

Methods for Sampling and Inorganic Analysis of Coal

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Methods for Sampling and Inorganic Analysis of Coal

Edited by D.W. GOLIGHTLY and F.O. SIMON

This manual presents a collection of detailed procedures used in geochemical laboratories of the U.S. Geological Survey for the chemical characterization of coal.

U.S. GEOLOGICAL SURVEY BULLETIN 1823

DEPARTMENT OF THE INTERIOR
MANUEL LUJAN, JR., Secretary

U.S. GEOLOGICAL SURVEY
Dallas L. Peck, Director



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ACRONYMS

AAS	atomic absorption spectrometry
AES	atomic emission spectrography (or spectrometry)
AFT	ash fusion temperature
ASTM	American Society for Testing and Materials
BCR	Community Bureau of Reference (Commission of the European Communities, Brussels)
CAL	calorific value
CRM	certified reference material (BCR)
FSI	free swelling index
HGI	Hardgrove grindability index
ICP	inductively coupled plasma
INAA	instrumental neutron activation analysis
ISA	infrared spectrometric sulfur analyzer
ISE	ion selective electrode
LOI	loss on ignition
MINTEK	Council for Mineral Technology, South Africa
NBS	National Bureau of Standards
NCRDS	National Coal Resources Data System (USGS)
PVC	polyvinylchloride
RSD	relative standard deviation
SARM	South African reference material (MINTEK)
SPGR	specific gravity
SRM	standard reference material (NBS)
TRIGA	thermal reactor installation—General Atomic [Company]
USCHEM	United States Chemistry data base within NCRDS
USGS	United States Geological Survey
WDXRF	wavelength dispersive x-ray fluorescence
XRF	x-ray fluorescence

Methods for Sampling and Inorganic Analysis of Coal

INTRODUCTION

By D.W. Golightly and F.O. Simon

Abstract

Methods used by the U.S. Geological Survey for the sampling, comminution, and inorganic analysis of coal are summarized in this bulletin. Details, capabilities, and limitations of the methods are presented.

INTRODUCTION

The large body of chemical information (for example, see Averitt and Lopez, 1972; O'Gorman and Walker, 1972; Zubovic and others, 1980) available to the modern coal scientist has been provided by diverse instrumental and chemical methods of analysis. The methods used in U.S. Geological Survey laboratories (Golightly and others, 1986; Simon and Huffman, 1978; Swanson and Huffman, 1976) change with the requirements for investigations of coal composition and with refinements in the instrumentation and approaches to chemical analysis. Detailed descriptions of most of the methods routinely used in U.S. Geological Survey laboratories for determining the inorganic composition of coal are provided in this bulletin. In addition to the descriptions of methods, one section is dedicated to the important topic of coal sampling and another treats the comminution of field samples prior to analysis.

Concentrations of more than 70 elements important to investigations of coal are determined by diverse methods established for the chemical and instrumental analysis of both whole coal and coal ash. This diversity results from the different capabilities of the individual methods, the quality of information sought, and the cost of this information. The measurement techniques used for the determination of major, minor, and trace elements in coal and coal ash include atomic emission spectrography (AES), atomic absorption spectrometry (AAS), X-ray fluorescence (XRF) spectrometry, instrumental neutron activation analysis (INAA), and ion-selective electrode (ISE). The conventional routing of

samples and types of analyses are illustrated by the chart in figure 1.

For the routine quantitative analysis of coal ash (ashing temperature of 525 °C), the elements Cd, Cu, Li, Mg, Mn, Na, Pb, and Zn are determined by AAS, and Al, Ca, Fe, K, Mg, Mn, Na, P, S, Si, and Ti are determined by XRF spectrometry. Rapid chemical methods, described in this bulletin, offer an alternative approach for measurements of the same elements determined by XRF spectrometry. After a special ashing procedure and fusion of the resulting ash with NaOH, fluorine concentrations are measured by ISE. An automated, semiquantitative direct-current (dc) arc AES method is applied to the analysis of all coal ashes for the determination of 64 elements. Lower determination limits for the methods used for the analysis of coal ash are listed in table 1.

For the routine quantitative analysis of whole coal, Hg is determined by cold-vapor AAS; Cl and P are measured by XRF spectrometry; and As, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Hf, Hg, K, La, Lu, Na, Nd, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, U, W, Yb, and Zn are determined by INAA. Total sulfur and sulfur species (forms of sulfur) are determined by gas-phase infrared absorption spectrometry that is combined with chemical separation methods. Lower determination limits for these methods are summarized in table 1.

In addition to analyzing coal for the elements indicated in table 1, the U.S. Geological Survey routinely analyzes coals by methods recommended by the American Society for Testing and Materials (ASTM) for calorific value, proximate analysis (moisture, ash, volatile matter, and fixed carbon), ultimate analysis (C, H, N, O, and S), and physical parameters, such as Hardgrove grindability, ash-fusion temperature, specific gravity, and free-swelling index. Equilibrium moisture is determined on selected samples. The "1984 Annual Book of ASTM Standards" (ASTM, 1984) provides

Table 1. Lower determination limits (in $\mu\text{g/g}$) for elements in whole coal or coal ash, listed by method of analysis

H																	He
Li 2 68	Be 1											B 3	C	N	O	F 20 ISE	Ne
Na 1 100 10 22	Mg 1 100 22											Al 100 460	Si 500 46	P 100 680	S 100	Cl 100	Ar
K 100 100 680	Ca 100 10	Sc 0.01 1	Ti 100 32	V 1	Cr 1 1	Mn 2 100 1 1	Fe 100 100 74	Co 0.2 1	Ni 500 1.5	Cu 10 1	Zn 1 1 10	Ga 5 1.5	Ge 5	As 1 100	Se 1	Br 1	Kr
Rb 5	Sr 50 1	Y 1.5	Zr 100 3	Nb 7	Mo 10 1	Tc	Ru 2	Rh 2	Pd 1	Ag 0.1	Cd .02 32	In 10	Sn 5	Sb 0.1 68	Te	I	Xe
Cs 0.1	Ba 100 1.5	La 0.02 10	Hf 0.1 15	Ta 0.03 320	W 0.1 15	Re 10	Os 15	Ir 0.01 15	Pt 2	Au 0.005 7	Hg .01 CVAAS 1	Tl 10	Pb 20 7	Bi 10	Po	At	Rn
Fr	Ra	Ac															

Ce 0.5 43	Pr 100	Nd 2 32	Pm	Sm 0.5 10	Eu 0.02 2	Gd 2 32	Tb 0.1 32	Dy 10 22	Ho 0.5 7	Er 5	Tm 0.5 5	Yb 0.2 0.2	Lu 0.01 15
Th 0.1 46	Pa	U 0.5 220	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

Key:

Lower determination limit, $\mu\text{g/g}$, in the coal or coal ash measured by:

Element

Na	AAS
	XRF
	INAA
	DCA

Atomic Absorption Spectrometry [ash], Hg by Cold-Vapor AAS [whole coal];
 X-Ray Fluorescence spectrometry [ash, whole coal];
 Instrumental Neutron Activation Analysis [whole coal];
 Direct-Current Arc spectrography, semiquantitative [ash].
 ISE: Ion-Selective Electrode (fluorine only).

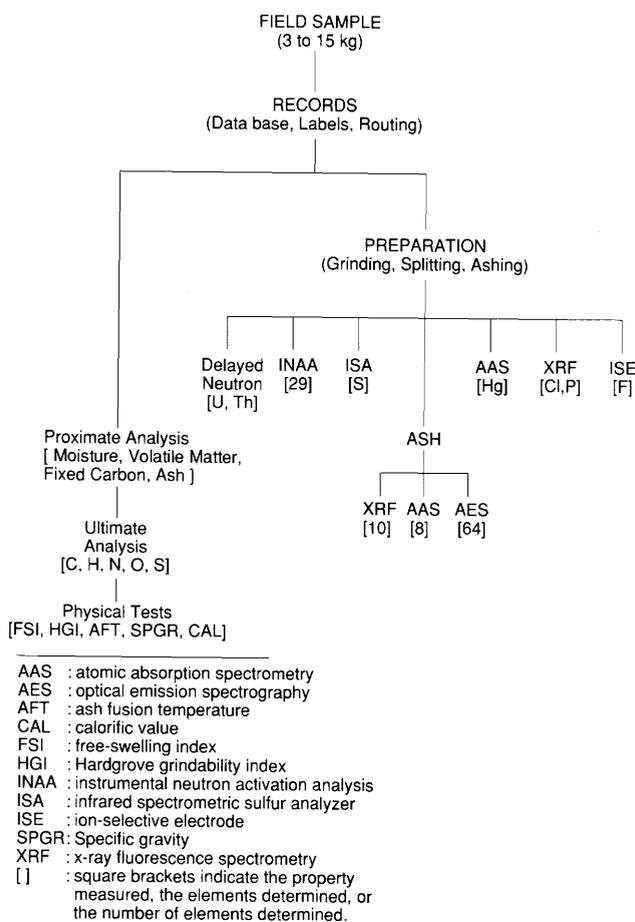


Figure 1. Flowchart for samples and analyses of coals.

detailed descriptions of the standard procedures used. A list of the pertinent ASTM methods appears in table 2.

All data for coals and associated rocks analyzed by the U.S. Geological Survey reside in the National Coal Resources Data System (NCRDS) (Carter and others, 1981). The NCRDS is an interactive computerized storage, retrieval, and display system created to assess the quantity and quality of the nation's coal resources. Currently, the NCRDS USCHEM data bases contain analytical data on approximately 10,000 point-located coal and associated rock samples from all coal regions of the United States. Other data bases contain information on approximately 50,000 samples that are area located. In addition, the geochemical data bases contain geologic and geographic data for each sample. A total of 128 parameters, including the analytical data, can be stored for each sample. The geologic and geographic data include State, county, latitude, longitude, coal province, region, coal field, district, formation group, coal bed, member, zone, series, location name, quadrangle, collector, point identification, date, estimated rank, calculated rank, laboratory identification number, and sample type.

The accuracy of analysis by the U.S. Geological Survey methods, each of which is the topic of a section of this bulletin, is ultimately linked to a standard reference material (Uriano and Gravatt, 1977). These standard coals and coal ashes are provided by various agencies, such as the National Bureau of Standards, and commercial laboratories, such as Alpha Resources, Inc. Representative materials are described in the appendix to this bulletin, where the addresses of suppliers are also given. A significant new development is underway at the Argonne National Laboratory where eight premium coal standards are being prepared (see the appendix).

In addition to this bulletin, a large body of information on the chemical and physical characterizations of coal is available to the coal scientist. The general methodologies used for inorganic analysis of coal, critically reviewed recently by Swaine (1985) for bituminous coal, are described in various journal articles and books. Valkovic (1983) has provided a comprehensive review of both the chemistry and the methodology used for the characterization of coal. Mills and Belcher (1981) surveyed atomic spectrometric methods for the analysis of coal, coke, ash, and mineral matter. The "1984 Annual Book of ASTM Standards" (ASTM, 1984) provides detailed descriptions of standard procedures for sampling, grinding, and analyzing coal and coke. Volumes edited by Babu (1975) and Karr (1978) describe numerous instrumental and chemical methods for the characterization of coal. Mineral matter and trace-element associations are treated in these two books and in a recently published book by Vorres (1986).

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Table 2. Selected ASTM standard methods (ASTM, 1984)

Designation	Title
D121-78(1983)	Standard Definitions of Terms Relating to Coal and Coke, p. 207-208.
D167-73(1979)	Standard Test Method for Specific Gravity and Porosity of Lump Coke, p. 209-212.
D388-82	Standard Classification of Coals by Rank, p. 242-246.
D409-71(1978)	Standard Test Method for Grindability of Coal by the Hargrove-Machine Method, p. 247-253.
D-720-83	Standard Test Method for Free-Swelling Index of Coal, p. 272-278.
D1412-74(1979)	Standard Test Method for Equilibrium Moisture of Coal at 96 to 97 percent Relative Humidity and 30° C, p. 279-281.
D1757-80	Standard Test Methods for Sulfur in Ash from Coal and Coke, p. 286-290.
D1857-68(1980)	Standard Test Method for Fusibility of Coal and Coke Ash, p. 292-297.
D2013-72(1978)	Standard Method of Preparing Coal Samples for Analysis, p. 298-312.
D2015-77(1978)	Standard Test Method for Gross Calorific Value of Solid Fuel by the Adiabatic Bomb Calorimeter, p. 320-328.
D2234-82	Standard Methods for Collection of a Gross Sample of Coal, p. 329-345.
D2361-83	Standard Test Method for Chlorine in Coal, p. 346-349.
D2492-84	Standard Test Methods for Forms of Sulfur in Coal, p. 350-354.
D2795-84	Standard Methods of Analysis of Coal and Coke Ash, p. 366-373.
D2796-82	Standard Definitions of Terms Relating to Megascopic Description of Coal and Coal Seams and Microscopical Description and Analysis of Coal, p. 374-377.
D3172-73(1979)	Standard Method for Proximate Analysis of Coal and Coke [moisture, volatile matter, fixed carbon (by difference), and ash], p.397.
D3173-73(1979)	Standard Test Method for Moisture in the Analysis Sample of Coal and Coke, p. 398-400.
D3174-82	Standard Test Method for Ash in the Analysis Sample of Coal and Coke From Coal, p. 401-404.
D3175-82	Standard Test Method for Volatile Matter in the Analysis Sample of Coal and Coke, p. 405-408.
D3176-84	Standard Method for Ultimate Analysis of Coal and Coke [C,H,S,N,O,Ash], p. 409-412.
D3177-84	Standard Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke, p. 413-417.
D3178-84	Standard Test Methods for Carbon and Hydrogen in the Analysis Sample of Coal and Coke, p. 418-423.
D3179-84	Standard Test Methods for Nitrogen in the Analysis Sample of Coal and Coke, p. 424-430.
D3180-84	Standard Test Method for Calculating Coal and Coal Analysis from the As-Determined to Different Bases, p. 431-434.
D3286-82	Standard Test Method for Gross Calorific Value of Solid Fuel by the Isothermal-jacket Bomb Calorimeter, p. 435-444.
D3302-82	Standard Test Method for Total Moisture in Coal, p. 445-454.
D3682-78(1983)	Standard Test Methods for Major and Minor Elements in Coal and Coke Ash by Atomic Absorption [Si,Al,Fe,Ca,Mg,Na,K,Ti,Mn,P] p. 458-465.
D3683-78(1983)	Standard Test Method for Trace Elements in Coal and Coke Ash by Atomic Absorption [Be,Cd,Cr,Cu,Mn,Ni,Pb,V,Zn], p. 466-469.
D3684-78(1983)	Standard Test Method for Total Mercury in coal by the Oxygen Bomb Combustion - Atomic Absorption Method, p. 470-473.
D3761-79(1984)	Standard Test Method for Total Fluorine by the Oxygen Bomb Combustion - Ion Selective Electrode Method, p. 474-477.
D4208-83	Standard Test Method for Total Chlorine in Coal by the Oxygen Bomb Combustion - Selective Ion Electrode Method, p. 480-483.
D4239-83	Standard Test Method for Sulfur in the Analysis Sample of Coal and Coke using High Temperature Tube Furnace Combustion Methods, p. 484-495.
D4326-84	Standard Test Method for Major and Minor Elements in Coal and Coke Ash by X-Ray Fluorescence, p. 496-499.
D4182-82	Standard Practice for Evaluation of Laboratories using ASTM Procedures in the Sampling and Analysis of Coal and Coke, p. 478-479.

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SAMPLING OF COAL BEDS FOR ANALYSIS

By Ronald W. Stanton

Abstract

Channel and core samples are the primary types of samples collected and analyzed to establish the chemical composition, or quality, of coal beds. The choice between channel or core samples may be predicated on cost and accessibility to the coal bed. The purpose of the investigation or program determines the nature of the sample to be taken and the materials to be included in the sample. Impurities, such as mineral-rich layers, may be included in the sample, depending on the intended use of the data.

A channel or core sample should (1) represent an equal volume from the top to the bottom of the coal bed and (2) experience minimal comminution and (3) not be split in the field. Discrimination between impure coal, carbonaceous shale, and coal sometimes is subjective and consequently affects the precision of the sampling method. A coal bed can be described and sampled by facies by delimiting the laterally continuous subunits of the bed and by evaluating their effect on bed quality, particularly in the collection of channel samples. Descriptions of core samples are facilitated by geophysical logging techniques and by X-ray radiography.

The number of samples required to characterize adequately a coal bed depends on the thickness, quality variability, and size of the deposit. In general, the locations for sampling in mines should be separated by distances that are comparable to spacings of other outcrop or core locations in the same bed. Additionally, two to three closely spaced locations (10 to 100 m) may yield useful data on local variability of certain quality parameters.

PURPOSES OF SAMPLING A COAL BED

Samples submitted for chemical and physical analyses are collected for a variety of reasons, but the collection of each sample should always conform to certain guidelines. The application of precise techniques in sample collection helps to ensure that data from each analysis performed on the samples will be useful. For interpretations and comparisons of elemental compositions of coal beds to be valid, the samples must be collected so that they are comparably representative of the coal bed. Such interpretations and comparisons should never be based on data from different types of samples.

The purpose in sample collection and the kinds of analyses to be performed on the sample dictate the type and nature of the sample that should be collected (see table 3). For samples used in determining rank, mineral-rich layers greater than 1 cm must be excluded so that only the coal intervals are sampled (ASTM, 1986a). In contrast, samples intended for chemical analysis commonly include mineral-rich layers that are less than 10 cm thick (Swanson and Huffman, 1976); samples obtained for petrographic analysis generally consist of lithologically distinct parts of the coal bed taken at separate intervals; and samples intended for washability testing may consist of all material, rock and coal, between the roof and the floor of the coal bed.

Table 3. Types of samples and purposes for which samples are commonly collected

		CLASSIFICATION BY RANK	APPARENT RANK	GEOLOGIC STUDIES	RESOURCE STUDIES	RESERVE QUALITY	ENVIRONMENTAL QUALITY	PRODUCT QUALITY	WASHABILITY TESTING
CHANNEL	COAL ONLY	X			X			?	
	WHOLE BED		X			X	X	X	X
	BENCH FACIES		X	X		X	X	?	X
CORE	COAL ONLY		X		X			?	
	WHOLE BED		X			X	X	X	X
	BENCH FACIES		X	X		X	X	?	X

COAL ONLY = Sample taken using exclusionary rule
 WHOLE BED = All material between roof and floor of bed
 BENCH = All mineral layers and coal between mineral layers
 FACIES = Laterally extensive subunits of coal bed
 ? = Possible sampling for product quality

Other purposes may also be best served by channel or core samples. If the objective is to represent the resources of a coal bed for mine planning and future extraction methods, channel and core samples are necessary. In resource and reserve characterization, coal sample subtypes include those that represent the whole bed, coal facies (laterally extensive parts of the bed), and total coal interval. Stratigraphic descriptions of the coal bed at and between sample localities should enable correlations of subunits, or facies, of the coal bed (fig. 2). This procedure will aid in understanding abrupt quality or thickness changes in the bed. In contrast, if the purpose in sample collection is to represent a mined product, a properly obtained conveyor-belt sample (ASTM, 1986c) may be preferable to channel or core samples.

In some cases, obtaining channel samples may not be possible, thus leaving core samples as the only practical alternative. Some supplementary coal-quality data can be obtained by down-hole geophysical techniques (Lavers and Smits, 1976), regardless of whether a core is recovered.

HISTORICAL PERSPECTIVE OF SAMPLING

The methods of sampling described by Burrows (1907) and Holmes (1911) involve an exclusionary procedure in which the sampler eliminates partings or impurities (mineral-rich layers) greater than 1 cm and lenses or concretions of sulfur or other impurities greater than 5 cm in diameter and 1.3 cm thick "if in the judgement of the sampler, they are being excluded by the miner from the coal as loaded out of the mine or as shipped" (Holmes, 1911, p. 1). The reason for such a procedure is "to obtain samples that represent, as nearly as possible, the coal that is produced commercially from the mine" (Holmes, 1911, p. 8). This was the purpose of sampling coal during the early 1900's by the U.S. Bureau of Mines and the U.S. Geological Survey (Burrows, 1907; Campbell, 1907). For the fuel inspectors of the U.S. Bureau of Mines, the sampling purpose was qualified to represent the particular mining practice at an individual mine and at a specific time. In contrast, the samplers from the U.S. Geological Survey attempted to approximate the average composition of produced coal without regard to site-specific mining practices; therefore, their samplers strictly followed the exclusionary procedure. In both methods, partings and pyrite of certain thicknesses were excluded from the sample. The U.S. Bureau of Mines inspectors excluded only those partings excluded by the miner, and the U.S. Geological Survey samplers excluded layered, mineral-rich material of certain thicknesses.

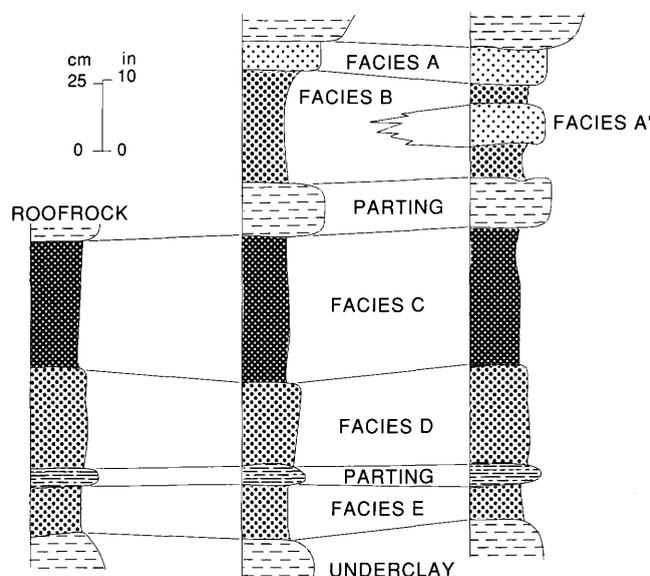


Figure 2. Correlation of facies of a single coal bed.

SAMPLING FOR RANK CLASSIFICATION

To classify coal by rank, the American Society for Testing and Materials (ASTM) refers to the publication by Holmes (1911) as the method of sampling (ASTM, 1986a). In addition, the procedure described by Schopf (1960), which restates the rule for exclusion of material, attempts to discriminate obvious partings from impure coal; the latter is sampled as part of the coal bed. For purposes of rank classification, perhaps either variation of the procedure is adequate. However, objective criteria to distinguish precisely coal from noncoal layers are not available. In the calculation of rank-determining values, the fixed carbon or calorific-value mineral matter is "removed mathematically." This continued practice of excluding mineral layers in samples from a bed, even by a mathematical correction for mineral matter, is probably an outgrowth of concerns by such early workers as Fieldner and Selvig (1930), who proposed that coal rank be calculated on a pure-coal or unit-coal basis.

If an approximation of the characteristics of the mined product is needed, perhaps a better sample for determining rank would be some mechanical separation of a whole-bed sample. The original purpose of the exclusion of partings was to approximate or verify more closely ash and sulfur concentrations for coal delivered by train cars from mined areas (Burrows, 1907; Campbell, 1907). During the days of blasting and hand loading of coal, discrimination among impurities could be made by those handling the coal. However, high-production equipment, such as a continuous miner or long-wall mining equipment, does not differentiate between the coal and the partings during extraction. Parting material generally is removed by jigs or air tables in the first stage of coal preparation.

SAMPLING FOR CHEMICAL ANALYSIS

Another purpose for collecting a channel or core sample is to evaluate the chemical composition of the coal. Known concentrations and distributions of major, minor, and trace elements in a coal bed enable an assessment of the possible environmental impacts and technological problems that could occur from use of the coal. A modification of the exclusionary procedure is commonly used because rock partings may contribute to the variability in concentrations of certain elements or to quality parameters. Shale, siltstone, or nonbanded, impure-coal (bone) layers less than 10 cm thick are included in whole-bed channel samples if it is probable that these materials will be mined along with the coal (Swanson and Huffman, 1976). Swanson and Huffman (1976) also recommended that special samples of non-coal materials be collected to determine their contribution to abnormal elemental concentrations. However, "judgement . . . must be applied toward obtaining samples which will be most representative of the coal bed" (Swanson and Huffman, 1976, p. 2).

SAMPLING FOR OTHER PURPOSES

Other purposes of sampling, such as determining the coal and the noncoal facies and predicting the geometry and quality of a coal bed, may require detailed sampling procedures by bench or by coal facies. In these procedures, the effects of including or excluding parting materials must be assessed. The combined effects of the laterally extensive layers of the bed on the quality of the whole bed also can be evaluated.

In all attempts to sample coal beds, the purpose of collecting a coal sample determines the criteria applied to sampling. Precautions must be taken when comparing certain elemental concentration values so that samples taken for different purposes are not directly compared. For example, in samples collected and analyzed to estimate rank, mineral layers greater than 1 cm thick are excluded, and for samples collected and analyzed to determine the trace-element composition, mineral layers less than 10 cm thick are excluded. Direct comparisons of data from these two suites of samples are suspect. Thus, ash or sulfur isopleth maps generated from this mixed-sample-type set should not be interpreted as being related to coal-forming processes. Furthermore, the application of the exclusionary procedure does not reflect present mining practices. Other questionable comparisons may be made if data from bench or facies samples are mixed with data from whole-bed samples.

PROCEDURE FOR CHANNEL SAMPLING

For both surface and deep mines, the ASTM (1986a) standard for collecting channel samples of coal

should be followed. The following procedures are used to collect channel samples of coal.

1. Select a freshly exposed face to sample. Avoid coal ribs or faces that have been "rock dusted" or show obvious signs of oxidation, such as red-brown stains or efflorescence. In a deep mine, sampling of a new face may be possible just after the roof has been bolted and before the next cut is made. In a surface mine, a fresh face can be sampled following the loading stage of mining.
2. Select a face having a plane that is normal to bedding. Coal may be cut back with a hand pick at the top and bottom to produce a proper surface.
3. Spread a 3- × 4-m nylon-reinforced vinyl tarpaulin on the floor.
4. Mark two parallel, vertical lines (using crayon) about 10 cm apart on the coal face, and select the units to be included in the sample. If the exclusionary procedure is to be followed, the excluded layers should be clearly marked.
5. Using a pick, begin at the bottom of the coal bed and chip out the coal between the lines to a depth of approximately 8 cm; repeat this step from the bottom to the top of the channel.
6. Carefully square the back of the channel so that the channel cut is of uniform volume. In surface mines, gas-powered masonry cut-off saws may be used to cut small channels on either side of the 10-cm-wide block to be sampled. In deep mines, an analogous procedure involves drilling a series of holes by hand auger, from top to bottom, on both sides of the 10-cm wide block to expose a column for sampling.
7. Transfer the entire sample into polyethylene-lined canvas bags or drums. Representative splitting can be done later in the laboratory. In the past, samples were split in the mine to prevent loss of moisture from the freshly removed material. Schopf (1960) suggests that a separate sample, solely for moisture determination, be taken from part of the coal bed and sealed in an air-tight container.
8. Place a properly marked sample tag inside the innermost bag, label the outside container, and seal each container separately.
9. Record a description of the channel, with particular emphasis on the thickness of the coal bed subunits.

PROCEDURE FOR SAMPLING DRILL CORE

The drill core should be the most representative type of sample of a coal bed. However, in some cases, coal is lost during coring, and the complete bed is not represented by the recovered drill core. In any case, geophysical techniques, such as gamma and gamma-gamma (density) logs, should be used to compare the

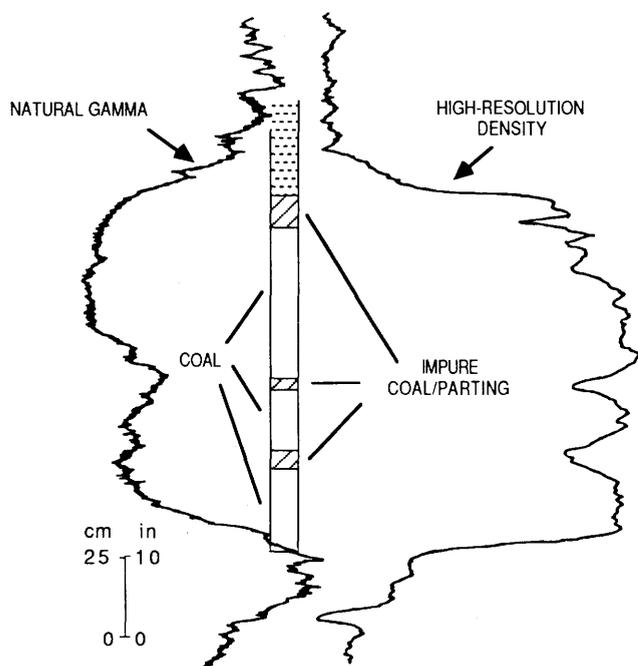


Figure 3. Natural gamma and high-resolution density logs of a coal bed showing log responses of coal and impure coal or parting.

thickness of the bed to the thickness of the core recovered (fig. 3).

After the drill core barrel is brought to the surface, the collection of a core should involve the following procedure:

1. For the split barrel, remove half of the barrel from the core. Position split polyvinylchloride (PVC) pipe over the exposed core. Remove the barrel after the core, barrel, and pipe are rolled over together. For the solid barrel, place the PVC pipe at one end of the barrel; extrude the core onto the PVC pipe.
2. Arrange the core with no gaps between pieces. Then, measure and describe the core.
3. Place the second half of the PVC pipe over the core, cap and tape the ends of the pipe, and clearly label the pipe.
4. Pull a polyethylene sleeve over the pipe, and seal the ends to prevent moisture loss. A moist sponge can be placed in the sleeve to prevent further moisture loss.

Next, X-ray radiography (Standards Association of Australia, 1982; Stanton and others, 1983) should be performed on the core. If the exclusionary procedure is used, radiography is a reliable technique for discerning coal from noncoal layers. The use of PVC pipe (fig. 4) to encase the coal core provides a way to transport the core without major disorientation and, in many cases, without further breakage.

