National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2682c

Subbituminous Coal

(Nominal Mass Fraction 0.5 % 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 2682c consists of 50 g of subbituminous coal that was ground to pass a 250 µm (60 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.

Reference Values: The reference values for bromine, chlorine, magnesium, and manganese, 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. 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 [2]. Information values cannot be used to establish metrological traceability.

Expiration of Certification: The certification of **SRM 2682c** is valid, within the measurement uncertainty specified, until **31 January 2037**, 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 2682c was provided by T.W. Vetter of the NIST Chemical Sciences Division.

Analytical measurements leading to certification were made by S.J. Christopher, S.E. Long, A.F. Marlow, J. Ness, R. Oflaz, 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

Gaithersburg, MD 20899
Certificate Issue Date: 17 September 2015

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

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 and 200 mg for bromine, chlorine, magnesium, manganese, and mercury should be used for analytical determinations.

Drying Instructions: To relate 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 16 %. 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 900 kg of coal was obtained from the Amax Coal Company Belle Ayr Mine near Gillette in Campbell County, WY. This mine is an open pit mine that produces subbituminous coal from the Wyodak–Anderson coal seam that is part of the Powder River Basin. The coal was oven dried prior to processing in accordance with procedures outlined in ASTM D 2013 [5]. At least 500 kg of the coal was reduced in size to 250 µm (60 mesh) and screened prior to blending. The coal was blended in a stainless steel cone blender (approximate capacity 0.85 m^3). Additional information on sampling and preparation can be obtained from the NIST Special Publication 260-84 [6].

Portions of the bulk material had been used to make SRM 2682, SRM 2682a, and SRM 2682b. The remaining bulk material was divided using the spinning riffler technique into 50 g units and subsequently issued as SRM 2682c.

Heterogeneity Testing: Twenty bottles of SRM 2682c were selected for heterogeneity assessment. Duplicate test portions from each bottle were analyzed by wavelength-dispersive X-ray fluorescence spectrometry (WDXRF) for chlorine, magnesium, manganese, and sulfur. For bromine and manganese, duplicate test portions from each of ten bottles were analyzed by instrumental neutron activation analysis (INAA). For mercury, duplicate test portions from each of eight bottles were analyzed by isotope dilution cold vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS).

Statistical tests do not detect significant heterogeneity for chlorine, magnesium, or sulfur, as measured by WDXRF, or for bromine, as measured by INAA. However, these tests detected significant heterogeneity for manganese, as measured by INAA, and for mercury, as measured by ID-CV-ICP-MS. In addition, graphical displays of the bromine data show evidence of heterogeneity.

VALUE ASSIGNMENT

Except for magnesium, certified and reference values are expressed with an expanded uncertainty, $U = ku_c$ and are calculated in a manner that is consistent with the ISO/JCGM Guide [7]. Measurement replication is assessed using linear mixed effects statistical models that are estimated using the Bayesian inference paradigm [8]. The Monte Carlo method [9] is used to propagate all of the components of uncertainty. For chlorine and sulfur, 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 2682c, because the underlying mass fraction is assumed to be the same for each bottle. For magnesium, u_c represents, at the level of one median absolute deviation from the median, the estimated uncertainty in the mass fraction for the mean of all bottles of SRM 2682c, because the underlying mass fraction is assumed to be the same for each bottle. The median absolute deviation is used in place of the standard deviation for magnesium, because the standard deviation of the distribution of values obtained by Monte Carlo uncertainty propagation is not defined. For

[(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.

bromine, manganese, and mercury, 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 2682c, 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.

Metrological Traceability: The measurands in Table 1 are the total mass fraction for the elements. The measurands in Table 2 are the total mass fraction for the elements as determined by the method listed below. Metrological traceability is to the SI derived units for mass fraction, expressed as milligrams per kilogram for all the elements except sulfur, for which it is expressed as a percentage [1].

Certified Mass Fraction Values: The certified values and the corresponding expanded uncertainty are given in Table 1. The certified value and expanded uncertainty for mercury are based on measurements by ID-CV-ICP-MS [10]. Major sources of uncertainty included measurement replication, instrument background 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 [11], 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 inter-laboratory 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 mass discrimination/bias. For the CANSPEX inter-laboratory 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 2682c

Element	Mass Fraction (mg/kg)
Mercury (Hg)	0.1051 ± 0.0093
	Mass Fraction (%)
Sulfur (S)	0.4906 ± 0.0083

Reference Mass Fraction Values: The reference values and the corresponding expanded uncertainty are given in Table 2. The reference values and expanded uncertainties are based on measurements by INAA. Major sources of uncertainty, which varied for each element, included measurement replication, calibration standards, counting geometry, and possible heterogeneity. The coverage factor is $k = 2$, except that $k = 2.39$ for Mg.

