test Method

4.1 This test method is used to determine the acid and ester content of ethylene glycol by titration. The sample is titrated to the phenolphthalein end point with 0.02 N NaOH to determine the acidity. Then a known amount of base is added and the sample is heated at 100°C to hydrolyze the esters. It is then back-titrated with 0.02 N sulfuric acid to determine the ester content.

5. Significance and Use

5.1 The presence of acids or glycol esters in the ethylene glycol used to produce engine coolant is undesirable. Under conditions in an engine cooling system, the esters can hydrolyze to form glycol and an acid. The acid will react with the corrosion inhibitors, thereby reducing the useful life of the coolant. This method can determine the amount of acid and glycol ester present in the ethylene glycol.

6. Interferences

6.1 This test method is based on a color change titration. Glycol with a strong color could interfere with the results of this method.

6.2 High pH recycled glycols streams will affect the results of this test method.

7. Apparatus

7.1 *250 mL Borosilicate Glass Bottles,* with screw caps.

8. Reagents and Materials

8.1 *Phenolphthalein Solution*—Dissolve 0.5 g of phenolphthalein in methanol or ethanol and dilute to 100 mL.

8.2 *Sodium Hydroxide (NaOH),* 0.02 N in water.

8.3 *Sulfuric Acid (H_2SO_4),* 0.02 N in water.

8.4 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II or III of Specification D1193.

8.5 *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,

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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 D15.04 on Chemical Properties.

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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.

where such specifications are available.[3] 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.

9. Sampling

9.1 Sample the material in accordance with Practice D1176.

10. Procedure

10.1 *Acid Content:*

10.1.1 *Adjustment of pH*—Pipet 25.00 mL of deionized water into each of three 250 mL bottles. Add 3 drops of phenolphthalein solution to each. Titrate with 0.02 N sodium hydroxide to the first pink end point permanent for at least 15 seconds. Do not record this volume of titrant. Repeat for each bottle.

10.1.2 *Determination of Sample Acidity:*

10.1.2.1 Add an amount of sample as indicated in Table 1 to the nearest 0.1 g into the bottle of deionized water prepared in 10.1.1.

10.1.2.2 Titrate each sample with 0.02 N sodium hydroxide to the first pink end point permanent for at least 15 s. This volume of titrant is used to calculate the percent acid.

NOTE 1—If the ester content is completely unknown, a trial titration beginning with 25 g of sample may be conducted to develop a preliminary estimate before the actual test titration is performed. If the trial suggests concentration of over 0.10 wt % (1000 ppm) then reduce the sample to 10 g and repeat. The second trial should provide enough information to direct an appropriate choice of the sample quantity to be used.

10.2 *Total Ester Content:*

10.2.1 *Hydrolysis of the Esters*—Pipet 25.00 mL of 0.02 N sodium hydroxide into each bottle used in 10.1.2. Prepare a blank for each sample by pipetting 25.00 mL of 0.02 N sodium hydroxide into three clean, 250 mL bottles. Immerse the pairs of bottles in a boiling water bath for 1 h. (Tap water is suitable.) The weight of the bottles should prevent tipping. Leave caps slightly loose to prevent pressure buildup.

10.2.2 *Determination of the Ester Content*—Remove bottles from the bath and cool to room temperature. When cool, add 3 drops of phenolphthalein solution to each and titrate with 0.02 N H_2SO_4 until disappearance of pink color.

TABLE 1 Recommended Sample Sizes

Estimated Ester Content, wt %	Sample Size, g	Sample Method
< 0.10	25.0	Weigh the sample to the nearest 0.1 g into the bottle of water prepared in 10.1.1
0.10 to 0.20	10.0	
0.20 to 0.50	5.0[A]	

[A] Report as ">0.50 wt %" if the titration determination exceeds 0.50 %.

11. Calculation

11.1 *Acidity:*

$$\% \text{ acetic acid} = \frac{(mL\ NaOH)\ (N\ NaOH)\ (60.0\ g/equivalent)\ (1\ L/1000\ mL)}{g\ of\ sample} \times 100$$

where:

N = normality of the NaOH used.

11.2 *Ester Content:*

$$\% \text{ esters (as acetic acid)} = \frac{(B - A)\ (N\ H_2SO_4)\ (60.0g/equivalent)\ (1\ L/1000\ mL)}{g\ of\ sample} \times 100$$

$$esters,\ ppm\ (as\ acetic\ acid) = \%\ esters\ (as\ acetic\ acid) \times 10\ 000$$

where:

N = normality of the H_2SO_4 used,
B = H_2SO_4 used to titrate the blank, mL, and
A = H_2SO_4 used to titrate the sample, mL.

12. Report

12.1 Report the average of the three determinations of acidity as mass percent acetic acid.

12.2 Report the average of the three determinations of the ester content as ppm acetic acid.

13. Precision and Bias

13.1 The precision of this test method is based on an interlaboratory study conducted in 2009. Each of four laboratories tested four different materials. Every "test result" represents an individual determination. All laboratories were asked to report duplicate test results from a single operator for every material. Except for the limited number of laboratories involved, and the inability of all participants to report all requested replicates, Practice E691 was followed for the design and analysis of the data; the details are given in RR:D15-1031.[4]

13.1.1 *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.

13.1.1.1 Repeatability limits are listed in Table 2.

13.1.2 *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.

13.1.2.1 Reproducibility limits are listed in Table 2.

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

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[3] *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.

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D15-1031.

TABLE 2 Esters, ppm

Material	Average, $\bar{x}$ [A]	Repeatability Standard Deviation, S_r	Reproducibility Standard Deviation, S_R	Repeatability Limit, r	Reproducibility Limit, R
Sample 1	7.25	1.41	5.22	3.96	14.62
Sample 2	394.63	7.52	17.94	21.07	50.23
Sample 3	48.88	2.76	12.56	7.73	35.18
Sample 4	203.50	1.12	11.30	3.13	31.65

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

13.1.4 Any judgment in accordance with statements 13.1.1 and 13.1.2 would normally have an approximate 95% probability of being correct, however the precision statistics obtained in this interlaboratory study (ILS) shall not be treated as exact mathematical quantities that are applicable to all circumstances and uses. The limited number of materials tested and laboratories reporting replicate results guarantees that there will be times when differences greater than predicted by the ILS results will arise, sometimes with considerably greater or smaller frequency than the 95% probability limit would imply. Consider the repeatability limit and the reproducibility limit as general guides, and the associated probability of 95% as only a rough indicator of what can be expected.

13.2 *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.

13.3 The precision statement was determined through statistical examination of 28 results, from four laboratories, on four materials. These materials were described as follows:
Sample 1: Low esters sample,
Sample 2: High esters sample,
Sample 3: Moderate esters sample, and
Sample 4: Elevated esters sample.

13.4 To judge the equivalency of two test results, it is recommended to choose the material closest in characteristics to the test material.

14. Keywords

14.1 acid content; acidity; antifreeze; engine coolant; ester; ethylene glycol; glycol ester