Designation: D 2929 – 89 (Reapproved 2000)

Standard Test Method for Sulfur Content of Cellulosic Materials by X-ray Fluorescence[1]

This standard is issued under the fixed designation D 2929; 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 determination of sulfur content of cellulosic materials by X-ray fluorescence.

1.2 Using appropriate standards, the range of the procedure is from approximately 10 ppm to 20 % sulfur.

1.3 This test method is proposed specifically as an alternative to Test Methods D 871, Sections 29 to 33, and Test Methods D 817, Sections 39 to 43. As applied to cellulose esters it measures the combined sulfur and sulfur in the accompanying inorganic salts.

1.4 To determine combined sulfur, the sample, when soluble, must first be reprecipitated into dilute acid to remove the noncombined sulfur compounds.

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

1.6 *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 3.

2. Referenced Documents

2.1 *ASTM Standards:*

D 817 Test Methods of Testing Cellulose Acetate Propionate and Cellulose Acetate Butyrate[2]

D 871 Test Methods of Testing Cellulose Acetate[2]

3. Summary of Test Method

3.1 The sulfur content of cellulose, cellulose modification, or cellulose derivative is determined by measuring the intensity of the secondary sulfur Kα X rays emitted on irradiation of the sample with primary X rays of higher energy from an X-ray tube with a target of tungsten or chromium. The sulfur Kα radiation is diffracted with a suitable analyzing crystal and detected with a flow proportional counter. The entire path of the secondary radiation is purged with hydrogen or helium, or evacuated to a pressure of 0.5 mm Hg or less. The intensity of the sulfur Kα rays, as established by a standard counting period and corrected for background radiation, is then converted to percent sulfur from calibration data.[3]

4. Significance and Use

4.1 This procedure provides a method for determining sulfur content in cellulosic materials by nondestructive means. Sulfur may be in the form of sulfate esters that may contribute to thermal instability. Sulfur can also be present as salts that can cause haze in solutions.

5. Apparatus

5.1 *Wiley Mill*, equipped with 60-mesh screen.

5.2 *Sample Mold*—Chrome steel die of a size depending on the sample holder to be used.

5.3 *Laboratory Press*, capable of exerting at least 5000 psi.

5.4 *X-Ray Spectrograph*, with following equipment: tungsten or chromium target X-ray tube; hydrogen or helium purging system or vacuum system to reach 0.5 mm Hg (or less, if desired); 20-mil Soller slits; flow proportional counter with 90 % argon-10 % methane gas mixture; and NaCl, ethylenediamine dextro tartrate (EDT), or pentaerythritol (PET) analyzing crystal.

NOTE 1—Radiation from a chromium target tube appears to be more effective than radiation from a tungsten target tube for exciting sulfur Kα. This may be because a larger part of the "white" radiation of the chromium tube is at the longer wavelength region of the spectrum, or because of the use of thinner windows in the chromium tube. However, either the chromium or the tungsten target tube is suitable for sulfur analysis. If a pulse height analyzer is available as a part of the X-ray instrumentation, its use is very helpful in reducing background radiation. Use of a pulse height analyzer is mandatory for the determination of sulfur below 100 to 200 ppm level.

6. Reagents

6.1 *Ethyl Cellulose Phthalate.*

6.2 *Microcrystalline Cellulose.*

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[1] 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 D01.36 on Cellulose and Cellulose Derivatives.

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[2] *Annual Book of ASTM Standards*, Vol 06.03.

[3] This test method is compiled from four techniques, by incorporating certain features of each, as follows: "Sulfur in Cellulose Esters by X-ray Emission Spectroscopy," Eastman Kodak Co.; "Sulfur in Cellulose Acetate by X-ray Fluorescence," Tennessee Eastman Co.; "X-ray Fluorescence Analysis of Modified Cottons" by Tripp, Piccolo, Mitcham and O'Connor. *Textile Research Journal*, Vol 34, 1964, p. 773, and FMC Corp., American Viscose Div. information furnished by L. H. Phifer and W. B. Swann.

