



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2684b

Sulfur and Mercury in Coal

This Standard Reference Material (SRM) is intended primarily for use in the evaluation of techniques employed in the determination of sulfur, mercury, ash content, and calorific value ($\text{MJ}\cdot\text{kg}^{-1}$) in coal and materials of a similar matrix. SRM 2684b 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 and mercury, expressed as mass fractions [1] on a dry basis, are provided in Table 1. The certified values are based on single NIST primary 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 September 1998 (CANSPECS No. 57). 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 are noncertified values with no uncertainty assessed that are provided for information purposes only. In addition, data from the CANMET CANSPECS 57 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 and mercury and should **NOT** be used as substitutes for NIST values.

Expiration of Certification: The certification of SRM 2684b 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. Return of the attached registration card will facilitate notification.

The coordination of the technical measurements leading to certification was performed by G.C. Turk and M.R. Winchester of the NIST Analytical Chemistry Division.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by B.S. MacDonald.

Willie E. May, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 06 February 2001

Nancy M. Trahey, Chief
Standard Reference Materials Program

Certification analyses for sulfur were performed by W.R. Kelly and R.D. Vocke 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. Moisture analyses were performed by J.L. Mann and W.R. Kelly 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 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 and mercury 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 $107\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$ 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. During drying at NIST, the mass loss of SRM 2684b samples was observed to stabilize after approximately 2.5 hours. The average mass loss measured at NIST for SRM 2684b was 3.08 % ($1\text{ s} = 0.20\text{ }\%$, $n = 8$).

At NIST a study was also conducted to quantify the difference between drying in air and nitrogen atmospheres for SRM 2684b. The average weight loss determined at NIST for SRM 2684b dried in a convection oven in air at $105\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ for two hours was 2.87 % ($1\text{ s} = 0.19\text{ }\%$, $n = 8$).

PREPARATION, HOMOGENEITY, AND ANALYSIS¹

Source and Preparation of Material: Approximately 900 kg of coal was obtained from the Delta mine of the Amax Coal Company, Marion, Illinois. The mine is a surface mine that produces bituminous coal with a sulfur content, after cleaning, of 2.8 % to 2.9 % (dry basis). The coal mined at the Delta mine was obtained from the Illinois No. 6 Herrin seam. 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 m³). 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 2684 and SRM 2684a. The remaining bulk material was divided using the spinning riffler technique into 50 g units and subsequently issued as SRM 2684b.

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 [4] on 12 bottles from the SRM 2684b lot selected by stratified random sampling. The standard deviation of random bottle-to-bottle differences in sulfur mass fraction is estimated to be 0 % relative to the certified sulfur mass fraction, with a range of 0 % to 0.64 % at the 95 % confidence level.

¹Certain 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.

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] of SRM 2684a. The material designated SRM 2684b is a portion of the same bulk material that was used to prepare SRM 2684a. The sulfur concentration of SRM 2684a and SRM 2684b lots were directly compared by combustion-infrared detection to verify uniformity between lots. The certified sulfur value for SRM 2684b is based on the ID-TIMS measurements of the 2684a 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) [8].

Table 1. Certified Values (Dry basis) for SRM 2684b

Element	Mass Fraction	
Sulfur	3.076 %	± 0.031 %
Mercury	97.4 µg/kg	± 4.7 µg/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 Guide [6]. 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 2684a was recomputed in accordance to ISO Guidelines before being used in the calculation of the expanded uncertainty for SRM 2684b), 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, $k = 2.170$, is determined from the Student's t -distribution with 12.43 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 [6]. 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 [7]. 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, $k = 2.450$, is determined from the Student's t -distribution with 5.97 degrees of freedom and a confidence level of 95 %.

Reference Values and Uncertainties: The reference value for ash content is based on data obtained from 38 laboratories using method ASTM D 3174 [2] in the CANMET CANSPECS Coal 57 Round Robin. The reference value for the gross calorific value is based on data obtained from 53 laboratories using conventional calorific methods in the CANMET CANSPECS Coal 57 Round Robin.

Table 2. Reference Values (Dry basis) for SRM 2684b

Ash Content	10.85 %	± 0.36 %
Gross Calorific Value	28.56 MJ·kg ⁻¹	± 0.28 MJ·kg ⁻¹
	(12 278 Btu _{th} ·lb ⁻¹)	± 119 Btu _{th} ·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 [6]. Prediction intervals were used to account for variability in the ash content and gross calorific value of this material [7]. 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 35.60 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 45.61 degrees of freedom and a confidence level of 95 %.