Table 2. Reference Mass Fraction Values (Dry-Mass Basis) for SRM 2682c

Element	Mass Fraction (mg/kg)
Bromine (Br)	3.64 ± 1.14
Chlorine (Cl)	20.1 ± 3.9
Magnesium (Mg)	1575 ± 289
Manganese (Mn)	25.4 ± 1.6

Information Values: Particle size measurements were made using a laser-based light scattering system. Approximately 0.5 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 $d_{0.1}$ = 4 µm and $d_{0.9}$ = 55 µm. The volume weighted mean is 14 µm. The fraction of material smaller than 10 µm in diameter is 36 %. The particle size distribution is shown in Figure 1.

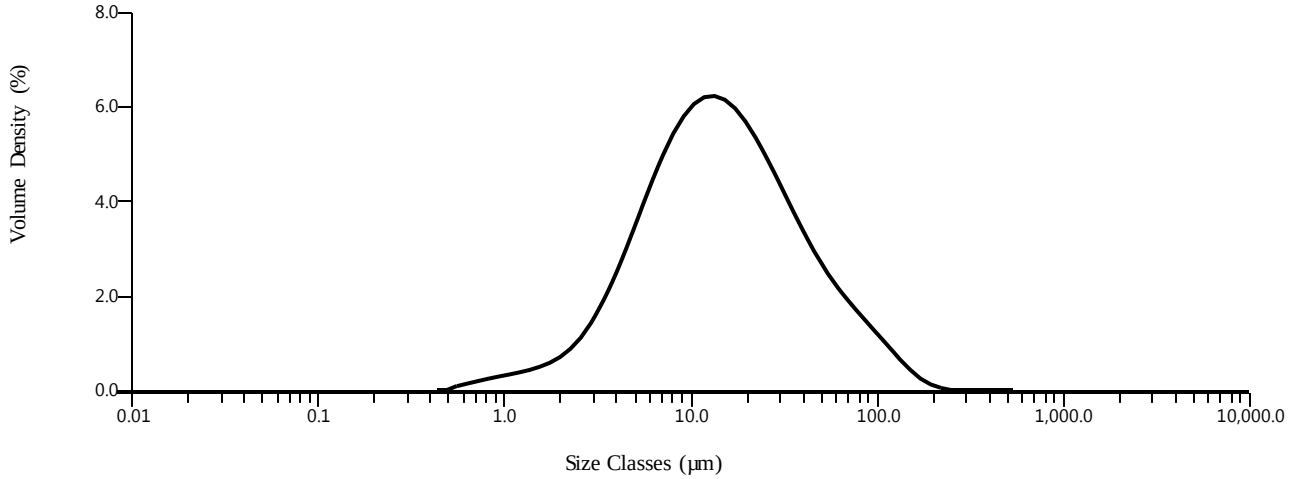

Figure 1. Particle size distributions in SRM 2682c

SUPPLEMENTAL INFORMATION

Summary statistics reported by Quality Associates International, Ltd. (Sechelt, BC, Canada) for the Coal and Ash Sample Proficiency Exchange (CANSPEX) 2011-4 inter-laboratory study using SRM 2682c as an unknown coal sample are provided in the Appendix (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 inter-laboratory 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 2015).

[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 2015).

[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 D2013/D2013M-122; *Standard Practice for Preparing Coal Samples for Analysis*; Annu. Book ASTM Stand. Vol. 05.06, pp. 442–449 (2014).

[6] Gills, T. E.; Seward, R. W.; Collins, R. J.; Webster, W. C.; *Standard Reference Materials: Sampling, Materials Handling, Processing, and Packaging of NBS Sulfur in Coal Standard Reference Materials 682, 2683, 2684, and 2685*; NIST Special Publication 260-84; U.S. Government Printing Office: Washington, DC (1983); available at http://www.nist.gov/srm/upload/SP260-84.PDF (accessed Sep 2015).

[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 2015); 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 2015).

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

[9] 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 2015).

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[11] 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

Test portions of SRM 2682c were analyzed as unknown samples in the inter-laboratory study CANSPEX 2011-4, 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 completed. 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 2682c CANSPEX Round Robin Results

SRM 2682x 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 (%)	15.133	0.131	0.088	0.611	119
Ash (% dry basis)	6.188	0.044	0.064	0.194	115
Volatile (% dry basis)	46.71	0.35	0.26	1.44	94
Btu/lb (dry basis)	10959	12	21	51	105
Carbon (% dry basis)	66.39	0.27	0.22	0.86	61
Hydrogen (% dry basis)	4.298	0.073	0.051	0.219	57
Nitrogen (% dry basis)	0.981	0.022	0.023	0.067	59
Total Sulfur (% dry basis)	0.488	0.006	0.010	0.025	112
Pyritic Sulfur (% dry basis)	0.016	0.005	0.003	0.007	17
Sulfate Sulfur (% dry basis)	0.068	0.020	0.006	0.034	18
Chlorine (µg/g dry basis)	59	15	4	41	42
Fluorine (µg/g dry basis)	50	6	3	13	32
Mercury (ng/g dry basis)	109	6	4	15	38
Selenium (µg/g dry basis)	0.78	0.15	0.09	0.20	13
Free Swelling Index (FSI)	Non Agglomerating				

