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The Chemical Analysis of Argonne Premium Coal Samples

U.S. Geological Survey
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and Frank G. Walthall

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CHAPTER A

An Introduction to the Chemical Analysis of Argonne Premium Coal Samples

by Curtis A. Palmer

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The Chemical Analysis of Argonne Premium Coal Samples

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An Introduction to the Chemical Analysis of Argonne Premium Coal Samples

by Curtis A. Palmer

INTRODUCTION

This volume contains papers discussing chemical analysis of the eight Argonne Premium Coal Samples performed by the United States Geological Survey. The papers present analytical results obtained from all the methods used in the analyses and give a comparison of the results for elements where more than one technique was used. This paper will describe the samples, explain the numbering protocol which will be used throughout this volume, and list the elements determined by each technique used.

DISCUSSION

A detailed description of the samples, the reasons for their collection and other background information have been reported by Vorres (1990). Table 1 contains the sample identification for the eight Argonne Premium Coal Samples used in this study, with the seam, location, rank and ash content for each. The samples come from seven different states and vary in rank from Lignite to Low Volatile Bituminous. The sample identification protocol is similar to that used by Vorres (1990). It consists of a two to four letter identifier which represents either the state or the seam from which the sample was obtained, followed by one or more spaces, and the letters PC for Premium Coal then a dash followed by the sample number 1 through 8. In the chapters to follow splits will be identified by the addition of a dash and another number after the sample number. For example, split two of Premium Coal Sample one would be identified as UF PC-1-2 with UF designated the Upper Freeport coal seam from which the Premium Coal Sample number one was obtained.

Table 1. Sample identification, location, rank and ash content of the eight Argonne Premium Coal Samples analyzed in this work. Ash contents are taken from Doughten and Gillison, Table 6, this volume.

Sample ID		Seam	State	Rank	Ash Content (%)
UF	PC-1	Upper Freeport	PA	Medium Volatile Bituminous	13.5
WY	PC-2	Wyodak-Anderson	WY	Subbituminous	8.5
IL	PC-3	Illinois #6	IL	High Volatile Bituminous	16.2
PITT	PC-4	Pittsburgh (#8)	PA	High Volatile Bituminous	9.2
POC	PC-5	Pocahontas #3	VA	Low Volatile Bituminous	5.3
UT	PC-6	Blind Canyon	UT	High Volatile Bituminous	4.6
WV	PC-7	Lewiston-Stockton	WV	High Volatile Bituminous	19.4
ND	PC-8	Lignite	ND	Lignite	9.5

Thirteen different procedures using seven different techniques were used to determine 58 different elements. Six of these procedures required coal ash and the other seven used the whole ground coal. Table 2 shows the elements which were determined by each procedure. Two direct-current atomic optical emission spectrography (DCAES) procedures, one on the ash and one on the whole coal, four X-ray fluorescence spectrometry (XRF) procedures including both wavelength and energy dispersive procedures for the analysis of both the whole coal and the ash and three atomic absorption spectrometry (AAS) procedures (flame AAS and graphite furnace AAS on the ash, and cold vapor AAS for Hg on the whole coal) were used in the analysis of the Premium Coal Samples. The other techniques include instrumental neutron activation analysis (INAA), ion-selective electrode (ISE) and instrumental analyses for carbon, nitrogen and hydrogen (CHN) which were determined on the whole coal only, and inductively coupled argon plasma-atomic emission spectroscopy (ICAP-AES) analyses were made on the ash only. Ash content (Doughten and Gillison, 1991) and moisture content (Krasnow and Finkelman, 1991) are also reported. A detailed description of each of these procedures is given in the following chapters.

In addition to the values of 35 elements reported by DCAES on the ash, upper limits were reported for another 27 elements making a total of 62 elements reported by DCAES in chapter C. Of the 58 different elements with reported values, 33 were determined by more than one technique. Comparison of the results by different techniques are reported by Palmer (1991) in this volume.

Table 2. Tabulation of elements determined by different techniques.

Technique	DCAES		XRF		INAA	ICAP-AES	AAS	CVAA	ISE	CHN	Total Number of procedures	
Material Analyzed	WC	ASH	WC	ASH	WC	ASH	ASH	WC	WC	WC		
Element												
H										X	1	H
Li							X^2				1	Li
Be		X				X					2	Be
B		X									1	B
C										X	1	C
N										X	1	N
F									X		1	F
Na		X		X^1	X	X					4	Na
Mg	X	X		X^1		X					4	Mg
Al	X	X		X^1		X					4	Al
Si	X	X		X^1							3	Si
P		X	X^1	X^1		X					4	P
S				X^1							1	S
Cl			X^1								1	Cl
K		X		X^1	X	X					4	K
Ca	X	X		X^1		X					4	Ca
Sc		X			X						2	Sc
Ti	X	X		X^1		X					4	Ti
V	X	X				X					3	V
Cr	X	X	X	X	X	X					6	Cr
Mn	X	X		X^1		X					4	Mn
Fe	X	X		X^1	X	X					5	Fe
Co	X	X			X		X^2				4	Co
Ni	X	X	X	X	X	X					6	Ni
Cu	X	X	X	X		X					5	Cu
Zn	X		X	X	X	X					5	Zn
Ga	X	X									2	Ga
Ge	X	X									2	Ge
As		X			X						2	As
Se					X						1	Se
Br					X						1	Br
Rb			X	X	X						3	Rb
Sr		X	X	X	X	X					5	Sr
Y		X	X	X		X					4	Y
Zr	X	X	X	X							4	Zr
Nb		X	X	X							3	Nb
Mo		X									1	Mo
Ag		X									1	Ag
Cd							X^3				1	Cd
Sn		X									1	Sn
Sb					X						1	Sb
Cs					X						1	Cs
Ba	X	X	X	X	X	X					6	Ba
La		X	X	X	X						4	La
Ce		X	X	X	X						4	Ce
Nd		X			X						2	Nd
Sm		X			X						2	Sm
Eu					X						1	Eu
Tb					X						1	Tb
Yb		X			X						2	Yb
Lu					X						1	Lu
Hf					X						1	Hf
Ta					X						1	Ta
W					X						1	W
Hg								X			1	Hg
Pb	X	X					X^3				3	Pb
Th					X						1	Th
U					X						1	U
TOTALS	18	35	14	23	29	18	4	1	1	3	146	

DCAES	Direct-Current Arc Spectrography. Those elements with only upper limits reported are not included (Skeen and others, 1991).
XRF	X-Ray Fluorescence Spectrometry [1] Wavelength dispersive procedure; all other XRF procedures are energy dispersive procedures
INAA	Instrumental Neutron Activation Analysis
ICAP-AES	Inductively Coupled Plasma Emission Spectroscopy
AAS	Atomic Absorption Spectrometry [2] Flame AAS [3] Graphite Furnace AAS
CVAA	Cold-Vapor AAS
ISE	Ion-Selective Electrode
CHN	Carbon-Hydrogen-Nitrogen elemental analysis
WC	Whole Coal

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CHAPTER B

Rehydration of Desiccated Argonne Premium Coal Samples

by Marta R. Krasnow and Robert B. Finkelman

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Rehydration of Desiccated Argonne Premium Coal Samples

by Marta R. Krasnow and Robert B. Finkelman

INTRODUCTION

The Argonne National Laboratory has taken measures to ensure that their eight Premium Coal Samples retain their original properties during storage by sealing them in glass ampoules filled with an inert gas (argon) (Vorres, 1989). However, once the ampoules are opened in a laboratory, sample alteration, such as dehydration and oxidation, can occur.

EXPERIMENTAL

We experienced a situation in which Argonne coal samples were stored in our laboratory for two to four years in polyethylene bottles which allowed the samples to dehydrate (see columns 1 and 2 of Table 1). A substantial amount of moisture had been lost from each sample during storage.

This note is intended to illustrate the degree of dehydration and to discuss the possibility of rehydrating the samples.

Table 1. Moisture[1] of Argonne Premium Coal Samples Under Different Conditions. Values are in weight percent.

Sample Identification			(1)	(2)	(3)
Sample		Rank[2]	"Fresh" Samples[3]	"Aged" Samples	After Resaturation
UF	PC-1	Bit.	1.13	0.17 (15)[4]	0.16 (14)[4]
WY	PC-2	Sub.	28.09	8.79 (31)	9.76 (35)
IL	PC-3	Bit.	7.97	1.41 (18)	6.77 (85)
PITT	PC-4	Bit.	1.65	0.97 (59)	1.57 (95)
POC	PC-5	Bit.	0.65	0.10 (15)	0.23 (35)
UT	PC-6	Bit.	4.63	0.21 (05)	3.29 (71)
WV	PC-7	Bit.	2.42	0.85 (35)	1.29 (53)
ND	PC-8	Lig.	32.24	1.94 (06)	11.90 (37)

[1] All moisture values were determined using the ASTM recommended procedure (ASTM, 1988).

[2] Bit. = bituminous, Sub. = subbituminous, Lig. = lignite.

[3] Samples in ampoules, data from Vorres, 1989.

[4] Percent of original moisture content.

From 41 to 95 percent of the original moisture was lost during the unregulated storage of the "aged" samples. Sample WY PC-2 lost almost 20 weight percent moisture and ND PC-8 lost more than 30 weight percent. Sample POC PC-5 lost the least absolute amount of moisture, slightly more than 0.5 weight percent.

To resaturate the samples, weighed splits of -100 mesh coal were placed in uncovered petri dishes in a vacuum desiccator containing a barometer and a thermometer. Approximately 800 milliliters of deionized water was added to the base of the desiccator. The samples were kept under atmospheric pressure in the desiccator at 90 percent relative humidity and 72° F for 24 hours after which they were removed from the desiccator and weighed. Several samples had increases far in excess of the original moisture loss. For example, sample UF PC-1, which had lost about one weight percent moisture, increased over 5 weight percent. This "excess" moisture may be due to condensation on the coal particles. We therefore allowed the resaturated samples to equilibrate with the ambient atmosphere for 24 hours (72-74° F, 60-64 percent relative humidity) prior to determining the moisture (referred to as resaturated moisture) by the ASTM (1988) procedure (Table 1, column 3).

After the 24 hour residency in the desiccator at the 90 percent relative humidity and subsequent equilibration, there were substantial increases in moisture in most samples. Sample IL PC-3 regained 67 percent of the original moisture (Table 1, column 1), and UT PC-6 regained 66 percent. Sample IL PC-3 regained 5.36 weight percent moisture and ND PC-8 gained almost 10 weight percent. Only sample UF PC-1 showed no gain in moisture. Despite the substantial increases in moisture for most samples, none of the samples, with the possible exception of PITT PC-4, recovered all the moisture lost on drying.

Experiments on water desorption and adsorption have been conducted by varying vapor pressure and holding the temperature constant, usually less than 40° C (Gauger, 1945; Allardice and Evans, 1978). Results of the experiments indicate that, once dry, a coal sample will not adsorb enough water to regain its original moisture content. There is no generally accepted mechanism to explain this phenomenon (Allardice and Evans, 1978), however, several theories have been offered. These include: 1) the shrinking of coal upon drying which causes a collapse of some capillaries, so that the dried material can no longer hold or take up as much water as it held originally: 2) the replacement of moisture on the walls of some capillaries by adsorbed gases making it difficult to re-wet the capillaries (Gauger, 1945).

Vorres and others (1988) and Vorres and Kolman (1988) conducted drying and rehydration studies of Argonne Premium Coal Samples. They concluded that coal rank, particle size, and degree of oxidation affected moisture removal and replacement.

The Argonne Premium Coal Samples behave in a typical fashion with respect to rehydration. Improper storage can lead to substantial moisture loss. Resaturation generally will restore some of the lost moisture. These observations on moisture loss are important if measurements of physical properties are to be made on samples that have been stored under non-controlled conditions for any length of time. These observations are also important for calculations involving chemical analysis of the raw coal (for example, instrumental neutron activation analysis or X-ray fluorescence analysis). Assuming that the coal samples have retained their original moisture contents can lead to errors of as much as 30 percent for low-rank coals (lignites and subbituminous: ND PC-8 and WY PC-2, respectively). Even for higher-rank coal (e. g. IL PC-3) the errors can be as high as 6.5 percent.

