National Institute of Standards and Technology

Certificate of Analysis

Standard Reference Material® 2692b

Bituminous Coal

(Sulfur, Mercury, and Chlorine)

This Standard Reference Material (SRM) is intended primarily for use in the evaluation of techniques employed in the determination of sulfur, mercury, chlorine, ash content, and calorific value ($MJ \cdot kg^{-1}$) in coal and materials of a similar matrix. A unit of SRM 2692b 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 Values: The certified values for sulfur, mercury, and chlorine, expressed as mass fractions [1] on a dry basis, are provided in Table 1. The certified values for sulfur and mercury are based on single NIST primary methods while the chlorine value is the average of two independent NIST methods. 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 accounted for by NIST.

Reference Values: The reference values for ash content [2] and calorific value are provided in Table 2. These reference values are based on the statistical analysis by NIST of data from laboratories participating in the CANSPEX 2000-2 interlaboratory study done in June 2000 in conjunction with Quality Associates International, Ltd., Douglas, Ontario, Canada.[1] Reference values are noncertified values that are the 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.

Supplemental Information: Summary statistics reported by CANSPEX for SRM 2692b are provided in the addendum to this certificate to demonstrate user experience with this material using conventional methods and to more fully characterize the matrix. The CANSPEX 2000-2 results were not used in calculating the certified values for sulfur, mercury, and chlorine and should **NOT** be used as substitutes for NIST values.

Expiration of Certification: The certification of SRM 2692b is valid, within the measurement uncertainties specified, until **31 December 2012** provided the SRM is handled in accordance with the instructions given in this certificate (see "Instructions for Use"). This certification is nullified if the SRM is 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.

The coordination of the technical measurements leading to certification was performed by W.R. Kelly and R.D. Vocke, Jr. of the NIST Analytical Chemistry Division.

Stephen A. Wise, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 08 August 2007
See Certificate Revision History on Page 4

Robert L. Watters, Jr., Chief
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[1] Certain commercial organizations, services, equipment, or materials are identified in this certificate to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by National Institute of Standards and Technology nor does it imply that the organizations, services, materials, or equipment identified are necessarily the best available for the purpose.

Certification analyses for sulfur were performed by W.R. Kelly, J.L. Mann, and R.D. Vocke, Jr. of the NIST Analytical Chemistry Division. Certification analyses for mercury were performed by S.E. Long and W.R. Kelly of the NIST Analytical Chemistry Division. Certification analyses for chlorine were performed by R.M. Lindstrom, J.L. Mann, R.O. Spatz, and R.D. Vocke, Jr. of the NIST Analytical Chemistry Division. Moisture analyses were preformed by J.L. Mann of the NIST Analytical Chemistry Division.

Statistical analyses leading to certified and reference values were performed by W.F. Guthrie and D.D. Leber of the NIST Statistical Engineering Division.

The support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

INSTRUCTIONS FOR USE

Sampling: The unit should be thoroughly mixed by rotating the bottle before sampling. A minimum sample mass of 100 mg should be used for analytical determinations to be related to the sulfur, mercury, and chlorine values provided. The calorific value and ash content were 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 [3] or equivalent technique. For the purposes of certification, constant mass was 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 [4]. During drying at NIST, the mass loss of SRM 2692b samples was observed to stabilize after approximately 70 minutes. The average mass loss measured at NIST for SRM 2692b was 1.24 % (1 s = 0.03 %, n =6).

PREPARATION, HOMOGENEITY, AND ANALYSIS

Source and Preparation of Material: Approximately 700 kg of coal was obtained from the Elk Creek #2 Gas Seam near Holden, WV. This single-seam coal was washed, crushed, and air-dried prior to being pulverized and screened at 250 μm (60 mesh). The resulting fraction of clean coal less than 250 μm (approximately 320 kg) was divided into two portions using the spinning riffler technique. One portion was divided into the 50 g units bottled under an argon atmosphere and issued as SRM 2692a in September of 1994. The other portion was stored in bulk under argon for five years, then divided using the spinning riffler technique into 50 g units and bottled under an argon atmosphere for subsequent issuance as SRM 2692b.

