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## NBS SPECIAL PUBLICATION 260-94

U.S. DEPARTMENT OF COMMERCE/National Bureau of Standards

*Standard Reference Materials:*

### **Methods and Procedures Used at the National Bureau of Standards To Certify Sulfur in Coal SRM's for Sulfur Content, Calorific Value, Ash Content**

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he National Bureau of Standards<sup>1</sup> was established by an act of Congress on March 3, 1901. The Bureau's overall goal is to strengthen and advance the nation's science and technology and facilitate their effective application for public benefit. To this end, the Bureau conducts research and provides: (1) a basis for the nation's physical measurement system, (2) scientific and technological services for industry and government, (3) a technical basis for equity in trade, and (4) technical services to promote public safety. The Bureau's technical work is performed by the National Measurement Laboratory, the National Engineering Laboratory, the Institute for Computer Sciences and Technology, and the Center for Materials Science.

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Provides the national system of physical and chemical measurement; coordinates the system with measurement systems of other nations and furnishes essential services leading to accurate and uniform physical and chemical measurement throughout the Nation's scientific community, industry, and commerce; provides advisory and research services to other Government agencies; conducts physical and chemical research; develops, produces, and distributes Standard Reference Materials; and provides calibration services. The Laboratory consists of the following centers:

- Basic Standards<sup>2</sup>
- Radiation Research
- Chemical Physics
- Analytical Chemistry

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Provides technology and technical services to the public and private sectors to address national needs and to solve national problems; conducts research in engineering and applied science in support of these efforts; builds and maintains competence in the necessary disciplines required to carry out this research and technical service; develops engineering data and measurement capabilities; provides engineering measurement traceability services; develops test methods and proposes engineering standards and code changes; develops and proposes new engineering practices; and develops and improves mechanisms to transfer results of its research to the ultimate user. The Laboratory consists of the following centers:

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- Fire Research
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Conducts research and provides measurements, data, standards, reference materials, quantitative understanding and other technical information fundamental to the processing, structure, properties and performance of materials; addresses the scientific basis for new advanced materials technologies; plans research around cross-country scientific themes such as nondestructive evaluation and phase diagram development; oversees Bureau-wide technical programs in nuclear reactor radiation research and nondestructive evaluation; and broadly disseminates generic technical information resulting from its programs. The Center consists of the following Divisions:

- Inorganic Materials
- Fracture and Deformation<sup>3</sup>
- Polymers
- Metallurgy
- Reactor Radiation

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<sup>1</sup>Headquarters and Laboratories at Gaithersburg, MD, unless otherwise noted; mailing address Gaithersburg, MD 20899.

<sup>2</sup>Some divisions within the center are located at Boulder, CO 80303.

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# Methods and Procedures Used at the National Bureau of Standards To Certify Sulfur in Coal SRM's for Sulfur Content, Calorific Value, Ash Content

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Thomas E. Gills, Editor

Office of Standard Reference Materials  
National Measurement Laboratory  
National Bureau of Standards  
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## PREFACE

As part of its congressional mandate, the National Bureau of Standards (NBS) is charged with the essential function of preparing and distributing reference materials for use in chemical analysis and the development of methods for chemical analysis. At NBS, the Office of Standard Reference Materials brings together "state-of-the-art" measurement methods and homogeneous, stable materials to produce Standard Reference Materials (SRM's). These SRM's are used by laboratories around the world to calibrate instruments, to test the accuracy of new methods, and in routine programs of measurement quality assurance.

One of the most important facets of NBS SRM's is that certification is given at a stated level of accuracy. This is generally accomplished using one or more of three modes: reference methods, two or more independent methods, or interlaboratory comparison.

The Sulfur-in-Coal SRM's are certified through measurements performed in the NBS National Measurement Laboratory. Systematic and random errors of the methods used were sufficiently well known to provide an uncertainty level for each property certified. We hope this publication of methods and procedures will help other analysts to perform measurements with accuracy comparable to those obtained during certification.

Stanley D. Rasberry, Chief  
Office of Standard  
Reference Materials

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# 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 calorific value ( $\text{MJ}\cdot\text{K}^{-1}$ ) and ash content. 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 by procedures recommended in standard ASTM methods (see references in Table 1). The certification data 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: These SRM's are sold individually rather than in sets; however, only one Certificate of Analysis is provided. Therefore, the user must be careful to use the data specific to the SRM being used.

The uncertainty of a certified 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 heating values the uncertainty also includes additional allowances for possible limited sample degradation due to aging or normal oxidation.

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, Chief of the Inorganic Analytical Research Division.

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.

February 7, 1983  
(Revision of Certificate  
dated 12-14-82)

(over)

George A. Uriano, Chief  
Office of Standard Reference Materials

Table 1  
 Certified Values for SRM's 2682, 2683, 2684, and 2685

SRM No.	Coal Type	Sulfur <sup>1,2,3</sup> Wt. %	Furnace <sup>4</sup> Ash Wt. %	HHV <sub>2</sub> <sup>5,6</sup> MJ·Kg <sup>-1</sup> (BTU·lb <sup>-1</sup> )
2682	Sub-bituminous	0.47 ± 0.03	6.37 ± 0.18	27.45 ± 0.56 (11800 ± 240)
2683	Bituminous	1.85 ± 0.06	6.85 ± 0.02	32.70 ± 0.14 (14060 ± 60)
2684	Bituminous	3.00 ± 0.13	11.09 ± 0.18	29.68 ± 0.47 (12760 ± 200)
2685	Bituminous	4.62 ± 0.18	16.53 ± 0.15	28.15 ± 0.42 (12100 ± 180)

<sup>1</sup> ASTM D3177 Standard Test Method for Total Sulfur in the Analysis Sample of Coal and Coke

<sup>2</sup> Ion Chromatography with Bomb Combustion

<sup>3</sup> Thermal Ionization Mass Spectrometry, Sealed Glass Tube Digestion

<sup>4</sup> ASTM D3174, Standard Test Method for Ash in the Analysis Sample of Coal and Coke

<sup>5</sup> ASTM D2015 Standard Test Method for Gross Calorific Value of Solid Fuel by the Adiabatic Bomb Calorimeter

<sup>6</sup> ASTM D3180 Standard Test Method for Calculating Coal and Coke Analyses from As-Determined to Different Bases

HHV<sub>2</sub> (Higher Heating Value - Moisture Free)

Note: The calorific values (MJ·Kg<sup>-1</sup>) may decrease upon the aging or normal oxidation of the coals. NBS will continue to monitor these calorific values and report any substantive change to the purchaser. The uncertainty of the heating value includes an additional allowance of 0.12 MJ·Kg<sup>-1</sup> for possible sample degradation. The reference date for the calorific data is October 1982.

#### PREPARATION AND TESTING

Approximately one ton 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 1000 pounds 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 packaged into individual 50-g bottled units. Homogeneity testing was done on the bulk materials and 50-g bottled units. The homogeneity analyses were performed 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 ( $\text{MJ}\cdot\text{Kg}^{-1}$ ) 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 calibrations made on the calorimeter using a benzoic acid standard that is traceable to the NBS SRM 39i, Benzoic Acid.

Major and Minor Elements: Analyses for major and minor elements were performed by thermal neutron activation analysis and neutron capture gamma-ray activation analysis. These values 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 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 24 hours at 105 °C. Typical moisture loss using the recommended methods for drying are the following: SRM 2682, 1.8%; SRM 2683, 1.4%; SRM 2684, 3.6%; and SRM 2685, 1.8%.

### SUPPLEMENTAL INFORMATION

The values listed below 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  
 Inorganic Constituents in SRM's 2682, 2683, 2684, and 2685  
 Mean Concentrations ( $\mu\text{g/g}$ ) 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

METHODS AND PROCEDURES USED AT THE  
NATIONAL BUREAU OF STANDARDS TO CERTIFY  
SULFUR IN COAL SRM'S FOR SULFUR  
CONTENT, CALORIFIC VALUE, ASH CONTENT

Thomas E. Gills, Editor

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ABSTRACT

This Special Publication consists of a collection of analytical methods used at NBS for the determination of total sulfur, calorific value, and ash content in four different coals, SRM's 2682, 2683, 2684, and 2685, with nominal sulfur contents of 0.5, 2.0, 3.0, and 4.5 percent, respectively. Also, included are descriptions of methods and procedures used for providing noncertified values for approximately 30 elements including carbon, hydrogen, and nitrogen. These procedures were selected and often specifically developed, by the scientific staff members of NBS, to provide measurements with the best obtainable accuracy and precision.

The materials for these SRM's were obtained and processed by Valley Forge Laboratories under a grant from the National Bureau of Standards. Material preparation of the four coal SRM's is described in NBS Special Publication 260-84, "Sampling, Materials Handling, Processing, and Packaging of Standard Reference Coal Materials."

Key Words: analytical procedures; coal analysis; gravimetry; ion chromatography; isotope dilution thermal ionization mass spectrometry; prompt gamma activation analysis; sample preparation; thermal neutron activation analysis.

DISCLAIMER

In order to describe adequately materials and experimental procedures discussed in this work, it was occasionally necessary to identify commercial products by manufacturer's name or label. In no instance does such identification imply endorsement by NBS of the particular product or equipment as being best available for that purpose.

## INTRODUCTION

Recently, there have been some important developments in coal utilization technology in the areas of coal liquefaction, coal gasification, and advanced methods of coal combustion to generate electric power. Equally important, the combustion of coal produces an ash which may offer an economical raw material for resource recovery. The problems associated with these activities, i.e., environmental pollution, have mandated new approaches to produce more efficient and cleaner coal combustion technologies. In response to these newer technologies, new techniques and methods have emerged to serve as monitors of the coal composition, combustion processes, and coal combustion by-products.

As part of its environmental and energy standards program, NBS has produced a series of four new coal SRM's, 2682, 2683, 2684, and 2685, certified for sulfur content, heating value and ash content. Additionally, noncertified values, for information only, were determined for approximately 30 elements and/or constituents. These materials are intended primarily for use as analytical standards to evaluate methods and procedures used in routine coal analyses.

This Special Publication is a collection of the analytical methods used at NBS to certify and analyze these SRM's. These methods include: ion chromatography, isotope dilution thermal ionization mass spectrometry, neutron capture prompt-gamma activation analysis, thermal neutron activation analysis and ASTM methods for coal analyses, D2015, D3180, D3177, D3173, D3174, and D1552. The certified values are based on the use of two or more of these independent methods of analysis or an ASTM reference method. The noncertified values are based on a single method of analysis and are provided for information only.

The materials for these SRM's were procured and processed as part of a grant to Valley Forge Laboratories and Webster and Associates. The details of the collection processing and preparation of the base materials for these SRM's are documented in NBS Special Publication 260-84 "Sampling, Materials Handling, Processing, and Packaging of NBS Sulfur in Coal Standard Reference Materials."

The analytical methods described in this publication are believed to provide the best measuring capabilities available at this time. However, they will be reviewed periodically and the certified values updated as a part of the NBS update certification program.



