National Bureau of Standards

Certificate of Analysis

Standard Reference Materials 2682, 2683, 2684, and 2685

Sulfur in Coal

These Standard Reference Materials (SRM's) are intended primarily for use as analytical standards for the-determination of sulfur in coal. In addition to sulfur they are certified for their ash content and calorific value ($MJ \cdot kg^{-1}$) except for SRM 2682. The Higher Heating Value-Moisture Free (HHV2) for SRM 2682 was removed from certification because the HHV2 value of the bottled material is changing at an unpredictable rate.

SRM's 2682-2685 each consists of a 50-g bottle of a different coal composition. Each material was ground to pass a 60-mesh sieve and homogenized. The certification of the materials for sulfur is based on at least a 250-mg sample of the dried material, the minimum amount that should be used for analysis (see drying instructions). The calorific values were determined using procedures recommended in ASTM methods (see references in Table 1). The certified values for the four different coals are given in Table 1 along with methods used for certification. Noncertified values for major and minor elements are given in Table 2. These values are provided for information only.

Notice to Users: The certified calorific values ($MJ \cdot kg^{-1}$) decreases upon the aging or normal oxidation of the coals. NBS redetermines these values each year and revises the Certificate of Analysis. The user must be careful to use the most current revised certificate. The reference date for the calorific data in this revised certificate is October 1987.

Certification analyses were performed by W.R. Kelly, W.F. Koch, P.J. Paulsen, and J.W. Stolz of the Inorganic Analytical Research Division and J.C. Colbert and D.R. Kirklin of the Chemical Thermodynamics Division.

Analyses for supplemental information were performed in the Inorganic Analytical Research Division by R. Fleming, R. Greenberg, and R.M. Lindstrom.

The statistical analysis of the certification data was performed by R.C. Paule of the National Measurement Laboratory.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of E.L. Garner.

The technical and support aspects involved in the preparation, certification, and issuance of these Standard Reference Materials were coordinated through the Office of Standard Reference Materials by T.E. Gills.

October 30, 1987
Gaithersburg, MD 20899
(Revision of Certificates
dated 12-14-82, 2-7-83,
2-25-85, and 6-30-86)

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

Table 1

Certified Values for SRM's 2682, 2683, 2684, and 2685

SRM No.	Coal Type	Sulfur[1,2,3] Wt. %	Furnace[4] Ash Wt. %	HHV2[5,6] $MJ \cdot kg^{-1}$ (Btu. lb^{-1})
2682	Subbituminous	0.47 ± 0.03	6.37 ± 0.18	
2683	Bituminous	1.85 ± 0.06	6.85 ± 0.02	32.40 ± .16 (13930 ±70)
2684	Bituminous	3.00 ± 0.13	11.09 ± 0.18	29.03 ± .46 (12480 ±200)
2685	Bituminous	4.62 ± 0.18	16.53 ± 0.15	27.38 ± .35 (11770 ±150)

1 ASTM D3177 Standard Test Method for Total Sulfur in the Analysis Sample of Coal and Coke.
2 Ion Chromatography with Bomb Combustion.
3 Thermal Ionization Mass Spectrometry, Sealed Glass Tube Digestion.
4 ASTM D3174 Standard Test Method for Ash in the Analysis Sample of Coal and Coke.
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.
7 ASTM D3173 Standard Test Method for Moisture in the Analysis Sample of Coal and Coke.

The uncertainty of a certified value, except the calorific value, is expressed as two times the standard error and includes observed variability within and between measurement methods and any observed material heterogeneity. For the certified calorific values the uncertainty is expressed as two times the standard deviation for the certified HHV2 value. The uncertainty includes the observed variability within and between HHV2 measurements, as well as any observed sample heterogeneity. An allowance for sample degradation, equivalent to one year's degradation, has also been added to the uncertainty.

PREPARATION AND TESTING

Approximately 900 kg of coal was obtained from each of four different coal mine locations. All coals were oven dried prior to processing in accordance with procedures outlined in ASTM D2013. At least 500 kg of each of the four coals were reduced in size to -60 mesh and screened prior to blending. Each of the -60 mesh coals was blended in a stainless steel cone blender (approximate capacity 0.85 cubic meter). The coals were then bottled into individual 50-g units. Homogeneity testing was done on both the bulk materials and 50-g bottled units using x-ray fluorescence analysis. Replicate analyses indicated the material variability for sulfur to be within ± 2% (relative) for all four SRM's.

