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Standard Test Method for Forms of Sulfur in Coal¹

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¹ This test method is under the jurisdiction of ASTM Committee ~~D-5~~ D05 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

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1. Scope

1.1 This test method applies to the determination of sulfate sulfur and pyritic sulfur in coal and calculates organic sulfur by difference. This test method is not applicable to coke or other carbonaceous materials. Monosulfides (pyrites and FeS₂ are disulfides) of iron and elements such as cadmium, lead, vanadium, and zinc can be present in coal. In the range of 0 to 100 ppm, these monosulfides do not contribute significantly to the total inorganic sulfide content.

1.2 The values stated in SI units are to be regarded as 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 determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water²

~~D 2013 Method of 2013 Practice for Preparing Coal Samples for Analysis³~~

D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke³

D 3177 Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke³

D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases³

D 4239 Test Methods for Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion Methods³

E 832 Specification for Laboratory Filter Papers⁴

3. Summary of Test Method

3.1 *Sulfate Sulfur:*

3.1.1 Sulfate sulfur is extracted from the analysis sample with dilute hydrochloric acid. The sulfate sulfur in the extract is determined gravimetrically. Sulfates are soluble in hydrochloric acid, but pyritic and organic sulfur are not.

3.2 *Pyritic Sulfur:*

3.2.1 Pyritic sulfur is calculated as a stoichiometric combination with iron.

3.2.2 *Methods:*

3.2.2.1 *Referee Method*, which can be used in cases of dispute or arbitration. The iron combined in the pyritic state is extracted with dilute nitric acid from the coal residue remaining after sulfate extraction (see Note 1). The iron is determined by atomic absorption techniques (see Note 2).

NOTE 1—The sulfate extraction step also removes hydrochloric acid soluble iron (nonpyritic iron) from the test specimen. A test specimen separate from that used for the sulfate extraction could be used for the nitric acid extraction of iron. In this case, both nonpyritic and pyritic iron are extracted from the test specimen. Since there is evidence that for some coals the extraction of nonpyritic iron by nitric acids falls short of the amount extracted by hydrochloric acid,^{5,6} the use of a separate test specimen for the nitric acid extraction of iron with subsequent correction for the contribution of nonpyritic iron is not included in this test method.

² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 05.056.

⁴ *Annual Book of ASTM Standards*, Vol 14.04.

⁵ Edwards, A. H., Daybell, G. N., and Pringle, W. J. S., "An Investigation into Methods for the Determination of Forms of Sulfur in Coal," *Fuel*, Vol 37, 1958, pp. 47–59.

⁶ Burns, M. S., "Determination of Pyritic Sulfur in Australian Coals," *Fuel*, Vol 49, 1970, pp. 126–33.

NOTE 2—Round-robin testing of the coal samples used to generate data for the precision statement in this test method indicates that plasma emission techniques give results equivalent to those from atomic absorption analysis for the determination of iron. However, emission analysis is highly susceptible to interferences from other analytes that may be dissolved during the extraction of iron. Selection of a wavelength that is free from interferences and linear over the range of iron anticipated for emission analysis can require a detailed compositional analysis of the coal mineral matter, thus limiting the practicality of this approach.

3.2.2.2 *Alternative Method*, which can be used in routine practice or when the concerned parties agree on this test method. The iron originally combined in the pyritic state can be extracted with dilute hydrochloric acid from the ash obtained by incinerating the coal residue remaining after sulfate extraction. The iron is determined by atomic absorption techniques (see Note 2).

4. Significance and Use

4.1 This test method provides for a separation of coal-associated sulfur into two commonly recognized forms: pyritic and sulfate. Organic sulfur is calculated by difference. Results obtained by the test method are used to serve a number of interests, including the evaluation of coal preparation and processing operations designed to reduce coal sulfur levels.

5. Analysis Sample

5.1 The analysis sample is that sample which has been pulverized to pass No. 60 (250- μ m) sieve as prepared in accordance with Test Method D 2013. Moisture shall be determined in accordance with Test Method D 3173 to permit calculations to other than as-analyzed bases.

6. Sulfate Sulfur

6.1 Apparatus:

6.1.1 *Balance*, sensitive to 0.1 mg.