## SECTION I

### Determination of Sulfur in NBS Coals by Ion Chromatography

W. F. Koch and J. W. Stolz

Six bottles of each of four levels of coal (SRM's 2682-5) were analyzed for sulfur content by ion chromatography. Single analyses were done on two bottles and duplicate analyses were carried out on the remaining four bottles. The sequence of analysis was randomized; however, each level used the identical sequence. The order of analysis is indicated in Tables 1-4. SRM's 1635 and 1632a, Trace Elements in Coal, were run as controls. In addition, an alternate drying procedure was investigated on four bottles at each level.

Drying: Samples were dried for 24 hours in a vacuum drying oven at 23 °C, final pressure 15 microns. A liquid nitrogen cold trap was between the pump and the oven. The alternate procedure was to dry at 105 °C at atmospheric pressure.

Combustion: Samples of 250 mg were combusted in a high-pressure oxygen calorimetric bomb (30 atm. O<sub>2</sub>, 20 mL H<sub>2</sub>O scrubber) and then diluted with a carbonate buffer solution. Quantitative transfer of the sample from the bomb was not required.

Ion Chromatography: After dilution, the samples were injected into the ion chromatograph through a 0.2 micron syringe filter. SRM's 2682-4 were analyzed using standard anion separator columns; SRM 2685 was analyzed on new fast-run columns. The following conditions were employed: eluent, 3 mmol/L NaHCO<sub>3</sub> and 2 mmol/L Na<sub>2</sub>CO<sub>3</sub>; flow rate 2.5-3 mL/min.; suppressor column regenerated with H<sub>2</sub>SO<sub>4</sub>. Calibrant-solutions were prepared from coulometrically standardized sulfuric acid. For each level, three calibrants were prepared which bracketed the concentration of sulfate in the combusted and diluted samples. Quantitation was by interpolation of the calibration curve, peak height versus concentration. Calibration sets were run before every second sample. Each sample was injected twice in alternate calibration sets.

Results: The results are detailed in Tables 1-5 and summarized in Table 6. Vacuum drying and drying at 105 °C can be used without changing the value of the sulfur content.

Table 1  
Sulfur in Coal, SRM 2682  
by Ion Chromatography

<u>Sample #</u>	<u>Weight Loss</u> <u>%</u>	<u>Sulfur</u> <u>Wt. %</u>
<u>A</u>		
1227-1	18.9	0.466
410-1	15.3	0.465
1227-2	19.0	0.468
1500	19.0	0.474
398	19.1	0.457
410-2	14.5	0.472
241-1	18.8	0.450
809-1	19.1	0.470
241-2	19.1	0.478
809-2	<u>19.2</u>	<u>0.469</u>
	Mean = 18.2	0.467
	Std. Dev.* = 1.8	0.008
<u>B</u>		
1635-1	10.6	0.326
1635-2	20.3	0.349
<u>C</u>		
1227-3	18.8	0.473
1227-4	18.9	0.466
410-3	14.8	0.468
809-3	<u>18.8</u>	<u>0.456</u>
	Mean = 17.8	0.466
	Std. Dev.* = 2.0	0.007

A - Dried in vacuum oven, 23 °C

B - Controls, SRM 1635

C - Dried at 105 °C

\*Standard Deviation for a single measurement

Table 2  
Sulfur in Coal, SRM 2683  
by Ion Chromatography

<u>Sample #</u>	<u>Weight Loss</u> %	<u>Sulfur</u> Wt. %
<u>A</u>		
1227-1	1.11	1.82
410-1	1.72	1.84
1227-2	1.41	1.90
1500	1.78	1.90
398	1.71	1.85
410-2	1.77	1.90
241-1	1.12	1.85
809-1	1.19	1.82
241-2	1.25	1.89
809-2	<u>1.20</u>	<u>1.86</u>
	Mean = 1.43	1.86
	Std. Dev.* = 0.29	0.03
<u>B</u>		
1632a-1	2.62	1.56
1632a-2	2.83	1.59
1632a-3	1.33	1.58
1632a-4	1.29	1.59
<u>C</u>		
1227-3	1.07	1.874
1227-4	1.14	1.873
410-3	1.67	1.870
809-3	<u>1.09</u>	<u>1.872</u>
	Mean = 1.24	1.872
	Std. Dev.* = 0.29	0.002

A - Dried in vacuum oven, 23 °C

B - Controls, SRM 1632a

C - Dried at 105 °C

\*Standard Deviation for a single measurement

Table 3  
Sulfur in Coal, SRM 2684  
by Ion Chromatography

<u>Sample #</u>	<u>Weight Loss</u> %	<u>Sulfur</u> Wt. %
<u>A</u>		
1227-1	4.20	3.05
410-1	3.77	3.06
1227-2	4.06	3.03
1500	3.98	3.10
398	3.40	3.05
410-2	3.82	3.03
241-1	2.93	3.03
809-1	3.64	3.04
241-2	3.00	3.02
809-2	<u>3.59</u>	<u>3.03</u>
	Mean = 3.64	3.04
	Std. Dev.* = 0.43	0.02
<u>B</u>		
1632a-5	1.91	1.58
1632a-6	2.00	1.56
<u>C</u>		
1227-3	3.54	2.98
1227-4	3.52	3.03
410-3	3.23	3.06
809-3	<u>3.10</u>	<u>3.05</u>
	Mean = 3.35	3.03
	Std. Dev.* = 0.22	0.04

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A - Dried in vacuum oven, 23 °C

B - Controls, SRM 1632a

C - Dried at 105 °C

\*Standard Deviation for a single measurement

Table 4  
Sulfur in Coal, SRM 2685  
by Ion Chromatography

<u>Sample #</u>	<u>Weight Loss</u> <u>%</u>	<u>Sulfur</u> <u>Wt. %</u>
<u>A</u>		
1227-1	1.78	4.70
410-1	1.83	4.56
1227-2	1.77	4.70
1500	1.92	4.66
398	1.90	4.70
410-2	1.75	4.68
241-1	2.03	4.66
809-1	1.69	4.61
241-2	1.77	4.55
809-2	<u>1.80</u>	<u>4.69</u>
	Mean = 1.82	4.65
	Std. Dev.* = 0.10	0.06
<u>B</u>		
1632a-7	2.06	1.57
1632a-8	2.00	1.57
<u>C</u>		
1227-3	----	4.63
1227-4	1.31	4.61
410-3	1.17	4.61
809-3	<u>1.11</u>	<u>4.63</u>
	Mean = 1.20	4.62
	Std. Dev.* = 0.10	0.01

A - Dried in vacuum oven, 23 °C

B - Controls, SRM 1632a

C - Dried at 105 °C

\*Standard Deviation for a single measurement

Table 5

## Sulfur in Coal, Control Standards

<u>SRM #</u>	<u>Sulfur Wt. %</u>
<u>A</u>	
1635-1	0.326
1635-2	<u>0.349</u>
Mean = 0.338	
Certified Value = 0.33 ± 0.03	
<u>B</u>	
1632a-1	1.56
1632a-2	1.59
1632a-3**	1.58
1632a-4**	1.58
1632a-5	1.58
1632a-6	1.56
1632a-7	1.57
1632a-8	<u>1.57</u>
Mean = 1.57	
Std. Dev.* = 0.01	
Certified Value = 1.58 ± 0.04	

\*Standard Deviation for a single measurement

\*\* - Dried at 105 °C for 2 hours.  
All others were dried at 23 °C in a vacuum oven (P < 50 microns).

Table 6

Summary of Sulfur in Coal  
by Ion Chromatography

<u>SRM #</u>	<u>Sulfur, Wt. % Vacuum Drying</u>	<u>n</u>	<u>Sulfur, Wt. % 105 °C Drying</u>	<u>n</u>
2682	0.467 ± 0.008*	10	0.466 ± 0.007*	4
2683	1.86 ± 0.03*	10	1.872 ± 0.002*	4
2684	3.04 ± 0.02*	10	3.03 ± 0.04*	4
2685	4.65 ± 0.06*	10	4.62 ± 0.01*	4

\* Standard deviation of a single measurement

## SECTION II

### Determination of Sulfur in NBS Coals by Isotope Dilution Thermal Ionization Mass Spectrometry

W. R. Kelly and P. J. Paulsen

Sulfur was determined in four different NBS coal SRM's by isotope dilution thermal ionization mass spectrometry. In this procedure the relative sulfur isotopic abundances were measured as the thermally produced  $AsS^+$  molecular ion. This technique is capable of measuring sulfur over a wide concentration range in a variety of matrices with relative measurement precisions of 0.1 percent (1s). The application of this technique to the determination of Sulfur in Coal SRM's is presented. Additional information is given in papers by Paulsen and Kelly [1] and Kelly and Paulsen [2].

#### Experimental Procedure

##### Sample Preparation and Dissolution

For each SRM approximately 0.7 g of coal from six different bottles were placed in weighing bottles for drying. In the case of SRM 2682, which has a high moisture content, the material in the weighing bottles was pre-dried in a desiccator over  $Mg(ClO_4)_2$  for 46 hours at room temperature. The weight losses ranged from 14.9-16.3 percent. All samples were then dried in two groups at room temperature: (1) SRM's 2682, 2683, and (2) SRM's 2684, 2685. After 24 hours of pumping, the pressure in the vacuum oven, as measured by a thermocouple, was 14 microns Hg for the first group and 10 microns Hg for the second group. The weight losses for each sample are given in Tables 2-6.

Weighed samples of about 0.1-0.2 g of dried coal were transferred to modified Carius tubes using a glass transfer boat. Approximately  $1 \mu g$  of  $^{34}S$  enriched tracer per 3  $\mu g$  natural S was added by weight to each sample followed by 10 g of  $HNO_3$  and 4g HCl. The acids and water used in these procedures were produced at NBS by subboiling distillation [3] unless otherwise noted. The tubes were cooled immediately to  $-78^\circ C$  in a  $CO_2-CCl_4-CHCl_3$  slush and sealed with a gas-oxygen torch. Each sealed tube along with 25 g of solid  $CO_2$  was placed in a steel shell equipped with a threaded cap. The shells were sealed and placed in an oven at  $240^\circ C$  for 24 hours. This process completely dissolved the organic fraction of the coal and oxidized all S to sulfate which insures equilibration of tracer and natural sulfur isotopes. After the steel shells were cooled to room temperature, the Carius tubes were removed and placed behind an explosion shield. The Carius tubes were cooled again to  $-78^\circ C$  and the neck heated with a torch until a small vent blew open and released the internal pressure. Each tube was scored 5 cm below the shoulder and fire opened. The samples were transferred to 50 mL beakers, covered with watch glasses, placed on a hotplate under a glass dome (3 L volume), which was continuously purged with dry  $N_2$  (2 L/min), and evaporated to dryness. Two mL of HCl were added to rinse the side of each beaker and the samples were heated to dryness. The last step was repeated twice using 1 mL HCl each time. The repeated additions of HCl destroy all nitrates which would interfere with the reduction step. The dried sample was dissolved in 5 mL HCl.

##### Reduction of Sulfate to $H_2S$ and Precipitation as $As_2S_3$

The sulfur in each sample was reduced to  $H_2S$  using hypophosphorous acid as the reducing agent. A master reducing solution was made from a mixture of ACS Reagent Grade  $H_3PO_2$  (61 mL), HCl (205 mL), and HI (125 mL) [1].

