National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2685b

Sulfur, Mercury and Chlorine in Coal

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. SRM 2685b 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 a single NIST primary method, 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 data from laboratories participating in an interlaboratory study done in conjunction with the Canada Centre for Mineral and Energy Technology (CANMET) Service Program for the Evaluation of Codes and Standards (CANSPECS) in December 1998 (CANSPECS No. 58). 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.

Information Values: Information values for selected elements, expressed as mass fractions on a dry basis, are provided in Table 3. These noncertified values, with no assessed uncertainties, are provided for information purposes only. In addition, data from the CANMET CANSPECS 58 Coal Round Robin 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 CANMET CANSPECS 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 2685b is valid, within the measurement uncertainties specified, until **31 December 2010**, 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 representative samples of this SRM over the period of its certification. If substantive 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 G.C. Turk, M.R. Winchester, and R.D. Vocke, Jr. of the NIST Analytical Chemistry Division.

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

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Certificate Issue Date: 21 May 2007
See Certificate Revision History on Page 5

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Certification analyses for sulfur were performed by W.R. Kelly, J.L. Mann, K.H. Murphy and M.R. Winchester 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 W.R. Kelly and J.L. Mann of the NIST Analytical Chemistry Division.

Homogeneity testing of the bulk material by X-ray fluorescence was performed by A.F. Marlow and P.A. Pella of the NIST Analytical Chemistry Division. The comparative sulfur analysis and bottle-to-bottle homogeneity testing was performed at the Electric Fuels Corporation Central Laboratory under the direction of the NIST Analytical Chemistry and Statistical Engineering Divisions.

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

INSTRUCTIONS FOR USE

Sampling: The unit should be thoroughly mixed by rotating the bottle before sampling. A minimum sample mass of 150 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, NIST operationally defined constant mass 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 2685b samples was observed to stabilize after approximately 2.5 hours. The average mass loss measured at NIST for SRM 2685b was 2.32 % (1 s = 0.06 %, n = 8).

At NIST a study was also conducted to quantify the difference between drying in air and nitrogen atmospheres for SRM 2685b. The average weight loss determined at NIST for SRM 2685b dried in a convection oven in air at 105 °C ± 1 °C for two hours was 2.14 % (1 s = 0.06 %, n = 8).

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 the Consolidation Coal Co., Ohio Valley Division, located in Captina, WV, approximately 20 miles south of Wheeling along the Ohio River in Marshall County. This mine produces bituminous coal with a sulfur content of about 4.5 % (dry basis) after washing. This coal was obtained from an underground mine that is part of the Pittsburgh, No. 8 coal seam, which is in the northern West Virginia coal field. The coal was oven dried prior to processing in accordance with procedures outlined in ASTM D 2013. At least 500 kg of the coal was reduced in size to –60 mesh and screened prior to blending. The –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 the NBS Special Publication 260-84 Sampling, Materials Handling, Processing, and Packaging of NBS Sulfur in Coal Standard Reference Materials.

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

Homogeneity Testing: Homogeneity testing on the bulk material was done by X-ray fluorescence. Homogeneity testing for sulfur on 50 g bottled units was done using a combustion-infrared detection analyzer according to ASTM D 4239 [5] on 12 bottles from the SRM 2685b lot selected by stratified random sampling.

[1]Certain commercial equipment, instrumentation, 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 materials or equipment identified are necessarily the best available for the purpose.

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) [6] of SRM 2685a. The material designated SRM 2685b is a portion of the same bulk material that was used to prepare SRM 2685a. The sulfur concentration of SRM 2685a and SRM 2685b lots were directly compared by combustion-infrared detection to verify uniformity between lots. The certified sulfur value for SRM 2685b is based on the ID-TIMS measurements of the 2685a lot, with an adjustment for the differences observed between lots and adjustment to report the certified value based on drying in a nitrogen atmosphere.

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) [7].

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 [8] and Instrumental Neutron Activation Analysis (INAA).

Table 1. Certified Values (dry basis) for 2685b

Element	Mass Fraction		
Sulfur	4.730 %	±	0.068 %
Mercury	146.2 µg/kg	±	10.6 µg/kg
Chlorine	517 mg/kg	±	13 mg/kg

The uncertainty in the certified value for sulfur is expressed as an expanded uncertainty, $U = ku_c$, calculated according to the methods in the ISO and NIST Guides [9]. The quantity u_c represents, at the level of one standard deviation, the potential combined effects of the uncertainty due to combustion/infrared detection measurement variability, ID-TIMS measurement variability (the ID-TIMS measurement variability for SRM 2685a was recomputed in accordance to ISO Guidelines before being used in the calculation of the expanded uncertainty for SRM 2685b), and conversion of values to nitrogen drying basis. The quantity k is the coverage factor used to obtain an expanded uncertainty with an approximate confidence level of 95 %. The value of the coverage factor, $k = 2.366$, is determined from the Student's t-distribution with 6.98 degrees of freedom and a confidence level of 95 %.

The uncertainty in the certified value for mercury is expressed as an expanded uncertainty, $U = ku_c$, calculated according to the methods in the ISO Guide [9]. The observed mercury variation was much greater than expected for the analytical technique used. Therefore a prediction interval was used to account for the mercury variability in this material [10]. The quantity u_c represents, at the level of one standard deviation, the potential combined effects of the uncertainties due to measurement variability and mercury inhomogeneity. The quantity k is the coverage factor used to obtain an expanded uncertainty with an approximate confidence level of 95 %. The value of the coverage factor, $k = 2.519$, is determined from the Student's t-distribution with 5.36 degrees of freedom and a confidence level of 95 %.