6.1.2 *Crucibles*, porcelain, platinum, alundum, or silica of 10- to 25-mL capacity for ignition of barium sulfate (BaSO_4).

6.1.3 *Hot Plate*, electric or gas-heated with capability for temperature control.

6.1.4 *Muffle Furnace*, electrically heated and capable of regulating the temperature at $800 \pm 25^\circ\text{C}$ for igniting BaSO_4 .

6.2 Reagents and Materials:

6.2.1 *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.⁷ Other grades may be used, provided that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

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

6.2.3 *Ammonium Hydroxide* (14.9N, sp. gr. 0.90)—concentrated aqueous ammonia.

6.2.4 *Ammonium Hydroxide Solution* 1.5N, (1 + 10)—Mix one volume of concentrated aqueous ammonia with ten volumes of water.

6.2.5 *Barium Chloride Solution* (100 g/L)—Dissolve 100 g of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in water and dilute to 1 L.

6.2.6 *Bromine Water* (saturated)—Add an excess of bromine to 1 L of water. (**Caution—Store Warning—Store** in a dark bottle and keep in a hood.) (Solubility, 42 g/L.)

6.2.7 *Ethanol*, reagent grade, denatured.

6.2.8 *Filter Paper*—Unless otherwise indicated, references to filter paper shall be understood to mean filter paper conforming to Specification E 832.

6.2.9 *Hydrochloric Acid*, 12N (sp. gr. 1.19)—Concentrated aqueous hydrochloric acid (HCl).

6.2.10 *Hydrochloric Acid*, 4.8N (2 + 3)—Mix two volumes of concentrated aqueous hydrochloric acid (HCl, sp. gr. 1.19) with three volumes of water.

6.2.11 *Methyl Orange Indicator Solution*, (0.02 g/100 mL)—Dissolve 0.02 g of methyl orange in 100 mL of hot water.

6.2.12 *Silver Nitrate Solution*, (0.43 g/100 mL)—Dissolve 0.43 g of silver nitrate in 100 mL of water. Store in an amber glass bottle.

6.3 Procedure:

6.3.1 *Extraction*—Weigh to the nearest 1 mg a 2- to 5-g test specimen of analysis sample (see Note 3) and transfer to a 250-mL Erlenmeyer flask or beaker. Add 50-mL HCl (2 + 3) in small increments while stirring to wet the coal thoroughly. A few drops of ethanol added to the coal facilitates the wetting process. Place on a hotplate and boil gently for $\frac{1}{2}$ h. Carefully filter the contents into a 400-mL beaker, using a Type II, Class F filter paper. Wash the filter paper and contents with sufficient small water washings to ensure the transfer of all HCl extract to the beaker. Save the filter paper with extracted residue for subsequent extraction of pyrites.

⁷ *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.

NOTE 3—It is practical to limit the sample weight to 2 g when the total sulfur level is 2 % or above, to avoid handling an excessive amount of iron in the pyritic extraction.

6.3.2 Add 5 mL of bromine water to the extract and boil for at least 5 min to oxidize iron and expel excess bromide. Cool to room temperature.

6.3.3 Precipitate the iron by slowly adding aqueous ammonium hydroxide (sp. gr. 0.90) until a slight excess is present as measured by pH indicator paper. Add 5 mL more with constant stirring to coagulate the ferric hydroxide. Filter on a Type II, Class E filter paper into a 400-mL or larger beaker. Wash the filter paper several times with hot ammoniacal solution (6.2.4).

6.3.4 *Precipitation*—Add two or three drops of methyl orange solution and neutralize the filtrate (6.3.3) by cautiously adding aqueous HCl (sp. gr. 1.19) until the solution turns pink. Add 1 mL in excess. Heat to boiling and, while stirring slowly, add 10 mL of BaCl₂ solution. Continue boiling gently for 10 to 15 min and allow to stand overnight at room temperature or for 4 h between 70 and 100°C covered with a watch glass. Filter through a Type II, Class G filter paper and wash with intermittent small washings of hot water until one drop of silver nitrate solution produces no more than a slight opalescence when added to 8 to 10 mL of the filtrate.