COAL BED DESCRIPTIONS

Channel-sampled coal faces should be described as completely as possible. Minimally, the thickness of the bed, the thickness and stratigraphic positions of partings, the pyrite layers, and the mineral-bleat fillings should be measured and described. Subunits, or facies, that are lithologically distinct and that have lateral continuity can be identified by the frequency and thickness of vitrain bands and attritus (Schopf, 1960). Individual layers, such as vitrain (bright, homogeneous layers greater than 1 mm thick) and fusain ("charcoal"), generally are not laterally continuous; they are commonly lenticular because they form from compressed plant stems, leaves, and roots. For the most part, facies are composed of assemblages of vitrain and attrital layers or other rock that can be identified and recognized in the coal bed (fig. 5). These facies frequently can be mapped for miles, and commonly have a narrow range of coal quality (fig. 6).

Visual descriptions of core are difficult to make unless the core is broken. Visual descriptions can be complemented with data from common down-hole, geophysical measurement techniques, such as gamma, gamma-gamma (density), and resistivity (Lavers and Smits, 1976). A high-resolution geophysical density log can provide data that aid in the identification of coal facies (fig. 3). High-resolution density logging also can provide measurements of thickness to the nearest 3 cm and a profile of the quality of the coal bed (fig. 3). X-ray radiography (fig. 7), combined with visual observation of the core and density log, provides another tool for recognizing the dominant facies in a core. Comparison of an X-ray radiograph to a density log can be used to (1) discriminate between layers of pyrite and clay, impure coal, and coal, (2) determine which parts of the

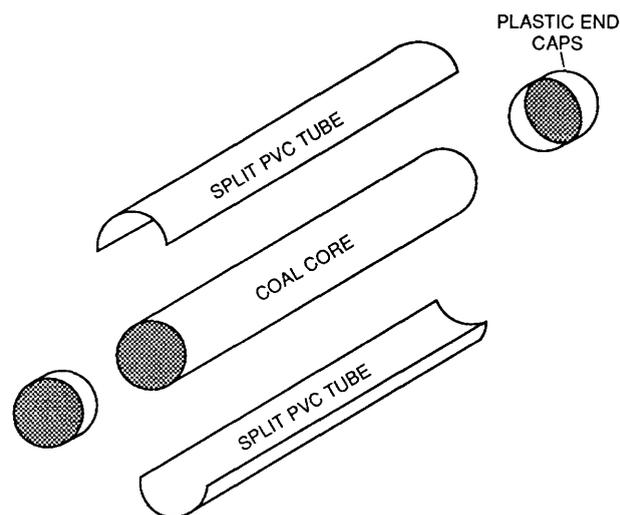


Figure 4. Container for collection of core samples.

coal bed were not recovered in the core, and (3) identify the different facies of the coal bed.

IDENTIFICATION OF CARBONACEOUS SHALE LAYERS

High-ash coal or mineral-rich partings generally are visually distinct in a coal bed. However, in most cases, criteria or tests cannot be applied objectively in the field to differentiate impure coal (25 to 50 weight percent ash) from carbonaceous shale (>50 weight percent ash). Any classification that involves such terms as “bone,” “billy coal,” or “rash” generally has only local significance and is not useful for coals of different rank or type (Schopf, 1960). Some field methods may provide aid in discriminating carbonaceous shale from coal. In surface mines, a gamma-ray scintillometer (a hand-held instrument) is used to locate impure layers in low-ash coal. For the drill core, an X-ray radiograph and a gamma-gamma (density) down-hole geophysical log can be compared with the coal core.

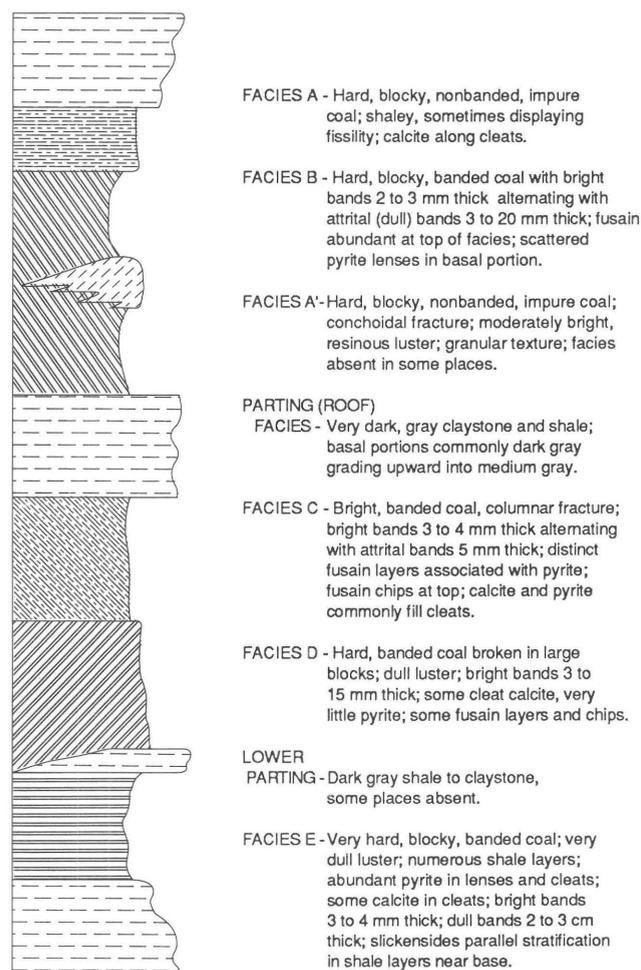


Figure 5. Example of description of generalized stratigraphic section of the Upper Freeport coal bed.

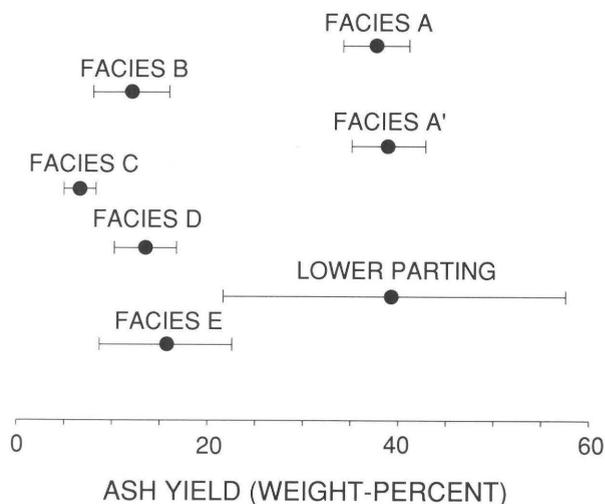


Figure 6. Ash yields of 134 facies samples of the Upper Freeport coal bed.

For sample collection from deep mines, no comparable instrument that is “mine safe” is available. This deficiency in instrumentation creates difficulty when applying the exclusionary procedure. However, even if this procedure is not followed, another difficulty exists in precisely sampling a coal bed at the points of contact with adjacent rock strata. Commonly, coal bed contacts between the floor and roof rocks are sharp. However, in places, contacts are interbedded, transitional, or located in a nonbanded layer, particularly at the top of the bed.

SAMPLING THICK COAL BEDS

A common practice of sampling thick coal beds (greater than 10 m thick), either by core or by channel, is to divide the bed into intervals no thicker than 1.5 m. In many cases, thick coals are sampled in 0.7 m sections; such sampling provides a detailed stratigraphic section of the bed. Core samples are best for thick-bed sampling. Beds greater than approximately 3 m thick are difficult to sample reliably by the channel method, and in many places the thick beds are mined in layers in surface mines, thus decreasing the probability of obtaining a fresh sample of the entire bed. Where a high resolution density log is obtained, the core can be subdivided into lithologically distinct units.

SUMMARY

Proper collection of coal samples requires representative material from a coal bed. Uniform volumes by core samples, by channel samples, or by properly collected stream (run-of-mine) samples (ASTM, 1986b) are the common types. The selection of sample types is determined by the purposes of the sampling project or program. Certain sample types may not be appropriate for particular analyses or comparisons.

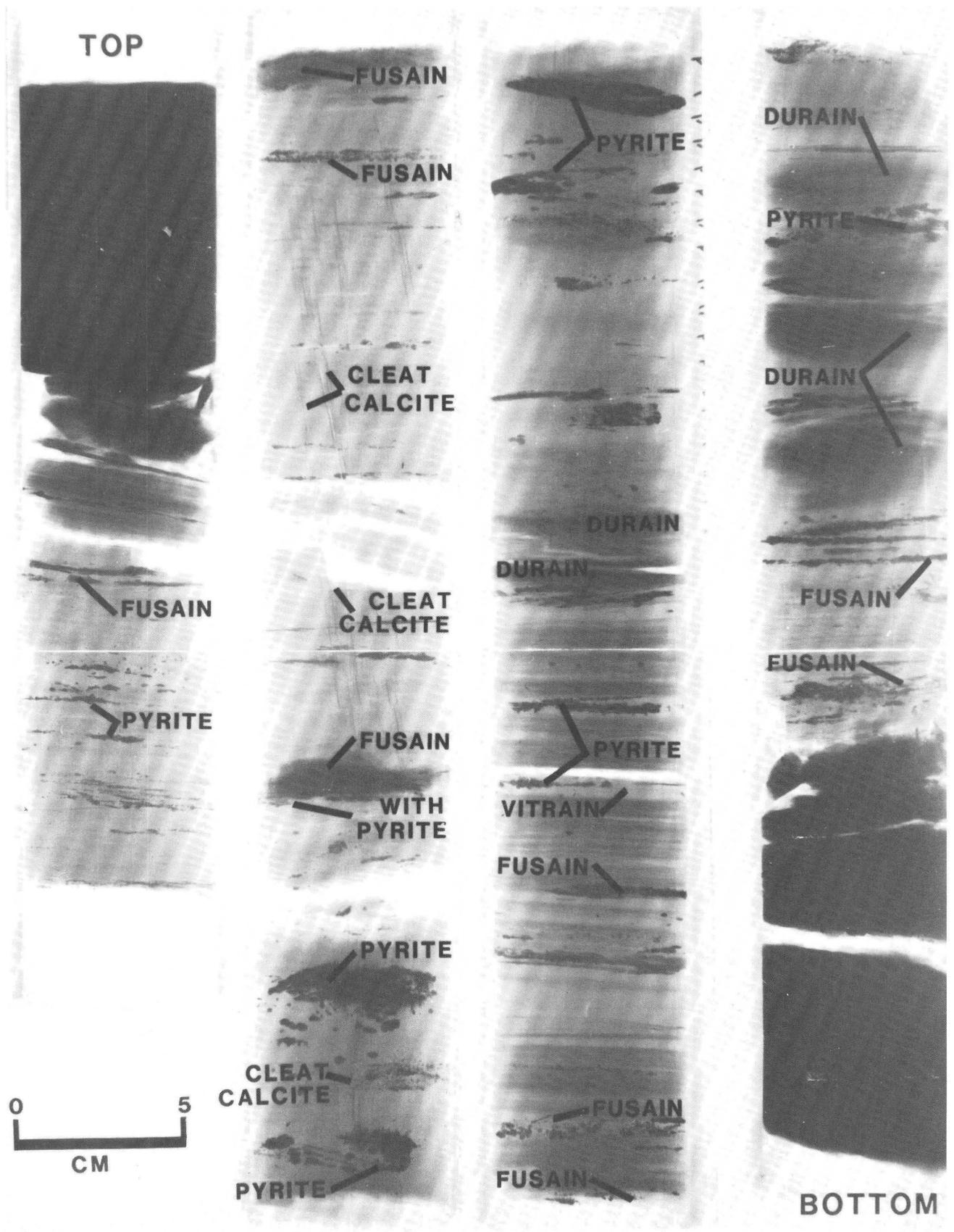


Figure 7. X-ray radiograph of an undisturbed coal core showing mineral impurities and coal lithotype layers.

Valid comparisons of analytical data are the user's responsibility and depend largely on (1) the types of samples, (2) the nature of the samples, such as whole bed or bench, and (3) whether mineral layers or coal partings are excluded from the sample or are sampled separately.

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PREPARATION OF COAL FOR ANALYSIS

By F.G. Walthall *and* S.L. Fleming, II

Abstract

Bulk quantities of coal weighing 3 to 15 kg are individually reduced to approximately 150 μm (100 mesh) by comminution procedures that minimize contamination by grinding surfaces or by other samples. Seventy grams of each pulverized coal sample is oxidized at 525 °C for 36 h to determine the percent ash and to provide ash required for chemical and instrumental analyses.

INTRODUCTION

All procedures described in subsequent sections of this bulletin on the chemical and instrumental analysis of coals depend upon the comminution step. The pulverization of bulk coal samples from the field serves both to homogenize the coal, which typically is quite heterogeneous, and to reduce the material to small particles needed for rapid ashing and dissolution. The comminution of a field sample and the splitting of the resulting pulverized sample into portions to be distributed to various laboratories, while minimizing contamination from grinding surfaces, sieves, and other coals, are essential to the success of all subsequent chemical measurements. Thus, the comminution process is of critical importance, and all aspects of the laboratory arrangement and of procedures for grinding coals must be carefully planned (Swaine, 1985).

Coals submitted for chemical analysis are first received and prepared by the sample preparation (grinding) laboratory. The typical sizes of individual field samples vary from 3 to 15 kg. The normal preparation procedure requires that each air-dried coal sample pass through a jaw crusher; one subsample (split) of the crushed material (2 to 4 mm, or 5 to 10 mesh) is then taken for the ultimate and proximate analyses, and another split is reduced to approximately 150 μm (100 mesh) by a vertical grinder for chemical analysis. An additional split is kept for archival storage, and the excess sample is returned to the submitter.

EQUIPMENT AND PROCEDURES

Sample Preparation (Grinding) Laboratory— Equipment

The instrumentation, equipment, and related items required for the safe operation and maintenance of a grinding laboratory for coal are listed here. The kiln and balance are included because this laboratory both determines the ash from coal and supplies coal ash to other laboratories for chemical analysis.

1. Jaw crusher, partially corrugated manganese steel jaw plates, model 2X6, Sturtevant Mill Company, Boston, MA.
2. Vertical grinder, alumina ceramic plates with aluminum ring, aluminum ore pan, model 6R (catalog no. 242-72A), Bico Braun, Inc., Burbank, CA.
3. Rolls crusher, 8X5, Sturtevant Mill Company, Boston, MA.
4. Mixer-mill, model 8000, Spex Industries, Edison, NJ.
5. Kiln, 6 kW.
6. Laboratory balance, 0.005 to 500 g.
7. Riffle splitter, with pans, Wards Natural Science Establishment, Inc., Rochester, NY.
8. Plastic bag sealmaster, Packaging Aids Corporation, San Francisco, CA.
9. Sieves, nylon screen in methacrylate rings, 100 mesh, Spex Industries, Edison, NJ.
10. Exhaust hoods, size and location shown in figure 8.
11. Aluminum pans (23 cm circular “pie” pans).
12. Plastic drying pans, sides less than 38 mm high, sample spread less than 25 mm deep.
13. Porcelain crucibles, 65 to 70 g.
14. Wire brush, stainless steel.
15. Spatula, stainless steel.
16. Polystyrene jars, 120 mL, 5.8-cm diameter, with lids.
17. Polystyrene vials (26 mL) with caps.
18. Polyethylene vials (polyvials, 3.7 mL) with snap caps.
19. Paper cartons, 0.55 L, 8.5-cm diameter.

20. Plastic bags, 15 × 30 cm, sealed by plastic bag sealmaster (item 8).
21. Wax paper, 30 × 46 cm.
22. Lint-free paper towels.
23. Cleaning sand (clean quartz sand).
24. Compressed-air supply, filtered, with hose and nozzle. (For safety, the pressure at which the compressed air is supplied should be kept below 0.2 kPa (30 psi).)

Safety Equipment and Provisions

1. Safety goggles for protection of eyes from small projectiles and dust from grinding machines, Macalaster Bicknell Company, Millville, NJ.
2. Ear covers (muff type) or inserts for protection from loud noises emitted by grinding machinery.
3. Laboratory coats or coveralls.
4. Plastic gloves, disposable.
5. Safety shoes with protective steel toes.
6. Fire extinguishers (ABC tri-class dry chemical, 5.25 kg).
7. Explosion-proof switches and light fixtures in grinding laboratory.
8. Respirator masks with interchangeable paper filters.

Safety Procedures

As in all procedures for the comminution of geologic materials, precautions must be taken to protect the operator of grinding equipment from dust inhalation, the noise of the machinery, small projectiles emanating from the grinding process for a sample, and injury (especially to the hands) that can be inflicted by the powerful machinery required for grinding of samples. Moreover, high concentrations of coal dust in air can constitute an explosion hazard. Thus, an adequate ventilation system and the complete absence of high-temperature sources (cigarettes, sparks from electrical switches, electrostatic sparks, flames, etc.) are essential for a safe grinding facility for coal.

Safety goggles, ear protection, a laboratory coat, and an air-filter mask should be used at all times while operating the crushing and grinding equipment. A rapid stream of compressed air, used in cleaning grinder surfaces, should always be directed away from the operator. Electrical power to grinding equipment should be switched off before hands or tools are inserted into the machinery. Periodic medical examinations, which may include chest X-ray examinations to reveal developing respiratory disorders such as silicosis, are generally considered to be a good preventive measure.

Maintenance of Equipment

Adequate maintenance of equipment basically consists of regular lubrication and replacement of worn components. The following procedure is suggested for the grinding laboratory.

1. Identify all grease fittings and keep the fittings capped.
2. Lubricate each piece of equipment in accordance with an established schedule that is posted near the device.
3. Replace worn parts on jaw crusher.
4. Resurface worn ceramic plates that are used on the vertical grinder.
5. Replace worn drive belts.
6. Keep drawings and brochures related to equipment on file for lists of proper replacement parts and for instructions on proper lubrication.

Sample Preparation (Grinding) Laboratory—Facilities

The grinding laboratory, which contains heavy machinery that is capable of producing significant floor vibrations, should be located on the ground floor of a building. The laboratory should have no overhead water plumbing, including fire-sprinkler systems, because the failure, or breakup, of such plumbing presents a serious hazard to both the equipment and the operator. Fire extinguishers that use carbon dioxide or halonTM are suggested.

The arrangement of the laboratory currently used by the U.S. Geological Survey for all grinding procedures on coal is shown in figure 8. This laboratory occupies an area of 51 m² and has four specially constructed exhaust hoods that are ducted to a “rotocone” dust collector. Electrical power for equipment is made available through eight duplex outlets (single phase, 110-V alternating current, 20 A) and four outlets providing three-phase, 220-V alternating current, 30 A. Compressed air is provided at five outlets, and hot and cold tapwater are available at the sink. A water drain is located in the center of the floor.

Adjacent to the laboratory is an office area (31 m²), in which field samples are received and information concerning each sample is recorded. A sample-drying room (20 m²) is used both for short-term storage and for drying of samples. Archives of samples are stored in a separate area of the facility.

Crushing and Grinding

The coal sample, as received from the field, consists of 3 to 15 kg of material that first is reduced to a particle size of 2 to 4 mm (5 to 10 mesh) in a jaw crusher. This crushed material is then divided into three splits.

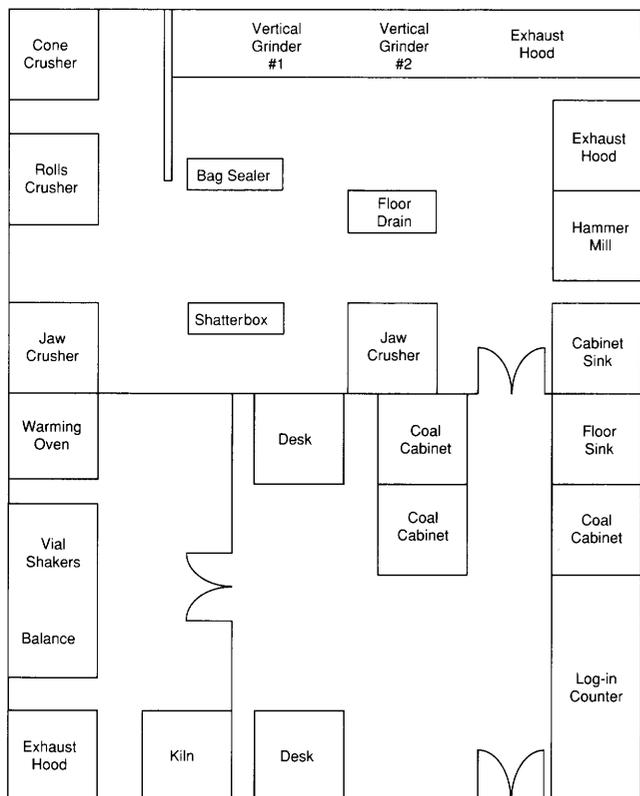


Figure 8. Sample preparation laboratories.

The first split is forwarded to a laboratory for standard ultimate and proximate analyses. The second split, which is intended for chemical analysis and archiving within the U.S. Geological Survey, is pulverized to 150 μm (100 mesh) in a vertical grinder. The remaining split is returned to the submitter. These and subsequent steps are outlined in figure 9, which is a flowchart that shows the treatment and routing of each sample.

Description of Procedure

1. Generally, samples are received in plastic bags that are tightly packed into a cubic box that has a 30-cm edge. The individual plastic bags, which have been labeled in the field, are removed from the box and necessary recordkeeping is first completed. Special grinding and routing instructions that accompany the sample are noted on a form that also has descriptive information pertaining to the coal.
2. Samples that need air drying are identified. Typically, moisture is readily apparent on these samples, or the coal powder commonly present in the samples does not move about freely as the container is agitated. Each of these samples is poured into a plastic or aluminum pan, and each of the sample numbers is written on a strip of masking tape

attached to the pan. The empty plastic bag is placed under the pan for later use. Wet samples typically are air dried for one week; however, longer drying times may be required for samples that tend to stick to surfaces during grinding.

3. Containers needed for sample splits from the crushing process are cleaned with a stream of air and labeled prior to the crushing procedure.
4. Samples are taken into the grinding laboratory to be crushed one at a time, while the remainder of the samples are stored on a cart outside the door of the grinding laboratory. This practice reduces the possibility of cross contamination.
5. Just prior to crushing the first sample, the gap between the jaws of the jaw crusher is adjusted to approximately 4 mm.
6. After crushing the entire sample, the sample is homogenized by rolling it on a sheet of waxed paper. Then, the homogeneous, crushed sample is fed into a riffle splitter (fig. 10) to produce splits A and B. A minimum of 100 g of sample from the first split is poured into the container for samples that are intended for ultimate and proximate analyses (fig. 10, split A). The second split (fig. 10, split B) is fed again into the riffle splitter (fig. 10, splits C and D), and a 15-cm-long plastic bag is filled from split D for return to the submitter. Split C (fig. 10)

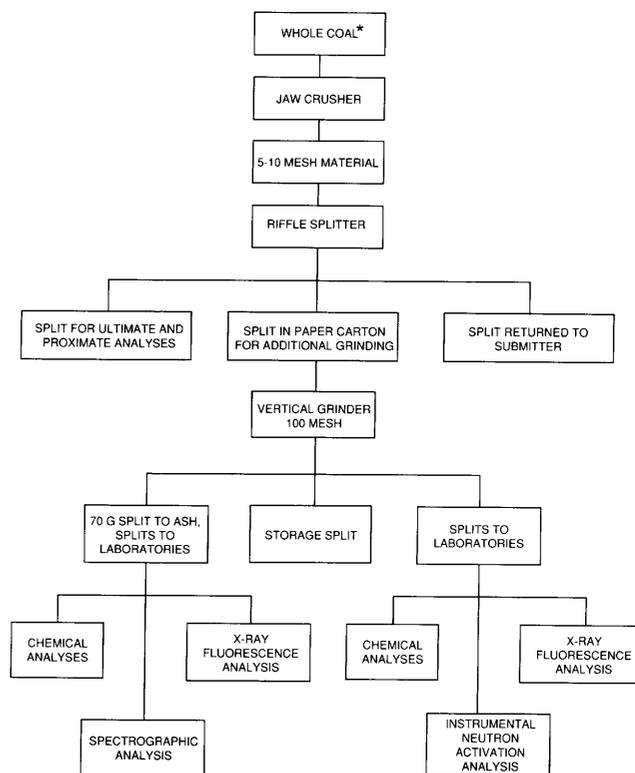


Figure 9. Sample preparation procedure for coals.

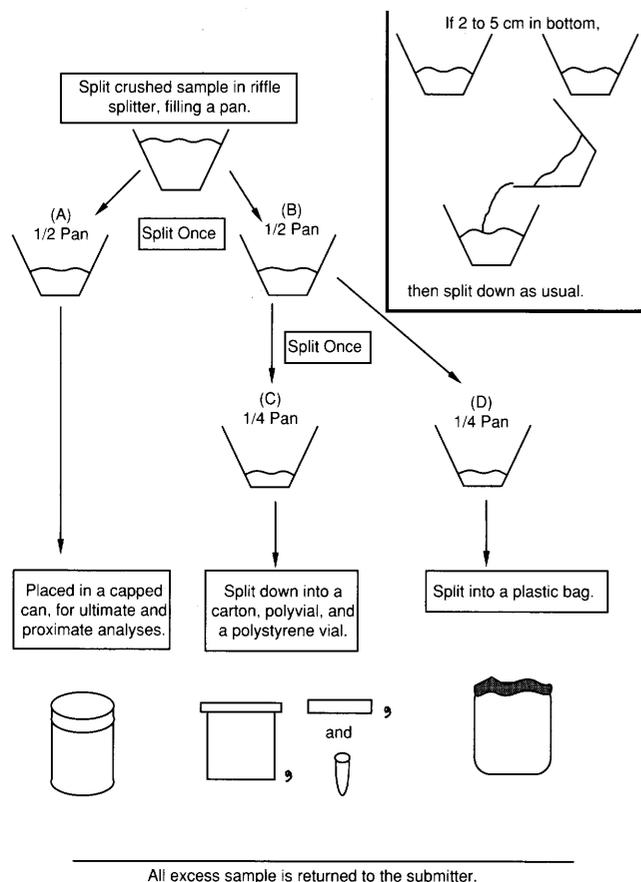


Figure 10. Splitting procedure.

is distributed into a paper carton (550 mL), a polystyrene vial (26 mL), and a snap-cap polyvial (3.7 mL); the paper carton and the polystyrene vial are filled approximately two-thirds full, and the polyvial is filled to within 3 mm of the top. These individual portions are to be used for ashing and for subsequent chemical and instrumental analyses. All remaining sample is placed in the original plastic bag, which is then resealed and returned to the submitter.

7. The simultaneous use of two vertical grinders is recommended. This arrangement enables a machine operator to pulverize one sample while the previously pulverized sample is being split and the other grinder is being cleaned. Each sample is split by a riffle splitter inside a hood (46 × 61 × 61 cm).
8. Splits must be prepared for five laboratories: a 20-g split for analysis by neutron activation is packaged in a paper carton; a separate 3.5-g sample for delayed-neutron determinations of uranium and thorium is placed in a polyvial; a 140-g split for the ultimate and proximate analyses is placed in a metal can; 70 g of coal is split for high-temperature

(525 °C) ashing; and the submitter receives a 140-g portion in plastic bags.

A similar method for preparing coal samples is described in the ASTM (1984a) book of standards.

Ashing Procedure

Pulverized coal samples are ashed in an electrically heated kiln that can ash 40 samples simultaneously. The steps followed in the ashing process are listed here.

1. Forty sequentially numbered porcelain crucibles (or evaporating dishes) are cleaned and dried prior to ashing the coal samples. The weight of each crucible, approximately 70 g, is sufficiently constant to make repeated weighings unnecessary for each ashing cycle.
2. Approximately 70 g of sample is weighed into each crucible. Appropriate records are maintained for the weights of the sample and the crucible and for the sample number or name used by the laboratory.
3. The crucibles are placed in the kiln. The electrical power to the kiln is switched on, and the kiln is slowly heated to 200 °C. After the kiln is operated at 200 °C for 1.5 h, the temperature is increased to 350 °C and is maintained at that temperature for 2 h. Finally, the temperature is increased to 525 °C and the ashing is completed at that temperature; generally, a period of 36 h is required.
4. After 36 h, the electrical power is switched off and the kiln and samples are allowed to cool (1 to 2 h). After the crucibles have cooled to room temperature, the “crucible-plus-ash” weight is measured for each sample. These data are recorded, and the percent ash is calculated.

$$\text{Percent ash} = \left(\frac{\text{Weight ash}}{\text{Weight coal}} \right) \times 100$$

5. Forty 118 mL polystyrene jars are labeled, and three 6-mm-diameter glass beads are placed in each jar.
6. Ash from each crucible is then transferred into an individual polystyrene jar, and the jar is closed. Each jar subsequently is placed into a mixer-mill and agitated for 30 s. These homogenized samples are provided to the chemical laboratories for analysis.

Another method for determining ash in coal and coke is described by the ASTM (1984a) book of standards.

Cleaning of Work Area and Equipment

1. Make certain that the vents on the hoods are open; switch on electrical power to the exhaust system.
2. For the jaw crusher,
 - a. Remove loose dust on the plates and surrounding area with a fast stream of air from the compressed-air line.

- b. Remove buildup of sample on the crusher plates with a wire brush, and again blow away loose material with a fast stream of air from the compressed-air line.
 - c. Wipe off the plates with a water-dampened sponge, and dry the plates with a stream of air from the compressed-air line.
 - d. Finally, wipe off the plates with a Kimwipe™ tissue soaked with acetone.
 - e. Blow away loose dust from the pan with a stream of air; then, clean the pan with a water-dampened sponge.
3. For the vertical grinder,
 - a. Blow away loose dust from the plates and pan with a stream of air.
 - b. Pass clean sand through the grinder, as you would in grinding a coal sample, and repeat step 3.a.
 4. In the work area and hood,
 - a. Wipe the inside of the hood and the counter space with a water-dampened sponge.
 - b. Dry the cleaned surfaces with a stream of air.
- c. Once each week, thoroughly clean the entire floor with a broom and dust pan. Vacuum cleaning with a cleaner that does not generate sparks is quite appropriate.

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AUTOMATED SEMIQUANTITATIVE DIRECT-CURRENT ARC SPECTROGRAPHIC DETERMINATION OF 64 ELEMENTS IN COAL ASH

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Abstract

A semiquantitative, direct-current arc spectrographic method is routinely used to determine 64 elements in coal ash. The automated method is rapid and economical for evaluating both major and trace-element concentrations. The method, a listing of the spectral lines used in the analytical scheme, and data from analyses of National Bureau of Standards standard reference coal fly ashes are presented.

