National Institute of Standards and Technology

Certificate of Analysis

Standard Reference Material® 2693

Bituminous Coal

(Nominal Mass Fraction 0.5 % Sulfur)

This Standard Reference Material (SRM) is intended primarily for use in the evaluation of techniques employed in the determination of sulfur, mercury, chlorine, and ash content in coal and materials of a similar matrix. A unit of SRM 2693 consists of 50 g of bituminous coal ground to pass a 250 µm (60 mesh) sieve, homogenized, and packaged in an amber glass bottle and then sealed in an aluminized bag.

Certified Mass Fraction Values: Certified values for sulfur, mercury, and chlorine, expressed as mass fractions [1] on a dry-mass basis, are provided in Table 1. The certified values for sulfur and mercury are based on a single NIST primary method while the chlorine value is the average of two independent NIST methods. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or taken into account [2]. A certified value is the present best estimate of the true value.

Reference Mass Fraction Value: The reference value for ash content [3] on a dry-mass basis, is provided in Table 2. A reference value is a non-certified value that is the best estimates of the true value; however, the value does not meet NIST criteria for certification and is provided with an associated uncertainty that may reflect only measurement precision and may not include all sources of uncertainty [2].

Supplemental Information: Summary statistics reported by CANSPEX for SRM 2693 are provided in Appendix A of this certificate to demonstrate user experience with this material using conventional methods and to more fully characterize the matrix. The CANSPEX 2002-4 results were not used in calculating the certified values for sulfur, mercury, and chlorine and should **NOT** be used as substitutes for NIST values.

Expiration of Certification: The certification of **SRM 2693** is valid, within the measurement uncertainties specified, until **31 December 2021,** provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Storage and Use"). This certification is nullified if the SRM is contaminated or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Coordination of the technical measurements leading to certification was performed by W.R. Kelly and R.D. Vocke, Jr. of the NIST Chemical Sciences Division.

Certification analyses for sulfur were performed by W.R. Kelly, J.L. Mann, and R.D. Vocke, Jr. of the NIST Chemical Sciences Division. Certification analyses for mercury were performed by S.E. Long and W.R. Kelly of the NIST Chemical Sciences Division. Certification analyses for chlorine were performed by R.M. Lindstrom, J.L. Mann, R.O. Spatz, and R.D. Vocke, Jr. of the NIST Chemical Sciences Division. Homogeneity analysis was performed by A.F. Marlow, B.R. Norman, and J.R. Sieber of the NIST Chemical Sciences Division. Moisture analyses were performed by J.L. Mann.

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Gaithersburg, MD 20899
Certificate Issue Date: 19 October 2016
Certificate Revision History on Page 4.

Stephen J. Choquette, Director
Office of Reference Materials

Statistical analyses leading to certified and reference values were performed by W.F. Guthrie and D.D. Leber of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

The coal for this SRM was donated by Consol Coal Sales, Inc., Pittsburgh, PA[(1)].

INSTRUCTIONS FOR STORAGE AND USE

Storage: The SRM should be stored in its original tightly sealed bottle away from sunlight and intense sources of radiation.

Use: The unit should be thoroughly mixed by rotating the bottle before sampling. A minimum sample mass of 100 mg should be used for analytical determinations to be related to the sulfur, mercury, and chlorine values provided. The ash content was determined using a nominal sample mass of 1 g.

Drying Instructions: To relate measurements to the certified and reference values that are expressed on a dry-mass basis, users should determine a drying correction at the time of each analysis. The correction is determined by oven drying a separate 1 g sample in a nitrogen atmosphere at 107 °C ± 3 °C to a constant mass [4] or by an equivalent technique. For the purposes of certification, constant mass is operationally defined as the average mass of the first occurring three to five consecutive masses for which the absolute change in mass from one weighing to the next is less than the observed pooled standard deviation of the weighing of at least three gold wires included as controls, or the sample mass when the loss of mass reaches a slope of zero. Constant mass for this SRM was identified at the minimum (modeling the data using a polynomial fit and identifying the point where the first derivative vanishes) because this coal gained mass after initially losing mass during drying (*positive* behavior) [5]. During drying at NIST, the mass loss of SRM 2693 samples was observed to stabilize just before 1 h. The average mass loss measured at NIST for SRM 2693 was 0.75 % (1s = 0.048 %, n = 9).

SOURCE PREPARATION, HOMOGENEITY, AND ANALYSIS

Source and Preparation of Material: Approximately 320 kg of cleaned metallurgical coal was obtained from the Line Creek Mine of the Consol Coal Company in Sparwood, British Columbia, Canada. This multi-seam coal was crushed and air-dried prior to being pulverized and screened at 250 µm (60 mesh). The resulting fraction of clean coal, less than 250 µm, was divided into two portions using the spinning riffler technique. One portion was stored in bulk. The other portion was divided using the spinning-riffler technique into the 50 g units and bottled.