6.3.5 *Sulfate Blank*—Prepare a sulfate blank following the same procedure and using the same amounts of all reagents as described in 6.3.1-6.3.4. Save the filter paper from 6.3.1 of the blank test for the pyritic iron blank in 7.3.3.

6.3.6 *Determination*—Preignite crucibles (6.1.2) at 800 ± 25°C for 30 min. Cool in a desiccator and weigh to the nearest 0.1 mg. Place the specimen filter paper from 6.3.4 and the blank filter paper from 6.3.5 in separate preignited crucibles. Fold the filter papers over loosely to allow free access of air. Smoke the paper off gradually to prevent spattering. At no time allow to burn with flame. After the filter paper is practically consumed, raise the temperature to 800 ± 25°C and maintain for 1 h. Cool the crucibles in a desiccator until equilibrium is reached. Weigh the crucibles and contents to the nearest 0.1 mg. Ignition is considered to be complete when the weight of the crucible and contents do not change by more than 0.2 mg after reheating at 800 ± 25°C for 30 min.

6.4 *Calculation:*

6.4.1 Calculate the percentage of sulfate sulfur as follows:

$$\text{Sulfate sulfur \%} = \frac{[(S - C_s) - (B - C_B)] \times 13.735}{W} \quad (1)$$

where:

S = weight of sample crucible plus ignited BaSO₄ precipitate, ~~g~~, g_s

C_s = weight of sample crucible, ~~g~~, g_s

B = weight of blank crucible plus ignited sulfate blank, g,

C_B = weight of blank crucible, ~~g~~ and, g, and

W = weight of test specimen used (6.3.1), g.

METHODS FOR PYRITIC SULFUR

7. Referee Method—Using Coal Residue Remaining After Sulfate Extraction

7.1 *Apparatus:*

7.1.1 *Atomic Absorption Spectrophotometer.*

7.1.2 *Balance,* see 6.1.1.

7.1.3 *Hot Plate,* see 6.1.3.

7.2 *Reagents and Materials:*

7.2.1 *Purity of Reagents,* see 6.2.1.

7.2.2 *Purity of Water,* see 6.2.2.

7.2.3 *Filter Paper,* see 6.2.8.

7.2.4 *Hydrochloric Acid, 12N* (sp. gr. 1.19)—see 6.2.9.

7.2.5 *Hydrochloric Acid, 4.8N* (2 + 3)—see 6.2.10.

7.2.6 *Hydrochloric Acid, 0.24N, (1 + 49)*—Mix 1 volume of concentrated aqueous hydrochloric acid (HCl, sp. gr. 1.19) with 49 volumes of water.

7.2.7 *Iron Standard, (400 ppm)*—Weigh 0.4000 g ± 0.1 mg of clean, pure iron wire or 0.5179 g ± 0.1 mg of high purity iron (III) oxide into a 250-mL beaker. Add 50 mL of HCl (7.2.5) and cover with a watch glass. Heat until the solution boils gently for ½ h or until no visible particles are left. Quantitatively transfer the contents to a 1000-mL volumetric flask and dilute to the mark with water. Alternatively, an appropriate commercially available iron standard with an equivalent acid concentration may be used.

7.2.8 *Lanthanum Solution*—Dissolve 175 g of lanthanum chloride (LaCl₃) or 265 g of hydrated lanthanum chloride (LaCl₃·7H₂O) in water and dilute to 1 L. Alternatively, slurry 115 g of lanthanum oxide (La₂O₃) in 200 mL of water. Slowly add 200 mL of concentrated aqueous hydrochloric acid (HCl, sp. gr. 1.19), while mixing continually with the flask under cold water, to dissolve the oxide. Dilute to 1 L.

7.2.9 *Nitric Acid, 2N* (1 + 7)—Mix one volume of concentrated aqueous nitric acid (HNO₃, sp. gr. 1.42) with seven volumes of water.

7.3 *Procedure:*

7.3.1 *Extraction*—Transfer the filter paper and extracted residue from 6.3.1 to a 250-mL Erlenmeyer flask. Slowly add 50 mL of HNO₃ (1 + 7) with stirring, to ensure complete wetting and to help disintegrate the filter paper. Either boil gently for 30 min or let stand overnight at room temperature. Filter the flask and contents through a Type II, Class F filter paper into a 400- to 600-mL beaker. Wash the residue at least six times with small increments of water, keeping the total volume of filtrate between 100 and 200 mL.

