



## Standard Test Method for Sulfated Ash from Lubricating Oils and Additives<sup>1</sup>

This standard is issued under the fixed designation D874; 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 U.S. Department of Defense.*

### 1. Scope

1.1 This test method covers the determination of the sulfated ash from unused lubricating oils containing additives and from additive concentrates used in compounding. These additives usually contain one or more of the following metals: barium, calcium, magnesium, zinc, potassium, sodium, and tin. The elements sulfur, phosphorus, and chlorine can also be present in combined form.

1.2 Application of this test method to sulfated ash levels below 0.02 % by mass is restricted to oils containing ashless additives. The lower limit of the test method is 0.005 % by mass sulfated ash.

NOTE 1—This test method is not intended for the analysis of used engine oils or oils containing lead. Neither is it recommended for the analysis of nonadditive lubricating oils, for which Test Method D482 can be used.

NOTE 2—There is evidence that magnesium does not react the same as other alkali metals in this test. If magnesium additives are present, the data is interpreted with caution.

NOTE 3—There is evidence that samples containing molybdenum can give low results because molybdenum compounds are not fully recovered at the temperature of ashing.

1.3 Fatty acid methyl ester (FAME) conforming to EN 14213 and EN 14214, when tested using this test method, were shown to meet its precision.

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

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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In the IP, this test method is under the jurisdiction of the Standardization Committee. This test method has been approved by the sponsoring committees and accepted by the cooperating societies in accordance with established procedures.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:<sup>2</sup>

- D482 Test Method for Ash from Petroleum Products
- D1193 Specification for Reagent Water
- D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
- D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
- D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

#### 2.2 CEN Standards:<sup>3</sup>

- EN 14213 Heating Fuels—Fatty Acid Methyl Esters (FAME)—Requirements and Test Methods
- EN 14214 Automotive Fuels—Fatty Acid Methyl Esters (FAME) for Diesel Engines—Requirements and Test Methods

### 3. Terminology

#### 3.1 Definitions:

3.1.1 *sulfated ash, n*—the residue remaining after the sample has been carbonized, and the residue subsequently treated with sulfuric acid and heated to constant weight.

### 4. Summary of Test Method

4.1 The sample is ignited and burned until only ash and carbon remain. After cooling, the residue is treated with sulfuric acid and heated at 775 °C until oxidation of carbon is

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> Available from European Committee for Standardization (CEN), Avenue Marnix 17, B-1000, Brussels, Belgium, <http://www.cen.eu>.

complete. The ash is then cooled, re-treated with sulfuric acid, and heated at 775 °C to constant weight.

## 5. Significance and Use

5.1 The sulfated ash can be used to indicate the concentration of known metal-containing additives in new oils. When phosphorus is absent, barium, calcium, magnesium, sodium and potassium are converted to their sulfates and tin (stannic) and zinc to their oxides (**Note 4**). Sulfur and chlorine do not interfere, but when phosphorus is present with metals, it remains partially or wholly in the sulfated ash as metal phosphates.

**NOTE 4**—Since zinc sulfate slowly decomposes to its oxide at the ignition temperature specified in the test method, samples containing zinc can give variable results unless the zinc sulfate is completely converted to the oxide.

5.2 Because of above inter-element interferences, experimentally obtained sulfated ash values may differ from sulfated ash values calculated from elemental analysis. The formation of such non-sulfated species is dependent on the temperature of ashing, time ashed, and the composition of metal compounds present in oils. Hence, sulfated ash requirement generally should not be used in product specifications without a clear understanding between a buyer and a seller of the unreliability of an ash value as an indicator of the total metallic compound content.<sup>4</sup>

## 6. Apparatus

6.1 *Evaporating Dish or Crucible*; 50 mL to 100 mL for samples containing more than 0.02 % by mass sulfated ash, or 120 mL to 150 mL for samples containing less than 0.02 % by mass sulfated ash, and made of porcelain, fused silica, or platinum. (**Warning**—Do not use platinum when the sample is likely to contain elements such as phosphorus, which attack platinum under the conditions of the test.)

