National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2683c

Bituminous Coal
(Nominal Mass Fraction 2 % Sulfur)

This Standard Reference Material (SRM) is intended primarily for use in the evaluation of techniques employed in the determination of sulfur, mercury, and chlorine in coal and materials of a similar matrix. A unit of SRM 2683c consists of 50 g of bituminous coal ground to pass a 250 µm (60 mesh) sieve, homogenized, packaged in an amber glass bottle under an argon atmosphere, and sealed in an aluminized bag.

Certified Mass Fraction Values: The certified values for mercury and sulfur, expressed as mass fractions [1] on a dry-mass basis, are provided in Table 1. The certified values are based on or directly traceable to a single NIST primary method. 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 Mass Fraction Value: The reference value for chlorine, expressed as a mass fraction [1] on a dry-mass basis, is 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 2683c** is valid, within the measurement uncertainty specified, until **01 August 2021**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Handling, 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.

Technical measurements leading to certification were coordinated by T.W. Vetter of the NIST Chemical Sciences Division. Analytical measurements leading to certification were made by W.R. Kelly, S.E. Long, E.A. Mackey, J.L. Mann, A.F. Marlow, T.L. Quinn, J.R. Sieber, and R.D. Vocke of the NIST Chemical Sciences Division and by CONSOL Energy Inc. (Pittsburgh, PA).

Statistical analyses were performed by W.F. Guthrie and S.D. Leigh of the NIST Statistical Engineering Division.

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

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Gaithersburg, MD 20899
Certificate Issue Date: 10 September 2019
Certificate Revision History on Page 4

Steven J. Choquette, Director
Office of Reference Materials

INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

Sampling: Before it is sampled, the unit should be thoroughly mixed by carefully inverting and rotating the tightly sealed bottle. A minimum test portion of 250 mg should be used for analytical determinations to be related to the certified values for sulfur and mercury provided and a 750 mg minimum should be used to be related to the reference value for chlorine. The SRM should be stored in its original bottle, tightly sealed and away from sunlight and intense sources of radiation.

Drying Instructions: To relate their measurements directly to the certified and reference values, which 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 separate 1 g test portions in a nitrogen atmosphere at 107 °C ± 3 °C to a constant mass [3] or an equivalent technique. The dry-mass basis was determined at NIST using a thermogravimetric method [4]. During drying at NIST, the mass loss of SRM 2683c samples (n = 8) stabilized after approximately 75 minutes in nitrogen and approximately 60 minutes in air. The average mass loss measured was 3.30 % ± 0.052 % in nitrogen and 3.31 % ± 0.022 % in air. The uncertainty in the mass loss value is expressed as an expanded uncertainty, $U = ku_c$, calculated according to the methods in the ISO/JCGM Guide [5], with coverage factor, k = 2.31 (approximately 95 % level of confidence).

SOURCE, PREPARATION, AND HOMOGENEITY ASSESSMENT[(1)]

Preparation: SRM 2683c is a 50/50 blend of Illinois State Geological Survey IBC-112 coal (Herrin, Il No. 6 coal) and Electric Fuels Corporation SPC-B coal (a blend of coal from various seams found in Harlan County, KY). Each coal was crushed to a nominal 4.76 mm (8 mesh) particle size and subsequently pulverized until the entire lot passed a 250 μm sieve (60 mesh). Next, the two coals were combined and mixed into a single lot. The entire lot was then divided by the spinning riffle technique into two portions. One portion was divided further by the spinning riffle technique into units of SRM 2683b (the previous issue of this material) and bottled under an argon atmosphere. The other portion was stored in bulk under an argon atmosphere and, at a later date, was divided further by the spinning riffle technique into units of SRM 2683c and bottled under an argon atmosphere.

Homogeneity Testing: Twenty-four bottles of SRM 2683c were selected for homogeneity assessment. Duplicate test portions from each bottle were analyzed by X-ray fluorescence spectrometry for sulfur and chlorine. Measured gross count rates were used to assess homogeneity. For both elements, one-way analyses of variance conform with the null hypothesis of no bottle effect, which is indicative of material homogeneity (sulfur P-value = 0.465, chlorine P-value = 0.171).

VALUE ASSIGNMENT

Measurements were performed to determine uniformity between SRM 2683c and SRM 2683b, which are from the same original bulk material (see “Preparation”). No significant differences were found as discussed below.

Certified Mass Fraction Values: Each certified mass fraction value is expressed with an expanded uncertainty, $U = ku_c$, calculated according to the method in the ISO/JCGM Guide [5]. The quantity u_c represents, at the level of one standard deviation, the combined effects of uncertainty due to components associated with material and measurement variability. The quantity, k, is the coverage factor used to obtain an expanded uncertainty with an approximately 95 % level of confidence.