Twenty-five mL of the master solution was added to each reduction flask and refluxed at  $120^\circ C$  for 45 min. After the solution cooled to room temperature, the dissolved samples were added and refluxed for 45 min. The  $H_2S$  formed was flushed from the flask and passed through a 5 mL distilled water trap and was then trapped in a 15 mL centrifuge tube containing 1 mL aqueous ammonia solution and  $1000 \mu g As^{+3}$ . During the collection step the  $NH_3-As^{+3}$  solution was cooled in an ice bath to retard the loss of  $NH_3$ . The trapped S was precipitated as  $As_2S_3$  by the dropwise addition of HCl to the solution. The precipitate was centrifuged for 10 min to insure that all particles of  $As_2S_3$  were removed from the solution. The supernate, which contained a large amount of dissolved  $NH_4Cl$ , was removed with a pipet. The  $As_2S_3$  was washed 5 times with 5 mL portions of distilled water. The washed  $As_2S_3$  was dissolved in an  $As-NH_3$  solution to a S concentration of  $100 \mu g S/mL$  and an As/S atom ratio of 2. This solution was used for the ratio measurement by mass spectrometry.

## Mass Spectrometry

Sample loading was performed in a plastic box flushed with  $N_2$  to prevent sulfur contamination from ambient air. About  $1.5 \mu\text{g S}$  and about  $100 \mu\text{g}$  silica gel were added to a rhenium flat filament and  $\text{AsS}^+$  ions were thermally ionized at  $950^\circ\text{C}$ .

The zone refined rhenium filaments were outgassed at  $1500^\circ\text{C}$  at  $10^{-7}$  torr for 1/2 hour and stored overnight before use. The silica gel was prepared from high purity quartz that was fused with  $\text{Na}_2\text{CO}_3$  and washed repeatedly with quartz distilled water. A mixture of silica gel and  $\text{H}_3\text{PO}_4$  was prepared, which contained  $20 \text{ mg silica gel/mL of } 0.4\text{M H}_3\text{PO}_4$ . This mixture was neutralized with high purity  $\text{NH}_3$ . The  $\text{H}_3\text{PO}_4$  was prepared from high purity  $\text{P}_2\text{O}_5$  and quartz distilled water.

A detailed description of the sample loading and mass spectrometric measurement procedure is given below. The silica gel- $\text{H}_3\text{PO}_4$  solution is shaken vigorously to disperse the silica gel and  $1 \text{ cm } (5 \mu\text{L})$  is drawn into a  $5 \text{ cm}$  length of intermedic tubing and placed in the center of the filament. A current of  $0.9 \text{ A}$  is passed through the filament until the silica gel is dry and then heated an additional  $15 \text{ sec}$ . A  $3 \text{ cm}$  length (equivalent to  $1.5 \mu\text{g S}$ ) of the sample solution is drawn into the tubing and added as single drops to the dried silica gel. After the first drop is added the filament current is adjusted to  $1.5 \text{ A}$ . The silica gel will break up and disperse within the sample drop. The remainder of the sample is added without allowing the solution on the filament to evaporate to dryness between additions. After the sample is dry it is heated for  $15 \text{ sec}$ . The current is increased and the sample dried at approximately  $700^\circ\text{C}$  for  $5 \text{ sec}$ . No fumes are observed during this final heating step. If excess  $\text{H}_3\text{PO}_4$  is present and fumes of  $\text{P}_2\text{O}_5$  are observed, it causes decomposition of  $\text{As}_2\text{S}_3$  and the loss of sulfur as  $\text{H}_2\text{S}$ . For this reason the silica gel and  $\text{H}_3\text{PO}_4$  were premixed (neutralized with  $\text{NH}_3$ ) in a ratio designed to maximize both signal intensity and stability while avoiding excess amounts of  $\text{H}_3\text{PO}_4$ .

The sample is loaded into the mass spectrometer with a total exposure to room atmosphere of two minutes or less. Heating of the filament is started when the pressure drops below  $2 \times 10^{-7}$  torr. A liquid  $N_2$  cold finger is used to reduce the pressure in the source. The filament is initially heated to  $800^\circ\text{C}$  which typically gives a  $\text{AsS}^+$  beam of 2 to 5 volts with a  $10^{14}\Omega$  feedback resistor. At this temperature the signal is decaying rapidly. The filament temperature is increased to  $950^\circ\text{C}$  in  $50^\circ\text{C}$  increments at  $5 \text{ min. intervals}$ . The source is focused for maximum intensity after each temperature adjustment. The ion current at  $950^\circ\text{C}$  is stable and normally in the  $10\text{V}$  range. Larger ion currents can be obtained above  $950^\circ\text{C}$  but they are unstable. The signal increases and then decays after each temperature increase. Data collection commences at  $30 \text{ min}$ . The major isotope is either on the  $10\text{V}$  or  $3\text{V}$  scale and decaying at a moderate rate ( $5\%/ \text{min.}$ ). Three data sets are collected. Each data set consists of 6 integrations of the mass 107 current and 5 integrations of the mass 109 current using an integration time of  $15 \text{ sec}$ . Delay times of  $14 \text{ sec}$  and  $10 \text{ sec}$  are used for ratios of 20/1 and 1/1, respectively. Background signals and electronic offsets are read before each set. Typical precision for a single set is  $0.05 \text{ percent (1s)}$ . During the 21 minutes of data collection, the observed decrease in the 107/109 ratio as a result of isotopic fractionation is less than  $0.1 \text{ percent}$ .

## Results and Discussion

Isotope dilution is based upon the equilibration of a known amount of enriched isotope with the isotopes of the element being determined and the measurement of the isotopic ratio of the resulting mixture. Sulfur has four stable isotopes with the following abundances:  $^{32}\text{S}$  95 percent,  $^{33}\text{S}$  0.75 percent,  $^{34}\text{S}$  4.2 percent, and  $^{36}\text{S}$  0.02 percent. Using sulfur enriched in  $^{34}\text{S}$  as the tracer, the most precise data are obtained by measuring the  $^{32}\text{S}/^{34}\text{S}$  ratio. The measured ratio in the mixture is given by the following equation:

$$\left(\frac{^{32}\text{S}}{^{34}\text{S}}\right)_m = \frac{\left(\frac{^{32}\text{S}}{^{34}\text{S}}\right)_{\text{sample}} + \left(\frac{^{32}\text{S}}{^{34}\text{S}}\right)_{\text{tracer}}}{\left(\frac{^{34}\text{S}}{^{34}\text{S}}\right)_{\text{sample}} + \left(\frac{^{34}\text{S}}{^{34}\text{S}}\right)_{\text{tracer}}} \quad (1)$$

Equation (1) can be rearranged to give the following:

$$\left(\frac{^{32}\text{S}}{^{34}\text{S}}\right)_{\text{sample}} = \left(\frac{^{34}\text{S}}{^{34}\text{S}}\right)_{\text{tracer}} \frac{\left(\frac{^{32}\text{S}}{^{34}\text{S}}\right)_t - \left(\frac{^{32}\text{S}}{^{34}\text{S}}\right)_m}{\left(\frac{^{32}\text{S}}{^{34}\text{S}}\right)_m \left(\frac{^{32}\text{S}}{^{34}\text{S}}\right)_s - 1} \quad (2)$$



It is obvious from equation (2) that to determine the moles of  $^{32}\text{S}$  in the sample, only ratios need be measured and, therefore, the accuracy of an isotope dilution determination is independent of chemical yields provided blanks are relatively small. The concentration of sulfur in a sample is given by the following relation:

$$\mu\text{g of S/g} = \frac{(^{32}\text{S})_s(\text{at.wt})}{(^{32}\text{A})_s(\text{wt})_s} \times 10^6 \quad (3)$$

where the numerator equals the moles of  $^{32}\text{S}$  times the atomic weight of sulfur and the denominator equals the fractional abundance of  $^{32}\text{S}$  ( $^{32}\text{A}$ ) in the sample times the sample weight in grams.

For the vast majority of elements the isotopic composition is invariant in nature. However, sulfur is one of the few elements which exhibits variability in nature as a result of isotopic fractionation during biological processing by certain types of bacteria [4]. Therefore, the isotopic composition of the sulfur in all samples was measured on unspiked samples to preclude bias from this effect which could be 1 percent or larger if average isotopic abundance values were assumed.

#### Calibration of $^{34}\text{S}$ Enriched Tracer

The accuracy of an isotope dilution determination can be no better than the accuracy of the tracer concentration. Therefore, considerable effort was made to insure that the  $^{34}\text{S}$  enriched tracer solution was accurately calibrated. The  $^{34}\text{S}$  tracer used in this study was obtained from Oak Ridge National Laboratory in the form of elemental sulfur. It was converted to sulfate in  $\text{HNO}_3\text{-HCl}$  and diluted to an approximate concentration of 300  $\mu\text{g}$  total sulfur per gram of solution. The  $^{34}\text{S}$  tracer was calibrated against gravimetrically prepared solutions of high purity  $\text{K}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  plus three different lots of coulometrically assayed sulfuric acid solutions. All five of these solutions showed measurable differences in their sulfur isotopic compositions. An accurately weighed portion of a natural solution and  $^{34}\text{S}$  enriched tracer solution were added to a Teflon beaker, mixed thoroughly, and added directly to the reduction flask. Blanks were determined concurrently with the calibration mixtures and resulted in corrections of less than 0.02 percent relative in all cases. The results of ten calibration mixes are given in Table 1. There is good agreement between the six sulfuric acid mixes and the four salt mixes. The high precision of the mean of all ten mixes reflected in the 0.14 percent relative standard deviation demonstrates the high precision capabilities of this technique.

#### Results

The sulfur concentrations in the five SRM coals, as determined by isotope dilution thermal ionization mass spectrometry, are given in Tables 2-6. The sulfur concentrations listed in the tables are a single determination from one bottle of the SRM. The standard deviation was computed from the individual determinations. The blank uncertainty was negligible for all samples.

#### References

1. Paulsen, P. J., and Kelly, W. R., Determination of Sulfur by Isotope Dilution Thermal Ionization Mass Spectrometry as  $\text{AsS}^+$  Ions, *Anal. Chem.* 56, 708-713 (1984).
2. Kelly, W. R. and Paulsen, P. J., Precise Determination of Sulfur at High Concentrations by Isotope Dilution Thermal Ionization Mass Spectrometry, submitted to *Talanta*.
3. Kuehner, E. C.; Alvarez, R.; Paulsen, P. J.; and Murphy, T. J.; Production and Analysis of High Purity Acids Purified by Sub-boiling Distillation. *Anal. Chem.* 44: 2050-2056 (1972).
4. Krouse, H. R., Sulfur Isotopes in our Environment, in *Handbook of Environmental Isotope Geochemistry*, P. Fritz and J. Ch. Fontes, eds., Elsevier, 435-471 (1980).

