Designation: D3175 − 17

Standard Test Method for
Volatile Matter in the Analysis Sample of Coal and Coke[1]

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 gaseous products, exclusive of moisture vapor, as volatile matter in the analysis sample of coal or coke from coal.

1.2 The test method for the determination of volatile matter is empirical.

1.3 *Units*—The values stated in SI units are to be regarded as standard.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D121 Terminology of Coal and Coke
D346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis
D388 Classification of Coals by Rank
D2013 Practice for Preparing Coal Samples for Analysis
D3173/D3173M Test Method for Moisture in the Analysis Sample of Coal and Coke
D3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases
D5142 Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures (Withdrawn 2010)[3]
D6374 Test Method for Volatile Matter in Green Petroleum Coke Quartz Crucible Procedure
D3173/D3173M Test Method for Moisture in the Analysis Sample of Coal and Coke
D7582 Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions:*

3.1.1 *popping*—unseating of the crucible cover due to swelling of the test sample resulting in mechanical loss of the test material.

3.1.1.1 *Discussion*—This phenomenon is normally associated with strongly swelling coals.

3.1.2 *sparking*—the evolution of gaseous products at a rate sufficient to mechanically carry solid particles out of the crucible. Those particles escaping at higher temperatures become incandescent when they are emitted, creating sparks.

3.1.2.1 *Discussion*—This phenomenon is normally associated with non-swelling coals but can also be associated with swelling coals as well as cokes.

3.1.3 *swelling*—the change in volume which takes place when coal is heated under conditions allowing the softened coal to expand freely in a direction normal to the plane of heating.

3.2 Refer to Terminology D121 for additional definitions of terms used in this test method.

4. Summary of Test Method

4.1 Volatile matter is determined by establishing the mass loss resulting from heating a coal or coke under rigidly controlled conditions. The measured mass loss, corrected for moisture as determined in Test Method D3173/D3173M establishes the volatile matter content. Two procedures are described to permit conformity with differences in sample behavior.

4.2 In this empirical test method, the use of platinum crucibles shall be considered the standard reference method for volatile matter. Platinum crucibles shall be used in determining the volatile matter determined for classification of coals by rank. Volatile matter determinations by some laboratories using alternate nickel-chromium alloy crucibles having the physical

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[1] This test method is under the jurisdiction of ASTM Committee D05 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

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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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

***A Summary of Changes section appears at the end of this standard**

dimensions specified in 6.1 have been shown to differ from those obtained using platinum crucibles. A laboratory utilizing nickel-chromium crucibles shall first determine if a relative bias exists between the use of nickel-chromium and platinum crucibles on the coals being tested using the test method set forth in Annex A1. Where a relative bias is shown to exist, the volatile matter determined using nickel-chromium crucibles shall be corrected by a factor determined through comparison of volatile matter results from both crucible types on coals being tested or analysis of samples of known proximate analysis.

5. Significance and Use

5.1 Volatile matter, when determined as herein described, can be used to establish the rank of coals, to indicate coke yield on carbonization process, to provide the basis for purchasing and selling, or to establish burning characteristics.

6. Apparatus

6.1 *Platinum Crucible,* with closely fitting cover, for coal. The crucible shall be of not less than 10 or more than 20 mL capacity, not less than 25 or more than 35 mm in diameter, and not less than 30 or more than 35 mm in height.

6.2 *Platinum Crucible,* with closely fitting cover, for coke. The crucible shall be of 10 mL capacity, with capsule cover having thin flexible sides fitting down into crucible. Or the double-crucible method can be used, in which the sample is placed in 10 mL platinum crucible, which is then covered with another crucible of such a size that it will fit closely to the sides of the outer crucible and its bottom will rest 8.5 to 12.7 mm (⅓ to ½ in.) above the bottom of the outer crucible.

6.3 *Alternate Crucible Materials,* Nickel-chromium crucible with closely fitting cover. The crucible shall not be less than 10 or more than 20 mL capacity, not less than 25 or more than 35 mm in diameter, and not less than 30 or more than 35 mm in height. Nickel-chromium crucibles shall be heat-treated for 4 h at 500°C to ensure that they are completely oxidized prior to use.

6.3.1 Quartz crucible with closely fitting cover for coke samples. The crucible shall be the same type as specified for use with Test Method D6374.

6.4 *Vertical Electric Tube Furnace,* for coal or coke. The electric furnace shall be a vertical tube furnace. The furnace can be of the form shown in Fig. 1. It shall be regulated to maintain a temperature of 950 ± 20°C in the crucible, as measured by a thermocouple positioned in the furnace. The furnace shall accommodate sparking coals and meet the specifications set forth in 8.3.2.

6.5 *Balance,* sensitive to 0.1 mg.

7. Reagents and Materials

7.1 *Desiccants*—Use freshly regenerated self-indicating desiccants. Suitable materials are listed as follows.

7.1.1 *Anhydrous Calcium Sulfate*

7.1.2 *Silica Gel*

8. Procedure

8.1 The sample shall be the material pulverized to 250 µm (No. 60) sieve in accordance with Practice D2013 or Practice D346.

8.1.1 Carry out a moisture determination in accordance with Test Method D3173/D3173M on a separate portion of the analysis sample preferably on the same day but not more than 24 h apart from the volatile matter determination so that reliable corrections to other bases can be made.

8.2 *Procedure for Nonsparking Coals and Cokes:*

8.2.1 Record the mass of the crucible and cover to the nearest 0.0001 g. For coals place 1 g of the sample in a platinum crucible. For coke samples platinum, nickel-chromium or quartz crucibles are permitted. Close with a cover which fits closely enough so that the carbon deposit from bituminous, subbituminous, and lignite coals does not burn away from the underside. Record the total mass of the crucible, sample and cover to the nearest 0.0001 g. Place the crucible on platinum or nickel-chromium wire supports and insert directly into the furnace chamber, which shall be maintained at a temperature of 950 ± 20°C, and lower immediately to the 950°C zone. Regulation of the temperature to within the prescribed limits is critical. After the more rapid discharge of volatile matter has subsided, as shown by the disappearance of the luminous flame, or in the case of coke, after 2 or 3 min, inspect the crucible (see Note 1) to verify that the lid is still properly sealed. If necessary, reseat the lid to guard against the admission of air into the crucible. Do this as rapidly as possible by raising the crucible to the top of the furnace chamber, reposition the lid to more perfectly seal the crucible, then lower the crucible immediately back to the 950°C zone. After heating for a total of exactly 7 min, remove the crucible from the furnace and without disturbing the cover, allow it to cool. Coke should be cooled in a desiccator. Weigh as soon as cold. The percentage loss of weight minus the percentage moisture equals the volatile matter. With some strongly caking low-volatile and medium-volatile bituminous coals, the coke button can be broken with explosive violence due to the liberation of volatile matter within the button. This is usually designated as popping. Such popping can blow the lid off the crucible and cause mechanical losses of the coked material. When such popping is observed, the determination shall be rejected and the test repeated until popping does not occur.