The mercury mass fraction value of SRM 2683c was measured by isotope dilution cold-vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS) [6] and no statistically significant difference from the certified value determined for SRM 2683b was found. The certified mercury value and uncertainty for SRM 2683b (also determined by ID-CV-ICP-MS) have been assigned to SRM 2683c. The coverage factor, k = 2.424, is determined from the Student’s t-distribution for 6.24 degrees of freedom and 95 % confidence.

For the certified mass fraction value of sulfur, SRM 2683c and SRM 2683b were compared directly by combustion with infrared detection and by X-ray fluorescence spectrometry. Considering that both materials originate from the same lot of bituminous coal, and that no statistically significant difference was found between them using these methods, the sulfur value for SRM 2683b has been assigned to SRM 2683c. The certified sulfur value for SRM 2683b was based on measurements by isotope dilution thermal ionization mass spectrometry (ID-TIMS) [7]. The expanded uncertainty, U = 0.044 % (95 % confidence, coverage factor k = 2), associated with the value assigned

[(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.

to SRM 2683c, is larger than the corresponding uncertainty listed for SRM 2683b: this reflects the extra comparison that was made for value assignment to SRM 2683c. The measurands are mercury and sulfur as listed in Table 1. Sulfur is metrologically traceable to the SI derived units for mass fraction in grams per 100 grams, expressed as percent. Mercury is metrologically traceable to the SI derived units for mass fraction in micrograms per kilogram.

Table 1. Certified Mass Fraction Values (Dry-Mass Basis) for Mercury and Sulfur in SRM 2683c

Element	Mass Fraction
	(µg/kg)
Mercury (Hg)	90.0 ± 3.6
	(%)
Sulfur (S)	1.955 ± 0.044

Reference Mass Fraction Value: The reference mass fraction value for chlorine is based on measurements by prompt gamma-ray activation analysis (PGAA) of SRM 2683c. The uncertainty in the reference value for chlorine is expressed as an expanded uncertainty, $U = ku_c$, calculated according to the method in the ISO/JCGM Guide [5], with coverage factor, $k = 2$. The measurand is chlorine as listed in Table 2. Metrological traceability is to the SI derived units for mass fraction (expressed as milligrams per kilogram); as determined by the methods used.

Table 2. Reference Mass Fraction Value (Dry-Mass Basis) for Chlorine in SRM 2683c

Element	Mass Fraction
	(mg/kg)
Chlorine (Cl)	1127 ± 20

SUPPLEMENTAL INFORMATION

Summary statistics reported by Quality Associates International, Ltd. (Sechelt, BC Canada) for the Coal and Ash Sample Proficiency Exchange (CANSPEX) 2010-4 round robin using SRM 2683c 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. The CANSPEX round robin results were not used in calculating the assigned values for sulfur, mercury, and chlorine and should **NOT** be used as substitutes for NIST 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 https://www.nist.gov/pml/special-publication-811 (accessed Sep 2019).

[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 https://www.nist.gov/sites/default/files/documents/srm/SP260-136.PDF (accessed Sep 2019).

[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 (2010).

[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] 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 https://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Sep 2019); 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 https://www.nist.gov/pml/nist-technical-note-1297 (accessed Sep 2019).

[6] 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).

[7] 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, pp. 2505–2513 (1994).

Certificate Revision History: 10 September 2019 (Change of expiration date; editorial changes); **19 December 2016** (Change of expiration date; editorial changes); **22 May 2012** (Revision of uncertainty for sulfur; editorial changes); **20 April 2011** (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 https://www.nist.gov/srm.

APPENDIX A

Test portions of SRM 2683c were analyzed as unknown samples in the round robin study CANSPEX 2010-4, conducted by Quality Associates International, Ltd. Summary results shown in Tables A1 and A2 were provided by Quality Associates International, Ltd. These results are included to demonstrate user experience with this material using conventional methods and to better characterize the matrix. Results from this study should NOT be used as substitutes for the NIST values.

Table A1. SRM 2683c CANSPEX Round Robin Results

Parameter	Most Likely Value[a]	Unit	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	3.185	%	0.057	0.057	0.270	124
Ash	9.870	%	0.017	0.050	0.062	122
Volatile	35.84	%	0.18	0.18	0.77	100
Btu	13 003	per lb	11	20	44	111
Carbon	73.38	%	0.22	0.26	0.72	62
Hydrogen	4.886	%	0.040	0.042	0.120	58
Nitrogen	1.635	%	0.018	0.022	0.054	58
Total Sulfur	1.954	%	0.016	0.018	0.073	119
Pyritic Sulfur	0.541	%	0.033	0.011	0.062	21
Sulfate Sulfur	0.199	%	0.014	0.006	0.024	21
Chlorine	1053	µg/g	37	36	102	48
Fluorine	82	µg/g	8.2	4.2	18.3	30
Mercury	89	ng/g	3	5	7	37
Selenium	1.92	µg/g	0.34	0.12	0.49	14
FSI[b]	2.2		0.2	0.4	0.3	55

