National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material 2692a

Sulfur in Coal

This Standard Reference Material (SRM) 2692a is intended primarily for use in the evaluation of methods and the calibration of instruments used in the determination of sulfur in coal. It is also certified for ash content and calorific value ($MJ \cdot kg^{-1}$). SRM 2692a consists of a 50 g bottle of a bituminous coal that was ground to pass a 60 mesh (250 μm) sieve and homogenized.

The certified value for sulfur is based on at least a 150 mg sample of the dried material, the minimum amount that should be used for analysis (see drying instructions). The uncertainty was calculated according to NIST Technical Note 1297 [1]. It has an approximate level of confidence of 95%, and includes material variability. The certified calorific value and ash content were determined in two laboratories using procedures recommended in ASTM methods and are given in Table 1 with method citations. Uncertified values based on a 70-laboratory round robin are given in Table 2.

The certified value for HHV2 is based on the interlaboratory mean and anticipates material degradation; it is given as the midpoint of the degradation line for 24 months after certification. Using data about laboratory differences, material variability and uncertainty in predicting material degradation, approximate 95% confidence bands were placed about the anticipated degradation line. The uncertainty is the distance between the certified value and the upper bound on the line over the 24 month period. The certified value for ash is the mean of results from two laboratories. The uncertainty is based on the 95% prediction interval for the true concentration, and includes allowances for differences among laboratories, material variability, and random measurement error. This interval predicts the ash concentration in 95% of the samples of this material.

Certification analyses were performed at NIST by W.R. Kelly and R.D. Vocke, Jr., of the NIST Inorganic Analytical Research Division, and by D.R. Kirklin of the Chemical Kinetics and Thermodynamics Division. Corroborating analyses were performed by L.W. Rosendale of Consol Inc., Library, PA and by L. Janke of Canada Center for Mineral and Energy Technology, Ottawa, Canada.

The statistical analysis of the certification data was performed by S.B. Schiller of the NIST Statistical Engineering Division.

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

Gaithersburg, MD 20899
September 19, 1994
(Revision of certificate dated 1-26-94)

Thomas E. Gills, Chief
Standard Reference Materials Program

(over)

Table 1. Certified Values for SRM 2692a

Sulfur[1,2] Wt %*	Furnace[2,3] Ash, Wt %	HHV2[3,4,5,6] $MJ \cdot kg^{-1}$ $Btu \cdot lb^{-1}$
1.184 ± 0.036	7.94 ± 0.07	32.64 ± 0.32 (14033 ± 137)

*Wt % = mg/kg x 10^{-4}

Note: $MJ \cdot kg^{-1} = 429.9226\ Btu_{th} \cdot lb^{-1}$ was used for the calorific value conversion.

[1]Thermal Ionization Mass Spectrometry, Sealed Glass Tube Digestion.
[2]ASTM D5142-90 Standard Test Methods for the Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures.
[3]ASTM D3174 Standard Test Method for Ash in the Analysis Sample of Coal and Coke.
[4]ASTM D1989 Standard Test Method for Gross Calorific Value of Coal and Coke by Microprocessor-Controlled Isoperibol Calorimeters.
[5]ASTM D2015 Standard Test Method for Gross Calorific Value of Solid Fuel by the Adiabatic Bomb Calorimeter.
[6]ASTM D3180 Standard Test Method for Calculating Coal and Coke Analyses from As-Determined to Different Bases.

Use: The SRM must be thoroughly mixed in the original bottle before sampling. Natural materials such as coal tend to segregate with time.

NOTICE TO USERS

The certified calorific value ($MJ \cdot kg^{-1}$) decreases upon the aging and/or normal oxidation of the sample. The National Institute of Standards and Technology (NIST) redetermines the calorific value periodically and revises the Certificate of Analysis. The user must be careful to use the most current certificate. The reference date for the certified calorific value for this SRM is September 1993.

Material Preparation: Approximately twelve hundred 50 g bottles of a bituminous coal were obtained from a commercial supplier under contract to NIST. These coals were prepared according to NIST procurement specifications and protocols.