NOTE 1—Inspection of the crucible can be aided by the use of a mirror held above the furnace well.

8.3 *Modified Procedure for All Sparking Fuels:*

8.3.1 Fuels that do not cake or cake weakly when volatile matter is determined shall be watched closely for sparking during the heating period (see 8.3.3); also, at the end of the test the crucible cover shall be inspected for ash deposits, and the presence of such deposits shall be considered as evidence of sparking.

8.3.2 All fuels that spark when the volatile matter is determined by the methods described in 8.1 shall be treated as follows: The sample shall be given a preliminary gradual heating such that a temperature of 600 ± 50°C is reached in 6 min (8.3.3). After this preliminary heating the sample shall be

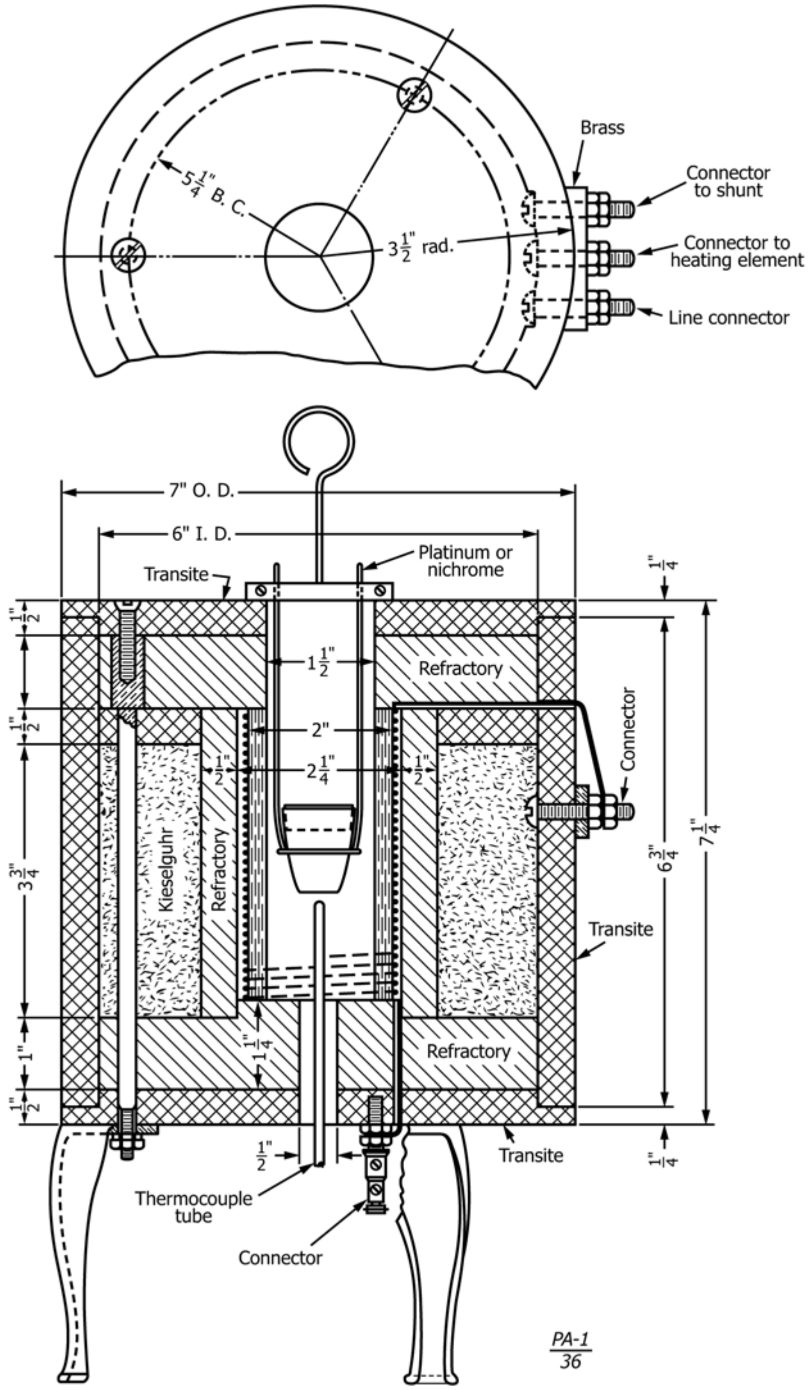

FIG. 1 Electric Furnace for Determining Volatile Matter

heated for exactly 6 min at 950 ± 20°C. If sparking is then observed, the determination shall be rejected and the test repeated until no sparking occurs either during the preliminary heating or during the 6 min period at 950°C. Remove the crucible from the furnace, cool on a metal cooling block, and weigh. To ensure uniformity of results, keep the cooling period constant and do not prolong beyond 15 min. The percentage loss in weight minus the percent moisture in accordance with Test Method D3173/D3173M, is the volatile matter. All analyses by this test method shall be so marked when reported to indicate that the modified procedure was used.

8.3.3 If a tubular furnace of the Fieldner type (Fig. 1) is used for the determination of volatile matter, the preliminary gradual heating can be accomplished by moving the crucible to predetermined positions in the cooler top zone of the furnace. Due to variations in the heating characteristics of the furnace, the operator shall predetermine by thermocouple the proper positions to meet a preliminary heating rate as specified in

8.3.2. A mechanical device to lower the crucible into the furnace can be used to facilitate control of the lowering operation.

9. Calculation

9.1 Calculate the percent mass loss on heating as follows:

$$\text{mass loss }\%, \text{D} = 100 \times [(B - C) / (B - A)] \quad (1)$$

where:

A = mass of crucible and cover, g,
B = mass of crucible and cover and contents before heating, g, and
C = mass of crucible and cover and contents after heating, g.