DISCUSSION

We recommend the following procedures to minimize errors caused by desiccation (especially for low-rank coal):

1) After opening the ampoules, samples should be stored in such a way as to minimize dehydration.

2) Moisture content of the coal samples should be determined just prior to chemical analysis of whole coal.

3) If there is insufficient sample for moisture determination, rehydrate the sample to minimize the error.

The ASTM method for determining equilibrium moisture (ASTM, 1988, D 1412) could be used to rehydrate the sample, but the method requires at least a 20 gram sample, more time and equipment than the procedure described in this note.

An alternative method would be to analyze a moisture-free sample by drying it (105°C for 24 hours) prior to analysis. Two assumptions are necessary, 1) that the published moisture value is applicable so that the chemical analysis can be recalculated to an as-received basis, 2) that the sample does not pick up moisture between drying and weighing for analysis.

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CHAPTER C

Automated Semiquantitative Direct-Current Arc Spectrographic Analysis of Eight Argonne Premium Coal Ash Samples

By C.J. Skeen, B.J. Libby and W.B. Crandell

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Automated Semiquantitative Direct-Current Arc Spectrographic Analysis of Eight Argonne Premium Coal Ash Samples

by C.J. Skeen, B.J. Libby and W.B. Crandell

ABSTRACT

The automated semiquantitative direct-current arc spectrographic method was used to analyze 62 elements in eight Argonne Premium Coal Ash Samples. All eight coal ash samples were analyzed in triplicate to verify precision and accuracy of the method. The precision for most elements was within ± 10%. The evaluation of the accuracy of this method is assumed to be limited to +50% or -33% because of the nature of the standard curves for each of the elements. Adjustments to the computer program were implemented to account for unique matrix interferences in these particular coal ash samples.

INTRODUCTION

Emission spectrographic analysis is based on the emission of light by atoms and ions returning to ground state after excitation in a direct-current arc. The light is passed through the slit of a spectrograph, diffracted by a grating, and focussed on a photographic plate. Wavelength positions indicate the elements present, and the darkness of the resulting specific elemental image is proportional to the concentration of the specific element present.

The automated d.c.-arc emission spectrographic analysis of a wide variety of geologic materials is a rapid, economical method for evaluating both the major and trace element composition. A total of 62 elements can be determined (Dorrzapf, 1973). This computerized procedure is semiquantitative, because it calculates concentrations using prestored coefficients calculated from previously arced standards.

EXPERIMENTAL

In preparation for arcing of samples, 15 mg of sample (-100 mesh) is mixed with 30 mg of graphite and transferred to a graphite crater electrode. The spectrograph is adjusted and photographic developing solutions are prepared using the standard operating procedures listed in Table 1 (Dorrzapf and others, 1988). The Helz jet is used in preference to a Stallwood jet, because it simplifies the procedure for changing samples (Helz, 1964; Shaw and others, 1958; Stallwood, 1954). An iron bead is arced first and exposed on the plate for the iron calibration reference. Then each sample is arced at 5 amps for 20 seconds and then at 15 amps for 130 seconds. For the iron and each sample and standard, a cadmium lamp is exposed in two windows as a reference to be used on the scanning microphotometer.

Table 1. Photoplate preparation conditions

Electrodes	Cathode: ASTM type C-6, 50 mm long. Anode: 6.3 mm diameter thin-walled graphite (Ultra Carbon no. 3170).
Electrode charge	15 mg sample + 30 mg graphite (type UCP-2, 200 mesh).
Spectrograph	3.4-m Ebert (JARRELL-ASH Mark III).
Power source	325 V, open circuit.
Excitation	15 A dc arc, set with empty graphite electrodes.
Arc gap	4 mm, maintained throughout arcing.
Exposure	20 s at 5 A followed by 130 s at 15 A, continuous arcing.
Atmosphere	70% Ar + 30% 0_2; 6.6 liters/min flow rate, with top of Helz jet nozzle 2 mm below top of electrode.
Wavelength range	230.0-470.0 nm; first order.
Grating	600 grooves/nm; 0.5 nm/mm reciprocal linear dispersion.
Slit	25 μm wide and 2 mm high.
Filter	14% transmission neutral-density filter at slit.
Illumination	Arc image focused on collimator by 450-mm focal-length cylindrical quartz lens at slit.
Mask at collimator	18 mm.
Emulsion	Kodak III-0 (102 X 508 mm plates).
Processing	Kodak D-19 developer, 3.25 min at 20°C stirred by nitrogen bursts; Kodak indicator stop bath, 30 s; Kodak fixer, 10 min; wash, 20-30 min at 20°C; Kodak photoflow, 1 min; and dry with warm air for 30 min.

The photoplate is developed and processed according to standard USGS procedures (Helz and others, 1969). The plate is recorded by a scanning microphotometer (Helz, 1965; Helz, 1973). The data are processed by an HP 2100 computer, and a report is generated with the 64-element concentration information. This report is evaluated, and the analyst chooses the values to report based upon data supplemental to the report (Dorrzapf and others, 1988; Golightly and others, 1977).

DATA REDUCTION

Programs for data collection and interpretation that were written (Walthall, 1974) for use on a mainframe computer were adapted for use on a minicomputer system (Thomas, 1979). A two-step procedure is used for emulsion calibration. A single Fe burn is exposed through a two-step filter. The recorded Fe spectrum is divided into ten 25-nm segments. Then twenty-six Fe lines are used to define the preliminary plate emulsion curve in each 25-nm segment. In Figure 1, the preliminary plate emulsion curve is a plot of the natural logarithm of the percent transmittance of the unfiltered step, the abscissa, versus the natural logarithm of the percent transmittance of the filtered step, the ordinate. This second-degree curve is represented by the quadratic equation, $y = ax^2+bx+c$. The 45° tangent to this curve is used as a starting place for finding the inflection point of the natural logarithm of the relative intensity versus the natural logarithm of the percent of transmittance for the final plate emulsion curve. Figure 2 shows the final plate emulsion calibration curve as it relates percentage transmittance to intensity. 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 natural logarithm percent transmittance scale.

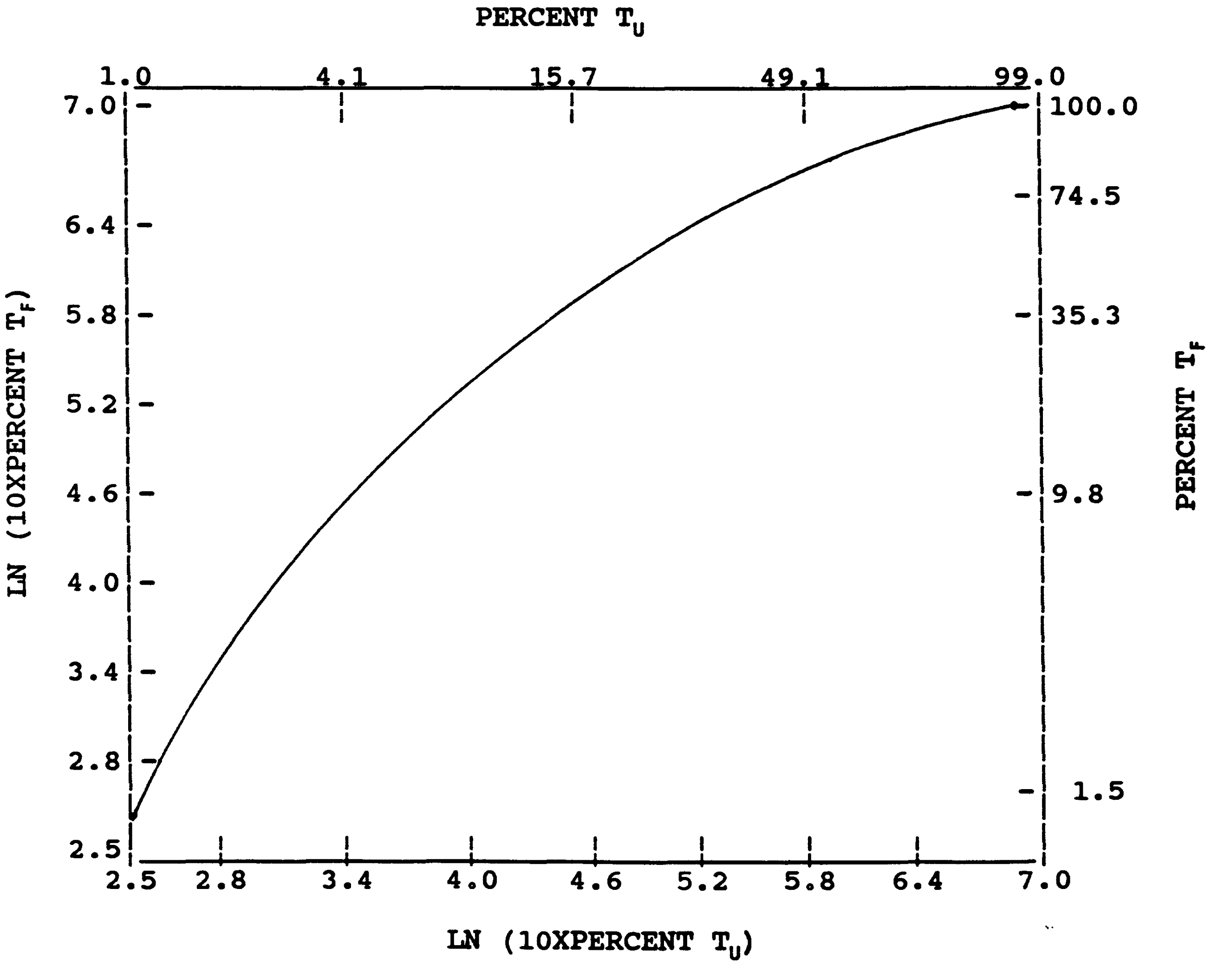

Figure 1. Preliminary plate emulsion calibration curve relating transmittance from the unfiltered step, T_U, to the filtered step, T_F.

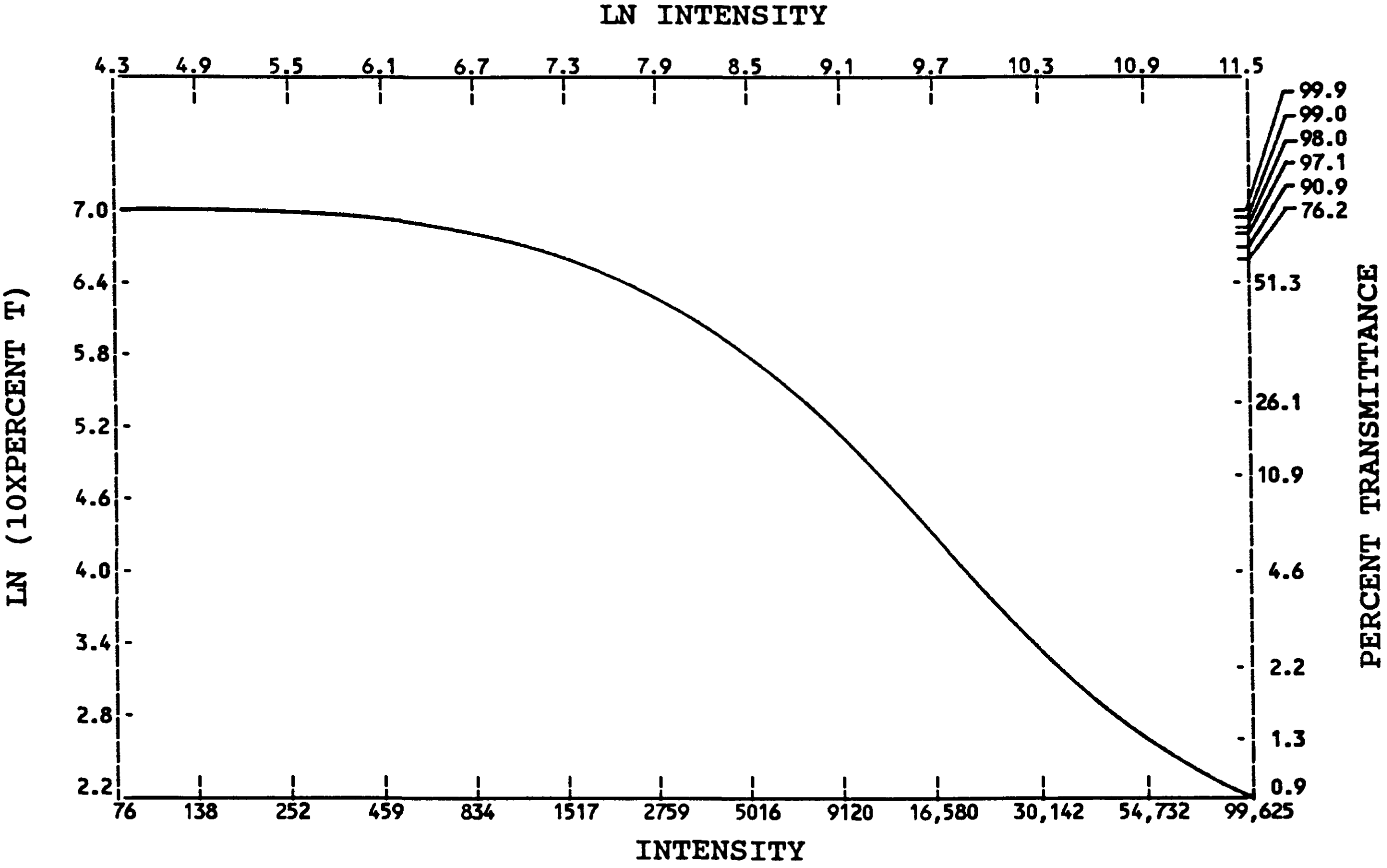

Figure 2. Final plate emulsion calibration curve relating intensity to transmittance.

