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## Standard Test Method for Ester Value of Solvents and Thinners<sup>1</sup>

This standard is issued under the fixed designation D 1617; 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.*

### 1. Scope

1.1 This test method covers the determination of the ester value of solvents and thinners used in lacquers and other coatings.

1.2 *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.* For a specific hazard statement, see Note 2.

1.3 For hazard information and guidance, see the supplier's Material Safety Data Sheet.

### 2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water<sup>2</sup>

### 3. Summary of Test Method

3.1 The specimen is reacted with a measured excess of aqueous potassium hydroxide, using isopropanol as a mutual solvent if necessary. The amount of potassium hydroxide consumed, which is determined by titrating the excess with standard mineral acid, is a measure of the ester originally present.

3.2 Since this determination is based on an acidimetric titration, a suitable correction should be applied if the acidity of the sample exceeds the limit of the specification.

### 4. Significance and Use

4.1 This test method is useful in determining the assay of solvents and thinners which are esters or solutions of esters of carboxylic acid. The ester value is calculated as percent ester. This test method has its greatest application where the solvent or thinner is not a pure ester. This test method may be used in assessing compliance to specification.

### 5. Interferences

5.1 Organic chlorides, nitriles, and amides may be hydro-

lyzed by the reagent, particularly at 98°C, and are a possible source of error. Ketones interfere only slightly with this procedure. Aldehydes consume some alkali, but the error introduced by small amounts is negligible.

### 6. Apparatus

6.1 *Pressure Bottle*,<sup>3</sup> 200 to 350-mL capacity, made from heat-resistant glass.

6.2 *Container for Pressure Bottle*—A suitable safety device to contain the pressure bottle. A metal container with hinged top and perforated bottom, a strong synthetic fabric or canvas bag, or a safety shield may be used.

6.3 *Ampoule*, 1 or 2-mL capacity.

6.4 *Weighing Pipet*, Lunge or similar type.

6.5 *Erlenmeyer Flasks*, 250-mL glass-stoppered.

6.6 *Buret*, 50-mL capacity.

6.7 *Boiling Water Bath*.

### 7. Reagents

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 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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type IV of Specification D 1193.

7.3 *Hydrochloric Acid, Standard (0.5 N)*—Prepare 0.5 N hydrochloric acid (HCl) and standardize to four significant figures.

7.4 *Isopropyl Alcohol (99 %)*.

7.5 *Phenolphthalein Indicator Solution*—Dissolve 1 g of phenolphthalein in 100 mL of methanol, ethanol, or isopropyl alcohol.

<sup>3</sup> Bottles of this type, equipped with lever-type closures, can be obtained from Preiser Scientific, PO Box 1330, 94 Oliver St., St. Albans, WV 25177.

<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 Pharmacopoeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.35 on Solvents, Plasticizers, and Chemical Intermediates.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

7.6 *Potassium Hydroxide, Standard Solution (1.0 N)*—Dissolve 66 g of potassium hydroxide (KOH) pellets in water and dilute to 1 L with water (see Note 1).

7.7 *Sulfuric Acid, Standard (0.5 N)*—Prepare 0.5 N sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and standardize to four significant figures.

## 8. Procedure

8.1 Prepare a sufficient number of 250-mL, glass-stoppered Erlenmeyer flasks to make all blank and test determinations in duplicate. Use heat-resistant pressure bottles if sealed glass ampoules are required or if the reaction is conducted at 98°C.

8.2 Into each of the flasks or bottles, carefully introduce 25 mL of 1.0 N KOH solution (Note 1) by means of a suitable transfer pipet. Use the same pipet for each transfer.

NOTE 1—Do not substitute sodium hydroxide (NaOH) solution. The reaction conditions given in Table 1 are valid only when 1.0 N KOH solution is used.

8.3 Add the amount of isopropyl alcohol prescribed in Table 1 but never add more than 40 mL. Stopper and reserve two of the flasks or bottles for the blank determinations.

8.4 Into each of the other flasks or bottles introduce an amount of sample containing not more than 0.016 mol (16 milliequivalents) of the ester. For substantially pure material, weigh the specimen to the nearest 0.1 mg, using the amount and procedure specified in Table 1. Stopper the flasks after addition of the specimen.

8.5 If a sealed glass ampoule is used, add several pieces of fire-polished 8-mm glass rod to each bottle, stopper, and shake the bottle vigorously to break the ampoule.

8.6 *Reaction at 98°C (Precaution—See Note 2.)*—Place the specimens and blanks as close together as possible in a boiling water bath maintained at least at 98°C for the time prescribed in Table 1. Maintain sufficient water in the bath to just cover the liquid in the bottles. Remove the bottles from the bath and allow them to cool to room temperature. When the bottles have cooled, remove them from the safety device and uncap them carefully to release any pressure. Continue as described in 8.8.