9.2 Calculate the percent volatile matter in the analysis samples as follows:

$$\text{Volatile matter in analysis sample, } \% = D - E \quad (2)$$

where:

D = mass loss, %, and
E = moisture in analysis sample, %, as determined by Test Methods D3173/D3173M and D7582.

9.3 The calculated volatile matter in the analysis sample is the as-determined volatile matter.

10. Report

10.1 Report the volatile matter in the analysis sample along with the sample moisture from 8.1.1.

10.2 Report the procedure employed for the determination of volatile matter. Report as the D3175 Procedure for Nonsparking Fuels or the D3175 Procedure for Sparking Fuels.

10.3 The volatile matter result can be reported in any of a number of bases differing in the manner in which the moisture is treated. Procedures for converting the test result obtained on an analysis sample to other bases are described in Practice D3180.

10.4 Use Classification D388 for reporting volatile matter on a dry mineral matter free basis.

11. Precision and Bias

11.1 The precision of this test method for the determination of Volatile Matter in Coal are shown in Table 1. Coal Repeatability and Reproducibility limits for this test method were determined using only platinum crucibles. Coal Repeatability and Reproducibility limits for nickel-chromium crucibles have not been determined.

11.1.1 *Repeatability Limit (r)*—The value below which the absolute difference between two test results 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, can 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 carried out in different laboratories, using samples taken at random from a single quantity of material that is as homogeneous as possible, can be expected to occur with a probability of approximately 95 %.

11.2 The precision of this test method for the determination of Volatile Matter in Coke are shown in Table 2. The precision characterized by repeatability (S_r, r) and reproducibility (S_R, R) is described in Table A2.1 in Annex A2.

11.2.1 The inter-laboratory proficiency test data employed to derive the r and R values for cokes include 48 samples covering a period of 11 years. Some of the samples were distributed as many as three separate times. All crucible types were included for the derivation of the precision statement for coke offered in this test method. There are a number of reasons for this. Of the 20 to 22 participants taking part in the proficiency testing program only 10 to 12 reported volatile matter by D3175. The remaining participants employed Test Method D5142 or other standard test methods. Of the 10 to 12 employing D3175, the majority (6 to 7) employed quartz crucibles. The number of labs employing platinum crucibles varied from 2 to 4. The remaining employed nickel or nickel-chromium crucibles. Practice E691 recommends at least 8 laboratories take part in an ILS. The reason for this is that the r and R estimates can exhibit a variance of as much as 25 % for 8 laboratories and that increases to as much as 30 % for 6 laboratories. Thus it was necessary to include all crucible types in the derivation of the precision statement for coke. This has an additional effect of not having to include the same relative bias requirement in an Annex for alternate crucibles as is required for coal.

11.3 *Bias*—Since this is an empirical test method when utilizing platinum crucibles to analyze coal, the degree of absolute bias can not be determined. Bias between the use of platinum and nickel-chromium crucibles shall be determined in the laboratory on coal being tested using the test method set forth in Annex A1.

11.3.1 No information can be presented on the bias of the procedure in this test method for determining the volatile matter in the analysis sample of cokes because this is an

TABLE 1 Limits for Repeatability and Reproducibility of Volatile Matter in Coal

Rank	Repeatability Limit, *r*	Reproducibility Limit, *R*
Anthracite	0.3	0.6
Semianthracite, bituminous,	0.5	1.0
Subbituminous	0.7	1.4
Lignite	1.0	2.0

TABLE 2 Concentration Range and Limits for Repeatability and Reproducibility of Volatile Matter in Coke

	Range	Repeatability Limit, *r*	Reproducibility Limit, *R*
Coke	0.49 to 2.50 %	0.20	$0.27 + 0.27\ \bar{x}$[A]

[A] Where $\bar{x}$ is the average of two single test results.

empirical test method and no material having an accepted reference value is available.

ANNEXES

A1. METHOD FOR DETERMINING RELATIVE BIAS BETWEEN PLATINUM AND NICKEL-CHROMIUM ALLOY CRUCIBLES

A1.1 Scope

A1.1.1 This method describes the procedure for determining the component of relative bias between platinum and alternate nickel-chromium alloy crucibles.

A1.2 Apparatus

A1.2.1 All Apparatus and equipment shall conform to the apparatus and equipment specifications given in the "Apparatus" Section of Test Method D3175 with the additional requirement that temperatures shall be measured with a Type K or N thermocouple with a standard tolerance of ± 2.2 C°.

A1.3 Procedure

A1.3.1 Apply one of the two alternate methods given in the "Procedure" section of ASTM D3175 to a minimum of twenty pairs of the materials being tested, one member of each pair consisting of a one-gram analysis sample in a platinum crucible, and the other member of each pair consisting of a one-gram analysis sample of the same material in a nickel-chromium alloy crucible.

A1.3.2 The following additional limitations apply:

A1.3.2.1 The materials in the study group shall all be of the same groupings listed in Table 1:

1. Anthracite
2. Semianthracite, Bituminous
3. Subbituminous
4. Lignite

A1.3.2.2 The range of volatile matter contents within the study group shall not exceed 10% absolute. If the range of volatile matter routinely analyzed and within the same Table 1 grouping exceeds 10% absolute, analyze multiple groups to accommodate the expected range of volatile matter. Apply the appropriate relative bias to samples within the same volatile matter range. The relative bias shall be applicable only to analyses performed in the laboratory in which it is originally determined.

A1.3.2.3 All values determined in any experiment upon members of the study group shall be used in the statistical analysis (unless there is undeniable evidence that the data to be rejected is technically invalid).

A1.3.2.4 All materials within the study group shall be analyzed the same number of times.

A1.3.2.5 Confirmatory analyses for each study group (redetermination of relative bias) shall be conducted at least once per year to ascertain that normal wear of equipment (crucibles, thermocouples, furnace, etc.) does not result in changes to the conclusions of the experiment. See Table A1.2 as an example.

