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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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OTHER NBS PUBLICATIONS IN THIS SERIES

Catalog of NBS Standard Reference Materials (1984-85 edition), Catherine H. Hudson, ed., NBS Spec. Publ. 260 (February 1984).

Michaelis, R. E., and Wyman, L. L. Standard Reference Materials: Preparation of White Cast Iron Spectrochemical Standards. NBS Misc. Publ. 260-1 (June 1964). COM74-11061**

Michaelis, R. E., Wyman, L. L., and Flitsch, R., Standard Reference Materials: Preparation of NBS Copper-Base Spectrochemical Standards. NBS Misc. Publ. 260-2 (October 1964). COM74-11063**

Michaelis, R. E., Yakowitz, H., and Moore, G. A., Standard Reference Materials: Metallographic Characterization of an NBS Spectrometric Low-Alloy Steel Standard. NBS Misc. Publ. 260-3 (October 1964). COM74-11060**

Hague, J. L. Mears, T. W., and Michaelis, R. E., Standard Reference Materials: Sources of Information, NBS Misc. Publ. 260-4 (February 1965). COM74-11059

Alvarez, R., and Flitsch R., Standard Reference Materials: Accuracy of Solution X-Ray Spectrometric Analysis of Copper-Base Alloys. NBS Misc. Publ. 260-5 (March 1965). PB168068**

Shultz, J. I., Standard Reference Materials: Methods for the Chemical Analysis of White Cast Iron Standards, NBS Misc. Publ. 260-6 (July 1965). COM74-11068**

Bell, R. K., Standard Reference Materials: Methods for the Chemical Analysis of NBS Copper-Base Spectrochemical Standards. NBS Misc. Publ. 260-7 (October 1965). COM74-11067**

Richmond, M.S., Standard Reference Materials: Analysis of Uranium Concentrates at the National Bureau of Standards. NBS Misc. Publ. 260-8 (December 1965). COM74-11066**

Anspach, S. C., Cavallo, L. M. Garfinkel, S. B. Hutchinson, J. M. R., and Smith, C. N., Standard Reference Materials: Half Lives of Materials Used in the Preparation of Standard Reference Materials of Nineteen Radioactive Nuclides Issued by the National Bureau of Standards NBS Misc. Publ. 260-9 (November 1965). COM74-11065**

Yakowitz, H., Vieth, D. L., Heinrich, K. F. J., and Michaelis, R. E., Standard Reference Materials: Homogeneity Characterization of NBS Spectrometric Standards II: Cartridge Brass and Low-Alloy Steel, NBS Misc. Publ. 260-10 (December 1965). COM74-11064**

Napolitano, A., and Hawkins, E. G., Standard Reference Materials: Viscosity of Standard Lead-Silica Glass, NBS Misc. Publ. 260-11 (November 1966). NBS Misc. Publ. 260-11**

Yakowitz, H., Vieth, D. L., and Michaelis, R. E., Standard Reference Materials: Homogeneity Characterization of NBS Spectrometric Standards III: White Cast Iron and Stainless Steel Powder Compact, NBS Misc. Publ. 260-12 (September 1966). NBS Misc. Publ. 260-12**

Spijkerman, J. L., Snediker, D. K., Ruegg, F. C., and DeVoe, J. R., Standard Reference Materials: Mossbauer Spectroscopy Standard for the Chemical Shift of Iron Compounds, NBS Misc. Publ. 260-13 (July 1967). NBS Misc. Publ. 260-13**

Menis, O., and Sterling, J. T., Standard Reference Materials: Determination of Oxygen in Ferrous Materials - SRM 1090, 1091, and 1092, NBS Misc. Publ. 260-14 (September 1966). NBS Misc. Publ. 260-14**

Passaglia, E., and Shouse, P. J., Standard Reference Materials: Recommended Method of Use of Standard Light-Sensitive Paper for Calibrating Carbon Arcs Used in Testing Textiles for Colorfastness to Light, NBS Misc. Publ. 260-15 (June 1967). (Replaced by NBS Spec. Publ. 260-41.)