[a] Values are expressed on a dry-mass basis for all parameters except moisture. The moisture value is expressed on an "as received" basis.
[b] Free Swelling Index

Parameter	Total Number of Labs	Table A2. Derived Standard Deviations (in %) of Repeatability (s_r) and Reproducibility (s_R), and Tally of Published Methods Used in CANSPEX Round Robin[a]																																
		Standards Australia (AS)				ASTM International				British Standards Institution (BSI)				Deutsches Institut für Normung (DIN)				China National Standards (GB)				International Organization for Standardization				Association Francaise de Normalisation (NF)				South African Bureau of Standards (SABS)				In-House[b]
		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 (%)	124	1038.3	0.04	-[c]	1	D2013	0.04	0.10	1	1016	0.04	-	1	51718	0.07	-	2	212	0.07	-	1	589	0.11	-	1	3-037	-	-	1	925	-	-	1	9
						D3173	0.04	0.10	55													11722	0.04	-	7									
						D3302	0.04	0.10	13													5068	0.07	-	1									
						D5142	0.08	0.12	27																									
						D7582	0.09	0.2801	3																									
Ash (%)	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	2	212	0.07	0.11	1	1171	0.07	0.11	11	3-003	-	-	1		-	-		8
						D5142	0.09	0.13	32																									
						D7582	0.07	0.11	3																									
Volatile (%)	100	1038.3	0.07	0.35	1	D3175	0.18	0.35	47	1016	0.11	0.35	1	51720	0.38	0.51	2	212	0.18	0.35	1	562	0.38	0.51	12									7
						D5142	0.28	0.82	27																									
						D7582	0.13	0.47	2																									
Btu (per lb)	111	1038.5	20	46	1	D1989	23	39	4	1016	18	43	1	51900	18	46	5	213	18	46	1	1928	43	106	13									4
						D2015	24	38	3																									
						D3286	18	35	2																									
						D5865	24	38	77																									
Carbon (%)	62	1038.6.4	0.11	0.21	1	D3178	0.11	-	0					51732	-	-	1	476	0.18	0.35	1	609	0.09	0.18	2									5
						D5373	0.16	0.35	49													12902	-	-	3									
Hydrogen (%)	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 (%)	58	1038.6.4	0.01	0.03	1	D3179	0.09	0.15	1					51732	-	-	1	476	0.03	0.05	1	333	0.02	0.04	2									4
						D5373	0.02	0.05	45													12902	-	-	3									
Total Sulfur (%)	119	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	1	3-038	-	-	1		-	-		15
						D4239	0.03	0.07	92																									
						D5016	0.06	0.21	2																									
Pyritic Sulfur (%)	21	1038.11	0.02	0.05	1	D2492	0.05	0.10	19									215	0.02	0.04	1													0
Sulfate Sulfur (%)	21	1038.11	0.007	0.011	1	D2492	0.007	0.014	19									215	0.01	0.04	1													0
Chlorine (µg/g)	48		-	-		D2361	106	213	2	1016	177	177	0	51727	71	106	2	3558	35	71	1					3-009	-	-	0		-	-		16
						D4208	66	157	20																									
						D6721	23	28	7																									
Fluorine (µg/g)	30					D3761	5	5	14					51723	8	14	1	4663	6	7	1	11724	4	7	3	03-009	-	-	1					7
						D5987	4	7	3																									
Mercury (ng/g)	37					D6414	8	9	5					22022	-	-	0																	9
						D6722	3	7	23																									
Selenium (µg/g)	14					D4606	0.246	0.24	4																									10
FSI	55	1038.17	0.18	0.35	1	D720	0.35	0.71	45	1016	-	-	1	51741	-	-	1	5448	0.35	0.53	1	501	0.35	0.18	4									2

[a]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. Values are expressed on a dry-mass basis for all parameters except moisture. The moisture value is expressed on an "as received" basis.

[b]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.

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

The above referenced methods are available through the following websites:

AS https://www.standards.org.au/ (accessed Sep 2019)
ASTM https://www.astm.org/ (accessed Sep 2019)
BSI https://www.bsigroup.com/ (accessed Sep 2019)
DIN https://www.din.de/en (accessed Sep 2019)
GB http://www.standardsportal.org.cn/zmen/English/Resources/ (accessed Sep 2019)
ISO https://www.iso.org/standards-catalogue/browse-by-ics.html(accessed Sep 2019)
NF https://www.afnor.org/en/ (accessed Sep 2019)
SABS https://www.sabs.co.za/ (accessed Sep 2019)