TABLE A1.1 Factors for Maximum Difference That Could Escape Undetected 5% of the Time[A]

n	γ
10	1.29
11	1.22
12	1.15
13	1.10
14	1.05
15	1.01
16	0.97
17	0.94
18	0.91
19	0.88
20	0.85
21	0.83
22	0.81
23	0.79
24	0.77
25	0.76
26	0.74
27	0.72
28	0.71
29	0.70
30	0.68
31	0.67
32	0.66
33	0.65
34	0.64
35	0.63
36	0.62
37	0.61
38	0.60
39	0.59
40	0.59

[A] Multiply standard deviation of the Differences by γ for Number of Differences

A1.4 Assessment and Uses of Relative Bias Test Results

A1.4.1 Compute the differences between the matched pairs, subtracting the result obtained with the platinum crucible from the result obtained with the nickel-chromium alloy crucible results. Calculate the mean and the standard deviation of the differences. Multiply the standard deviation of the differences by the value of y corresponding to the number of pairs (0.85 for 20 pairs) from Table A1.1. This is the limit of bias at the 95% confidence level that could accidentally pass undetected by reason of statistical error. If this limit exceeds one-half the repeatability limits in Table 1, do not use nickel-chromium alloy crucibles for volatile determinations. If this limit is less than one-half the repeatability limits in Table 1, nickel-chromium alloy crucibles can be used provided the results obtained with nickel-chromium alloy crucibles are corrected by subtracting algebraically the test mean of the differences from nickel-chromium crucible results. Subtracting a negative value algebraically corresponds to adding the absolute value.

TABLE A1.2 Example of Data for a Relative Bias Experiment

Sample ID	VM-NiCr	VM-Pt	NiCr-Pt
1	37.66	37.14	0.52
2	41.98	41.83	0.15
3	39.50	38.89	0.61
4	40.35	39.93	0.42
5	40.35	40.09	0.26
6	39.77	39.30	0.47
7	33.90	33.43	0.47
8	36.18	35.74	0.44
9	33.81	33.65	0.16
10	36.36	36.09	0.27
11	38.19	37.41	0.78
12	41.06	40.68	0.38
13	42.29	41.70	0.59
14	34.73	34.34	0.39
15	42.03	41.87	0.16
16	38.01	37.47	0.54
17	40.55	39.76	0.79
18	37.51	37.15	0.36
19	38.09	37.83	0.26
20	40.78	40.68	0.10
21	41.84	41.84	0.00
22	38.44	38.14	0.30
23	41.69	41.53	0.16
MEAN			0.37
SD			0.21
SD*0.79			0.16
MINIMUM		33.43	
MAXIMUM		41.87	

From Table A1.1, with n = 23, y = 0.79 and from Table A1.2, the standard deviation of the differences (SD) of the 23 sets is 0.21. The limit of bias is the product of these two values, SD * y = 0.21% * 0.79 = 0.16%. The limit of the bias cannot exceed ½ of the repeatability value given in Table A1.1 for the rank of coal being considered. The example category is "Semianthracite, Bituminous" for which the repeatability limit, r, is 0.5% (absolute) and, therefore, for which ½ r = 0.25%. The determined limit of bias for the data set in Table A1.2 is 0.16%, and this value is less than ½ r = (0.25%). This set of data passes the relative bias experiment and nickel-chromium crucibles may be used in testing these types of materials (with volatile matter values in the range from 33.43% thru 41.87%

A1.4.2 Once the relative bias testing is concluded and acceptable results obtained, if the corrected volatile value obtained on any subsequent test specimen falls outside the range of values determined on the samples used in conducting the relative bias test (the range of values being that determined with Pt crucibles), because the value is outside of the method validation range, discard the results and perform the determination with a platinum crucible.

A1.4.3 For client and audit purposes, maintain records of all relative bias studies and volatile matter tests in such a manner that it can be ascertained how the values were corrected.

A2. PRECISION STATISTICS FOR COKE SAMPLES

A2.1 The precision of this test method, characterized by repeatability (S_r, r) and reproducibility (S_R), R) has been determined for the following cokes as listed in Table A2.1.[4]

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[4] Information for coke was calculated per Practice E 691 using 48 sets of data for 24 coke samples from a commercially available inter-laboratory proficiency test program. The cokes used in this study included furnace coke, foundry coke and coke breeze. Details and supporting information are given in Research Report RR:D05-1039.

TABLE A2.1 Repeatability (S_r, r) and Reproducibility (S_R, R) Parameters used for Calculation of Precision Statement for Coke

Material	Average	S_r	S_R	r	R
CK980108 - Furnace	0.95	0.07	0.21	0.20	0.58
CK980312 - Furnace	0.81	0.05	0.22	0.15	0.63
CK980716 - Foundry	0.69	0.08	0.19	0.21	0.52
CKReference2 - Furnace	0.49	0.06	0.15	0.17	0.44
CKNIST01 - Foundry	1.36	0.06	0.27	0.17	0.76
CKNIST02 - Furnace	1.02	0.03	0.15	0.10	0.43
CK0303 - Foundry	1.25	0.07	0.29	0.19	0.81
CK9903 - Foundry	0.97	0.06	0.14	0.17	0.40
CK9904 - Furnace	1.25	0.08	0.30	0.23	0.85
CK0001 - Furnace	1.26	0.07	0.19	0.20	0.53
CK0401 - Furnace	1.30	0.07	0.16	0.20	0.46
CK0002 - Breeze	3.02	0.06	0.22	0.17	0.61
CK0302 - Breeze	3.13	0.05	0.25	0.13	0.72
CK0003 - Foundry	0.69	0.03	0.17	0.09	0.48
CK0101 - Furnace	0.74	0.06	0.16	0.18	0.46
CK0504 - Furnace	0.84	0.04	0.27	0.10	0.76
CK0701 - Furnace	0.80	0.05	0.12	0.14	0.34
CK0102 - Furnace	0.93	0.06	0.15	0.16	0.41
CK0301 - Furnace	0.96	0.09	0.19	0.26	0.53
CK0404 - Furnace	1.01	0.08	0.14	0.22	0.40
CK0103 - Furnace	1.72	0.06	0.56	0.17	1.57
CK0304 - Furnace	1.67	0.08	0.19	0.24	0.53
CK0601 - Furnace	1.75	0.06	0.23	0.17	0.66
CK0903 - Furnace	1.70	0.04	0.14	0.12	0.39
CK0104 - Furnace	0.71	0.06	0.08	0.18	0.22
CK0503 - Furnnace	0.83	0.05	0.20	0.13	0.57
CK0201 - Furnace	0.95	0.06	0.24	0.17	0.67
CK0501 - Furnace	1.07	0.04	0.13	0.11	0.37
CK0802 - Furnace	1.19	0.06	0.21	0.18	0.59
CK0904 - Furnace	1.03	0.06	0.08	0.17	0.22
CK0202 - Furnace	0.80	0.03	0.11	0.08	0.32
CK0502 - Furnace	0.87	0.07	0.18	0.20	0.51
CK0603 - Furnace	1.06	0.05	0.20	0.13	0.56
CK0203 - Furnace	0.71	0.08	0.10	0.23	0.28
CK0403 - Furnace	0.62	0.06	0.16	0.17	0.46
CK0604 - Furnace	0.62	0.04	0.17	0.13	0.48
CK0801 - Furnace	0.66	0.04	0.21	0.10	0.59
CK0204 - Breeze	2.42	0.06	0.29	0.16	0.82
CK0402 - Breeze	2.44	0.09	0.22	0.24	0.63
CK0602 - Breeze	2.54	0.08	0.36	0.24	1.01
CK0704 - Breeze	2.57	0.05	0.44	0.13	1.24
CK0702 - Furnace	1.53	0.06	0.27	0.17	0.76
CK0902 - Furnace	1.54	0.06	0.20	0.16	0.57
CK0703 - Coke	2.04	0.06	0.27	0.17	0.77
CK0803 - Furnace	1.32	0.07	0.19	0.18	0.53
CK0804 - Furnace	1.26	0.05	0.22	0.13	0.62
CK0901 - Coke	0.72	0.03	0.10	0.09	0.27
CK1001 - Furnace	0.85	0.05	0.17	0.15	0.49