The filter factor is the ratio of the percentage transmittances of the unfiltered half of the filter and the filtered half of the filter. The Newton method of successive approximation is used to find this point on the preliminary curve (Abramowitz, 1964). The inflection point is then translocated to the final curve so that it falls on the line with a 315° slope that passes through the point where the relative intensity equals 10,000 and the percent transmittance equals 10.0 percent (Figure 2).

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

RESULTS AND DISCUSSION

For these Premium Coals, an in-depth study was made for specific interference corrections which were not automatically performed. Due to heterogeneity problems associated with Ba coupled with the suppression of the most sensitive analytical lines for Ba due to the matrices of these coals, values from less sensitive lines were used. The values for Sr were improved after making adjustments for interferences from Fe and Ni.

This semiquantitative approach achieves ranges and detectability comparable to those of the visual estimation procedure (Myers and others, 1961). Since the standards used do not closely match the approximate composition of the samples to be analyzed, the expected accuracy is limited to ± 1 step, which corresponds to roughly +50% or -33%.

In the analyses of these Premium Coals, NIST Standard Reference Materials 1633 and 1633a (National Bureau of Standards, 1975 and 1979) were included as control samples for evaluation of both precision and accuracy of this method. Table 2 lists the concentrations provided by NIST certificates, the mean concentrations determined over a 5-month period, and the associated relative standard deviations. Compositions determined for coal ashes 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 and others, 1985). Heterogeneity possibly explains the large range of values for barium and zirconium in the Premium Coals as well as the interferences discussed above.

Table 3 lists data for all 62 elements in these eight Argonne Premium Coals. The < symbol indicates the lower limit for a value for that element, and a > symbol indicates the highest value determined for that element. An "H" denotes the occurrence of an unresolved interference. Major elements are reported in percent, and the trace elements in μg/g.

Table 2. D.C. Arc Spectrographic Analyses of (NIST) Standard Reference Material Coal Fly Ash. [Concentration units are % for the first group of elements, including Si through Mn, and µg/g for the group of elements that includes As through Zr.]

Element	1633 NIST Value[a] (mean ± SD)	1633 USGS Average[b]	1633A NIST Value[a] (mean ± SD)	1633A 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 ± 0.08
As(µg/g)	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 ± 30	830 ±30*	900 ± 140
V	214 ± 8*	200 ± 24	300	240 ± 36
Y		53 ± 7.8		
Yb		6.6 ± 0.9		
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.

Table 3. Concentrations in % for First 10 Elements and µg/g for the Other 54 Elements in the Argonne Premium Coal Samples

Sample	UF PC-1-1	UF PC-1-2	UF PC-1-3	WY PC-2-1	WY PC-2-2	WY PC-2-3	IL PC-3-1	IL PC-3-2	IL PC-3-3
Si %	22	22	25	15	15	17	22	20	25
Al %	15	19	19	5.0	6.4	7.2	12	12	13
Fe %	12	9.9	13	3.0	3.0	3.6	14	14	16
Mg %	0.98	1.1	1.2	3.9	4.6	4.4	0.69	0.68	0.77
Ca %	5.1	4.4	4.7	12	15	17	9.6	9.4	11
Na %	0.31	0.35	0.34	1.4	1.9	1.4	0.99	0.89	0.91
K %	2.3	2.1	2.2	0.36	0.44	0.36	1.5	1.6	1.7
Ti %	0.45	0.29	0.44	0.35	0.43	0.48	0.38	0.40	0.45
P %	< 0.068	< 0.068	< 0.068	0.24	0.31	0.39	< 0.068	< 0.068	< 0.068
Mn %	0.041	0.038	0.043	0.049	0.032	0.036	0.066	0.064	0.070
Ag µg/g	1.4	1.5	1.6	0.65	0.85	0.88	2.2	2.6	2.4
As µg/g	230	280	160	< 100	< 100	< 100	< 100	< 100	100
Au µg/g	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8
B µg/g	140	350	180	870	740	860	730	680	780
Ba µg/g	300	320	290	3400	3700	4200	320	330	470
Be µg/g	11	8.9	11	1.6	1.6	1.8	5.5	5.9	6.6
Bi µg/g	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Cd µg/g	< 32	< 32	< 32	< 32	< 32	< 32	< 32	< 32	< 32
Ce µg/g	< 63	74	< 63	74	120	110	< 200	< 200	170
Co µg/g	28	22	29	12	17	16	22	21	26
Cr µg/g	160	130	140	56	74	70	220	220	260
Cu µg/g	130	120	140	130	160	160	82	69	58
Dy µg/g	< 22	< 22	< 22	< 22	< 22	< 22	< 22	< 22	< 22
Er µg/g	< 4.6	< 4.6	< 4.6	< 4.6	< 4.6	< 4.6	< 4.6	< 4.6	< 4.6
Eu µg/g	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2
Ga µg/g	45	47	47	26	31	29	29	27	31
Gd µg/g	< 32	< 32	< 32	< 32	< 32	< 32	< 32	< 32	< 32
Ge µg/g	26	25	29	< 4.6	< 4.6	< 4.6	52	52	60
Hf µg/g	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15
Ho µg/g	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8
In µg/g	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Ir µg/g	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15
La µg/g	64	39	50	56	77	84	54	55	63
Lu µg/g	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15
Mo µg/g	12	9.3	12	7.6	7.8	8.2	34	30	32
Nb µg/g	12	10	15	14	15	21	12	14	20
Nd µg/g	75	< 32	37	< 68	< 68	< 68	< 68	< 68	40
Ni µg/g	100	95	110	57	64	64	130	120	150

Table 3. (continued)

Sample	UF PC-1-1	UF PC-1-2	UF PC-1-3	WY PC-2-1	WY PC-2-2	WY PC-2-3	IL PC-3-1	IL PC-3-2	IL PC-3-3
Os µg/g	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15
Pb µg/g	77	74	82	31	48	41	87	78	88
Pd µg/g	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Pr µg/g	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100
Pt µg/g	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2
Re µg/g	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Rh µg/g	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2
Ru µg/g	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2
Sb µg/g	< 68	< 68	< 68	< 68	< 68	< 68	< 68	< 68	< 68
Sc µg/g	19	11	16	12	17	18	16	16	17
Sm µg/g	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Sn µg/g	13	12	12	6.4	10	14	10	15	20
Sr µg/g	490	420	490	2000	2800	3100	250	230	270
Ta µg/g	< 320	< 320	< 320	< 320	< 320	< 320	< 320	< 320	< 320
Tb µg/g	< 32	< 32	< 32	< 32	< 32	< 32	< 32	< 32	< 32
Th µg/g	< 46	< 46	< 46	< 46	< 46	< 46	< 46	< 46	< 46
Tl µg/g	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Tm µg/g	< 4.6	< 4.6	< 4.6	< 4.6	< 4.6	< 4.6	< 4.6	< 4.6	< 4.6
U µg/g	< 220	< 220	< 220	< 220	< 220	< 220	< 220	< 200	< 200
V µg/g	130	99	130	86	110	120	140	140	160
W µg/g	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15
Y µg/g	46	22	36	28	36	42	27	29	32
Yb µg/g	6.2	6.1	6.4	2.7	3.5	4.1	3.5	3.6	4.2
Zr µg/g	96	55	89	140	200	250	86	96	140
Majors Recalculated as oxides									
SiO_2 %	47	47	54	32	32	36	47	43	54
Al_2O_3 %	28	36	36	9.5	12	14	23	23	25
Fe_2O_3 %	17	14	19	4.3	4.3	5.2	20	20	23
MgO %	1.6	1.8	2.0	6.5	7.6	7.3	1.1	1.1	1.3
CaO %	7.1	6.2	6.6	17	21	24	13	13	15
Na_2O %	0.42	0.47	0.46	1.9	2.6	1.9	1.3	1.2	1.2
K_2O %	2.8	2.5	2.7	0.43	0.53	0.43	1.8	1.9	2.1
TiO_2 %	0.75	0.48	0.73	0.58	0.72	0.80	0.63	0.67	0.75
P_2O_5 %	< 0.16	< 0.16	< 0.16	0.55	0.71	0.89	< 0.16	< 0.16	< 0.16
MnO %	0.053	0.049	0.056	0.063	0.041	0.047	0.085	0.083	0.090

Table 3. (continued)

Sample	PITT PC-4-1	PITT PC-4-2	PITT PC-4-3	POC PC-5-1	POC PC-5-2	POC PC-5-3
Si %	26	29	32	18	17	19
Al %	24	21	24	12	14	14
Fe %	19	20	22	9.8	8.3	10
Mg %	0.71	0.70	0.97	1.9	2.0	2.0
Ca %	5.0	3.6	4.7	10	11	12
Na %	0.42	0.36	0.40	2.4	2.4	2.5
K %	1.4	1.3	1.5	0.65	0.63	0.73
Ti %	0.64	0.57	0.64	0.53	0.47	0.58
P %	< 0.068	< 0.068	< 0.068	< 0.068	< 0.068	< 0.068
Mn %	0.033	0.041	0.042	0.045	0.043	0.050
Ag µg/g	0.95	0.94	1.0	1.8	1.8	2.0
As µg/g	210	180	160	350	210	270
Au µg/g	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8
B µg/g	530	580	570	320	310	360
Ba µg/g	390	370	490	3600	3600	4900
Be µg/g	12	13	13	14	11	13
Bi µg/g	22	17	< 10	< 10	< 10	< 10
Cd µg/g	< 32	< 32	< 32	< 32	< 32	< 32
Ce µg/g	< 200	< 200	< 200	220	190	270
Co µg/g	31	25	30	45	44	56
Cr µg/g	220	190	220	170	150	180
Cu µg/g	58	89	66	420	290	380
Dy µg/g	< 22	< 22	< 22	< 22	< 22	< 22
Er µg/g	< 4.6	< 4.6	< 4.6	< 4.6	< 4.6	< 4.6
Eu µg/g	< 2.2	< 2.2	< 2.2	< 2.2	< 4.2	< 2.2
Ga µg/g	57	43	54	42	40	47
Gd µg/g	< 32	< 32	< 32	< 32	< 32	< 32
Ge µg/g	13	13	12	8.7	8.2	9.2
Hf µg/g	< 150	< 150	< 150	< 15	< 15	< 15
Ho µg/g	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8
In µg/g	< 10	< 10	< 10	< 10	< 10	< 10
Ir µg/g	< 15	< 15	< 15	< 15	< 15	< 15
La µg/g	60	66	62	130	130	150
Lu µg/g	< 15	< 15	< 15	< 15	< 15	< 15
Mo µg/g	9.4	7.4	9.0	37	41	46
Nb µg/g	18	22	18	24	14	22
Nd µg/g	47	46	35	100	130	110
Ni µg/g	150	130	150	120	110	140