The chlorine value was obtained by averaging the ID-TIMS and INAA measurements while the uncertainty was derived by combining the respective Type A uncertainties using the BOB method [11]. The uncertainty in the certified value for chlorine is expressed as an expanded uncertainty, $U = ku_c$, calculated according to the methods in the ISO Guide [9]. The quantity u_c represents, at the level of one standard deviation, the 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 %. The value of the coverage factor, $k = 2.16$, is determined from the Student's t-distribution with 13.9 degrees of freedom and a confidence level of 95 %.

Reference Values and Uncertainties: The reference value for ash content, listed in Table 2, is based on data obtained from 41 laboratories using method ASTM D 3174 [2] in the CANMET CANSPECS Coal 58 Round Robin. The reference value for the gross calorific value (Table 2) is based on data obtained from 55 laboratories using conventional calorific methods in the CANMET CANSPECS Coal 58 Round Robin.

Table 2. Reference Values (dry basis) for SRM 2685b

Ash Content	15.94 %	±	0.30 %
Gross Calorific Value	26.94 $MJ \cdot kg^{-1}$	±	0.28 $MJ \cdot kg^{-1}$
	(11 582 $Btu_{th} \cdot lb^{-1}$	±	120 $Btu_{th} \cdot lb^{-1}$)

The uncertainties in the reference values for ash content and gross calorific value are each expressed as expanded uncertainties, $U = ku_c$, calculated according to the methods in the ISO Guide [9]. Prediction intervals were used to account for variability in the ash content and gross calorific value of this material [10]. 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 drying 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, $k = 2.03$, is determined from the Student's t-distribution with 37.07 degrees of freedom and a confidence level of 95 %. For gross calorific value, the value of the coverage factor, $k = 2.01$, is determined from the Student's t-distribution with 52.98 degrees of freedom and a confidence level of 95 %.

Supplemental Information: The SRM 2685b mass fraction values listed in Table 3 for the major and minor elements are provided as additional information on the matrix.

Table 3. Information Values for SRM 2685b

(Mean Mass Fraction (mg/kg) Unless Otherwise Noted)

Element	Mean Mass Fraction	Element	Mean Mass Fraction
Aluminum	1.7 %	Lanthanum	10
Antimony	0.36	Magnesium	0.1 %
Arsenic	12	Manganese	41
Barium	105	Nitrogen	1.1 %
Boron	109	Potassium	0.26 %
Bromine	5.6	Rubidium	17
Calcium	0.52 %	Samarium	1.7
Carbon	64.6 %	Scandium	3.7
Cerium	18	Selenium	1.9
Cesium	1.3	Sodium	0.08 %
Chromium	22	Thorium	2.7
Cobalt	4.6	Titanium	0.09 %
Europium	0.36	Tungsten	1.2
Hafnium	0.91	Uranium	0.95
Hydrogen	4.5 %	Vanadium	31
Iron	3.9 %	Zinc	17

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] ASTM D 4239-94; *Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods*; Annu. Book of ASTM Stand.,Vol. 05.05.

[6] 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).

[7] 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).

[8] 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, 1423 (2004).

[9] 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/.

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

[11] 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).

Certificate Revision History: 21 May 2007 (Technical addition of chlorine certified value); 06 February 2001 (Original certificate date).

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® 2685b

Sulfur, Mercury, and Chlorine in Coal

CANSPECS 58 Coal Round Robin Results: SRM 2685b was included as an unknown in the December 1998 CANSPECS 58 Coal Round Robin. Summary statistics reported by CANSPECS 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 CANSPECS 58 Coal Round Robin results should **NOT** be used as substitutes for NIST values.

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Addendum Issue Date: 06 February 2001

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Summary of Analysis Reported by CANSPECS

CANSPECS 58 Coal Sample NIST SRM 2685b

Parameter	Consensus Value	ASTM Method Reference for Reproducibility and Repeatability	ASTM Reproducibility Standard Deviation	CANSPECS Reproducibility Standard Deviation	ASTM Repeatability Standard Deviation	CANSPECS Repeatability Standard Deviation	Number of Labs	Number of Methods
Moisture wt %	2.21	ASTM D 3173	0.11	0.12	0.07	0.06	85	22
Ash wt % db	15.93	ASTM D 3174	0.18	0.10	0.11	0.07	86	22
Volatiles wt % db	37.61	ASTM D 3175	0.35	0.79	0.18	0.15	68	17
BTU/lb db	11555	ASTM D 5865	44	47	18	16	83	16
Carbon wt % db	64.59	ASTM D 5373	0.89	0.69	0.23	0.18	37	14
Hydrogen wt % db	4.45	ASTM D 5373	0.11	0.11	0.06	0.03	36	13
Nitrogen wt % db	1.07	ASTM D 5373	0.06	0.08	0.04	0.02	37	13
Sulfur wt % db	4.69	ASTM D 4239c	0.12	0.17	0.08	0.03	86	18
Pyritic Sulfur wt % db	1.15	ASTM D 2492	0.16	0.06	0.06	0.01	16	4
Sulfate Sulfur wt % db	1.08	ASTM D 2492	0.01	0.06	0.01	0.01	15	3
Chlorine µg/g db	530	ASTM D 4208	114	161	42	24	28	10
Fluorine µg/g db	94	ASTM D 3761	5	45	5	4	17	6
Mercury ng/g db	143	ASTM D 3684	11	30	7	11	11	8
Selenium µg/g db	1.82	ASTM D 4606	0.25	0.41	0.18	0.09	7	7
Free Swelling Index (FSI)	4.5	ASTM D 720	1.0	1.0	0.5	0.3	30	4