National Institute of Standards and Technology

Certificate of Analysis

Standard Reference Material® 2692c

Bituminous Coal

(Nominal Mass Fraction 1 % 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 2692c consists of 50 g of bituminous coal ground to pass a 250 µm (60 mesh) sieve, homogenized, and packaged in an amber glass bottle.

Certified Mass Fraction Values: 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]. A certified value is the present best estimate of the true value. The certified value for sulfur is based on weighted least squares regression analysis [3] while the certified value for mercury is based on the unweighted mean of the analytical measurements. The uncertainty listed with each value is an expanded uncertainty based on a 95 % confidence interval and is calculated according to the method in the ISO/JCGM Guide [4,5]. Both certified values are based on a single NIST primary method.

Reference Mass Fraction Values: The reference values for chlorine and ash content [6,7] expressed as mass fractions [1] on a dry-mass basis, are provided in Table 2. The reference value for chlorine is based on data obtained using one NIST technique. The reference value for ash content is based on data provided by the CANSPEX Program in collaboration with NIST. Reference values are non-certified values that are the present best estimates of the true values; however, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision and may not include all sources of uncertainty [2]. The uncertainty listed with each value is an expanded uncertainty based on a 95 % confidence interval and is calculated according to the method in the ISO/JCGM Guide [4,5].

Supplemental Information: CANSPEX 2009-2 summary data and statistics are provided in the appendix to this certificate for selected elements, expressed as mass fractions on a dry-mass basis. These values are considered to be of interest to the SRM user, but insufficient information is available to assess the uncertainties associated with the values [2] and is provided for information purposes only. The CANSPEX 2009-2 results were not used in calculating the values for sulfur, mercury, and chlorine and should NOT be used as substitutes for NIST values.

Expiration of Certification: The certification of **SRM 2692c** is valid, within the measurement uncertainty specified, until **30 September 2019**, provided the SRM is handled and stored in accordance with instructions given in this certificate (see "Instructions for Storage and Use"). The 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 the certification of this SRM was under the direction of J.L. Mann formerly of the NIST Analytical Chemistry Division.

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Stephen J. Choquette, Director
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Gaithersburg, MD 20899
Certificate Issue Date: 04 November 2016
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Analyses for value assignment were performed by R. Bindel, L. Francini, W.R. Kelly, S.E. Long, E.A. Mackey J.L. Mann, and R.D. Vocke, Jr. of NIST. Homogeneity testing of the bulk material by X-ray fluorescence was performed by J.R. Sieber and R.L. Temple, Jr. of NIST. Additional analyses were performed as part of an interlaboratory study in conjunction with the Quality Assurance Insurance CANSPEX Program run by Quality Associates International, Ltd. (Douglas, ON, Canada) in June 2009 (CANSPEX 2009-2)[(1)].

Statistical consultation was provided by W.F. Guthrie of the NIST Statistical Engineering Division.

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

INSTRUCTIONS FOR STORAGE AND USE

Sampling: The unit should be thoroughly mixed by rotating the bottle end-over-end before sampling. To relate measurements of the sulfur, mercury, and chlorine content to values provided in this certificate, a minimum sample mass of 100 mg, 250 mg, and 750 mg are recommended for analytical determinations, respectively. The ash content value was determined using a nominal sample mass of 1 g. The SRM should be stored in its original tightly sealed bottle away from sunlight and intense sources of radiation.

Drying: In order 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 [6] or use of an equivalent technique. The dry mass basis was determined at NIST using a thermogravimetric method described elsewhere [7]. 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. During drying at NIST, it was determined that this material exhibited positive behavior, in which there is a gain in mass after initially losing mass [7] when drying in air and nitrogen. This positive behavior permits a unique end point to be defined as the minimum of the curve or point of equilibrium. For the purposes of certification, the mass loss curve was modeled using a third-order polynomial and the minimum was taken as the point where the first derivative vanished. Although this minimum does not correspond to the true water content and is likely an overlap of several processes (moisture loss, volatilization, oxidation), the minimum may be the closest/best estimate of the true moisture value that can be determined using the thermogravimetric technique. The mass loss of SRM 2692c samples was observed to stabilize after approximately 50 minutes. The average mass loss measured for SRM 2692c was 0.66 % (1 s = 0.064 %, U = 0.018 %, n = 8).

SOURCED, PREPARATION, HOMOGENEITY, AND ANALYSIS[(1)]

Source and Preparation of Material: The coal for SRM 2692c was provided by Alpha Coal Sales Company, LLC, Pittsburgh, PA. Approximately 550 kg of a washed low-volatile coal from the Upper Freeport seam of Cambria County, PA was collected and shipped to the U.S. Geological Survey (USGS) in Denver, CO. The coal was subsequently air-dried, pulverized to pass a 250 µm (60 mesh) screen, blended in a cross-flow V-blender, and divided using the spinning riffler technique. Bulk material weighing approximately 150 kg was divided using a spinning riffler into amber glass bottles. All material was then shipped to NIST in Gaithersburg, MD, where bottles were back filled with argon and then sealed in Mylar bags.