Yakowitz, H., Michaelis, R. E., and Vieth, D. L., Standard Reference Materials: Homogeneity Characterization of NBS Spectrometric Standards IV: Preparation and Microprobe Characterization of W-20% MO Alloy Fabricated by Powder Metallurgical Methods, NBS Spec. Publ. 260-16 (January 1969). COM74-11062**

Catanzaro, E. J., Champion, C. E., Garner, E. L., Marinenko, G., Sappenfield, K. M., and Shields, W. R., Standard Reference Materials: Boric Acid; Isotopic and Assay Standard Reference Materials, NBS Spec. Publ. 260-17 (February 1970). Out of Print.

Geller, S. B., Mantek, P.A., and Cleveland, N. G., Standard Reference Materials: Calibration of NBS Secondary Standard Magnetic Tape (Computer Amplitude Reference) Using the Reference Tape Amplitude Measurement "Process A," NBS Spec. Publ. 260-18 (November 1969). (See NBS Spec. Publ. 260-29.)

Paule, R. C., and Mandel, J., Standard Reference Materials: Analysis of Interlaboratory Measurements on the Vapor Pressure of Gold (Certification of Standard Reference Material 745). NBS Spec. Publ. 260-19 (January 1970). PB190071**

Paule, R. C., and Mandel. J., Standard Reference Materials: Analysis of Interlaboratory Measurements on the Vapor Pressures of Cadmium and Silver, NBS Spec. Publ. 260-21 (January 1971). COM74-11359**

Yakowitz, H., Fiori, C. E., and Michaelis, R. E., Standard Reference Materials: Homogeneity Characterization of Fe-3 Si Alloy, NBS Spec. Publ. 260-22 (February 1971). COM74-11357**

Napolitano, A., and Hawkins, E. G., Standard Reference Materials: Viscosity of a Standard Borosilicate Glass, NBS Spec. Publ. 260-23 (December 1970). COM71-00157**

Sappenfield, K. M., Marineko, G., and Hague, J. L., Standard Reference Materials: Comparison of Redox Standards, NBS Spec. Publ. 260-24 (January 1972). COM72-50058**

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

Hust, J. G., and Giarratano, P. J., Standard Reference Materials: Thermal Conductivity and Electrical Resistivity Standard Reference Materials: Electrolytic Iron, SRM's 734 and 797 from 4 to 1000 K, NBS Spec. Publ. 260-50 (June 1975). $1.00* SN003-003-01425-7

Mavrodineanu, R., and Baldwin, J. R., Standard Reference Materials: Glass Filters As a Standard Reference Material for Spectrophotometry; Selection; Preparation; Certification; Use-SRM 930, NBS Spec. Publ. 260-51 (November 1975). $1.90* SN003-003-01481-8

Hust, J. G., and Giarratano, P. J., Standard Reference Materials: Thermal Conductivity and Electrical *Resistivity Standard Reference Materials* 730 and 799, from 4 to 3000 K, NBS Spec. Publ. 260-52 (September 1975). $1.05* SN003-003-01464-8

Durst, R. A., Standard Reference Materials: Standardization of pH Measurements, NBS Spec. Publ. 260-53 (December 1975, Revised). $1.05 SN003-003-01551-2

Burke, R. W., and Mavrodineanu, R., Standard Reference Materials: Certification and Use of Acidic Potassium Dichromate Solutions as an Ultraviolet Absorbance Standard, NBS Spec. Publ. 260-54 (August 1977). $3.00* SN003-003-01828-7

Ditmars, D. A., Cezairliyan, A., Ishihara, S., and Douglas, T. B., Standard Reference Materials: Enthalpy and Heat Capacity; Molybdenum SRM 781, from 273 to 2800 K, NBS Spec. Publ. 260-55 (September 1977). $2.20* SN003-003-01836-8

Powell, R. L., Sparks, L. L., and Hust, J. G., Standard Reference Materials: Standard Thermocouple Materials, Pt.67: SRM 1967, NBS Spec. Publ. 260-56 (February 1978). $2.20* SN003-003-018864

Cali, J. P. and Plebanski, T., Guide to United States Reference Materials, NBS Spec. Publ. 260-57 (February 1978). $2.20* PB 277173

Barnes, J. D., and Martin, G. M., Standard Reference Materials: Polyester Film for Oxygen Gas Transmission Measurements SRM 1470, NBS Spec. Publ. 260-58 (June 1979) $2.00* SN003-003-02077

Chang, T., and Kahn, A. H. Standard Reference Materials: Electron Paramagnetic Resonance Intensity Standard; SRM 2601, NBS Spec. Publ. 260-59 (August 1978) $2.30* SN003-003-01975-5

