



# Standard Test Methods for Ashing Cellulose<sup>1</sup>

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## 1. Scope

1.1 These test methods cover four ashing methods for cellulose. These are intended for use on unbleached and bleached cellulose in sheeted or bulk fiber form. Each one of the test methods has advantages, so that preference applications exist for all four.

1.2 The test methods appear as follows:

	Sections 6 to 11
Test Method A—Ash in Cellulose at 575°C	
Test Method B—Sulfated Ash in Cellulose at 575°C	12 to 17
Test Method C—Ashing Cellulose by Schoniger Oxidation	18 to 22
Test Method D—Wet Ashing of Cellulose for Inorganics	23 to 29

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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.* For a specific hazard statement, see 20.6.1.

## 2. Referenced Documents

2.1 *ASTM Standards:*

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

D 1348 Test Methods for Moisture in Cellulose<sup>3</sup>

## 3. Summary of Test Methods

3.1 *Test Method A, Ash in Cellulose at 575°C*—This test method measures the ash content of cellulose, which is defined for this test as the residue remaining after ignition at  $575 \pm 25^\circ\text{C}$  until all carbon has been burned off. It is the simplest of the four test methods for the determination of ash content only, and it should not be considered as a standard preparative procedure for elemental analysis.

NOTE 1—The ash content at this ignition temperature is a reasonable measure of the mineral salts and inorganic foreign matter in the cellulose. The weight of ash obtained varies with the temperature of ignition. Higher

temperatures ( $850^\circ\text{C}$ ) will convert calcium carbonate and other carbonates to the oxides and thus give lower values for ash. The composition of ash may vary with the pulping process employed for manufacture, which limits the significance of the ash determination in absolute terms.

3.2 *Test Method B, Sulfated Ash in Cellulose at 575°C*—In this ashing procedure the metal salts are converted to sulfates by treatment with sulfuric acid and ignition at  $575 \pm 25^\circ\text{C}$  to overcome limitations of Test Method A. It should not be considered as a standard preparative test method for elemental analysis.

NOTE 2—Conventional dry ashing at high temperature (over  $850^\circ\text{C}$ ) results in loss of carbon dioxide from metal carbonates, decomposition of magnesium sulfate, and loss of sodium salts. Ashing at lower temperatures ( $575^\circ\text{C}$ ) gives a better estimate of the inorganic impurities, but has the disadvantage of requiring a long ignition time and also the heat produced by the burning pulp can raise the temperature far above  $575^\circ\text{C}$  for a short period of time, converting calcium carbonate to the oxide in varying amounts. The sulfated ash method overcomes these objectionable features and has additional advantages. It is relatively insensitive to ignition time. Ash weight remains constant during weighing, and because the ash does not melt it will not attack the crucible.

3.3 *Test Method C, Ashing Cellulose by Schoniger Oxidation*—This test method is generally applicable to ashing cellulose for subsequent analysis of inorganic constituents. The procedure utilizes the Schoniger technique in which the cellulose is burned in a combustion flask and all combustion products are dissolved in an aqueous medium, thus avoiding the possibility of physical loss of sample such as can occur in dry ashing (Test Methods A and B). A limitation is the relatively small sample of 1 g, which can be ashed without excessively large apparatus in which to carry out the oxidation step. Small specimens may not be adequately representative where a particulate contaminate is involved.

3.4 *Test Method D, Wet Ashing of Cellulose for Inorganics*—This test method is recommended for ashing cellulose for subsequent analysis of inorganic constituents. The procedure employs saturation of the cellulose with a concentrated solution of hydrogen peroxide followed by incremental addition to a small volume of concentrated sulfuric acid. It has the advantage over Test Method C of not requiring special apparatus and can be readily applied to samples of 5 to 10 g. The test method becomes tedious and less convenient for use where larger specimens such as 50 or 100 g are required. Specimens this large, although not generally required, may be necessary for the determination of trace levels of constituents such as manganese or silica. Smaller samples may not be

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

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 06.03.

adequately representative where a particulate contaminate is involved.

#### 4. Significance and Use

4.1 Ash content gives an estimation of the inorganic content of cellulose samples. The presence of high levels of ash can be expected to be detrimental to the process of making cellulose derivatives. It also provides a rough estimate of silica content which can have a significant effect on the performance of filters in cellulose derivative manufacturing facilities.

#### 5. Purity of Reagents

5.1 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.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined in Specification D 1193.