INTRODUCTION

A semiquantitative, direct-current (dc) arc spectrographic method is routinely used to determine 64 elements in coal ash. The automated data acquisition and analysis system used in conjunction with this approach is an outgrowth of a scanning microphotometer concept (Helz, 1965; Helz and others, 1969) that ultimately was extended to its present form. The system maintains long-term consistency of results and provides archival storage capability on both photoplates and microfiche. The dc-arc spectrographic method is applicable in laboratories without the scanning microphotometer system.

THE METHOD

This semiquantitative approach achieves analytical ranges and detectability comparable to those of visual estimation procedures (Myers and others, 1961). Standards are diluted with a synthetic silicate matrix to provide six evenly spaced logarithmic divisions (steps) per decade of concentration. When available, natural rock standards are preferred over synthetic standards and are diluted to correspond to the six steps: 1, 1.47, 2.15, 3.16, 4.64, and 6.81. Because the standards used generally do not match the approximate composition of the samples analyzed, the expected accuracy is limited to ± 1 step, which corresponds to roughly +50 or -33 percent. The procedure is semiquantitative because the

computer algorithm extrapolates concentrations based on prestored coefficients calculated from previously arced standards. Analytical curves are not established from spectra of standards on the same plate as the samples.

EXPOSURE PROCEDURE

The operating conditions and the spectrograph are described in table 4 (Dorrzapf, 1973). Dilution of the sample with graphite increases the uniformity of the introduction of the sample into the arc. The spectrograph has been modified to include a two-position mask near the focal plane (Helz, 1973). In one position, the mask allows only the wavelength regions adjacent to the cadmium lines at 274.8 and 441.5 nm to be exposed. The spectral lines from a cadmium Osram lamp serve as fiducial lines for wavelength calibration. In the other mask position, the cadmium "windows" are blocked, but the remainder of the spectral region from 230 to 470 nm is exposed. Thus, spectra from the cadmium lamp and the dc arc are coexposed without moving the photoplate. The Helz jet (Helz, 1964) was chosen rather than a Stallwood jet (Stallwood, 1954; Shaw and others, 1958) because the procedure for changing samples was simplified if there was no jet dome to be cleaned. An argon-oxygen atmosphere minimizes cyanogen-band formation and thus frees the wavelength region from approximately 350 to 420 nm for measurements of sensitive lines for Cr, Eu, Gd, K, Mo, Pr, Sc, Sr, Th, Tl, W, and Yb.

THE SCANNING MICROPHOTOMETER SYSTEM

A scanning microphotometer (Helz, 1973) provides the basis for all spectral measurements. The optical system for the microphotometer follows conventional practices for good resolution, high contrast, and low scattered or diffuse light detection. The fixed

Table 4. Instrumentation and operating conditions

Instrument or Function	Operating Conditions
Spectrograph	3.4-m Ebert (Jarrell-Ash Mark III). Grating has 600 grooves per mm, and is blazed for the first-order ultraviolet region. A 2-mm high central portion of the arc is focused on the collimator by a cylindrical quartz lens that has a focal length of 45 cm and is located at the slit. The slit is 0.025 mm wide and 2.0 mm high. The two-step neutral density filter used for emulsion calibration and a 14 percent transmission neutral density filter are located near the slit. The height of the mask at the collimator is 18 mm.
Dispersion	0.5 nm/mm reciprocal linear dispersion, first order.
Wavelength range	230.0 to 470.0 nm; first order.
Excitation	15-A direct-current arc; current is set with a set of graphite electrodes in place (the anode cup is empty). The open-circuit voltage from the power supply is 325 volts.
Arcing of sample	15 mg of sample, mixed with 30 mg of pure graphite powder, is arced for 20 s at a current of 5 A, then the current is switched (without interruption of the arc) to 15 A for a period of 130 s.
Arc gap	4 mm, maintained constant throughout arcing process.
Upper electrode	Cathode: ASTM type C-6, 3.2-mm diameter \times 50-mm long graphite rod.
Lower electrode	Anode: Ultra Carbon No. 3170, 6.3-mm diameter, thin-walled graphite.
Atmosphere	Mixture of 70 percent argon plus 30 percent oxygen; flow of 6.6 L/min directed by a ceramic jet concentric to the anode (Helz, 1964). The top of the jet nozzle is positioned 2 mm below the top of the anode.
Photoplates	Eastman-Kodak III-0 emulsion, 102 \times 508 mm glass plate. Exposed emulsion is processed in D-19 for 3.25 min, fixed for 10 min, washed for 30 min, and dried by a flow of warm air for 30 min.

entrance slit consists of a precision ruled window (100 μ m wide) in a mirror. A 32-mm focal length Micro-TessarTM lens focuses an image one-tenth the slit size on the plane of the spectrum. The optics are designed to sample a portion of the spectrum 1 mm high by 7 μ m wide (about a quarter of the width of a spectral line).

The optical system is mounted on a Moore^R no. 3 measuring machine. Lateral motion of the milling machine bed, on which the photoplate rests, is accomplished by a precision lead screw. The signal produced by light passing through the photographic emulsion and detected by a solid-state detector is sampled by an

analog-to-digital (A/D) converter that is gated by a rotating shaft encoder attached directly to the ring motor that drives the screw. A scanning speed of 70 s per spectrum provides a practical interval for data collection and minimizes vibrational effects on the optical system and thermal and mechanical wear on the screw. The photoelectric signal is sampled at 5- μ m increments of plate motion that correspond to wavelength changes of 0.0025 nm. Spectral lines can be located with a reproducibility of ± 0.005 nm. During a scan of the spectrum from 230.0 to 470.0 nm, approximately 92,000 transmission measurements are made, corresponding to a sampling rate of 1.3 kHz.

THE MINICOMPUTER CONFIGURATION

The heart of the signal processing system is a Hewlett-Packard^R 2100S minicomputer that has 32 kilobytes of random-access memory.

The operator of the microphotometer controls the computer via a model 2615A terminal when recording plates. The portion of computer memory that remains after installation of the real time executive operating system (RTE II) is divided into a small foreground (5 kilobytes) and a large background area (16 kilobytes). Programs are run concurrently in both areas. The data acquisition program runs in the foreground, while data reduction programs are operating in the background. The Hewlett-Packard^R 91000A A/D converter uses a differential input when sampling voltages and is gated by a square-wave timing pulse from the shaft encoder. A specially written assembly language driver, which allows a sampling rate up to 40 kHz, controls the operation of the A/D converter. All 92,000 voltage measurements, which constitute a scan, are dumped into a file on the Hewlett-Packard^R 7900A 5-megabyte disk. Although the resolution of the A/D converter is 1 part in 10,235, only 1 part in 1,000 is needed for this work.

Within 5 min of recording the last spectrum on a photoplate, the necessary number of two-page report forms listing the concentrations of 64 elements for as many as 10 samples are printed on a model 2607A line printer. Information about effective arc temperature and electron pressure during each arcing (Golightly and others, 1977) and the calculated total oxides (considering only major constituents) for each sample are printed on a separate page. The program next writes an ASCII magnetic tape that contains detailed data on plate emulsion calibration and on each spectral line. These data are processed on an International Business Machine^R 370 computer to produce a second tape that is organized for input to the Quantor^R 105 microfiche recorder. However, information can also be printed out on the line printer to provide the detailed analysis immediately.

DATA HANDLING

Programs for data collection and interpretation have been written by Walthall (1974) to use on a mainframe computer and by Thomas (1979) to use on the minicomputer system just described.

WAVELENGTH CALIBRATION

The two cadmium fiducial lines coexposed on each spectrum, through specially masked windows, are used for wavelength calibration. The computer program searches each of these windows for the first line with a transmittance below some predetermined threshold. The lines thus located are accepted as the cadmium fiducial lines. The number of readings (transmission measurements) between these cadmium lines is compared with the expected number of readings; a discrepancy of more than ± 1 reading is assumed to correspond to an expansion or contraction of the spectrum due to temperature variation or a change in the optics. The first task, then, is to calculate the estimated positions of iron and analyte lines relative to Fe 233.2 nm, using the dispersion of the spectrograph-microphotometer system in units of the number of percent transmission readings per nanometer. The expected positions of all the other iron or analyte lines are calculated by applying corrections to their estimated positions relative to Fe 233.2 nm.

CONCENTRATION CALIBRATION

Both single- and multiple-element standards are used to provide the working relationships between concentration and spectral line intensity required for the analytical curve for each spectral line of each analyte element. For each analyte line, a series of programs produce a single page of output on which are tabulated intensities of the line in all the spectra on the photoplate. The tabulation includes the percent transmittances of the peak and background of the analyte line and neighboring lines within ± 0.0175 nm, the relative intensity of the analytical line, and the concentration. The output also presents an evaluation of the suitability of the line for analyses that is based on the shape and intensity of the line and the number of readings away from the estimated position at which the line was located in each spectrum.

The computer algorithm calculates the coefficients of first- and second-degree polynomials for the analytical curve of the natural logarithm of intensity versus the natural logarithm of concentration. It evaluates the curve for range, goodness of fit, and slope, and suggests a working concentration range for the line, with a lower limit defined by a signal-to-noise ratio of 2.

The analyst evaluates the analytical usefulness of each line on the basis of profile, intensity, and location. The coefficients of the analytical curve are automatically entered into a data base. When the process is complete for each analyte line, the data base is defined as the wavelength table for the system. For each analyte line in wavelength order, the table contains the element symbol, wavelength, line priority, determination limits, and coefficients of the second-degree polynomial that are used to determine the concentration of the analyte in the sample. A list of the spectral lines and determination limits for each line are given in table 5.

SPECTRAL-INTERFERENCE CORRECTIONS

On the basis of elemental concentrations determined for standard reference materials, interferences can be identified and line priorities and concentration ranges adjusted to minimize systematic errors (Thomas, 1979).

Generalized interference treatments are of two types, subtraction or line switching. The subtraction routine makes corrections by subtracting an equivalent concentration contributed by the interfering line. This subtraction uses predetermined coefficients, relating the concentration of interference to apparent concentration of analyte.

The line-switching treatments are of three types. Two are used when the analyte line is hidden by an interference. One type gives no estimate of concentration. The computer then checks the concentration of the interference to be sure that it is high enough to interfere and checks the computerized evaluation of the profile of the line to be sure that the line is obscured. In the second type, if both of the previous conditions are met, the computer algorithm switches to an auxiliary line, which may give a concentration greater than the upper limit of the last interference-free line in the priority scheme. The third line-switching treatment is designed to guard against spurious answers from band lines, scratches, or ghosts. Here, one or two similar, more abundant, elements, such as platinum and palladium for the noble metals series, are monitored. For this example, if platinum or palladium is not reported, the algorithm switches to a less-sensitive line for ruthenium and reports less than its lower limit of determination.

PLATE EMULSION CALIBRATION

A modified (Walthall, 1974) Churchill two-step procedure is used for emulsion calibration. The recorded spectrum is divided into ten 25-nm segments. Twenty-six iron lines are used to define the preliminary plate emulsion curve in each 25-nm segment. These iron lines

Table 5. Spectral lines used in spectrographic analysis, listed in order of decreasing intensity

Element	Wavelength (nm)	Determination limits (cg/g)		Element	Wavelength (nm)	Determination limits (cg/g)		Element	Wavelength (nm)	Determination limits (cg/g)	
Ag . . .	328.068	0.000010	- 0.00215	Ho . . .	345.600	0.000681	- 0.0147	Ru . . .	349.894	0.000215	- 0.0100
	338.289	0.000100	- 0.00215		339.898	0.00100	- 0.0316		343.674	0.000464	- 0.0215
	235.792	0.100	- 1.00		328.198	0.00681	- 0.100		408.060	0.000681	- 0.0681
Al . . .	266.039	0.0464	- 1.47	In . . .	451.132	0.00100	- 0.0147		291.626	0.00464	- 1.00
	265.249	0.0464	- 3.16		303.936	0.00100	- 0.0464	Sb . . .	259.806	0.00681	- 0.215
	237.841	0.316	- 31.6		325.856	0.00147	- 0.147		326.750	0.0100	- 0.681
	266.917	2.15	- 31.6		293.262	0.00316	- 1.00		267.064	0.0681	- 1.00
As . . .	286.045	0.0100	- 1.00		271.027	0.0464	- 1.00		268.276	0.147	- 1.00
	234.984	0.0147	- 1.00	Ir . . .	322.778	0.00147	- 0.464	Sc . . .	424.683	0.000100	- 0.00316
	289.871	0.464	- 1.00		247.512	0.0147	- 1.00		391.181	0.000100	- 0.00464
Au . . .	267.595	0.000681	- 0.0316		404.414	0.0681	- 2.15		402.040	0.000147	- 0.00681
	242.795	0.00147	- 0.147	K . . .	404.720	0.147	- 3.16		335.373	0.000147	- 0.0100
	249.773	0.000316	- 0.0215		344.637	1.00	- 10.4		255.326	0.00215	- 0.100
B	249.679	0.000681	- 0.0464	La . . .	404.291	0.00100	- 0.0681	Si . . .	251.921	0.00464	- 0.0681
Ba . . .	455.404	0.000147	- 0.00316		433.373	0.00215	- 0.0464		253.238	0.100	- 14.7
	413.066	0.00215	- 0.0681		324.512	0.00215	- 0.215		243.878	0.215	- 21.5
	350.112	0.00464	- 0.681		350.999	0.0215	- 1.00		257.713	2.15	- 34.3
	307.159	0.0215	- 3.16	Li . . .	323.261	0.00681	- 0.316	Sm . . .	429.675	0.00100	- 0.0100
Be . . .	313.042	0.000100	- 0.00147		427.328	0.215	- 3.16		321.640	0.00316	- 0.100
	313.107	0.000100	- 0.00316	Lu . . .	291.139	0.00147	- 0.100		340.867	0.00464	- 0.100
	234.861	0.000100	- 0.00681		451.857	0.0147	- 0.100	Sn . . .	317.502	0.000464	- 0.0464
	332.134	0.000215	- 0.0147	Mg . . .	277.983	0.00215	- 0.147		283.999	0.00147	- 0.0464
	332.109	0.000215	- 0.0147		278.142	0.00316	- 0.681		286.333	0.00681	- 0.100
	265.062	0.000215	- 0.0215		332.993	0.100	- 4.64		242.169	0.0100	- 1.00
	249.473	0.00100	- 0.0681		293.854	0.147	- 10.0	Sr . . .	407.771	0.000100	- 0.000464
Bi . . .	306.772	0.00100	- 0.0215		457.115	4.64	- 30.4		460.733	0.000215	- 0.00681
	289.796	0.00316	- 0.316	Mn . . .	279.827	0.000100	- 0.0147		346.446	0.00147	- 0.100
	302.464	0.00464	- 0.681		280.106	0.000147	- 0.0215		416.179	0.0147	- 0.464
Ca . . .	317.933	0.00100	- 0.147		294.921	0.000316	- 0.0464		293.183	0.316	- 14.7
	315.887	0.00464	- 0.316		293.306	0.00100	- 0.147		330.753	0.464	- 21.5
	299.731	0.0681	- 10.0		291.460	0.0215	- 3.16		256.947	1.47	- 31.6
	272.165	0.681	- 31.6		271.333	0.464	- 21.5	Ta . . .	271.467	0.0316	- 1.00
Cd . . .	326.106	0.00316	- 0.147		238.702	10.0	- 46.4		296.555	0.0464	- 1.00
	346.620	0.00316	- 0.215	Mo . . .	317.035	0.000100	- 0.0316		284.425	0.0464	- 1.00
	325.253	0.100	- 1.00		320.883	0.00100	- 0.100		294.022	0.100	- 1.00
Ce . . .	418.660	0.00430	- 0.136		281.615	0.00215	- 0.100	Tb . . .	329.307	0.00316	- 0.100
	416.561	0.00632	- 0.200	Na . . .	330.232	0.00215	- 0.464		365.888	0.00464	- 0.100
	320.171	0.0200	- 0.928		330.299	0.00681	- 1.00		427.851	0.0215	- 0.100
	314.528	0.0200	- 2.00		285.303	0.100	- 7.96	Th . . .	401.913	0.00464	- 0.215
Co . . .	345.351	0.000100	- 0.00681		285.283	0.147	- 7.96		340.270	0.0100	- 1.00
	341.234	0.000215	- 0.0147	Nb . . .	316.340	0.000681	- 0.100		332.513	0.0147	- 0.681
	344.917	0.000215	- 0.0316		319.498	0.000681	- 0.100		411.672	0.0316	- 0.681
	341.263	0.000464	- 0.0464		295.088	0.00100	- 0.100		287.041	0.0147	- 1.00
	339.538	0.00215	- 0.0681	Nd . . .	430.357	0.00316	- 0.0681	Ti . . .	264.426	0.00316	- 2.15
	335.438	0.00316	- 0.316		435.817	0.00681	- 0.316		264.110	0.0100	- 2.15
	326.082	0.0316	- 1.47		438.566	0.0215	- 0.464		267.993	0.0464	- 10.0
	238.346	0.0316	- 2.15	Ni . . .	436.863	0.0464	- 1.00		245.044	1.47	- 46.4
Cr . . .	357.869	0.000100	- 0.00147		305.082	0.000147	- 0.0316	Tl . . .	377.572	0.00100	- 0.0215
	302.435	0.000681	- 0.100		342.371	0.000316	- 0.0464		351.924	0.00100	- 0.0464
	301.519	0.00100	- 0.100		310.188	0.000681	- 0.0681		276.787	0.00215	- 0.316
	342.121	0.00316	- 0.681		294.391	0.00464	- 0.316		352.943	0.0147	- 0.316
Cu . . .	324.754	0.000100	- 0.00147		299.260	0.00464	- 0.316		237.969	0.100	- 1.00
	327.396	0.000100	- 0.00464		282.129	0.0316	- 1.00	Tm . . .	346.220	0.000464	- 0.0215
	282.437	0.00316	- 0.147		340.953	0.0464	- 1.47		409.418	0.00215	- 0.0464
	301.084	0.0215	- 0.147	Os . . .	330.156	0.00147	- 0.464		325.804	0.00215	- 0.100
Dy . . .	345.433	0.00215	- 0.100		326.795	0.00316	- 0.464		339.995	0.00464	- 0.100
	331.989	0.00464	- 0.100		290.906	0.00316	- 0.681	U	286.568	0.0215	- 1.00
Er . . .	323.059	0.000464	- 0.0681	P	255.493	0.0681	- 6.81		378.284	0.0464	- 1.00
	332.320	0.00147	- 0.100	Pb . . .	283.307	0.000681	- 0.0316		424.437	0.100	- 1.00
	322.073	0.0100	- 0.100		368.347	0.000681	- 0.0316	V	310.230	0.000100	- 0.0215
Eu . . .	412.973	0.000215	- 0.00681		363.958	0.00147	- 0.0464		318.341	0.000215	- 0.0316
	420.504	0.000316	- 0.00681		261.418	0.00215	- 0.100		311.838	0.000215	- 0.0464
	281.395	0.00147	- 0.100		266.317	0.00681	- 0.100		319.801	0.00147	- 0.100
	290.668	0.00464	- 0.100	Pd . . .	324.270	0.000100	- 0.0100		267.932	0.00464	- 0.100
	272.778	0.00464	- 0.100		351.694	0.000464	- 0.0147	W . . .	400.875	0.00147	- 0.215
Fe . . .	283.244	0.00743	- 1.60		346.077	0.000681	- 0.0215		289.645	0.00681	- 1.00
	294.134	0.0160	- 3.45		306.531	0.00316	- 0.464		294.698	0.0100	- 1.00
	317.545	0.0743	- 7.43	Pr . . .	405.654	0.0100	- 0.100	Y	321.668	0.000147	- 0.0147
	236.202	0.345	- 23.5		414.126	0.0147	- 0.100		324.228	0.000147	- 0.0147
	239.147	1.09	- 23.5	Pt . . .	403.936	0.0147	- 0.100		332.788	0.000147	- 0.0316
Ga . . .	294.364	0.000147	- 0.0316		306.471	0.000215	- 0.0464		319.562	0.000681	- 0.0681
	294.418	0.00147	- 0.100		299.797	0.000681	- 0.100		434.879	0.0464	- 1.00
Gd . . .	354.937	0.00316	- 0.100		265.945	0.000681	- 0.100	Yb . . .	328.937	0.000015	- 0.00215
	302.761	0.00316	- 0.100		283.030	0.00315	- 0.215		398.799	0.000100	- 0.00316
	333.139	0.00464	- 0.100		262.803	0.0215	- 0.464		289.138	0.000681	- 0.0464
Ge . . .	265.118	0.000464	- 0.0316		331.505	0.0316	- 1.00		345.407	0.00316	- 0.100
	303.906	0.000464	- 0.0316	Re . . .	346.047	0.00100	- 0.147		334.502	0.00100	- 0.100
	326.949	0.00147	- 0.147		346.472	0.00147	- 0.147	Zn . . .	334.557	0.00681	- 0.681
	265.158	0.00316	- 0.147		334.620	0.100	- 1.00		277.087	0.0681	- 1.00
	241.737	0.0147	- 1.00		350.306	0.147	- 1.00	Zr . . .	327.305	0.000316	- 0.100
Hf . . .	291.648	0.00147	- 0.464		264.905	0.316	- 1.00		327.927	0.000464	- 0.147
	339.980	0.00316	- 0.464	Rh	339.685	0.000215	- 0.0100		347.939	0.000681	- 0.316
	310.912	0.0147	- 1.00		346.204	0.000464	- 0.0316		348.115	0.00464	- 0.316
					318.905	0.0215	- 1.00		408.122	0.00681	- 0.464
									272.261	0.0100	- 2.15
									270.013	0.0147	- 2.15

and the exposure time for the two-step iron spectrum are selected so that the transmittance regions <20 percent, 20 to 80 percent, and >80 percent are approximately equally represented. The preliminary emulsion calibration curve (natural logarithm of percent transmittance of filtered step versus the natural logarithm of percent transmittance of unfiltered step) is represented by a quadratic equation. The 45° tangent to the curve is used as a starting place for finding the inflection point of the logarithm of relative intensity versus the logarithm of percent transmittance of the final plate emulsion curve. The actual inflection point is defined as the point from which one step of the filter factor on either side produces an equal change on the logarithm percent transmittance scale. The Newton method of successive approximation (Abramowitz, 1964) is used to find this point on the preliminary curve. The inflection point is then translocated to the final curve so that it falls on the line with a 45° slope that passes through the point where the relative intensity equals 10⁶ and the percent transmittance equals 0.1 percent.

QUALITY CONTROL

Two other computer programs detect possible analysis errors. Each photoplate contains spectra from one to three reference materials in addition to spectra from up to 23 samples and an iron two-step calibration spectrum. The reference materials are selected from 20 well-characterized standards, such as U.S. Geological Survey (USGS) diabase W-2, USGS granite G-2, or National Bureau of Standards (NBS) 1633a coal ash, chosen to represent the variety of materials commonly analyzed. The analyst selects standards that are compositionally similar to the samples on the basis of the description of the samples provided by the scientist requesting the analyses. The computer program recognizes these standards and compares the concentrations determined for Si, Al, Fe, Ca, Mg, Ti, Co, Pb, and Zr with accepted analyte concentrations for these standards. These nine elements include the major rock constituents, have a wide range of volatility in the dc arc, and enable checks for loss of refractory elements that would occur if a molten bead is lost from the anode during the arcing process. If the concentration computed for any of these elements is more than one step away from the accepted concentration, a message is printed comparing the reported value with the accepted value. Another program computes and tabulates total oxides, effective temperature, and electron pressure for each sample. Total concentration of oxides is computed by converting concentrations of the rock-forming elements (Si, Al, Fe, Mg, Ca, Na, K, Ti, P, and Mn) to concentrations of the individual oxides and by summing the results. Ideally, the total concentration of oxides for a silicate rock equals 100 percent.

In the analyses of coal ash, for evaluation of both precision and accuracy of this method, NBS standard reference materials 1633 and 1633a (NBS, 1975, 1979) are routinely included as control samples in the analytical procedure. Table 6 lists the concentrations provided by NBS certificates, the mean concentrations determined in U.S. Geological Survey laboratories over an 11-month period, and the associated relative standard deviations. These data were accumulated during a period that coincides with the analyses of over 2,000 coal-ash samples.

CONCLUSIONS

The automated dc arc emission spectrographic analysis of coal ash is a rapid, economical method for evaluating both major and trace-element concentrations. Concentrations determined for coal ash are within the limits of precision and accuracy for which the method was designed. The high relative standard deviations for barium and zirconium indicate the heterogeneity documented for these reference materials (Filby, 1985). The system has the capability for the analysis of 4,000 samples, or 256,000 determinations, per year of effort by a single analyst.

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Table 6. D.C. Arc Spectrographic Analyses of NBS Standard Reference Material Coal Fly Ash
 [Concentration units are % (cg/g) for the first group of elements, including Si through Mn, and ppm ($\mu\text{g/g}$) for the group of elements that includes As through Zr.]

ELEMENT	1633			1633A				
	NBS VALUE ^a		USGS AVERAGE ^b		NBS VALUE ^a		USGS AVERAGE ^c	
Si (%)			27	± 3.3	22.8	± 0.8*	26	± 2.6
Al			17	± 2.8	14		18	± 3.1
Fe			8.0	± 0.93	9.40	± 0.10*	11	± 1.7
Mg			2.2	± 0.32	0.455	± 0.010*	0.71	± 0.14
Ca			5.4	± 1.2	1.11	± 0.01*	1.3	± 0.31
Na			0.25	± 0.03	0.17	± 0.01*	0.16	± 0.03
K	1.72		1.3	± 0.15	1.88	± 0.06*	1.5	± 0.19
Ti			0.80	± 0.15	0.8		0.85	± 0.18
Mn	0.0493	± 0.0007*	0.076	± 0.011	0.0190		0.026	± 0.0777
As(ppm)	61	± 6*	<100 ^d		145	± 15*	190	± 49
B	430		440	± 46			32	± 4.0
Ba			1600	± 490	1500		910	± 160
Be	12		15	± 1.5	12		14	± 1.9
Ce			170	± 29	180		160	± 53
Co	38		38	± 4.9	46		38	± 6.2
Cr	131	± 2*	120	± 23	196	± 6*	180	± 33
Cu	128	± 5*	100	± 25	118	± 3*	93	± 21
Eu			3.1	± 0.5	4		3.4	± 0.6
Ga	49		39	± 5.8	58		54	± 11
La			96	± 13				
Mo			-	-	29		28	± 6.2
Nd			60	± 15			100	± 29
Ni	98	± 3*	110	± 15	127	± 4*	140	± 19
Pb	70	± 4*	74	± 9.0	72.4	± 0.4*	76	± 12
Sc			25	± 4.0	40		29	± 5.7
Sr	1380		1700	± 230	830	± 30*	900	± 140
V	214	± 8*	200	± 24	300		240	± 36
Y			53	± 7.8				
Yb			6.6	± 0.9				
Zn	210	± 20*	260	± 21	220	± 10	270	± 41
Zr			180	± 29				

^a certified values indicated with *; others not certified

^b average of 35 determinations 2/83 to 7/83

^c average of 31 determinations 6/83 to 3/84

^d lower limit of determination

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THE DETERMINATION OF 41 ELEMENTS IN WHOLE COAL BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

By C.A. Palmer and P.A. Baedecker

Abstract

Forty-one elements have been determined in coal by a combination of short and long irradiations using instrumental neutron activation analysis (INAA). The factors that lead to errors in analysis, such as spectral overlaps, low sensitivity, and multiple sources of the indicator radionuclide, are discussed. Detection limits for the elements determinable by INAA are given and data for National Bureau of Standards coal and fly ash standards are presented.

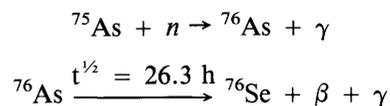
INTRODUCTION

Instrumental neutron activation analysis (INAA) is a versatile technique for elemental analysis because it has very low detection limits for many elements, lends itself to automation, and provides precise data for many major, minor, and trace elements. The application of INAA to the analysis of coal has been described in a number of publications (e.g., Block and Dams, 1973; Ondov and others, 1975; Rowe and Steinnes, 1977a, b; Swaine, 1985). For analyses based on the measurement of long-lived nuclides ($t^{1/2} > 1$ day), 30 elements can be determined routinely in most coal samples. Two additional elements can be determined in certain coals. Extension of the technique to the measurement of short-lived activities, with rapid sample transfer and short irradiation and counting times, makes possible the determination of an additional nine elements.

ACTIVATION ANALYSIS

Activation analysis is based on the measurement of the activity from radionuclides that are produced by nuclear reactions on naturally occurring isotopes of the element to be determined in the sample. Reactor neutrons are most commonly used for inducing the nuclear transformations because of their availability, their relatively high probability for neutron-induced reactions, and their relative freedom from problems due to matrix

effects (self-shielding). For example, the determination of arsenic is carried out by the following reaction:



where the amount of arsenic in the sample is determined by counting the induced ${}^{76}\text{As}$ activity. The activity of the indicator radionuclide produced during the irradiation is directly proportional to the amount of element of interest in the sample, and the analytical determination is generally made by comparing the activity induced in the sample against the activity measured for well-characterized standard samples. The activities of the samples and standards are most commonly measured by gamma-ray spectroscopy because potentially interfering activities can generally be discriminated against by looking at gamma-rays having unique energies for the indicator radionuclide and because gamma counting is relatively free from matrix effects (self-absorption). Semiconductor detectors, such as high-purity germanium and lithium-drifted germanium (Ge(Li)) diodes, are generally used for gamma-ray spectroscopy because of their excellent resolution, which permits the separation of closely spaced lines. These devices convert the gamma-ray signal for the irradiated samples to electrical signals that can be sorted according to amplitude by an analog-to-digital converter; the pulses within each amplitude interval are counted by a multichannel scaler, with each channel corresponding to a given interval of gamma energy. A typical gamma-ray spectrum of an irradiated coal sample, measured 5 days after irradiation, is shown in figure 11. The radioactivity in the sample is thus measured by determining the area of a specific gamma photopeak of interest above an underlying background continuum.