Table 1  
Calibration of  $^{34}\text{S}$  Enriched Spike Solution

Natural Sulfur	Concentration Determined in Tracer $\mu\text{g S/g}^a$
$\text{H}_2\text{SO}_4\text{-135}^b$	
Mix #1	313.47
Mix #2	313.63
$\text{H}_2\text{SO}_4\text{-137}^b$	
Mix #1	313.60
Mix #2	313.39
$\text{H}_2\text{SO}_4\text{-139}^b$	
Mix #1	314.30
Mix #2	314.26
Mean of 6 acids	313.78 $\pm$ 0.40 (1s)
$\text{K}_2\text{SO}_4$	
Mix #1	313.98
Mix #2	312.88
$\text{Na}_2\text{SO}_4$	
Mix #1	313.27
Mix #2	313.73
Mean of 4 salts	313.47 $\pm$ 0.49 (1s)
Grand mean of 10 measurements	313.65 $\pm$ 0.44 (1s)

<sup>a</sup> Total  $\mu\text{g}$  of S per gram of solution.

<sup>b</sup> The three  $\text{H}_2\text{SO}_4$  acid natural solutions were prepared from three different lots of acids.

Table 2

Sulfur Concentration in SRM 2682, Coal,  
as Determined by Thermal Ionization Mass Spectrometry

<u>OSRM Bottle #</u>	<u>Weight Loss (%)</u>	<u>Dry Sample Weight (g)</u>	<u>S%</u>
1453	18.85	0.15805	0.4908
156	18.88	0.16186	0.4897
394	18.40	0.22883	0.4924
510	18.61	0.21871	0.4952
899	17.71	0.20537	0.4934
1178	18.77	0.15608	<u>0.4992</u>

Mean = 0.4935

St. Dev\* = 0.0034

\* Standard Deviation of single measurement

Table 3

Sulfur Concentration in SRM 2683, Coal,  
as Determined by Thermal Ionization Mass Spectrometry

<u>OSRM Bottle #</u>	<u>Weight Loss (%)</u>	<u>Dry Sample Weight (g)</u>	<u>S%</u>
121	1.29	0.13593	1.877
133	1.56	0.13511	1.907
529	1.58	0.16290	1.895
900	1.37	0.11518	1.897
1033	0.943	0.11492	1.889
1178	1.52	0.12194	<u>1.911</u>

Mean = 1.896

Std. Dev\* = 0.012

\* Standard Deviation of single measurement

Table 4

Sulfur Concentration in SRM 2684, Coal,  
as Determined by Thermal Ionization Mass Spectrometry

<u>Bottle #</u>	<u>Weight Loss (%)</u>	<u>Dry Sample Weight (g)</u>	<u>S%</u>
481	3.29	0.10161	3.109
492	3.70	0.10821	3.074
816	3.75	0.10555	3.108
1178	3.72	0.10903	3.076
1260	3.13	0.10321	3.062
1475	3.50	0.13460	<u>3.026</u>
		Mean =	3.076
		Std. Dev* =	0.031

\* Standard Deviation of single measurement

Table 5

Sulfur Concentration in SRM 2685, Coal,  
as Determined by Thermal Ionization Mass Spectrometry

<u>OSRM Bottle #</u>	<u>Weight loss (%)</u>	<u>Dry Sample Weight (g)</u>	<u>S%</u>
498	1.79	0.11576	4.853
504	1.78	0.09934	4.811
505	1.75	0.11391	4.762
848	1.70	0.11119	4.670
1178	1.79	0.12793	4.764
1452	1.64	0.11427	<u>4.703</u>
		Mean =	4.761
		Std. Dev. =	0.067

\* Standard Deviation of single measurement

Table 6  
 Sulfur Concentration in SRM 1635, Coal,  
 as Determined by Thermal Ionization Mass Spectrometry

<u>Sample #</u>	<u>Weight Loss (%)</u>	<u>Dry Sample Weight (g)</u>	<u>S%</u>
1	18.80	0.16489	0.3576
2	18.80	0.10232	0.3525
3	18.80	0.17319	<u>0.3530</u>

Mean = 0.3544

Std. Dev.\* = 0.0028

\* Standard Deviation of single measurement

Certified Value = 0.33 ± 0.03

## SECTION III

### Determination of Sulfur, Calorific Value and Ash Content in NBS Coals Using ASTM Procedures D2015, D3180, D3177, D3173, and D3174

J. C. Colbert and D. R. Kirklín

Twenty-four bottled samples of the NBS coal SRM's (2682, 2683, 2684, and 2685) were analyzed for sulfur content by the gravimetric method, gross calorific value by bomb calorimetry, furnace ash and moisture content.

In addition, one bottle each of the SRM's 1632a and 1635, certified for trace elements in coal, was used as a control sample for purposes of establishing a point of reference for the sulfur content.

The coal SRM's are primarily certified for sulfur content with the additional measurements made to certify the gross calorific value and furnace ash content.

#### Sample Preparation

The coal samples for analysis were taken directly from the bottles as issued. No special sample preparation was made.

#### Procedure

Standard bomb calorimetric techniques were used; however, procedures used at NBS contain some modifications that are essentially covered in the ASTM Standards listed below.

ASTM D2015	Standard Test Method for Gross Calorific Value of Solid Fuel by the Adiabatic Bomb Calorimeter
ASTM D3180	Standard Method for Calculating Coal and Coke Analyses from As-Determined to Different Bases HHV1---as determined HHV2---moisture-free HHV3---moisture-ash-free
ASTM D3177	Standard Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke
ASTM D3173	Test for Moisture in the Analysis Sample of Coal and Coke
ASTM D3174	Test for Ash in the Analysis Sample of Coal and Coke

For each coal sample submitted for testing three one-gram samples were weighed in analysis crucibles. Each measurement for moisture ash and gross calorific value required a separate one-gram sample. The three samples were weighed in the same time period to ensure that effects due to ambient room conditions of relative humidity and temperature were the same.

For moisture determination, the weighed analysis sample together with the analysis crucible were dried for 2 hours in a circulating air oven held at  $107 \pm 3$  °C. The loss in weight on drying was calculated as the moisture in the analysis sample and that value is used to convert the calorific value to a moisture free basis.

For the ash determination, the weighed analysis sample and crucible were placed in a muffle furnace capable of maintaining a temperature of  $725 \pm 25$  °C. The sample was ignited, cooled in a desiccator and weighed. The calculated amount of ash is used to convert the calorific value to an ash-free basis. The procedure is detailed in ASTM standard D3174.

The weighed analysis sample and combustion crucible for calorific value were burned in an adiabatic bomb calorimeter with the procedure being followed as described in ASTM D2015. After combustion, the interior of the bomb was washed and the washings collected for HNO<sub>3</sub> titration and sulfur determination as described in ASTM D2015 and D3177, respectively. A weighed aliquot of the total washings was taken for each determination. The ratio of the aliquot and total washings was used in the individual calculations for HNO<sub>3</sub> and sulfur.

## Benzoic Acid Calibrations

All measurements were made in a Parr adiabatic bomb calorimeter of the type used in many commercial laboratories. A series of 5 calibrations was made on the Parr calorimeter using benzoic acid supplied by the Parr Company (which is traceable to NBS SRM 391). The calibrations were done with a precision of 0.07 percent.

## Results

The results of the measurements made on the four coal SRM's, 2682, 2683, 2684, and 2685 are tabulated in Tables 1a through 1d. The tables include data on residual moisture, dry furnace ash (as weight percent), higher heating value-1 (HHV1---as determined), HHV2-(moisture free), HHV3 (moisture-ash-free) in BTU.lb<sup>-1</sup>, and dry sulfur content in weight percent. Table 2 contains the data summary for the coals, including mean value, standard deviation of a single measurement and percent standard deviation for moisture, ash, sulfur content, HHV1, HHV2, and HHV3. A conversion to MJ.kg<sup>-1</sup> is given for each mean calorific value. The conversion factor of 1 MJ.kg<sup>-1</sup> = 429.9226 BTU.lb<sup>-1</sup> was used to calculate the values presented in parenthesis.

Table 3 lists the mean value (+1 standard deviation for a single measurement) for the dry sulfur content in weight percent for SRM's 2682 through 2685. Each is a mean of ten determinations.

Three determinations each were made on the control coals 1632a and 1635. There were no moisture corrections made on these controls due to their being pre-dried before testing; therefore, the as-determined data (HHV1) and the moisture-free data (HHV2) are the same.

Table 4 gives the individual experimental results on the control coals. The data included are SRM number, dry furnace ash (as a fraction), dry sulfur in weight percent HHV1, HHV2, and HHV3. Table 5 gives the data summary for the control coals, including mean, standard deviation and percent standard deviation of a single measurement for furnace ash, sulfur content and the calorific values calculated to the three basis.

Table 6 compares the experimental sulfur data to the certified values given for sulfur on the SRM certificate for 1632a and 1635. The experimental data is a mean of three determinations (+1 standard deviation of a single measurement).

Table 1a

SRM No	Bottle No	Moist Wt. %	Fur Ash Wt. %	HHV1	HHV2 (BTU/LB)	HHV3	Sulfur Wt. %
2682	609	18.667	6.465	9677.69	11898.85	12721.25	0.35261
2682	432	17.264	6.501	9643.94	11656.28	12466.80	0.50822
2682	911	18.647	6.656	9519.59	11701.58	12536.00	0.39365
2682	1086	18.938	6.500	9603.42	11847.01	12670.59	0.39590
2682	1086	19.262	6.226	9583.86	11870.32	12658.48	0.46726
2682	1293	19.280	6.150	9547.86	11828.37	12603.44	0.45976
2682	432	17.335	6.130	9656.31	11681.26	12444.02	0.40597
2682	1293	19.148	6.078	9531.19	11788.44	12551.27	0.46002
2682	156	19.041	6.292	9634.09	11899.96	12698.99	0.43877
2682	156	18.990	6.647	9568.13	11811.05	12652.07	0.44926
Ave		18.657	6.365	9596.61	11798.31	12600.29	0.433
S.D.		+0.747*	+0.216	+55.17	+89.69	+96.71	+0.046

HHV1 - as received  
 HHV2 - moisture free  
 HHV3 - moisture-ash-free

\* Standard deviation of a single measurement

Table 1b

SRM No	Bottle No	Moist	Fur Ash Wt. %	HHV1	HHV2	HHV3	Sulfur Wt. %
				(BTU/LB)			
2683	609	1.443	6.829	13854.40	14057.25	15087.50	1.68397
2683	432	1.547	6.832	13852.01	14069.67	15101.34	1.86585
2683	156	1.200	6.842	13886.76	14055.43	15087.75	1.93237
2683	911	1.516	6.856	13855.27	14068.55	15104.08	1.77527
2683	1086	1.451	6.828	13864.12	14068.25	15099.23	1.77964
2683	1086	1.381	6.899	13855.50	14049.52	15090.67	1.80972
2683	1293	1.446	6.894	13844.65	14047.78	15087.89	1.78642
2683	432	1.497	6.858	13851.97	14062.49	15097.85	1.76395
2683	1293	1.436	6.813	13848.76	14050.53	15077.75	1.80421
2683	156	1.258	6.846	13902.17	14079.29	15114.02	1.73143
Ave S.D.*		1.418	6.850	13861.56	14060.88	15094.81	1.793
		+ 0.110	+ 0.028	+ 18.41	+ 10.49	+ 10.47	+ 0.068