A3. INVESTIGATION OF THE VOLATILE MATTER PRECISION FOR COAL SAMPLES

A3.1 An evaluation of the precision of results for the determination of volatile matter in coal from laboratories indicating they are employing Test Method D3175 was conducted on results taken from three independent sources. This evaluation indicates the precision estimates in D3175 can be achieved for all ranks of coal from subbituminous to low volatile bituminous. All precision estimates were derived employing Practice E691 by setting the critical *h* and *k* factors at a 0.005 level of significance as specified in Practice E691. Table A3.1 summarizes the median, maximum and minimum repeatability and reproducibility by rank group investigated in the evaluation. Table A3.2 describes the design scheme for each source of data employed in the investigation. The 1991 ASTM ILS was conducted to evaluate a pellet method for the determination of volatile matter in sparking coal.

TABLE A3.1 Repeatability (r) and Reproducibility (R) by Rank Group

Rank Group	*r* Min	*r* Median	*r* Max	*R* Min	*R* Median	*R* Max
hvAb-lvb	0.08	0.32	0.81	0.28	0.72	1.50
hvCb-hvBb	0.18	0.40	0.74	0.41	0.66	1.69
Sub	0.23	0.66	1.54	0.63	0.97	2.46

TABLE A3.2 Design Scheme by Data Source

Source	Rank Range	Number of Samples	Number of Labs	Number of Days	Number of Results per Day	Crucible Types
LQSi	hvAb-lvb	6	21 to 25	1	2	Pt: Ni-Cr
CANSPEX	sub-lvb	44	30 to 45	2	2	Pt: Ni-Cr : Quartz
ASTM	sub	8	4	2	2	Pt

A3.2 It is evident from Table A3.2 there are dissimilarities in the design scheme for each source. A common design framework was developed for the derivation of precision estimates from each source. The CANSPEX and ASTM data were separated into sub groups for Day 1 and Day 2. In the case of CANSPEX, a group of 7 laboratories known to use the ASTM final soak temperature of 950 °C, a common source of quartz crucibles, a furnace capable of recovering to the final soak temperature of 950 °C within the prescribed limits specified in D3175 and which strictly adhere to the procedures for non-sparking coal as well as sparking coal were extracted from the CANSPEX data set. The LQSi data set was separated into laboratories employing platinum crucibles and those employing nickel-chromium crucibles. This generates the investigation design scheme shown in Table A3.3. Table A3.4 lists the *r* and *R* estimates for each rank group by crucible type.

TABLE A3.3 Investigation Design Scheme

Source	Rank Range	Number of Samples	Number of Labs	Day	Number of Results	Crucible Types
LQSi	hvAb-lvb	6	14 to 19	1	2	Pt
LQSi	hvAb-lvb	6	3 to 6	1	2	Ni-Cr
CANSPEX-1	sub-lvb	44	7	1	2	Quartz
CANSPEX-2	sub-lvb	44	7	2	2	Quartz
ASTM-1	sub	8	4	1	2	Pt
ASTM-2	sub	8	4	2	2	Pt

TABLE A3.4 Repeatability (*r*) Reproducibility (*R*) by Crucible Type

Rank Group	Repeatability *r*			Reproducibility *R*		
	Pt	Ni-Cr	Quartz	Pt	Ni-Cr	Quartz
hvAB-lvb	0.32	0.22	0.34	0.74	0.82	0.65
hvCb-hvBb	NR	NR	0.40	NR	NR	0.66
Sub	0.71	NR	0.55	1.10	NR	0.77

A3.3 Table A3.5 provides a detailed summary of the precision estimate for each sample subjected to Practice E691 analysis. The table lists the precision estimates by data source for all 58 samples. The table also includes sample average reference values. The LQSi reference values are from the LQSi report from which the LQSi data was taken. They are the LQSi E691 estimates of the average value. Differences from the values shown in this report appear to be due to a different choice of the level of significance for the critical *k* and *h* values. The CANSPEX reference values are the median result of all labs excluding the 7 laboratories employed for derivation of the precision estimates. This includes laboratories employing platinum and nickel crucibles as well as single and multiple throat furnace configurations. Inclusion of these results essentially eliminates any possibility of complicity between the 7 CANSPEX laboratories employed in this investigation.