#### TEST METHOD A—ASH IN CELLULOSE AT 575°C

#### 6. Apparatus

6.1 *Balance*, with an accuracy to 0.05 g is required for weighing cellulose samples.

6.2 *Analytical Balance*, with a sensitivity of 0.1 mg is required. It should be checked with Class S weights.

6.3 *Drying Oven*, with the capability of maintaining a temperature of  $105 \pm 2^\circ\text{C}$ .

6.4 *Desiccator*, such as silica gel, indicating drierite, or magnesium perchlorate are suitable.

6.5 *Muffle Furnace*, electric, capable of maintaining a temperature of  $575 \pm 25^\circ\text{C}$ , is recommended.

NOTE 3—Back to front temperatures in muffle furnaces frequently exceed the  $\pm 25^\circ\text{C}$  range, so that operating limits should be established for a given furnace.

6.6 *Dish*, platinum, 100-mL capacity or larger. Porcelain crucibles are not recommended.

6.7 *Tongs*, approximately 0.5 m (20 in.) long, with nickel-chromium or platinum tips.

#### 7. Test Specimen

7.1 The amount of cellulose selected for each ash determination depends on the ash content of the test specimen and should be varied so that the weight of the ash will be not less than 10 mg and preferably over 20 mg. Table 1 gives suggested sample sizes.

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

TABLE 1 Suggested Sample Sizes

Ash, %	Moisture-Free Cellulose, g
Over 0.5	5
0.20 to 0.5	10
0.12 to 0.2	20
0.08 to 0.12	30
0.04 to 0.08	40
Less than 0.04	50

7.2 Selection of the specimen shall be in such a manner as to be representative of the lot being tested.

NOTE 4—No set sampling procedure has been established to be applicable to all samples. It will suffice to specify that the specimen shall be representative of the lot being sampled.

#### 8. Procedure

8.1 Weigh out, to the nearest 0.05 g, sufficient cellulose to give the correct range of ash weight (see Table 1). At the same time, a separate specimen (3 to 5 g) should be weighed and dried at  $105^\circ\text{C}$  for a moisture determination.

NOTE 5—Test Methods D 1348, Method B is suitable. However, accuracy of the moisture test is not critical for the ash determination and any method capable of obtaining the percent oven dry within 0.5 % of the true value is adequate.

8.2 Heat the platinum dish in the muffle furnace at  $575^\circ\text{C}$  for 15 min, cool and weigh to the nearest 0.1 mg. Place the weighed cellulose in the platinum dish and place the dish on the open door of the muffle furnace, previously set and allowed to reach equilibrium at  $575^\circ\text{C}$ . Allow the cellulose to char without flame by gradually moving the dish into the muffle, and continue ashing with the door closed for 1 h.

NOTE 6—With some pulps, the character of the ash inhibits complete carbon removal and gray or black specks persist after 3 h of ignition. The addition of a few drops of distilled water to the ash after 8.3 followed by drying and reignition at  $575^\circ\text{C}$  for 1 h or more may be required. Extreme cases may require a second treatment with water.

NOTE 7—If the sample is too large, either separate ashings are required or successive additions of cellulose are made with extreme care so as not to disturb the ash. 8.2 is then repeated between each addition.

8.3 Remove the dish from the muffle furnace and allow to cool somewhat. Place it in the desiccator and allow it to cool to room temperature.

NOTE 8—Care must be taken at all times to keep drafts away from the light, fluffy ash.

8.4 Weigh the dish and ash to the nearest 0.1 mg. Reignite for a 15-min period and reweigh. Repeat as required to obtain constant weight.

#### 9. Calculation

9.1 Calculate the ash percent of moisture-free cellulose,  $E$ , as follows:

$$E = \frac{(C - B)(100)(100)}{(A)(D)} \quad (1)$$

where:

$A$  = weight of specimen as is, g,

$B$  = weight of dish, g,

$C$  = weight of dish plus ash, g, and  
 $D$  = oven dry cellulose in specimen, %

## 10. Report

10.1 Report the results to the nearest 0.01 %. Duplicate determinations should check within approximately 5 %.

## 11. Precision and Bias

11.1 A precision of 8 % relative at the 95 % confidence level is found for specimens at the 0.05 % ash level.

11.2 No statement of bias can be made as no suitable reference material exists for determining bias.

### TEST METHOD B—SULFATED ASH IN CELLULOSE AT 575°C

## 12. Apparatus and Reagent

12.1 *Hot Plate.*

12.2 Additional apparatus shall be in accordance with Section 6.

12.3 *Sulfuric Acid*—Concentrated  $H_2SO_4$ .

