National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2685c

Bituminous Coal

(Nominal Mass Fraction 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 2685c consists of 50 g of bituminous coal ground to pass a 250 µm (60 mesh) sieve, homogenized, and packaged in an amber glass bottle under an argon atmosphere, and sealed in an aluminized bag.

Certified Mass Fraction Values: The certified values for sulfur and mercury, 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].

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].

Expiration of Certification: The certification of **SRM 2685c** is valid, within the measurement uncertainty specified, until **31 January 2021**, provided the SRM is handled 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) will facilitate notification.

Coordination of the technical measurements leading to certification of SRM 2685c was provided by T.W. Vetter of the NIST Chemical Sciences Division. Analytical measurements leading to certification were made by S.J. Christopher, W.C. Davis, S.E. Long, J.L. Mann, A.F. Marlow, 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
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Gaithersburg, MD 20899
Certificate Issue Date: 22 October 2013
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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, mercury, magnesium, and manganese 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].

Mass loss determined during three different time periods (January, May, and August), which is reported ***for information purposes only***, was found to vary from 1.94 % to 2.43 %, depending on ambient relative humidity. 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 McElroy mine and coal preparation plant of Consol Energy, located in Glen Easton, WV. This underground mine that is part of the Pittsburgh, No. 8 coal seam, which is in the northern West Virginia coal field, produces bituminous coal with a sulfur mass fraction of about 4.5 % (dry-mass basis) after washing. The coal was oven dried prior to processing in accordance with procedures outlined in ASTM D2013 [5]. At least 500 kg of the coal was reduced in size to 250 µm (60 mesh) and screened prior to blending. The 250 µm (60 mesh) 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 reference 6.

Portions of the bulk material had been used to make SRM 2685, SRM 2685a, and SRM 2685b. The remaining bulk material was divided using the spinning riffler technique into 50 g units and subsequently issued as SRM 2685c.

Homogeneity Testing: Twenty-four bottles of SRM 2685c were selected for homogeneity assessment. Duplicate test portions from each bottle were analyzed by wavelength-dispersive X-ray fluorescence spectrometry for carbon, chlorine, magnesium, and sulfur. 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). For bromine and manganese, duplicate test portions from each of 11 bottles were analyzed by instrumental neutron activation analysis (INAA). For all elements, statistical hypothesis tests for differences in the bottle means fail to reject the hypothesis of no differences at the 0.05 significance level, which is consistent with material homogeneity; however, the results for mercury (p-value = 0.052) are considered to be only weakly consistent with homogeneity.

VALUE ASSIGNMENT

Certified and reference values are expressed with an expanded uncertainty, $U = ku_c$, calculated using Bayesian methods [7] in a manner that is consistent with the ISO/JCGM [8]. The quantity u_c represents, at the level of one standard deviation, the estimated uncertainty in the average mass fraction over all bottles of SRM 2685c, with the exception of mercury. For mercury, u_c represents, at the level of one standard deviation, the estimated uncertainty in a single bottle. The quantity, k, is the coverage factor used to obtain an expanded uncertainty that provides an approximately 95 % coverage interval.

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(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.

Certified Mass Fraction Values: The certified values and their corresponding expanded uncertainties and coverage factors are given in Table 1. The certified value and expanded uncertainty for mercury are based on measurements by ID-CV-ICP-MS [9]. Major sources of uncertainty included mass discrimination, dead-time correction, background, and possible heterogeneity. Because the ANOVA results for Hg are considered to be only weakly consistent with homogeneity, possible heterogeneity is accounted for in the uncertainty by using a coverage interval for the expected value for a single bottle of SRM 2685c. The effective 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 reference 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 source of uncertainty was measurement variability. For the CANSPEX interlaboratory study, the sources of uncertainty explicitly accounted for were between-lab and within-lab variability. The effective coverage factor is $k = 2.17$. The expanded uncertainty in the sulfur certified value represents a symmetric, approximately 95 % coverage interval for the mean of all bottles of SRM 2685c.