Homogeneity Testing: Homogeneity testing by the NIST Chemical Sciences Division is based on X-ray fluorescence spectrometric analysis of aliquots taken from 25 bottles, selected by stratified random sampling from the SRM 2693 lot. No evidence was found to indicate that the material is inhomogeneous for sulfur or for 20 other elements, with the possible exception of iron.

[(1)] Certain commercial organizations, services, equipment, or materials are identified in this certificate to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by National Institute of Standards and Technology nor does it imply that the organizations, services, materials, or equipment identified are necessarily the best available for the purpose.

VALUE ASSIGNMENT

Certified Mass Fraction Values: The certified values for sulfur, mercury, and chlorine are reported in Table 1 as a mass fractions [1] on a dry-mass basis (see "Instructions for Storage and Use"). The sulfur value is based on measurements by isotope dilution thermal ionization mass spectrometry (ID-TIMS) [6]. The mercury value is based on measurements by isotope dilution cold vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS) [7]. The chlorine value is based on measurements by negative-ion ID-TIMS [8] and Instrumental Neutron Activation Analysis (INAA). The uncertainties in the certified values for sulfur, mercury, and chlorine are expressed as an expanded uncertainty, $U = ku_c$, calculated according to the methods in the ISO/JCGM and NIST Guides [9]. The observed sulfur and mercury variations by isotope dilution methods were greater than expected for the analytical technique used. Therefore a prediction interval was used to account for the sulfur and mercury variability in this material [10]. The chlorine value was obtained by averaging the values and combining the Type A uncertainties of the IDMS and INAA measurements using the BOB method [11]. The quantity u_c represents, at the level of one standard deviation, the combined effects of the uncertainties due to the measurement variability and material inhomogeneity. The quantity k is the coverage factor used to obtain an expanded uncertainty with an approximate confidence level of 95 %. For sulfur, the value of the coverage factor, $k = 2.31$, is determined from the Student's t-distribution with 8.35 degrees of freedom and a confidence level of 95 %. For mercury, the value of the coverage factor, $k = 2.31$, is determined from the Student's t-distribution with 8.14 degrees of freedom and a confidence level of 95 %. For chlorine, the value of the coverage factor, $k = 2.45$, is determined from the Student's t-distribution with 6.8 degrees of freedom and a confidence level of 95 %.

Table 1. Certified Values (Dry-mass Basis) for SRM 2693

Element	Mass Fraction		
Sulfur[(a)]	0.4571 %	±	0.0067 %
Mercury[(b)]	37.3 µg/kg	±	7.7 µg/kg
Chlorine[(c)]	369.6 mg/kg	±	5.7 mg/kg

[(a)] The measurand is the total mass fraction of sulfur and the value listed is metrologically traceable to the SI unit of mass, expressed as a percent on a dry-mass basis.

[(b)] The measurand is the total mass fraction of mercury listed and the value listed is metrologically traceable to the SI unit of mass, expressed as micrograms per kilogram on a dry-mass basis.

[(c)] The measurand is the total mass fraction of chlorine and the value listed is metrologically traceable to the SI unit of mass, expressed as milligrams per kilogram on a dry-mass basis.

Reference Mass Fraction Value: The reference value for ash content (Table 2) is based on data obtained from 43 laboratories using ASTM 3174 method [3] in the CANSPEX 2002-4 Coal Round Robin completed in November 2002 in conjunction with Quality Associates International, Ltd., Douglas, Ontario, Canada. The uncertainty in the reference value for ash content is expressed as an expanded uncertainty, $U = ku_c$, calculated according to the methods in the ISO/JCGM and NIST Guides [9]. A prediction interval was used to account for the potential variability in this material [10]. The quantity u_c represents, at the level of one standard deviation, the combined effects of within-laboratory measurement uncertainty, between-laboratory uncertainty, and material inhomogeneity. The quantity k is the coverage factor used to obtain an expanded uncertainty with an approximate confidence level of 95 %. For ash content, the value of the coverage factor, $k = 1.96$, was obtained from the standard normal distribution and a confidence level of 95 %. The measurand is the mass fraction of the ash content listed as determined by the CANSPeX Round Robin and the value listed is metrologically traceable to the SI unit of mass, expressed as a percent on a dry-mass basis.

Table 2. Reference Value (Dry-mass Basis) for SRM 2693

	Mass Fraction		
Ash Content	9.4 %	±	0.1 %

REFERENCES

[1] Thompson, A.; Taylor, B.N.; *Guide for the Use of the International System of Units (SI)*; NIST Special Publication 811; U.S. Government Printing Office: Washington, DC (2008); available at http://www.nist.gov/pml/pubs/index.cfm/ (accessed Oct 2016).

[2] May, W.E.; Parris, R.M.; Beck II, C.M.; Fassett, J.D.; Greenberg, R.R.; Guenther, F.R.; Kramer, G.W.; Wise, S.A.; Gills, T.E.; Colbert, J.C.; Gettings, R.J.; MacDonald, B.R.; *Definition of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260-136 (2000); available at http://www.nist.gov/srm/publications.cfm (accessed Oct 2016).