**NOTE 5**—For best results on samples containing less than 0.1 % by mass sulfated ash, platinum dishes are used. The precision values shown in Section 13 for this type of sample were so obtained.

6.2 *Electric Muffle Furnace*—The furnace shall be capable of maintaining a temperature of 775 °C ± 25 °C and preferably have apertures at the front and rear to allow a slow natural draft of air to pass through the furnace.

6.3 *Balance*, capable of weighing to 0.1 mg.

## 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, or to other recognized

standards for reagent chemicals.<sup>5</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 defined by Types II or III of Specification **D1193**.

7.3 *Low-Ash Mineral Oil*—White oil having a sulfated ash lower than the limit capable of being determined by this test method.

**NOTE 6**—Determine the sulfated ash of this oil by the procedure given in **9.1 – 9.11** below using 100 g of white oil weighed to the nearest 0.5 g in a 120 mL to 150 mL platinum dish. Deduct the sulfuric acid blank as described in **9.11**.

7.4 *Sulfuric Acid (relative density 1.84)*—Concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). (**Warning**—Poison. Corrosive. Strong oxidizer.)

7.5 *Sulfuric Acid (1 + 1)*—Prepare by slowly adding 1 volume of concentrated sulfuric acid (relative density 1.84) to 1 volume of water with vigorous stirring. (**Warning**—Mixing this acid into water generates considerable heat. When necessary, cool the solution before adding more acid. Do not allow the solution to boil.)

7.6 *Propan-2-ol*, (**Warning**—Flammable, can be explosive when evaporated to or near dryness.) 99 % minimum purity.

7.7 *Toluene*, (**Warning**—Flammable, toxic.) 99 % minimum purity.

7.8 *Quality Control (QC) Samples*, preferably are portions of one or more liquid petroleum materials that are stable and representative of the samples of interest. These QC samples can be used to check the validity of the testing process as described in Section 12.

## 8. Sampling

8.1 Obtain samples in accordance with the instructions in Practice **D4057** or **D4177**. The sample shall be thoroughly mixed before removal of the laboratory test portion.

## 9. Procedure

9.1 Select the size of the evaporating dish or crucible according to the quantity of sample necessary (see **9.3**).

9.2 Heat the evaporating dish or crucible that is used for the test at 775 °C ± 25 °C for a minimum of 10 min. Cool to room temperature in a suitable container and weigh to the nearest 0.1 mg.

**NOTE 7**—The container in which the dish is cooled does not contain a desiccating agent.

9.3 Weigh into the dish a quantity of sample given as follows:

<sup>4</sup> Further discussion of these interferences can be found in Nadkarni, R. A., Ledesma, R. R., and Via, G. H., "Sulfated Ash TM: Limitations of Reliability and Reproducibility," SAE Technical Paper No. 952548, available from SAE, 400 Commonwealth Drive, Warrendale, PA 15096-0001, U.S.A.

<sup>5</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.

$$W = 10/a \quad (1)$$

where:

$W$  = mass of test specimen, g, and  
 $a$  = expected sulfated ash, mass %.

However, do not take a quantity in excess of 80 g. In the case of lubricating oil additives yielding a sulfated ash of 2 % by mass or more, dilute the weighed sample in the dish with approximately 10 times its weight of low-ash mineral oil. If the amount of sulfated ash found differs from the expected amount by more than a factor of two, repeat the analysis with a different weight of sample calculated from the first analysis unless the calculated sample size >80 g.

9.4 Heat the dish or crucible and sample carefully until the contents can be ignited with a flame. Maintain at such a temperature that the sample continues to burn at a uniform and moderate rate. When burning ceases, continue to heat gently until no further smoke or fumes are evolved.

9.4.1 If the sample contains sufficient moisture to cause foaming and loss of material from the dish, discard the sample and to an additional sample add 1 mL to 2 mL of 99 % propan-2-ol (**Warning**—Flammable) before heating. If this is not satisfactory, add 10 mL of a mixture of equal volumes of toluene (**Warning**—Flammable, Vapor harmful.) and propan-2-ol and mix thoroughly. Place several strips of ashless filter paper in the mixture and heat; when the paper begins to burn, the greater part of the water will have been removed.