7.3.2 *Preparation of Test Solution*—Transfer the filtrate from 7.3.1 to a 200-mL volumetric flask and dilute to volume with water. Transfer a 10-mL aliquot of the diluted filtrate to a 100-mL volumetric flask. Add 10 mL of lanthanum solution (7.2.8) and dilute to volume with HCl (1 + 49). This is the test solution.

7.3.3 *Preparation of Blank Test*—Perform a parallel blank test following the same procedure and reagents as described in 7.3.1 and 7.3.2 using the filter paper generated in 6.3.1 of the sulfate blank test.

7.3.4 *Determination of Iron by Atomic Absorption:*

7.3.4.1 *Spectrometric Conditions*—Suitable conditions for the determination of iron are as follows:

Wavelength 248.3 nm (0- to 5-ppm Fe)

Wavelength 372.0 nm (5- to 100-ppm Fe)

Wavelength 344.1 nm (>100-ppm Fe)

Flame: air/acetylene (lean)

7.3.4.2 *Preparation of Calibration Solutions*—Prepare a set of calibration solutions to cover the expected range of concentration in the test solution (7.3.2) by transferring appropriate volumes of the iron standard solution (7.2.7) to a series of 100-mL volumetric flasks. Add 10 mL of lanthanum solution (7.2.8). Dilute to the mark with HCl (1 + 49).

7.3.4.3 *Calibration*—Measure the absorbance of the calibration solutions (7.3.4.2) using the atomic absorption spectrometer (7.1.1) using the appropriate conditions (7.3.4.1). By regression analysis, construct a calibration curve (see Note 4) of absorbance against iron content for the calibration solutions (7.3.4.2).

NOTE 4—For guidance on appropriate procedures for construction of calibration curve, see pages 72 to 78 of Wernimont.⁸

7.3.4.4 *Determination of Iron in the Test Solution and Blank Test*—Measure the absorbance of the test solution (7.3.2) and the blank test (7.3.3) using the same conditions as used for the calibration solutions (7.3.4.3). Read the concentration of the test solution and the blank test by reference to the calibration curve (7.3.4.3).

7.4 *Calculation:*

7.4.1 Calculate the percentage of pyritic sulfur as follows:

$$\text{Pyritic sulfur, \%} = [F \times A \times V \times C \times P \times (T - B)]/W \quad (2)$$

where:

F = 1.148, dimensionless, the stoichiometric ratio of sulfur to iron in iron disulfide (FeS₂);₂

A = 20, dimensionless, the aliquot factor indicating proportion of filtrate used to prepare the test solution in 7.3.2;₂

V = 100 mL, the volume of the test solution from 7.3.2;₂

C = 10⁻⁶ g/μg conversion factor from micrograms to grams;₂

P = 100, dimensionless, conversion factor from weight fraction to percentage by weight;₂

T = concentration of iron in the test solution, μg/mL;₂

B = concentration of iron in the blank test, μg/mL;₂ and

W = weight of the test specimen (6.3.1), g.

8. Alternative Method—Using Ash Remaining After Incineration of Residue from Sulfate Extraction

8.1 *Apparatus:*

8.1.1 *Atomic Absorption Spectrophotometer*, see 7.1.1.

8.1.2 *Balance*, see 6.1.1.

8.1.3 *Crucibles*, porcelain, platinum, alundum, or silica of 10- to 25-mL capacity for incineration of coal residue remaining after sulfate extraction.

8.1.4 *Hot Plate*, see 6.1.3.

8.1.5 *Muffle Furnace*, electrically heated and capable of regulating the temperature at 700 to 750°C for incineration of the coal residue remaining after sulfate extraction.

8.1.6 *Tongs*, platinum tipped or tips covered with rubber policemen.

8.2 *Reagents and Materials:*

8.2.1 *Purity of Reagents*—see 6.2.1.

8.2.2 *Purity of Water*—see 6.2.2.

8.2.3 *Filter Paper*—see 6.2.8.

8.2.4 *Hydrochloric Acid*, 12*N* (sp. gr. 1.19)—see 6.2.9.

