



Standard Test Method for Sulfated Ash of Organic Materials by Thermogravimetry¹

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1. Scope

1.1 This standard describes the determination of sulfated ash content (sometimes called residue-on-ignition) of organic materials by thermogravimetry. The method converts common metals found in organic materials (such as sodium, potassium, lithium, calcium, magnesium, zinc, and tin) into their sulfate salts permitting estimation of their total content as sulfates or oxides. The range of the test method is from 0.1 to 100 % metal content.

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 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 to determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:²

D874 Test Method for Sulfated Ash from Lubricating Oils and Additives

D914 Test Methods for Ethylcellulose

D3516 Test Methods for Ashing Cellulose

E473 Terminology Relating to Thermal Analysis and Rheology

E1131 Test Method for Compositional Analysis by Thermogravimetry

E1142 Terminology Relating to Thermophysical Properties

E1582 Practice for Calibration of Temperature Scale for Thermogravimetry

E2040 Test Method for Mass Scale Calibration of Thermogravimetric Analyzers

¹ This test method is under the jurisdiction of ASTM Committee E37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.01 on Calorimetry and Mass Loss.

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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.

2.2 Other Standards:

The United States Pharmacopeia XXII and The National Formulary XVII, United States Pharmacopeial Convention, Rockville, MD, 1990, Section 281, p. 1527

3. Terminology

3.1 *Definitions*—Technical terms used in this standard are defined in Terminologies E473 and E1142.

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

3.1.2 *residue-on-ignition, ROI, n*—a commonly used alias for sulfated ash.

3.1.3 *volatiles, n*—for the purpose of this test, those materials evolving as gas at temperatures below 160°C in an air atmosphere.

4. Summary of Test Method

4.1 A test specimen is ignited and burned in an air atmosphere at temperatures up to 600°C until only ash remains. After cooling, the residue is treated with sulfuric acid and heated to 800°C to constant weight. The residue remaining is identified as sulfated ash.

4.2 This test method is similar to Test Method D874 for lubricating oils and additives, Test Methods D914 for ethyl cellulose, Test Methods D3516 cellulose, and that of The United States Pharmacopeia XXII and makes use of thermogravimetric apparatus to perform the determination.

5. Significance and Use

5.1 The sulfated ash may be used to indicate the level of known metal-containing additives or impurities in an organic material. When phosphorus is absent, barium, calcium, magnesium, sodium and potassium are converted to their sulfates. Tin and zinc are converted to their oxides.

5.2 This standard may be used for research and development, specification acceptance and quality assurance purposes.

6. Interferences

6.1 If phosphorus is present with metals, it partially or wholly remains in the sulfated ash as metal phosphates.

6.2 Sulfur and chlorides do not interfere.

7. Apparatus

7.1 *Thermogravimetric Analyzer (TGA)*—The essential instrumentation required to provide the minimum thermogravimetric analytical capability for this standard includes:

7.1.1 A thermobalance composed of:

7.1.1.1 A furnace to provide uniform controlled heating of a specimen to a constant temperature of 850°C and at a constant rate of 5 to 60°C/min

7.1.1.2 A temperature sensor to provide an indication of the specimen or furnace temperature to $\pm 1^\circ\text{C}$.

7.1.1.3 A continuously recording balance to measure the specimen mass with a minimum capacity of 50 mg and a sensitivity of ± 0.01 mg.

7.1.1.4 A means of maintaining the specimen or container under atmospheric control of air at a purge flow rate of 50 to 100 mL/min ± 5 mL/min.

7.1.2 A temperature controller capable of executing a specific temperature program by operating the furnace between selected temperature limit at a rate of 5 to 60°C/min and to an isothermal temperature of up to 850°C which is maintained constant to $\pm 10^\circ\text{C}$ for a minimum of 70 minutes.

7.1.3 A recording device, capable of recording and displaying any fraction of the specimen mass signal (TGA curve) including signal noise.

7.1.4 Containers (pans, crucibles, etc.) that are inert to the specimen and to concentrated sulfuric acid and that will remain gravimetrically stable up to 850°C. Platinum is a common material of construction for this purpose.

7.2 Graduated micropipette with capacity of 40–50 μL

8. Reagents and Materials

8.1 Sulfuric acid, concentrated (98 %), with a relative density of 1.84. (**Warning**—Poison. Corrosive. Strong Oxidizer.)

8.2 *Air*—Zero grade or better purity

9. Hazards

9.1 Sulfuric acid may be corrosive to some thermogravimetric apparatus. A regular visual inspection of the apparatus will determine if any corrosion is taking place.

9.2 The exhausted purge gas from the apparatus will contain sulfuric acid fumes. This purge gas shall be treated by exhausting to a acid hood or by bubbling through a solution of sodium bicarbonate to absorb the acidic fumes.

10. Preparation of Apparatus

10.1 After turning the power on, allow the instrument to equilibrate for at least one hour prior to any measurements.

10.2 Perform any cleaning and calibration procedures described by the manufacturer in the apparatus Operator's Manual.

11. Calibration and Standardization

11.1 Perform temperature calibration of the thermogravimetric analyzer according to Practice E1582 using reference materials suitable for the temperature range of this method, namely 25 to 800°C.

11.2 Perform mass calibration of the thermogravimetric analyzer according to Test Method E2040.

12. Procedure

12.1 Transfer 30 to 40 mg of the sample into a tared, clean, and dry sample container. Assemble the thermogravimetric analyzer for operation. Record the initial weight of the test specimen as W_o to within ± 0.01 mg

NOTE 1—The sample container may be preconditioned by heating in an air atmosphere to 800°C.