If only relatively long-lived ($t^{1/2} > 12$ h) indicator radionuclides are employed in the analysis, up to 32

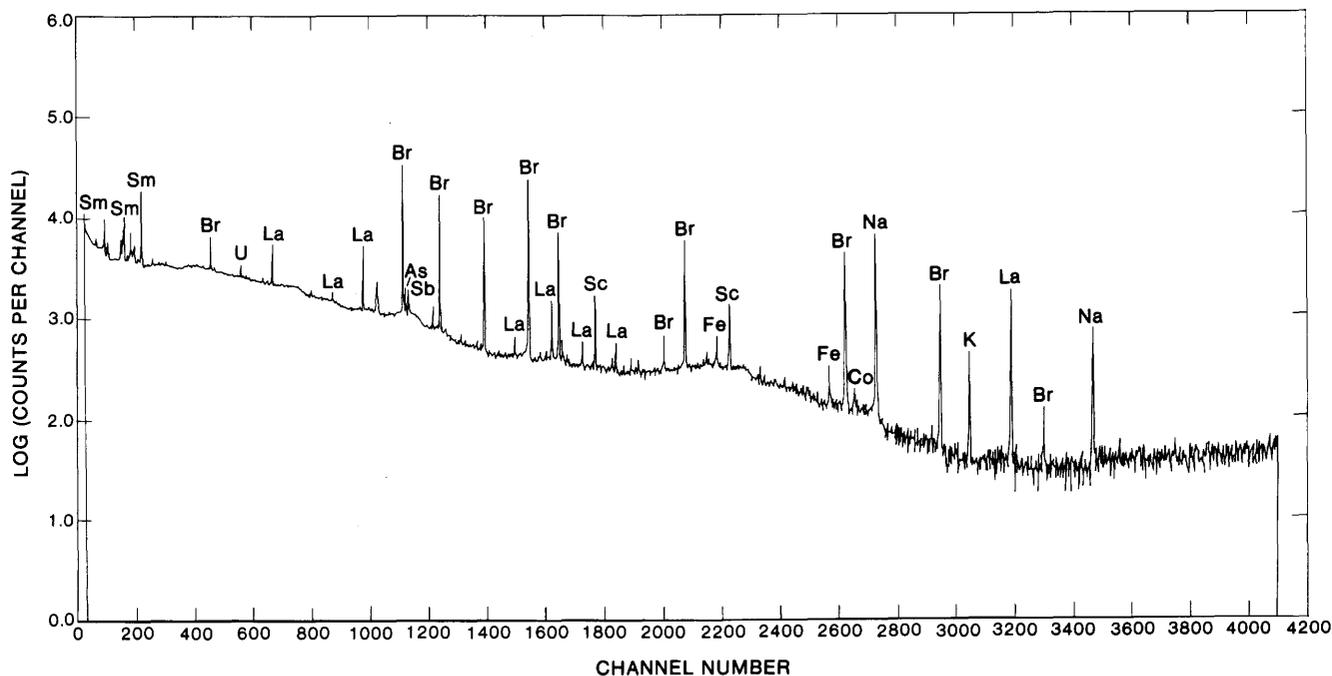


Figure 11. Spectrum of NBS coal standard 1632 collected 5 days after irradiation.

elements can be determined using relatively long irradiations and two sample counts following irradiation. The elements, their indicator radionuclides, half-lives, gamma-ray lines, detection limits, and potential spectral interferences are listed in table 7. The estimation of detection limits for INAA is subject to considerable uncertainty. This uncertainty exists because the estimate is based on the signal-to-background ratio for each photopeak of each sample being counted and the Ge(Li) detector employed, where the Compton continuum from higher-energy gamma-rays contributes to the background. The detection limits are therefore dependent on sample composition. These detection limits, presented in table 7, are for coal samples having concentrations of Na, Sc, Fe, Co, and La similar to National Bureau of Standards (NBS) standard coal 1632, because the gamma-rays from the activation products of these elements dominate the spectrum of most activated coal samples and limit the sensitivities for the determinations of other elements.

The pertinent information for the short-lived species that can be measured for the determination of nine additional elements is listed in table 8. Those species with half-lives of less than 1 h are generally measured after irradiation for 5 min at a flux of 3×10^{12} units in the pneumatic tube system of the U.S. Geological Survey 1 MW TRIGA reactor in Denver, Colo., and counted after approximately 10 min of decay. Manganese and dysprosium are measured after a 2 h irradiation and approximately 3 h of decay.

EXPERIMENTAL METHODS AND PROCEDURES

Sample Preparation

The TRIGA research reactor facility of the U.S. Geological Survey is utilized for most of the INAA work conducted in our laboratories. Powdered samples, weighing 500 mg, are heat sealed in 1.5-cm³ polyethylene vials. Eighty samples, including standards, can be irradiated in the "lazy susan" facility of the reactor for 8 h at a flux of 6×10^{12} n/cm² s. The samples are packaged in 7.4-cm³ snap-top polyethylene vials and inserted into a single TRIGA tube in the "lazy susan." Because of a modest flux variation along the tube, the 40 samples and standards on each level are treated as separate sample sets during the subsequent counting and data processing procedures.

Samples, as small as 2 mg, can be analyzed after irradiation in the U.S. Geological Survey TRIGA reactor by increasing the irradiation time to 16 or 24 h. The sensitivity is reduced for the determination of several elements in samples weighing less than 200 mg, and less than 20 elements can be detected for most samples weighing less than 10 mg.

Standards

Three multiple-element standards, or flux monitors, are currently used for the routine analysis of coal: NBS 1632 (coal) and 1633 (fly ash) and Eastman-

Table 7. Long-lived (>10 h) radionuclides

Element	Indicator Radionuclide	Half-life	Preferred γ -energy	Limit of Determination ppm ($\mu\text{g/g}$) except % (cg/g) as indicated	Potential Spectral Interferences			
					Radio-nuclide	Energy	Radio-nuclide	Energy
Na	²⁴ Na	15.0 h	1368.6 2753.9	10				
K	⁴² K	12.4 h	1524.7	0.01%				
Sc	⁴⁶ Sc	84 d	1120.5	0.01				
Cr	⁵¹ Cr	27.8 d	320.1	0.5	¹⁷⁷ Lu	321.3	¹⁴⁷ Nd	319.4
Fe	⁵⁹ Fe	45.6 d	1099.3 1291.5	50 75	¹⁸² Ta	1289.1		
Co	⁶⁰ Co	5.3 yr	1173.2 1332.5	0.2 0.2				
Zn	⁶⁵ Zn	245 d	1115.4	1	¹⁶⁰ Tb	1115.1		
Ga	⁷² Ga	14.1 h	834.1	0.1	⁵⁴ Mn	834.8		
As	⁷⁶ As	26.4 h	559.0	0.1				
Se	⁷⁵ Se	120.0 d	264.6	0.1	¹⁸² Ta	264.1		
Br	⁸² Br	35.4 h	554.3 776.5	0.5 0.5				
Rb	⁸⁶ Rb	18.7 d	1076.8	5				
Sr	⁸⁵ Sr	64.0 d	514.0	50				
Zr	⁹⁵ Nb ⁹⁵ Zr	35.1 d 65.0 d	765.8 756.7	200 200	¹⁵² Eu ¹⁵⁴ Eu	764.8 756.8	¹⁶⁰ Tb	765.3
Mo	⁹⁹ Mo	66.7 h	140.5	10				
Sb	¹²² Sb ¹²⁴ Sb	67.2 h 60.0 d	564.0 1691.0	0.05 0.1				
Cs	¹³⁴ Cs	2.1 yr	795.8	0.1				
Ba	¹⁰¹ Ba	12.0 d	496.3	100	¹⁰³ Ru	497.0		
La	¹⁴⁰ La	40.2 h	1596.6 487.0	0.02 0.05				
Ce	¹⁴¹ Ce	32.5 d	145.4	0.5	¹⁵⁴ Eu	145.6		
Nd	¹⁴⁷ Nd	11.1 d	531.0	2				
Sm	¹⁵³ Sm	46.8 h	103.2	0.5	²³⁹ Np	103.7		
Eu	¹⁵² Eu	12.7 yr	779.1 1408.1	0.04 0.01				
Tb	¹⁶⁰ Tb	72.1 d	298.6 1178.1	0.05 0.1	²³³ Pa	299.9		
Yb	¹⁷⁵ Yb	101.0 h	396.1 282.6	0.1 0.2	¹⁴⁷ Nd	398.2	²³³ Pa	398.2
Lu	¹⁷⁷ Lu	6.7 d	208.4	0.01	²³⁹ Np	209.7		
Hf	¹⁸¹ Hf	42.5 d	482.2 133.1	0.1 0.05				
Ta	¹⁸² Ta	115.1 d	1221.3 1189.2	0.02 0.03				
W	¹⁸⁷ W	24.0 h	479.5 685.7	0.1 0.1	¹⁴⁷ Nd	685.9		
Hg	²⁰³ Hg	46.6 d	279.2	0.1	⁷⁵ Se	279.5		
Th	²³³ Pa	27.0 d	311.9	0.1				
U	²³⁹ Np	2.3 d	277.6	0.5				

Table 8. Short-lived indicator radionuclides

Element	Indicator Radionuclide	Half-life	Preferred γ -energy (keV)	Limits of Determination	Potential Spectral Interferences (keV)
$t_{1/2} > 1 \text{ h}, < 3 \text{ h}$					
Mn	^{56}Mn	2.58 h	846.7 1811.2	1	
Dy	^{165}Dy	2.36 h	94.7	0.1	
$t_{1/2} < 1 \text{ h}$					
Mg	^{27}Mg	9.5 min	844.0 1014.1	1%	^{56}Mn 846.7
Al	^{28}Al	2.27 min	1778.9	50	
S	^{37}S	5.04 min	2081.8 3103.8	1%	
Cl	^{38}Cl	37.3 min	1642.0	100	
Ca	^{49}Ca	8.8 min	2062.5	0.5%	
Ti	^{51}Ti	5.8 min	320.1	0.1%	
V	^{52}V	3.76 min	1434.0	50	

Kodak gelatin multicomponent reference material (TEG-50-B). The concentration values used for NBS 1632 and 1633 are those of Ondov and others (1975). Standard TEG-50-B has been calibrated against single-element standards for As, Co, Cu, Hg, Sb, Se, and Zn. In addition, NBS standard reference materials 1632a and 1633a have been characterized in the U.S. Geological Survey laboratories for use as standards. Data for all five standard samples are listed in table 9. Antimony has been observed to be inhomogeneous in NBS 1632 (Ondov and others, 1975) and has a low concentration in NBS 1633. Thus, TEG-50-B is used as a standard for antimony. For short irradiations, these standards are supplemented with analytical-grade sulfur and spectroscopic grade CaCO_3 and MgO . Recently, work has begun on a new U.S. Geological Survey standard that will consist of a spiked coal from the Lower Bakerstown coal bed. After testing of this standard is complete, the NBS standards will probably be used only for quality-control purposes.

Counting Facilities

Following an 8-h irradiation in the U.S. Geological Survey reactor in Denver, Colo., and the subsequent four days of transcontinental shipping of the samples, all samples are placed in 7.4-cm³ polyethylene vials. These vials serve as transfer containers for the automatic sample changers used with the high-resolution coaxial Ge(Li) detectors for gamma-ray spectroscopy. The detectors are coupled to multichannel pulse-height analyzers, which are capable of dividing the spectrum into 4,096 energy increments or channels. The analyzers automatically repeat a cycle of data acquisition, sample changing, and read-out of the spectral data to disk storage. The automatic sample changer used with each detector is mechanically identical to that described by Massoni and

others (1973), but the electronic interface has been completely redesigned to employ solid-state circuitry. Eight sample changers are controlled by a single interface. At the end of each preset counting period, the multichannel analyzer signals the controller to change samples. The sample changer is a gravity feed device that uses compressed air to eject a sample from the counting station after counting is completed.

Data Reduction

All spectra are processed using the computer program SPECTRA (Baedecker, 1976, 1980; Grossman and Baedecker, 1986). The program contains algorithms for smoothing the spectral data; searching out all peaks in the spectrum; determining the areas of both well-resolved, single peaks and unresolved (or overlapping) multiple peaks; and determining the energies of the photopeaks (including corrections for zero and gain drift of the spectrometer). The calculations of elemental concentrations include corrections for spectral interferences, decay, and neutron-flux variations, as well as pulse pileup effects. When a gamma-ray line has been specified for use in the analysis and has been observed in a standard material but not in a sample, the program computes an upper limit to the concentration of the element in question. The peak area used for the calculation is 10 times the standard deviation of the background within the normal integration limits at the expected peak location in the spectrum. The program corrects for overlapping spectral lines that are too poorly resolved to be recognized as multiplets when an interference-free line of the interfering radionuclide can be observed in the spectrum and used for correction. For example, the area of the 264.6-keV line of ^{75}Se can be corrected for interference from the 264.1-keV line of ^{182}Ta . This correction is accomplished by using the peak area of the 1221.3-keV line of ^{182}Ta and the known ratio of the intensity of the 264.1-keV line to the intensity of the 1221.3-keV line.

Thus, elemental concentration data, based on each specified peak, are stored in a disk file that is generated during execution of the SPECTRA program. A second program, SUMMARY1, is executed after the successful execution of SPECTRA, to average the results from multiple lines for a given element and to generate a report of analysis for a single counting of a sample set. Peaks that are averaged are specified to the program in order of decreasing priority. Results from lower-priority peaks are included in the reported result only if they agree within 2 standard deviations of the mean based on the peak(s) given higher priority. Each result included in the mean is weighted by its estimated standard deviation based on counting statistics. The weighted average results and the estimated standard deviations for each element are stored in a disk file for long-term storage.

Table 9. Concentrations of 40 elements in multiple-element standards used for the analysis of coal ($\mu\text{g/g}$, unless percent indicated)

[Sulfur was not included because it was below the detection limit for all these standards, and elemental sulfur was used as a standard.]

Element	Standards				
	1632*	1632a	1633*	1633a	TEG-50-B
Na	414 ± 20	90 ± 1	3200 ± 400	2000 ± 100	397 ± 5
Mg %	0.20 ± 0.05	—	1.8 ± 0.4	—	—
Al %	1.85 ± 0.13	—	12.7 ± 0.5	—	—
Cl	890 ± 125	—	42 ± 10	—	—
K %	0.28 ± 0.03	0.40 ± 0.02	1.61 ± 0.15	2.1 ± 0.3	—
Ca %	0.43 ± 0.05	—	4.7 ± 0.6	—	—
Sc	3.7 ± 0.3	6.0 ± 0.1	27 ± 1	41.8 ± 0.4	—
Ti	1040 ± 110	—	7400 ± 300	—	—
V	36 ± 3	—	235 ± 13	—	—
Cr	19.7 ± 0.9	32.4 ± 0.4	127 ± 6	212 ± 6	47 ± 3
Mn	43 ± 4	—	496 ± 19	—	—
Fe	0.84 ± 0.04	1.09 ± 0.02	6.2 ± 0.3	10.4 ± 0.2	—
Co	5.7 ± 0.4	6.2 ± 0.18	41.5 ± 1.2	44.5 ± 0.5	46 ± 2
Zn	30 ± 10	30 ± 2	216 ± 25	260 ± 15	53 ± 4
Ga	5.8 ± 0.4 [†]	7.0 ± 0.05	40.7 ± 1.2 [†]	—	—
As	6.5 ± 1.4	9.6 ± 0.1	58 ± 4	177 ± 4	105 ± 5
Se	3.4 ± 0.2	2.35 ± 0.05	10.2 ± 1.4	10.9 ± 0.9	43 ± 3
Br	19.3 ± 1.9	44 ± 1	12 ± 4	7.8 ± 0.6	—
Rb	19.4 ± 2.3 [†]	—	110 ± 9 [†]	—	—
Sb	3.9 ± 1.3	0.61 ± 0.03	6.9 ± 0.6	6.2	44 ± 4
Sr	161 ± 16	88 ± 6	1700 ± 300	940 ± 40	—
Zr	—	—	301 ± 20	—	—
Mo	3.1 ± 0.1 [†]	—	25 ± 2 [†]	—	—
Cs	1.4 ± 0.1	2.1 ± 0.5	8.6 ± 1.1	11.0 ± 0.3	—
Ba	352 ± 30	127 ± 8	2700 ± 200	1500 ± 60	—
La	10.7 ± 1.2	15 ± 7	82 ± 2	94 ± 1	—
Ce	19.5 ± 1	28 ± 1	146 ± 15	184 ± 8	—
Nd	8.7 ± 1.0 [†]	12 ± 1	57.8 ± 1.6 [†]	79 ± 3	—
Sm	1.7 ± 0.2	2.0 ± 0.1	12.4 ± 0.9	14 ± 2	—
Eu	0.33 ± 0.04	0.49 ± 0.01	2.5 ± 0.4	3.9 ± 0.1	—
Tb	0.23 ± 0.05	0.31 ± 0.01	1.9 ± 0.3	2.8 ± 0.2	—
Dy	1.12 ± 0.06 [†]	—	9.4 ± 0.5 [†]	—	—
Yb	0.7 ± 0.1	1.2 ± 0.1	7 ± 3	9.2 ± 0.2	—
Lu	0.14 ± 0.01	0.15 ± 0.01	1.0 ± 0.1	1.2 ± 0.1	—
Hf	0.96 ± 0.05	1.23 ± 0.02	7.9 ± 0.4	6.5 ± 0.1	—
Ta	0.24 ± 0.04	0.41 ± 0.01	1.8 ± 0.3	2.4 ± 0.1	—
W	0.75 ± 0.17	0.76 ± 0.03	4.6 ± 1.6	5 ± 1	—
Hg	—	0.22 ± 0.03	—	—	60 ± 5
Th	3.2 ± 0.2	4.3 ± 0.1	24.8 ± 2.2	27.5 ± 5	—
U	1.41 ± 0.07	1.3 ± 0.1	12.0 ± 0.5	11.4 ± 0.3	—

* From Ondov and others (1975) (except as noted).

[†] From Rowe and Steinnes (1977 a).

Errors based on standard deviation of 12 replicates.

Following the completion of all counts on each set of samples during a 2-month decay period, a third program, SUMMARY2, is executed to average the results from multiple counts and to generate a report of analysis. Again, the mean value for each element is a weighted mean based on the estimated counting error. If uranium has been determined via the 2.35-day ^{239}Np , SUMMARY2 corrects for fission product interferences in the determination of Zr, Mo, La, Ce, Nd, and Sm using the correction factors listed in table 10. Where the magnitude of the correction exceeds 20 percent of the value reported, the value is flagged in the report of analysis. The calculation of the fission product interference for lanthanum is complicated by the fact that the fission product ^{140}Ba has a longer half-life (12.7 days) than its daughter product, the indicator radionuclide ^{140}La . We have not measured the fission product interference for lanthanum at the normal decay time of 6 days for coal samples. We use the calculated value of 0.02 part per million of lanthanum per part per million of uranium for computing the fission product interference, which is generally less than 1 percent for most coal samples. The experimental values for other elements listed in table 10 are not decay dependent and were measured at a decay time of 10 days after irradiation. Because the experimental values agree with the calculated values to within 25 percent and the fission product interferences for most coals are below 2 percent, small errors in the interference-correction factor result in negligible errors in the data.

Quality Control

An estimate of the precision for each sample set is made by using replicate samples to determine the reproducibility of the measurements. Several replicate samples are generally determined within each sample set. In addition, many elements are determined by two or more counting cycles.

Agreement in both cases is usually within errors determined by counting statistics. When this is not the case, the results are flagged in the data reduction procedures using programs described by Grossman and Baedecker (1986). An estimate of the accuracy of the data is obtained by running control standards that can then be compared to "best values" determined from the literature or from previously determined averages. Reference materials 1632a and 1633a are most commonly used as control standards. "Best values" for these are given in table 9. This procedure also allows for an estimate of the precision of the data between different sample sets. Computerized procedures (including graphic presentation of the quality-control data) for comparing measured values with "best values" were also described by Grossman and Baedecker (1986).

Table 10. Interferences in INAA due to neutron-induced fission of ^{235}U (in μg of the elements (apparent) per μg of U)

Isotope	Fission Yield	(n, γ) Cross Section (barns)	I (calc.) [*]	I (exp.) [*]
^{95}Zr	6.5	0.08	7.5	11.5 ± 0.3
^{99}Mo	6.1	0.51	0.85	1.01 ± 0.13
^{140}La	6.3	8.9	0.020 [†]	—
^{141}Ce	5.9	0.6	0.27	0.29 ± 0.01
^{147}Nd	2.26	2	0.17	0.22 ± 0.01
^{153}Sm	0.16	210	0.00008	

^{*} Error estimates are 70 percent confidence limits on the mean of four determinations.

[†] 6 days following irradiation.

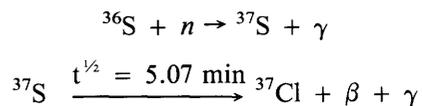
^{*} Calculation assumes that the cross section for fission of ^{235}U is equal to 580 barns.

DISCUSSION

Up to 41 elements can be determined in coal and fly ash by a combination of short and long irradiations for INAA. Except for dysprosium, all the elements determined using short-lived indicator radionuclides are light or first-row transition elements, which can be better determined by other multiple-element instrumental techniques. The use of short irradiations and counting times is primarily useful for the analysis of small samples where it is desirable to get as complete an analysis as is possible on a single sample (e.g., mineral, size, or density separates). Of the elements with half-lives of less than 1 h, the lines from the activation products of Mg, Al, and V are most readily observed in the spectra obtained within 10 min of irradiation. The remaining four elements listed in table 8 (S, Cl, Ca, and Ti) are determinable with a detectability poorer than that for Mg, Al, and V.

The following discussions provide more detailed evaluations of the problems associated with the determination of specific elements.

Sulfur is determined in the short counting cycle, 5 min after irradiation. It is determined from the reaction



The determination of sulfur is subject to error due to natural variation in the isotopic abundance of ^{36}S . A maximum error of ± 29 percent has been calculated, but errors from +4.4 to -6.5 percent have been observed for results on natural material when compared with a standard with $\delta^{34}\text{S} = 0$. Because of the low natural abundance of ^{36}S (0.01 percent) and its low cross section (0.14 b), the determination of sulfur has poor sensitivity, and errors from counting statistics are likely to be much higher than errors in isotopic composition for most moderate- to low-sulfur coals.

Although the concentration of magnesium is moderately high in most coal samples, it is relatively difficult to measure, because ^{27}Mg is produced in the reactor from two sources: from the (n, γ) reaction or ^{26}Mg and from the (n, p) reaction or ^{27}Al . Because most coal samples having high magnesium concentrations commonly have even higher aluminum concentrations, large corrections must be made. The correction, which depends on the neutron spectrum for a given reactor, is about 35 percent for NBS 1632 irradiated in the pneumatic tube of the U.S. Geological Survey Denver reactor.

The accuracy for the determination of gallium is greatly dependent on concentrations of iron and the speed with which the sample is counted. The major photopeak of ^{31}Ga (834 keV) has an interference from the 835-keV photopeak of ^{54}Mn that is formed from the (n, p) reaction of ^{54}Fe . Although the ^{54}Fe peak is relatively small for most coal samples, the half-life of gallium is only 14 h. For samples having high concentrations of iron or a large counting delay, this interference can be a major problem. For NBS 1632, the relative error is 1.2 percent after 3 days, but the error increases to 70 percent after 6 days.

The determination of chromium suffers from potential spectral interference from ^{177}Lu and ^{147}Nd . For NBS 1632, the corrections for these interferences amount to ≤ 1 percent, but they can be higher in coals with lower concentrations of chromium or higher contents of the lanthanide elements.

The 1,115-keV photopeak of ^{65}Zn falls on the low-energy tail from the 1,120-keV photopeak from ^{46}Sc , which complicates the evaluation of the base area for the photopeak. This ^{65}Zn photopeak is normally treated by the computer algorithm as part of a triplet along with the 1,112-keV photopeak of ^{152}Eu . Also, a small interference exists from ^{160}Tb , which amounts to 1 percent zinc in NBS 1632.

The 264.6-keV photopeak from selenium is best measured in coal samples in a count taken from 3 weeks to 2 months after irradiation. A correction must generally be made for an interference from ^{182}Ta . The correction is 8 percent of the measured selenium in NBS 1632.

Zirconium is difficult to determine by INAA due to spectral interferences from ^{152}Eu , ^{154}Eu , and ^{160}Tb , which interfere with the lines from ^{92}Zr and its daughter product, 35.1-day ^{95}Nb . For NBS 1632, the correction on the ^{95}Nb 765.8-keV line is 10 percent. Also, a correction is necessary for the fission product interference based on the measured uranium content, which for fly ash NBS 1632 amounts to 45 percent. For these reasons, the determination of zirconium is semiquantitative at best.

Molybdenum, like zirconium, falls near the low-mass maximum of the fission yield curve of ^{235}U , and a

large fission-interference correction is generally required. The interference correction would be roughly 46 percent of the value for NBS 1632 and 1633.

The determination of barium is based on the measurement of the most intense ^{131}Ba line at 496.3 keV in the Ge(Li) spectrum taken within a week of irradiation. There is a potential spectral interference from fission product ^{103}Ru , which cannot be corrected because of the absence of any other interference-free line from ^{103}Ru of sufficient intensity. An estimate of the interference calculated from fundamental parameters and confirmed by experiment is $2.9 \times e^{0.0402 t}$ (apparent parts per million of barium per part per million of uranium), where t is the time after irradiation in days. For NBS 1632, ^{103}Ru contributes 1.5 percent to the intensity of the barium photopeak seven days after irradiation, and for NBS 1633, it contributes 1.7 percent.

The determination of lanthanum also can be affected by fission product interferences. The measurement is complicated by the relatively long lived, 12.8-day ^{140}Ba , which is a fission product precursor to the indicator radionuclide ^{140}La . Four days after irradiation, the interference from ^{140}Ba is 0.0084 (apparent parts per million of lanthanum per part per million of uranium), or a 0.1-percent correction for NBS 1632. For later counts, the correction will increase; at a counting time of 10 days, the interference is 0.092, or a 1.2-percent correction for NBS 1632.

The determination of terbium is made difficult by spectral interferences. The most intense line in the Ge(Li) spectrum, at 298.6 keV, occasionally suffers from interferences from the ^{233}Pa 299.9-keV line. The computer program must first check to see if both lines have been detected and resolved by the multiplet analysis algorithm; if not, the program then applies a correction for the interference, which for NBS 1632 will be 50 percent, at a decay time of two months. The 879.4-keV line is also observed in most spectra as a weak line on the low-energy tail of the generally intense ^{146}Sc 889.3-keV line, which renders the base area difficult to evaluate. The 965.8-keV line may suffer from interference from ^{152}Eu , and while the 1,177.9-keV line is free from interferences, it has much poorer sensitivity.

Photopeaks from 101-h ^{175}Yb and 32-day ^{169}Yb are normally detected in Ge(Li) spectra of activated coal. Most photopeaks from both nuclides incur spectral interferences, although ytterbium is generally well determined using the 396.1-keV line of the shorter-lived isotope. There are minor interferences from ^{147}Nd and ^{233}Pa ; the correction is 3 percent for NBS 1632.

Mercury can be determined in many coal samples by measuring the intensity of the 279.2-keV line of the 46.6-day ^{203}Hg . A substantial spectral-interference correction is generally required due to ^{75}Se (60 percent for NBS 1632). Because the ^{175}Se 264.6-keV line, which is used to make the correction, suffers from a generally

small interference from ^{182}Ta , the algorithm must treat the 264.6-keV line before computing a mercury content from the 279.2-keV photopeak.

Rowe and Steinnes (1977a, b) have described the application of epithermal neutron irradiations to the analysis of coal. Many of the spectral and fission product interferences discussed in this section can be reduced and greater sensitivity realized by this technique, particularly for the determination of Ni, Mo, Rb, Sr, Cs, Tb, Ta, W, and U. However, the technique is limited to small (~50 mg) samples and requires special packaging in aluminum foil and irradiation inside cadmium capsules. Because of the added cost and labor involved in the special handling of samples for epithermal neutron activation analysis (and increased radiological hazard of handling radioactive coal powders), the technique is not suitable for routine application but is useful for special problems.

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THE DETERMINATION OF MAJOR AND MINOR ELEMENTS IN COAL ASH AND OF CHLORINE AND PHOSPHORUS IN WHOLE COAL BY X-RAY FLUORESCENCE SPECTROMETRY

By R.G. Johnson, G.A. Sellers, and S.L. Fleming, II

Abstract

Methods for the X-ray fluorescence spectrometric analysis of 11 elements in coal ash (Na, Mg, Al, Si, P, S, K, Ca, Ti, Mn, and Fe) and of two elements in whole coal (Cl and P) are described. Coal-ash samples are fused with lithium tetraborate to produce glass disks; whole-coal samples are briquetted with a cellulose binder prior to analysis. Calibration for all elements in both whole coal and coal ash is accomplished by using a simple linear regression of X-ray intensity versus concentration. Silicate rock standards are used for calibration in coal ash analysis, and whole-coal analyses are based on coal standards from the National Bureau of Standards (NBS), on coals analyzed by independent methods, and on synthetic standards. Precision, expressed as the relative standard deviation, is 2 to 5 percent for coal ash and 10 percent for determinations of elements in the whole coal.

INTRODUCTION

X-ray fluorescence (XRF) spectrometry is a rapid technique for accurate and precise elemental analysis of solid and liquid specimens. As such, it is suited to the determination of certain important elements that occur in coal and has been used extensively for the analysis of both whole coal and coal ash (Kuhn and others, 1975; Giaque and others, 1979; Mills and others, 1981; Wheeler, 1983). In practice, most XRF spectrometer systems are not able to detect elements having atomic numbers lower than 11, the atomic number of sodium. Thus, concentrations of the most abundant elements in the coal matrix (C, H, N, and O) must be determined by other methods.

In general, the accuracy of XRF spectrometric determinations of inorganic elements depends on concentration, particle size, matrix effects, surface roughness, the quality of standard materials, and other related

factors. The accuracy of analysis usually falls between 2 and 10 percent (relative) depending on how well these factors have been controlled. The lower limit of determination is as low as 1 $\mu\text{g/g}$ for elements having atomic numbers greater than 26, the atomic number of iron, and ranges to several hundred micrograms per gram for aluminum and silicon and to several thousand micrograms per gram for sodium. The upper limits for quantitative XRF spectrometric analysis are determined by the availability of standard reference materials.