8.2.5 *Hydrochloric Acid*, 4.8*N* (2 + 3)—see 6.2.10.

⁸ Wernimont, G. T., "Use of Statistics to Develop and Evaluate Analytical Methods," AOAC, Arlington, VA, 1987.

8.2.6 *Hydrochloric Acid, 0.24N (1 + 49)*—see 7.2.6.

8.2.7 *Iron Standard, (400 ppm)*—see 7.2.7.

8.2.8 *Lanthanum Solution*—see 7.2.8.

8.3 *Procedure:*

8.3.1 *Ashing of Residue from Sulfate Extraction*—Transfer the filter paper and extracted residue from 6.3.1 to a crucible (8.1.3). Place the crucible in a cold muffle furnace and heat gradually at such a rate that the temperature reaches 95°C in 45 min. Hold at this temperature for 90 min (see Note 5). Char the coal without ignition (see Note 6). Once charring is complete, continue heating so that the temperature reaches 700 to 750°C in another hour. Continue incineration for an additional 6 h or until no unburned particles are observed. Remove the crucible from the muffle furnace and allow to cool to room temperature.

NOTE 5—This hold step should prevent spattering of sample onto the sides of the crucible. Material deposited on the sides of the crucible is not dissolved by boiling in HCl.

NOTE 6—Residues from coals of anthracitic and bituminous rank, in the majority of cases, can be charred without ignition by gradually raising the temperature from 300 to 450°C over a period of 2 h. Residues from coals of subbituminous and lignite rank, in the majority of cases, can be charred without ignition by gradually raising the temperature from 200 to 450°C over a period of 4 h. Ignition of the coal residue can result in localized temperatures in the sample, which could result in the production of oxides of iron such as Fe₃O₄, which would not dissolve in the digestion step outlined in 8.3.2.

8.3.2 *Digestion of Ash*—Place the crucible on its side in a 250-mL beaker which contains 100 mL of HCl (2 + 3). Place a stirring bar in the beaker and cover with a watch glass. Transfer the beaker to a hot plate and heat to just below the boiling point; maintain at this temperature for ½ h with gentle stirring. Carefully remove the crucible with a set of tongs. Immerse only tips of the tongs in the solution. Rinse the crucible and tips of the tongs with deionized water, collecting the washings in the beaker. Continue to heat the solution while stirring until it boils moderately (see Note 7) for a period of ½ h or until no reddish particles are visible in the residue.

NOTE 7—If the solution does not reach the boiling point, the hydrochloric acid-soluble iron compounds may not dissolve completely.

8.3.3 *Preparation of Test Solution*—Filter the contents of the beaker through a Type II, Class F filter paper into a 200-mL volumetric flask. Wash the beaker, filter paper, and residue with sufficient small water washings to ensure transfer of all the hydrochloric acid extract to the volumetric flask. Dilute to the mark with deionized water. Transfer a 10-mL aliquot of the diluted filtrate to a 100-mL volumetric flask. Add 10 mL of lanthanum solution (7.2.8, Note 8). Dilute to volume with HCl (1 + 49). This is the test solution.

NOTE 8—Experimental tests have shown that addition of the lanthanum solution to the hydrochloric acid extract from digestion of the ash is not essential to the determination of pyritic iron. However, to permit comparison of results from the referee and alternative method on a common calibration basis, the addition of the lanthanum solution is included.

8.3.4 *Preparation of Blank Test*—Perform a parallel blank test following the same procedure and reagents as described in 8.3.1-8.3.3, using the filter paper generated in 6.3.1 of the sulfate blank test.

8.3.5 *Determination of Iron by Atomic Absorption*—Determine the iron content of the test solution (8.3.3) and blank test (8.3.4) as described in 7.3.4.1-7.3.4.4.

8.4 *Calculation*—Calculate the percent by weight of pyritic sulfur in the sample, according to Eq 2.

9. Organic Sulfur

9.1 When analyses are expressed on a common moisture basis, the percentage of organic sulfur is obtained by subtracting the sum of the percentages of sulfate sulfur and pyritic sulfur from the percentage of total sulfur as determined by Test Methods D 3177 or D 4239.