Homogeneity Testing: Homogeneity testing was based on X-ray fluorescence analysis of aliquots taken from 24 bottles selected by stratified random sampling from the SRM 2692c lot. The within-bottle and between-bottle measurement data for sulfur, mercury, and chorine are not significantly different at the 95 % level of confidence.

VALUE ASSIGNMENT

The certified value for sulfur is based on measurements by isotope dilution thermal ionization mass spectrometry (ID-TIMS) [8]. The certified value for mercury is based on measurements by isotope dilution cold vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS) [9]. The reference value for chlorine is

[(1)]Certain commercial entities, equipment, instruments, or materials are identified in this report to specify adequately 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.

based on measurements by prompt-gamma activation analysis (PGAA) [10]. The reference value for ash content is based on data obtained as a part of the Quality Assurance Insurance CANSPEX 2009-2 Interlaboratory Exercise with participation of 117 laboratories employing five different methods of analysis including ASTM D5142 [6], ASTM D3174 [11], ISO 1171 [12], DIN 51719 [13], and in-house methods.

Metrological Traceability: The measurands in Table 1 are the total mass fractions for mercury and sulfur. The measurands in Table 2 are the mass fractions for chlorine and ash content as determined by the method listed in this certificate. Metrological traceability is to the SI derived units for mass fraction, expressed as micrograms per gram for mercury and chorine; sulfur and ash are expressed as a percentage [1].

Certified Mass Fraction Values: The uncertainty listed with each value is an expanded uncertainty, *U*, about the mean, with coverage factor *k*, calculated according to the method described in the ISO/JCGM Guide [4,5]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined effects of inherent sources of uncertainty. For sulfur, the value of the coverage factor, $k = 2.19$, is determined from the Student's *t*-distribution with 11.28 effective degrees of freedom. For mercury, the value of the coverage factor, $k = 2.10$, is determined from the Student's *t* distribution with 18 effective degrees of freedom. The values of the coverage factors correspond to a level of confidence of approximately 95 %.

The certified value, expressed as a mass fraction on a dry-mass basis, for mercury is the mean of measurements obtained using ID-CV-ICP-MS. The certified value, expressed as a mass fraction on a dry-mass basis, for sulfur is the value derived from the slope of the weighted least squares regression of the results obtained using ID-TIMS [3].

Table 1. Certified Mass Fraction Values (Dry-Mass Basis) for SRM 2692c

Constituent	Mass Fraction (µg/g)		
Mercury (Hg)	0.1790 µg/g	±	0.0069 µg/g
	Mass Fraction (%)		
Sulfur (S)	1.064 %	±	0.013 %

Reference Mass Fraction Values: The uncertainty listed with each value is an expanded uncertainty, *U*, about the mean, with coverage factor k, calculated according to the method described in the ISO/JCGM Guide [4,5]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined effects of inherent sources of uncertainty. For chlorine, the value of the coverage factor, $k = 2.00$, is determined from the Student's *t*-distribution with 60 effective degrees of freedom. For ash content, the value of the coverage factor, $k = 2.78$, is determined from the Student's *t* distribution with 4 effective degrees of freedom. The values of the coverage factors correspond to a level of confidence of approximately 95 %.

The reference concentration value, expressed as a mass fraction on a dry-mass basis, for Cl is the mean of measurements obtained using PGAA. The reference concentration value, expressed as a mass fraction on a dry-mass basis, for ash content is the mean of the method means [14].

Table 2. Reference Mass Fraction Values (Dry-Mass Basis) for SRM 2692c

Constituent	Mass Fraction (µg/g)		
Chlorine (Cl)	1338 µg/g	±	22 µg/g
	Mass Fraction (%)		
Ash Content	7.499 %	±	0.024 %

REFERENCES

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Certificate Revision History: 04 November 2016 (Title change; editorial changes); 29 September 2010(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

SRM 2692c was included as an unknown in the June 2009 CANSPEX 2009-2 Coal Round Robin. CANSPEX 2009-2 summary statistics are provided to demonstrate user experience with this material using conventional methods and to better characterize the matrix. The CANSPEX Coal Round Robin results should **NOT** be used as substitutes for NIST values.