## 13. Test Specimen

13.1 The amount of cellulose selected for each ash determination depends upon the sulfated ash content of the test specimen and should be varied so that the weight of the ash will be not less than 10 mg and preferably over 20 mg. Table 1 gives suggested specimen sizes for Test Method A. The table is applicable to sulfated ash also, providing the percent ash column is taken as percent sulfated ash.

NOTE 9—The sulfated ash values will be higher than the ash obtained by ignition of the cellulose without addition of the sulfuric acid. The magnitude of the difference will depend upon the proportions of different inorganic salts present, but based on the following conversion factors for the salts commonly present, will generally be about twice the regular ash:

$$\frac{MgSO_4}{MgO} = 2.99; \frac{CaSO_4}{CaO} = 2.43; \frac{MgSO_4}{MgCO_3} = 1.43 \quad (2)$$

$$\frac{CaSO_4}{CaSO_3} = 1.36; \frac{Na_2SO_4}{Na_2CO_3} = 1.34 \quad (3)$$

13.2 Selection of the specimen shall be in such a manner as to be representative of the lot being tested (see Note 4).

## 14. Procedure

14.1 Weigh out to the nearest 0.05 g sufficient cellulose to give the correct range of ash weight (see Table 1). At the same time, weigh a separate specimen (3 to 5 g) and dry to constant weight at  $105 \pm 2^\circ C$  for a moisture determination (see Note 5).

14.2 See 8.2.

14.3 Remove the dish and allow it to cool to room temperature (see Note 7 and Note 8).

14.4 Moisten the ash with 1 to 2 mL of concentrated  $H_2SO_4$  and heat on a hot plate until all the dense white fumes of sulfur trioxide ( $SO_3$ ) are liberated.

14.5 Place in the muffle furnace and ignite at  $575^\circ C$  for 1 h. If carbon persists repeat 14.3, 14.4, and 14.5.

14.6 After the last trace of carbon has disappeared, ignite in the muffle furnace for 1 h at  $575^\circ C$ .

14.7 Remove the dish and allow it to cool somewhat before placing it in desiccator and cooling to room temperature.

14.8 Weigh the dish and sulfated ash to the nearest 0.1 mg. Reignite for a 15-min period and reweigh. Repeat as required to obtain constant weight.

NOTE 10—To remove the ash from the dish, clean with boiling hydrochloric acid.

NOTE 11—On igniting sulfated ash at  $575^\circ C$ , there should be no fusion with the dishes, even when ashing cellulose that gives an alkaline ash.

14.9 Prepare a reagent blank for the  $H_2SO_4$  corresponding to the number of millilitres of  $H_2SO_4$  used in 14.4 and 14.5, by the addition of the acid to a platinum dish after ignition and true weight was determined, and carrying through 14.4–14.8 as they apply.

## 15. Calculation

15.1 Calculate the sulfated ash,  $S$ , as percent of moisture-free cellulose, as follows:

$$S = \frac{(C - B - R)(100)(100)}{(A)(D)} \quad (4)$$

where:

$A$  = weight of specimen, g,

$B$  = weight of dish, g,

$C$  = weight of dish plus sulfated ash, g,

$R$  = weight of  $H_2SO_4$  reagent blank residue, g, and

$D$  = oven-dry cellulose in specimen, %.

## 16. Report

16.1 Report the results to the nearest 0.01 %. Duplicate determinations should check within approximately 5 %.

## 17. Precision and Bias

17.1 A precision of 15 % relative is found for specimens in the 0.1 to 0.3 % ash range.

17.2 No statement of bias can be made as no suitable reference material exists for determining bias.

### TEST METHOD C—ASHING CELLULOSE BY SCHONIGER OXIDATION

## 18. Apparatus

18.1 *Combustion Flasks*, 5000 mL, round bottom, borosilicate glass, with 65/40 ball and joint stopper. The flasks are equipped with perforated platinum specimen carriers sealed into the extended stem of the flask stopper.

18.2 *Igniter*, suitable for igniting the specimen in the flask. An infrared igniter is preferred.

18.3 *Specimen Wrappers*, black paper.

18.4 *Pipet*, 5 mL.

18.5 *Volumetric Flask*, 50 mL.

## 19. Reagents

19.1 *Deionized Water*, high-purity, with a conductivity  $< 1.0 \mu\text{mho/cm}$  at  $25^\circ C$ .

19.2 *Absorption Solution*—0.2 N  $H_2SO_4$  prepared from concentrated  $H_2SO_4$ .