HHV1 - as received

HHV2 - moisture free

HHV3 - moisture-ash-free

\* Standard deviation of a single measurement

Table 1c

SRM No	Bottle No	Moist	Fur Ash Wt. %	HHV1	HHV2	HHV3	Sulfur Wt. %
				(BTU/LB)			
2684	609	3.199	1.074	12277.15	12682.88	14262.33	2.87425
2684	911	3.246	1.244	12474.89	12893.41	14526.80	2.91589
2684	1086	3.283	1.191	12334.97	12753.67	14360.85	2.89642
2684	156	3.962	1.029	12371.54	12749.17	14329.53	2.85126
2684	432	3.135	1.064	12321.74	12720.53	14302.99	2.86697
2684	1086	3.364	1.107	12317.79	12746.59	14339.19	2.89740
2684	1293	3.485	1.050	12318.19	12762.98	14348.51	2.81185
2684	432	3.217	1.059	12341.56	12751.79	14337.32	2.88786
2684	1293	3.423	1.098	12303.86	12739.95	14330.31	2.87180
2684	156	3.048	1.898	12352.95	12741.31	14299.72	2.86248
Ave S.D.*		3.236	1.081	12341.46	12754.23	14343.76	2.874
		+ 0.163	+ 0.093	+ 53.67	+ 53.89	+ 70.31	+ 0.029

HHV1 - as received

HHV2 - moisture free

HHV3 - moisture-ash-free



Table 1d

Moisture, Furnace Ash, Heating Values and Sulfur Content  
in Individual SRM Coal 685

SRM No	Bottle No	Moist Wt. %	Fur Ash Wt. %	HHV1	HHV2	HHV3	Sulfur Wt. %
2685	609	1.466	6.592	11870.27	12046.88	14443.36	4.36829
2685	432	1.523	6.576	12012.07	12197.84	14621.58	4.44933
2685	911	1.469	6.648	11964.77	12143.15	14568.44	4.45855
2685	1086	1.469	6.555	11876.49	12053.56	14444.95	4.48801
2685	156	1.469	6.573	11891.28	12039.00	14415.34	4.43629
2685	1086	1.418	6.485	11868.29	12039.00	14415.34	4.43629
2685	1293	1.349	6.429	11927.49	12090.59	14467.38	4.48301
2685	432	1.645	6.535	11986.45	12186.92	14601.24	4.33383
2685	1293	1.464	6.386	11908.50	12085.43	14453.82	4.51483
2685	156	1.467	6.451	11872.76	12049.53	14422.17	4.54138
Ave.		1.474	16.523	11917.84	12096.15	14490.44	4.448
S.D.		± 0.075	± 0.082	± 52.85	± 59.04	± 76.46	± 0.064

Table 2

Summary of Data on SRM Coals 2682, 2683, 2684, and 2685

(Calorific Values in  $\text{Btu} \cdot \text{lb}^{-1}$  ( $\text{MJ} \cdot \text{kg}^{-1}$ ))

SRM No	Residual Moisture Wt. %	Furnace Ash Wt. %	Sulfur Wt. %	HHV1 <sup>a</sup>	HHV2	HHV3
2682						
Mean	18.657	6.365	0.433	9596.61 (22.3217)	11798.31 (27.4429)	12600.29 (29.3083)
Std. Dev.*	.747	.216	0.046	55.17 (.1283)	89.685 (.0286)	96.706 (.2249)
% S.D.	4.004	3.394	0.11	.5749 (.0013)	.7601 (.0018)	.7675 (.0018)
2683						
Mean	1.418	6.850	1.793	13861.56 (32.2420)	14060.88 (32.7056)	15094.81 (35.1105)
Std. Dev.*	.110	.028	0.068	18.41 (.0428)	10.4488 (.0243)	10.4654 (.0243)
% S.D.*	7.757	.409	0.04	.1328 (.0003)	.0743 (.0002)	.0693 (.0002)
2684						
Mean	3.236	11.081	2.874	12341.46 (28.7062)	12754.23 (29.6663)	14343.76 (33.3636)
Std. Dev.*	.163	.093	0.029	53.67 (.1248)	53.8880 (.1253)	70.3141 (.1636)
% S.D.	5.037	.839	0.01	.4349 (.0010)	.4225 (.0010)	.4902 (.0011)
2685						
Mean	1.474	16.523	4.448	11917.84 (27.7209)	12096.15 (28.1357)	14490.44 (33.7048)
Std. Dev.*	.075	.082	0.064	52.85 (.1229)	59.0447 (.1373)	76.4561 (.1778)
% S.D.	5.088	.496	0.01	.4435 (.0010)	.4881 (.0011)	.5276 (.0012)

<sup>a</sup> Additional decimal places were added to eliminate rounding errors when making conversions between  $\text{BTU} \cdot \text{lb}^{-1}$  and  $\text{MJ} \cdot \text{kg}^{-1}$ .

\* Standard deviation of single measurement.

Table 3  
Sulfur Content - SRM's 2682, 2683, 2684, 2685

<u>SRM No.</u>	<u>Mean <math>\pm</math> 1 S.D.*</u>
2682	0.433 $\pm$ .046
2683	1.793 $\pm$ .068
2684	2.874 $\pm$ .029
2685	4.448 $\pm$ .064

\*Standard Deviation of a single measurement

Table 4  
Furnance Ash, Sulfur Content and Heating Values of  
SRM Coals 1632a and 1635

SRM No	Fur Ash (FRAC)	Sulfur Wt.%	<u>HHV1*</u>	<u>HHV2</u> (BTU/LB)	<u>HHV3</u>
1632a	0.21846	1.56282	11156.59	11156.59	14275.13
632a	0.21846	1.54388	11229.92	11229.92	14368.96
1632a	0.21816	1.48872	11233.67	11233.67	14368.25
1635	0.04009	0.31641	11613.23	11613.23	12098.25
1635	0.03945	0.31830	11813.07	11813.07	12298.24
1635	0.03908	0.30779	11862.46	11862.46	12344.90

\* HHV1 = HHV2, sample dried before combustion.

Table 5

Summary of Data on Controls 1632a and 1635  
(Calorific Value in Btu<sup>1</sup>lb<sup>-1</sup> (MJ<sup>1</sup>kg<sup>-1</sup>))

SRM No	Furnace Ash Wt. %	Sulfur Wt. %	HHV1*	HHV3
1632a				
Mean	21.836	1.532	11207.73 (26.06685)	14337.45 (33.34891)
Std. Dev.*	.017	0.039	43.460 (.10109)	53.969 (.12553)
% S.D.*	.078		.38780 (.0009)	.37642 (.00088)
1635				
Mean	3.954	0.314	11762.92 (27.36055)	12257.13 (28.48683)
Std. Dev.*	.051	0.006	131.967 (.30696)	131.028 (.30477)
% S.D.*	1.290		1.12189 (.00261)	1.06987 (.00249)

\* HHV1 = HHV2, sample dried before combustion.

HHV3 = Moisture-ash-free.

\* Standard deviation of single measurement.

Certified Sulfur Values

1632a	1.58 ± 0.04
1635	0.33 ± 0.03

Table 6

Sulfur Content - SRM 1632a, 1635  
(wt. percent)

SRM No.	This Report (Mean ± 1 S.D.*)	Certificate
1632a	1.532 ± .039	1.58 ± 0.04
1635	0.314 ± .006	0.33 ± .03

\*Standard Deviation of a single measurement

## SECTION IV

### Determination of Sulfur in NBS Coals by a Modified High Temperature Method (D1552)

P. T. S. Pei and S. Weeks

The method used in the analyses was the modified ASTM D1552, Standard Test Method for Sulfur in Petroleum Products (High Temperature Method.) This method involves the burning of a coal sample in a stream of oxygen at a sufficiently high temperature to convert the sulfur to sulfur dioxide. A standardization factor was employed for obtaining accurate analysis results. For this work, SRM fuel oil standards were used for the standardization factor as required in Section 7-2 of the ASTM Method D1552. The combustion products are passed onto an absorber containing an acid solution of potassium iodide and starch indicator. A slight blue color is developed in the absorber solution by the addition of standard potassium iodate solution. As combustion proceeds, bleaching the blue color, more iodate is added. The amount of standard iodate consumed during combustion is a measure of the sulfur content of the sample. The sample preparation procedures, apparatus and fuel oil standards used for the analyses of the coal SRM's are given below.

#### 1. Apparatus

An induction furnace was used for the combustion of the samples. An automatic titrator was used for the titration of the sulfur dioxide evolved during the combustion of the sample.

#### 2. Preparation of Samples

Coal samples were dried in a vacuum oven at room temperature for 24 hours before analysis. The sample preparation procedure for the induction - type furnace is followed with the following modification. During the preparation of the sample, a drop of high viscosity and sulfur free mineral oil ( 20 mg) is added onto the coal sample and also a light layer of magnesium oxide ( 50 mg) is added to cover the coal sample before the addition of the iron powder and tin.

#### 3. Determination of Standardization Factor

SRM fuel oil standards have been used for the standardization factor stated in Section 7-2 of the method.

SRM 1623a (0.21%) for 0.5% Sulfur coal  
SRM 1622b (1.98%) for 2.0% Sulfur coal  
SRM 1634a (2.85%) for 3.0% Sulfur coal  
SRM 1620a (4.5 %) for 4.5% Sulfur coal

#### 4. Sample Size and Titrant Conc.

The sample sizes of the coal and  $KIO_3$  titrant conc. for sulfur analysis are:

<u>Sample #</u>	<u>Sample Wt.</u>	<u>Conc. of <math>KIO_3</math></u>
2682	50 mg	0.0006238N
2683	40 mg	0.006238N
2684	25 mg	0.006238N
2685	20 mg	0.006238N

#### 5. Results

The individual results for total sulfur in SRM's 2682-4 are given in Table 1 along with the mean and standard deviation of a single measurement. The moisture content determined by drying the coals for 24 hours under vacuum at 24 °C are shown in Table 2.

Table 1

% Sulfur in SRM Coal Samples of Different Concentrations  
as Determined by Modified ASTM D1552

<u>Sample #</u>	<u>2682</u>	<u>2683</u>	<u>2684</u>	<u>2685</u>
767	0.464	1.77	2.91	4.59
1-1	0.489	1.79	2.71	4.65
544-1	0.468	1.79	2.97	4.70
491-1	0.456	1.82	3.15	4.69
1176	0.476	1.82	3.17	4.51
128	0.464	1.81	2.91	4.67
876-1	0.461	1.88	3.09	4.78
491-2	0.461	1.81	3.08	4.51
968	0.470	1.78	2.97	4.73
1370-1	0.490	1.86	2.82	4.60
716	0.493	1.86	3.03	4.62
544-2	0.471	1.77	2.94	4.75
876-2	0.506	1.83	3.11	4.60
1022	0.489	1.77	2.99	4.66
1-2	0.474	1.87	3.05	4.78
71	0.462	1.74	2.99	4.68
370	0.501	1.76	3.11	4.47
1370-2	0.494	1.84	3.02	4.68
1486	0.474	1.81	2.94	4.43
Mean	0.477	1.81	3.00	4.64
Std. Dev.*	0.015	0.04	0.11	0.10

Note: Sample #1178 was not available at the analysis time.