NOTE 2—**Precaution:** Enclose each bottle securely in a suitable safety device to restrain fragments of glass should the pressure bottle rupture.

8.7 *Reaction at Room Temperature*—Allow the specimen to stand together with the blanks at room temperature for the length of time specified in Table 1.

TABLE 1 Specimen Size and Reaction Conditions

Ester	Specimen, g <sup>A</sup>	Isopropyl Alcohol Added, mL	Minimum Reaction Conditions	
			Time, min	Temperature, °C
Amyl acetate	1.4 to 1.6	40	30	98
Dibutyl phthalate	1.4 to 2.0	30	30	98
2-Ethoxyethyl acetate	1.3 to 2.1	0	30	25
Ethyl acetate	0.9 to 1.4 <sup>B</sup>	0	30	25
Isobutyl acetate	1.2 to 1.9	25	45	25
Isopropyl acetate	1.0 to 1.6 <sup>B</sup>	10	30	25
Methyl amyl acetate	1.4 to 2.3	30	30	98
Normal butyl acetate	1.2 to 1.9	25	45	25
Normal propyl acetate	1.0 to 1.6 <sup>B</sup>	10	30	25
sec-Butyl acetate	1.2 to 1.9	25	45	98

<sup>A</sup> Use a suitable weighing pipet unless otherwise specified.

<sup>B</sup> Use a sealed glass ampoule.

8.8 If a white precipitate develops in the specimen flasks or bottles, add sufficient water to dissolve the salt. Add the same amount of water to each of the blanks. Add 6 to 8 drops of the phenolphthalein indicator solution to each flask or bottle and titrate with 0.5 N H<sub>2</sub>SO<sub>4</sub> just to the disappearance of the pink color. If more than 25 mL of isopropyl alcohol were added in accordance with 8.3, titrate with 0.5 N HCl.

8.9 Measure the temperature of the acid titrant. If the temperature of the reagent at the time the ester determination is made is not the same as it was at the time the reagent was standardized, apply a temperature correction of 0.00014/°C to the normality.

## 9. Calculation

9.1 Calculate the percent of ester, *E*, as follows:

$$E = [(B - V)N \times F] / S \times 100 \quad (1)$$

where:

*V* = 0.5 N H<sub>2</sub>SO<sub>4</sub> (or HCl) required for titration of the specimen (8.8), mL

*B* = 0.5 N H<sub>2</sub>SO<sub>4</sub> (or HCl) required for titration of the blanks (8.8), avg, mL,

*N* = normality of the H<sub>2</sub>SO<sub>4</sub> (or HCl) corrected for temperature,

*F* = factor specified in Table 2 for the ester being determined, and

*S* = specimen used, g.

NOTE 3—If the acidity of the ester exceeds the limit of the specification, it is recommended that a suitable correction be applied to the ester value. Table 2

## 10. Report

10.1 Report the following information:

10.1.1 All results to the nearest 0.1 %. Duplicate determinations that agree within 0.38 %, absolute, are acceptable for averaging (95 % confidence level).

## 11. Precision and Bias

11.1 *Precision*—The precision statements are based upon an interlaboratory study in which two analysts in each of four different laboratories analyzed one sample of ethyl acetate, 88 %, and one sample of dibutyl phthalate, 99 %, in duplicate on three different days. The within-laboratory coefficient of variation was found to be 0.154 % at 40 df, and the between-laboratory coefficient of variation was found to be 0.313 % at approximately 16 df. Based on these coefficients of variation, the following criteria should be used in judging the acceptability of results at the 95 % confidence level.

TABLE 2 Ester Factors

Ester	Factor <sup>A</sup>
Amyl acetate	0.1302
Dibutyl phthalate	0.1392
2-Ethoxyethyl acetate	0.1322
Ethyl acetate	0.0881
Isobutyl acetate	0.1162
Isopropyl acetate	0.1021
Methyl amyl acetate	0.1442
Normal butyl acetate	0.1162
Normal propyl acetate	0.1021
sec-Butyl acetate	0.1162

<sup>A</sup> Factor = molecular weight of compound/number of reacting groups × 1000.

11.1.1 *Repeatability*—Two results, each the mean of duplicates, obtained by the same operator on different days should be considered suspect if they differ by more than 0.44 % relative.

11.1.2 *Reproducibility*—Two results, each the mean of duplicates, obtained by operators in different laboratories should be considered suspect if they differ by more than 0.94 % relative.

11.2 *Bias*—Any material or contaminant (see Section 5 and Note 3) that will react with potassium hydroxide under the test conditions will affect the results.

## 12. Keywords

12.1 ester value; solvents; thinner

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