## 20. Procedure

20.1 By hand, tear a 2- to 3-g air-dried test portion of the

sample into 1 to 1.5-cm pieces and store in closed airtight, glass or polyethylene bottles.

20.2 Weigh a 1-g portion of the prepared sample to  $\pm 1$  mg, and wrap in a square of black ignition paper.

20.3 Weigh a second portion of sample, approximately 1 g to  $\pm 1$  mg, and determine the moisture content in accordance with Test Methods D 1348. This test method determines the weight loss on a 1-g specimen placed in a gravity convection oven at 105°C for 4 h.

20.4 Add by pipet, 10 mL of 0.2 N H<sub>2</sub>SO<sub>4</sub> as an absorption solution to the combustion flask.

20.5 Place the specimen contained in the wrapper into the platinum carrier and insert into the flask.

20.6 Allow a stream of oxygen from a low-pressure, regulated supply (2 to 3 lb./in.<sup>2</sup> (14 to 21 kPa)) to flow into the flask for a period of 30 s to displace the air. Secure the stopper in the flask with the pinch clamp and place the expansion balloon on the side tube.

20.6.1 **Warning:** It is required that laboratory goggles be worn during 20.6, 20.7, and 20.8 as a safety measure.

20.7 Place the flask behind a safety shield or in a hood with a protective door.

20.8 Turn on the igniter and focus the infrared light beam on the fuse strip of the black paper wrapper until ignition occurs. Allow the specimen to burn completely and cool the flask for 1 h so that all vapors are absorbed in the solution.

20.9 Transfer the solution to a 150-mL beaker and rinse the flask with two 15-mL portions of deionized water and add to the absorption solution in the beaker.

20.10 Transfer the contents of the beaker to a 50-mL volumetric flask and rinse with 2 to 4-mL portions of deionized water. Add water to bring to 50-mL volume. *Identify as Schoniger ash solution.*

20.11 Ash a black wrapper identical in weight to one used for wrapping the specimen by following 20.4 to 20.10. Identify as *wrapper and absorption solution blank.*

## 21. Calculation

21.1 Calculate the concentration equivalent for oven-dry cellulose, *C*, in Schoniger ash solution, as follows (Note 12):

$$C = \frac{(A)(B)}{(50)(100)} \quad (5)$$

where:

*A* = weight of cellulose specimen, and

*B* = oven-dry cellulose in specimen, %

NOTE 12—Use of the solution for subsequent analysis assumes parallel treatment of both the Schoniger ash solution and the wrapper absorption solution blank to provide for the analytical blank correction.

NOTE 13—The purpose in specifying the calculation of equivalent oven-dry cellulose in grams per millilitre is to provide for convenient use of aliquots for subsequent elemental analyses.

## 22. Precision and Bias

22.1 A precision of 20 % relative is found for specimens at the 0.2 % ash content level. The operator's technique is very important in keeping the precision at a high level.

22.2 No statement on bias can be made as no suitable reference material exists for determining bias.

## TEST METHOD D—WET ASHING OF CELLULOSE FOR INORGANICS

### 23. Summary of Test Method

23.1 A test specimen of pulp is torn into small pieces approximately 1 cm across, saturated with a solution of hydrogen peroxide, and added one piece at a time to a small volume of concentrated sulfuric acid.

23.2 The cellulose is oxidized to carbon dioxide and water. The water is volatilized by the heat of the reactions involved.

23.3 An analyst experienced with the technique can ash 30 g of pulp into an initial volume of only 10 mL of sulfuric acid in about 30 min. Total procedural time for converting a 30-g specimen to solution in a form suitable for aliquoting for metals analysis is about 2 h.

### 24. Apparatus

24.1 *Balance*, sensitivity to  $\pm 0.01$  g.

24.2 *Beakers*, Berzelius, 300-mL.

24.3 *Beakers*, 150-mL.

24.4 *Cylinder*, graduated-pharmaceutical, 50-mL.

24.5 *Forceps*, 20-cm stainless steel, TFE-fluorocarbon tipped.

24.6 *Hot Plate*, sensitive temperature control, ceramic-top surface or alternative suitable for use with platinum ware. Metal surfaces are not suitable.

24.7 *Pipet*, 10-mL.

24.8 *Rubber Bulb*, for filling pipet.

### 25. Reagents

25.1 *Hydrogen Peroxide*, 50 % H<sub>2</sub>O<sub>2</sub>.