Table 3. (continued)

Sample	PITT PC-4-1	PITT PC-4-2	PITT PC-4-3	POC PC-5-1	POC-5-2	POC-5-3
Os µg/g	< 15	< 15	< 15	< 15	< 15	< 15
Pb µg/g	79	75	84	220	160	220
Pd µg/g	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Pr µg/g	< 100	< 100	< 100	< 100	< 100	< 100
Pt µg/g	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2
Re µg/g	< 10	< 10	< 10	< 10	< 10	< 10
Rh µg/g	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2
Ru µg/g	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2
Sb µg/g	< 68	< 68	< 68	< 68	< 68	< 68
Sc µg/g	20	19	22	24	24	28
Sm µg/g	< 10	< 10	< 10	14	13	16
Sn µg/g	18	11	13	2800	550	720
Sr µg/g	960	900	1100	2000	1900	2300
Ta µg/g	< 320	< 320	< 320	< 320	< 320	< 320
Tb µg/g	< 32	< 32	< 32	< 32	< 32	< 32
Th µg/g	< 46	< 46	< 46	< 46	< 46	< 46
Tl µg/g	< 10	< 10	< 10	< 10	< 10	< 10
Tm µg/g	< 4.6	< 4.6	< 4.6	< 4.6	< 4.6	< 4.6
U µg/g	< 220	< 220	< 220	< 220	< 220	< 220
V µg/g	130	130	150	130	120	150
W µg/g	< 15	< 15	< 15	< 15	< 15	< 15
Y µg/g	31	36	33	86	81	92
Yb µg/g	6.9	5.5	5.2	8.7	8.8	7.9
Zr µg/g	110	160	120	250	200	220
Majors Recalculated as Oxides						
SiO_2 %	56	62	69	39	36	41
Al_2O_3 %	45	40	45	23	27	27
Fe_2O_3 %	27	29	32	14	12	14
MgO %	1.2	1.2	1.6	3.2	3.3	3.3
CaO %	7.0	5.0	6.6	14	15	17
Na_2O %	0.57	0.49	0.54	3.2	3.2	3.4
K_2O %	1.7	1.6	1.8	0.78	0.76	0.88
TiO_2 %	1.1	0.95	1.1	0.88	0.78	0.97
P_2O_5 %	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16
MnO %	0.043	0.053	0.054	0.058	0.056	0.065

Table 3. (continued)

Sample	UT PC-6-1	UT PC-6-2	UT PC-6-3	WV PC-7-1	WV PC-7-2	WV PC-7-3	ND PC-8-1	ND PC-8-2	ND PC-8-3
Si %	16	20	20	22	30	28	5.7	6.6	6.6
Al %	6.8	7.8	6.3	17	22	21	2.2	3.0	2.2
Fe %	4.6	5.9	5.1	1.8	2.3	2.1	3.7	4.5	3.5
Mg %	0.93	0.82	0.89	0.66	0.43	0.40	5.5	5.4	5.3
Ca %	6.0	6.3	6.3	0.40	0.31	0.49	13	14	15
Na %	1.9	1.4	1.4	0.19	0.18	0.19	H	2.6	H
K %	0.47	0.31	0.36	2.0	1.7	1.8	0.40	0.35	0.41
Ti %	0.40	0.43	0.40	0.95	0.91	0.90	0.18	0.18	0.20
P %	< 0.068	< 0.068	< 0.068	0.086	< 0.068	< 0.068	< 0.13	0.11	0.098
Mn %	0.014	0.010	0.016	0.0092	0.012	0.010	0.11	0.11	0.11
Ag µg/g	12	8.9	9.6	2.6	2.2	2.2	< 0.10	< 0.10	< 0.10
As µg/g	< 220	< 220	< 220	< 220	< 220	< 220	< 220	< 220	< 220
Au µg/g	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8
B µg/g	> 1000	> 1000	> 1000	150	480	250	500	800	810
Ba µg/g	750	670	900	660	740	640	5300	7400	5700
Be µg/g	3.3	5.2	4.4	15	16	16	2.8	3.5	2.4
Bi µg/g	< 22	< 22	< 22	< 22	< 22	< 22	< 22	< 22	< 22
Cd µg/g	< 22	< 22	< 22	< 22	< 22	< 22	< 22	< 22	< 22
Ce µg/g	160	160	130	130	140	130	< 63	< 63	< 63
Co µg/g	15	13	14	36	30	31	5.7	6.0	5.7
Cr µg/g	110	85	120	220	180	210	25	25	26
Cu µg/g	69	52	66	90	85	68	41	40	75
Dy µg/g	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Er µg/g	< 4.6	< 4.6	< 4.6	< 4.6	< 4.6	< 4.6	< 4.6	< 4.6	< 4.6
Eu µg/g	< 0.68	< 0.68	2.5	2.4	2.5	4.6	< 0.68	< 0.68	< 0.68
Ga µg/g	32	19	28	68	56	59	19	16	20
Gd µg/g	< 22	< 22	< 22	< 22	< 22	< 22	< 22	< 22	< 22
Ge µg/g	< 4.6	< 4.6	< 4.6	5.5	< 4.6	6.2	< 4.6	< 4.6	< 4.6
Hf µg/g	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Ho µg/g	< 1.5	< 1.5	< 1.5	3.2	< 1.5	1.7	< 1.5	< 1.5	< 1.5
In µg/g	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8
Ir µg/g	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
La µg/g	66	64	62	72	74	64	37	40	39
Lu µg/g	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8	< 6.8
Mo µg/g	12	8.4	11	7.0	8.4	6.3	8.6	8.2	8.7
Nb µg/g	10	11	12	13	19	23	6.6	5.3	6.4
Nd µg/g	64	< 150	< 150	97	100	90	< 32	< 32	< 150
Ni µg/g	84	89	87	120	100	110	17	17	22

Table 3. (continued)

Sample	UT PC-6-1	UT PC-6-2	UT PC-6-3	UV PC-7-1	UV PC-7-2	UV PC-7-3	ND PC-8-1	ND PC-8-2	ND PC-8-3
Os µg/g	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Pb µg/g	45	36	43	93	81	69	28	22	32
Pd µg/g	< 0.68	< 0.68	< 0.68	< 0.68	< 0.68	< 0.68	< 0.68	< 0.68	< 0.68
Pr µg/g	9.5	9.3	8.4	10	9.3	< 6.8	< 6.8	< 6.8	7.3
Pt µg/g	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5
Re µg/g	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Rh µg/g	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5
Ru µg/g	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Sb µg/g	< 32	< 32	< 32	< 32	< 32	< 32	< 32	< 32	< 32
Sc µg/g	16	15	14	36	31	32	9.2	9.1	10
Sm µg/g	8.0	8.2	7.8	8.9	8.7	< 3.2	< 3.2	< 3.2	4.9
Sn µg/g	8.8	5.9	9.4	11	8.4	10	< 4.6	< 4.6	13
Sr µg/g	1800	2000	2000	390	320	370	6200	6300	7300
Ta µg/g	< 320	< 320	< 320	< 320	< 320	< 320	< 320	< 320	< 320
Tb µg/g	< 32	< 32	< 32	< 32	< 32	< 32	< 32	< 32	< 32
Th µg/g	< 46	< 46	< 46	< 46	< 46	< 46	< 46	< 46	< 46
Tl µg/g	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Tm µg/g	< 3.2	< 3.2	< 3.2	< 3.2	< 3.2	< 3.2	< 3.2	< 3.2	< 3.2
U µg/g	< 150	< 150	< 150	< 150	< 150	< 150	< 150	< 150	< 150
V µg/g	82	78	79	160	180	150	38	38	37
W µg/g	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Y µg/g	41	42	34	50	52	39	24	27	25
Yb µg/g	4.9	4.4	4.6	9.2	7.3	7.1	2.3	2.0	2.1
Zr µg/g	260	280	200	200	150	140	130	130	140
Majors Recalculated as Oxides									
SiO_2 %	34	43	43	47	64	60	12	14	14
Al_2O_3 %	13	15	12	32	42	40	4.2	5.7	4.2
Fe_2O_3 %	6.6	8.4	7.3	2.6	3.3	3.0	5.3	6.4	5.0
MgO %	1.5	1.4	1.5	1.1	0.71	0.66	9.1	9.0	8.8
CaO %	8.4	8.8	8.8	0.56	0.43	0.69	18	20	21
Na_2O %	2.6	1.9	1.9	0.26	0.24	0.26	H	3.5	H
K_2O %	0.57	0.37	0.43	2.4	2.1	2.2	0.48	0.42	0.49
TiO_2 %	0.67	0.72	0.67	1.6	1.5	1.5	0.30	0.30	0.33
P_2O_5 %	< 0.16	< 0.16	< 0.16	0.20	< 0.16	< 0.16	0.30	0.25	0.23
MnO %	0.018	0.013	0.021	0.012	0.016	0.013	0.14	0.14	0.14

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CHAPTER D

The Determination of 18 Elements in Five Whole Argonne Premium Coal Samples by Direct-Current Arc Spectrography

by Janet D. Fletcher and Carol J. Skeen

U.S. GEOLOGICAL SURVEY OPEN-FILE REPORT 91-638

The Chemical Analysis of Argonne Premium Coal Samples

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TABLES

The Determination of 18 Elements in Five Whole Argonne Premium Coal Samples by Direct-Current Arc Spectrography

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ABSTRACT

Quantitative multiple-element analysis of whole Argonne Premium Coal Samples by direct-current arc spectrography is accomplished through the use of a lithium carbonate buffer. Two spectrographic methods are described for the determination of 18 trace elements in 100-mg samples of coals. Overall concentrations for calibration standards range from a low of 2 μg/g to a high of 3%. For concentrations well above the lower determination limit, the typical accuracy is within ± 20%, and the general precision of the method is ± 10%.

INTRODUCTION

Most atomic-spectrometric methods are designed for the analysis of ash from pulverized coals that have been oxidized at 500°C or 750°C (ASTM, 1984). The direct-current (d.c.) arc functions well for ash that is mixed with graphite powder, and many elements are effectively preconcentrated by the ashing process, thus providing improved detectability (Dorrzapf, 1973). However, certain elements associated with organic phases, such as porphyrins, organometallics, or acid salts, may be volatilized and lost during the ashing process. The elements Ag, B, Ga, Ge, Mo, Ni, and Ti, which potentially can be determined by d.c.-arc spectrometry, are at least partially associated with organic phases in coals (Finkelman, 1980; Ruch, and others, 1974; Gluskoter, and others, 1977). Direct, multiple-element analysis of whole coals circumvents the long intervals required for ashing, the losses due to volatilization, and the extra exposures of samples to possible contamination. This paper describes the two atomic-emission spectrographic methods that have produced accurate determinations of 28 elements in the pulverized whole coal (Fletcher and Golightly, 1985). Only 18 elements were determined for these Premium Coals. These methods, which principally have been applied to the analysis of coal microlithotypes, offer the basis for efficient, low-cost, multiple-element analysis of whole coals.

EXPERIMENTAL

Approach

A principal difficulty encountered in attempts to directly arc small quantities of pulverized coal focuses on the rapid evolution of gases that occurs immediately following initiation of the arc and on the subsequent burning of the organic phases that remain in a cup-shaped electrode (anode). The rapidly-evolved gases usually blow material from the anode cup, thus creating uncontrolled losses of the previously weighed sample, and the erratic flaming of the organic phase can produce unwanted spectral bands from carbon-based free radicals. These events constitute very irreproducible processes that control the transport of material from the hot anode cup into the arc discharge. Such severe problems related to the arcing process have been solved by mixing powdered coal with a lithium carbonate buffer. This controls sample transport and excitation conditions in the arc column and greatly diminishes the possibility for flaming of the hot coal dissociation products. With these very important aspects of arcing well controlled for coal samples, the methodology for d.c. arc spectrographic analysis becomes quite conventional.

Method

The Sample

The spectrographic laboratory generally receives pulverized samples (-100 mesh) from the sample-preparation laboratory, but small, unground samples of coals are pulverized by hand-grinding with an agate mortar and pestle (Fletcher and Golightly, 1985).