This section describes procedures for the analysis of 2 minor elements (Cl and P) in whole-coal samples, and 11 major elements (Na, Mg, Al, Si, P, S, K, Ca, Ti, Mn, and Fe) in the corresponding high-temperature (525 °C) coal ash.

EXPERIMENTAL METHODS AND PROCEDURES

Equipment and Supplies

The instruments and reagents required in the XRF spectrometric methods are listed here.

1. For the preparation of a coal-ash fusion disk the following items are required.

Analytical balance	1-mg sensitivity
Automatic fluxer	Corporation Scientifique Claisse, Quebec, Canada
Pt-Au crucibles and molds (95 percent Pt alloyed with 5 percent Au)	Johnson Matthey, Inc. Seabrook, NH
Lithium tetraborate	Spectroflux 100 Johnson Matthey, Inc. Seabrook, NH

Storage desiccators

2. For the preparation of whole-coal briquettes the following items are required.

Analytical balance	1-mg sensitivity
Mixer-mill and accessories	Spex Industries
Cellulose powders	Whatman microgranular (CC-31), Whatman fibrous (CF-1)
Hydraulic press	276 MPa (40,000-psi) capacity, minimum

3. Standard reference materials can be obtained from the National Bureau of Standards (NBS), Office of Standard Reference Materials, Room B311, Chemistry Building, Gaithersburg, MD 20899.

Coal Ash

Because coal ash represents the dominant mineral portion of coal, XRF spectrometric analysis of this material is very similar to the XRF analysis of silicate rocks (Rose and others, 1963; Norrish and Hutton, 1969). Samples are prepared by fusion with lithium tetraborate flux, and silicate rock standards are used to construct calibration curves for each element. Extensive matrix correction techniques are not required because of the almost eightfold dilution of the sample by the flux. Fusion is the preferred method of preparation because it eliminates particle-size effects and mineralogical heterogeneity and thus allows for the highest precision possible.

A sample is prepared by thoroughly mixing 600 mg of coal ash with 5.400 g of lithium tetraborate in a Pt-Au crucible (95 percent Pt and 5 percent Au). To this mixture is added 5 drops of a 15-percent hydrobromic acid solution, which acts as a nonwetting agent during the fusion. Samples are fused for 20 min by a commercial fluxer (Claisse^R) that produces a temperature in the range of 1,100 to 1,200 °C. Alternatively, samples may be fused for 1 h at 1,100 °C by a U.S. Geological Survey "in-furnace" device (Taggart and Wahlberg, 1980a), and finally cast in Pt-Au molds (Taggart and Wahlberg, 1980b) to produce glass disks. Caution is advised here. Preliminary evidence indicates that the higher temperature effected by the Meeker burner in the Claisse^R fluxer may volatilize sodium from certain samples during the fusion process.

A Diano^R model XRD-8300 wavelength-dispersive XRF (WDXRF) spectrometer is used to make all intensity measurements; instrumental parameters and operating conditions are listed in table 11.

Calibration of the instrument consists of plotting X-ray intensity versus concentration of the standard

Table 11. Instrumental operating conditions for XRF analysis of coal ash

Element	Anode	kV	mA	Crystal
Na	Cr	60	33	Ovonyx ^a
Mg	Cr	60	33	Ovonyx
Al	Cr	50	40	PET
Si	Cr	50	40	PET
P	Cr	50	40	Ge
S	Cr	50	40	PET
K	Cr	50	10	LiF(200)
Ca	Cr	50	10	LiF(200)
Ti	Cr	50	30	LiF(200)
Mn	W	50	40	LiF(200)
Fe	W	50	10	LiF(200)

^a The Ovonyx crystal is a synthetic multiple-layer structure with a d-spacing of 2.28 nm.

reference materials for each element and calculating slope and intercept through simple linear regression analysis. Silicate rock standards are used for every element except sulfur because of their availability and similarity to the composition of most coal ashes. The ranges of concentration (Abbey, 1983) covered by these reference materials for 10 elements (excluding sulfur) are listed in table 12. Results from a typical calibration for iron are shown in table 13 in the form of accepted and calculated concentrations generated by the simple linear regression model.

Because many coal ashes contain much higher levels of sulfur than do the available reference materials, the preparation of separate standards for use in determining sulfur is necessary. To prepare these standards, a typical rock standard is spiked with sulfur and diluted in steps with the unspiked material to produce a set of secondary standards covering the intended concentration range. The mixture is fused with lithium tetraborate flux, and sulfur in the product is determined by an independent method (LECO^R sulfur analyzer) because some sulfur is lost during the fusion process.

Table 12. Concentration ranges provided by rock standards for the XRF analysis of coal ash

Oxide	Concentration (percent)	
	Lowest standard	Highest standard
Na ₂ O	0.06	8.37
MgO	0.10	43.50
Al ₂ O ₃	0.73	54.53
SiO ₂	4.43	87.21
P ₂ O ₅	0.01	34.50
K ₂ O	0.03	10.03
CaO	0.08	50.50
TiO ₂	0.01	2.69
MnO	0.01	0.77
Fe ₂ O ₃	1.00	25.76

Table 13. XRF calibration of iron in coal ash: simple linear regression analysis results

Standard	Concentration (percent)	
	Accepted	Calculated
AGV-1	6.78	6.83
DNC-1	9.85	9.72
W-1	11.11	10.90
QLO-1	4.29	4.15
G-1	1.94	1.49
ANV	7.48	7.56
SCO-1	5.22	5.47
SDC-1	6.85	7.27
ANQ	2.26	2.10
ANY	13.85	14.19
BCR-1	13.41	13.73
BHVO-1	12.23	12.07
GSP-1	4.30	4.05
STM-1	5.20	5.47
W-2	10.77	10.97
CRPG-Fe	25.76	24.92
G-2	2.69	2.36
RGM-1	1.89	1.55
ANW	5.33	5.51
ANX	4.25	4.37
BIR-1	11.25	11.45

The sulfur reference standards used for this work were produced by spiking U.S. Geological Survey basalt BIR-1 with ignited calcium sulfate. Serial dilutions of this mixture with BIR-1 were made to cover the concentration range of 0.1 to 10 percent sulfur. Samples were prepared in duplicate, and one of each was crushed, ground, and analyzed by a LECO^R sulfur analyzer. Calibration for sulfur is accomplished in the same way as the calibrations for other elements.

The XRF spectrometric determinations of major elements in coal ash compare well with other analytical methods. Because the chemistry (or at least the range of composition of the major elements) of coal ash is similar to that of silicate rocks, the accuracy is approximately the same. This accuracy is estimated to be ± 2 to 5 percent (relative error) depending on the element and the concentration level.

Whole Coal

One advantage of analyzing whole coal is that volatile elements normally lost in ashing or fusion can be determined. The analysis of whole coal may include practically any element, at concentrations approaching 1 $\mu\text{g/g}$ for many. One problem, however, is that calibration standards for XRF spectrometric analysis of whole coal must themselves be whole coals. Only a few coal standards exist, and these are certified for only a few elements. Thus, additional reference materials must be established by analysis of existing coals by other methods or by preparation of synthetic standards.

Specimen preparation normally involves grinding a coal sample with a binder, followed by compression to form a briquette. A low weight-ratio of sample to binder is used because the XRF spectrometric analysis of whole coal usually involves the determination of certain trace elements for which the best possible detection limits are desired. This section describes procedures used in the determination of phosphorus and chlorine in whole coal. Similar procedures could be used for the determination of other elements.

Air-dried coal samples (80 mesh) to be prepared for XRF analysis are further dried for three hours at 105 °C. Then, 0.500 g of coal is mixed with an equal portion of microgranular cellulose that serves as a binder. The mixture is transferred to a 26-mL polystyrene vial containing two 6-mm-diameter polycarbonate beads (to aid mixing) and is shaken on a mixer-mill for 10 min to ensure homogeneity. This mixture is pressed against an equal volume of fibrous cellulose (to provide a strong backing) in a hydraulic press at 276 MPa (40,000 psi) for 30 s to produce a 2.54-cm-diameter briquette.

Measurements are made by a Diano^R model XRD-8300 WDXRF spectrometer; instrumental operating conditions are listed in table 14.

Table 14. Operating conditions for XRF analysis of whole coal

Element	Anode	kV	mA	Crystal
P	Cr	50	40	Ge
Cl	Cr	50	40	PET

Standards used for the determination of chlorine and phosphorus in whole coal include three NBS reference materials, coals that have been analyzed by other methods, and synthetic standards. The NBS coal standards include NBS 1633, 1633a, and 1635. NBS 1633 is no longer available, and NBS 1632b has only recently become available. The NBS coals are used in determinations of both chlorine and phosphorus; concentration values are taken from Germani and others (1980) and from Ondov and others (1975) because the concentrations of these elements are not certified by NBS.

Standards for the determination of chlorine in whole coal consist of a set of coals from three power plants. These coals were analyzed by instrumental neutron activation analysis (R.B. Finkelman, written commun., 1980) for 18 elements, including chlorine. A second set of five coals was the subject of an American Society for Testing and Materials (ASTM) cooperative program investigating XRF analysis of whole coals (ASTM D.05.29.02); although the coal samples were not intended to be distributed as standards, they were extensively analyzed by a variety of methods for the 10 major elements and phosphorus.

Finally, when the available standard reference material is not sufficient to meet analytical needs, it is possible to produce synthetic standards. The use of synthetic standards is the least desirable alternative because of the uncertainty in the composition of the final product due to preparation error and the considerable time and effort required to produce such material.

Phosphorus standards can be produced by thoroughly mixing a sample with a known concentration of phosphorus (for example, NBS 120a, a phosphate rock standard) or a pure compound (Na_3PO_4) with spectrographically pure graphite and then diluting this mixture in steps to give a series of samples that define the concentration range needed. These samples are then mixed with cellulose and briquetted as described previously.

Likewise, chlorine standards are prepared by spiking graphite with a substance such as sodium chloride and then diluting the mixture with graphite in steps to produce a series of standards. Standards for other elements can be prepared in a similar fashion.

Calibration for each element is accomplished by plotting concentration and intensity for all the available standards and calculating slope and intercept by a simple linear regression analysis. Results from a typical calibration for phosphorus are shown in table 15, where accepted and calculated concentrations are given. (The standards Syn-C through Syn-H were prepared synthetically, as described in the text. RM-120 through RM-124 were analyzed by other methods. The value for NBS 1632 is from Ondov and others (1975), and the value for NBS 1632a is from Germani and others (1980).) Although mathematical correction for absorption and enhancement by the other matrix elements may improve results (because minimal dilution is used), in practice, such corrections are difficult to accomplish because of the lack of well-characterized standards. Most matrix correction algorithms require that concentrations for all major and minor elements for the standards be known.

Table 15. XRF calibration of P_2O_5 in whole coal: simple linear regression analysis results

Standard	Concentration ($\mu\text{g/g}$)	
	Accepted	Calculated
Syn-C	2,610	2,590
Syn-D	1,310	1,310
Syn-E	653	622
Syn-F	327	321
Syn-G	163	153
Syn-H	82	77
RM-120	300	304
RM-121	350	354
RM-122	600	650
RM-123	270	200
RM-124	160	150
NBS-1632	300	280
NBS-1632a	500	512

Precision is determined by the sample preparation, instrument stability, and counting time and is generally in the 1- to 2-percent range. Because of the lack of appropriate standard reference materials and because of the uncertainty associated with those materials that are being used as reference standards in the calibrations, assessment of the accuracy of the chlorine and phosphorus determinations is difficult. In addition, there are no other methods for determining either of these two elements now in routine use at the U.S. Geological Survey to provide values for comparison. However, based on the few primary standards available, we estimate the relative precision of the method to be approximately 10 percent.

CONCLUSIONS

Methods based on XRF spectrometry are capable of determining 11 inorganic elements in coal, providing relative precision and accuracy of 2 to 5 percent for the determination of sulfur and major oxides in coal ash, and 10 percent for the determinations of chlorine and phosphorus in whole coal. The most important factor limiting the accuracy of analysis is the restricted availability of standard reference materials. Another significant factor that affects accuracy is that many coal samples not stored in a cool, dry, inert atmosphere decompose over time and, consequently, are subject to changes in composition. In addition, other elements, such as Mg, Al, Si, K, Ca, Ti, Mn, Fe, Cu, Ni, Zn, Rb, Sr, Y, Zr, Nb, and Ba have been determined in whole coal by methods quite similar to those previously described.

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ANALYSIS OF COAL ASH BY ATOMIC ABSORPTION SPECTROMETRIC AND SPECTROPHOTOMETRIC METHODS

By Floyd W. Brown and Hezekiah Smith

Abstract

Methods for determining Al, Ca, Fe, Mg, Mn, P, K, Si, Na, and Ti in coal ash are described. A bead formed by fusing a mixture of sample and lithium metaborate-lithium tetraborate flux at 1,000 °C for 45 min is dissolved in dilute nitric acid. Measurements are made by atomic absorption spectrometry and by spectrophotometry on portions of the resulting solution. Selected silicate standards are used as control samples to assure the quality of measurements. The precision of the methods commonly ranges from 1 to 10 percent relative standard deviation. The methods are both accurate and inexpensive and provide a good alternative to measurements by X-ray fluorescence spectrometry.

INTRODUCTION

The determination of major elements in coal ash requires the analysis of high-temperature ash residues having compositions that resemble those of silicate rocks. Thus, methods used in U.S. Geological Survey laboratories for routinely determining major elements (Al, Ca, Fe, K, Mg, Mn, Na, P, Si, and Ti) in silicate rocks (Shapiro, 1975) are, with certain modifications, applicable to coal-ash residues. The elements Al, P, Si, and Ti are determined spectrophotometrically, and the other six elements (Ca, Fe, K, Mg, Mn, and Na) are determined by flame atomic absorption spectrometry (AAS). The procedures were developed to facilitate the analysis of large numbers of samples.

Each sample, which consists of 100 to 200 mg of coal ash ground to pass through a 100-mesh sieve, is mixed with a reagent-grade lithium metaborate—lithium tetraborate flux and fused at 1,000 °C for 45 min in a graphite crucible. Use of a mixed flux (1 part anhydrous lithium metaborate (LiBO_2) and 2 parts anhydrous lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$)) prevents strong adhesion of the final bead to the wall of the graphite crucible. This feature is particularly important for samples having iron concentrations greater than 15 percent.

Also, the use of the mixed flux produces more reliable values for silica than do fusions with only lithium tetraborate.

In a practical procedure for determining major elements, the flux-to-sample ratio should be kept low to avoid the introduction of impurities, but the ratio must be high enough to assure complete decomposition of the sample. Concentrations of the major elements in solution must be sufficiently high to accommodate the least sensitive determinations but low enough to prevent silica from precipitating. These requirements are satisfied if 0.2 g of sample is used with 1.2 g of flux. The same flux-to-sample ratio (6 to 1) is used with different sample sizes. The bead that results from the fusion of 0.2 g of sample is dissolved in dilute nitric acid and diluted to 250 mL. Concentrations of major elements in this solution are determined by either spectrophotometry or by AAS.

SPECTROPHOTOMETRIC PROCEDURES

Silicon (as SiO_2) is determined spectrophotometrically by measuring the absorbance of a molybdenum complex at 640 nm (Bunting, 1944). In concentrations greater than 200 $\mu\text{g}/\text{mL}$, silica forms polymers that do not react with the molybdate reagent. Formation of these polymers is prevented by the addition of fluoride, as sodium fluoride, to each solution. Because the fluoride solution dissolves glass, thus giving erratic results in determinations of silica, containers made of polyethylene, TeflonTM, or some similar material should be used. The interference caused by phosphate, which forms a phosphomolybdic acid complex, is avoided by adding tartaric acid to destroy the complex.

Aluminum (as Al_2O_3) is determined spectrophotometrically by measuring the absorbance at 475 nm of the aluminum complex with calcium alizarin red-S (Parker and Goddard, 1950). Iron and titanium also form colored complexes that absorb at 475 nm, but these

interferences are eliminated by the addition of potassium ferricyanide and thioglycolic acid as complexing agents.

The titanium determination (as TiO_2) is based on the use of disodium-1,2-dihydroxybenzene-3,5-disulfonate (Tiron) as a spectrophotometric reagent. The reagent forms a lemon-yellow titanium complex that has a high molar absorptivity (Yoe and Armstrong, 1947). The absorbance of this titanium complex is nearly independent of pH over the range 4.3 to 9.6. Ferric iron also reacts with Tiron to produce a purple complex, but this interference is eliminated by reducing the ferric iron with sodium dithionite solution buffered at pH 4.7. The absorbance of the yellow titanium complex at 430 nm is measured spectrophotometrically.

Phosphorus (as P_2O_5) is determined spectrophotometrically by measurement of the absorbance of a heteropoly molybdenum-blue complex that forms upon reduction of heteropoly phosphomolybdic acid with stannous chloride solution. For the conditions used, only the molybdenum combined with phosphorus is reduced, and the excess molybdic acid is unaffected.

ATOMIC ABSORPTION SPECTROMETRIC METHODS

An aliquot of the original sample solution is diluted with lanthanum solution, and the absorption for Ca, Fe, K, Mg, Mn, or Na is measured by AAS. Operating conditions for the AAS instrument are presented in table 16.

Table 16. Operating conditions for atomic absorption spectrometry

Element	Wavelength (nm)	Hollow Cathode Lamp Current (mA)	Spectral Bandpass (nm)	Flame Type
Ca	422.673	10 to 25	0.7	Air-Acetylene Reducing
Fe	248.327	30	0.2	Air-Acetylene Oxidizing (lean, blue)
K	766.491	12	2.0	Air-Acetylene Oxidizing (lean, blue)
Mg	285.213	6 to 15	0.7	Air-Acetylene Oxidizing (lean, blue)
Mn	279.482	20 to 30	0.2	Air-Acetylene Oxidizing (lean, blue)
Na	588.995	8 to 10	0.7	Air-Acetylene Oxidizing (lean, blue)

PRECISION OF ANALYSIS

The precision for major-element analyses, which is defined as the reproducibility of replicate determinations of a particular analyte, is described in table 17. The values of relative standard deviation in this table are estimates based on replicate determinations of major elements in both standards and samples.

Table 17. Estimated precision of analysis

Concentration (percent, w/w)	Relative Standard Deviation (percent)
>10	1 to 2
1 to 10	2 to 10
0.1 to 1	10 to 50
<0.1	50 to 100

PREPARATION OF SAMPLE SOLUTION

Reagents and Supplies

1. Flux mixture: 1 part reagent grade lithium metaborate ($LiBO_2$) and 2 parts anhydrous lithium tetraborate ($Li_2B_4O_7$) are thoroughly mixed and stored in a closed container. Several hundred grams of the flux mixture should be prepared at one time.
2. Standard control samples: Several U.S. Geological Survey silicate standards, such as W-2, BHVO-1, AGV-1, G-2, and RGM-1 and National Bureau of Standards (NBS) 1633a coal fly ash are analyzed along with the samples. Other established standards may be substituted.
3. Graphite crucibles: Cylindrical, 25-mm outside diameter (20-mm inside diameter), high-purity graphite.
4. Dilute nitric acid, 8 M: Prepare several liters.
5. Polyethylene bottles: 250 mL, with caps.

Procedure

1. Weigh 0.2000 g of coal ash sample and mix thoroughly with 1.2 g of flux mixture on glassine paper. Transfer the sample-flux mixture into a graphite crucible.
2. Weigh the standard control samples along with the other samples. Also, take through the procedure a crucible that contains only the flux mixture as a blank.
3. Fuse the sample-flux mixtures in a muffle furnace at 1,000 °C for 45 min.

- Remove the crucibles from the furnace and allow them to cool to room temperature. In most cases, the beads produced are easily dislodged from the crucibles by gentle tapping. If the iron content of a particular sample is exceptionally high, a spatula may be needed to remove the bead.
- Place each bead into a 250-mL polyethylene bottle, and add a TeflonTM-covered, 39-mm magnetic stirring bar.
- Add 50 mL of boiling distilled water to each bottle from a polyethylene graduated cylinder, and transfer the bottle to a magnetic stirrer. Then, add 5 mL of 8 M nitric acid to each bottle.
- Stir each solution rapidly for approximately 60 min. Visually examine the bottle to be sure that dissolution of the bead is complete before going to the next step of the procedure.
- Remove the bottles from the stirrer, and add approximately 100 mL of distilled water to each. Catch the magnetic stirring bar in a funnel while pouring each solution into a separate 250-mL volumetric flask. Rinse the bottle, add water to the volumetric flask to mark, and mix. Pour the solution back into the polyethylene bottle for storage.

DETERMINATION OF SILICON (AS SiO₂)

Reagents and Equipment

- Ammonium molybdate solution: Dissolve 6.0 g of ammonium molybdate [(NH₄)₆Mo₇O₂₄·4H₂O] in 1 L of distilled water.
- Tartaric acid solution: Dissolve 16 g of tartaric acid [H₂C₂H₄O₆] in 1 L of distilled water.
- Reducing solution: Dissolve 0.28 g of sodium sulfite, 3.6 g of sodium bisulfite, and 0.06 g of 1-amino-2-naphthol-4-sulfonic acid in 1 L of distilled water. Prepare this solution within 48 h of use.
- Dilute sodium fluoride solution: Dilute 20 mL of a 3-percent sodium fluoride solution and 5 mL of 9 M sulfuric acid to 1 L with distilled water.
- Ultraviolet-visible spectrophotometer, with 1-cm cell.

Procedure

- Transfer 0.500-mL aliquots of solutions of the blank, the standards, and the samples into a series of 100-mL polyethylene beakers. Use a high-precision, 0.500-mL piston-type pipet to make these transfers. If the silica concentration is expected to be low, larger aliquots of sample solutions should be used. The following reagents then are added by a pipeting machine.

- Add 25 mL of the dilute sodium fluoride solution to each beaker and let the mixture sit for 5 min.
- Add 25 mL of the molybdate solution to each beaker, and let the mixture sit for 10 min.
- Add 25 mL of the tartaric acid solution to each beaker.
- Add 25 mL of the reducing solution to each beaker, and let the mixture sit for at least 45 min. The color of the complex is stable for at least 6 h.
- Set the concentration scale of the spectrophotometer to zero for a wavelength of 640 nm with the blank solution in the absorption cell. Then, set the concentration scale with a solution having a known concentration of silica (standard silicate reference material), and determine directly the percent silica in each of the samples.

DETERMINATION OF ALUMINUM (AS Al₂O₃)

Reagents, Supplies, and Equipment

- Complexing solution: To 880 mL of distilled water add 0.3 g of potassium ferricyanide [K₃Fe(CN)₆], 40 mL of 10 percent hydroxylamine hydrochloride [NH₂OH·HCl] solution, and 80 mL of calcium chloride solution. The calcium chloride solution is prepared by dissolving 14 g of calcium carbonate (CaCO₃) in 30 mL of concentrated hydrochloric acid and diluting to 1 L. The complexing solution should be prepared on the same day that it is to be used.
- Thioglycolic acid solution: Dilute 3 mL of the pure acid to 1 L with distilled water.
- Buffer solution: Dissolve 80 g of sodium acetate [NaC₂H₃O₂·3H₂O] in 975 mL of distilled water and add 24 mL of glacial acetic acid.
- Alizarin red-S stock solution, 0.10 percent: Dissolve 1.0 g of the pure dye in 1 L of distilled water and filter the resulting solution.
- Alizarin red-S, 0.02 percent: Dilute 200 mL of the stock solution to 1 L with distilled water.
- Ultraviolet-visible spectrophotometer, with 1-cm cell.

Procedure

- Transfer 0.750 mL of the blank, standard solution, and each of the sample solutions into a series of 150-mL beakers using a high-precision piston pipet. Add the following reagents to each beaker by pipeting machine.
- Add 25 mL of the complexing solution.
- Add 25 mL of the thioglycolic acid solution, and let the mixture sit for 5 min.

4. Add 25 mL of the buffer solution, and let the mixture sit for 10 min.
 5. Add 25 mL of the 0.02-percent alizarin red-S solution, and let the mixture sit for 45 to 75 min.
 6. Set the concentration scale of the spectrophotometer to zero for a wavelength of 475 nm with the blank solution in the absorption cell. Then, set the concentration scale with a solution having a known concentration of alumina (standard silicate reference material), and determine directly the percent alumina in each of the samples.
2. Buffer solution: Dissolve 80 g of ammonium acetate $[\text{NH}_4\text{C}_2\text{H}_3\text{O}_2]$ and 30 mL of glacial acetic acid in 2 L of distilled water.
 3. Sodium dithionate $[\text{Na}_2\text{S}_2\text{O}_4]$ (sometimes sold as sodium hydrosulfite): Dry reagent powder.

Procedure

1. Transfer 10-mL aliquots of the blank, each of the standards, and each of the sample solutions to a series of 150-mL beakers.
2. Add 125 mg of Tiron reagent powder to each beaker.
3. Add, by pipeting machine, 25 mL of the buffer solution to each beaker. Then, add 50 mL of distilled water to each beaker.
4. Add 10 to 20 mg of sodium dithionate to the blank and mix gently. Avoid vigorous mixing, which causes sulfur to precipitate. Then, set the concentration scale of the spectrophotometer to zero for a wavelength of 430 nm with the blank solution in the absorption cell.
5. Add sodium dithionate to one of the standard solutions and set the concentration scale of the spectrophotometer to the known concentration value (standard silicate reference material). Determine directly the percent TiO_2 in each of the samples. Sodium dithionate may be added to six solutions at a time.

DETERMINATION OF PHOSPHORUS (AsP_2O_5)

Reagents and Equipment

1. Ammonium molybdate stock solution: Dissolve 12.5 g of ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ in 340 mL of distilled water. Then, add 160 mL of 9 M sulfuric acid.
2. Dilute ammonium molybdate solution: Dilute 20 mL of stock ammonium molybdate solution to 1 L.
3. Stannous chloride solution: Dissolve 0.600 g of stannous chloride $[\text{SnCl}_2\cdot 2\text{H}_2\text{O}]$ in 25 mL of concentrated hydrochloric acid and dilute to 1 L with distilled water. This solution should be freshly prepared just prior to use.
4. Ultraviolet-visible spectrophotometer, with 1-cm cell.

Procedure

1. Transfer 10-mL aliquots of the blank, standards, and the sample solution to a series of 100-mL polyethylene beakers.
2. Add 25 mL of the dilute molybdate solution, and let the mixture sit for 10 min.
3. Add 25 mL of the stannous chloride solution. The developed color is stable for approximately 40 min.
4. Set the concentration scale of the spectrophotometer to zero for a wavelength of 640 nm with the blank solution in the absorption cell. Then, set the concentration scale with a solution having a known concentration of phosphorus pentoxide (standard silicate reference material), and determine directly the percent phosphorus pentoxide in each of the samples.

DETERMINATION OF TITANIUM (AS TiO_2)

Reagents and Equipment

1. Disodium-1,2-dihydroxybenzene-3,5-disulfonate (Tiron): Dry reagent powder.

DETERMINATION OF CALCIUM, IRON, MAGNESIUM, MANGANESE, POTASSIUM, AND SODIUM

Reagents and Equipment

1. Lanthanum solution: Transfer 140 g of lanthanum oxide (La_2O_3 , 99.997 percent pure) into a 2-L beaker. Slowly add 300 mL of concentrated hydrochloric acid, allowing time for the reaction to be completed after each addition of acid. Then, add 200 mL of distilled water. Each 4 mL of the final solution contains approximately 1 g of lanthanum.
2. Manganese stock solution: Transfer 0.3872 g of pure manganese metal into a glass beaker, add 20 mL of hot 8 M nitric acid, and gently boil the nitric acid for several minutes. After the resulting solution has cooled to room temperature, transfer the solution to a 500-mL volumetric flask and dilute to volume with distilled water. The concentration of MnO in this solution is 1,000 $\mu\text{g}/\text{mL}$.
3. Stock multiple-element standard solution: Transfer 0.8924 g of CaCO_3 , 0.9435 g of NaCl, 0.7915 g of KCl, and 2.4556 of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4\cdot 6\text{H}_2\text{O}$, [all

reagent-grade purity] and 0.3045 g of magnesium ribbon to a 500-mL volumetric flask. (Magnesium ribbon generally is 99 percent magnesium; therefore, the weight of the ribbon includes a 1-percent correction.) Add 50 mL of distilled water and 10 mL of concentrated hydrochloric acid. Boil the dilute acid to dissolve all the constituents. After the solution cools to room temperature, add 50.0 mL of the manganese stock solution (1,000 $\mu\text{g}/\text{mL}$ of MnO), dilute to volume with distilled water, and thoroughly mix the final solution. This solution contains the equivalent of 1.00 mg/mL each of Fe_2O_3 , CaO , MgO , Na_2O , and K_2O , and 0.1 mg/mL of MnO .

4. Working standard solutions: To six 250-mL volumetric flasks, add 0, 6, 12, 18, 24, and 30 mL of the standard stock solution. Then, add 1.2 g of flux mixture, 5 mL of 8 M nitric acid, and approximately 200 mL of distilled water. Agitate the nitric acid solution to dissolve the flux mixture. Then, add distilled water to make the final volume 250 mL and make the solution homogeneous by vigorous mixing. These six solutions represent a blank and 3-, 6-, 9-, 12-, and 15-percent (equivalent in the sample) standard solutions. For MnO , the same six solutions represent a blank and 0.3-, 0.6-, 0.9-, 1.2-, and 1.5-percent standard solutions.

Procedure for Calcium, Iron, Magnesium, and Manganese

1. Transfer 0.750 mL of blank, sample, and standard solutions into small vials or beakers.
2. Dilute 8 mL of lanthanum solution with 200 mL of distilled water. Add 6.5 mL of this solution to all standards, samples, and blanks.
3. Calibrate the atomic absorption spectrometer by setting the concentration scale to zero for the recommended wavelength (table 16) while the blank solution is nebulized into the flame. Then, set the concentration scale with the 6-percent working standard, and verify this setting with solutions of silicate standards. Directly measure the concentrations of calcium, iron, magnesium, and manganese in each of the samples. Most available atomic absorption spectrometers are suitable for these measurements; the optimum operating conditions for each element usually are discussed in the manual provided with the spectrometer. Importantly, the individual measurements of concentra-

tion (or, absorbance) for a sample should be "bracketed" between those of standards because the instrumental responses are usually not linear.