TABLE A3.5 Practice E691 Precision Estimates by Sample^{A}

PTP	Sample	Rank	Crucible	Average	Refernce	Labs Reporting	Labs Retained	Sr	SR	r	R
LQSi	6147	lvb	Pt	20.29	20.29	17	15	0.14	0.18	0.39	0.50
LQSi	6147	lvb	NiCr	20.37	20.34	7	6	0.06	0.30	0.16	0.84
LQSi	6148	mvb	NiCr	24.37	24.37	6	6	0.04	0.52	0.10	1.44
LQSi	6148	mvb	Pt	24.39	24.39	19	18	0.11	0.21	0.32	0.58
LQSi	6143	hvAb	Pt	35.44	35.42	17	16	0.11	0.22	0.29	0.61
LQSi	6143	hvAb	NiCr	35.56	35.56	5	4	0.10	0.53	0.27	1.50
LQSi	6144	hvAb	NiCr	35.19	35.19	5	5	0.22	0.26	0.61	0.72
LQSi	6144	hvAb	Pt	35.60	35.60	18	17	0.11	0.37	0.31	1.04
LQSi	6145	hvAb	Pt	38.06	38.16	18	17	0.12	0.31	0.33	0.87
LQSi	6145	hvAb	NiCr	38.21	38.21	4	4	0.10	0.28	0.28	0.79
LQSi	6146	hvAb	Pt	30.09	30.61	17	15	0.08	0.43	0.22	1.20
LQSi	6146	hvAb	NiCr	30.75	30.94	4	3	0.04	0.27	0.11	0.77
CANSPEX-1	20071	lvb	Quartz	17.30	17.48	7	7	0.12	0.25	0.34	0.71
CANSPEX-2	20071	lvb	Quartz	17.36	17.47	7	7	0.12	0.23	0.32	0.63
CANSPEX-2	20084	lvb	Quartz	19.78	19.98	7	7	0.04	0.13	0.11	0.36
CANSPEX-1	20084	lvb	Quartz	19.94	19.97	7	6	0.03	0.34	0.08	0.95
CANSPEX-2	20092	lvb	Quartz	19.87	20.13	7	7	0.08	0.18	0.24	0.49
CANSPEX-1	20092	lvb	Quartz	19.90	20.04	7	7	0.14	0.20	0.39	0.56
CANSPEX-2	20101	lvb	Quartz	16.42	16.74	7	7	0.09	0.11	0.25	0.31
CANSPEX-1	20101	lvb	Quartz	16.43	16.69	7	7	0.07	0.10	0.20	0.28
CANSPEX-1	20061	mvb	Quartz	23.67	24.20	6	6	0.11	0.25	0.32	0.69
CANSPEX-2	20061	mvb	Quartz	23.76	24.22	6	6	0.18	0.22	0.51	0.61
CANSPEX-1	20112	mvb	Quartz	20.75	20.82	7	6	0.18	0.21	0.50	0.60
CANSPEX-2	20112	mvb	Quartz	20.81	20.84	7	6	0.14	0.16	0.39	0.44
CANSPEX-2	20052	hvAb	Quartz	30.47	30.29	5	5	0.03	0.24	0.09	0.66
CANSPEX-1	20052	hvAb	Quartz	30.48	30.45	5	5	0.08	0.32	0.22	0.89
CANSPEX-1	20063	hvAb	Quartz	34.83	34.89	6	5	0.12	0.18	0.34	0.50
CANSPEX-2	20063	hvAb	Quartz	34.89	34.91	6	5	0.10	0.31	0.28	0.87
CANSPEX-2	20073	hvAb	Quartz	35.98	36.27	7	6	0.20	0.21	0.56	0.59
CANSPEX-1	20073	hvAb	Quartz	36.05	36.27	7	7	0.19	0.40	0.53	1.11
CANSPEX-2	20091	hvAb	Quartz	36.16	36.36	7	7	0.13	0.29	0.38	0.80
CANSPEX-1	20091	hvAb	Quartz	36.30	36.40	7	7	0.29	0.47	0.81	1.31
CANSPEX-2	20093	hvAb	Quartz	37.95	38.27	7	7	0.15	0.19	0.42	0.54
CANSPEX-1	20093	hvAb	Quartz	38.06	38.35	7	7	0.21	0.26	0.58	0.73
CANSPEX-2	20094	hvAb	Quartz	36.28	36.67	7	7	0.11	0.34	0.31	0.96
CANSPEX-1	20094	hvAb	Quartz	36.30	36.55	7	7	0.12	0.26	0.34	0.73
CANSPEX-2	20051	hvBb	Quartz	39.24	39.65	5	5	0.21	0.22	0.57	0.61
CANSPEX-1	20051	hvBb	Quartz	39.38	39.64	5	4	0.10	0.21	0.28	0.59
CANSPEX-1	20054	hvBb	Quartz	40.84	41.09	5	5	0.19	0.42	0.54	1.18
CANSPEX-2	20054	hvBb	Quartz	40.86	41.16	5	5	0.16	0.29	0.44	0.80
CANSPEX-2	20113	hvBb	Quartz	37.67	38.03	7	7	0.11	0.16	0.32	0.45
CANSPEX-1	20113	hvBb	Quartz	37.74	38.20	7	7	0.19	0.24	0.54	0.69
CANSPEX-2	20062	hvCb	Quartz	38.48	38.85	6	6	0.07	0.18	0.21	0.51
CANSPEX-1	20062	hvCb	Quartz	38.57	38.84	6	6	0.15	0.24	0.41	0.66
CANSPEX-2	20064	hvCb	Quartz	35.63	36.03	6	6	0.10	0.25	0.28	0.71
CANSPEX-1	20064	hvCb	Quartz	35.70	36.00	6	6	0.20	0.28	0.56	0.79
CANSPEX-2	20074	hvCb	Quartz	35.20	35.79	7	7	0.15	0.27	0.41	0.77
CANSPEX-1	20074	hvCb	Quartz	35.39	35.85	7	7	0.20	0.34	0.56	0.95
CANSPEX-2	20081	hvCb	Quartz	35.08	35.68	7	6	0.11	0.15	0.32	0.42
CANSPEX-1	20081	hvCb	Quartz	35.09	35.63	7	5	0.09	0.21	0.26	0.59
CANSPEX-2	20082	hvCb	Quartz	39.50	39.68	7	7	0.16	0.21	0.45	0.58
CANSPEX-1	20082	hvCb	Quartz	39.64	39.54	7	6	0.06	0.17	0.18	0.49
CANSPEX-2	20102	hvCb	Quartz	34.66	35.19	7	6	0.14	0.24	0.39	0.67
CANSPEX-1	20102	hvCb	Quartz	34.79	35.28	7	7	0.12	0.61	0.33	1.69
CANSPEX-2	20103	hvCb	Quartz	39.65	39.93	7	7	0.13	0.23	0.37	0.65
CANSPEX-1	20103	hvCb	Quartz	39.69	39.79	7	7	0.07	0.36	0.19	1.00
CANSPEX-1	20104	hvCb	Quartz	36.16	36.04	7	7	0.27	0.22	0.74	0.63
CANSPEX-2	20104	hvCb	Quartz	36.19	36.06	7	6	0.14	0.15	0.40	0.41
CANSPEX-2	20111	hvCb	Quartz	38.65	39.40	7	7	0.17	0.32	0.49	0.90
CANSPEX-1	20111	hvCb	Quartz	38.78	39.36	7	7	0.19	0.28	0.55	0.77
CANSPEX-2	20053	sub	Quartz	31.26	32.53	5	4	0.11	0.24	0.31	0.67
CANSPEX-1	20053	sub	Quartz	31.36	32.57	5	5	0.08	0.52	0.23	1.45
CANSPEX-2	20072	sub	Quartz	43.92	43.99	7	6	0.16	0.32	0.45	0.89
CANSPEX-1	20072	sub	Quartz	43.94	43.91	7	5	0.18	0.35	0.50	0.98
CANSPEX-1	20083	sub	Quartz	44.26	44.85	7	6	0.26	0.27	0.73	0.76
CANSPEX-2	20083	sub	Quartz	44.49	44.88	7	6	0.21	0.27	0.58	0.75
CANSPEX-2	20114	sub	Quartz	45.82	47.06	7	7	0.20	0.22	0.56	0.63
CANSPEX-1	20114	sub	Quartz	45.94	47.01	7	7	0.31	0.28	0.86	0.77
ASTM-1	1	sub	Pt	45.55	NA	4	3	0.23	0.26	0.66	0.74
ASTM-2	1	sub	Pt	45.57	NA	4	4	0.34	0.41	0.94	1.15
ASTM-2	2	sub	Pt	45.24	NA	4	4	0.20	0.52	0.56	1.46
ASTM-1	2	sub	Pt	45.39	NA	4	3	0.21	0.35	0.60	0.97
ASTM-2	3	sub	Pt	44.56	NA	4	2	0.30	0.23	0.85	0.64
ASTM-1	3	sub	Pt	44.66	NA	4	3	0.24	0.31	0.67	0.87