Preparation of Sample

A 100 mg of a pulverized coal sample, a 100 mg of lithium carbonate and a 50 mg of pure graphite powder are thoroughly mixed and ground with an agate mortar and pestle to obtain a final homogeneous mixture. For samples that have especially high concentrations of analyte elements, a higher weight ratio (<10:1) of lithium carbonate to sample may be necessary. Twenty-five mg of the final homogeneous mixture is transferred into the appropriate graphite electrode and firmly tamped (Dorrzapf, 1973). These filled electrodes are dried in an oven at 110°C for 4 hours immediately before arcing. The drying step is necessary because it removes water and other readily volatilized components that can cause the loss of sample material from the anode just after initiation of the arc discharge.

Preparation of Standards

Calibration standards consist of homogeneous mixtures of oxides and carbonates of the analyte elements in a lithium carbonate matrix. Dilutions of commercially available standards, which contain 43 elements in lithium carbonate (Spex Industries, Metuchen, New Jersey), provide calibration standards for the concentration range from 1 to 1000 ug/g for each element of interest. Individual standards are diluted on a weight-weight basis with high purity lithium carbonate (<10 μg/g total impurities).

Reference standards are prepared from National Institute of Science and Technology (NIST) formerly NBS, coals 1632, 1632a, and 1635, which can be diluted with lithium carbonate in the same fashion as the samples. Drying and handling of NIST standards should follow the procedure used for samples.

Arcing of Samples and Standards

All samples and standards are arced in an argon-oxygen, or argon, laminar stream that is concentric to the anode and is introduced through an alumina nozzle arrangement known as a Helz jet (Helz, 1964). Both the arcing conditions and the atmosphere (Table 1) were chosen to give complete volatilization of analyte elements from an anode cup into the arc column and to effectively excite those atomic energy levels giving the spectral lines listed in Table 1, without causing high spectral background. For the volatile elements (Group II, Table 1), the objective is to vaporize and to excite these elements over a relatively long interval while distilling insignificant amounts of matrix elements into the arc column. The present method is one adapted from that of Annell (1967) for volatile elements in silicate and carbonate rocks. For elements in chemical forms that exhibit low volatility (Group 1, Table 1), total vaporization of each sample into the arc column is necessary for an accurate determination.

Complete details on the spectrographic equipment and the conditions for arcing samples and for making the necessary measurements are given in Table 2. Maintaining a 4-mm gap between the tips of the electrodes is essential to the achievement of the accuracy and precision that this approach is capable of producing.

ACCURACY AND PRECISION

The accuracy of analysis by d.c. arc spectrography is dependent on the successful element-by-element calibrations of an instrument with standard materials that closely resemble the materials to be analyzed. For coals, the effective matrix of the "arced sample" has been modified through the use of a lithium carbonate buffer. This modification of the sample matrix makes the arced sample resemble the lithium carbonate matrix of the Spex calibration standards. The quantity of lithium carbonate, relative to that of the sample in any given arced sample, is sufficient to control the fusion, vaporization, transport, and excitation processes. The concentration ranges for the elements capable of being determined by the d.c. arc spectrographic methods described in the present work, are summarized in Table 1. Elements exhibiting the largest deviations are Al, Ca, Mn, and Si. Experience in the analyses of other coals, vitrinites, exinites, and inertinites indicates that the deviations for these elements observed here are random, rather than systematic. Measurement errors for the spectrographic method are typically ± 20%, and the precision of the methods is ± 10% for concentrations well above (> 5X) the determination limits.

Table 1. Elements, Spectral Lines, and Determination Limits.

Group I[a]	Wavelength[b], nm	Spectrum[b]	Determination Limits, %[c]		
Al	265.248	I	0.01	-	2.0
	266.039	I	0.01	-	2.0
B	249.773	I	0.005	-	0.1
Ba	455.403	II	0.002	-	0.05
Ca	315.887	II	0.01	-	0.3
	422.673	I	0.005	-	0.01
Co	345.350	I	0.0002	-	0.05
Cr	302.156	I	0.002	-	0.2
	425.435	I	0.0002	-	0.02
Cu	327.396	I	0.0002	-	0.02
Fe	259.837	II	0.05	-	2
	302.107	I	0.002	-	1.0
Mg	277.983	I	0.01	-	0.2
	285.213	I	0.0002	-	0.02
Mn	279.482	I	0.0002	-	0.1
	279.827	I	0.0002	-	0.2
Mo	317.035	I	0.0005	-	0.2
Nb	316.340	II	0.002	-	0.1
Ni	305.082	I	0.002	-	0.1
	341.476	I	0.0002	-	0.05
	349.296	I	0.01	-	0.2
Si	251.920	I	0.2	-	3.0
Ti	308.940	II	0.002	-	0.2
	316.257	II	0.005	-	0.2
V	318.341	I	0.0005	-	0.1
Zr	327.926	II	0.001	-	0.2
Group II[a]					
Ag	338.289	I	0.0002	-	0.02
As	278.020	I	0.02	-	0.2
Bi	306.772	I	0.0002	-	0.005
Cd	326.106	I	0.0002	-	0.1
Ga	294.364	I	0.0002	-	0.05
Ge	265.118	I	0.0005	-	0.05
	303.906	I	0.0005	-	0.005
Hg	253.652	I	0.002	-	0.1
Pb	283.306	I	0.0002	-	0.01
Sn	317.505	I	0.0002	-	0.02
Tl	276.787	I	0.0002	-	0.02
Zn	334.502	I	0.001	-	0.05

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[a] Group I and Group II refer to the involatile and volatile groups of elements, respectively.

[b] Wavelength and spectrum are from the NIST Wavelength Tables (Meggers and others, 1975). I line emitted by normal atom; II line emitted by singly ionized atom

[c] Lower and upper limits for each element are in units of weight percent.

Table 2. Spectrographic Equipment and Operating Conditions.

Subject	Group I Elements (Involatile)	Group II Elements (Volatile)
Sample	100 mg pulverized whole coal mixed with 100 mg Li_20_3 powder (American Potash) and 50 mg graphite powder (-200 mesh, Ultra Carbon). 25 mg of mixture tamped into anode cup.	100 mg pulverized whole coal mixed with 100 mg Li_20_3 powder (American Potash) and 100 mg graphite powder (-200 mesh, Ultra Carbon). 50 mg of mixture tamped into anode cup.
Spectrograph	Ebert mounting, 3.4 m focal length, 0.5 nm/mm reciprocal linear dispersion in first order, grating: 600 grooves/mm, blazed for 300 nm.	Eagle mounting, 3 m focal length, 0.55 nm/mm reciprocal linear dispersion dispersion in first order, grating: 590 grooves/mm, blazed for 300 nm.
Slit	25 μm x 2 mm for spectra from standards and samples. 25 μm x 4 mm for spectra from iron arc.	25 μm x 2.5 mm for spectra from standards and samples. 25 μm x 5 mm for spectra from iron arc.
Wavelength Range	240 - 360 nm, first order.	250 - 340 nm, second order.
Illumination	Arc image focused on collimator mirror by a 450 mm focal length cylindrical quartz lens located at the entrance slit.	Arc image focused on grating by a 450 mm focal length cylindrical quartz lens located near the entrance slit.
Filters	Neutral density, 35% T plus 75% T, for exposures of samples and standards. Two-step neutral density filter, 40% T: 100% T, for iron arc exposures used in calibration of the photographic emulsion.	None for exposures of samples and standards. Two-step neutral density filter, 50% T: 100% T, for iron arc exposure used in calibration of the photographic emulsion.

Table 2 (Continued). Spectrographic Equipment and Operating Conditions.

Subject	Group I Elements (Involatile)	Group II Elements (Volatile)
Electrodes	Cathode: 3.2 mm (0.125 inch) diameter x 3.8 cm (1.5 inches) long graphite rod (Ultra Carbon no. 5001). Anode: 3.6 mm (0.14 inch) diameter, thin-walled graphite electrode (Ultra Carbon no. 1590).	Cathode: Same as for Group I. Anode: 5.7 mm (0.225 inch) diameter graphite electrode (Ultra Carbon no. 3170).
Excitation	Arc Current: Stepped arc current, 5 A d.c. for 10 s, 15 A d.c. for 95 s, across constant 4 mm arc gap. Voltage source of 300 V, open circuit. Electrode supporting the sample is the anode. Atmosphere: 80% Ar, 20% 0_2; 6.6 L/min through Helz jet (Helz, 1964).	Arc Current: Stepped arc current, 8 A d.c. for 10 s, 25 A for 110 s, across constant 4 mm arc gap. Voltgage source of 300 V, open circuit. Electrode supporting the sample is the anode. Atmosphere: Ar, 6.6 L/min through Helz jet (Helz, 1964).
Photography	Eastman-Kodak III-0 emulsion on 101 x 254 mm (4 x 10 inch) glass substrate. Emulsion processed in Kodak D-19 developer for 3 min (20°C), short stop solution for 30 s, and fixer for 10 min. Then, the plate was washed in tap water for 10 to 20 min, allowed to drain, and dried with warm air for 5 min.	Same as for Group I elements.
Microphotometry	All microphotometry was done by conventional methods, such as those described by ASTM (ASTM, 1971).	Same as for Group I Elements.

RESULTS AND DISCUSSION

Only 18 elements were analyzed in five of the eight whole Premium Coals. The results of these analyses are shown in Table 3 and Table 4. Ag, B, and Mo required special treatment and preparation time so they were eliminated from the request for analysis. As, Bi, Cd, Hg, Nb, Sn and Tl were not able to be analyzed because of the nature of the matrix of these particular coals.

Only five of the eight Argonne Premium Coals were available for analysis when this method was developed. Because this method is labor intensive and the accuracy and precision for this method at the detection limits for a majority of the elements are not better than the other methods implemented in the analysis of these coals, the characterization of the other three coals was not carried out. The standard deviation for accuracy was ± 20%, while precision had a standard deviation of ± 10%.

Table 3. Concentration in % of Seven Elements in Argonne Premium Coals.

		Mg (WT.%)	Al (WT.%)	Ca (WT.%)	Ti (WT.%)	Mn (WT.%)	Si (WT.%)	Fe (WT.%)
UF	PC-1-1	0.097	2.0	0.57	0.10	0.0053	3.0	2.0
UF	PC-1-2	0.10	2.0	0.54	0.10	0.0059	4.0	3.0
UF	PC-1-3	0.10	2.0	0.63	0.10	0.0048	3.0	2.0
WY	PC-2-1	0.20	0.47	1.0	0.048	0.0010	0.80	0.34
WY	PC-2-2	0.20	0.54	1.0	0.046	0.0016	1.0	0.33
WY	PC-2-3	0.20	0.44	1.0	0.038	0.0014	0.52	0.20
IL	PC-3-1	0.096	2.0	2.0	0.089	0.015	3.0	2.0
IL	PC-3-2	0.099	2.0	2.0	0.10	0.015	4.0	2.0
IL	PC-3-3	0.10	2.0	1.0	0.086	0.017	3.0	3.0
PITT	PC-4-1	0.045	1.0	0.24	0.086	0.0016	2.0	1.0
PITT	PC-4-2	0.048	2.0	0.34	0.090	0.0028	3.0	1.0
PITT	PC-4-3	0.052	2.0	0.28	0.097	0.0018	2.0	2.0
POC	PC-5-1	0.079	0.80	0.69	0.084	0.0016	0.83	0.60
POC	PC-5-2	0.074	0.92	0.93	0.084	0.0024	1.0	0.80
POC	PC-5-3	0.079	0.84	0.79	0.078	0.0017	0.80	0.68

Table 4. Concentration in μg/g of Eleven Elements in Argonne Premium Coals.