Velapoldi, R. A., Paule, R. C., Schaffer, R., Mandel, J., and Moody, J. R., Standard Reference Materials: A Reference Method for the Determination of Sodium in Serum, NBS Spec. Publ. 260-60 (August 1978). $3.00* SN003-003 01978-0

Verdier, P. H., and Wagner. H. L., Standard Reference Materials: The Characterization of Linear Polyethylene (SRM 1482, 1483, 1484), NBS Spec. Publ. 260-61 (December 1978). $1.70* SN003-003-02006-1

Soulen, R. J., and Dove, R. B., Standard Reference Materials: Temperature Reference Standard for Use Below 0.5 K (SRM 768). NBS Spec. Publ. 260-62 (April 1979). $2.30* SN003-003-02047-8

Velapoldi, R. A., Paule, R. C., Schaffer, R. Mandel, J., Machlan, L. A., and Gramlich, J. W., Standard Reference Materials: A Reference Method for the Determination of Potassium in Serum. NBS Spec. Publ. 260-63 (May 1979). $3.75* SN003-003-02068

Velapoldi, R. A., and Mielenz, K. D., Standard Reference Materials: A Fluorescence Standard Reference Material Quinine Sulfate Dihydrate (SRM 936), NBS Spec. Publ. 260-64 (January 1980). $4.25* SN003-003-02148-2

Marinenko, R. B., Heinrich, K. F. J., and Ruegg, F. C., Standard Reference Materials: Micro-Homogeneity Studies of NBS Standard Reference Materials, NBS Research Materials, and Other Related Samples. NBS Spec. Publ. 260-65 (September 1979). $3.50* SN003-003-02114-1

Venable, W. H., Jr., and Eckerle, K. L., Standard Reference Materials: Didymium Glass Filters for Calibrating the Wavelength Scale of Spectrophotometers (SRM 2009, 2010, 2013). NBS Spec. Publ. 260-66 (October 1979). $3.50* SN003-003-02127-0

Velapoldi, R. A., Paule, R. C., Schaffer, R., Mandel, J., Murphy, T. J., and Gramlich, J. W., Standard Reference Materials: A Reference Method for the Determination of Chloride in Serum, NBS Spec. Publ. 260-67 (November 1979). $3.75* SN003-003-02136-9

Mavrodineanu, R. and Baldwin, J. R., Standard Reference Materials: Metal-On-Quartz Filters as a Standard Reference Material for Spectrophotometry-SRM 2031, NBS Spec. Publ. 260-68 (April 1980). $4.25* SN003-003-02167-9

Velapoldi, R. A., Paule, R. C., Schaffer, R., Mandel, J., Machlan, L. A., Garner, E. L., and Rains, T. C., Standard Reference Materials: A Reference Method for the Determination of Lithium in Serum, NBS Spec. Publ. 260-69 (July 1980). $4.25* SN003-003-02214-4

Marinenko, R. B., Biancaniello, F., Boyer, P. A., Ruff, A. W., DeRobertis, L., Standard Reference Materials: Preparation and Characterization of an Iron-Chromium-Nickel Alloy for Microanalysis, NBS Spec. Publ. 260-70 (May 1981). $2.50* SN003-003-02328-1

Seward, R. W., and Mavrodineanu, R., Standard Reference Materials: Summary of the Clinical Laboratory Standards Issued by the National Bureau of Standards, NBS Spec. Publ. 260-71 (November 1981). $6.50* SN003-003-02381-7

Reeder, D.J., Coxon, B., Enagonio, D., Christensen, R. G., Schaffer, R., Howell, B. F., Paule, R. C., Mandel, J., Standard Reference Materials: SRM 900, Antiepilepsy Drug Level Assay Standard, NBS Spec. Publ. 260-72 (June 1981). $4.25* SN003-003-02329-9

U. S. Department of Commerce
Malcolm Baldrige
Secretary

National Bureau of Standards
Ernest Ambler, Director

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 ($MJ \cdot Kg^{-1}$) 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 2

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

Mean Concentrations ($\mu g/g$) 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

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 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, 18%; 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.

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 moniters 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.

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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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.