9.5 Allow the dish to cool to room temperature, then completely moisten the residue by the dropwise addition of sulfuric acid (relative density 1.84). Carefully heat the dish at a low temperature on a hot plate or over a gas burner, avoiding spattering, and continue heating until fumes are no longer evolved.

9.6 Place the dish in the furnace at  $775\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$  for 30 min  $\pm 5$  min until oxidation of the carbon is complete or almost complete.

9.7 Allow the dish to cool to room temperature. Add 3 drops of water and 10 drops of sulfuric acid (1 + 1). Move the dish so as to moisten the entire residue. Again heat the dish in accordance with 9.5.

9.8 Again place the dish in the furnace at  $775\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$  and maintain at that temperature for 30 min  $\pm 5$  min (see **Note 8**). Cool the dish to room temperature in a suitable container (see **Note 7**). Zinc dialkyl or alkaryl dithiophosphates and blends containing these additives can give a residue that is partially black at this stage. In this case, repeat 9.7 and 9.8 until a white residue is obtained.

**NOTE 8**—A study conducted by two separate laboratories investigating whether heating sulfated ash residues for extended periods of time (for example, overnight) in a furnace at  $775\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$  as opposed to 30 min as required in 9.8 revealed that a significant difference in sulfated ash results can exist. The study indicated that lower sulfated ash results were obtained on the samples left in the furnace overnight versus those that were heated in 30 min cycles. A thermogravimetric analysis also confirmed that the samples evaluated continued to lose weight at  $775\text{ }^{\circ}\text{C}$  as a function of time. As such, it is essential that the 30 min heating time requirement be adhered to in performing the test method. Details

concerning the study can be found in ASTM Research Report RR:D02-1597.<sup>6</sup>

9.9 Weigh the dish and residue to the nearest 0.1 mg.

9.10 Repeat 9.8 and 9.9 until two successive weighings differ by no more than 1.0 mg.

**NOTE 9**—Normally one repeat will suffice, unless a high proportion of zinc is present, when three or four heating periods can be required.

9.11 For samples expected to contain 0.02 % mass or less of sulfated ash, determine a sulfuric acid blank by adding 1 mL of the concentrated sulfuric acid to a tared platinum dish or crucible, heating until fumes are no longer evolved and then heating in the furnace at  $775\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$  for 30 min  $\pm 5$  min. Cool the dish or crucible to room temperature in a suitable container (see **Note 7**) and weigh to the nearest 0.1 mg. If any ash is found in the sulfuric acid, make an adjustment to the weight of sulfated ash obtained by subtracting the weight of ash contributed by the sulfuric acid, determined from the total volume of sulfuric acid used and the weight of ash found for the 1 mL blank, from the total grams of sulfated ash for the sample. Use this corrected weight,  $w$ , in calculating the percent sulfated ash.

## 10. Calculation

10.1 Calculate the sulfated ash as a percentage of the original sample as follows:

$$\text{Sulfated ash, mass \%} = (w/W) \times 100 \quad (2)$$

where:

$w$  = grams of sulfated ash, and  
 $W$  = grams of sample used.

## 11. Report

11.1 Report the result to the nearest 0.001 % by mass for samples below 0.02 % by mass and to the nearest 0.01 % by mass for higher levels as the sulfated ash, Test Method D874.

## 12. Quality Control

12.1 Confirm the performance of the instrument or the test procedure by analyzing a QC sample (see 7.8).

12.1.1 When QC/Quality Assurance (QA) protocols are already established in the testing facility, these may be used to confirm the reliability of the test result.

12.1.2 When there is no QC/QA protocol established in the testing facility, **Appendix X1** can be used as the QC/QA system.