		V (μg/g)	Cr (μg/g)	Ni (μg/g)	Cu (μg/g)	Zn (μg/g)	Ga (μg/g)	Co (μg/g)	Ge (μg/g)	Zr (μg/g)	Ba (μg/g)	Pb (μg/g)
UF	PC-1-1	38	32	22	20	30	11	5.0	4.0	36	88	8.0
UF	PC-1-2	45	38	29	18	30	11	5.0	4.0	29	72	10
UF	PC-1-3	41	26	24	16	40	8.0	5.0	3.0	34	84	6.0
WY	PC-2-1	10	8.0	< 10	5.0	< 20	4.0	< 5.0	< 2.0	< 20	200	< 2.0
WY	PC-2-2	14	6.0	< 10	10	< 20	2.0	< 5.0	< 2.0	< 20	260	< 2.0
WY	PC-2-3	17	8.0	< 10	6.0	< 20	3.0	< 5.0	< 2.0	< 20	300	< 2.0
IL	PC-3-1	52	54	28	9.0	250	8.0	< 5.0	8.0	22	140	9.0
IL	PC-3-2	59	57	35	10	260	5.0	< 5.0	7.0	25	120	8.0
IL	PC-3-3	44	47	37	9.0	320	7.0	< 5.0	12	16	92	6.0
PITT	PC-4-1	20	23	13	5.0	20	6.0	< 5.0	3.0	23	66	4.0
PITT	PC-4-2	25	27	14	6.0	30	5.0	< 5.0	< 2.0	21	72	3.0
PITT	PC-4-3	27	21	11	7.0	30	5.0	< 5.0	< 2.0	28	60	5.0
POC	PC-5-1	16	17	11	18	< 20	4.0	5.0	< 2.0	25	400	5.0
POC	PC-5-2	21	17	11	13	< 20	3.0	5.0	< 2.0	34	460	4.0
POC	PC-5-3	18	14	< 10	27	< 20	4.0	5.0	< 2.0	32	500	5.0

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CHAPTER E

Analysis of Eight Argonne Premium Coal Samples by X-ray Fluorescence Spectrometry

by John R. Evans, George A. Sellers, Robert G. Johnson, Davison V. Vivit, and Judy Kent

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The Chemical Analysis of Argonne Premium Coal Samples

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Analysis of Eight Argonne Premium COAL Samples by X-Ray Fluorescence Spectrometry

by John R. Evans, George A. Sellers, Robert G. Johnson,
Davison V. Vivit, and Judy Kent

ABSTRACT

X-ray fluorescence spectrometric methods were used in the analysis of eight Argonne Premium Coal Samples. Trace elements (Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, La, and Ce) in both coal ash and whole coal were determined by energy-dispersive X-ray fluorescence spectrometry; major elements (Na, Mg, Al, Si, P, S, K, Ca, Ti, Mn, and Fe) in coal ash and trace elements (Cl and P) in whole coal were determined by wavelength-dispersive X-ray fluorescence spectrometry. The results of this study will be used in a geochemical database compiled for these materials from various analytical techniques. The experimental XRF methods and procedures used to determine these major and trace elements are described.

INTRODUCTION

Energy-dispersive X-ray fluorescence (EDXRF) spectrometry and wavelength-dispersive X-ray fluorescence (WDXRF) spectrometry are used routinely in the determination of major and trace elements in silicate rocks (Johnson, 1984; Norrish and Hutton, 1969); however, the analysis of whole coals by XRF spectrometric techniques is more difficult due to the problem of the very light coal matrix and the scarcity of reliable coal standards. Since coal ash is similar to silicate matrix rocks, EDXRF and WDXRF techniques developed for silicates can be used for the determination of major and trace elements in coal ash samples.

The rapidity, sensitivity, accuracy, and precision of X-ray fluorescence spectrometric methods are well documented for a wide range of geological materials (Johnson, 1984; Johnson, and others, 1986; Johnson and Fleming, 1987; Evans and Jackson, 1989; Rose, and others, 1963; Norrish and Hutton, 1969). The successful characterization of silicate matrix rocks can be similarly applied to coal ash samples, as mentioned above. Further, analysis of whole coal by XRF spectrometric techniques has also proven to be successful in many studies (Kuhn, and others, 1975; Johnson, and others, 1989). Therefore, the determinations of major and minor elements in eight Argonne Premium Coal Samples by XRF spectrometric techniques contributed an important part of the geochemical database compiled for these materials. This study was not intended to include interpretations of the differences of behavior between various coal ranks of the samples studied. Rather, it was merely to document the analytical values of the major and trace components of both the ash and whole coal.

The following sections will describe the experimental procedures used in the analysis of the eight Argonne Premium Coal Samples by both energy-dispersive and wavelength-dispersive X-ray fluorescence spectrometry.

EXPERIMENTAL

Coal Ash - EDXRF

All the Argonne Premium Coal Samples were first ashed at 525 °C. From the standpoint of differences in ashing temperature from our method and the ASTM method (750 °C), our method (525 °C) eliminated all combustible material while retaining the same or higher concentrations of volatile material. Sample preparation of coal ash samples followed procedures described in other publications (Johnson, 1984; Johnson, and others, 1986; Evans and Jackson, 1989). A Kevex 700 EDXRF spectrometer with a Kevex 8000 analyzer was used to fluoresce coal ash samples powdered to approximately 100 mesh. These powders were pressed into cups made of Mylar film (0.00025 inch) pulled tightly over an aluminum ring with a teflon collar. The resultant surface appears to be exceedingly planar.

Using appropriate secondary targets (Table 1), each sample was fluoresced and intensity measurements were determined after making background and spectral overlap corrections. The ratio of the analyte line intensity to the secondary target Compton scatter intensity was used to determine elemental concentrations. The Compton ratio method corrects for matrix effects, particle size variations, packing density variations, heterogeneity effects, instrumental fluctuations as well as other sources of error inherent in EDXRF determinations.

Table 1. Secondary targets used for EDXRF analysis

Element(s)	Secondary target
Cr	Fe
Ni, Cu, Zn	Ge
Rb, Sr, Y, Zr, Nb	Ag
Ba, La, Ce	Gd

Trace element concentrations for coal ash samples were determined from calibration graphs. Calibration graphs were constructed by plotting the intensity ratio with the known concentrations for a selected set of standard reference materials (Abbey, 1983).

Whole Coal - EDXRF

Whole coal samples were prepared similarly to those procedures described for EDXRF analyses of the coal ash (Johnson, 1984; Johnson, and others, 1986; Evans and Jackson, 1989). All intensity measurements were made on a Kevex 700 spectrometer with a Kevex 7000 analyzer. Each whole coal sample was fluoresced using a secondary target (Table 1).

Corrections for background interferences and spectral line overlaps were made before integration of the analyte line intensity.

Trace elements in whole coal samples by EDXRF were determined using inter-element influence coefficients calculated from fundamental parameters (Johnson and Fleming, 1987). Characterizations of the coal samples by other analytical techniques must be made before trace element determinations can be obtained with this method. Even though carbon, hydrogen, nitrogen, and oxygen comprise the largest percentage of the whole coal, these elements have very little bearing on absorption and enhancement effects. Major element concentrations as determined from the coal ash (see the next section, Coal Ash - WDXRF) identify the most important influences on absorption and enhancement effects. In order to generate accurate inter-element influence coefficients from the fundamental parameters algorithm, the composition of the coal matrix must be determined.

The complexities of the fundamental parameters algorithms used in this study are beyond the scope of this paper. For a detailed explanation of all equations and variables inherent in the matrix correction procedures, we direct the reader to Rousseau, 1984, Sherman, 1959, and, Johnson and Fleming, 1987.

The lack of available whole coal standards and the ultimate degradation over time of these standards are the major difficulties involved in the characterization of coals. For these reasons, it is not possible to construct calibration graphs of standard reference materials for elements of interest; therefore, we must utilize the fundamental parameters algorithm. Using this algorithm, discussed above, allows the investigator to make accurate trace element determinations in whole coal with as few as one well characterized standard. In this study, National Institute of Standards and Technology (NIST, formerly National Bureau of Standards - NBS) whole coal reference materials, NBS 1632a and NBS 1632b, were used to calculate pure element intensities.

Coal Ash - WDXRF

The fusion method was used to produce glass disks of the coal ash samples (Johnson, et al., 1989). This method eliminates the need for matrix correction routines since the significant dilution of the sample by the flux corrects for heterogeneity effects, particle size variations, and other sources of error from instrumental fluctuations. The sample/flux ratio is chosen to yield linear calibration curves over the range of concentrations found in our samples and standards, without the use of a heavy absorber, such as La_2O_3. This is due to the low final concentrations of sample components in the sample/flux mix.

A 1:9 dilution of sample to flux is obtained by mixing 0.600 grams of the coal ash with 5.400 grams of a 2:1 mixture of lithium tetraborate to lithium metaborate. This mixture is carefully transferred to a platinum - gold crucible and three drops of a 15 percent hydrobromic acid solution is added. An automatic Claisse fluxer is used to heat/mix the sample to temperatures reaching 1,200 °C for approximately 20 minutes. After cooling to room temperature, a thin glass disk with a planar analytical surface is produced which is adequate for WDXRF analysis. All elemental intensity measurements were made on a Diano XRD-8300 wavelength-dispersive X-ray fluorescence spectrometer.

Standards used in the construction of calibration graphs were silicate matrix materials selected from those tabulated by Abbey, 1983. Since the coal ash matrix closely resembles silicate materials in composition, calibration graphs obtained from silicate standard reference materials are reliable for major element determinations in coal ash. Standards are prepared for WDXRF analysis in a manner identical to that described above. Calibration graphs were constructed by plotting the analyte intensity with the known concentration for a selected set of standard reference materials for each element of interest. The intensities for the major elements in the coal ash samples were then used in the individual calibration graphs.

A set of synthetic standards was prepared for sulfur analysis since the typical silicate rock matrix does not approximate the concentrations found in the coal ash matrix. A LECO sulfur analyzer was used to determine the actual sulfur concentration in the fused "spiked" silicate standards, since some sulfur is volatilized during fusion.

Whole Coal - WDXRF

Briquettes of the whole coal samples were produced by mixing 0.500 grams of the coal with 0.500 grams of microgranular cellulose for 10 minutes on a shaker mill and subsequently pressing the mixture against a fibrous cellulose backing at 40,000 pound/in^2 for approximately 30 seconds (Johnson, and others, 1989).

The difficulties experienced in the analysis of whole coals by EDXRF also apply for WDXRF. Reliable whole coal standard reference materials are scarce. Since these standards are not commercially available, synthetic standards as well as coal samples characterized by other laboratories were used. Only three NIST coal standards were used in this study (NBS 1633, 1633a, and 1635). Spiked graphite samples with varying concentrations of chlorine and phosphorus served as the synthetic whole coal standards. All standards were prepared identically to the whole coal samples described above. All intensity measurements for chlorine and phosphorus were made on a Diano XRD-8300 wavelength-dispersive X-ray fluorescence spectrometer.

Calibration graphs were constructed by plotting the analyte intensity with the known concentration for a set of standards. The intensities for chlorine and phosphorus in the whole coal samples were then used to calculate Cl and P concentrations from the regression curves.

RESULTS AND DISCUSSION

In this study eight Argonne premium coal samples were analyzed by energy-dispersive and wavelength-dispersive X-ray fluorescence spectrometry. Determinations for major elements in the coal ash are detailed in Table 2; trace elements in coal ash in Table 3; chlorine and phosphorus in the whole coal in Table 4; and, trace elements in the whole coal in Table 5.

