National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2684c

Bituminous Coal

(Nominal Mass Fraction 3 % Sulfur)

This Standard Reference Material (SRM) is intended primarily for use in the evaluation of techniques used in the analysis of coals and materials of a similar matrix. A unit of SRM 2684c consists of 50 g of bituminous coal that was ground to pass a 212 µm (70 mesh) sieve, homogenized, packaged in an amber glass bottle under an argon atmosphere, and then sealed in an aluminized bag.

Certified Mass Fraction Values: Certified values for mercury and sulfur, expressed as mass fractions [1] on a dry-mass basis, are provided in Table 1. 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 based on the results of analyses performed at NIST and collaborating laboratories.

Reference Values: Reference values for aluminum, bromine, calcium, chlorine, magnesium, manganese, potassium, sodium, and vanadium, expressed as mass fractions [1] on a dry-mass basis, are provided in Table 2. A reference value is a non-certified value that is the best estimate 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].

Information Values: Information values for particle size fractions are provided in Figure 1. An information value is considered to be a value that will be of interest to the SRM user, but insufficient information is available to assess the uncertainty associated with the value or only a limited number of analyses were performed [1]. Information values cannot be used to establish metrological traceability.

Expiration of Certification: The certification of **SRM 2684c** is valid, within the measurement uncertainty specified, until **30 September 2027**, 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 damaged, 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 of SRM 2684c was provided by T.W. Vetter of the NIST Chemical Sciences Division. Analytical measurements leading to certification were made by B.L. Catron, S.J. Christopher, S.E. Long, A.F. Marlow, J. Ness, R. Oflaz, R.L. Paul, J.R. Sieber, and T.W. Vetter of the NIST Chemical Sciences Division.

Statistical analyses were performed by A.L. Pintar of the NIST Statistical Engineering Division.

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

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Robert L. Watters, Jr., Director
Office of Reference Materials

Gaithersburg, MD 20899
Certificate Issue Date: 22 September 2014

INSTRUCTIONS FOR STORAGE AND USE

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

Use: Before it is sampled, the unit should be thoroughly mixed by carefully inverting and rotating the tightly sealed bottle. A minimum test portion mass of 100 mg for sulfur, 200 mg for aluminum, bromine, chlorine, magnesium, manganese, sodium and vanadium, 250 mg for mercury, and 500 mg for calcium and potassium should be used for analytical determinations.

Drying Instructions: To relate their measurements directly to the certified and reference values that are expressed on a dry-mass basis, users should determine a drying correction at the time of the 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 [3] or equivalent technique. Attainment of constant mass is defined according to the ASTM thermogravimetric (TG) method as either a mass loss of ≤ 0.05 %, relative, over a nine-minute period or the mass loss after one hour of heating [3]. The mass losses determined in both manners, and in both nitrogen and air, were similar. Similar mass losses were determined using a TG method applied to previous coal SRMs [4].

The mass loss determined in both a nitrogen and air atmosphere, which is reported ***for information purposes only***, was nominally 1.3 %. The mass loss determined by the user may be different, depending on ambient conditions when the bottle is sampled.

SOURCE, PREPARATION, HOMOGENEITY, AND ANALYSIS(1)

Source and Preparation of Material: Approximately 600 kg of coal was obtained from the Loveridge Mine of CONSOL Energy (currently owned by Murray Energy and operating under the name Marion County Coal Mine), located in Fairview, WV. This underground mine that is part of the Pittsburgh coal seam, which is in the northern West Virginia coal field, produces bituminous coal with a sulfur mass fraction of about 3 % (dry-mass basis), after washing. The coal was air-dried prior to processing in accordance with procedures in ASTM D3302 [5]. Approximately 560 kg of the coal was reduced in size to 212 µm (70 mesh) and screened prior to blending. The 212 µm (70 mesh) coal was blended by spin riffling in a stainless steel rotary sample divider to ensure negligible heterogeneity. A portion of the bulk material was reserved for use in a future issue of this SRM. The remaining bulk material was divided using the spinning riffler technique into 50 g units and subsequently issued as SRM 2684c.

Heterogeneity Testing: Twenty-three bottles of SRM 2684c were selected for heterogeneity assessment. Duplicate test portions from each bottle were analyzed by wavelength-dispersive X-ray fluorescence spectrometry (WDXRF) for aluminum, calcium, carbon, chlorine, potassium, magnesium, sodium, and sulfur. For bromine, manganese, and vanadium, duplicate test portions from each of seven bottles and a single replicate from an eighth bottle were analyzed by instrumental neutron activation analysis (INAA). For mercury, test portions from each of eight bottles were analyzed by isotope dilution cold vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS).