The homogeneity studies were performed by T.E. Gills and M. Watson of the Office of Standard Reference Materials and P.A. Pella of the Gas and Particulate Science Division.

ANALYSIS

Sulfur: The certified sulfur content is based upon the results of 3 independent methods of analysis: ion chromatography, gravimetry, and thermal ionization mass spectrometry. Agreement with the certified values was found using 2 additional independent techniques, prompt-gamma activation analysis, and a combustion IR technique.

Calorific value ($MJ \cdot kg^{-1}$) and Ash Content: The certified values for the calorific values and ash contents were determined using measurements made in an adiabatic bomb calorimeter of the type used in commercial laboratories. This calorimeter is capable of reproducing determinations on benzoic acid to a precision of 0.07% (relative). This statement of precision was arrived at by averaging 5 measurements made on the calorimeter using a benzoic acid standard that is traceable to NBS-SRM 39i, Benzoic Acid.

Major and Minor Elements: Analyses for major and minor elements were performed using thermal neutron activation analysis and neutron capture gamma-ray activation analysis. These values, provided as Supplemental Information (Table 2) are not certified but are to be used for information only.

STABILITY

The long-term physical and chemical stability of these SRM's has not been rigorously established. However, NBS recommends that the material be stored in the tightly sealed bottle away from sunlight and intense sources of radiation. NBS will continue to monitor these materials and any substantive change in their certification or analysis will be reported to the purchaser.

INSTRUCTIONS FOR DRYING

The certification of sulfur in these SRM's is based upon a properly dried sample. The recommended procedures for drying are vacuum drying at ambient temperature for 24 hours or oven drying for 2 hours at 105 °C. Typical moisture losses using the recommended methods for drying are the following: SRM 2682, 18%; SRM 2683, 1.4%; SRM 2684, 3.6%; and SRM 2685, 1.8%. However, for the calorific values, the ASTM D3173 Method is to be used wherein a moisture determination is made on a duplicate analysis sample of coal and the moisture value is used for calculating the calorific value to a dry basis.

SUPPLEMENTAL INFORMATION

The values listed in Table 2 are based on measurements made using a single method or technique and are given for information only. While no reason exists to suspect systematic bias in these numbers, no attempt was made to determine if such bias attributable to the methods exists.

The analyses of SRM's 2682-2685 for major and minor elements were made using NBS SRM's 1632a and 1635, Trace Elements in Coal, as controls.

Table 2

Noncertified Concentrations of
Inorganic Constituents in SRM's 2682, 2683, 2684, and 2685

Mean Concentrations (μg/g) Unless Noted

Element/SRM	2682	2683	2684	2685
Al %	0.46	0.86	1.1	1.7
As	1.0	3.6	3.9	12
B	39	67	114	109
Ba	382	71	41	105
Br	3.7	17	11	5.6
C %	75	79	68	66
Ca %	1.1	0.20	0.44	0.52
Ce	10	9	12	18
Co	1.7	2.2	3.9	4.6
Cr	15	11	17	22
Cs	<0.1	0.4	1.2	1.3
Eu	0.17	0.18	0.23	0.36
Fe %	0.24	0.76	1.5	2.9
H %	4.7	5.0	4.8	4.6
Hf	0.60	0.42	0.57	0.91
K %	0.01	0.08	0.20	0.26
La	5.2	5.1	6.7	10
Mg %	0.2	0.05	0.08	0.1
Mn	26	13	36	41
N %	0.8	1.6	1.6	1.1
Na %	0.10	0.05	0.03	0.08
Rb	<2	5.3	15	17
Sb	0.19	0.28	0.35	0.36
Sc	1.5	1.9	2.7	3.7
Se	0.91	1.2	1.9	1.9
Sm	0.78	0.86	1.1	1.7
Th	1.5	1.4	2.0	2.7
Ti %	0.05	0.04	0.06	0.09
U	0.52	0.42	0.90	0.95
V	15	14	22	31
W	1.8	0.48	0.56	1.2
Zn	8.6	9.5	110	17