SRM 2692c CANSPEX Round Robin Results					
Parameter	**Mean Value[a]**	**95 % Coverage Interval of Mean Value**	**Pooled Within-Lab Standard Deviation (S_W)**	**Pooled Between-Lab Standard Deviation (S_B)**	**Total Number of Labs**
Moisture wt %	0.695	0.029	0.038	0.154	117
Ash wt % db	7.497	0.014	0.045	0.076	117
Volatile wt % db	19.92	0.10	0.16	0.47	94
BTU/lb db	14512[b,c]	8	20	41	106
Carbon wt % db	83.16	0.32	0.26	1.18	56
Hydrogen wt % db	4.499	0.037	0.036	0.130	51
Nitrogen wt % db	1.514	0.017	0.023	0.059	52
Sulfur wt % db	1.075	0.008	0.014	0.039	108
Pyritic Sulfur wt % db	0.563	0.036	0.020	0.075	19
Sulfate Sulfur wt % db	0.016	0.10	0.005	0.015	16
Chlorine µg/g db	1271	63	40	208	46
Fluorine µg/g db	59.3	8.1	4.0	21.0	30
Mercury ng/g db	167	10	7	28	36
Selenium µg/g db	1.18	0.33	0.07	0.55	14
Free Swelling Index (FSI)	9.00	0.1	0.4	0.2	53

db – dry basis

[a] Estimates of the mean and standard deviation are based on a robust estimator using Rousseeuw’s Qn [15].

[b] Please note that the gross calorific value may decrease upon aging, and this decrease will accelerate after the unit has been removed from the Mylar packaging (see “Instructions for Use”).

[c] Btu_{th}/lb • 2324.444 = J/kg [1]

Derived Standard Deviations (in %) of Repeatability (s_r) and Reproducibility (s_R), and Tally of Published Methods Used in CANSPEX™ Round Robin*

Parameter	Total Number of Labs	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 %	117	**1038.3**	0.04	-	1	**D2013**	0.03	0.09	1	**1016**	0.04	-	1	**51718**	0.07	-	2	**212**	0.07	-	1	**589**	0.11	-	2	**3-037**	-	-	1	**925**	-	-	1	8
						D3173	0.03	0.09	55													**11722**	0.04	-	5									
						D3302	0.03	0.09	11													**5068**	0.07	-	1									
						D5142	0.07	0.09	27																									
Ash % dry basis	117	**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	9	**3-003**	-	-	1		-	-		8
						D5142	0.08	0.11	32																									
Volatile % dry basis	94	**1038.3**	0.07	0.35	1	**D3175**	0.18	0.35	47	**1016**	0.11	0.35	1	**51720**	0.21	0.28	2	**212**	0.18	0.35	1	**562**	0.21	0.28	11									7
						D5142	0.20	0.55	24																									
Btu/lb dry basis	106	**1038.5**	20	46	1	**D1989**	23	39	5	**1016**	18	43	0	**51900**	18	46	4	**213**	18	46	1	**1928**	43	106	11									5
						D2015	24	38	3																									
						D3286	18	35	4																									
						D5865	24	38	72																									
Carbon % dry basis	56	**1038.6.4**	0.11	0.21	1	**D3178**	0.11	-	2					**51732**	-	-	1	**476**	0.18	0.35	1	**609**	0.09	0.18	2									10
						D5373	0.16	0.35	36													**12902**	-	-	3									
Hydrogen % dry basis	51	**1038.6.4**	0.04	0.07	1	**D3178**	0.02	-	3					**51732**	-	-	1	**476**	0.05	0.09	1	**609**	0.04	0.09	2									6
						D5373	0.04	0.09	34													**12902**	-	-	3									
Nitrogen % dry basis	52	**1038.6.4**	0.01	0.03	1	**D3179**	0.08	0.13	3					**51732**	-	-	1	**476**	0.03	0.05	1	**333**	0.02	0.04	2									7
						D5373	0.02	0.05	34													**12902**	-	-	3									
Total Sulfur % dry basis	108	**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	1	**214**	0.04	0.09	1	**351**	0.02	0.04	3	**3-038**	-	-	1		-	-		9
						D4239	0.02	0.04	83																									
						D5016	0.04	0.15	5																									
Pyritic Sulfur % dry basis	19	**1038.11**	0.02	0.05	1	**D2492**	0.05	0.11	16									**215**	0.02	0.04	1													1
Sulfate Sulfur % dry basis	16	**1038.11**	0.007	0.011	1	**D2492**	0.007	0.014	14									**215**	0.01	0.04	1													0
Chlorine µg/g dry basis	46		-	-		**D2361**	106	213	2	**1016**	177	177	1	**51727**	71	106	2	**3558**	35	71	1					**3-009**	-	-	1		-	-		13
						D4208	76	175	18																									
						D6721	28	34	8																									
Fluorine µg/g dry basis	30					**D3761**	5	5	10					**51723**	8	14	2	**4663**	6	7	1	**11724**	4	7	2	**03-009**	-	-	1					11
						D5987	4	7	3																									
Mercury ng/g dry basis	36					**D6414**	11	16	6					**22022**	-	-	1																	7
						D6722	3	10	22																									
Selenium µg/g dry basis	14					**D4606**	0.193	0.16	3																									11
FSI	53	**1038.17**	0.18	0.35	1	**D720**	0.35	0.71	46	**1016**	-	-	1	**51741**	-	-	1	**5448**	0.35	0.53	1	**501**	0.35	0.18	3									

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