For the heterogeneity assessment of aluminum, calcium, carbon, chlorine, potassium, magnesium, sodium, and sulfur by WDXRF, statistical hypothesis tests for differences in the bottle means at the 0.05 significance level were conducted. For aluminum (p-value = 0.047) and sulfur (p-value = 0.022), those tests suggest evidence of heterogeneity. In addition, probability distributions quantifying the value of bottle-to-bottle variability for aluminum, calcium, sodium and sulfur suggest evidence of heterogeneity. For the heterogeneity assessment of bromine, manganese and vanadium by INAA, statistical hypothesis tests for differences in the bottle means at the 0.05 level suggest evidence of heterogeneity for vanadium (p-value = 0.028). Further, probability distributions quantifying the value of bottle-to-bottle variability suggest evidence of heterogeneity for bromine and vanadium. For mercury, the lack of duplicate test portions does not allow a heterogeneity assessment.

VALUE ASSIGNMENT

Certified and reference values are expressed with an expanded uncertainty, $U = ku_c$, calculated by estimating a statistical model using the Bayesian inference paradigm [6] in a manner that is consistent with the ISO/JCGM [7] for all elements, except mercury, for which the Monte Carlo Method [8] was used. For chlorine, potassium,

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

magnesium, and manganese, the quantity u_c represents, at the level of one standard deviation, the estimated uncertainty in the mass fraction for the mean of all bottles of SRM 2684c, because the underlying mass fraction is assumed to be the same for each bottle. For aluminum, bromine, calcium, mercury, sodium, sulfur, and vanadium, the quantity u_c represents, at the level of one standard deviation, the estimated uncertainty for the mean of a single randomly chosen bottle of SRM 2684c, which accounts for possible material heterogeneity. The quantity, k, is the coverage factor used to obtain an expanded uncertainty that provides a symmetric approximately 95 % coverage interval.

Certified Mass Fraction Values: The certified values and their corresponding expanded uncertainties and coverage factors are given in Table 1. The measurand is the total mass fraction of mercury and sulfur. Sulfur is metrologically traceable to the SI unit of mass fraction in gram per 100 gram, expressed as a percent in Table 1, on a dry-mass basis. Mercury is metrologically traceable is to the SI unit of mass, as expressed in Table 1, on a dry-mass basis [1].

The certified value and expanded uncertainty for mercury are based on measurements by ID-CV-ICP-MS [9]. The major sources of uncertainty included measurement replication, mass discrimination, dead-time correction, and possible heterogeneity. The coverage factor is $k = 2$.

The certified value and expanded uncertainty for sulfur are calculated by combining two sets of results using the approach in [10], the first from sample decomposition by microwave-induced combustion with measurements by isotope dilution sector field inductively coupled plasma mass spectrometry (ID-SF-ICP-MS), and the second from a CANSPEX interlaboratory study, which is described in the “Supplemental Information” section. For the determination of sulfur by ID-SF-ICP-MS, the major sources of uncertainty were measurement replication and spike calibration. For the CANSPEX interlaboratory study, the sources of uncertainty explicitly accounted for were between-lab and within-lab variability.

Table 1. Certified Mass Fraction Values (Dry-Mass Basis) for SRM 2684c

Element	Mass Fraction
	(mg/kg)
Mercury (Hg)	0.0688 ± 0.0041
	(%)
Sulfur (S)	3.027 ± 0.074

Reference Mass Fraction Values: The reference values and their corresponding expanded uncertainties are given in Table 2. The reference value and expanded uncertainty for chlorine are calculated by combining two sets of results using a mixed linear effects model estimated by the Bayesian inference paradigm [6] in a manner that is consistent with the GUM [7]. The first set of results was from INAA and the second from prompt gamma activation analysis (PGAA). All other reference values and expanded uncertainties are based on measurements using INAA only. Major sources of uncertainty, which varied for each element, included measurement variability, sample mass, and calibration standards. The measurand is the mass fraction of each element as determined by the methods indicated in the text. Metrological traceability is to the SI unit of mass as expressed in Table 2, on a dry-mass basis [1].