Procedure for Potassium and Sodium

1. Transfer 0.200 mL of blank, sample solutions, working standards, and silicate standards into a small vial or beaker.
2. Dilute 1.2 mL of lanthanum solution with 200 mL of distilled water. Add 5.0 mL of this solution to the blank and to each of the standards and samples.
3. Calibrate the atomic absorption spectrometer using the concentration mode with the 6-percent working standard, and check appropriate silicate standards for known values. Measure directly the concentration of samples.

CONCLUSIONS

Methods based on AAS and spectrophotometry provide accurate determinations of 10 inorganic elements in coal ash. Although not as rapid as X-ray fluorescence (XRF) spectrometry, these methods furnish an approach to determining major oxides in coal ash that is both inexpensive and accurate (table 18). The agreement between our measurements and the NBS-certified concentrations for 10 elements in NBS 1633a coal fly ash, demonstrated by data in table 18, is quite acceptable. Results from XRF spectrometry for SiO_2 , Al_2O_3 , and Fe_2O_3 in ash sample number 1 and for SiO_2 in sample number 7 (table 18) are outside the range covered by the standards used for calibration. Thus, extrapolations beyond this range could introduce error into these determinations.

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Table 18. Compositions of coal ashes determined by methods based on atomic absorption spectrometry (AAS) or spectrophotometry (S^a) and on X-ray fluorescence (XRF) spectrometry^b

Sample	Concentration (percent ^c)																			
	SiO ₂		Al ₂ O ₃		Fe ₂ O ₃ ^d		MgO		CaO		Na ₂ O		K ₂ O		TiO ₂		P ₂ O ₅		Mno	
	AAS,S	XRF	AAS,S	XRF	AAS,S	XRF	AAS,S	XRF	AAS,S	XRF	AAS,S	XRF	AAS,S	XRF	AAS,S	XRF	AAS,S	XRF	AAS,S	XRF
NBS 1633A	48.6	48.8	27.1	27.0	13.5	13.4	0.78	0.75	1.6	1.6	0.19	0.23	2.2	2.3	1.4	1.3	0.42	ND	0.05	0.02
Ash 1	6.2	9.9	4.0	4.1	67.4	60.3	0.28	ND	9.0	9.4	0.26	ND	0.30	0.26	0.18	0.13	0.02	0.05	0.08	0.09
Ash 2	37.5	38.1	24.2	25.2	12.3	11.9	0.52	ND	9.5	9.5	0.75	ND	1.2	1.2	1.0	0.97	0.21	0.18	0.06	0.06
Ash 3	53.4	54.5	22.3	23.8	13.4	15.3	1.0	ND	0.44	0.40	0.49	ND	2.9	2.8	1.0	1.2	0.16	0.09	0.03	0.03
Ash 4	26.2	26.3	12.0	10.9	47.6	45.5	0.59	ND	3.4	3.6	0.38	ND	1.2	1.2	0.59	0.64	0.15	0.12	0.06	0.07
Ash 5	56.9	57.6	24.5	25.3	7.3	7.5	1.2	ND	0.67	0.57	0.43	ND	3.3	3.3	1.2	1.3	0.39	0.30	0.02	0.02
Ash 6	51.5	47.6	30.3	30.4	6.2	6.1	0.96	ND	0.40	0.40	0.25	ND	4.1	4.0	1.2	1.1	0.12	0.15	0.01	0.05
Ash 7	15.1	18.9	22.0	21.2	26.6	28.2	1.2	ND	9.3	10.2	0.43	ND	0.10	0.13	0.88	0.87	2.4	2.8	0.02	0.03
Ash 8	48.6	47.5	26.9	29.8	15.8	16.9	0.40	ND	1.8	1.7	0.15	ND	0.57	0.62	0.94	0.94	0.17	0.12	0.01	0.03
Ash 9	45.4	48.5	15.4	18.7	4.7	4.4	2.2	ND	16.6	17.3	0.12	ND	1.1	1.1	1.4	1.3	0.15	0.25	0.10	0.11

^a Only Al₂O₃, P₂O₅, SiO₂, and TiO₂ were determined by spectrophotometric methods.^b Analyst: George Sellers.^c ND: not determined.^d Total Fe is reported as Fe₂O₃.

THE DETERMINATION OF SELECTED ELEMENTS IN COAL ASH BY ATOMIC ABSORPTION SPECTROMETRY

By Jean S. Kane

Abstract

Methods for the determination of eight elements in coal ash by atomic absorption spectrometry are described. Results from analyses of two National Bureau of Standards (NBS) standard reference materials, coal fly ashes NBS 1633 and 1633a, and four quality-control samples are reported. Possible sources of error in each method are discussed, and steps in the procedure critical to accuracy and precision are identified. Accuracy of the methods is established by comparisons of measured concentrations for elements in NBS standards 1633 and 1633a with certified values and with other values reported in the literature.

INTRODUCTION

The elements Cd, Cu, Li, Mg, Mn, Na, Pb, and Zn are determined in coal ash by methods based on atomic absorption spectrometry (AAS). These methods are described, and results are reported from the analyses of two National Bureau of Standards (NBS) standard reference materials, coal ashes NBS 1633 and 1633a, and four U.S. Geological Survey in-house, quality-control samples. Comparisons of elemental concentrations determined for NBS 1633 and NBS 1633a to certified concentrations and to other values reported in the literature establish the accuracy of the methods.

EXPERIMENTAL METHODS AND PROCEDURES

Dissolution of Samples

A coal-ash sample, 500 ± 1 mg, is weighed into a 50-mL TeflonTM beaker to which 10 mL of hydrochloric acid, 3 mL of perchloric acid, and 10 mL of hydrofluoric acid are added. Each of these acids is concentrated and of reagent-grade quality. The mixture of acids and sample is heated in an uncovered beaker for 1 h on a hot plate having a surface temperature of 200 °C. Then, the

beaker is removed from the hot plate and allowed to cool for 5 min, and 2 mL of nitric acid is added. The beaker is returned to the hot plate and heated until dense fumes of perchloric acid are formed and the acid volume has been reduced to ≤ 3 mL. The beaker is again removed from the hot plate and allowed to cool for 5 min, and 2 mL of nitric acid plus 5 mL of hydrochloric acid are added. The beaker is returned to the hot plate, and the mixture within is evaporated overnight to complete dryness. Finally, the beaker and its contents are cooled for 5 min, 2.5 mL hydrochloric acid is added, and the wall of the beaker is washed with approximately 5 mL of distilled water to dissolve the residue. Gentle warming of this solution for 5 to 10 min completes the dissolution and produces a clear solution that is transferred to a 50-mL linear polyethylene volumetric flask. This flask is filled to the volume mark with water after the solution reaches room temperature. For this approach, the concentration of an element in a sample of coal ash equals the concentration of the element in the sample solution times 100.

Determinations of Cu, Li, Pb, Mn, and Zn are made directly on each final solution. However, determinations of Na and Mg are made only after diluting each solution 1 to 100 with a matrix-modifier solution containing lanthanum at a concentration of 1,000 $\mu\text{g/mL}$. The cadmium determination requires extraction of the element with dithizone into xylene.

Cadmium Extraction

Typically, 12 samples, 2 blanks, and 4 calibration standards are extracted as a set. The concentrations of the calibration standards should range from 1 to 15 ng/mL in solutions freshly prepared by diluting a stock solution that contains 100 $\mu\text{g/mL}$ of cadmium.

Pipet 5 mL of the sample solution, blank, or calibration solution, described later, into a 60-mL separatory funnel. Add 0.50 mL of 20 percent (w/v) hydroxylamine hydrochloride, 5 mL of 10 percent (w/v) sodium potassium tartrate, and 5 mL of 10 percent (w/v) sodium hydroxide. Then, add 15 mL 0.10 percent (w/v) dithizone in xylene, and mix for 5 min by an air bubbler or by a mechanical shaker. Allow the layers to separate, and discard the aqueous layer.

The xylene (upper) layer varies in color from pale straw to pink to a deep, almost-black purple, depending on the amounts of Zn, Pb, and Mn that coextract with the Cd. The coextracted elements are not extracted from the xylene layer in subsequent steps. The aqueous layer should be distinctively orange.

After discarding the aqueous layer, wash the xylene phase twice with 5 mL of 0.10 percent (w/v) ammonium hydroxide, agitate the mixture for 1 min, and discard the aqueous wash solution each time.

Back extract the cadmium into 5 percent (v/v) hydrochloric acid by adding 10 mL of 5 percent hydrochloric acid to the xylene phase in each funnel, and then mix each solution for 10 min with either an air bubbler or a mechanical shaker. Rinse the stem of each separatory funnel with distilled water, and dry each stem with a Kimwipe™. Then, collect the aqueous phase, which is needed for the AAS measurement. The concentration of cadmium in the coal-ash sample is equal to the concentration of cadmium measured in the stripped solution times 200.

Calibration Solutions

Solutions for calibration of the atomic absorption spectrometer are prepared to contain Cu, Li, Mn, and Zn in 5 percent (v/v) hydrochloric acid at concentrations ranging from 0.10 to 20 µg/mL by serial dilutions of single-element stock solutions in which each element has a concentration of 1,000 µg/mL. Four to five solutions are prepared to calibrate over each decade of concentration.

Solutions of lead, which have the same range of concentrations as the previous multiple-element solutions, are matched to the matrix of a typical coal ash by adding an aliquot of a concentrated iron solution to give a final iron concentration of 5,000 µg/mL. The use of solutions that contain the principal elements aluminum, calcium, and iron provide no improvement in matrix matching over the iron solution alone.

Concentrations of magnesium and sodium in calibration solutions range from 0.05 to 2.0 µg/mL. These calibration solutions contain 0.10 percent lanthanum to minimize errors originating from matrix suppression of the magnesium absorption and from ionization effects on sodium.

Calibration solutions for cadmium are taken through the extraction procedure previously described. Without this extraction, background correction by use of a deuterium lamp is inadequate in the determination of cadmium.

INSTRUMENTATION

All measurements by flame AAS are made by either a Perkin-Elmer^R model 603 or model 5000 atomic absorption spectrometer that has background correction based on a deuterium arc lamp. Measurements of cadmium by electrothermal-atomization AAS are accomplished with a Perkin-Elmer^R model 603 atomic absorption spectrometer that has deuterium-lamp background correction, a graphite atomizer (model 500 or model 2100), a model AS40 autosampler, and a model 56 strip chart recorder. Solution volumes of 20 µL are injected into nonpyrolytic graphite tubes that are purged by argon. Each hollow cathode lamp used in these measurements is operated at the current recommended by the manufacturer.

Instrumental operating parameters for each of the elements determined are listed in table 19. Although the

Table 19. Operating parameters: flame and graphite-furnace atomization

Element	Wavelength (nm)	Bandpass (nm)	Background Correction	Cell ^a	Matrix
Cd	228.8	0.7	Yes	Graphite Furnace	0.5% ash solution; extract in 5% HCl
Cu	324.7	0.7	No	Flame	1% ash solution in 5% HCl
Li	670.8	1.4	No	Flame	1% ash solution in 5% HCl
Mg	285.2	0.7	No	Flame	0.01% ash solution in 5% HCl
Mn	279.5	0.2	No	Flame	1% ash solution in 5% HCl
Na	589.0	0.2	No	Flame	0.1% ash solution in 5% HCl
Pb	217.0	0.7	Yes	Flame	0.1% ash solution in 5% HCl
Zn	213.9	0.7	Yes	Flame	1% ash solution in 5% HCl

^a Flame: Fuel-lean air-acetylene.

Graphite furnace: 20-µL sample, argon sheath gas, conventional graphite tube. Furnace sequence: (1) Dry for 20 s at 110 °C. (2) Char for 25 s at 250 °C. (3) Atomize for 5 s at 2,100 °C with 1 s ramp to temperature. Interrupt gas flow (default to 50 mL/min with the model 2100 HGA.)

Table 20. Detection limits, sensitivities, and calibration ranges for flame and graphite-furnace atomic absorption spectrometry

Element	Wavelength (nm)	Concentration ^{a,b} in Solution for			
		Detection Limit	Sensitivity ^c	Upper Limit of Linear Calibration	Usable Nonlinear Range
Cd ^a	228.8	0.05	0.065	5.0	5 - 20
Cu ^b	324.7	0.02	0.07	5.0	5 - 15
Li ^b	670.8	0.02	0.035	2.0	2 - 10
Mg ^b	285.2	—	0.008	0.5	0.5 - 2
Mn ^b	279.5	0.04	0.07	3.0	3 - 10
Na ^b	589.0	—	0.02	1.0	1 - 5
Pb ^b	217.0	0.08	0.2	5.0	5 - 25
Zn ^b	213.9	0.01	0.02	2.0	2 - 10

^a Graphite-furnace AAS (ng/mL).

^b Flame AAS ($\mu\text{g/mL}$).

^c For 0.0044 absorbance.

operation of a fuel-lean (blue) flame and the use of an observation height of five units on the vernier of the burner head are common to all measurements reported here, the accuracy of these measurements is relatively insensitive to variations in flame stoichiometry and observation height. Thus, an inability to reset exactly these parameters on a day-to-day basis should be of no consequence.

Detection limits, sensitivities, and approximate upper limits of linearity for calibration curves are listed in table 20. Detection limits for the cited elements are a simple function of dilution and thus can be improved by as much as a factor of 5 by decreasing the extent to which the dissolved sample is diluted. For cadmium, a change in the extraction factor can improve the detection limit by up to a factor of 10. For most coal ashes, the sensitivities for individual elements need to be reduced much more frequently than the detection limits need to be improved. Such a reduction in sensitivity can be accomplished either through serial dilutions of the sample solution until the analyte concentration is within the linear calibration range or through a reduction of the effective length of the flame that is accomplished by rotation of the burner head. Only positions at 30°, 60°,

and 90° can be reproducibly set on the Perkin-Elmer^R model 603 spectrometer, but the model 5000 permits the continuous variation of the burner position through 90°. For copper, manganese, and lead, the option of using less-sensitive spectral lines for measurements is available. Alternate operating parameters that can produce reduced sensitivity are listed along with detection limits, sensitivities, and calibration ranges in table 21. Also, alternative approaches are available through standard methods described in American Society for Testing and Materials (1984a, b) publications.

DISCUSSION OF RESULTS

The accuracy of analysis for the AAS methods described here is verified by comparisons of measurements on NBS standard reference materials 1633 (table 22) and 1633a (table 23) with certified concentrations and with concentrations determined by instrumental neutron activation analysis (Ondov and others, 1975; Rowe and Steinnes, 1977). U.S. Geological Survey "in-house" standards, designated ASH1, S1, S2, and S3 in table 23, are used as references to provide long-term accuracy and to conserve supplies of NBS standard

Table 21. Alternate operating parameters for flame atomic absorption spectrometry and calibration ranges

Element	Wavelength (nm)	Bandpass (nm)	Background Correction	Burner Head Position, Oxidant Fuel	Calibration Range ($\mu\text{g/mL}$ in solution)	
					Linear	Nonlinear
Cu	324.7	0.7	No	Rotated 60°, Air-acetylene	5 - 300	300 - 700
Mg	285.2	0.7	No	Rotated 60°, Air-acetylene	2 - 10	
Mn	280.1	0.2	No	Rotated 60°, Air-acetylene	5 - 50	50 - 200
Zn	213.9	0.7	Yes	Rotated 60°, Air-acetylene	1 - 20	
				Rotated 90°, Nitrous oxide-acetylene	5 - 50	

Table 22. Concentrations of eight elements in the NBS 1633 coal fly ash determined by atomic absorption spectrometric methods

Element	Concentration ($\mu\text{g/g}$)				
	This Work (<i>n</i>) ^a	Certificate of analysis	EPA-NBS Round Robin ^b (Range)	Literature	Reference
Cd	1.56 \pm 0.26(17)	1.45 \pm 0.06	0.88 - 6.0	1.5 \pm 0.2	Gladney (1980)
Cu	130 \pm 6(16)	128 \pm 5	-	127 \pm 8 115 \pm 8	Gladney (1980) Rowe and Steinnes (1977)
Li	170 \pm 13(17)	-	-	110 \pm ?	Gladney (1980)
Mg	1.17 \pm 0.049(14)	-	-	1.6 \pm 0.3 1.78 \pm 0.20	Gladney (1980) Rowe and Steinnes (1977)
Mn	496 \pm 34(17)	493 \pm 7	181 - 636	492 \pm 24 509 \pm 20 488 \pm 14	Gladney (1980) Ondov and others (1975) Rowe and Steinnes (1977)
Na	0.295 \pm 0.023(11)	-	-	0.320 \pm 0.034 0.283 \pm 0.014	Gladney (1980) Rowe and Steinnes (1977)
Pb	67 \pm 4(10)	70 \pm 4	18.7 - 110	72 \pm 5	Gladney (1980)
Zn	210 \pm 10(18)	210 \pm 20	54.2 - 244	213 \pm 13 216 \pm 25 201 \pm 6	Gladney (1980) Ondov and others (1975) Rowe and Steinnes (1977)

^a The number of replicate determinations = *n*.

^b Laboratory averages from round-robin analyses by AAS (EPA, 1977).

EPA: U.S. Environmental Protection Agency.

NBS: National Bureau of Standards.

reference materials. The precision of each method is expressed as the standard deviation for 10 or more replicate determinations. Factors that are important to the maintenance of accuracy and precision are treated in the following discussions on individual elements.

Manganese

In general, determinations of manganese are biased low for measurements on Mn 279.42 nm if spectral background corrections are based on the use of a deuterium arc lamp. Iron lines at 279.42, 279.47, and

279.50 nm, which occur within the spectrometer band-pass for the Mn 279.42-nm line, absorb the continuum radiation from the deuterium lamp and thus produce an overcorrection for background (Zander, 1976). Because of the close proximity of the iron lines to Mn 279.42 nm, reduction of the spectrometer slit width produces no improvement. Also, at minimal slit widths, analyte absorption of the continuum radiation produces overcorrection for background. Furthermore, matrix matching cannot be used to eliminate this error because of the variability of concentrations of iron in coal ashes. For best accuracy, a background correction should not be made for manganese.

Table 23. Concentrations of analytes determined for NBS standard reference material 1633a and for quality-control samples ($\mu\text{g/g}$)^a

Analyte	NBS 1633a					
	This Work	Certificate	ASH1	S1	S2	S3
Cd	0.98 \pm 0.08	1.0 \pm 0.15	0.71 \pm 0.13	1.4 \pm 0.2	0.52 \pm 0.09	0.49 \pm 0.1
Cu	114 \pm 7	118 \pm 3	141 \pm 7	65 \pm 4	81 \pm 3	127 \pm 4
Li	184 \pm 14	-	153 \pm 10	96 \pm 13	273 \pm 9	200 \pm 23
Mg(%)	0.436 \pm 0.005	0.455 \pm 0.01	0.51 \pm 0.03	0.65 \pm 0.04	0.46 \pm 0.02	0.58 \pm 0.04
Mn	160 \pm 12	190 ^b 190 ^c	160 \pm 11	251 \pm 10	124 \pm 9	222 \pm 22
Na(%)	0.158 \pm 0.014	0.170 \pm 0.01	0.18 \pm 0.03	0.44 \pm 0.04	0.13 \pm 0.02	0.22 \pm 0.02
Pb	62 \pm 4	72.4 \pm 0.4	185 \pm 17	60 \pm 8	44 \pm 13	53 \pm 7
Zn	211 \pm 11	220 \pm 10	147 \pm 8	66 \pm 13	89 \pm 4	106 \pm 6

^a Concentration units for Mg and Na are percent, or cg/g.

^b Concentration listed "for information only" by NBS, that is, the value is not certified.

^c From Gladney (1980).

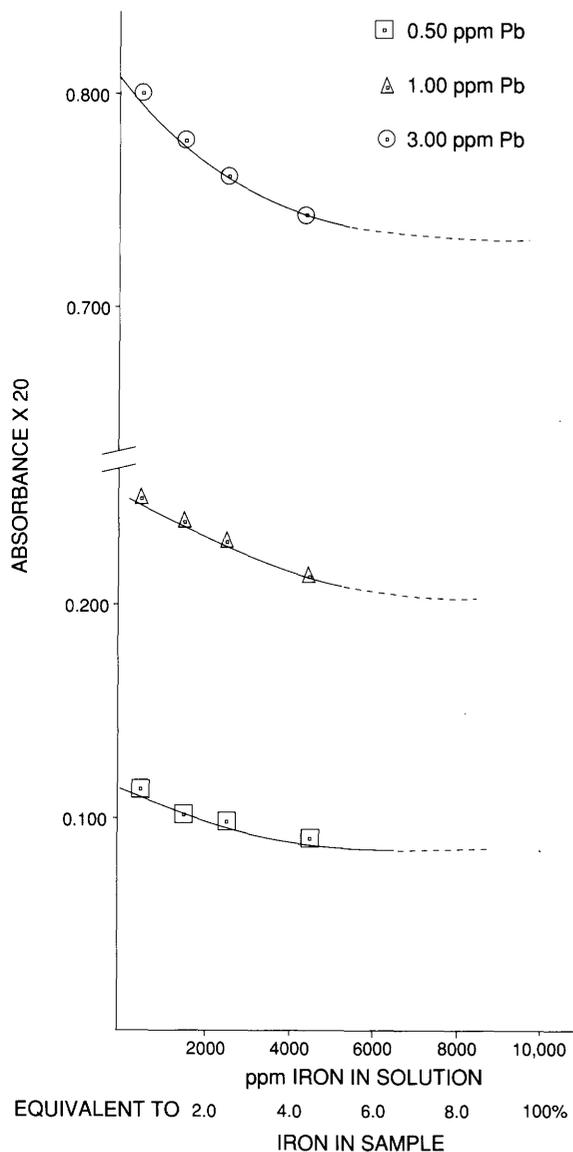


Figure 12. Lead absorbance as a function of iron concentration in the sample matrix.

Lead

As the concentration of iron increases from 0 to 1,000 $\mu\text{g}/\text{mL}$, the lead atomic absorption signal is sharply suppressed. Further increments in iron concentration up to 4,000 to 5,000 $\mu\text{g}/\text{mL}$ produce little further suppression of lead absorption, as illustrated in figure 12. Typically, matrix matching can be used to correct for this suppression over most of the concentration range encountered in the analysis of coal ash. Lead calibration solutions, each containing iron at a concentration of 1,000 $\mu\text{g}/\text{mL}$, are well suited for this purpose. However, this approach overcorrects when iron occurs at concentrations below 5 percent in the ash and is inadequate for iron concentrations above 40 to 50 percent in the ash. In the latter case, removal of the iron

from solution by extraction with concentrated hydrochloric acid into methylisobutylketone is necessary before measuring lead absorbance. The method of standard additions is unsatisfactory in correcting for the suppression of lead absorption signal because of the greatly reduced sensitivity for lead absorption measurements. Furthermore, the extraction of lead by diethylammonium diethyldithiocarbamate prior to measurement is unsuccessful because of the coextraction of iron by this reagent.

Although most AAS methods use the Pb 283.3-nm line, the more sensitive 217.0-nm line is recommended for detectability that is better by a factor of 2.5. Background correction at this wavelength is essential. The Sb 217.59-nm line potentially can cause overcorrection for background (Vajda, 1981), but Pb-to-Sb concentration ratios in coal ash are so high that this error is rarely significant.

Zinc

The concentrations of zinc in NBS 1633 determined by AAS are in excellent agreement with the NBS certificate value. Background correction is required at the Zn 213.86-nm line. Positive bias can occur for zinc determinations in coal ashes having high iron concentrations because of the direct spectral overlap of iron 213.859 nm on zinc 213.856 nm. For a concentration of 10 percent iron in the ash, the error is equivalent to 15 ppm of zinc. For typical coal ashes, which have zinc concentrations between 200 and 1300 ppm, the relative error is less than 5 percent. Precision of measurements, which generally is ± 5 percent, is illustrated by the plot in figure 13 of zinc concentrations measured for duplicate dissolutions of various samples. Data for the other seven elements are quite similar and thus are not shown here.

Copper

Measurements of copper in NBS 1633 by AAS show the best accuracy and precision of the eight elements determined. Background corrections are not needed.

Lithium

Prior to 1980, values for lithium concentrations in coal-ash standards were unavailable in the literature. Thus, accuracy of analysis was evaluated from concurrent measurements of lithium concentrations in several U.S. Geological Survey standard rocks. The dissimilarities of both matrices and concentration ranges for lithium cause problems in comparisons. For example, the lithium concentrations determined for standard rocks generally have relative standard deviations of 5 percent, which is only half that observed for coal ashes.

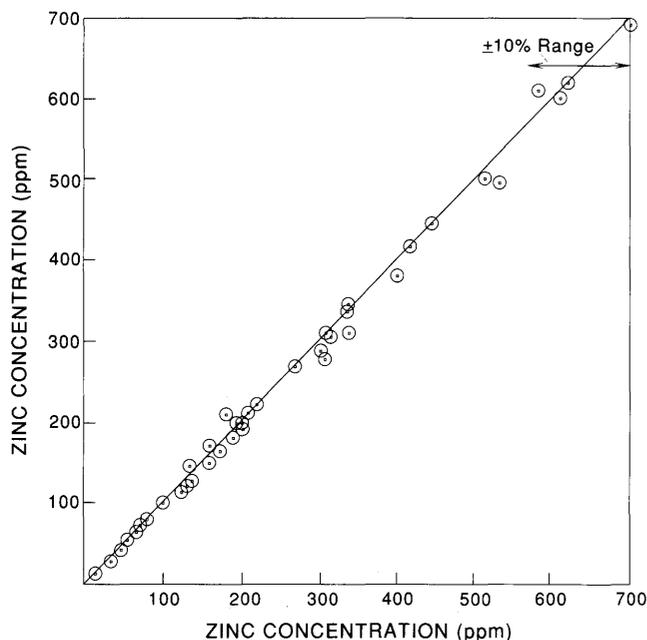


Figure 13. Zinc correlation plot.

Solutions of coal ash naturally contain concentrations of total alkalis (Na + K) that approach 2,000 $\mu\text{g/mL}$. Thus, additional ionization buffering is unnecessary for the determination of lithium. Nonetheless, the precision of this determination is poorer for the coal ash than that for silicate rocks and is poorer than that for determinations of copper or manganese in coal ash.

Sodium

The use of glass volumetric flasks in determinations of sodium in solutions of NBS 1633 produces values that are consistently high by 10 to 100 percent. Replacement of all glassware with linear polyethylene containers eliminates this bias, enabling sodium values to agree within 7 percent of literature values. Also, the precision for the method is 8-percent relative standard deviation. The concentration of sodium in solutions from coal ash frequently exceeds the linear range of absorbance for the Na 589.0-nm line. However, detection of sodium often requires the use of this line in preference to the somewhat less sensitive doublet at 589.0–589.6 nm. Use of several calibration solutions that span a small concentration range enables accurate determinations of sodium in the nonlinear portion of the calibration curve.

Magnesium

The accurate determination of magnesium is quite dependent on the dissolution procedure. The use of hydrofluoric acid is necessary for the decomposition of

siliceous materials, but the formation of insoluble MgF_2 can lead to losses of magnesium if the hydrofluoric acid is not completely evaporated. The initial fuming of the sample in a mixture of nitric and perchloric acids must be followed by evaporation in aqua regia and by thorough drying of the resulting residue. Without this treatment, losses of magnesium can approach 50 percent.

Curvature of calibration curves for magnesium occurs above concentrations of 0.5 $\mu\text{g/mL}$. With sufficient calibration points, the useful range can be extended to 3 $\mu\text{g/mL}$. Concentrations of magnesium in solutions of coal ash are rarely high enough to allow the use of the 202.6-nm line, which is less sensitive (by a factor of 24) than the 285.6-nm line.

Cadmium

Several factors affect the overall accuracy and precision of the cadmium determination. Control of the chemical blank is the most important factor. Commonly, acids used for dissolving samples produce blanks having cadmium concentrations that greatly exceed those of cadmium in solutions of coal ash. Containers of such acids should be avoided in sample preparation.

Adsorption of cadmium on the walls of a separatory funnel or a volumetric flask from samples having very high concentrations of cadmium can contaminate the next sample placed in the same vessel. Thorough cleaning of glassware with 50 percent nitric acid, followed by repeated rinsing with distilled water, minimizes this type of error. Autosampler cups made of linear polyethylene must be used to prevent initial contamination from the cups because the slightly coextracted organic phase in the solution dissolves the polystyrene cups. The cups should be cleaned between uses, along with the glassware, to avoid cross contamination from one sample to the next. The pipet tip of the autosampler has been observed to cause cross contamination that results from inadequate rinsing if the sample-to-sample variation of cadmium concentration is 1,000-fold or more. This cross contamination decreases rapidly with repeated pipetings and is readily identified by making three or more successive absorption measurements at each autosampler position. Concentrations of cadmium in coal ashes are directly correlated with zinc concentrations. The latter can reach quite high levels in coals that are located near ore bodies (Ruch and others, 1974).

When cadmium concentrations in the extract are expected to be well above the normal calibration range for graphite-furnace AAS, that is, above 100 ng/mL , flame AAS can be used to minimize the possibility of carry-over contamination. As illustrated in table 24, high concentrations of cadmium are sometimes encountered in analyses of coal ash.

Table 24. Some typical concentration ranges^a of analytes in coal ashes originating from different regions of the United States

Analyte	Concentration Range ($\mu\text{g}/\text{mL}$)					
	Cd	Cu	Li	Mn	Pb	Zn
Appalachian Range ^a	0.02 - 0.8	27 - 980	11 - 760	11 - 5200	3 - 590	17 - 3800
Interior Eastern ^a	0.1 - 66	20 - 790	12 - 410	41 - 2800	10 - 2900	39 - 5400
Interior Western ^a	0.1 - 700	22 - 670	10 - 270	32 - 4700	25 - 6600	36 - 100000
Western ^a	0.1 - 25	0.8 - 1300	0.3 - 490	2 - 11000	5 - 2900	5 - 3700
Northern Plains ^a	0.01 - 32	16 - 630	1 - 220	7 - 11000	5 - 680	10 - 2500
Analyzed Samples ^b	<0.1 - 100	5 - 3200	11 - 440	29 - 11,000	<10 - 60	10 - 48,000
Notes	c	d	e	f		g

^a Source: Robert Finkelman (personal commun., 1987).