\*Standard Deviation of a single measurement

Table 2

Moisture Content in SRM Coal Samples

<u>Sample #</u>	<u>2682</u>	<u>2683</u>	<u>2683</u>	<u>2684</u>
767	19.3	1.4	3.6	1.6
1-1	-	1.6	3.7	1.6
544-1	18.7	1.6	3.5	1.5
491-1	18.3	1.5	-	1.8
1176	18.4	1.4	3.6	1.7
128	18.7	1.4	3.5	1.6
876	18.2	1.5	3.3	1.7
491-2	18.7	1.3	3.6	1.7
968	18.8	1.7	3.6	1.6
1370	18.3	1.7	3.5	1.6
716	19.5	1.6	3.5	1.6
544-2	19.0	1.7	3.6	1.7
876-2	19.1	1.8	3.4	1.5
1022	19.0	1.8	2.8	1.6
1-2	19.3	1.7	3.8	1.6
71	18.8	1.7	3.6	1.8
370	19.3	1.7	3.6	1.6
1370-2	19.2	1.8	3.6	1.5
1486	19.3	1.7	3.5	1.7
Mean	18.9	1.6	3.5	1.6
Std. Dev.*	+0.4*	+0.2	+0.2	+0.1

\*Standard Deviation of a single measurement

## SECTION V

### Determination of Sulfur and Major Inorganic Constituents by Neutron-Capture Prompt- Activation Analysis - H, B, C, N, Al, and S

R. M. Lindstrom

#### Procedure

Vacuum-dried samples of coal (0.5-1.0 g) were pressed into 13-mm pellets, heat-sealed into cleaned Mylar bags, and irradiated in the prompt-facility of the National Bureau of Standards Reactor (NBSR) for 7-40 hours. Compton-suppressed  $\gamma$ -ray spectra were collected in the memory of a data acquisition system and stored on disk and the spectral peaks integrated. Corrections for background and for interfering peaks were carried out by hand calculation. The apparatus and procedures have been described elsewhere [1].

#### Results and Discussion

The high hydrogen content of coals required that account be taken of enhanced signal (due to neutron thermalization in the sample) and increased background (due to scattering into the surrounding apparatus) over that of standards containing low hydrogen. Allowance has been made for these effects by using homogeneous standards and backgrounds to calibrate the system.

The individual values obtained in these analyses are given in Tables 1, 2, 3, and 4. The error estimates in these tables are computed from counting statistics alone and therefore are lower limits to the true uncertainty, particularly for H and B where the analytical signal is strong. For these elements, the intersample reproducibility is a more realistic estimate of accuracy. The weighted mean values for each SRM and recommended values are summarized in Table 5, together with estimated standard deviations computed from both sources of inaccuracy.

Two samples of SRM 1632a, Trace Elements in Coal, were analyzed in parallel as controls. The concentrations found are compared with previous values in Table 6.

[1] M. P. Failey, et al., Anal. Chem., 51, 2209 (1979).

Table 1

Data for Major Constituents in NBS Coal Samples, SRM 2682

Sample No. Bottle No. Weight, g	1 516 1.0727	2 1465 1.0007	3 893 0.6471	4 893 0.5807
% H (2223)	4.74 ± 0.01	4.56 ± 0.01	4.59 ± 0.01	4.87 ± 0.01
ppm B (478)	38.5 ± 0.4	37.7 ± 0.4	39.5 ± 0.4	41.0 ± 0.4
% C (3684)	68.6 ± 2.0	68.5 ± 1.9	74.1 ± 2.5	81.6 ± 4.3
% N (1884)	1.13 ± 0.30	1.03 ± 0.27	0.68 ± 0.35	1.26 ± 0.68
(3678)	1.46 ± 0.20	1.12 ± 0.21	0.85 ± 0.28	1.88 ± 0.47
% Al (1779)	0.51 ± 0.05	0.48 ± 0.04	0.56 ± 0.06	0.54 ± 0.07
% S (840)	0.451 ± .016	0.435 ± .015	0.437 ± .020	0.486 ± .034
(2379)	0.456 ± .024	0.454 ± .023	0.444 ± .028	0.437 ± .052
(3220)	0.420 ± .038	0.446 ± .037	0.471 ± .048	0.483 ± .094

The number in parentheses is the energy KeV of the gamma ray used for quantitation. Uncertainties are given as the standard deviation based on counting statistics alone, and thus are lower limits to the true uncertainty.

Table 2

Data for Major Constituents in NBS Coal Samples, SRM 2683

Sample No. Bottle No. Weight, g	1 1021 0.9886	2 1451 1.0023	3 127 0.7199	4 122 0.8342
% H (2223)	4.99 ± 0.01	4.85 ± 0.01	5.21 ± 0.02	5.05 ± 0.01
ppm B (478)	66.9 ± 0.4	64.1 ± 0.4	69.8 ± 0.6	67.6 ± 0.5
% C (3684)	78.9 ± 1.7	75.4 ± 2.1	83.4 ± 2.9	74.6 ± 4.3
% N (1884)	1.72 ± 0.47	1.99 ± 0.58	1.38 ± 0.67	2.03 ± 0.89
(3678)	2.80 ± 0.28	0.85 ± 0.26	0.73 ± 0.39	1.56 ± 0.53
% Al (1779)	0.91 ± 0.04	0.91 ± 0.04	0.54 ± 0.07	0.88 ± 0.08
% S (840)	1.82 ± 0.02	1.77 ± 0.03	1.90 ± 0.03	1.84 ± 0.04
(2379)	1.82 ± 0.04	1.74 ± 0.05	1.89 ± 0.06	1.93 ± 0.07
(3220)	1.76 ± 0.07	1.77 ± 0.07	1.71 ± 0.08	1.81 ± 0.11

The number in parentheses is the energy KeV of the gamma ray used for quantitation. Uncertainties are given as the standard deviation based on counting statistics alone, and thus are lower limits to the true uncertainty.

Table 3

Data for Major Constituents in NBS Coal Samples, SRM 2684

Sample No.	1	2	3	4
Bottle No.	1204	482	864	1209
Weight, g	1.0106	1.0191	0.9433	0.8098
% H (2223)	4.62 ± 0.01	4.82 ± 0.01	4.74 ± 0.01	4.87 ± 0.01
ppm B (478)	111.0 ± 0.4	113.2 ± 0.4	115.0 ± 0.4	118.4 ± 0.5
% C (3684)	66.5 ± 1.9	69.2 ± 1.3	69.4 ± 3.6	64.8 ± 5.0
% N (1884)	1.75 ± 0.48	1.95 ± 0.44	1.81 ± 0.89	0.8 ± 0.9
(3678)	1.64 ± 0.29	1.79 ± 0.33	1.79 ± 0.46	0.7 ± 0.6
% Al (1779)	1.13 ± 0.04	1.18 ± 0.03	1.12 ± 0.07	1.11 ± 0.10
% S (840)	2.88 ± 0.03	2.95 ± 0.03	3.00 ± 0.04	3.01 ± 0.06
(2379)	2.87 ± 0.07	3.02 ± 0.06	2.99 ± 0.08	2.86 ± 0.10
(3220)	2.85 ± 0.10	3.04 ± 0.11	3.02 ± 0.13	2.60 ± 0.15

The number in parentheses is the energy KeV of the gamma ray used for quantitation. Uncertainties are given as the standard deviation based on counting statistics alone, and thus are lower limits to the true uncertainty.

Table 4

Data for Major Constituents in NBS Coal Samples, SRM 2685

Sample No.	1	2	3	4
Bottle No.	1474	481	487	847
Weight, g	0.9824	0.5326	0.7870	0.8934
% H (2223)	4.39 ± 0.01	4.95 ± 0.02	4.75 ± 0.01	4.70 ± 0.01
ppm B (478)	103.9 ± 0.4	114.1 ± 0.8	113.9 ± 0.5	111.4 ± 0.5
% C (3684)	63.5 ± 1.8	66.2 ± 2.5	71.9 ± 3.3	65.2 ± 3.2
% N (1884)	1.6 ± 0.5	1.2 ± 0.8	1.7 ± 0.7	0.9 ± 0.7
(3678)	1.0 ± 0.3	1.2 ± 0.5	0.9 ± 0.4	1.0 ± 0.4
% Al (1779)	1.69 ± 0.04	1.74 ± 0.06	1.85 ± 0.06	1.84 ± 0.06
% S (840)	4.39 ± 0.05	4.80 ± 0.06	4.73 ± 0.06	4.71 ± 0.06
(2379)	4.35 ± 0.09	4.91 ± 0.11	4.81 ± 0.11	4.76 ± 0.11
(3220)	4.54 ± 0.15	4.87 ± 0.17	4.60 ± 0.16	4.58 ± 0.17

The number in parenthesis is the energy KeV of the gamma ray used for quantitation. Uncertainties are given as the standard deviation based on counting statistics alone, and thus are lower limits to the true uncertainty.



Table 5

Summary of Concentrations for Major Constituents  
in NBS Coal Samples

Element	SRM 2682	SRM 2683	SRM 2684	SRM 2685
% H	4.7 ± 0.1	5.0 ± 0.1	4.8 ± 0.1	4.6 ± 0.2
g/g B	39 ± 1	67 ± 2	114 ± 3	109 ± 5
% C	76 ± 4	79 ± 4	68 ± 2	66 ± 3
% N	0.8 ± 0.3	1.6 ± 0.9	1.6 ± 0.4	1.1 ± 0.3
% Al	0.51 ± 0.03	0.86 ± 0.14	1.15 ± 0.03	1.76 ± 0.08
% S	0.447 ± 0.013	1.82 ± 0.05	2.94 ± 0.07	4.64 ± 0.19

The uncertainties quoted are an estimate of the standard deviation of individual single measurements including both counting statistics and intersample precision.

Table 6

## Analysis of SRM 1632a, Coal

Element Peak Energy KeV	Sample A	Sample B	Previous Analysis	Reference
% H (2223)	4.3 ± 0.1	4.3 ± 0.1	4.17 ± 0.01	2
g/g B (478)	59 ± 5	60 ± 5	53 ± 2	2
% C (3684)	61 ± 2	59 ± 4	62.70 ± 0.06	2
% N (1884) (3678)	1.5 ± 0.5 1.4 ± 0.2	0.7 ± 0.7 1.6 ± 0.5	1.26 ± 0.03	2
% Al (1779)	3.14 ± 0.05	3.05 ± 0.09	(3.07)	1
% S (840) (2379) (3219)	1.57 ± 0.02 1.54 ± 0.04 1.46 ± 0.06	1.57 ± 0.04 1.54 ± 0.07 1.63 ± 0.11	(1.64)	1

1 - NBS Certificate of Analysis, October 1983. Values in parentheses are not certified.

2 - E.S. Gladney, Anal. Chim Acta, 18, 385 (1980) and references therein.