Table 2. Reference Mass Fraction Values (Dry-Mass Basis) for SRM 2684c

Element	Mass Fraction (mg/kg)	Coverage factor, k
Aluminum (Al)	8730 ± 210	2
Bromine (Br)	11.1 ± 1.2	2.15
Calcium (Ca)	3220 ± 93	2
Chlorine (Cl)	975 ± 30	2
Potassium (K)	981 ± 68	2.06
Magnesium (Mg)	494 ± 37	2.06
Manganese (Mn)	20.51 ± 0.44	2
Sodium (Na)	606 ± 16	2
Vanadium (V)	16.3 ± 1.1	2.09

Information Values: Particle size measurements were made using a laser-based light scattering system. Approximately 1 g of material (refractive index: 2.42, absorption index: 1.0) was measured using water as the dispersant, (refractive index: 1.33) and 0.1 % Triton X-100 as a pre-wetting surfactant. Calculated 10th percentile ($d_{0.1}$) and 90th percentile ($d_{0.9}$) particle sizes (percent volume of particles smaller than the value) are $d_{0.1}$ = 11 µm and $d_{0.9}$ = 180 µm. The volume weighted mean is 77 µm. The fraction of material smaller than 10 µm in diameter is 9 %. The particle size distribution is shown in Figure 1.

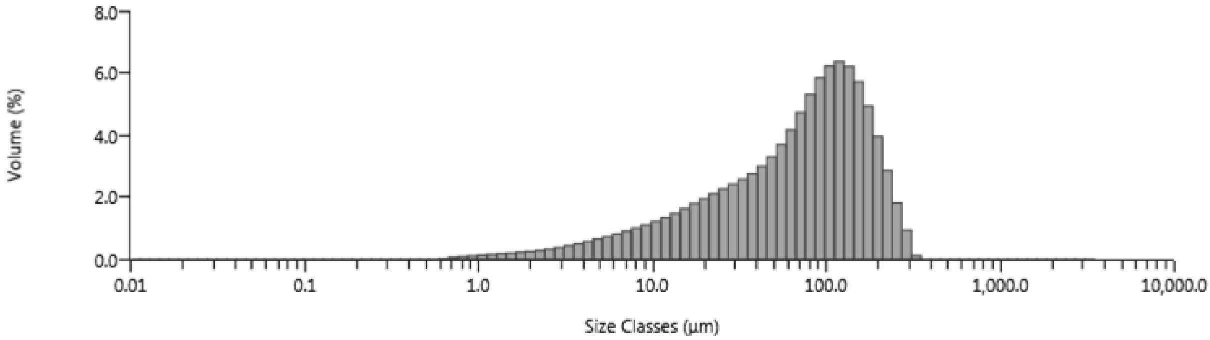

Figure 1. Particle size distribution in SRM 2684c

SUPPLEMENTAL INFORMATION

Summary statistics reported by Quality Associates International, Ltd. (Sechelt, BC, Canada) for the Coal and Ash Sample Proficiency Exchange (CANSPEX) 2012-2 interlaboratory study using SRM 2684c as an unknown coal sample are provided in the Appendix A (Tables A1 and A2) to this certificate to demonstrate user experience with this material using conventional methods and to better characterize the matrix. Although the CANSPEX data and NIST data were used to calculate the sulfur certified value, no other CANSPEX interlaboratory study results were used in value assignments and should **NOT** be used as substitutes for certified or reference values.

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 Sep 2014).

[2] May, W.; Parris, R.; Beck, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G..; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements;* NIST Special Publication 260-136; U.S. Government Printing Office: Washington, DC (2000); available at http://www.nist.gov/srm/publications.cfm (accessed Sep 2014).

[3] ASTM D7582-10 *Standard Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis*; Annu. Book ASTM Stand., Vol 05.06, pp. 812–820 (2012).

[4] 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, pp. 3585–3591 (2002).

[5] ASTM D3302-12 *Standard Test Method for Total Moisture in Coal*; Annu. Book ASTM Stand. Vol. 05.06, pp. 499–506 (2012).

[6] Gelman, A.; Carlin, J.B.; Stern, H.S.; Rubin, D.B.; *Bayesian Data Analysis*; Chapman & Hall (2004).

[7] 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 (JCGM) (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Sep 2014); 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/index.cfm (accessed Sep 2014).