Homogeneity testing was performed on 12 randomly selected 50 g bottles of coal using X-ray fluorescence spectrometry. Replicate analysis indicated that there was evidence of some heterogeneity for sulfur, amounting to 1.17% relative to the certified sulfur value; calcium showed similar heterogeneity. Other elements determined, Al, Ca, Cu, K, Si, and Zn, showed no heterogeneity.

The homogeneity studies with respect to elemental concentrations were performed by P.A. Pella and A.F. Marlow of the NIST Inorganic Analytical Research Division. The homogeneity with respect to BTU and ash content was assessed from the certification data, for which significant sample to sample variability was observed.

ANALYSIS

Sulfur: The certified sulfur content is based upon the results of thermal ionization isotope dilution mass spectrometry (ID-TIMS). The sulfur determinations were made on as-received samples and corrected to a dry weight basis using results of moisture determined according to ASTM standard method D5142-90. The ID-TIMS results were confirmed by high temperature combustion with infrared detection according to ASTM D4239 Test Method and gravimetry according to ASTM D3177 Test Method.

Calorific Value ($MJ \cdot kg^{-1}$) and Ash Content: The certified value for the calorific value was determined using measurements made in an adiabatic bomb calorimeter following the ASTM D2015 Standard Test Method. The calorimeter is capable of reproducing determinations on benzoic acid to a precision of 0.05% relative, as determined using the standardization procedure outlined in the method with SRM 39i, Benzoic Acid as the calibrant. The uncertainty of the calorific value includes within laboratory variability, material variability, between lab differences, and an allowance for the expected change in calorific value due to aging/oxidiation of the coal for a period of 2 years from the certification date.

Stability: The long-term physical and chemical stability of this SRM, except for the calorific value, has not been rigorously established. The predicted change with time in calorific value for this coal is based on historical data for other low moisture coals which have been certified and monitored for changes in calorific value over the past ten years. It is recommended that the material be stored in the tightly sealed bottle away from sunlight and intense sources of radiation. NIST will continue to monitor this SRM and any substantive change in its certification or analysis will be reported to the user. NIST will recertify the calorific value approximately two years from the reference date of the current measurement (Sept. 1993). It is important that the attached registration form be completed and returned to NIST for obtaining proper notification of calorific value recertification and any other change in the certified values.

Instructions for Drying: The certifications of sulfur and BTU are reported on a dry-weight basis. The recommended procedures for drying are vacuum drying at ambient temperature for 24 h, oven drying for two h at 105 °C, or drying in a controlled dry nitrogen gas environment following ASTM Standard Test Method D5142-90. Samples for sulfur analysis may be analyzed after drying according to one of these procedures, or analyzed as received, with results corrected for moisture. Calorific values are always obtained on as-received samples and corrected to a dry-weight basis. The typical moisture loss for SRM 2692a using the recommended drying procedures is approximately 1.5-1.6%.

SUPPLEMENTAL INFORMATION

SRM 2692a was analyzed by more than 70 laboratories participating in the Canada Center for Mineral and Energy Technology (CANMET) program for the evaluation of coal codes and standards. Data from that program [3] provides information on the chemical composition of this coal. The values, which are not certified, are given in Table 2.

Table 2. Non-Certified Values

	Concentration in Wt. %		Concentration in mg/kg
C	(79.45)	As	(15)
H	(4.97)	Be	(6)
N	(1.32)	Cd	(0.6)
Al	(1.08)	Co	(8)
Ca	(0.080)	Cr	(12)
Fe_{Tot}	(0.77)	Cu	(19)
K	(0.23)	Hg	(0.20)
Mg	(0.079)	Mn	(17)
Na	(0.029)	Ni	(17)
P	(0.003)	Pb	(7)
Si	(1.82)	V	(27)
Ti	(0.049)	Zn	(21)

REFERENCES

[1] *"Guide to the Expression of Uncertainty in Measurement"*, ISBN 92-67-10188-9, 1st Ed. ISO, Switzerland, 1993.

[2] Canspec 40 Coal Report, March 10, 1994, Natural Resources Canada, Energy Research Laboratories, CANMET, Ottawa, Canada.