10. Report

10.1 Report the following information:

- 10.1.1 Date of the test,
- 10.1.2 Identification of sample tested,
- 10.1.3 Basis for expression of results,
- 10.1.4 The method used in the case of pyritic sulfur,
- 10.1.5 The instrumental conditions used for the determination of pyritic iron,
- 10.1.6 A note to the effect that organic sulfur is calculated by difference,
- 10.1.7 Any unusual features noted during the determinations, and
- 10.1.8 Any operation not included in the standard or regarded as optional.

11. Precision and Bias ⁹

11.1 Where applicable, these

⁹ Supporting data are available from ASTM Headquarters. Request RR:D5-1009.

11.1 The precision of this test method for the determination of Forms of Sulfur in Coal are calibrated with solutions that are similar shown in Table 1.⁹

11.1.1 *Repeatability Limit (r)*—The value below which the absolute difference between two test results calculated to a dry basis (Practice D 3180) of separate and consecutive test determinations, carried out on the same sample, in the same laboratory, by the same operator, using the same apparatus on samples taken at random from a single quantity of homogeneous material, may be expected to occur with a probability of approximately 95 %.

11.1.2 *Reproducibility Limit (R)*—The value below which the absolute difference between two test results calculated to a dry basis (Practice D 3180), carried out in different laboratories, using samples taken at random from a single quantity of material that is as homogeneous as possible, may be expected to occur with a probability of approximately 95 %.

11.2 *Precision Statement for Sulfate Sulfur:*

11.2.1 *Repeatability*—Results of consecutive determinations performed on the same sample, in the same laboratory, by the same operator, and using the same apparatus should not differ by more than the following:

$$\text{Sulfate Sulfur } 0.02 \% \text{ by weight} \quad (3)$$

11.2.2 *Reproducibility*—The means of the results of duplicate determinations carried out by different laboratories, on representative samples taken from the same bulk sample after the last stage of reduction should not differ by more than the following:

$$\text{Sulfate Sulfur } 0.04 \% \text{ by weight} \quad (4)$$

11.3 *Precision Statement for Pyritic Sulfur:*

11.3.1 *Referee Method Using Coal Residue Remaining After Sulfate Extraction*—The relative precision of this test method for the estimation of pyritic sulfur covers the concentration range of 0.10 to 12.00 weight % on a dry basis.

11.3.1.1 *Repeatability*—The difference in absolute value between two consecutive test results, calculated to a dry basis (Practice D 3180), performed on two separate test specimens of the same test unit of No. 60 (250- μ m) coal sample in the same laboratory, by the same operator, and using the same apparatus should not exceed the repeatability interval $I(r)$ by more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability interval, there is reason to question one or both of the test results. The repeatability interval is calculated using the following equation:

$$I(r) = 0.09 X + 0.08 \quad (5)$$

where X is the average of the two test results.

NOTE 9—Eq 3 applies to the relative spread of a measurement that is expressed as weight percent on a dry basis and is derived from statistical evaluation of round robin results.

Example—Two separate test specimens yielded test results for pyritic sulfur of 2.6 and 2.8 %. The average of the two test results is 2.7 %. The calculated repeatability interval $I(r)$ of 0.3 %. The difference between the two test results is 0.2 % and does not exceed the $I(r)$ of 0.3 %. Therefore, these two test results are acceptable at the 95 % confidence level.

11.3.1.2 *Reproducibility*—The difference in absolute value between test results, calculated to a dry basis (Practice D 3180), carried out in different laboratories on representative test units of No. 60 (250- μ m) coal sample prepared from the same bulk sample after the last stage of reduction, should not exceed the reproducibility interval $I(R)$ by more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility interval, there is reason to question the test result from one or both of the laboratories. The reproducibility interval is calculated using the following equation:

$$I(R) = 0.27 X + 0.15 \quad (6)$$

where X is the average of the test results from the two separate laboratories.

NOTE 10—Eq 4 applies to the relative spread of a measurement that is expressed as weight percent on a dry basis and is derived from statistical evaluation of round robin results. For the purposes of the reproducibility statement given in this standard, a laboratory test result consists of the average of results conducted on two separate test specimens in the same laboratory, which meet the repeatability requirements stipulated in 11.3.1.1.