[3] ASTM D 3174-93; *Test Method for Ash in the Analysis Sample of Coal and Coke from Coal*; Annu. Book ASTM Stand., Vol. 05.05.

[4] ASTM D 5142-90; *Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures*; Annu. Book ASTM Stand., Vol. 05.05.

[5] Mann, J.L.; Kelly, W.R.; MacDonald, B.S.; *Observations of Anomalous Mass-Loss Behavior in SRM Coals and Cokes on Drying*; Anal. Chem., Vol. 74, p. 3585 (2002).

[6] Kelly, W.R.; Paulsen, P.J.; Murphy, K.E.; Vocke, R.D.; Chen, L.-T.; *Determination of Sulfur in Fossil Fuels by Isotope Dilution Thermal Ionization Mass Spectrometry*; Anal. Chem., Vol. 66, p. 2505 (1994).

[7] Long, S.E.; Kelly, W.R.; *Determination of Mercury in Coal by Isotope Dilution Cold-Vapor Generation, Inductively Coupled Plasma Mass Spectrometry*; Anal. Chem., Vol. 74, p. 1477 (2002).

[8] Howard, M.E.; Vocke, R.D. Jr.; *A Closed System Digestion and Purification Procedure for the Accurate Assay of Chlorine in Fossil Fuels*; J. Anal. At. Spectrom., Vol. 19, p. 1423 (2004).

[9] JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement* (GUM 1995 with Minor Corrections); Joint Committee for Guides in Metrology (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Oct 2016); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at http://www.nist.gov/pml/pubs/tn1297/index.cfm (accessed Oct 2016).

[10] Hahn, G.J.; Meeker, W.Q.; *Statistical Intervals: A Guide for Practitioners*; John Wiley & Sons, Inc.: New York, NY (1991).

[11] Levenson, M.S.; Banks, D.L.; Eberhardt, K.R.; Gill, L.M.; Guthrie, W.F.; Liu, H.-K.; Vangel, M.G.; Yen, J.H.; Zhang, N.F.; *An Approach to Combining Results from Multiple Methods Motivated by the ISO GUM*; J. Res. Natl. Inst. Stand. Technol., Vol. 105, pp. 571–579 (2000).

Certificate Revision History: 19 October 2016 (Extension of certification date; editorial changes) 06 August 2014 (Changed addendum to appendix; changed name to include sulfur concentration; editorial changes); 15 August 2007 (Addition of chlorine certified value and re-title certificate); 20 October 2004 (Original certificate date).

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.

APPENDIX A

CANSPEX 2002-4 Coal Round Robin Results: SRM 2693 was included as an unknown in the November 24, 2002, CANSPEX 2002-4 Coal Round Robin. Summary statistics reported by CANSPEX are provided in the appendix to this certificate to demonstrate user experience with this material using conventional methods and to further characterize the matrix. The CANSPEX 2002-4 Coal Round Robin results should **NOT** be used as substitutes for the NIST values.

Summary of Analysis Reported by CANSPEX

CANSPEX 2002-4 Coal Round Robin: NIST SRM 2693

Parameter	Consensus Value	ASTM Method Referenced for Reproducibility and Repeatability	ASTM Reproducibility Standard Deviation	CANSPEX Reproducibility Standard Deviation	ASTM Repeatability Standard Deviation	CANSPEX Repeatability Standard Deviation	Number of Labs	Number of Methods
Moisture wt %	0.81	ASTM D 3173	0.11	0.11	0.07	0.03	81	15
Ash wt % db	9.42	ASTM D 3174	0.18	0.06	0.11	0.03	81	10
Volatiles wt % db	22.29	ASTM D 3175	0.35	0.63	0.18	0.09	67	12
BTU/lb db	14026	ASTM D 5865	36	43	18	16	79	12
Carbon wt % db	80.51	ASTM D 5373	0.89	0.70	0.23	0.20	40	10
Hydrogen wt % db	4.44	ASTM D 5373	0.11	0.24	0.06	0.03	37	8
Nitrogen wt % db	1.23	ASTM D 5373	0.06	0.06	0.04	0.02	36	8
Sulfur wt % db	0.46	ASTM D 4239c	0.02	0.01	0.01	0.005	81	17
Pyritic Sulfur wt % db	0.021	ASTM D 2492	0.06	0.01	0.03	0.005	14	5
Sulfate Sulfur wt % db	0.009	ASTM D 2492	0.01	0.006	0.007	0.0002	6	4
Chlorine µg/g db	386	ASTM D 4208	102	33	34	7	33	13
Fluorine µg/g db	88	ASTM D 3761	5	16	5	1	14	5
Mercury ng/g db	36	ASTM D 3684	11	15	7	1	16	9
Selenium µg/g db	0.84	ASTM D 4606	0.13	0.55	0.09	0.02	8	5
Free Swelling Index (FSI)	7.5	ASTM D 720	1.0	0.5	0.5	0.5	29	4