Note: The number in parenthesis is the energy KeV of the gamma ray used for quantitation. The uncertainties are given as the standard deviation of a single measurement based on country statistics alone and thus are lower limits to the true uncertainty.

## SECTION VI

### Determination of Minor Inorganic Constituents by Neutron Activation Analysis - Ca, Cl, K, Mg, Mn, Na, Ti, and V

R. F. Fleming

Samples for Analysis: One sample was taken from each of six bottles for each of the four SRM coals. Vacuum-dried samples of the powdered coal (0.35-0.67 g) were pressed into 0.5 inch diameter pellets and heat-sealed into cleaned 1 mil polyethylene bags.

Procedure: Each sample was irradiated for 60 seconds in the NBS Research Reactor (NBSR) irradiation facility, RT-4, and counted three times at 28 cm from the  $104 \text{ cm}^3$  Ge (Li) detector. The counts were begun typically at 15, 30, and 180 minutes after the irradiation. The photopeak data from the first two counts were used to quantify Ca, Cl, Mg, Ti, and V, while the third count gave the best results for K, Mn, and Na. The use of two gamma lines gave redundant results for Cl, Mn, and Na. The pure metals were used as standards for Mg, Mn, Ti, and V, while NBS certified SRMs were used for Ca (SRM 915), Cl and K (SRM 999), and Na (SRM 40h).

Results: The data for the eight elements are summarized in Table 1. No bottle-to-bottle variability was observed outside the indicated uncertainty except for the Cl result for SRM 2682. Here the range of results (-37% to +125%) was too great for any mean value or range to be estimated. The Cl data for the other three coals shows no variability at the  $\pm 3$  percent level, and the other eight elements measured for SRM 2682 are all consistent.

Table 1

SRM 2682, Raw Data  
Concentration -  $\mu\text{g/g}$  (dry weight basis)\*

Sample No.	Bottle No.	Ca 3084 KeV	C1 1642 KeV	Mg 1014 KeV	Mn 847 KeV	1811 KeV	K 1525 KeV	Na 1369 KeV	Ti 2754 KeV	V 1434 KeV
B-01	486	+300 11816	586 $\pm$ 11	1802 $\pm$ 10	+40 26.44	+70 26.35	348 $\pm$ 164	+15 1049	+21 1039	+38 15.06
B-02	498	+400 11921	1178 $\pm$ 16	1973 $\pm$ 225	+30 26.47	+50 26.86	128 $\pm$ 170	+9 1033	+16 1020	+72 13.33
B-03	514	+300 11314	373 $\pm$ 9	1645 $\pm$ 125	+30 25.79	+50 26.44	194 $\pm$ 166	+10 1034	+10 1045	+32 14.59
B-04	516	+240 11219	519 $\pm$ 13	1654 $\pm$ 125	+40 26.28	+50 25.44	310 $\pm$ 190	+8 1028	+12 1014	+32 14.68
B-05	893	+300 11392	524 $\pm$ 10	1682 $\pm$ 125	+40 26.29	+50 26.13	243 $\pm$ 121	+11 1032	+28 1011	+34 14.51
B-07	1465	+300 11254	506 $\pm$ 9	1724 $\pm$ 125	+40 25.96	+50 26.03	209 $\pm$ 123	+8 1040	+10 1019	+33 14.64
		Mean = 11430	***	1713	26.19	26.20	235	1035	1027	14.62
		2 $\sigma$ ** = 560		185	0.60	1.00	140	12	28	85

\* - The uncertainties in individual results are  $1\sigma$  counting statistics.

\*\* - The uncertainties quoted for the pooled results are an estimate of the standard deviation, including both counting statistics and intersample variability.

\*\*\* - The apparent bottle-to-bottle variability is too great for any mean value to be meaningful.

Table 2

S3M 2683, Raw Data  
Concentration -  $\mu\text{g/g}$  (dry weight basis)\*

Sample No.	Bottle No.	Ca 3084 KeV	C1 1642 KeV	Mg 1014 KeV	Mn 847 KeV	K 1525 KeV	Na 2754 KeV	Ti 320 KeV	V 1434 KeV
B-08	122	+130 1783	+14 1310	664 $\pm$ 145	+15 12.67	714 $\pm$ 236	494 $\pm$ 6	488 $\pm$ 7	1.0 14.10
B-09	127	+140 2057	+20 1278	427 $\pm$ 130	+27 13.97	782 $\pm$ 251	497 $\pm$ 6	490 $\pm$ 10	+49 13.63
B-10	498	+200 1892	+15 1248	407 $\pm$ 128	+30 12.72	911 $\pm$ 205	522 $\pm$ 8	509 $\pm$ 7	+44 13.65
B-11	535	+140 2016	+13 1305	357 $\pm$ 133	+20 13.57	874 $\pm$ 255	502 $\pm$ 10	499 $\pm$ 7	+47 14.19
B-12	1021	+150 2399	+13 1295	578 $\pm$ 131	+15 13.05	495 $\pm$ 216	499 $\pm$ 12	508 $\pm$ 8	+90 15.19
B-13	1451	+240 2330	+13 1297	267 $\pm$ 219	+15 12.89	760 $\pm$ 104	509 $\pm$ 7	507 $\pm$ 7	+2.06 16.20
		Mean = 2047	1293	465	13.04	756	503	501	14.0
		2 $\sigma$ ** = 200	47	265	0.84	240	20	20	1.1

\* - The uncertainties in individual results are  $1\sigma$  counting statistics.

\*\* - The uncertainties quoted for the pooled results are an estimate of the standard deviation, including both counting statistics and intersample variability.

Table 3

SRM 2684, Raw Data  
Concentration -  $\mu\text{g/g}$  (dry weight basis)\*

Sample No.	Bottle No.	Ca 3084 KeV	Cl 1642 KeV	Mg 1014 KeV	Mn 847 KeV	K 1811 KeV	Na 1369 KeV	Ti 2754 KeV	V 1434 KeV		
B-14	482	+400	+30	+13	+98	+83	+156		+1.24		
		4442	1292	1295	764 ± 181	35.25	34.68	1800	259 ± 6	259 ± 10	578 ± 70
B-15	858	+180	+14	+16	+25	+62	+369		±.55		
		4363	1304	1272	865 ± 150	35.46	35.60	1944	262 ± 6	252 ± 12	555 ± 71
B-16	864	+160	+20	+12	+30	+1.0	+140		+49		
		4344	1301	1309	691 ± 150	35.71	35.17	2049	266 ± 8	265 ± 9	493 ± 42
B-17	1204	+180	+14	+12	+38	+50	+226		±.66		
		4360	1304	1305	698 ± 150	35.30	35.49	2052	261 ± 6	262 ± 6	595 ± 53
B-18	1209	+170	+14	+12	+30	+89	+474		+56		
		4313	1271	1262	839 ± 150	35.58	35.25	2202	262 ± 8	264 ± 7	600 ± 67
B-19	1469	+180	+14	+13	+41	+1.0	+200		±.57		
		4388	1267	1285	790 ± 150	36.20	35.58	1985	265 ± 10	255 ± 6	677 ± 50
		Mean = 4355	1288	1289	775	35.6	35.4	262	260	580	21.9
		2 $\sigma$ ** = 200	36	38	150	0.6	0.6	8	10	150	1.2

\* - The uncertainties in individual results are 1 $\sigma$  counting statistics.

\*\* - The uncertainties quoted for the pooled results are an estimate of the standard deviation, including both counting statistics and intersample variability.

Table 4

SRM 2685, Raw Data  
Concentration -  $\mu\text{g/g}$  (dry weight basis)\*

Sample No.	Bottle No.	Ca 3084 KeV	Cl 1642 KeV	Mg 1014 KeV	Mn 847 KeV	K 1525 KeV	Na 2754 KeV	Tl 320 KeV	V 1434 KeV		
B-20	481	+200 5180	645 $\pm$ 15	974 $\pm$ 155	41.0 $\pm$ .5	40.9 $\pm$ .7	754 $\pm$ 10	767 $\pm$ 13	919 $\pm$ 65	31.1 $\pm$ .8	
B-21	482	+200 5564	653 $\pm$ 14	644 $\pm$ 13	1155 $\pm$ 154	42.2 $\pm$ .5	40.7 $\pm$ .9	768 $\pm$ 10	764 $\pm$ 13	914 $\pm$ 64	30.6 $\pm$ .8
B-22	487	+200 4925	649 $\pm$ 14	638 $\pm$ 13	887 $\pm$ 153	39.9 $\pm$ .4	38.7 $\pm$ .7	760 $\pm$ 10	763 $\pm$ 13	842 $\pm$ 63	29.2 $\pm$ .8
B-23	497	+200 5121	652 $\pm$ 13	650 $\pm$ 12	1108 $\pm$ 140	40.4 $\pm$ .4	39.5 $\pm$ .4	759 $\pm$ 10	758 $\pm$ 11	859 $\pm$ 62	30.3 $\pm$ .8
B-24	847	+200 5603	655 $\pm$ 14	636 $\pm$ 13	1214 $\pm$ 164	42.1 $\pm$ .5	41.1 $\pm$ .4	770 $\pm$ 10	772 $\pm$ 12	909 $\pm$ 63	30.9 $\pm$ .8
B-25	1474	+200 5004	645 $\pm$ 15	635 $\pm$ 15	1042 $\pm$ 145	41.8 $\pm$ .4	40.8 $\pm$ .6	765 $\pm$ 10	769 $\pm$ 12	901 $\pm$ 61	30.6 $\pm$ .7
		Mean = 5234	650	643	1061	41.1	40.3	765	765	890	30.5
		2 $\sigma$ ** = 500	13	14	150	1.0	1.0	14	15	65	1.3

\* - The uncertainties in individual results are 1 $\sigma$  counting statistics.

\*\* - The uncertainties quoted for the pooled results are an estimate of the standard deviation, including both counting statistics and intersample variability.

Table 5  
 Summary of Elemental Concentrations in SRM Coals  
 ( $\mu\text{g/g} \pm 2s$ )

<u>Element</u>	<u>SRM 2682</u>		<u>SRM 2683</u>		<u>SRM 2684</u>		<u>SRM 2685</u>	
Ca	11430	$\pm 560$	2047	$\pm 200$	4355	$\pm 200$	5234	$\pm 500$
Cl	---		1294	$\pm 40$	1292	$\pm 36$	647	$\pm 14$
K	235	$\pm 140$	756	$\pm 240$	1969	$\pm 250$	2705	$\pm 200$
Mg	1713	$\pm 185$	465	$\pm 265$	775	$\pm 150$	1061	$\pm 150$
Mn	26.2	$\pm 0.6$	13.0	$\pm 1.2$	35.6	$\pm 0.6$	40.7	$\pm 1.0$
Na	1030	$\pm 20$	502	$\pm 20$	261	$\pm 8$	764	$\pm 15$
Ti	505	$\pm 85$	438	$\pm 120$	577	$\pm 150$	890	$\pm 65$
V	14.6	$\pm 0.7$	14.0	$\pm 1.1$	21.9	$\pm 1.2$	30.5	$\pm 1.3$

The uncertainties are given as two times the standard deviation of single measurements

## SECTION VII

### Multielement Analysis of NBS Coals by Instrumental Neutron Activation Analysis

R. R. Greenberg

Procedure: One 250 mg sample of vacuum-dried coal from each of six or seven bottles of each coal was doubly sealed in polyethylene bags and irradiated for two hours in the RT-3 ( $5 \times 10^{15}$  n.cm.<sup>-2</sup>s.<sup>-1</sup>) pneumatic tube facility of the NBS Research Reactor along with multielemental standards, blank bags, and two samples of SRM 1632a. Mid-way through the irradiation, the rabbit was removed from the reactor, flipped end-over-end, and reinserted into the reactor, to provide a uniform neutron fluence within the rabbit. Beginning three days after irradiation, the outer bag of each sample was removed and discarded, and the samples were counted three times at a distance of 10 cm from a Gamma-X detector. Two different peak integration routines were used for all elements.