Example—Two separate test specimens in one laboratory yielded test results for pyritic sulfur that met the precision requirements for repeatability and gave an average 8.0 % pyritic sulfur as the laboratory test result. A laboratory test result of 10.0 % that met repeatability precision requirements was obtained in another laboratory. The average of the two laboratory test results is 9.0 %. The calculated reproducibility interval $I(R)$ is 2.6 %. The difference between the two test results is 2.0 % and does not exceed the $I(R)$ of 2.6 %. Therefore, these two laboratory test results are acceptable at the 95 % confidence level.

TABLE 1 Concentrations Range and Limits for Repeatability and Reproducibility for Forms of Sulfur in Coal

Sulfur Form	Range, wt %	Repeatability Limit, r	Reproducibility Limit, R
Sulfate Sulfur		0.02 % by weight	0.04 % by weight
Pyritic Sulfur	0.1 to 12		
Referee Method		$0.08 + 0.09 \bar{X}$ ^A	$0.15 + 0.27 \bar{X}$
Alternative Method		$0.06 + 0.11 \bar{X}$	$0.07 + 0.19 \bar{X}$

^AWhere \bar{X} is the average of two single test results.

11.3.2 *Alternative Method—Using Ash Remaining After Incineration of Residue from Sulfate Extraction*—The relative precision of this test method for the determination of pyritic sulfur covers the concentration range of 0.10 to 12.00 weight % on a dry basis.

11.3.2.1 *Repeatability*—The difference in absolute value between two consecutive test results, calculated to a dry basis (Practice D 3180), performed on two separate test specimens of the same test unit of No. 60 (250- μ m) coal sample in the same laboratory, by the same operator, and using the same apparatus, should not exceed the repeatability interval $I(r)$ by more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability interval, there is reason to question one or both of the test results. The repeatability interval is calculated using the following equation:

$$I(r) = 0.11X + 0.06 \quad (7)$$

where X is the average of the two test results.

NOTE 11—Eq 5 applies to the relative spread of a measurement that is expressed as weight percent on a dry basis and is derived from statistical evaluation of round robin results.

Example—Two separate test specimens yielded test results for pyritic sulfur of 4.4 and 4.8 %. The average of the two test results is 4.6 %. The calculated repeatability interval $I(r)$ is 0.6 %. The difference between the two test results is 0.2 % and does not exceed the $I(r)$ of 0.6 %. Therefore, these two test results are acceptable at the 95 % confidence level.

11.3.2.2 *Reproducibility*—The difference in absolute value between test results, calculated to a dry basis (Practice D 3180), performed in different laboratories on representative test units of No. 60 (250- μ m) coal sample prepared from the same bulk sample after the last stage of reduction, should not exceed the reproducibility interval $I(R)$ by more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility interval, there is reason to question one or both of the test results. The reproducibility interval is calculated using the following equation:

$$I(R) = 0.19X + 0.07 \quad (8)$$

where X is the average of the test results from the two separate laboratories.

NOTE 12—Eq 6 applies to the relative spread of a measurement that is expressed as weight percent on a dry basis and is derived from statistical evaluation of round robin results. For the purposes of the reproducibility statement given in this standard, a laboratory test result consists of the average of results conducted on two separate test specimens in the same laboratory, that meet the repeatability requirements stipulated in 11.3.2.1.

Example—Two separate test specimens in one laboratory yielded test results for pyritic sulfur that met the precision requirements for repeatability and gave an average 5.0 % pyritic sulfur as the laboratory test result. A laboratory test result of 7.0 % that met repeatability precision requirements was obtained in another laboratory. The average of the two laboratory test results is 6.0 %. The calculated reproducibility interval $I(R)$ is 1.2 %. The difference between the two test results is 2.0 % and exceeds the $I(R)$ of 1.2 %. Therefore, either one or both of the laboratory test results are suspect at the 95 % confidence level.

11.4 *Bias*⁹

11.4.2.1 *Absolute Bias*—Since no suitable certified reference materials for sulphate or pyritic sulfur are currently available, no statement on absolute bias can be made for this test method.

11.4.2.2 *Relative Bias*—Based on a matched paired comparison at the 95 % confidence level,⁸ the alternative method for the determination of pyritic sulfur was found to be biased high with respect to the referee method, with the minimum detectable bias being 0.06 %.

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