6.3 *Cystine*, NIST primary standard No. 143B.

7. Procedure

7.1 *Instrument Standardization Pellet*— Intimately mix ethyl cellulose phthalate, microcrystalline cellulose, or other selected matrix with finely divided cystine in a weight ratio of approximately 4:1. Press a portion into a pellet in the sample mold for 30 s using a pressure of 5000 lb on the mold. Make sure that the thickness of the sample pellet is 1.6 mm (1⁄16 in.) or greater.

7.2 *Standardization of Instrument*:

NOTE 2—Basic standardization techniques and operating parameters vary from instrument to instrument. The manufacturer's literature and the analyst's knowledge of the performance characteristics of the equipment should be used as a guide in performing this function.

7.2.1 Place a standardization pellet in the sample holder and center it so that it covers the entire window of the holder. Evacuate the X-ray path to a pressure of 0.5 mm Hg (or less, if desired) or flush the path with hydrogen or helium. Set the gas flow of the proportional counter as suggested by the manufacturer.

NOTE 3—**Precaution:** X rays are very hazardous. Do not turn the equipment on until the instruction manual has been read and understood.

7.2.2 Set the goniometer of the X-ray spectrograph at the appropriate sulfur Kα angle. Turn the X-ray tube on, using the manufacturer's recommended voltage and current. Selection of the operating voltage and current of the X-ray tube is governed by the type of tube used. Take care not to exceed the rated power output (in watts) of the X-ray tube. Make a plot of the sulfur X-ray intensity versus applied voltage to the detector. Make sure that the voltage chosen is approximately midway on the plateau.

7.2.3 If a pulse height analyzer is being used, a common way to arrive at the proper settings is to set the gain of the linear amplifier at approximately half of its maximum. Select the detector voltage about midway on the plateau. Set the minimum pulse rejection voltage at about 5 V and the ΔE at about 10 V. Observe the intensity without the pulse height analyzer on. With the pulse height analyzer on, change either the amplifier gain control or the detector voltage until as near as possible the same intensity as without the analyzer is obtained. Then increase or decrease the ΔE control just until a maximum intensity is reached.

7.3 *Calibration for Measurement of Sulfur*:

7.3.1 Select five or more representative cellulosic samples whose sulfur contents, as determined by chemical analysis according to Test Methods D 817 or D 871, completely cover the required range. Since X-ray fluorescence intensities are functions of concentrations per unit volume, prepare standards used to establish the calibration curve in a matrix as nearly identical to that of the sample as possible. Distribute the sulfur-containing component very uniformly in the matrix. The physical form of the matrix (powder, flake, pellet, or sheet) is a significant variable. For accurate work it may be necessary to have separate calibrations for each form of sample.

7.3.1.1 As a calibration standard for cellulose, microcrystalline cellulose containing intimately mixed known amounts of cystine may be used. A chemical analysis of the standards is generally not necessary.

7.3.2 Prepare the samples for analysis according to 7.4 and 7.5.

7.3.3 Measure the intensities of the sulfur Kα X rays of the standard samples according to 7.6.

7.3.4 Prepare a calibration curve relating sulfur Kα X-ray intensity expressed as net counts per second to percent sulfur.

7.4 *Treatment of Sample Prior to Analysis*:

7.4.1 To analyze for total sulfur content, no treatment is required prior to analysis. If the sample has a high absorbing coating (for example, saran, PVC, etc.) remove them or a standard containing a matrix of those materials in equivalent concentrations must be prepared.

7.4.2 When analyzing for combined sulfur content, as in a cellulose ester, remove the uncombined sulfur as follows:

7.4.2.1 Dissolve 25 g of sample in approximately 300 mL of acetone, depending on the viscosity. If the sample is of too high acetyl content to be directly soluble in acetone, cool in a dry ice cabinet overnight, then allow to come to room temperature while tumbling or stirring.