Table 1

Sulfur in Coal, SRM 2682 by Ion Chromatography

Sample #	Weight Loss %	Sulfur Wt. %
A		
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	19.2	0.469
Mean =	18.2	0.467
Std. Dev.* =	1.8	0.008
B		
1635-1	10.6	0.326
1635-2	20.3	0.349
C		
1227-3	18.8	0.473
1227-4	18.9	0.466
410-3	14.8	0.468
809-3	18.8	0.456
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

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_2, 20 mL H_2O 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 $NaHCO_3$ and 2 mmol/L Na_2CO_3; flow rate 2.5-3 mL/min.; suppressor column regenerated with H_2SO_4. 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 3

Sulfur in Coal, SRM 2684
by Ion Chromatography

Sample #	Weight Loss %	Sulfur Wt. %
A		
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	3.59	3.03
Mean =	3.64	3.04
Std. Dev.* =	0.43	0.02
B		
1632a-5	1.91	1.58
1632a-6	2.00	1.56
C		
1227-3	3.54	2.98
1227-4	3.52	3.03
410-3	3.23	3.06
809-3	3.10	3.05
Mean =	3.35	3.03
Std. Dev.* =	0.22	0.04

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

Sample #	Weight Loss %	Sulfur Wt. %
A		
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	1.80	4.69
Mean =	1.82	4.65
Std. Dev.* =	0.10	0.06
B		
1632a-7	2.06	1.57
1632a-8	2.00	1.57
C		
1227-3	----	4.63
1227-4	1.31	4.61
410-3	1.17	4.61
809-3	1.11	4.63
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

Mass Spectrometry

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

The zone refined rhenium filaments were outgassed at 1500 °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 Na_2CO_3 and washed repeatedly with quartz distilled water. A mixture of silica gel and H_3PO_4 was prepared, which contained 20 mg silica gel/mL of 0.4M H_3PO_4. This mixture was neutralized with high purity NH_3. The H_3PO_4 was prepared from high purity P_2O_5 and quartz distilled water.

A detailed description of the sample loading and mass spectrometric measurement procedure is given below. The silica gel-H_3PO_4 solution is shaken vigorously to disperse the silica gel and 1 cm (5 μL) is drawn into a 5 cm length of intermedic tubing and placed in the center of the filament. A current of 0.9 A is passed through the filament until the silica gel is dry and then heated an additional 15 sec. A 3 cm length (equivalent to 1.5 μg 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 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 sec. The current is increased and the sample dried at approximately 700 °C for 5 sec. No fumes are observed during this final heating step. If excess H_3PO_4 is present and fumes of P_2O_5 are observed, it causes decomposition of As_2S_3 and the loss of sulfur as H_2S. For this reason the silica gel and H_3PO_4 were premixed (neutralized with NH_3) in a ratio designed to maximize both signal intensity and stability while avoiding excess amounts of H_3PO_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 2×10^{-7} torr. A liquid N_2 cold finger is used to reduce the pressure in the source. The filament is initially heated to 800 °C which typically gives a AsS^+ beam of 2 to 5 volts with a $10^{11}\,\Omega$ feedback resistor. At this temperature the signal is decaying rapidly. The filament temperature is increased to 950 °C in 50 °C increments at 5 min. intervals. The source is focused for maximum intensity after each temperature adjustment. The ion current at 950 °C is stable and normally in the 10V range. Larger ion currents can be obtained above 950 °C but they are unstable. The signal increases and then decays after each temperature increase. Data collection commences at 30 min. The major isotope is either on the 10V or 3V scale and decaying at a moderate rate (5%/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 sec. Delay times of 14 sec and 10 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 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 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}S 95 percent, ^{33}S 0.75 percent, ^{34}S 4.2 percent, and ^{36}S 0.02 percent. Using sulfur enriched in ^{34}S as the tracer, the most precise data are obtained by measuring the $^{32}S/^{34}S$ ratio. The measured ratio in the mixture is given by the following equation:

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

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

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

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 μg of ^{34}S enriched tracer per 3 μg 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 °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 °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 °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 °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 μg 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 μg S/mL and an As/S atom ratio of 2. This solution was used for the ratio measurement by mass spectrometry.