[8] JCGM 101:2008, *Evaluation of Measurement Data — Supplement 1 to the "Guide to the Expression of Uncertainty in Measurement" — Propagation of Distributions Using a Monte Carlo Method*; Joint Committee for Guides in Metrology (JCGM) (2008); available at http://www.bipm.org/en/publications/guides/gum.html (accessed Sep 2014).

[9] 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, pp. 1477–1483 (2002).

[10] Stone, M.; *The Opinion Pool*; Ann. Math. Stat., Vol. 32, pp. 1339–1342 (1961).

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

Test portions of SRM 2684c were analyzed as unknown samples in the inter-laboratory study CANSPEX 2012-2, conducted by Quality Associates International, Ltd. Values are expressed on a dry-mass basis for all parameters except moisture, which is expressed on an "as-received" basis. The tables are included as shown in the summary report by Quality Associates International, Ltd. Table A1 shows the summary results and Table A2 shows the derived standard deviations and a tally of published methods used in the study. The values have not been altered. Tables A1 and A2 were formatted to fit on the page and minor editorial corrections for text and websites were made. These results are included to demonstrate user experience with this material using conventional methods and to better characterize the matrix. Results in this table should **NOT** be used as substitutes for certified or reference values.

Table A1. SRM 2684c CANSPEX Round Robin Results

SRM 2684x CANSPEX™ Round Robin Results					
Parameter	Most Likely Value	95 % Coverage Interval of Most Likely value	Pooled Within Lab Standard Deviation (s_W)	Pooled Between Lab Standard Deviation (s_B)	Total Number of Labs
Moisture (percent)	1.437	0.028	0.047	0.131	128
Ash (percent dry basis)	7.945	0.018	0.049	0.076	125
Volatile (percent dry basis)	39.40	0.16	0.17	0.69	102
Energy (British themal units per pound dry basis)	13851	11	21	48	115
Carbon (percent dry basis)	76.82	0.28	0.21	0.93	65
Hydrogen (percent dry basis)	5.173	0.039	0.037	0.122	61
Nitrogen (percent dry basis)	1.395	0.022	0.020	0.071	61
Total Sulfur (percent dry basis)	3.046	0.026	0.027	0.119	121
Pyritic Sulfur (percent dry basis)	0.881	0.031	0.020	0.053	20
Sulfate Sulfur (percent dry basis)	0.127	0.026	0.005	0.048	21
Chlorine (micrograms per gram dry basis)	916	32	19	95	52
Fluorine (micrograms per gram dry basis)	64	6	4	14	36
Mercury (nanograms per gram dry basis)	67	3	3	7	38
Selenium (micrograms per gram dry basis)	1.08	0.15	0.08	0.20	13
Free Swelling Index (FSI)	8.2	0.2	0.4	0.5	57