TABLE A3.5 *Continued*

ASTM-1	4	sub	Pt	44.21	NA	4	3	0.24	0.35	0.66	0.97
ASTM-2	4	sub	Pt	44.52	NA	4	3	0.34	0.33	0.94	0.92
ASTM-2	5	sub	Pt	39.63	NA	4	3	0.55	0.78	1.54	2.18
ASTM-1	5	sub	Pt	40.02	NA	4	4	0.23	0.37	0.64	1.05
ASTM-2	6	sub	Pt	40.97	NA	4	4	0.23	0.88	0.65	2.46
ASTM-1	6	sub	Pt	41.08	NA	4	3	0.19	0.49	0.53	1.38
ASTM-2	7	sub	Pt	39.72	NA	4	3	0.29	0.23	0.80	0.64
ASTM-1	7	sub	Pt	39.96	NA	4	4	0.30	0.76	0.84	2.13
ASTM-2	8	sub	Pt	40.84	NA	4	4	0.26	0.75	0.74	2.11
ASTM-1	8	sub	Pt	40.95	NA	4	4	0.51	0.55	1.43	1.55

[A] The LQSi values associated with nickel-chromium crucibles were not corrected for bias using Annex A1 in D3175. The tests were conducted prior to publication of the standard offering the Annex (2007).

APPENDIX

(Nonmandatory Information)

X1. CHRONOLOGY OF CHANGES TO ASTM D05 PROCEDURE FOR VOLATILE MATTER

X1.1 ASTM and in particular the Office of the Editor was of great assistance in providing archival information. The procedure for volatile matter in coal was traced back to ASTM D22-16 published in 1916. In 1927, D22 was incorporated into D271-27. In 1973, D271 was withdrawn. The sampling and analysis procedures for coal and coke in D271 were extracted and published as individual ASTM methods. The procedure for the determination of volatile matter was designated ASTM D3175 in 1973.

X1.2 The changes made to the ASTM D05 procedure for volatile matter have been established by comparing copies of D22-16, D271-27, D271-40, D271-58 and D271-68. Changes identified from these comparisons are further confirmed by technical reports, bulletins, and proceedings of conferences obtained from the U.S. Bureau of Mines (USBM), ASTM, and the digital libraries of several universities. These publications are listed as references (**1-10**).[5]

NOTE X1.1—Fieldner and Selvig are listed as authors for multiple publications. A.C. Fieldner (1881–1966) served as ASTM D05 Chairman for an unprecedented term from 1921 to 1948. W.A. Selvig (1886–1972) served as D05 Secretary during that same time period and as Chairman from 1949 to 1952.

X1.3 Table X1.1 compares the precision statements of D22-16, D271-27, D271-40, D271-58 and D3175 by rank of coal.

X1.4 Changes to the precision of the volatile matter procedure can be summarized as follows.

X1.4.1 From 1916 to 1940 there was no precision statement for anthracite, semianthracite, low-temperature coke, chars, subbituminous coals or peat.

X1.4.2 In 1943, USBM RI 3739 (**8**) proposed changes to the permissible differences.

X1.4.3 D271-58 confirms the changes to precision proposed in (**8**) were accepted by ASTM Committee D05. There is a separate precision statement for anthracite. Semianthracite, low-temperature coke, and chars are attributed a precision identical to that listed for bituminous coal. A separate set of precision values is added for subbituminous coal. Peat is attributed a precision identical to that listed for lignite.

X1.4.4 D3175 confirms the precision values listed in D271-58 were transferred directly to D3175 with the following changes: Low-temperature coke and chars as well as peat were removed.

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[5] The boldface numbers in parentheses refer to a list of references at the end of this standard.

TABLE X1.1

D22–16 (1916)	D271–27 (1927)	D271–40 (1940)	D271–58 (1958)	D3175 (current)	Repeatability *Permissible Difference Same Laboratory*	Reproducibility *Permissible Difference Different Laboratories*
...	...	...	Anthracite	Anthracite	0.3	0.6
Bituminous Coal	Bituminous Coal	Bituminous Coal	Semianthracite, bituminous coal, low temperature coke and chars	Semianthracite, bituminous	0.5	1.0
...	...	...	Subbituminous	Subbituminous	0.7	1.4
Lignite	Lignite	Lignite	Lignite & Peat	Lignite	1.0	2.0

X1.5 The apparatus specifications for heating the sample taken from respective versions of D22-16 and D271 are listed below.