Table 1

Calibration of ^{34}S Enriched Spike Solution

Natural Sulfur	Concentration Determined in Tracer µg S/g[a]
H_2SO_4-135[b]	
Mix #1	313.47
Mix #2	313.63
H_2SO_4-137[b]	
Mix #1	313.60
Mix #2	313.39
H_2SO_4-139[b]	
Mix #1	314.30
Mix #2	314.26
Mean of 6 acids	313.78 ± 0.40 (1s)
K_2SO_4	
Mix #1	313.98
Mix #2	312.88
Na_2SO_4	
Mix #1	313.27
Mix #2	313.73
Mean of 4 salts	313.47 ± 0.49 (1s)
Grand mean of 10 measurements	313.65 ± 0.44 (1s)

[a] Total µg of S per gram of solution.

[b] The three H_2SO_4 acid natural solutions were prepared from three different lots of acids.

It is obvious from equation (2) that to determine the moles of ^{32}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:

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

where the numerator equals the moles of ^{32}S times the atomic weight of sulfur and the denominator equals the fractional abundance of ^{32}S (^{32}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}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}S enriched tracer solution was accurately calibrated. The ^{34}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 HNO_3-HCl and diluted to an approximate concentration of 300 μg total sulfur per gram of solution. The ^{34}S tracer was calibrated against gravimetrically prepared solutions of high purity K_2SO_4 and Na_2SO_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}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 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 4

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

Bottle #	Weight Loss (%)	Dry Sample Weight (g)	S%
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	3.026
		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

OSRM Bottle #	Weight loss (%)	Dry Sample Weight (g)	S%
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	4.703
		Mean =	4.761
		Std. Dev. =	0.067

* Standard Deviation of single measurement

Table 2

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

OSRM Bottle #	Weight Loss (%)	Dry Sample Weight (g)	S%
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	0.4992
		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

OSRM Bottle #	Weight Loss (%)	Dry Sample Weight (g)	S%
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	1.911
		Mean =	1.896
		Std. Dev* =	0.012

* Standard Deviation of single measurement

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. Kirklin

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 ± 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 ± 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_3 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_3 and sulfur.

Table 6

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

Sample #	Weight Loss (%)	Dry Sample Weight (g)	S%
1	18.80	0.16489	0.3576
2	18.80	0.10232	0.3525
3	18.80	0.17319	0.3530
		Mean =	0.3544
		Std. Dev.* =	0.0028

* Standard Deviation of single measurement

Certified Value = 0.33 ± 0.03

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	11.081	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

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 39i). 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^{-1}, 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^{-1} is given for each mean calorific value. The conversion factor of 1 MJ.kg^{-1} = 429.9226 BTU.lb^{-1} 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	HHV3	Sulfur Wt.%
					(BTU/LB)		
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 3

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

SRM No.	Mean ± 1 S.D.*
2682	0.433 ± .046
2683	1.793 ± .068
2684	2.874 ± .029
2685	4.448 ± .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.%	HHV1*	HHV2	HHV3
				(BTU/LB)	
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 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 (BTU/LB)	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 $Btu \cdot lb^{-1}$ ($MJ \cdot kg^{-1}$)

SRM No	Residual Moisture Wt.%	Furnace Ash Wt.%	Sulfur Wt.%	HHV1[a]	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)

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

* Standard deviation of 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:

Sample #	Sample Wt.	Conc. of KIO_3
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 5

Summary of Data on Controls 1632a and 1635
(Calorific Value in Btu·lb^{-1} (MJ·kg^{-1}))

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 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 γ-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 hydrogeneous 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

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

Sample #	2682	2683	2684	2685
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

Sample #	2682	2683	2683	2684
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

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 1

Data for Major Constituents in NBS Coal Samples, SRM 2682

Sample No.	1	2	3	4
Bottle No.	516	1465	893	893
Weight, g	1.0727	1.0007	0.6471	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.	1	2	3	4
Bottle No.	1021	1451	127	122
Weight, g	0.9886	1.0023	0.7199	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.

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 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 ±3 percent level, and the other eight elements measured for SRM 2682 are all consistent.

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)	1.5 ± 0.5	0.7 ± 0.7	1.26 ± 0.03	2
(3678)	1.4 ± 0.2	1.6 ± 0.5		
% Al (1779)	3.14 ± 0.05	3.05 ± 0.09	(3.07)	1
% S (840)	1.57 ± 0.02	1.57 ± 0.04	(1.64)	1
(2379)	1.54 ± 0.04	1.54 ± 0.07		
(3219)	1.46 ± 0.06	1.63 ± 0.11		

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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.