Table 1. Certified Mass Fraction Values[(a)] (Dry-Mass Basis) for SRM 2685c

Element	Mass Fraction[(a)] (µg/kg)
Mercury (Hg)	149.4 ± 4.5
	Mass Fraction[(b)] (%)
Sulfur (S)	4.72 ± 0.10

[(a)] Traceability: The measurand is the total mass fraction of the constituent listed and the values listed are metrologically traceable to the SI unit of mass fraction in microgram analyte per kilogram sample on a dry-mass basis.
[(b)] Traceability: The measurand is the total mass fraction of the constituent listed and the values listed are metrologically traceable to the SI unit of mass fraction in percent analyte per kilogram sample on a dry-mass basis.

Reference Mass Fraction Values: The reference values and their corresponding expanded uncertainties are given in Table 2. All reference values and expanded uncertainties are based on measurements using INAA. Major sources of uncertainty, which varied for each element, included measurement variability, calibration standards, and irradiation and counting geometry. The expanded uncertainty in each reference value represents a symmetric, approximately 95 % coverage interval for the mean of all bottles of SRM 2685c. The effective coverage factor is $k = 2$.

Table 2. Reference Mass Fraction Values (Dry-Mass Basis) for SRM 2685c

Element	Mass Fraction[(a)] (mg/kg)
Bromine (Br)	4.94 ± 0.40
Chlorine (Cl)	554.0 ± 8.5
Magnesium (Mg)	814 ± 76
Manganese (Mn)	36.84 ± 0.75

[(a)] Traceability: The measurand is the total mass fraction of the constituent listed based on measurements using INAA and the values listed are metrologically traceable to the SI unit of mass fraction in milligram analyte per kilogram sample on a dry-mass basis.

SUPPLEMENTAL INFORMATION

Summary statistics reported by Quality Associates International, Ltd. (Sechelt, BC, Canada) for the Coal and Ash Sample Proficiency Exchange (CANSPEX) 2011-3 interlaboratory study using SRM 2685c 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, all other CANSPEX interlaboratory study results were not 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 Oct 2013).

[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 Oct 2013).

[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 D2013M-12 *Standard Practice for Preparing Coal Samples for Analysis*; Annu. Book ASTM Stand. Vol. 05.06, pp. 414–425 (2012).

[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/publications.cfm (accessed Oct 2013).

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

[8] 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 Oct 2013); 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 Oct 2013).

[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).

Certificate Revision History: 22 October 2013 (Corrected mass fraction unit in the traceability statement for Table 1, Footnote (a); editorial changes); 28 August 2013 (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.

Test portions of SRM 2685c were analyzed as unknown samples in the interlaboratory study CANSPEX 2011–3, 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 2685c 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 %	2.223	0.026	0.049	0.136	125
Ash % dry basis	15.950	0.023	0.056	0.113	122
Volatile % dry basis	37.61	0.16	0.16	0.79	101
Btu/lb dry basis	11558	13	18	67	112
Carbon % dry basis	64.68	0.18	0.16	0.68	63
Hydrogen % dry basis	4.506	0.034	0.045	0.116	58
Nitrogen % dry basis	1.081	0.016	0.019	0.057	61
Total Sulfur % dry basis	4.738	0.036	0.043	0.183	113
Pyritic Sulfur % dry basis	1.139	0.066	0.027	0.126	19
Sulfate Sulfur % dry basis	1.067	0.032	0.019	0.059	18
Chlorine µg/g dry basis	487	24	19	85	56
Fluorine µg/g dry basis	96	9	6	27	34
Mercury ng/g dry basis	146	3	5	5	38
Selenium µg/g dry basis	1.49	0.39	0.18	0.66	14
Free Swelling Index (FSI)	4.4	0.2	0.4	0.7	54

Table A2. CANSPEX Supplied Data

Table A2. Derived Standard Deviations (in %) of Repeatability (s_r) and Reproducibility (s_R), and Tally of Published Methods Used in CANSPEX^{TM} Round Robin*