Supplemental Information: The SRM 2684b 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 2684b

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

Element	Mean Mass Fraction	Element	Mean Mass Fraction
Aluminum	1.1 %	Lanthanum	6.7
Antimony	0.35	Magnesium	0.08 %
Arsenic	3.9	Manganese	36
Barium	41	Nitrogen	1.5 %
Boron	114	Potassium	0.20 %
Bromine	11	Rubidium	15
Calcium	0.44 %	Samarium	1.1
Carbon	69.3 %	Scandium	2.7
Cerium	12	Selenium	1.9
Cesium	1.2	Sodium	0.03 %
Chromium	17	Thorium	2.0
Cobalt	3.9	Titanium	0.06 %
Europium	0.23	Tungsten	0.56
Hafnium	0.57	Uranium	0.90
Hydrogen	4.6 %	Vanadium	22
Iron	1.5 %	Zinc	110

REFERENCES

- [1] Taylor, B.N., "Guide for the Use of the International System of Units (SI)," NIST Special Publication 811, 1995 Ed., (April 1995).
- [2] ASTM D 3174-93, "Test Method for Ash in the Analysis Sample of Coal and Coke from Coal," **05.05** ASTM Book of Standards, West Conshohocken, PA.
- [3] ASTM D 5142-90, "Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures," **05.05** ASTM Book of Standards, West Conshohocken, PA.
- [4] ASTM D 4239-94, "Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods," **05.05** ASTM Book of Standards, West Conshohocken, PA.
- [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.*, **66**, p. 2505, (1994).
- [6] *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st Ed. ISO, Geneva, Switzerland, (1993); see also Taylor, B.N. and 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/>.
- [7] Hahn, G.J. and Meeker, W.Q., "Statistical Intervals: A Guide for Practitioners," John Wiley & Sons, Inc., NY, (1991).
- [8] Christopher, S.J., Long, S.E., and Rearick, M.S., "Development of High Accuracy Vapor Generation ICP-MS and its Application to the Certification of Mercury in Standard Reference Materials," *Anal. Chem.*, Submitted for Publication, (November 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 (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet <http://www.nist.gov/srm>.

Addendum

Standard Reference Material[®] 2684b

Sulfur and Mercury in Coal

CANSPECS 57 Coal Round Robin Results: SRM 2684b was included as an unknown in the September 1998 CANSPECS 57 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 57 Coal Round Robin results should **NOT** be used as substitutes for NIST values.

Willie E. May, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Addendum Issue Date: 06 February 2001

Nancy M. Trahey, Chief
Standard Reference Materials Program

Summary of Analysis Reported by CANSPECS

CANSPECS 57 Coal Sample NIST SRM 2684b

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 %	3.84	ASTM D 3173	0.11	0.18	0.07	0.05	82	22
Ash wt % db	10.85	ASTM D 3174	0.18	0.13	0.11	0.06	84	22
Volatiles wt % db	36.43	ASTM D 3175	0.35	0.73	0.18	0.15	65	17
BTU/lb db	12268	ASTM D 5865	44	50	18	16	81	16
Carbon wt % db	69.25	ASTM D 5373	0.89	0.70	0.23	0.22	37	14
Hydrogen wt % db	4.59	ASTM D 5373	0.11	0.12	0.06	0.03	36	13
Nitrogen wt % db	1.45	ASTM D 5373	0.06	0.07	0.04	0.02	36	13
Sulfur wt % db	3.10	ASTM D 4239c	0.08	0.10	0.05	0.02	81	18
Pyritic Sulfur wt % db	0.52	ASTM D 2492	0.10	0.06	0.04	0.02	15	4
Sulfate Sulfur wt % db	0.81	ASTM D 2492	0.01	0.06	0.01	0.02	14	3
Chlorine µg/g db	1037	ASTM D 4208	156	103	65	36	30	10
Fluorine µg/g db	67	ASTM D 3761	5	11	5	5	15	6
Mercury ng/g db	90	ASTM D 3684	11	54	7	7	13	8
Selenium µg/g db	1.77	ASTM D 4606	0.22	0.42	0.16	0.15	10	7
Free Swelling Index (FSI)	1.5	ASTM D 720	0.7	0.4	0.4	0.2	30	4