Table 2

SRM 2683, Raw Data
Concentration - μg/g (dry weight basis)*

		Ca	Cl		Mg	Mn		K	Na		Ti	V
Sample No.	Bottle No.	3084 KeV	1642 KeV	2168 KeV	1014 KeV	847 KeV	1811 KeV	1525 KeV	1369 KeV	2754 KeV	320 KeV	1434 KeV
B-08	122	±130 1783	±14 1318	±24 1310	664 ± 145	±.15 12.67	±.48 12.24	714 ± 236	494 ± 6	488 ± 7	424 ± 38	1.0 14.10
B-09	127	±140 2057	±20 1278	±12 1296	427 ± 130	±.27 13.97	±.58 14.05	782 ± 251	497 ± 6	490 ± 10	368 ± 39	±.49 13.63
B-10	498	±200 1892	±15 1248	±12 1278	407 ± 128	±.30 12.72	±.35 12.17	911 ± 205	522 ± 8	509 ± 7	493 ± 39	±.44 13.65
B-11	535	±140 2016	±13 1305	±12 1279	357 ± 133	±.20 13.57	±.35 12.69	874 ± 255	502 ± 10	499 ± 7	440 ± 48	±.47 14.19
B-12	1021	±150 2399	±13 1295	±12 1326	578 ± 131	±.15 13.05	±.51 12.25	495 ± 216	499 ± 12	508 ± 8	494 ± 41	±.90 15.19
B-13	1451	±240 2330	±13 1297	±13 1304	267 ± 219	±.15 12.89	±.35 12.56	760 ± 104	509 ± 7	507 ± 7	257 ± 114	±2.06 16.20
	Mean =	2047	1293	1297	465	13.04	12.55	756	503	501	438	14.0
	2σ** =	200	47	38	265	0.84	1.20	240	20	20	120	1.1

---

* - **The uncertainties in individual results are 1σ counting statistics.**

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

Table 1

SRM 2682, Raw Data
Concentration - μg/g (dry weight basis)*

		Ca	Cl		Mg	Mn		K	Na		Ti	V
Sample No.	Bottle No.	3084 KeV	1642 KeV	2168 KeV	1014 KeV	847 KeV	1811 KeV	1525 KeV	1369 KeV	2754 KeV	320 KeV	1434 KeV
B-01	486	11816 ± 300	586 ± 11	560 ± 10	1802 ± 150	26.44 ± .40	26.35 ± .70	348 ± 164	1049 ± 15	1039 ± 21	499 ± 42	15.06 ± .38
B-02	498	11921 ± 400	1178 ± 16	1169 ± 15	1973 ± 225	26.47 ± .30	26.86 ± .50	128 ± 170	1033 ± 9	1020 ± 16	437 ± 67	13.33 ± .72
B-03	514	11314 ± 300	373 ± 9	381 ± 10	1645 ± 125	25.79 ± .30	26.44 ± .50	194 ± 166	1034 ± 10	1045 ± 10	473 ± 35	14.59 ± .32
B-04	516	11219 ± 240	519 ± 13	521 ± 12	1654 ± 125	26.28 ± .40	25.44 ± .50	310 ± 190	1028 ± 8	1014 ± 12	483 ± 61	14.68 ± .32
B-05	893	11392 ± 300	524 ± 10	527 ± 10	1682 ± 125	26.29 ± .40	26.13 ± .50	243 ± 121	1032 ± 11	1011 ± 28	503 ± 35	14.51 ± .34
B-07	1465	11254 ± 300	506 ± 9	497 ± 9	1724 ± 125	25.96 ± .40	26.03 ± .50	209 ± 123	1040 ± 8	1019 ± 10	567 ± 34	14.64 ± .33
	Mean =	11430	***		1713	26.19	26.20	235	1035	1027	505	14.62
	2σ** =	560			185	0.60	1.00	140	12	28	85	0.70

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* - The uncertainties in individual results are 1σ 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 4