Homogeneity Testing: Homogeneity testing by the NIST Analytical Chemistry Division is based on X-ray fluorescence analysis of aliquots taken from 24 bottles, selected by stratified random sampling, from the SRM 2692b lot. The standard deviation of random bottle-to-bottle differences in the sulfur mass fraction is negligible relative to the certified sulfur mass fraction at the 95 % confidence level.

Analysis: The certified value for sulfur, reported in Table 1 as a mass fraction [1] on a dry basis (see "Instructions for Use"), is based on measurements by isotope dilution thermal ionization mass spectrometry (ID-TIMS) [5].

The certified value for mercury, reported in Table 1 as a mass fraction [1] on a dry basis (see "Instructions for Use"), is based on measurements by isotope dilution cold vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS) [6].

The certified value for chlorine, reported in Table 1 as a mass fraction [1] on a dry basis (see "Instructions for Use"), is based on measurements by negative ion ID-TIMS [7] and Instrumental Neutron Activation Analysis (INAA).

Table 1. Certified Values (dry basis) for SRM 2692b

Element	Mass Fraction		
Sulfur	1.170 %	±	0.020 %
Mercury	133.3 µg/kg	±	4.1 µg/kg
Chlorine	1651 mg/kg	±	28 mg/kg

The uncertainties in the certified values for sulfur, mercury and chlorine are expressed as an expanded uncertainty, $U = ku_c$, calculated according to the methods in the ISO Guide [8]. The observed sulfur and mercury variations were greater than expected for the analytical technique used. Therefore a prediction interval was used to account for the sulfur and mercury variabilities in this material [9]. The chlorine value was obtained by averaging the values and combining the Type A uncertainties of the IDMS and INAA measurements using the BOB method [10]. The quantity u_c represents, at the level of one standard deviation, the potential combined effects of the uncertainties due to the measurement variability and material inhomogeneity. The quantity k is the coverage factor used to obtain an expanded uncertainty with an approximate confidence level of 95 %. For sulfur, the value of the coverage factor, $k = 2.306$, is determined from the Student's t-distribution with 8 degrees of freedom and a confidence level of 95 %. For mercury, the value of the coverage factor, $k = 2.235$, is determined from the Student's t-distribution with 9.77 degrees of freedom and a confidence level of 95 %. For chlorine, the value of the coverage factor, $k = 2.57$, is determined from the Student's t-distribution with 5.9 degrees of freedom and a confidence level of 95 %.

Reference Values and Uncertainties: The reference value for ash content (Table 2) is based on data obtained from 30 laboratories using method ASTM 3174 [2] in the CANSPEX 2000-2 Coal Round Robin. The reference value for the gross calorific value (Table 2) is based on data obtained from 41 laboratories using conventional calorific methods in the CANSPEX 2000-2 Coal Round Robin. Round robin dry ash and dry gross calorific data were converted to a dried in nitrogen atmosphere basis based on a drying study conducted at NIST.

Table 2. Reference Values (dry basis) for SRM 2692b

Ash Content (mass fraction)	7.90 %	±	0.30 %
Gross Calorific Value	32.81 MJ·kg^{-1}	±	0.18 MJ·kg^{-1}
	(14 104 Btu$_{th}$·lb^{-1}	±	77 Btu$_{th}$·lb^{-1})

The uncertainty in the reference values for ash content and gross calorific value are expressed as an expanded uncertainty, $U = ku_c$, calculated according to the methods in the ISO and NIST Guides [8]. A prediction interval was used to account for the potential variability in this material [9]. The quantity u_c represents, at the level of one standard deviation, the potential combined effects of within-laboratory measurement uncertainty, between-laboratory uncertainty, material inhomogeneity, and the uncertainty in the conversion of samples dried in air to a nitrogen basis. The quantity k is the coverage factor used to obtain an expanded uncertainty with an approximate confidence level of 95 %. For ash content, the value of the coverage factor, $k = 2.054$, is determined from the Student's t-distribution with 26.29 degrees of freedom and a confidence level of 95 %. For gross calorific value, the value of the coverage factor, $k = 2.025$, is determined from the Student's t-distribution with 37.90 degrees of freedom and a confidence level of 95 %.