^b Concentration ranges observed for more than 280 coal ashes analyzed by AAS in U.S. Geological Survey laboratories.

^c Correlation with Zn is 0.93.

^d High values in special mineral samples.

^e Variable concentrations; probably dependent on water contact.

^f Wide range in lithotypes.

^g Concentration is very high near ore beds.

The extraction yield for cadmium varies as a function of both pH and extraction time. Extraction for 5 min at pH 8.5, followed by back-extraction for 10 min, assures constant yields of 95 ± 5 percent for solutions prepared for calibration and for solutions of coal ashes. Variations in either pH or extraction time lead to irreproducible yields that deteriorate the precision of the method. Small changes in these two variables and the difficulty of exactly reproducing the chemical blank account for the 20-percent relative standard deviation of the method.

Losses of cadmium occur prior to atomization in the graphite furnace if the charring temperature exceeds 250 °C. Time constants of the Perkin-Elmer^R model 603 atomic absorption spectrometer and recorder are too long for accurate measurements of fast transient signals produced by rapid atomization. A sequence of temperatures for atomization that provides a heating rate matched to instrumental time constants is detailed in table 19. An increase in heating rate, either by adding programmable ramp features or by increasing the final atomization temperature above 2100 °C leads to loss of the absorption signal.

Without the extraction of cadmium before AAS measurements, serious errors in corrections for background can occur from Ni 228.73-nm, Ni 228.84-nm, and Co 228.78-nm lines that are within the bandpass of the spectrometer (Zander, 1976). Moreover, iron produces a severe suppression of the cadmium atomic absorption signal, particularly for furnace atomization.

Results of analyses for NBS 1633a coal ash and for four U.S. Geological Survey quality-control samples are summarized in table 23. Accuracy for analysis of NBS 1633a, as evident from comparisons of results from AAS methods with the certified values, is excellent. Except for manganese and lead, the determined concentrations agree with NBS-certified values within one standard deviation. The reason for the larger disparity

of manganese and lead values is not apparent. Measured concentrations of manganese and lead in NBS 1633 (table 22) agree with NBS-certified values well within one standard deviation.

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THE DETERMINATION OF MERCURY IN WHOLE COAL BY COLD-VAPOR ATOMIC ABSORPTION SPECTROMETRY

By Philip J. Aruscavage and Roosevelt Moore

Abstract

Concentrations of mercury in coal are determined by cold-vapor atomic absorption spectrometry. After decomposition of a 100-mg sample of pulverized coal in a mixture of perchloric and nitric acids, Hg II is reduced to the metal by stannous chloride. The mercury metal is removed from the solution in a stream of nitrogen and subsequently amalgamated with gold chips contained within a quartz tube that is located on the axis of a cylindrically wound induction coil. Rapid induction heating of the gold amalgam then releases the mercury, which is subsequently swept into a quartz cell where the peak absorption of Hg I 253.652 nm is measured. The determination limit of the method is 10 ng/g. The typical precision for measurements of concentrations of mercury is 5- to 10-percent relative standard deviation. Good accuracy is observed for concentrations of mercury determined for the National Bureau of Standards reference materials 1632, 1633, and 1633a.

INTRODUCTION

Although numerous methods exist for the determination of mercury in whole coal and related materials, the methods incorporating cold-vapor atomic absorption spectrometry (AAS) are used in many laboratories (Babu, 1975; Doolan, 1982; Swaine, 1985). The differences between the various cold-vapor AAS methods principally involve the processes used for decomposing, evolving, and collecting the mercury vapor prior to AAS measurements.

In the method recommended by the American Society for Testing and Materials (ASTM, 1984), a coal sample is decomposed in an oxygen bomb that contains nitric acid to collect the mercury. The resulting solution of mercury in nitric acid is treated with solutions of permanganate and hydroxylamine hydrochloride. Finally, stannous chloride solution is added to evolve the mercury vapor that is directly measured by the cold-vapor AAS technique.

In the method of Doolan (1982), a coal sample is heated in a high-temperature (1,250° to 1,450 °C) oxygen-rich atmosphere within a combustion-tube furnace. The liberated mercury is collected in a permanganate-sulfuric acid solution and finally is evolved, through reduction by a stannous chloride solution, into the cell of a cold-vapor AAS. Ebdon and others (1982) used nonoxidative pyrolysis of coal at 800 °C to remove mercury prior to its determination by atomic fluorescence spectrometry.

In a procedure used earlier in U.S. Geological Survey laboratories (Flanagan and others, 1982), mercury was removed from pulverized coal samples by nonoxidative pyrolysis in nitrogen at 900 °C, and the evolved combustion products were passed through a gas-washing bottle that contained a stannous chloride solution. Then, the mercury was amalgamated with gold and finally released by induction heating and determined by cold-vapor AAS. Although good results were obtained for most anthracite and bituminous coal samples, erratic results were commonly observed for mercury in subbituminous coal. Also, subbituminous coals produced contamination that was difficult to remove from equipment. Because of these problems, a wet oxidation procedure was found to be more appropriate. A simple decomposition with a mixture of perchloric and nitric acids in a Teflon™ digestion vessel gave adequate decomposition of coal samples. This conclusion is supported by comparisons of measured mercury concentrations with certified values for National Bureau of Standards (NBS) reference coal standards. Mercury losses from "spiked" coal samples also were negligible. The addition of hydrofluoric acid to the decomposition solution did not cause an increase in the concentration of mercury found in the whole-coal samples. This observation indicates that mercury did not remain in the undecomposed silicate materials. The addition of dichromate or permanganate to the digestion solution is

unnecessary if nitric acid is added to the hot digestion solution prior to the addition of distilled water and if the solutions do not stand for more than 2 to 3 h.

In the procedure described here, a 100-mg pulverized coal sample is decomposed by a solution of perchloric and nitric acids in a Teflon™ (PFA) container. The dissolved mercury is then reduced with a stannous chloride solution and removed from the solution in a stream of nitrogen. The free mercury is collected on 5 g of gold chips, which then is inductively heated to drive the mercury into a 30-cm-long quartz cell where the absorption at 253.7 nm is measured.

EXPERIMENTAL EQUIPMENT AND METHODS

Equipment

The arrangement for the cold-vapor AAS instrument is shown in figure 14. Individual apparatus and equipment items are listed here.

1. Teflon™ (PFA) digestion vials, 33 mL.
2. Aeration flask, Pyrex™ gas washing bottle with coarse-fritted cylinder, 250-mL capacity.
3. Quartz tube, 30-cm long by 7-mm diameter, drawn out in the center to approximately 3-mm diameter.
4. One-way check valves.
5. Three-way stopcocks, borosilicate glass.
6. Two-stage pressure regulator (Matheson^R model 8-580) and needle-valve flow regulator for nitrogen gas.
7. Flowmeter, precision ball-float rotameter with a range of 0.1 to 1 L/min.
8. Induction furnace, LECO^R model 521, with five-turn copper coil of 3-cm diameter.
9. Mercury monitor system, LDC^R model 1235, with dual gas quartz cell 30-cm long by 7.5-mm diameter and cell volume of 13.7 cm³.
10. Strip chart recorder, Perkin-Elmer^R model 56, 1- to 10-mV range.
11. Hot plate.

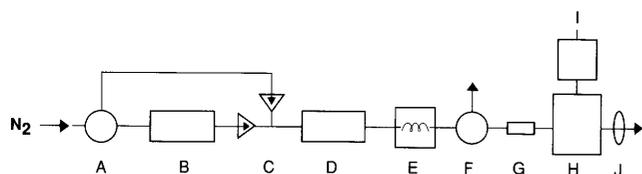


Figure 14. Diagram of arrangement of instrumentation for the measurement of mercury in coal.

Reagents

All chemical reagents are of reagent-grade or higher purity. Doubly-distilled water is used in the preparation of all solutions.

1. Perchloric acid, 72 percent.
2. Hydrochloric acid, 12 N.
3. Nitric acid, 14 N.
4. Gold chips, approximately 5 g, 99.99-percent pure, 0.5-mm diameter.
5. Mercury metal, high purity.
6. SnCl₂.
7. 5 percent (w/v) SnCl₂ in 12 N hydrochloric acid.
8. Nitrogen gas, 99-percent pure.
9. Anhydrous magnesium perchlorate (AnhydronTM)

Calibration Standards

1. Prepare an aqueous stock solution containing 1.00 mg/mL mercury and 10 percent nitric acid by dissolving high-purity metallic mercury in nitric acid.
2. Prepare a solution of 10 μg/mL mercury in 5 percent nitric acid by diluting an aliquot of the 1 mg/mL stock solution. This solution should be freshly prepared each month.
3. Freshly prepare a solution of 0.10 μg/mL mercury in 5 percent nitric acid each day from the 10 μg/mL mercury solution. Six different aliquots of the 0.10 μg/mL solution are pipeted into the aeration flask to effect calibration of the instrument.

Coal Standards

Coal standards NBS 1630, 1632, 1633, and 1633a are used to verify the accuracy of this analytical method.

PROCEDURES

Dissolution of Samples

Weigh 100 mg of air-dried, pulverized (100 mesh) coal into a 25-mL screw-cap Teflon™ digestion container. Add 5 mL of concentrated perchloric acid and 5 mL of concentrated nitric acid, and then heat the sample-acid mixture on a hot plate at 150 °C until 2 to 3 mL of solution remains (3 to 4 h). Add 1 mL of concentrated nitric acid to the hot solution, and finally add distilled water until the volume of the solution is approximately 25 mL. Immediately close the container with the screw cap, and mix the contents.

Determination of Mercury

Transfer the solution from the Teflon™ container to the aeration flask (fig. 14) and adjust the volume to

approximately 100 mL with distilled water. Add 6 mL of 5 percent (w/v) SnCl₂ solution and close the flask. Begin the flow of nitrogen (delivery pressure equals 34.5 kPa (5 psi); flow rate equals 0.5 L/min) into the aeration flask. The evolved mercury is collected on the gold chips within approximately 3 min. After the collection process is completed, turn the first three-way stopcock (fig. 14) to the position that allows the nitrogen flow to bypass the aeration flask and to pass directly over the gold chips, thus removing water vapor from the system (30 s). After the system has dried, turn the second three-way stopcock to direct the gas flow through the absorption cell. Power from the RF generator is then applied to the induction coil for 15.0 s to heat the gold chips, thus releasing the amalgamated mercury into the nitrogen stream. The mercury subsequently is transported into the cell of the mercury monitor system, where the peak absorption of Hg I 253.652 nm is measured and recorded on a strip chart recorder. The peak absorption signal for each sample is used to extrapolate the mercury concentration from a calibration curve established by separately pipeting 0, 5, 10, 15, 20, and 25 ng of mercury from a 0.10 µg/mL mercury solution into the aeration flask, adding the reagents, and recording the corresponding peak absorption signal.

DISCUSSION

NBS coal standards 1630, 1632a, and 1633 and a U.S. Geological Survey "in-house" coal standard are used as control standards in each measurement sequence. The detection limit of the method, based on twice the standard deviation for 10 determinations of mercury in a blank, is 1 ng of Hg, which is equivalent to 10 ng/g in a 100-mg sample. The sensitivity of the method is 1.1 mV/ng of mercury. The long-term precision of the method, estimated from repeated measurements of mercury concentrations in these standards over several years, is 5- to 10-percent relative standard deviation for the concentration range from 50 to 500 ng/g. Both the accuracy and precision of the method (table 25) are comparable to those for the methods using oxygen-bomb combustion (ASTM, 1984) or high-temperature oxidation in a tube furnace (Doolan, 1982). The proce-

Table 25. Concentrations of mercury determined by cold-vapor atomic absorption spectrometry for selected coal and fly-ash standards

Sample	Material	Hg Concentration (µg/g)	
		Measured ^a	Accepted ^b
NBS 1632	Bituminous Coal	0.11 ± 0.01 (15)	0.12 ± 0.02
USGS 24D	Subbituminous Coal	0.40 ± 0.02 (20)	—
NBS 1633	Coal Fly Ash	0.12 ± 0.01 (15)	0.14 ± 0.01
NBS 1633a	Coal Fly Ash	0.15 ± 0.01 (15)	0.16 ± 0.01

^a Uncertainty in concentration is the standard deviation for the number of measurements indicated in parentheses.

^b Concentrations of mercury in NBS 1632, 1633, and 1633a standard reference materials are certified values.

ure is simple and rapid and is applicable to a wide variety of coal samples.

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THE DETERMINATION OF FLUORIDE IN COAL BY ION-SELECTIVE ELECTRODE

By Herbert Kirschenbaum

Abstract

A method is described for determining the concentration of fluoride in coal. Coal ash is fused with sodium hydroxide, and the resulting melt is leached with distilled water. This solution is diluted with an ammonium citrate buffer to produce a final solution having a pH in the range of 5.5 to 7.0. The fluoride concentration then is determined by measurement of the potential produced by a fluoride ion-selective electrode. The lower limit for determination of fluorine in a 250-mg ash sample is 20 $\mu\text{g/g}$. The precision of the method is approximately 6-percent relative standard deviation.

INTRODUCTION

The method described herein for determining fluoride in coal (Ingram, 1970; Swanson and Huffman, 1976) requires that coal ash be fused with sodium hydroxide and that the resulting melt be leached with distilled water, filtered, and then diluted to a fixed volume with an ammonium citrate buffer. The pH of the resulting citrate-buffered solution must range from 5.5 to 7.0 for accurate measurement of the fluoride concentration with an ion-selective electrode (ISE). At a pH below 5.5, the measurement gives concentrations that are biased low because of the complexation of F^- by H^+ . A high bias in the measured concentration occurs at pH values above 7.0 because of the presence of high concentrations of OH^- or HCO_3^- .

EXPERIMENTAL METHODS AND PROCEDURES

Equipment

Measurements are made with an Orion Research IonalyzerTM (model 801), equipped with a fluoride-ion electrode (model 94-09) and a single-junction calomel reference electrode (model 90-01).

Reagents

The quality of each chemical reagent is reagent grade or better.

1. $\text{MgO-Mg}(\text{NO}_3)_2$ solution: Dissolve 38 g of MgO and 53 g of $\text{Mg}(\text{NO}_3)_2$ in 500 mL of distilled water.
2. 1 M ammonium citrate solution: Dissolve contents of a 454-g bottle of ammonium citrate in 2 L of distilled water. The pH of this solution is 4.7 to 4.9.
3. Sodium hydroxide pellets: Baker AnalyzedTM sodium hydroxide pellets, low in carbonates. These pellets are used in fusions described later.
4. Sodium fluoride standard: Purify the sodium fluoride by first adding from 10 to 15 mL of concentrated hydrofluoric acid to 3 g of sodium fluoride in a platinum dish. Evaporate the resulting solution to dryness on a steam bath. Transfer the purified NaF to a polyethylene vial.
5. Standard A: Prepare a stock solution of 1,000 $\mu\text{g/mL}$ of fluoride in distilled water by first dissolving 1.105 g of the purified NaF and then by diluting the resulting solution to 500 mL.
6. Standard B: Prepare a 100 $\mu\text{g/mL}$ fluoride standard by diluting 10.0 mL of standard A to 100 mL.
7. Standard C: Prepare a 10 $\mu\text{g/mL}$ fluoride standard by diluting 1.0 mL of standard A to 100 mL.
8. Calibration standards: Add 2.7 to 3.0 g (16 pellets) of NaOH to each of nine 100-mL volumetric flasks. Then, add approximately 20 mL of distilled water to each flask to dissolve the NaOH pellets.

The dilutions used to prepare the individual calibration solutions are detailed in table 26. The calibration standard having a F^- concentration of 8 $\mu\text{g/mL}$ is used to equilibrate between all measurements with the ISE on standards and samples. When these calibration standards are mixed 1 to 1 with the ammonium citrate buffer, the F^- concentration is diluted to half the value given in table 26.

Table 26. Dilutions for preparation of individual calibration standards

Pipet Volume (mL)	Standard Pipeted (B or C)	Dilute to Final Volume (mL)	Final Concentration of Fluorine ($\mu\text{g/mL}$)
0.02	B	100	0.02
0.05	B	100	0.05
1.0	C	100	0.10
0.15	B	100	0.15
2.0	C	100	0.20
4.0	C	100	0.40
8.0	C	100	0.80
10.0	C	100	1.0
8.0	B	100	8.0
8.0	B	100	8.0

Procedure

1. Thoroughly clean each 35-mL zirconium crucible by first fusing NaOH within the crucible and then washing the crucible in dilute (1 to 1) hydrochloric acid. This step is necessary to avoid contamination.
2. Weigh 0.250 g of pulverized (100 mesh) coal sample, and transfer the sample to a 35-mL zirconium crucible.
3. Add 1 mL of isopropanol into the crucible to wet the sample.
4. Add 1 mL of the $\text{MgO-Mg(NO}_3)_2$ solution to the wet sample and mix with a glass stirring rod. Rinse the stirring rod with a little distilled water while collecting the rinse solution in the crucible.
5. Place the crucible into an oven operated at 110 °C and dry the sample for 30 min.
6. Place the zirconium crucible that contains the sample into a muffle furnace and ash the sample in the following uninterrupted sequence: 200 °C for 30 min, 300 °C for 30 min, 400 °C for 90 min, and 525 °C for 135 min. If the coal is of high rank, such as an anthracite, then ash the sample overnight.
7. Allow the sample to cool to room temperature. Add 3 g of NaOH (approximately 16 pellets). Fuse in the uncovered crucible over an open Meeker burner at a "dull-red" temperature for 2 min.
8. Allow the sample to cool, add 25 mL of distilled water to the crucible, and place the crucible on a steam bath to leach the fused mass. After heating the crucible contents for approximately 30 min, transfer the contents of the crucible into a 100-mL polyethylene beaker. Do not put the crucible into the polyethylene beaker because contamination from the outside surface of the crucible is likely to occur.

9. Filter the contents of the beaker through a 9-cm-diameter Whatman^R number 40 paper into a 100-mL volumetric flask. Wash the residue on the paper three times with a 1 percent (w/v) NaOH solution. Dilute to the 100-mL mark with distilled water and mix well.

10. Pipet 10 mL of the sample solution into a 100-mL polyethylene beaker; pipet 10 mL of 1 M ammonium citrate solution into the beaker, and stir the resulting solution. Measure the fluoride concentration in this final solution by ISE. As previously explained, it is extremely important that the pH of this solution be in the range of 5.5 to 7.0.

Measurements of electrode potentials are accomplished in the following sequence. Prepare each solution for measurements in a 100-mL polyethylene beaker a few minutes before the potential is measured. Before each measurement on a sample solution, equilibrate the electrodes for 5 min in a 4 $\mu\text{g/mL}$ fluoride solution. Remove excess solution from the electrodes by blotting with laboratory tissue paper, such as KimwipeTM, and rinse the electrodes with a portion of the prepared solution in a 5-mL polyethylene beaker. Place the electrodes in the sample solution, and after exactly 10 min of equilibration, measure the potential produced by the fluoride-ion electrode. Typically, the potential ranges from 100 to 170 mV. The actual electrode potential has been observed to change as the electrodes age. The variability of single potential measurements commonly is ± 0.5 mV. Upon completion of all measurements of electrode potentials for samples and calibration standards, graphically establish the functional relation between fluoride concentration and electrode potential by plotting concentration (in micrograms per milliliter) versus measured potential (in millivolts). This plot generally is accomplished on one-cycle semilogarithmic paper, as shown in figure 15. For an ash sample weighing 250 mg, the concentration of fluorine in the sample (in micrograms per gram) equals 800 times the concentration of fluoride in solution (in micrograms per milliliter), as extrapolated from the calibration curve (fig. 15).

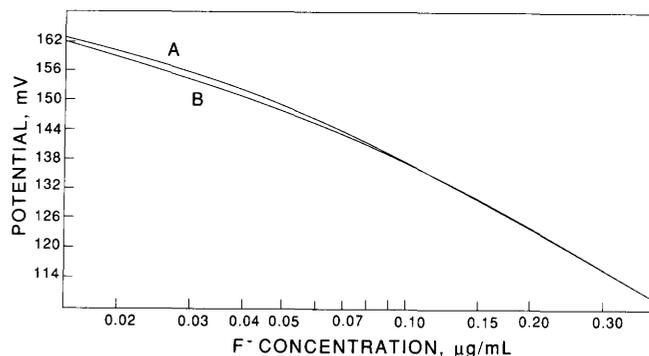


Figure 15. Two typical calibration curves (A and B).

ACCURACY, PRECISION, AND DETECTABILITY

Sets of coal-ash samples are always taken through the procedure with three blanks and National Bureau of Standards (NBS) coal standard reference material 1632. A fluoride concentration of approximately 10 $\mu\text{g}/\text{mL}$ is typical for the blank solutions. The mean value for 51 determinations of fluorine on ash from NBS standard reference material 1632 over a 1-year period is 83 $\mu\text{g}/\text{g}$, with a standard deviation of 5 $\mu\text{g}/\text{g}$. This value agrees quite well with 80 $\mu\text{g}/\text{g}$ reported by Gladney and others (1984) as the median of seven determinations by several different methods of analysis. The American Society for Testing and Materials (ASTM) method (ASTM, 1984) gives a fluorine concentration of $76 \pm 10 \mu\text{g}/\text{g}$ (Gladney and others, 1984). Swaine (1985) noted that the ASTM method generally gives lower results than those from pyrohydrolysis methods. The lower limit of determination by the ISE method for fluorine in a 250-mg sample is 20 $\mu\text{g}/\text{g}$.

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THE DETERMINATION OF FORMS OF SULFUR IN COAL

By Norma Rait and Philip J. Aruscavage

Abstract

Total sulfur, monosulfide ($S^=$), pyritic sulfur ($S_2^=$), and sulfate sulfur ($SO_4^=$) concentrations are determined in whole-coal samples. Total sulfur, monosulfide, and sulfate sulfur are determined by infrared absorption of the SO_2 produced by combustion of whole coal or of the separated forms of sulfur in an oxygen atmosphere. The pyritic sulfur concentration is measured indirectly by determining the iron concentration in a separated fraction by flame atomic absorption spectrometry. The organically bound sulfur concentration is calculated by subtracting the sum of the concentrations of monosulfide, sulfate sulfur, and pyritic sulfur from the total sulfur content. Coke and coal standards are used as control samples for measuring the accuracy and precision of the analytical procedures. The precision of the method for each form of sulfur, as determined from replicate analyses of standards, is approximately 5- to 10-percent relative standard deviation. The determination limit for sulfur is approximately 50 μg (30-percent relative standard deviation), which is equivalent to a 0.01 percent sulfur in 0.5 g of coal.

INTRODUCTION

Methods are described for the determination of total sulfur and of four forms of sulfur in coal (fig. 16): monosulfide ($S^=$), sulfate sulfur ($SO_4^=$), pyritic sulfur ($S_2^=$), and organically bound sulfur. The methods are modifications of those proposed by the American Society for Testing and Materials (ASTM) (1984).

EXPERIMENTAL EQUIPMENT AND METHODS

Sample Requirements

The whole-coal samples are received as air-dried, 80-mesh powders. Typically, 500 mg of sample is required for measurements of total sulfur and the four forms of sulfur.

Laboratory, Supplies, and Equipment

A steam bath in a fume hood is required. All chemicals and gases are of reagent-grade quality. Doubly distilled water is required for the preparation of all solutions.

1. Concentrated acids: hydrochloric and nitric.
2. 1- and 5-percent hydrochloric acid solutions.
3. 10 percent (w/v) $BaCl_2$ solution, approximately 1 L.
4. 20 percent (w/v) zinc acetate solution, approximately 1 L.
5. 50 percent (w/v) NaOH solution, for cleaning glassware.
6. 30 percent H_2O_2 solution, for cleaning glassware.
7. Cylinder of nitrogen gas and two-stage pressure regulator.
8. Cylinder of oxygen gas and two-stage pressure regulator.
9. V_2O_5 .
10. Anhydrous magnesium perchlorate (AnhydronTM).
11. LECO^R model SC-132 sulfur determinator, combustion boats, and accessories.
12. LECO^R coal standards used for calibration: 0.52, 1.10, 1.77, and 2.97 percent sulfur.
13. Alpha Resources, Inc., coke and coal standards numbered 771, 772, 774, 775, 780, and 782. These materials are analyzed along with samples as control standards.
14. Flame atomic absorption spectrometer, Perkin-Elmer^R model 370.
15. Iron standard solutions in 5 percent nitric acid: 0.5, 1, 3, 5, 7, 10, 20, 40, 60, and 100 $\mu\text{g}/\text{mL}$ iron.
16. Two laboratory hot plate—magnetic stirrer combinations.
17. Support-lattice frame to be used as a rack for equipment for forms of sulfur equipment (fig. 17).
18. Metal tube with five outlets and one inlet for nitrogen and associated Tygon tubing.
19. Round-bottom flasks, each having a volume of 200 mL and three necks. The two outside necks have

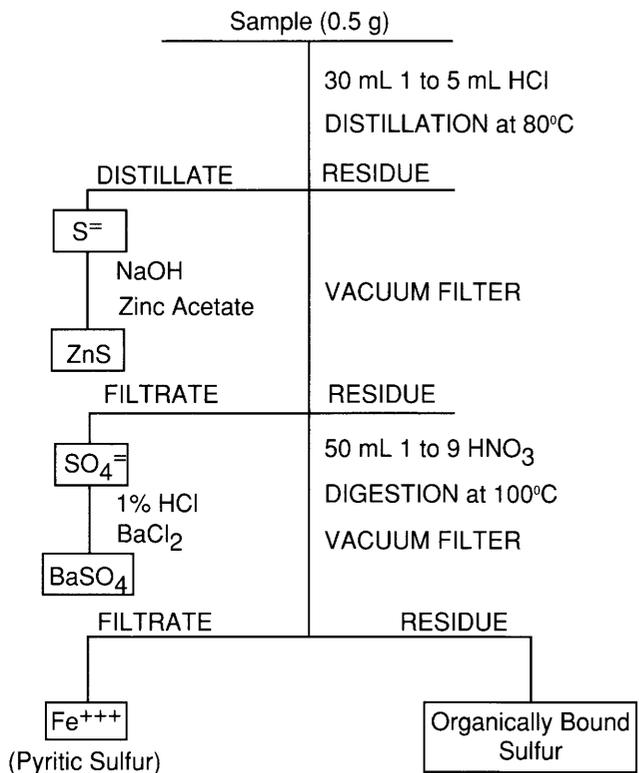


Figure 16. Flowchart for the separation of the forms of sulfur.

ground-glass joints 19/38; the center neck has a ground-glass joint 24/40 (fig. 18). These flasks are cleaned first with a solution of 50 percent NaOH and then with a 30 percent hydrogen peroxide solution. Finally, they are rinsed with tapwater and then with distilled water.

20. Heating mantel to fit 200-mL round-bottom flask, with accompanying Variac to regulate the temperature.
21. 70-mL test tubes and supporting laboratory jacks to raise and lower test tubes (fig. 17).
22. Thermometer (150 °C) having a ground-glass joint 10/30 (fig. 18).
23. Condenser (fig. 18) with ground-glass joint 14/35.
24. Pyrex™ ground-glass bushing-type reducing adapters, outer joint 24/40, inner joint 14/35 (fig. 18).
25. Pyrex reducing adapters: 19/38 to 10/30.
26. Vacuum flasks having volumes of 4 L and 250 mL, each fitted with a fritted-glass filter and a filter funnel and clamp. Each flask can be attached to a small vacuum pump.
27. Vacuum filters with diameters of 25 and 47 mm and a pore size of 0.45 μm and made of cellulose triacetate containing a small amount of wetting agent.
28. Pyrex™ standard-taper 10/30 inner ground-glass joint with a tube extension (outer diameter of 8 mm; length of 130 mm) (fig. 18).

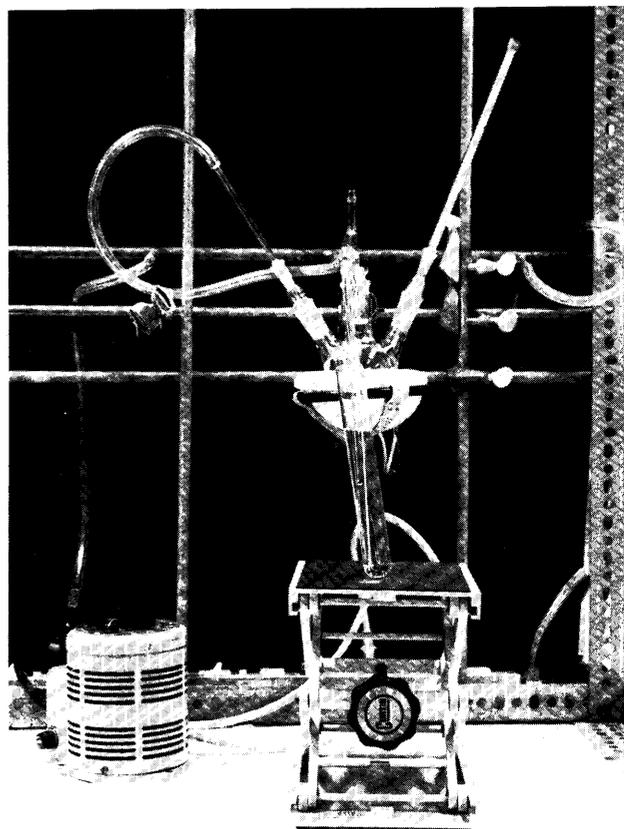


Figure 17. Photograph of setup. (Photograph by Deborah Dwornik.)