NOTE 2—Smaller quantities of test specimen will reduce the quantification capability of this method.

12.2 Heat the specimen from ambient to 600°C at 10°C/min under an air purge gas with a flow rate of 50 to 100 ± 5 mL/min and record the thermal curve.

12.3 Cool the heated sample and thermogravimetric apparatus to 20 to 25°C.

12.4 If desired, record the weight at 150°C (W_v) as the mass after apparent loss of volatiles. Record the weight at 600°C as the mass of the residue (W_r).

NOTE 3—Mass loss due to apparent loss of volatiles at 150°C and residue at 600°C are not required for the sulfated ash determination but may be recorded for additional sample characterization (see Test Method E1131.)

NOTE 4—The temperature at which the mass loss due to volatiles is determined may range from 100 to 160°C depending upon the material. Other values may be used but shall be reported.

12.5 Using a micropipette, add 30 – 40 μL of 98 % grade sulfuric acid to the sample residue (in the container). Reassemble the instrument for operation.

12.6 Heat the specimen from ambient to 800°C at 50°C/min and hold isothermally at $800 \pm 25^\circ\text{C}$ for 60 ± 1 minutes under an air purge at 50 to 100 ± 5 mL/min.

12.7 Cool the heated specimen and thermogravimetric apparatus to 20 to 25°C.

12.8 Record the residue mass W_s .

12.9 Calculate percent Sulfated Ash (S) using Eq 1.

12.10 In the absence of interferences and if the specific metal in the test specimen is known, then its mass percent (M) may be calculated by multiplying the sulfated ash value by the factors presented in Table 1 using Eq 2.

TABLE 1 Sulfated Ash Factors

| Metal | Sulfated Ash | Factor |
|----------------|--------------------------|--------|
| Sodium (Na) | Na_2SO_4 | 0.3237 |
| Potassium (K) | K_2SO_4 | 0.4487 |
| Lithium (Li) | Li_2SO_4 | 0.1263 |
| Calcium (Ca) | CaSO_4 | 0.2944 |
| Magnesium (Mg) | MgSO_4 | 0.2019 |
| Zinc (Zn) | ZnO | 0.8034 |
| Tin (Sn) | SnO | 0.8812 |

12.11 If desired, calculate the Percent Volatiles (V) and Percent Residue (R) using equations 3 and 4, respectively.

13. Calculation

13.1 Sulfated Ash (S) may be determined using the following equation:

$$S = W_s \times 100 \% / W_o \quad (1)$$

where:

S = Sulfated ash, mass %,
 W_s = Mass of sulfated ash from Section 12.8, mg,
 W_o = Original mass of the test specimen from Section 12.1, mg.

13.2 If the specific metal in the test specimen is known and if this is the only metal ion present, then its mass percent (M) may be calculated by multiplying the sulfated ash value by the factors presented in Table 1 using Eq 2.

$$M (\text{metal}) = \text{Factor} \times S \quad (2)$$

where:

M = Percent of the identified metal, mass %.

14. Report

14.1 Report the sulfated ash (S) to three significant figures.

14.2 Report to three significant figures the percent metal (M) when desired and the metal is known.

14.3 Provide a copy of the original thermal curve.

14.4 The specific dated version of this test method used.

15. Precision and Bias

15.1 An interlaboratory study was conducted in 2005 in which lithium cyclohexanebutyrate and calcium oxalate monohydrate were tested. Eight laboratories participated in the test using seven instrument models from two manufacturers. A Research Report is available from ASTM Headquarters.³

15.2 *Precision:*

³ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E37-1036.

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15.2.1 Within laboratory variability may be described using the repeatability value (r) obtained by multiplying the repeatability standard deviation by 2.8. The repeatability value estimates the 95 % confidence limit. That is, two results from the same laboratory should be considered suspect (at the 95 % confidence level) if they differ by more than the repeatability value.

15.2.1.1 The within laboratory repeatability standard deviation for lithium in lithium cyclohexanebutyrate was 0.057 % (RSD of 1.5 %) with 20 degrees of experimental freedom.

15.2.1.2 The within laboratory repeatability standard deviation for calcium in calcium oxalate monohydrate was 0.24 % (RSD of 0.92 %) with 20 degrees of experimental freedom.

15.2.2 Between laboratory variability may be described using the reproducibility value (R) obtained by multiplying the reproducibility standard deviation by 2.8. The reproducibility values estimates the 95 % confidence limit. That is, two results obtained from different laboratories, operators or apparatus should be considered suspect (at the 95 % confidence level) if they differ by more than the reproducibility value.

15.2.2.1 The between laboratory reproducibility standard deviation for lithium in lithium cyclohexanebutyrate was 0.10 % (RSD = 2.5 %) with 20 degrees of experimental freedom.

15.2.2.2 The between laboratory reproducibility standard deviation for calcium in calcium oxalate monohydrate was 0.32 % (RSD = 1.2 %) with 20 degrees of experimental freedom.

15.3 *Bias:*

15.3.1 Bias is the difference between the mean value obtained and an accepted reference value for the same material.

15.3.1.1 The lithium cyclohexanebutyrate used in this study was supplied (by Sigma-Aldrich, St. Louis, MO) with a Certificate of Analysis indicate an ICP assay of 3.9 % lithium. The sample is 3.94 % lithium by formula weight.

15.3.1.2 The mean value for lithium in lithium cyclohexanebutyrate characterized by this method was found to be 3.93 %, indicating no detectable bias in this method.

16. Keywords

16.1 ash; residue on ignition; sulfated ash; thermogravimetric analysis; thermogravimetry