X1.5.1 **D22-16**: "*(c) Vertical Electric Tube Furnace, or a Gas or Electrically Heated Muffle Furnace*—The furnace may be of the form shown in Fig. 5. It is to be regulated to maintain a temperature of 950 (± 20 ºC) in the crucible, as shown by a thermocouple kept in the furnace. A suitable form of furnace is shown in Fig. 5. If the determination of volatile matter is not an essential feature of the specifications under which the coal or coke is bought, a Meker burner may be used."

X1.5.2 **D271-27**: "*(c) Vertical Electric Tube Furnace, or a Gas or Electrically Heated Muffle Furnace, for Coal or Coke*—The furnace may be of the form shown in Fig. 5. It shall be regulated to maintain a temperature of 950 ± 20 C in the crucible, as shown by a thermocouple kept in the furnace. If the determination of volatile matter is not an essential feature of the specifications under which the coal or coke is bought, a Meker burner may be used."

X1.5.3 **D271-40**: "*(c) Vertical Electric Tube Furnace, or a Gas or Electrically Heated Muffle Furnace, for Coal or Coke*—The furnace may be of the form shown in Fig. 5. It shall be regulated to maintain a temperature of 950 ± 20 C in the crucible, as shown by a thermocouple kept in the furnace. If the determination of volatile matter is not an essential feature of the specifications under which the coal or coke is bought, a Meker burner may be used."

X1.5.4 **D271-58**: "*(c) Vertical Electric Tube Furnace, or a Gas or Electrically Heated Muffle Furnace, (Coal or Coke)*—The furnace may be of the form shown in Fig. 5. It shall be regulated to maintain a temperature of 950 ± 20 C in the crucible, as shown by a thermocouple kept in the furnace. If the determination of volatile matter is not an essential feature of the specifications under which the coal or coke is bought, a Meker burner may be used."

X1.5.5 **D271-68**: "*(c) Vertical Electric Tube Furnace, or a Gas or Electrically Heated Muffle Furnace, (Coal or Coke)*—The furnace may be of the form shown in Fig. 3. It shall be regulated to maintain a temperature of 950 ± 20 C in the crucible, as shown by a thermocouple kept in the furnace. If the determination of volatile matter is not an essential feature of the specifications under which the coal or coke is bought, a Meker burner may be used."

X1.6 Comparisons of these apparatus specifications show other devices for heating the sample were allowed for 52 years in addition to the vertical electric tube furnace. The descriptions for D22-16, D271-27, D271-40, D271-58 and D271-68 are essentially identical. The only method of heating not allowed, in cases when volatile matter is an essential feature of specifications for buying coal and coke, is the Meker burner. This indicates the precision for volatile matter had been confirmed for both the electrically heated muffle and the vertical tube furnace but not for the Meker burner.

X1.7 The following is taken from D3175. "6.4 Vertical Electric Tube Furnace, for coal or coke. The electric furnace shall be a vertical tube furnace. The furnace can be of the form shown in Fig. 1. It shall be regulated to maintain a temperature of 950 ± 20°C in the crucible, as measured by a thermocouple positioned in the furnace. The furnace shall accommodate sparking coals and meet the specifications set forth in 7.3.2."

X1.7.1 The allowed apparatus for heating the sample has been altered from D271. The vertical electric tube furnace is now mandatory.

X1.8 An unexplained contradiction arises with respect to the electrically heated muffle. The precision of the various designations for the ASTM volatile matter method for coal applied to both the vertical tube furnace and the electrically heated muffle from 1916 to 1968.

X1.8.1 The precision from D271 was transferred to D3175.

X1.8.2 The vertical tube furnace was transferred. The electrically heated muffle was not. The removal of an apparatus that conformed to the same precision requirements as the vertical electric tube furnace for 52 years appears unjustified.

X1.8.3 The Meker burner has been removed. Removal of the Meker burner as an allowed apparatus would be necessary unless a precision for that heating method is established as per ASTM requirements.

X1.9 Summary of Findings

X1.9.1 The precision values listed in the most current version of D3175 have been traced back to USBM report of investigations RI 3739 (**8**) published in 1943. Since that time there have been no modifications to those values or any ASTM E691 study that has confirmed those values. An examination of the approach employed for establishing the precision up to and including (**8**) coupled with an E691 study of precision of the method should be conducted.

X1.9.2 The electrically heated muffle has been removed from the apparatus specifications of ASTM D3175. This apparatus which was included in the apparatus specifications of all previous versions for the purposes of buying and selling coal conformed to the precision requirements specified in the current version of D3175. The historical evidence suggests that the electrically heated muffle should be reinstated in D3175 as an allowed apparatus pending a systematic examination of the precision and bias of the method.

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(7) Lowry, H.H. and Junge, Charles O. "Statistical Study of the Precision of Methods of Analysis of Coal and Coke." ASTM Proceedings Vol. 42, 1942, 870–888.

(8) Selvig, W.A. "Precision of the Volatile Matter Determination for Anthracite, Low Temperature Coke and Subbituminous Coal." US Bureau of Mines Report of Investigations RI 3739, 1943.

(9) Fieldner, A.C. and Selvig, W.A., "Methods of Analyzing Coal and Coke," US Bureau of Mines Bulletin 492, 1951.

(10) Rees, O.W, F. A. Coolican. and Pierron, E.D., "Comparison of Methods for Determination of Volatile Matter and Ash in Coal." Illinois State Geological Survey Circular 240, 1957.

SUMMARY OF CHANGES

Committee D05 has identified the location of selected changes to this standard since the last issue (D3175–11) that may impact the use of this standard.

(1) Subsections in the Scope, 1, were revised.
(2) Terms added to Terminology, Section 3.
(3) Revision made to subsection 4.2.
(4) Added subsections 6.3.1, 11.2.1, and 11.3.1.
(5) Revisions made to subsections 8.1.1, 8.2.1, and 8.3.3.
(6) Revisions made to 11.3.
(7) Revisions made to Calculation, section 9.
(8) Reagents and Materials section, 7, and Report section, 10 added.
(9) Added References section.
(10) Annex A3 and Appendix X1 added.