REFERENCES

[1] 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 (1995).

[2] ASTM D 3174-93; *Test Method for Ash in the Analysis Sample of Coal and Coke from Coal*; Annu. Book ASTM Stand., Vol. 05.05.

[3] ASTM D 5142-90; *Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures*; Annu. Book ASTM Stand., Vol. 05.05.

[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, p. 3585 (2002).

[5] Kelly, W.R., Paulsen, P.J., Murphy, K.E., Vocke, R.D., and Chen, L.-T.; *Determination of Sulfur in Fossil Fuels by Isotope Dilution Thermal Ionization Mass Spectrometry*; Anal. Chem., Vol. 66, p. 2505 (1994).

[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, p. 1477 (2002).

[7] Howard, M.E.; Vocke, R.D. Jr.; *A Closed System Digestion and Purification Procedure for the Accurate Assay of Chlorine in Fossil Fuels*; J. Anal. At. Spectrom., Vol. 19, p. 1423 (2004).

[8] ISO; *Guide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9, 1st ed.; International Organization for Standardization: Geneva, Switzerland (1993); 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://physics.nist.gov/Pubs/.

[9] Hahn, G.J. and Meeker, W.Q.; *Statistical Intervals: A Guide for Practitioners*; John Wiley & Sons, Inc.: NY, NY (1991).

[10] Levenson, M.S.; Banks, D.L.; Eberhart, K.R.; Gill, L.M.; Guthrie, W.F.; Liu, H.K.; Vangel, M.G.; Yen, J.H.; Zhang, N.F.; *An Approach to Combining Results From Multiple Methods Motivated by the ISO Guide*; J. Res. Natl. Inst. Stand., Vol. 105, p. 521 (2000).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (30l) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.

Addendum

Standard Reference Material 2692b

Bituminous Coal

(Sulfur, Mercury, and Chlorine)

CANSPEX 2000-2 Coal Round Robin Results: SRM 2692b was included as an unknown in the June 2000 CANSPEX 2000-2 Coal Round Robin. CANSPEX 2000-2 summary statistics are provided in the addendum to this certificate 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.

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Certificate Issue Date: 06 February 2001

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Summary of Analysis Reported by CANSPEX

CANSPEX 2000-2 Coal Sample NIST SRM 2692b

Parameter	Consensus Value	ASTM Method Referenced for Reproducibility and Repeatability	ASTM Reproducibility Standard Deviation	CANSPEX Reproducibility Standard deviation	ASTM Repeatability Standard Deviation	CANSPEX Repeatability Standard deviation	Number of Labs	Number of Methods
Moisture wt %	1.18	ASTM D 3173	0.11	0.17	0.07	0.04	85	22
Ash wt % db	7.88	ASTM D 3174	0.18	0.08	0.11	0.04	85	22
Volatiles wt % db	33.06	ASTM D 3175	0.35	0.61	0.18	0.14	68	17
BTU/lb db	14094	ASTM D 5865	44	59	18	15	84	16
Carbon wt % db	79.34	ASTM D 5373	0.89	0.92	0.23	0.18	37	14
Hydrogen wt % db	4.98	ASTM D 5373	0.11	0.15	0.06	0.05	35	13
Nitrogen wt % db	1.30	ASTM D 5373	0.06	0.09	0.04	0.02	36	13
Sulfur wt % db	1.19	ASTM D 4239c	0.05	0.05	0.03	0.01	85	18
Pyritic Sulfur wt % db	0.49	ASTM D 2492	0.10	0.02	0.05	0.01	14	4
Sulfate Sulfur wt % db	0.04	ASTM D 2492	0.01	0.01	0.01	0.00	14	3
Chlorine µg/g db	1593	ASTM D 4208	163	200	69	28	35	10
Fluorine µg/g db	65	ASTM D 3761	5	18	5	1	17	6
Mercury ng/g db	124	ASTM D 3684	11	19	7	5	19	8
Selenium µg/g db	3.18	ASTM D 4606	0.18	1.0	0.13	0.11	8	7
Free Swelling Index (FSI)	8.0	ASTM D 720	0.7	0.6	0.4	0.35	28	4