NOTE 14—The actual concentration is not critical, but the absolute minimum is 30 % below which the test fails. One should be aware that hydrogen peroxide solution tends to lose strength upon standing.

25.2 *Sulfuric Acid*, concentrated H<sub>2</sub>SO<sub>4</sub>.

### 26. Hazards

26.1 The procedure specifies many repetitive manual additions of a strong oxidant and organic material to concentrated acid. It is imperative that the analyst wears protective equipment for the eyes and hands, and works in a fume hood free of distraction during the steps in Section 28.

### 27. Sampling

27.1 Select an appropriate sized sample as specified in the methods for inorganic elements to be determined, with an allowance for a moisture determination.

27.2 Tear the pulp by hand into small pieces approximately 1 cm across.

27.3 Weigh the selected weight of the specimen to 0.01 g.

27.4 Determine the moisture content on a separate specimen in accordance with Test Methods D 1348.

27.5 Correct the specimen weight (27.3) to the oven-dry basis for subsequent calculations.

### 28. Procedure

28.1 Pipet 10 mL of H<sub>2</sub>SO<sub>4</sub> to a 300-mL tall form Berzelius beaker.

28.2 Place approximately 10 g of the weighed pulp specimen into a 150-mL beaker.

28.3 Pour approximately 50 mL of  $H_2O_2$  into a 50-mL graduated cylinder.

28.4 Distribute approximately 30 mL of the measured portion of  $H_2O_2$  over the 10 g of specimen allowing the pulp to saturate with it.

28.5 Add 2 to 3 mL of  $H_2O_2$  to the 10 mL of  $H_2SO_4$  by allowing it to run down the side of the beaker. Carefully swirl to mix, resulting in gas evolution. If mild boiling is not evident, heat gently on hot plate to induce it, then remove the beaker from the hot plate.

28.6 With stainless tongs, add the pulp saturated with  $H_2O_2$  one piece at a time allowing for almost complete destruction between each addition.

**NOTE 15**—A porcelain spatula has been used in place of stainless tongs to transfer the pulp to the acid and may be preferable for specimens in powdered state. Pulps vary in their behavior to the ashing step. Thirty grams of some pulps have been ashed with only 2 or 3 additions of  $H_2O_2$  separate from the pulp. These are required whenever the acid retains a brown or black residue after destruction of a pulp addition. With other pulps, ten or more 1 to 2 mL additions of hydrogen peroxide may be required.

28.7 After the initial 10-g portion of pulp has been ashed, repeat 28.2 to 28.6 on a second 10-g portion of the weighed specimen.

28.8 Repeat 28.7 until the total specimen is ashed.

28.9 Rinse the sides of the beaker containing ashed specimen with distilled water from a wash bottle. Use the minimum amount required.

28.10 Swirl the beaker to mix the rinse water with the acid.

28.11 Place the beaker on the hot plate and heat to the point that dense fumes of  $H_2SO_4$  evolve.

**NOTE 16**—If the acid discolors, remove the beaker from the hot plate, allow it to cool, and add 2 to 3 mL of  $H_2O_2$  to the beaker. Return the beaker to the hot plate and continue heating. Repeat this step as required to attain a colorless solution.

28.12 Continue heating to remove the excess acid.

**NOTE 17**—The final volume of acid is selected relative to subsequent analyses, however 2 to 3 mL has been satisfactory for most applications.

28.13 Remove the beaker from the hot plate, allow it to cool, and with extreme care add distilled water, allowing it to flow down the side of the beaker to the required dilution. Transfer it to a 25-mL volumetric flask and adjust to volume.

**NOTE 18**—If an ash-determination is desired, transfer the solution to a preweighed platinum dish, take to dryness, and ignite at approximately 400°C prior to weighing. The residue may then be taken up in distilled water for elemental analysis. Some sulfates may be difficult to solubilize, particularly ferric sulfate, requiring subsequent heating.

28.14 Prepare a reagent blank corresponding to the 10 mL of  $H_2SO_4$  and the volume of  $H_2O_2$  used by slow addition of increments of the peroxide to the acid followed by gentle heating to remove the oxygen and water. Complete the blank in accordance with 28.12 and 28.13.

28.15 The solutions from 28.13 and 28.14 are now suitable for subsequent elemental analysis.

## 29. Precision and Bias

29.1 A precision of 20 % relative is found for specimens at the 0.5 % ash content level.

29.2 No statement of bias can be made as no suitable reference material exists for determining bias.

## 30. Keywords

30.1 bleached; Schoniger oxidation; sulfated ash; wet ashing

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