Table 2. Major element concentrations (wt. %) in coal ash by WDXRF (reported on an ash basis)
Note: nd= not determined

Coal sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3
UF-PC-1-1	0.3	1.0	21.6	41.9	0.1	1.0	2.4	4.1	1.0	<0.1	21.0
UF-PC-1-2	0.2	1.0	21.6	42.7	0.1	nd	2.5	4.2	1.0	<0.1	19.9
UF-PC-1-3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WY-PC-2-1	1.6	4.9	15.0	31.0	0.7	6.4	0.4	18.1	1.0	<0.1	5.6
WY-PC-2-2	1.3	5.2	14.9	31.5	0.7	9.9	0.4	18.9	1.0	<0.1	5.4
WY-PC-2-3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
IL-PC-3-1	1.1	0.9	14.1	40.2	0.1	4.0	1.5	7.8	0.7	<0.1	23.9
IL-PC-3-2	0.8	0.9	14.0	40.2	0.1	3.6	1.5	7.7	0.7	<0.1	23.8
IL-PC-3-3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PITT-PC-4-1	0.6	0.6	20.3	45.4	0.2	2.0	1.5	3.1	1.1	<0.1	22.6
PITT-PC-4-2	0.4	0.6	20.0	45.8	0.2	1.9	1.5	3.0	1.1	<0.1	22.2
PITT-PC-4-3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
POC-PC-5-1	1.9	2.1	19.6	32.7	0.1	6.6	0.7	11.7	1.2	<0.1	14.0
POC-PC-5-2	1.8	2.1	19.5	32.2	0.1	6.0	0.7	11.7	1.2	<0.1	14.1
POC-PC-5-3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
UT-PC-6-1	3.8	1.4	15.2	41.5	0.1	8.3	0.6	12.2	0.8	<0.1	9.0
UT-PC-6-2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
UT-PC-6-3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WV-PC-7-1	0.3	0.7	30.8	54.0	0.1	0.7	2.9	0.4	2.1	<0.1	2.8
WV-PC-7-2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WV-PC-7-3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
ND-PC-8-1	7.1	7.3	9.0	17.3	0.4	20.5	0.4	22.6	0.3	0.1	6.7
ND-PC-8-2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
ND-PC-8-3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

Table 3. Trace element concentrations (µg/g) in coal ash by EDXRF (reported on an ash basis)
Note: nd= not determined

Coal sample	Cr	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb	Ba	La	Ce
UF-PC-1-1	186	104	146	162	160	440	74	205	20	380	52	112
UF-PC-1-2	196	118	152	142	154	450	72	196	16	405	60	136
UF-PC-1-3	196	84	158	150	158	450	84	205	20	370	70	130
WY-PC-2-1	86	50	142	114	40	3100	40	260	14	3200	<30	72
WY-PC-2-2	96	46	158	130	40	3000	42	275	12	3300	<30	50
WY-PC-2-3	108	44	154	130	44	3100	44	265	10	3100	<30	<30
IL-PC-3-1	265	88	66	984	90	188	30	146	12	465	<30	42
IL-PC-3-2	265	122	58	737	90	178	20	130	<10	460	<30	52
IL-PC-3-3	270	120	54	750	92	188	26	136	14	455	<30	40
PITT-PC-4-1	200	98	70	92	102	760	56	225	22	370	<30	80
PITT-PC-4-2	190	96	66	92	94	740	56	230	20	410	50	108
PITT-PC-4-3	195	112	66	88	100	710	48	215	20	385	46	104
POC-PC-5-1	235	132	240	82	50	2100	134	320	16	3200	30	100
POC-PC-5-2	225	146	245	100	40	2100	126	315	16	3600	50	162
POC-PC-5-3	235	150	225	88	42	2100	130	320	16	3500	44	168
UT-PC-6-1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
UT-PC-6-2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
UT-PC-6-3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WV-PC-7-1	238	91	130	64	218	393	110	412	40	567	75	145
WV-PC-7-2	234	83	115	57	232	402	99	411	43	577	91	163
WV-PC-7-3	237	87	120	59	224	411	118	421	46	552	96	154
ND-PC-8-1	26	25	36	61	nd	6700	nd	68	<10	5000	nd	nd
ND-PC-8-2	28	17	35	54	nd	6700	nd	74	<10	4900	nd	nd
ND-PC-8-3	29	19	34	55	nd	6700	nd	47	<10	4700	nd	nd

Table 4. Chlorine and phosphorous concentrations (wt. %) in whole coal by WDXRF

Coal sample	Cl	P_2O_5
UF-PC-1-1	0.15	<0.01
UF-PC-1-2	0.14	<0.01
UF-PC-1-3	0.15	<0.01
WY-PC-2-1	<0.01	0.06
WY-PC-2-2	<0.01	0.05
WY-PC-2-3	<0.01	0.06
IL-PC-3-1	0.05	<0.01
IL-PC-3-2	0.05	<0.01
IL-PC-3-3	0.06	<0.01
PITT-PC-4-1	0.06	0.02
PITT-PC-4-2	0.06	0.02
PITT-PC-4-3	0.07	0.02

Coal sample	Cl	P_2O_5
POC-PC-5-1	0.16	<0.01
POC-PC-5-2	0.16	<0.01
POC-PC-5-3	0.16	<0.01
UT-PC-6-1	<0.01	<0.01
UT-PC-6-2	<0.01	<0.01
UT-PC-6-3	<0.01	<0.01
WV-PC-7-1	0.04	<0.01
WV-PC-7-2	0.04	<0.01
WV-PC-7-3	0.05	<0.01
ND-PC-8-1	<0.01	0.04
ND-PC-8-2	<0.01	0.04
ND-PC-8-3	<0.01	0.04

Table 5. Trace element concentrations ($\mu g/g$) in whole coal by EDXRF
Note: nd= not determined

Coal sample	Cr	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb	Ba	La	Ce
UF-PC-1-1	15	27	20	35	23	61	nd	24	nd	54	31	27
UF-PC-1-2	23	22	18	32	21	63	nd	22	nd	68	9	46
UF-PC-1-3	19	21	17	31	20	61	nd	24	nd	59	9	48
WY-PC-2-1	3	9	18	26	14	292	nd	19	nd	404	4	18
WY-PC-2-2	5	7	17	29	14	300	nd	21	nd	407	4	21
WY-PC-2-3	nd	8	17	21	11	291	nd	17	nd	415	11	35
IL-PC-3-1	29	33	15	137	22	33	nd	24	nd	112	16	23
IL-PC-3-2	36	30	13	105	17	30	nd	22	nd	122	15	39
IL-PC-3-3	41	33	15	186	21	35	nd	24	nd	129	15	64
PITT-PC-4-1	6	17	10	17	8	59	nd	15	nd	46	23	19
PITT-PC-4-2	10	11	9	14	8	61	nd	17	nd	22	1	25
PITT-PC-4-3	9	15	10	15	8	69	nd	18	nd	19	2	6
POC-PC-5-1	5	11	16	14	5	86	nd	10	nd	134	1	4
POC-PC-5-2	7	9	16	14	4	77	nd	8	nd	124	4	19
POC-PC-5-3	4	12	19	15	5	93	nd	11	nd	164	10	8
UT-PC-6-1	<10	5	8	<2	3	58	2	20	<10	28	9	20
UT-PC-6-2	<10	5	8	<2	2	65	<2	17	<10	32	9	13
UT-PC-6-3	<10	5	8	<2	3	66	<2	16	<10	28	11	12
WV-PC-7-1	50	17	30	9	43	87	19	106	13	230	15	64
WV-PC-7-2	48	18	30	10	43	87	20	102	<10	202	18	54
WV-PC-7-3	48	19	32	10	40	83	17	101	13	200	14	48
ND-PC-8-1	<10	4	8	5	4	800	<2	20	<10	1000	8	21
ND-PC-8-2	<10	10	10	4	5	802	<2	19	<10	1040	6	19
ND-PC-8-3	<10	4	10	6	3	753	<2	17	<10	1060	10	17

Coal ash samples analyzed by EDXRF and WDXRF closely approximate the precision and accuracy determined for silicates. A study by Johnson, and others, 1989 estimated an average relative difference of ±2 to ±5 percent for WDXRF determinations of major elements (Na, Mg, Al, Si, P, S, K, Ca, Ti, Mn, and Fe) in coal ash samples. Trace element determinations (Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, La, and Ce) by EDXRF for silicate rocks were estimated to have an accuracy of < ±5 percent for the ratio-calibration graph method (Johnson, 1984). This level of accuracy is also expected for EDXRF trace element determinations on the coal ash.

The precision and accuracy of the whole coal samples analyzed by EDXRF and WDXRF were more difficult to estimate since a wide range of acceptable standards was not available. However, Johnson, and others, 1989 estimated the average relative difference for chlorine and phosphorus determinations on whole coals to be ± 10 percent. Trace element (Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, La, and Ce) determinations on the whole coal by EDXRF generally show close agreement (± 10 percent) between replicate samples. However, a wide variance was noted when the whole coal trace element results were compared to the results obtained on the coal ash. Further investigation is needed to more clearly evaluate the accuracy of the matrix correction method for whole coals.

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CHAPTER F

The Determination of 29 Elements in Eight Argonne Premium Coal Samples by Instrumental Neutron Activation Analysis

by Curtis A. Palmer

U.S. GEOLOGICAL SURVEY OPEN-FILE REPORT 91-638

The Chemical Analysis of Argonne Premium Coal Samples

CONTENTS

TABLES

The Determination of 29 Elements in Eight Argonne Premium Coal Samples by Instrumental Neutron Activation Analysis

by Curtis A. Palmer

ABSTRACT

Twenty-nine elements have been determined in triplicate splits of the eight Argonne Premium Coal Samples by instrumental neutron activation analysis. Data for control samples NBS 1633 (fly ash) and NBS 1632b are also reported. The factors that could lead to errors in analysis for these samples, such as spectral overlaps, low sensitivity and multiple sources of the interfering nuclear reactors, are discussed.

INTRODUCTION

Instrumental neutron activation analysis (INAA) has been used for the determination of major, minor and trace elements in thousands of coal samples by the United States Geological Survey (eg. Zubovic and others 1979, 1980, Oman and others 1981, Currens and others, 1986, 1987) and other labs (eg. Gluskoter and others, 1977). In addition, the application of INAA for the analysis of coal has been described in several papers (eg. Block and Dams, 1973; Ondov and others, 1975; Rowe and Steinnes, 1977a, b; Swaine, 1985 and Palmer and Baedecker, 1989). The analysis of coal by INAA is especially useful because determinations are made on the whole coal in contrast to other techniques where the ash is used as the sample matrix. Therefore, INAA can be used to measure elements which might be volatilized during ashing, such as Br. All elements are determined on the same sample split so that element ratios used in understanding geochemical environments are notaffected by inhomogeneities in a coal sample. In addition, INAA has very low detection limits for many elements, can be easily automated, and provides precise data for many major, minor and trace elements.

EXPERIMENTAL

Three splits of approximately 500 mg of each of the eight Premium Coal Samples (as received) were weighed and heat sealed in 1.5 cm^3 polyethylene vials. These samples were irradiated for eight hours in the TRIGA research reactor facility of the U.S. Geological Survey in Denver, Colorado at a neutron flux of 3 x 10^{12} n cm^{-2} sec^{-1}. After a delay of 3 days to eliminate or reduce short-lived activity, the samples were shipped by overnight delivery to our counting laboratories in Reston, Virginia.

The samples were counted at three different times on high resolution coaxial Ge and Ge(Li) detectors for gamma-ray spectroscopy. The first count was started approximately four days after irradiation or as soon as the samples were received. A second count was started at 17 days after irradiation after allowing the short-lived activities (especially ^{24}Na, $t_{1/2}$ = 15 hours) to decay, and then a third count was begun approximately 2 months after irradiation to obtain higher precision on the long-lived radionuclides. The gamma-ray detectors were coupled to multichannel pulse-height analyzers which are capable of dividing the spectrum into 4096 energy increments or channels. An automatic sample changer similar to that described by Massoni and others (1973) was used to change the samples. All spectra were processed using the computer program SPECTRA (Baedecker and Grossman, 1989).

SAMPLES AND STANDARDS

The eight Argonne National Laboratory Premium Coal Samples used in this study have been described previously (Vorres, 1990). The convention for sample identification is the same as described by Palmer (1991). Three multielement standards, NBS 1632a, NBS 1633a and Eastman Kodak TEG-50-B and one control sample NBS 1633 (fly ash; different from 1633a) and NBS 1632b, were included with each irradiation. The element concentration values for the NBS standards used for analysis have been reported previously (Palmer and Baedecker, 1989) and are largely based on the results of Ondov and others (1975).

A comparison of the results of this study with literature values for the control samples is given in Table 1. The analytical errors reported for the control NBS 1632b in this study are based on counting statistics at the one sigma level. NBS certified and informational values are shown for NBS 1632b. Our control 1632b agrees with all certified values within the stated errors and generally agrees, within 10%, of the NBS information values which have no reported errors.

RESULTS AND DISCUSSION

The concentrations and their associated errors based on counting statistics for 29 elements for each of the Premium Coal Samples are shown in Table 2. Iron is the only major element (concentrations >1%) determined and Na and K are the only minor elements (concentrations <1% >0.1%) determined. All other elements are trace elements. For many elements the concentration values ranged over a factor of 5 among the eight Argonne Premium Coal Samples.