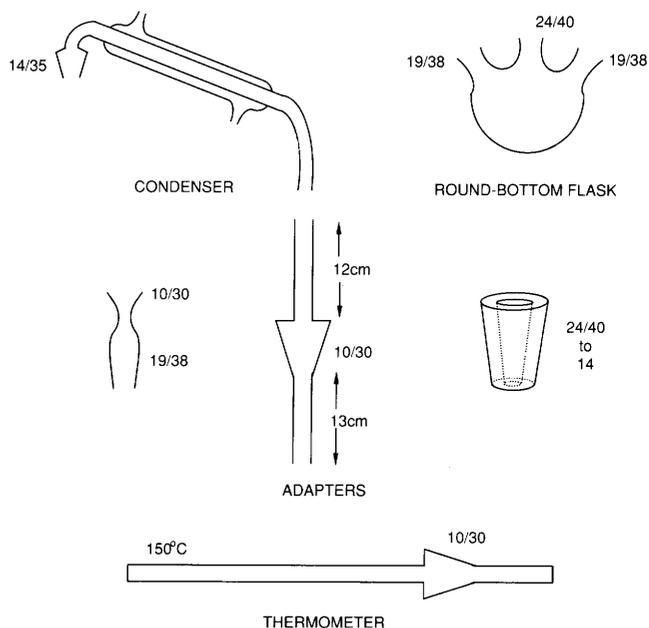


Figure 18. Diagrams of apparatus.

29. Pyrex™ ground-glass stoppers 19/38.
30. Graduated cylinders: 5, 10, and 50 mL.
31. Drying oven, maintained at 110 °C.
32. Volumetric flasks, 200 mL.
33. Beakers, 250 mL, with 9-cm-diameter Speedivap™ watch-glass covers.
34. Erlenmeyer flasks, 250 mL, and 5-cm-diameter watch-glass covers.
35. Balance with a sensitivity of 0.1 mg.

Methods

Total Sulfur

The total sulfur content of a sample is determined by use of the LECO^R SC132 sulfur analyzer (LECO Corporation, 1980; Kirschenbaum, 1983). Calibration of the sulfur analyzer is based on one of the LECO coal standards (LECO Corporation, 1980). After calibration, 200 mg of sample is weighed into a combustion boat then is placed in the combustion tube. This tube operates at a temperature of 1,370 °C in an oxygen atmosphere. The oxygen, which flows through the tube and over the boat, reacts with sulfur to form SO₂. The released SO₂ passes through the infrared absorption detector of the sulfur analyzer. After integrating the absorption signal over a period of 1 to 2 min, the instrument extrapolates and prints out the concentration of sulfur.

Laboratory Setup for the Separation of Forms of Sulfur

Within U.S. Geological Survey laboratories, the forms of sulfur are separated from 10 coal samples simultaneously. Ten three-neck, round-bottom flasks are placed in heating mantels. The first and fifth flasks have thermometers in one side neck (fig. 17), whereas the other eight flasks have stoppers in that side neck. Each flask has an air-cooled condenser attached to the center neck. The spout at the end of the condenser is placed in a 70-mL test tube that rests on a laboratory jack. Each of the 10 flasks has a bubble tube in one side neck. Nitrogen bubbles through each of the solutions in the round-bottom flasks and then passes through the condensers and into the test tubes. The rate of bubbling in a test tube is regulated by the height of the laboratory jack.

Monosulfide Sulfur Separation and Determination

1. Place 500 ± 1 mg of sample into each round-bottom flask. Use of a larger quantity of sample may cause difficulty in later filtering procedures.
2. Add 25 mL of distilled water to each sample.

3. Pour 15 mL of 20 percent zinc acetate solution and 285 mL of distilled water into a beaker. Place a magnetic stirring bar in this solution, and set the beaker on a hot plate. While stirring the diluted zinc acetate solution, add 3 mL of 50 percent NaOH solution. Warm, but do not boil, the resulting mixture.
4. Place 40 mL of this alkaline zinc acetate mixture into each test tube.
5. Bubble nitrogen through the system for 15 min to remove oxygen. Set the flow of nitrogen in each of the test tubes to approximately one bubble per second by adjusting the heights of the jacks.
6. Add 5 mL of concentrated hydrochloric acid to each flask.
7. Switch on the electrical power to the heating mantels, and maintain the temperature in the flasks at 80 °C. Continue to bubble the nitrogen through the system for 90 min. As the solution evaporates from a flask, add 5 percent hydrochloric acid to maintain the solution level.
8. Vacuum filter each alkaline zinc acetate mixture through a 47-mm filter.
9. Wash each precipitate thoroughly with doubly distilled water.
10. Discard the filtrate.
11. Place each filter on a marked watch glass and then transfer the watch glass into a drying oven that is maintained at 110 °C. Dry the filters overnight.
12. Transfer the dry precipitate on each filter to a separate combustion boat.
13. Place 500 mg of V₂O₅ over each precipitate.
14. Determine the percent sulfur by use of the LECO^R sulfur analyzer as described previously.
15. To determine the concentration of sulfur in a blank, place 500 mg of V₂O₅ in a combustion boat and measure the percent sulfur. Subtract this concentration from the previous result to obtain the percent of monosulfide sulfur in the sample.

Sulfate Sulfur Separation and Determination

1. Vacuum filter the solution in each round-bottom flask through a 25-mm filter.
2. Wash the residue thoroughly with 100 mL of 1 percent hydrochloric acid.
3. Place the residue in a 250-mL Erlenmeyer flask, and save it for the determination of pyritic sulfur.
4. Place the filtrate and washings in a 250-mL beaker.
5. Add distilled water until the volume of liquid in the beaker is 200 mL.
6. Place the beaker on a hot plate, and bring the solution to a boil.
7. Add 5 mL of 10 percent BaCl₂ to the boiling solution.

8. Place a SpeedivapTM watch glass on the beaker. Set the beaker on the large hot plate, and evaporate the solution to dryness (overnight).
9. Add 150 mL of 1-percent hydrochloric acid to the beaker containing dried residue, and bring the mixture to a boil. This prevents the formation of colloidal BaSO₄, which causes difficulty in filtering.
10. Filter the mixture through a 25-mm vacuum filter. Wash the beaker with 1 percent hydrochloric acid, and filter the wash solution.
11. Place the filter paper and precipitate on a marked watch glass, and dry them overnight in a drying oven at 110 °C.
12. Subsequently, place the filter paper and precipitate in a combustion boat. Spread approximately 500 mg of V₂O₅ over the precipitate, and determine the sulfur concentration by the sulfur analyzer. Subtract the blank from this result to give the concentration of sulfate sulfur.

Pyritic Sulfur Separation and Determination

1. Add 45 mL of distilled water to each of the residues in the Erlenmeyer flasks.
2. Add 5 mL of concentrated nitric acid to each flask.
3. Place a watch glass on top of each flask, and set the flask on a steam bath. Leave the flask on the steam bath for 90 min.
4. Vacuum filter the mixture in each flask through a 25-mm filter.
5. Wash the residue with distilled water; discard the residue.
6. Place the filtrate and washings in a 200-mL volumetric flask, and dilute to volume with distilled water.
7. Determine the iron leached from the sample by the nitric acid by flame atomic absorption spectrometry at the following conditions: 248.3 nm, 0.2-nm slit width, hollow cathode lamp, and an air-acetylene flame (oxidizing lean, blue).
8. Calculate the percent pyrite sulfur as follows:



$$\text{Atomic weight S} = 32.064 \text{ amu}$$

$$\text{Fe} = 55.847 \text{ amu}$$

$$\frac{(2 \times \text{S})}{\text{Fe}} = \frac{64.128}{55.847} = 1.148$$

$$\text{Weight of sample} = 0.500 \text{ g}$$

$$\begin{aligned} \text{Percent of Fe as pyrite in sample} &= \text{ppm Fe} \times \frac{0.0001}{0.500} \\ &= \text{ppm Fe} \times 0.0002 \end{aligned}$$

$$\text{Dilution factor} = 200$$

$$\begin{aligned} \text{Percent pyrite Sulfur} &= \text{ppm Fe} \times 0.0002 \times 200 \times 1.148 \\ &= \text{ppm Fe} \times 0.04592 \end{aligned}$$

Calculation of Organically Bound Sulfur

Organically bound sulfur is not determined by direct analysis but is determined by difference, as is shown in the following equation:

$$\begin{aligned} \text{Percent organically bound S} &= \text{Percent total S} \\ &- (\text{Percent monosulfide} + \text{Percent sulfate S} \\ &+ \text{Percent pyritic sulfur}) \end{aligned}$$

DISCUSSION

Tables 27 through 33 present results from determinations of forms of sulfur in coal standards; also shown are accepted values and standard deviations for replicate measurements.

Total sulfur concentrations from replicate determinations on nine coke and coal standards are shown in table 27. The accepted values (Alpha Resources, Inc., 1985) were obtained by using the ASTM recommended method for analysis for forms of sulfur (ASTM, 1984). The determination of total sulfur, from initial weighing of the sample to the result, requires about 3 min. This measurement time is comparable to those of other instrumental methods; moreover, the time is much less than that required for classical methods (Elliot, 1981). The determination limit for total sulfur is 0.02 percent for a 200-mg sample. The measured concentrations for total sulfur are in good agreement with the published values, and the precision is approximately 7-percent relative standard deviation.

The mean concentrations and standard deviations of monosulfide sulfur obtained for six Alpha Resources^R coal standards are shown in table 28. The results of

Table 27. Total sulfur in coal

Standard	Sulfur Concentration (percent)		
	Accepted ^a	Measured ^b	<i>n</i> ^b
771	0.59	0.60 ± 0.003	(10)
772	0.88	0.87 ± 0.01	(9)
774	0.63	0.65 ± 0.03	(9)
775	0.89	0.98 ± 0.01	(10)
780	2.06	2.17 ± 0.03	(11)
782	3.18	3.33 ± 0.05	(10)
NBS 1632a	1.58	1.59 ± 0.03	(11)
NBS 1635	0.33	0.32 ± 0.02	(10)
NBS 2683	1.85	1.96 ± 0.04	(10)

^a Sources: Accepted sulfur concentrations for standards 771, 772, 774, 775, 780, and 782 are from Alpha Resources, Inc. (1985). Accepted sulfur concentrations for NBS standards 1632a, 1635, and 2683 are from NBS (1984).

^b Sulfur concentrations measured in U.S. Geological Survey laboratories. Values shown for each coal standard are the arithmetic mean and standard deviation for *n* measurements, where *n* is the number in parentheses.

Table 28. Monosulfide sulfur in coal

Standard	Monosulfide Sulfur Concentration ^a (percent)	
	Measured ^b	<i>n</i> ^b
771	0.014 ± 0.004	(8)
772	0.095 ± 0.008	(5)
774	<0.01	(6)
775	<0.01	(6)
780	<0.01	(7)
782	<0.01	(6)

^a Accepted monosulfide sulfur concentrations not given by Alpha Resources, Inc. (1985).

^b Monosulfide sulfur concentrations measured in U.S. Geological Survey laboratories. Values shown for each coal standard are the arithmetic mean and standard deviation for *n* measurements, where *n* is the number in parentheses. For standard 771, three of the eight measurements indicated monosulfide sulfur concentrations of <0.01. The mean concentration shown is the average of the other five values.

monosulfide sulfur determinations for the coal standards numbered 774, 775, 780, and 782 are below the determination limit of the procedure, which is 0.01 percent sulfur.

The sulfate sulfur concentrations determined for standards numbered 772, 780, and 782 (table 29) are in good agreement with accepted values (Alpha Resources, Inc., 1985). Concentrations of sulfate sulfur in standards 771, 774, and 775 are below the determination limit of the method. The standard deviations for the concentrations measured for standards 772, 780, and 782 reflect the low precision of measurements in the proximity of the determination limit.

The pyritic sulfur concentrations determined for standards 771, 772, 774, 775, 780, and 782 are presented in table 30. The agreement between measured and accepted values of pyritic sulfur for standard 782 is not particularly good. The sample may contain an iron-bearing mineral that is incompletely dissolved in hydrochloric acid; thus, the iron appears as pyrite iron in a

Table 30. Pyritic sulfur in coal

Standard	Pyritic Sulfur Concentration (percent)		
	Accepted ^a	Measured ^b	<i>n</i> ^b
771	0.02	0.03 ± 0.03	(5)
772	0.03	0.02 ± 0.02	(3)
774	0.13	0.17 ± 0.05	(4)
775	0.43	0.41 ± 0.06	(5)
780	0.74	0.80 ± 0.08	(6)
782	1.19	1.43 ± 0.22	(4)

^a Source: Accepted pyritic sulfur concentrations for standards are from Alpha Resources, Inc. (1985).

^b Pyritic sulfur concentrations measured in U.S. Geological Survey laboratories. Values shown for each coal standard are the arithmetic mean and standard deviation for *n* measurements, where *n* is the number in parentheses.

Table 29. Sulfate sulfur in coal

Standard	Sulfate Sulfur concentration (percent)		
	Accepted ^a	Measured ^b	<i>n</i> ^b
771	0.01	<0.01	(7)
772	0.03	0.035 ± 0.012	(5)
774	0.01	<0.01	(6)
775	0.01	<0.01	(7)
780	0.13	0.13 ± 0.05	(6)
782	0.06	0.046 ± 0.046	(7)

^a Source: Accepted sulfate sulfur concentrations for standards are from Alpha Resources, Inc. (1985).

^b Sulfate sulfur concentrations measured in U.S. Geological Survey laboratories. Values shown for each coal standard are the arithmetic mean and standard deviation for *n* measurements, where *n* is the number in parentheses.

subsequent digestion with nitric acid. Iron-bearing minerals likely to occur in coal include siderite, hematite, marcasite, and goethite (Elliot, 1981). Pyritic sulfur, after oxidation by nitric acid and precipitation with BaCl₂, is determined as previously described for sulfate sulfur (table 31). Results for organically bound sulfur, which is determined on the filtered residue, appear in table 32. Calculations of organically bound sulfur (table 33) are in good agreement with the accepted values.

As illustrated by data in table 31, the concentrations determined for pyritic sulfur in standard 782 is again higher than the accepted value, but the value for organically bound sulfur in standard 782 (table 32) is lower. This observation indicates that the accepted concentration for pyritic sulfur may be low. However, organically bound sulfur may have been oxidized in the nitric acid digestion, thus, giving high values for pyritic sulfur in our determinations. Because the measurements of sulfur in standards 771 and 772 are near the determination limit of the method, the precision is low.

Table 31. Pyritic sulfur in coal by direct method

Standard	Pyritic Sulfur Concentration (percent)	
	Measured ^a	<i>n</i> ^b
771	0.018 ± 0.003	(3)
772	0.017 ± 0.004	(3)
774	0.17	(2)
775	0.39	(2)
780	0.87	(2)
782	1.47	(2)

^a Source: Standards are from Alpha Resources (1985).

^b Pyritic sulfur concentrations measured in U.S. Geological Survey laboratories. Values shown for each coal standard are the arithmetic mean and standard deviation for *n* measurements, where *n* is the number in parentheses.

Table 32. Organically bound sulfur in coal by direct method

Standard	Organic Sulfur Concentration (percent)	
	Measured ^a	<i>n</i> ^b
771	0.56 ± 0.02	(3)
774	0.49	(2)
775	0.59	(2)
780	1.08	(2)
782	1.61	(2)

^a Source: Standards are from Alpha Resources, Inc. (1985).

^b Organic sulfur concentrations measured in U.S. Geological Survey laboratories. Values shown for each coal standard are the arithmetic mean and standard deviation for *n* measurements, where *n* is the number in parentheses.

REFERENCES

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- American Society for Testing and Materials (ASTM), 1984, 1984 annual book of ASTM standards, petroleum products, lubricants, and fossil fuels, sect. 5, v. 05.05: Gaseous fuels, coal, and coke: Philadelphia, ASTM, p. 350-354.
- Elliot, Martin, ed., 1981, Chemistry of coal utilization, (2d

Table 33. Organically bound sulfur in coal by indirect method

Standard	Organic Sulfur Concentration (percent)		
	Accepted ^a	Measured ^b	<i>n</i> ^b
771	0.56	0.55 ± 0.03	(4)
772	0.75	0.69	(1)
774	0.49	0.48 ± 0.03	(3)
775	0.45	0.53 ± 0.03	(3)
780	1.19	1.27 ± 0.08	(3)
782	1.93	1.76 ± 0.18	(3)

^a Source: Accepted organic sulfur concentrations are from Alpha Resources, Inc. (1985).

^b Organic sulfur concentrations measured by difference in U.S. Geological Survey laboratories. Values shown for each coal standard are the arithmetic mean and standard deviation for *n* measurements, where *n* is the number in parentheses.

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- LECO Corporation, 1980, Instruction manual SC-132 sulfur system: St. Louis, Missouri.
- NBS Standard Reference Materials Catalog 1984-1985, National Bureau of Standards (NBS), 1984, Special Publication 260, Washington, D.C., U.S. Government Printing Office.

APPENDIX: REFERENCE MATERIALS FOR COAL ANALYSIS

By D.W. Golightly and F.O. Simon

The following tabulations list some of the reference materials available for use in the chemical analysis of coal. Data given in these tables are intended only to illustrate the degree to which the individual materials have been characterized. The analyst should always refer to specific certificates of analysis or other data provided directly by the supplier of the reference materials used.

Several coal standards now are being (or only recently have been) prepared by different laboratories; plans for preparation of these materials and available data are included in this section to alert the reader to these developments. The most significant program underway for the preparation and distribution of new coal standards is the Premium Coal Sample Program at Argonne National Laboratory. This program, described later, has produced eight new coal standards collected, analyzed, processed, and maintained for distribution to the coal research community. Important new coal and coal-ash standard reference materials for trace elements and radioactivity are expected to be available from the International Atomic Energy Agency in 1988. Also, the U.S. Geological Survey is preparing a new trace-element coal standard; preliminary data for this sample are included in this appendix.

SULFUR IN COAL: NBS STANDARDS 2682 THROUGH 2685

SRM ^a	Coal Type	Sulfur %	Furnace Ash %	Higher Heating Value ^b MJ/kg
2682	Subbituminous	0.47	6.37	27.08
2683	Bituminous	1.85	6.85	32.58
2684	Bituminous	3.00	11.09	29.21
2685	Bituminous	4.62	16.53	27.61

^a SRM: Standard Reference Material.

^b Moisture free.

These SRMs are intended primarily for use as analytical standards for the determination of **total sulfur in coal, ash content, and calorific value**. Semiquantitative data for these SRMs are available from NBS on 32 elements, including carbon, hydrogen, and nitrogen.

Source: National Bureau of Standards (NBS) certificate of analysis for standard reference materials 2682, 2683, 2684, and 2685, February 25, 1985.

TRACE MERCURY IN COAL: NBS STANDARD 1630

Mercury concentration = 0.13 µg/g

NBS-SRM 1630 is intended to be an analytical standard for the determination of trace mercury in coal. It consists of a commercially available coal crushed to particle size of 210 to 500 µm.

The concentration of selenium in this SRM is reported to be 2.1 µg/g, but the value is not certified by NBS.

Source: National Bureau of Standards (NBS) certificate of analysis, August 1, 1979.

CONCENTRATIONS OF ELEMENTS IN NBS-SRM COALS AND COAL FLY ASH^a

Element or Property	Concentration, µg/g ^b		
	1632b	1635	1633a
Al(%)	0.855	(0.32)	14.3
As	3.72	0.42	145
Ba	67.5	-	(0.15)
Be	-	-	(12)
Br	(17)	-	-
C(total, %)	78.11	-	-
Ca	0.204	-	1.11
Cd	0.0573	0.03	1.0
Ce	(9)	(3.6)	(180)
Cl	(1260)	-	-
Co	2.29	(0.65)	(46)
Cr	(11)	2.5	196
Cs	(0.44)	-	(11)
Cu	6.28	3.6	118
Eu	(0.17)	(0.06)	(4)
Fe(%)	0.759	0.239	9.4
Ga	-	(1.05)	(58)
H(%)	5.07	-	-
Hf	(0.43)	(0.29)	(8)
Hg	-	-	0.16
K(%)	0.0748	-	1.88
La	(5.1)	-	-
Li	(10)	-	-
Mg(%)	0.0383	-	0.455
Mn	12.4	21.4	179

Mo	(0.9)	-	(29)	Ba	78	304	372
N(%)	1.56	-	-	Be	4.1	2.8	2.5
Na(%)	0.0515	(0.24)	0.17	Br	(3)	(2)	(2)
Ni	6.10	1.74	127	Ca(%)	0.13	0.99	1.34
Pb	3.67	1.9	72.4	Ce	22	56	87
Rb	5.05	-	131	Cl	-	(32)	-
S(%)	1.89	0.33	(0.18)	Co	6.7	5.6	8.3
Sb	(0.24)	(0.14)	6.8	Cr	16	50	(67)
Sc	(1.9)	(0.63)	(40)	Cs	(1)	1.4	(2)
Se	1.29	0.9	10.3	Cu	5.9	13	18
Si(%)	(1.4)	-	22.8	Eu	(0.3)	(0.7)	(1)
Sm	(0.87)	-	-	Fe(%)	0.20	1.22	0.82
Sr	(102)	-	830	Ga	(8)	14	16
Th	1.34	0.62	24.7	Ge	(8)	13	-
Ti(%)	0.0454	(0.02)	(0.8)	Hf	1.7	5.4	4.8
Tl	-	-	5.7	Hg	(0.04)	(0.2)	(0.25)
U	0.436	0.24	10.2	K(%)	0.12	0.20	0.12
V	(14)	5.2	297	La	10	27	43
W	(0.48)	-	-	Li	(11)	(37)	(90)
Zn	11.9	4.7	220	Mg(%)	0.066	0.12	0.26
Ash(%)	6.79	-	-	Mn	22	157	80
Calorific Value (MJ/kg)	32.57	-	-	Mo	(1)	(2)	-
				Na(%)	0.0130	0.22	0.20
				Nb	(6)	(10)	(16)
				Ni	10.8	16	25
				P	30	130	610
				Pb	(5)	20	26
				Rb	8.1	9	10
				S(%)	0.56	1.49	0.51
				Sb	(0.3)	(0.3)	(0.4)
				Sc	4.3	7.6	10
				Se	-	(1)	0.8
				Si(%)	2.90	7.01	8.26
				Sm	2.0	4.9	6.3
				Sn	(1.0)	(3)	(4)
				Sr	44	126	330
				Ta	(0.3)	(0.8)	1.2
				Tb	(0.3)	(0.7)	(0.9)
				Th	3.4	12	18
				Ti(%)	0.0683	0.204	0.38
				U	1.5	5	4
				V	23	35	47
				W	(2)	(2)	(3)
				Y	(12)	(20)	29
				Yb	-	(2)	(2)
				Zn	5.5	12	17
				Zr	67	351	(180)
				L.O.I.(%) ^c	90.11	71.28	64.66

^a Source: National Bureau of Standards (NBS) certified values and information values, in parentheses, are from the following certificates of analysis:

1632b - Bituminous coal from Osage, W. Va., June 20, 1985.

1635 - Subbituminous coal from Erie, Colo., August 22, 1979.

1633a - Coal fly ash from Pennsylvania and West Virginia coals, January 5, 1985.

Further information and data on NBS standards are available from the following sources:

Gladney, E.S., and others, 1984, standard reference materials: 1982 compilation of elemental concentration data for NBS biological, geological, and environmental standard reference materials: NBS Special Publication 260-88, Washington, D.C., U.S. Government Printing Office, 221 pp.

Taylor, J.K., 1985, Standard reference materials: handbook for SRM users: NBS Special Publication 260-100, Washington, D.C., U.S. Government Printing Office, 85 pp.

National Bureau of Standards, 1984 Standard reference materials catalog 1984-85: NBS Special Publication 260, Washington, D.C., U.S. Government Printing Office.

Office of Standard Reference Materials, Room B311, Chemistry Building, National Bureau of Standards, Gaithersburg, MD 20899, telephone 301-921-2045.

^b Concentration units are percent, that is, centigrams per gram, for the elements Al, C, Fe, H, K, Mg, N, Na, S, Si, and Ti and for ash.

^a SARM: South African reference material.

^b Concentration units are micrograms per gram, unless indicated otherwise.

^c L.O.I.: Loss on ignition.

SARM 18 is a high-volatile, low-rank bituminous coal with a rank in the vitrinite category V_7 .

SARM 19 is a subbituminous to bituminous coal and is of generally very low rank (average V_4).

SARM 20 is a subbituminous to bituminous coal and is of generally low rank (average V_6).

Petrographic information is provided by Ring and Hansen (1984) on each SARM.

Source: Ring, E.J. and Hansen, R.G., 1984, The preparation of three South African coals for use as reference materials: MINTEK Report No. M169, 130 p. Council for Mineral Technology, 200 Hans Strijdom Road, Randburg, South Africa.

MINTEK COAL STANDARDS: SOUTH AFRICAN REFERENCE MATERIALS^a

Element	Concentration, $\mu\text{g/g}$ ^b		
	SARM 18	SARM 19	SARM 20
Al(%)	1.36	4.24	5.96
As	-	7	4.7
B	(30)	(90)	(90)

BCR REFERENCE MATERIALS

CRM 065 Coal

Property	Certified Value	95% Conf. Interval
Ash	39.1 mg/g	0.6 mg/g
Sulfur	8.3 mg/g	0.2 mg/g
Calorific Value	34.915 kJ/g	0.070 kJ/g

Source: Catalogue of BCR Reference Materials, Commission of the European Communities, Community Bureau of Reference, Brussels, 1982.

CRM 038 Fly Ash from Pulverized Coal

Element	Certified Concentration µg/g	95% Confidence Limit, µg/g
As	48.0	2.3
Cd	4.6	0.3
Co	53.8	1.9
Cu	176	9
Fe	338.10	7.10
Hg	2.10	0.15
Mn	479	16
Na	374.10	15.10
Pb	262	11
Zn	581	29

Particle size = 0.5 to 10 µm.

Source: Addendum to the Catalogue of BCR Reference Materials.

PREMIUM COAL SAMPLE PROGRAM, ARGONNE NATIONAL LABORATORY

This program was established to provide a suite of eight different premium coal samples to serve as standards for comparison. Coal samples designated "premium" have been selected, collected, transported, processed, and stored, while the original conditions were closely maintained. The coals selected represent a range of coalification, maceral content, mineral composition, and commercial significance. Each sample is kept in an inert atmosphere during transportation and in all processing steps. Prepared samples are sealed in glass ampoules and carboys. Each coal has been characterized by physical and chemical methods. The analyses planned include proximate, ultimate, calorific value, sulfur forms, Gieseler plasticity, and others. Information is available from the manager of the Premium Coal Sample Program: Dr. Karl S. Vorres, Chemistry Division, Building 211, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, telephone 312-972-7374.

COAL AND COAL ASH STANDARDS FOR TRACE ELEMENTS AND RADIOACTIVITY, INTERNATIONAL ATOMIC ENERGY AGENCY

Reference materials for trace elements and radioactivity will be available in 1988. Information is available through Dr. R. Schelenz, Head, Chemistry Unit, Analytical Quality Control Services, International Atomic Energy Agency, P.O. Box 100, A-1400 Vienna, Austria.

TRACE METALS IN COAL

Alpha Resources, Inc.

Element	Concentration ^a , µg/g				Method ^b
	AR-1800	AR-1801	AR-1802	AR-1803	
Ag	0.3 ^a	0.3 ^a	0.3 ^a	0.3 ^a	C
As	5.0	6.1	52.0	4.8	A
B	129	118	131	60	B
Be	3.9	3.3	3.9	0.3	C
Cd	0.2 ^a	0.2 ^a	0.2 ^a	0.2 ^a	C
Co	15	11	7	1	C
Cr	25	20	19	4	C
Cu	24	18	19	10	C
F	83	68	62	46	D
Ga	15 ^a	15 ^a	15 ^a	15 ^a	C
Ge	15	15	13	-	C
Hg	0.03	0.04	0.32	0.05	E
Li	32	17	13	4	C
Mn	15	14	33	11	C
Mo	2	2	3	1 ^a	C
Ni	82	58	22	5	C
Pb	8	8	64	4	C
Sb	0.9	0.9	0.8	1.2	A
Se	2.4	2.6	3.0	0.5	F
Sr	92	127	114	558	G
Tl	3 ^a	3 ^a	3 ^a	3 ^a	C
V	53	28	36	11	C
Zn	51	109	23	3	C

^a Concentration reported is at or below detection limit for method.

^b Method:

- HF-HCl digestion; gaseous hydride generation atomic absorption spectrometry (AAS).
- Na₂CO₃ fusion of ash; curcumin colorimetric.
- ASTM D3683-78-AAS.
- ASTM D3761-79 oxygen-bomb combustion; ion-selective electrode.
- ASTM D3684-78; oxygen-bomb combustion.
- Oxygen-bomb combustion; gaseous hydride generation AAS.
- HF-HCl dissolution; flame emission.

Alpha Resources, Inc., also has available coal standards for sulfur, with concentrations of sulfur that range from 0.2 to 6 percent sulfur, and 11 coal standards for sulfur forms (pyritic, sulfate, organic, and total sulfur). The latter standards have been characterized for proximate analysis (ash, volatile matter, fixed carbon, and calorific value), for ultimate analysis (carbon, hydrogen, nitrogen, chlorine, and ash), and for oxides (P₂O₅, SiO₂, Fe₂O₃, Al₂O₃, TiO₂, CaO, MgO, SO₃, K₂O, Na₂O).

Alpha Resources, Inc., Box 199, Stevensville, MI 49127.

U.S. GEOLOGICAL SURVEY COAL STANDARD:

Preliminary Data for Whole Coal^a

Element	Concentration, $\mu\text{g/g}^{\text{b}}$
As	20
Ba	<90
Br	61
Ce	8
Co	4.1
Cr	8.2
Cs	0.2
Eu	0.19
Fe(%)	0.73
Hf	0.3
Hg	0.14
K(%)	<0.30
La	5
Lu	0.07
Na(%)	0.02
Nd	<20
Rb	<20
Sb	0.9
Sc	1.5
Se	1.9
Sm	0.7
Sr	38
Ta	0.13
Tb	0.14
Th	1.2
U	0.4
W	<2
Yb	0.5
Zn	43

^a Preliminary data are from instrumental neutron activation analysis of whole coal, September 1983; S. Mee, analyst.

^b Concentration units are percent, that is, centigrams per gram, for the elements Fe, K, and Na.

SELECTED SERIES OF U.S. GEOLOGICAL SURVEY PUBLICATIONS

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Professional Papers are mainly comprehensive scientific reports of wide and lasting interest and importance to professional scientists and engineers. Included are reports on the results of resource studies and of topographic, hydrologic, and geologic investigations. They also include collections of related papers addressing different aspects of a single scientific topic.

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