7.4.2.2 Filter the solution, if necessary, through felt or a coarse sintered-glass crucible.

7.4.2.3 Precipitate with rapid stirring into a beaker or pail containing 2 to 3 L of acetic acid-water (1:49).

7.4.2.4 Filter through a cloth bag or a Büchner funnel and give two 15-min washes with water using mechanical agitation. A little Na_2CO_3 may be added to the last wash to stabilize samples of high sulfur content.

7.4.2.5 Filter and dry overnight at 60°C.

7.5 *Preparation of Specimen for Analysis*:

7.5.1 Grind the sample in a Wiley Mill to pass a 60-mesh screen. Mold a quantity of the sample for 30 s with a gage pressure to 5000 lb on the mold. Use sufficient sample to obtain a disk at least 1.6-mm (1⁄16-in.) thick.

7.5.2 Film specimens can be run directly (without grinding) by using a multiplicity of sheet thicknesses provided that the specimen contains no air trapped between the successive layers. If film specimens are coated with a high absorbing coating (for example, saran, PVC, or aluminum), these must be removed if the specimens are to be analyzed as multiple thicknesses. Similarly, a closely wrapped specimen of continuous filament yarn can also be tested directly.

7.6 *Measurement of Intensity of Sulfur Kα X rays*:

7.6.1 Place the specimen in the sample holder of the X-ray spectrograph and center so that it covers the entire sample-holder window.

7.6.2 Evacuate the X-ray path to a pressure of 0.5 mm Hg or less or flush the path with hydrogen or helium.

7.6.3 Record the X-ray count for a standard time period at the sulfur Kα angle.

7.6.4 Repeat the count on the opposite side of the specimen pellet if homogeneity is questioned.

7.6.5 If a sulfur-free specimen is available, record the background count. This is unnecessary if the standard's matrixes are identical to the samples.

NOTE 4—A background count is desirable at all concentration levels. It is mandatory for measurement of sulfur concentrations under 100 ppm.

NOTE 5—An indication of the precision of this test method is given by the standard counting error, which is:

$$s_c = \sqrt{N_T} + \sqrt{N_B} \tag{1}$$

where:

s_c = standard counting error of $N_T - N_B$,

N_T = counts accumulated at sulfur Kα angle during counting interval Δt, and

N_B = counts accumulated at background during same counting interval Δt.

This error level calculation should be used as a guide to counting time.

8. Calculation

8.1 Convert the standard time count values of the specimen and the background to counts per second.

8.2 If the background is measured subtract the background count rate from the count rate of the specimen pellet to obtain the net count rate of the specimen.

8.3 Convert the net count rate of the specimen to percent sulfur by using the calibration curve.

9. Precision and Bias

9.1 The precision of measurement, or standard deviation, σ, is calculated by normal statistical methods as follows.

$$\sigma = \sqrt{\frac{\Sigma(x - \bar{x})^2}{n - 1}} \tag{2}$$

where:

x = measured value,

$\bar{x}$ = mean value of n measurements, and

n = number of measurements.

9.1.1 The practical significance of σ is that 68 % of all results should be within ±1σ of the mean, 95 % with ±2σ and 99.7 % within ±3σ.

9.1.2 Since random processes are involved in x-ray analysis, precision can also be determined from the fact that standard deviation is equal to the square root of the number of counts, N, collected.

$$\sigma N = \sqrt{N} \tag{3}$$

9.1.3 It may be more relevant to express precision in terms of the coefficient of variaiton, E which is the standard deviation as a percent of the number of counts as follows:

$$E = \frac{\sqrt{N}}{N} \times 100 = \frac{100}{\sqrt{N}} \tag{4}$$

9.2 Bias has not been evaluated for this test method.

10. Keywords

10.1 cellulose esters; combined sulfur; salts; pulse height analyzer