Table A2. CANSPEX Supplied Data

Parameter	Total Number of Labs	Derived Standard Deviations (in %) of Repeatability (s_r) and Reproducibility (s_R), and Tally of Published Methods Used in CANSPEX™ Round Robin*																																
		Standards Australia				ASTM International				British Standards Institution				Deutsches Institut für Normung				China National Standards				International Organization for Standardization				Association Francaise de Normalisation				South African Bureau of Standards				In-house**
		AS	s_r	s_R	No.	ASTM	s_r	s_R	No.	BSI	s_r	s_R	No.	DIN	s_r	s_R	No.	GB	s_r	s_R	No.	ISO	s_r	s_R	No.	NF	s_r	s_R	No.	SABS	s_r	s_R	No.	No.
Moisture (percent)	**128**	**1038.3**	0.04	-	1	**D2013**	0.04	0.09	0	**1016**	0.04	-	1	**51718**	0.07	-	2	**212**	0.07	-	1	**589**	0.11	-	1	**3-037**	-	-		**925**	-	-	1	12
						D3173	0.04	0.09	55													**11722**	0.04	-	9									
						D3302	0.04	0.09	13													**5068**	0.07	-	1									
						D5142	0.08	0.10	19																									
						D7582	0.09	0.2801	12																									
Ash (percent, dry basis)	**125**	**1038.3**	0.04	0.05	1	**D3174**	0.08	0.11	63	**1016**	0.05	0.11	1	**51719**	0.07	0.11	2	**212**	0.07	0.11	1	**1171**	0.07	0.11	12	**3-003**	-	-			-	-		10
						D5142	0.08	0.11	22																									
						D7582	0.07	0.11	13																									
Volatile (percent, dry basis)	**102**	**1038.3**	0.07	0.35	1	**D3175**	0.18	0.35	49	**1016**	0.11	0.35	1	**51720**	0.42	0.56	2	**212**	0.18	0.35	1	**562**	0.42	0.56	14									8
						D5142	0.30	0.88	18																									
						D7582	0.13	0.47	8																									
Energy (British thermal unit per pound, dry basis)	**115**	**1038.5**	20	46	1	**D1989**	23	39	4	**1016**	18	43	1	**51900**	18	46	7	**213**	18	46	1	**1928**	43	106	13									5
						D2015	24	38	3																									
						D3286	18	35	1																									
						D5865	24	38	79																									
Carbon (percent, dry basis)	**65**	**1038.6.4**	0.11	0.21	1	**D3178**	0.11	-	0					**51732**	-	-	2	**476**	0.18	0.35	1	**609**	0.09	0.18	2									6
						D5373	0.16	0.35	49													**12902**	-	-	4									
Hydrogen (percent, dry basis)	**61**	**1038.6.4**	0.04	0.07	1	**D3178**	0.02	-	0					**51732**	-	-	2	**476**	0.05	0.09	1	**609**	0.04	0.09	2									3
						D5373	0.04	0.09	48													**12902**	-	-	4									
Nitrogen (percent, dry basis)	**61**	**1038.6.4**	0.01	0.03	1	**D3179**	0.07	0.11	0					**51732**	-	-	2	**476**	0.03	0.05	1	**333**	0.02	0.04	2									5
						D5373	0.02	0.05	47													**12902**	-	-	3									
Total Sulfur (percent, dry basis)	**121**	**1038.6.3.3**	0.01	0.02	1	**D3177**	0.02	0.04	1	**1016**	0.02	0.04	2	**51724-3**	0.01	0.02	2	**214**	0.04	0.09	1	**351**	0.02	0.04	2	**3-038**	-	-	1		-	-		17
						D4239	0.04	0.10	91																									
						D5016	0.09	0.29	3																									
Pyritic Sulfur (percent, dry basis)	**20**	**1038.11**	0.02	0.05	1	**D2492**	0.06	0.14	18									**215**	0.02	0.04	1													
Sulfate Sulfur (percent, dry basis)	**21**	**1038.11**	0.007	0.011	1	**D2492**	0.007	0.014	19									**215**	0.01	0.04	1													
Chlorine (micrograms per gram, dry basis)	**52**		-	-		**D2361**	106	213	3	**1016**	177	177		**51727**	71	106	1	**3558**	35	71	1	**587**	-	-	1	**3-009**	-	-	1		-	-		16
						D4208	59	146	21																									
						D6721	20	25	8																									
Fluorine (micrograms per gram, dry basis)	**36**					**D3761**	5	5	18					**51723**	8	14	2	**4663**	6	7	1	**11724**	4	7	2	**03-009**	-	-						11
						D5987	4	7	2																									
Mercury (nanograms per gram, dry basis)	**38**					**D6414**	7	7	2					**22022**	-	-																		9
						D6722	3	6	27																									
Selenium (micrograms per gram, dry basis)	**13**					**D4606**	0.186	0.15	2	**5.000**																								11
Free Swelling Index (FSI)	**57**	**1038.17**	0.18	0.35	1	**D720**	0.35	0.71	47	**1016**	-	-	1	**51741**	-	-	1	**5448**	0.35	0.53	1	**501**	0.35	0.18	4									2

* The above precision standard deviations are derived from the division of each method's published precision values by an estimate of the coverage factor used.

** Method is designated "In-house" if lab reports method as In-house; lab reports methods as modified; or does not report a method. CANSPEX does not provide repeatability or reproducibility information for In-house methods.

"-" indicates documentation confirming the repeatability or reproducibility is not available.

The above referenced methods are available through the following websites:

AS http://www.standards.org.au (accessed Sep 2014)
ASTM http://www.astm.org/. (accessed Sep 2014)
BSI http://www.bsigroup.com/ (accessed Sep 2014)
DIN http://www.din.de/cmd?level=tpl-home&languageid=en (accessed Sep 2014)
GB http://www.standardsportal.org.cn/zmen/English/Resources/ (accessed Sep 2014)
ISO http://www.iso.org/iso/iso_catalogue.htm (accessed Sep 2014)
NF http://www2.afnor.org/portail.asp?Lang=English (accessed Sep 2014)
SABS https://www.sabs.co.za/ (accessed Sep 2014)