Results and Discussions: The results of the coal analyses are listed in Tables 1-4. The observed sample-to-sample variations for all elements in SRM 2682, except Br, appeared to be consistent with the counting statistics. The observed standard deviation of a single measurement for Br was approximately 4-5 times greater than expected from the counting statistics, indicating some inhomogeneity for this element.

The observed standard deviation of a single measurement for As, Co, and Fe in SRM 2683 were more than twice as great as expected from the counting statistics indicating a degree of inhomogeneity for these elements. The possibility of problems during analysis such as geometry errors, counting errors, weighing errors, etc., can be eliminated since the observed standard deviation for Sc was only 0.4 percent (1s - relative), and these errors would affect Sc in the same manner as the other elements.

The observed standard deviation of a single measurement for As, Br, Cr, Fe, La, Sc, Sm, and Zn in SRM 2684 were more than twice as great as expected from the counting statistics indicating a degree of inhomogeneity for these elements. Although Br and Zn varied independently, the other elements, Cr, Fe, La, Sc, and Sm, exhibited similar behavior, in that bottles 858, 864, and 1024 had relatively higher concentrations of these elements than did bottles 482, 1209, and 1469. This variability could not be due to analytical problems arising from different geometrics, moisture content, weighing errors, dead time effects, etc., since these would affect the concentrations of each element within a sample to the same degree. The Fe concentration in bottle 858, for example, was considerably higher than in bottle 864,  $1.490 \pm 0.005$  percent (1s) vs.  $1.465 \pm 0.005$  percent, while the reverse was observed for Sm,  $1.114 \pm 0.002$   $\mu\text{g/g}$  (1s) compared to  $1.124 \pm 0.002$   $\mu\text{g/g}$ .

The observed standard deviation of a single measurement for As, La, and Fe in SRM 2685 were more than three times as great as expected from the counting statistics indicating a degree of inhomogeneity for these elements. The observed standard deviations for single measurements Sc and Sm, 0.5 percent and 0.4 percent (1s relative) although small, are approximately twice as great as expected from the counting statistics, and perhaps indicate some small inhomogeneity for these elements.



Table 1

## Summary of Concentrations Observed in Coal, SRM 2682

Mean Concentration ( $\mu\text{g/g}$ )  $\pm$  2s\*

As	1.00	$\pm$	0.04	La	5.17	$\pm$	0.05
Ba	382	$\pm$	10	Sb	0.189	$\pm$	0.018
Br	3.74	$\pm$	0.35**	Sc	1.524	$\pm$	0.010
Ce	9.87	$\pm$	0.16	Se	0.91	$\pm$	0.19
Co	1.66	$\pm$	0.06	Sm	0.776	$\pm$	0.008
Cr	15.4	$\pm$	0.5	Th	1.532	$\pm$	0.027
Eu	0.172	$\pm$	0.010	U	0.519	$\pm$	0.030
Fe	2420	$\pm$	30	W	1.81	$\pm$	0.05
Hf	0.60	$\pm$	0.03	Zn	8.6	$\pm$	1.8
K	117	$\pm$	28				

\*Two times the standard deviation of a single measurement

\*\*Variability more than twice as great as counting statistics.

Table 2

## Summary of Concentrations Observed in Coal, SRM 2683

Mean Concentration ( $\mu\text{g/g}$ )  $\pm$  2s\*

As	3.64	$\pm$	0.26**	La	5.05	$\pm$	0.07
Ba	71	$\pm$	6	Sb	0.279	$\pm$	0.015
Br	16.85	$\pm$	0.07	Sc	1.941	$\pm$	0.016
Ce	9.18	$\pm$	0.15	Se	1.23	$\pm$	0.17
Co	2.22	$\pm$	0.18**	Sm	0.859	$\pm$	0.010
Cr	11.02	$\pm$	0.36	Th	1.363	$\pm$	0.022
Cs	0.44	$\pm$	0.04	U	0.418	$\pm$	0.021
Eu	0.177	$\pm$	0.012	W	0.48	$\pm$	0.05
Fe	7620	$\pm$	380**	Zn	9.5	$\pm$	1.1
Hf	0.418	$\pm$	0.008				
K	750	$\pm$	20				

\*Two times the standard deviation of a single measurement

\*\*Variability more than twice as great as counting statistics.

Table 3

Summary of Concentrations Observed in Coal, SRM 2684

Mean Concentration ( $\mu\text{g/g}$  unless % indicated)  $\pm$  2s\*

As	3.867	$\pm$	0.269**	La	6.650	$\pm$	0.202**
Ba	41.4	$\pm$	5.5	Rb	14.6	$\pm$	2.2
Br	10.57	$\pm$	0.87**	Sb	0.354	$\pm$	0.016
Ce	11.51	$\pm$	0.36	Sc	2.665	$\pm$	0.041**
Co	3.85	$\pm$	0.10	Se	1.87	$\pm$	0.31
Cr	16.81	$\pm$	0.66**	Sm	1.109	$\pm$	0.023**
Cs	1.15	$\pm$	0.09	Th	1.955	$\pm$	0.032
Eu	0.226	$\pm$	0.018	U	0.901	$\pm$	0.020
Fe (%)	1.454	$\pm$	0.051**	W	0.562	$\pm$	0.043
Hf	0.565	$\pm$	0.025	Zn	110.0	$\pm$	23.6**
K	1969	$\pm$	31				

\*Two times the standard deviation of a single measurement

\*\*Variability more than twice as great as counting statistics.

Table 4

Summary of Concentrations Observed in Coal, SRM 2685

Mean Concentration ( $\mu\text{g/g}$  unless % indicated)  $\pm$  2s\*

As	12.28	$\pm$	0.76**	La	10.19	$\pm$	0.22**
Ba	105	$\pm$	11	Rb	16.8	$\pm$	2.6
Br	5.57	$\pm$	0.14**	Sb	0.357	$\pm$	0.023
Ce	17.88	$\pm$	0.35	Sc	3.700	$\pm$	0.038**
Co	4.57	$\pm$	0.11	Se	1.91	$\pm$	0.31
Cr	22.3	$\pm$	0.8	Sm	1.729	$\pm$	0.014**
Cs	1.31	$\pm$	0.13	Th	2.66	$\pm$	0.05
Eu	0.357	$\pm$	0.007	U	0.948	$\pm$	0.025
Fe (%)	2.396	$\pm$	0.130**	W	1.18	$\pm$	0.11
Hf	0.913	$\pm$	0.022	Zn	17.1	$\pm$	2.1
K	2592	$\pm$	89				

\*Two times the standard deviation of a single measurement

\*\*Variability at least twice as great as counting statistics.

## SECTION VIII

Statistical Analysis and Certification  
of NBS Sulfur in Coal SRM's

R. C. Paule

Statistical analyses have been made on a variety of data obtained from the proposed coal SRM's 2682-2685. The properties to be certified are sulfur content, ash content, and HHV2 heating value. A stratified random sampling plan was used to inspect the bottles of each coal for the above three properties. The data have been tabulated in Sections I-III.

Sulfur

The percent sulfur was certified based on three analytical methods: ion chromatography, gravimetry, and thermal ionization mass spectrometry. Two additional techniques, prompt-gamma activation analysis and a combustion technique, were used for confirmation and a test of the utility of the SRM's. The between-bottle variability for sulfur was not statistically significant for any of the four coals. The general approach for the statistical analyses of the SRM certificate has been reported in references (1) and (2).

All three analytical methods for sulfur analysis had relatively high internal precisions. The observed differences of results from the three methods, however, were appreciably greater than that expected from the internal precisions. Gravimetry gave the lowest results, ion chromatography gave intermediate results, and thermal ionization mass spectrometry gave the highest results. The uncertainty of the weighted average for each SRM is primarily determined by the variabilities between the three methods of analysis (1). For percent sulfur, the SRM weighted averages and associated two standard error values are as follows:

<u>SRM Number</u>	<u>2682</u>	<u>2683</u>	<u>2684</u>	<u>2685</u>
Wt. % Sulfur ±	.47±.03	1.85±.06	3.00±.13	4.62±.18
2 Std. Errors				

Calorific Value and Ash Content

The ash content and the HHV2 heating values for the four coals were each determined by a single method of analysis. Three of the four SRM's had moderate (but not statistically significant) between-bottle variabilities for ash content. These observed variabilities have been included in the overall SRM uncertainty statements. Since the between-bottle variability is not moderated by an averaging of results, this variability contributes appreciably to the overall uncertainty of the ash content for SRM's 2682, 2684, and 2685. For weight percent ash, the SRM weighted averages and associated two standard error values are as follows:

<u>SRM Number</u>	<u>2682</u>	<u>2683</u>	<u>2684</u>	<u>2685</u>
Wt. % Ash ±	6.37±.18	6.85±.02	11.09±.18	16.53±.15
2 std. errors				

For the HHV2 heating values, we observed statistically significant between-bottle variabilities for SRM's 2682, 2684, and 2685. These variabilities are included in the overall SRM statements of uncertainty. In addition, an allowance of 50 BTU/LB for possible sample degradation has been included in the overall uncertainty statements. The total uncertainty intervals given below are the sums of two standard errors plus the 50 BTU/LB degradation allowance. For HHV2 heating value, the SRM weighted averages and associated uncertainty intervals are as follows:

<u>SRM Number</u>	<u>2682</u>	<u>2683</u>	<u>2684</u>	<u>2685</u>
HHV2 in BTU/LB ±	11800 ± 240	14060 ± 60	12760 ± 200	12100 ± 180
Uncertainty Interval				

Major and Minor Elements

The information values for major and minor elements are based on measurements made by a single method or technique and were not carried through the statistical calculations. While no reason

exists to suspect systematic bias in these numbers, no attempt was made to determine if such bias attributable to the methods exist. Those values are not certified and are to be used for information only.

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- (1) Paule, R. C. and Mandel, J., Consensus Values and Weighting Factors, J. of Res. NBS, 87, 377 (1982).
  - (2) Mandel, J., and Paule, R. C., Interlaboratory Evaluation of a Material with Unequal Numbers of Replicates, Anal. Chem., 42, 1194 (1970) and Correction, Anal. Chem., 43, 1287 (1971).

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