SRM 2685, Raw Data
Concentration - μg/g (dry weight basis)*

		Ca	Cl		Mg	Mn		K	Na		Ti	V
Sample No.	Bottle No.	3084 KeV	1642 KeV	2168 KeV	1014 KeV	847 KeV	1811 KeV	1525 Kev	1369 KeV	2754 KeV	320 Kev	1434 KeV
B-20	481	±200 5180	645 ± 15	651 ± 11	974 ± 155	41.0 ± .5	40.9 ± .7	±141 2677	754 ± 10	767 ± 13	919 ± 65	31.1 ± .8
B-21	482	±200 5564	653 ± 14	644 ± 13	1155 ± 154	42.2 ± .5	40.7 ± .9	±247 2741	768 ± 10	764 ± 13	914 ± 64	30.6 ± .8
B-22	487	±200 4925	649 ± 14	638 ± 13	887 ± 153	39.9 ± .4	38.7 ± .7	±191 2870	760 ± 10	763 ± 13	842 ± 63	29.2 ± .8
B-23	497	±200 5121	652 ± 13	650 ± 12	1108 ± 140	40.4 ± .4	39.5 ± .4	±136 2776	759 ± 10	758 ± 11	859 ± 62	30.3 ± .8
B-24	847	±200 5603	655 ± 14	636 ± 13	1214 ± 164	42.1 ± .5	41.1 ± .4	±137 2694	770 ± 10	772 ± 12	909 ± 63	30.9 ± .8
B-25	1474	±200 5004	645 ± 15	635 ± 15	1042 ± 145	41.8 ± .4	40.8 ± .6	±166 2512	765 ± 10	769 ± 12	901 ± 61	30.6 ± .7
	Mean =	5234	650	643	1061	41.1	40.3	2705	763	765	890	30.5
	2σ** =	500	13	14	150	1.0	1.0	200	14	15	65	1.3

---

* - The uncertainties in individual results are 1σ 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 - μg/g (dry weight basis)*

		Ca	Cl		Mg	Mn		K	Na		Ti	V
Sample No.	Bottle No.	3084 KeV	1642 KeV	2168 KeV	1014 KeV	847 KeV	1811 Kev	1525 KeV	1369 KeV	2754 KeV	320 KeV	1434 KeV
B-14	482	±400 4442	±30 1292	±13 1295	764 ± 181	±.98 35.25	±.83 34.68	±156 1800	259 ± 6	259 ± 10	578 ± 70	±1.24 23.10
B-15	858	±180 4363	±14 1304	±16 1272	865 ± 150	±.25 35.46	±.62 35.60	±369 1944	262 ± 6	252 ± 12	555 ± 71	±.55 21.46
B-16	864	±160 4344	±20 1301	±12 1309	691 ± 150	±.30 35.71	±1.0 35.17	±140 2049	266 ± 8	265 ± 9	493 ± 42	±.49 21.93
B-17	1204	±180 4360	±14 1304	±12 1305	698 ± 150	±.38 35.30	±.50 35.49	±226 2052	261 ± 6	262 ± 6	595 ± 53	±.66 20.98
B-18	1209	±170 4313	±14 1271	±12 1262	839 ± 150	±.30 35.58	±.89 35.25	±474 2202	262 ± 8	264 ± 7	600 ± 67	±.56 21.76
B-19	1469	±180 4388	±14 1267	±13 1285	790 ± 150	±.41 36.20	±1.0 35.58	±200 1985	265 ± 10	255 ± 6	677 ± 50	±.57 22.67
	Mean =	4355	1288	1289	775	35.6	35.4	1970	262	260	580	21.9
	2σ** =	200	36	38	150	0.6	0.6	250	8	10	150	1.2

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* - The uncertainties in individual results are 1σ counting statistics.

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

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 (5×10^{13} n.cm.$^{-2}$ s^{-1}) 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 ± 0.005 percent (1s) vs. 1.465 ± 0.005 percent, while the reverse was observed for Sm, 1.114 ± 0.002 μg/g (1s) compared to 1.124 ± 0.002 μg/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 5

Summary of Elemental Concentrations in SRM Coals
(μg/g ± 2s)

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

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

Table 3

Summary of Concentrations Observed in Coal, SRM 2684

Mean Concentration (µg/g unless % indicated) ± 2s*

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

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*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 (µg/g unless % indicated) ± 2s*

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

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*Two times the standard deviation of a single measurement
**Variability at least twice as great as counting statistics.

Table 1

Summary of Concentrations Observed in Coal, SRM 2682

Mean Concentration (μg/g) ± 2s*

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

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*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 (μg/g) ± 2s*

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

*Two times the standard deviation of a single measurement

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

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).

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 activitation 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:

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

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:

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

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:

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

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