Parameter	Total Number of Labs	Standards Australia (AS)				ASTM International				British Standards Institution (BSI)				Deutsches Institut für Normung (DIN)				China National Standards (GB)				International Organization for Standardization (ISO)				Association Francaise de Normalisation (NF)				South African Bureau of Standards (SABS)				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 %	125	**1038.3**	0.04	-	1	D2013	0.04	0.10	1	1016	0.04	-	1	51718	0.07	-	1	212	0.07	-	1	589	0.11	-	1	3-037	-	-		925	-	-	1	10
						D3173	0.04	0.10	54													11722	0.04	-	9									
						D3302	0.04	0.10	13													5068	0.07	-	1									
						D5142	0.08	0.11	22																									
						D7582	0.09	0.28	9																									
Ash % dry basis	122	**1038.3**	0.04	0.05	1	D3174	0.08	0.11	62	1016	0.05	0.11	1	51719	0.07	0.11	1	212	0.07	0.11	1	1171	0.07	0.11	13	3-003	-	-			-	-		8
						D5142	0.14	0.18	26																									
						D7582	0.07	0.11	9																									
Volatile % dry basis	101	**1038.3**	0.07	0.35	1	D3175	0.18	0.35	47	1016	0.11	0.35	1	51720	0.40	0.53	1	212	0.18	0.35	1	562	0.40	0.53	14									8
						D5142	0.29	0.85	22																									
						D7582	0.13	0.47	6																									
Btu/lb dry basis	112	**1038.5**	20	46	1	D1989	23	39	3	1016	18	43	1	51900	18	46	5	213	18	46	1	1928	43	106	13									5
						D2015	24	38	3																									
						D3286	18	35	1																									
						D5865	24	38	79																									
Carbon % dry basis	63	**1038.6.4**	0.11	0.21	1	D3178	0.11	-	1					51732	-	-	1	476	0.18	0.35	1	609	0.09	0.18	2									5
						D5373	0.16	0.35	50													12902	-	-	2									
Hydrogen % dry basis	58	**1038.6.4**	0.04	0.07	1	D3178	0.02	-	1					51732	-	-	1	476	0.05	0.09	1	609	0.04	0.09	2									3
						D5373	0.04	0.09	46													12902	-	-	3									
Nitrogen % dry basis	61	**1038.6.4**	0.01	0.03	1	D3179	0.03	0.06	1					51732	-	-	1	476	0.03	0.05	1	333	0.02	0.04	2									6
						D5373	0.02	0.05	46													12902	-	-	3									
Total Sulfur % dry basis	113	**1038.6.3.3**	0.01	0.02	1	D3177	0.02	0.04	4	1016	0.02	0.04	1	51724-3	0.01	0.02	1	214	0.04	0.09	1	351	0.02	0.04	3	3-038	-	-	1		-	-		11
						D4239	0.06	0.16	87																									
						D5016	0.12	0.41	3																									
Pyritic Sulfur % dry basis	19	**1038.11**	0.02	0.05	1	D2492	0.06	0.16	17									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	56		-	-		D2361	106	213	2	1016	177	177		51727	71	106	2	3558	35	71	1	587	-	-	1	3-009	-	-	1		-	-		18
						D4208	40	111	23																									
						D6721	11	14	8																									
Fluorine µg/g dry basis	34					D3761	5	5	16					51723	8	14	2	4663	6	7	1	11724	4	7	2	03-009	-	-						10
						D5987	4	7	3																									
Mercury ng/g dry basis	38					D6414	10	14	5					22022	-	-																		8
						D6722	3	9	25																									
Selenium µg/g dry basis	9					D4606	0.216	0.19		5.000																								9
FSI	54	**1038.17**	0.18	0.35	1	D720	0.35	0.71	45	1016	-	-	1	51741	-	-		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 Oct 2013)
ASTM http://www.astm.org/. (accessed Oct 2013)
BSI http://www.bsigroup.com/ (accessed Oct 2013)
DIN http://www.din.de/cmd?level=tpl-home&languageid=en (accessed Oct 2013)
GB http://www.standardsportal.org.cn/zmen/English/Resources/ (accessed Oct 2013)
ISO http://www.iso.org/iso/iso_catalogue.htm (accessed Oct 2013)
NF http://www2.afnor.org/portail.asp?Lang=English (accessed Oct 2013)
SABS https://www.sabs.co.za/ (accessed Oct 2013)