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 (%)	119	1038.3	0.04	-	1	D2013	0.09	0.19	1	1016	0.04	-	1	51718	0.07	-	2	212	0.07	-	1	589	0.11	-	1	3-037	-	-		925	-	-	2	9
						D3173	0.09	0.19	53													11722	0.04	-	6									
						D3302	0.09	0.19	11													5068	0.07	-	1									
						D5142	0.14	0.27	20																									
						D7582	0.09	0.2801	10																									
Ash (% dry basis)	115	1038.3	0.04	0.05	1	D3174	0.08	0.11	60	1016	0.05	0.11	1	51719	0.07	0.11	2	212	0.07	0.11	1	1171	0.07	0.11	10	3-003	-	-			-	-		6
						D5142	0.07	0.10	24																									
						D7582	0.07	0.11	10																									
Volatile (% dry basis)	94	1038.3	0.07	0.35	1	D3175	0.18	0.35	46	1016	0.11	0.35	1	51720	0.50	0.66	2	212	0.18	0.35	1	562	0.50	0.66	11									6
						D5142	0.33	1.00	19																									
						D7582	0.13	0.47	7																									
Btu/lb (dry basis)	105	1038.5	20	46	1	D1989	23	39	4	1016	18	43	1	51900	18	46	6	213	18	46	1	1928	43	106	10									3
						D2015	24	38	3																									
						D3286	18	35	1																									
						D5865	24	38	75																									
Carbon (% dry basis)	61	1038.6.4	0.11	0.21	1	D3178	0.11	-						51732	-	-	2	476	0.18	0.35	1	609	0.09	0.18	2									5
						D5373	0.16	0.35	48													12902	-	-	2									
Hydrogen (% dry basis)	57	1038.6.4	0.04	0.07	1	D3178	0.02	-	1					51732	-	-	2	476	0.05	0.09	1	609	0.04	0.09	2									3
						D5373	0.04	0.09	45													12902	-	-	2									
Nitrogen (% dry basis)	59	1038.6.4	0.01	0.03	1	D3179	0.02	0.05	1					51732	-	-	2	476	0.03	0.05	1	333	0.02	0.04	2									6
						D5373	0.02	0.05	44													12902	-	-	2									
Total Sulfur (% dry basis)	112	1038.6.3.3	0.01	0.02	1	D3177	0.02	0.04	3	1016	0.02	0.04	1	51724-3	0.01	0.02	2	214	0.04	0.09	1	351	0.02	0.04	2	3-038	-	-			-	-		12
						D4239	0.01	0.02	87																									
						D5016	0.03	0.11	3																									
Pyritic Sulfur (% dry basis)	17	1038.11	0.02	0.05	1	D2492	0.03	0.05	15									215	0.02	0.04	1													
Sulfate Sulfur (% dry basis)	18	1038.11	0.007	0.011	1	D2492	0.007	0.014	16									215	0.01	0.04	1													
Chlorine (µg/g dry basis)	42		-	-		D2361	106	213	1	1016	177	177		51727	71	106	1	3558	35	71	1	587	-	-		3-009	-	-			-	-		12
						D4208	20	76	20																									
						D6721	2	4	7																									
Fluorine (µg/g dry basis)	32					D3761	5	5	14					51723	7	14	1	4663	6	7		11724	4	7	2	03-009	-	-						12
						D5987	4	7	3																									
Mercury (ng/g dry basis)	38					D6414	9	11	4					22022	-	-																		9
						D6722	3	8	25																									
Selenium (µg/g dry basis)	13					D4606	0.166	0.12	2	5.000																								11

* 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 2015)
ASTM http://www.astm.org/. (accessed Sep 2015)
BSI http://www.bsigroup.com/ (accessed Sep 2015)
DIN http://www.din.de/cmd?level=tpl-home&languageid=en (accessed Sep 2015)
GB http://www.standardsportal.org.cn/zmen/English/Resources/ (accessed Sep 2015)
ISO http://www.iso.org/iso/iso_catalogue.htm (accessed Sep 2015)
NF http://www2.afnor.org/portail.asp?Lang=English (accessed Sep 2015)
SABS https://www.sabs.co.za/ (accessed Sep 2015)