## 13. Precision and Bias<sup>6</sup>

13.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

13.1.1 For sulfated ash levels between 0.005 % and 0.10 % by mass.

13.1.1.1 **Repeatability**—The difference between two test results obtained by the same operator with the same apparatus

<sup>6</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1597. Contact ASTM Customer Service at service@astm.org.

**TABLE 1 Precision at Levels Below 0.10 %**

Sulfated Ash, mass %	Repeatability	Reproducibility
0.005	0.0005	0.0021
0.010	0.0009	0.0038
0.05	0.0037	0.0148
0.10	0.0066	0.0267

under constant operating conditions on identical test materials 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:

$$r = 0.047 X^{0.85} \quad (3)$$

where  $X$  = average of two results.

**13.1.1.2 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 in only one case in twenty:

$$R = 0.189 X^{0.85} \quad (4)$$

where  $X$  = average of two results.

**13.1.1.3 Specimen data** are shown in **Table 1**.

**NOTE 10**—The precision values in the range from 0.005 % to 0.10 % by mass sulfated ash were obtained by statistical examination of interlaboratory test results obtained in a joint ASTM-IP cooperative program conducted in 1975. Only platinum dishes were used.

**13.1.2** For sulfated ash levels between 0.11 % and 25 % by mass:

**13.1.2.1 Repeatability**—The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run in the normal and correct operation of the test method, exceed the following values in only one case in twenty:

$$r = 0.060 X^{0.75} \quad (5)$$

where  $X$  = average of two results.

**13.1.2.2 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 in only one case in twenty:

$$R = 0.142 X^{0.75} \quad (6)$$

**TABLE 2 Precision at Levels Above 0.10 %**

Sulfated Ash, mass %	Repeatability	Reproducibility
0.5	0.036	0.084
1.0	0.060	0.142
5.0	0.201	0.475
10.0	0.337	0.799
20.0	0.567	1.343
25.0	0.671	1.588

where  $X$  = average of two results.

**13.1.2.3 Specimen data** are shown in **Table 2**.

**NOTE 11**—The precision values in the range from 0.10 % to 25 % by mass sulfated ash were obtained by statistical examination of interlaboratory test results obtained in a joint ASTM-IP cooperative program conducted in 1981.

**13.1.3** Based on an interlaboratory study conducted in 2006 that included nine laboratories and six heavy duty engine oils meeting the API PC 10 specifications,<sup>7</sup> the following precision was obtained:<sup>8</sup>

Sulfated ash concentration level: 0.8 % to 1.6 % by mass  
 Repeatability:  $0.08068 X^{1.40}$   
 Reproducibility:  $0.1563 X^{1.40}$

**13.1.4** Examples of analysis precision are shown in **Table 3**.

**TABLE 3 Precision for API PC 10 Type Oils**

Sulfated Ash Concentration, mass %	Repeatability	Reproducibility
0.80	0.06	0.11
0.90	0.07	0.13
1.10	0.09	0.18
1.60	0.16	0.30

**13.2 Bias**—There is no accepted reference material suitable for determining the bias of the procedures in this test method for measuring ash.

## 14. Keywords

14.1 additives; ash; lubricating oils

<sup>7</sup> Available from American Petroleum Institute (API), 1220 L. St., NW, Washington, DC 20005-4070, <http://www.api.org>.

<sup>8</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1625. Contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org).



**APPENDIX****(Nonmandatory Information)****X1. QUALITY CONTROL**

X1.1 Confirm the performance of the instrument or the test procedure by analyzing a QC sample.

X1.2 Prior to monitoring the measurement process, the user of the test method needs to determine the average value and control limits of the QC sample (see Practice **D6299** and MNL 7).<sup>9</sup>

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process (see Practice **D6299** and MNL 7). Any out-of-control data should trigger investigation for root cause(s).

X1.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the

criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample is analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be checked against the ASTM test method precision to ensure data quality.

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions. See Practice **D6299** and MNL 7 for further guidance on QC and control charting techniques.

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<sup>9</sup> MNL 7, *Manual on Presentation of Data Control Chart Analysis*, 6<sup>th</sup> Ed., ASTM International, W. Conshohocken, PA.

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