The errors reported in Table 2 are based on counting statistics only. Generally, the precision of the data based on the replicate analyses is within the counting errors for elements where the reported error is greater than 5%. For some elements with small counting errors, the analytical precision is poorer due to the other sources of error such as sample homogeneity, positioning during counting, etc.

Table 1. Comparison of concentrations determined (µg/g) from this work with literature values.

Sample	Control 1633	Literature* 1633	Control 1632B	Literature** 1632B
Na	3060 ± 64	3200 ± 400	513 ± 5	515 ± 11
K	16000 ± 640	16100 ± 1500	740 ± 37	748 ± 28
Sc	27.3 ± 0.27	27 ± 1	2.060 ± 0.02	1.9
Cr	113.4 ± 8.6	127 ± 6	10.4 ± 0.3	11
Fe	62600 ± 630	62000 ± 3000	7780 ± 160	7590 ± 450
Co	40.8 ± 2.0	41.5 ± 1.2	2.33 ± 0.04	2.29 ± 0.17
Ni	92 ± 10	98 ± 9	8.1 ± 2	6.1 ± 0.27
Zn	183 ± 9.5	216 ± 25	11.7 ± 1.4	11.89 ± 0.78
As	56.0 ± 1.6	58.0 ± 4	3.80 ± 0.11	3.73 ± 0.09
Se	9.0 ± 0.54	10.2 ± 1.4	1.24 ± 0.10	1.29 ± 0.11
Br	6.5 ± 0.32	12 ± 4	21.3 ± 1.1	17
Rb	102 ± 6.3	125 ± 10	4.2 ± 0.76	5.05 ± 0.11
Sr	1340 ± 67	1700 ± 300	97 ± 5.8	102
Sb	6.61 ± 0.2	6.9 ± 0.6	0.259 ± 0.01	0.24
Cs	7.76 ± 0.23	8.6 ± 1.1	0.414 ± 0.012	0.44
Ba	2450 ± 74	2700 ± 200	69 ± 2.8	67.5 ± 2.1
La	80.4 ± 1.6	82 ± 2	4.80 ± 0.01	5.1
Ce	139.3 ± 2.7	146 ± 15	9.19 ± 0.18	9
Nd	55 ± 7.2	57.8 ± 1.6	<12	
Sm	14.23 ± 0.3	12.4 ± 0.9	0.899 ± 0.009	0.87
Eu	2.68 ± 0.08	2.5 ± 0.4	0.176 ± 0.004	0.17
Tb	1.79 ± 0.054	1.9 ± 0.3	0.104 ± 0.003	
Yb	5.99 ± 0.18	7 ± 3	0.366 ± 0.01	
Lu	1.12 ± 0.046	1.0 ± 0.1	0.099 ± 0.004	
Hf	7.12 ± 0.21	7.9 ± 0.4	0.410 ± 0.002	0.43
Ta	2.03 ± 0.06	1.8 ± 0.3	0.194 ± 0.03	
W	4.93 ± 0.25	4.6 ± 1.6	0.52 ± 0.05	0.48
Th	23.1 ± 0.46	24.8 ± 2.2	1.321 ± 0.026	1.342 ± 0.036
U	10.7 ± 0.9	12.0 ± 0.5	0.42 ± 0.05	0.436 ± 0.012

blank -- No values available from listed source

* Values taken from Ondov and others (1975)

** Values taken from NBS 1632B Certificate. Values with no error listed are NBS information values; all others are NBS certified values

Table 2. Concentration in µg/g of 29 elements in Argonne Premium Coal Samples. Errors are based on one sigma counting statistics only.

Sample	UF PC-1-1	UF PC-1-2	UF PC-1-3	WY PC-2-1	WY PC-2-2	WY PC-2-3	IL PC-3-1	IL PC-3-2	IL PC-3-3
Na	336. ± 2%	343. ± 2%	342. ± 3%	1140. ± 2%	1170. ± 2%	1130. ± 2%	1030. ± 2%	1010. ± 2%	1030. ± 2%
K	2640. ± 4%	2620. ± 4%	2800. ± 5%	268. ± 10%	340. ± 11%	270. ± 17%	1990. ± 4%	1860. ± 5%	1990. ± 6%
Sc	4.04 ± 1%	4.01 ± 1%	4.14 ± 1%	1.67 ± 2%	1.69 ± 2%	1.67 ± 1%	2.55 ± 1%	2.57 ± 1%	2.64 ± 1%
Cr	20.4 ± 3%	20.3 ± 3%	20.4 ± 5%	5.7 ± 6%	6.22 ± 4%	6.23 ± 4%	33.7 ± 2%	32.5 ± 3%	33.2 ± 2%
Fe	17600 ± 1%	18100 ± 1%	17900 ± 1%	3810. ± 2%	3790. ± 2%	3390. ± 2%	26600 ± 1%	26700 ± 1%	26800 ± 2%
Co	5.27 ± 2%	5.41 ± 2%	5.31 ± 2%	1.66 ± 3%	1.73 ± 2%	1.65 ± 2%	4.21 ± 6%	4.21 ± 6%	4.53 ± 2%
Ni	15.9 ± 16%	13.2 ± 18%	14.3 ± 19%	4.4 ± 29%	5.4 ± 24%	5.0 ± 24%	24.2 ± 11%	17.8 ± 13%	21.0 ± 12%
Zn	18.2 ± 8%	17.0 ± 14%	23.9 ± 5%	11.0 ± 4%	11.6 ± 5%	11.2 ± 9%	218. ± 2%	243. ± 3%	200. ± 2%
As	16.6 ± 3%	17.6 ± 3%	17.1 ± 3%	3.67 ± 3%	3.23 ± 3%	3.75 ± 3%	4.46 ± 4%	4.65 ± 4%	4.90 ± 3%
Se	2.09 ± 8%	1.88 ± 7%	1.8 ± 22%	1.57 ± 11%	1.49 ± 8%	1.63 ± 6%	3.78 ± 4%	4.03 ± 5%	5.07 ± 4%
Br	66. ± 8%	65. ± 8%	66. ± 8%	2.96 ± 8%	2.88 ± 8%	2.79 ± 8%	6.6 ± 8%	6.5 ± 8%	6.8 ± 8%
Rb	19.4 ± 8%	19.0 ± 8%	20.0 ± 8%	<5.	<5.	<5.	15.5 ± 14%	17.2 ± 11%	14.6 ± 11%
Sr	56. ± 16%	58. ± 19%	33. ± 22%	263. ± 5%	248. ± 5%	245. ± 5%	42. ± 29%	36. ± 22%	40. ± 18%
Sb	0.558 ± 5%	0.50 ± 8%	0.535 ± 5%	0.180 ± 6%	0.203 ± 5%	0.191 ± 5%	0.848 ± 3%	0.913 ± 3%	0.870 ± 3%
Cs	1.48 ± 3%	1.52 ± 3%	1.56 ± 3%	0.163 ± 7%	0.173 ± 12%	0.160 ± 11%	1.14 ± 4%	1.12 ± 3%	1.15 ± 3%
Ba	52. ± 14%	68. ± 11%	63. ± 15%	324. ± 3%	318. ± 3%	297. ± 3%	94. ± 7%	91. ± 7%	96. ± 7%
La	10.0 ± 2%	10.0 ± 2%	10.3 ± 3%	5.32 ± 3%	5.34 ± 3%	5.38 ± 3%	6.11 ± 3%	6.10 ± 3%	6.09 ± 3%
Ce	18.1 ± 3%	18.2 ± 3%	18.7 ± 2%	9.07 ± 3%	9.5 ± 5%	9.6 ± 5%	12.5 ± 3%	12.5 ± 3%	12.8 ± 3%
Nd	<20.	<18.	8.0 ± 29%	<13.	<11.	<9.	<10.	<8.	<11.
Sm	1.98 ± 2%	1.94 ± 2%	2.00 ± 2%	0.968 ± 2%	0.988 ± 2%	0.977 ± 2%	1.19 ± 4%	1.183 ± 2%	1.22 ± 3%
Eu	0.389 ± 3%	0.399 ± 3%	0.406 ± 6%	0.201 ± 4%	0.199 ± 4%	0.195 ± 6%	0.229 ± 3%	0.222 ± 5%	0.227 ± 4%
Tb	0.275 ± 5%	0.252 ± 4%	0.260 ± 4%	0.122 ± 7%	0.122 ± 4%	0.115 ± 5%	0.147 ± 5%	0.131 ± 5%	0.136 ± 5%
Yb	0.91 ± 4%	0.84 ± 5%	0.90 ± 4%	0.42 ± 8%	0.443 ± 5%	0.40 ± 8%	0.51 ± 7%	0.511 ± 5%	0.551 ± 5%
Lu	0.227 ± 5%	0.213 ± 5%	0.220 ± 5%	0.101 ± 5%	0.103 ± 5%	0.098 ± 5%	0.140 ± 12%	0.131 ± 8%	0.136 ± 10%
Hf	0.647 ± 4%	0.660 ± 4%	0.67 ± 9%	0.621 ± 3%	0.622 ± 3%	0.560 ± 5%	0.54 ± 8%	0.532 ± 4%	0.578 ± 4%
Ta	0.207 ± 5%	0.224 ± 5%	0.227 ± 5%	0.141 ± 5%	0.155 ± 5%	0.142 ± 7%	0.188 ± 5%	0.197 ± 5%	0.189 ± 6%
W	1.00 ± 6%	1.09 ± 7%	1.09 ± 8%	0.38 ± 10%	0.36 ± 12%	0.40 ± 12%	1.53 ± 5%	1.52 ± 6%	1.50 ± 6%
Th	2.59 ± 2%	2.64 ± 2%	1.547 ± 2%	1.56 ± 3%	1.58 ± 3%	2.01 ± 2%	1.95 ± 2%	1.95 ± 2%	1.99 ± 3%
U	0.81 ± 8%	0.81 ± 8%	0.86 ± 9%	0.55 ± 10%	0.54 ± 9%	0.52 ± 8%	4.46 ± 4%	4.06 ± 4%	4.28 ± 4%

Table 2. (Continued)

Sample:	PITT PC-4-1	PITT PC-4-2	PITT PC-4-3	POC PC-5-1	POC PC-5-2	POC PC-5-3	UT PC-6-1	UT PC-6-2	UT PC-6-3
Na	343. ± 2%	343. ± 3%	344. ± 3%	797. ± 2%	773. ± 2%	778. ± 2%	1485. ± 2%	1472. ± 2%	1425. ± 2%
K	1090. ± 5%	1120. ± 6%	1090. ± 7%	284. ± 11%	260. ± 14%	330. ± 15%	180. ± 25%	<250.	252. ± 12%
Sc	2.61 ± 2%	2.56 ± 1%	2.55 ± 1%	1.80 ± 2%	1.79 ± 2%	1.77 ± 1%	0.832 ± 2%	0.801 ± 1%	0.805 ± 2%
Cr	15.0 ± 3%	15.0 ± 3%	14.5 ± 3%	9.3 ± 4%	9.06 ± 3%	8.85 ± 3%	5.25 ± 4%	5.03 ± 4%	5.62 ± 3%
Fe	13600 ± 2%	13400 ± 2%	13300 ± 2%	5040. ± 2%	5210. ± 2%	5020. ± 2%	3270. ± 2%	3100. ± 2%	3150. ± 2%
Co	2.65 ± 3%	2.61 ± 4%	2.60 ± 6%	4.09 ± 2%	4.13 ± 2%	3.98 ± 2%	1.01 ± 2%	0.992 ± 3%	1.00 ± 2%
Ni	9.4 ± 21%	11.3 ± 17%	<12.	9.2 ± 17%	8.5 ± 19%	8.2 ± 19%	<3.	3.6 ± 32%	3.7 ± 26%
Zn	8.9 ± 4%	7.8 ± 7%	10.5 ± 12%	5.74 ± 5%	6.15 ± 5%	7.3 ± 5%	4.80 ± 5%	7.43 ± 4%	6.82 ± 4%
As	8.44 ± 3%	8.30 ± 3%	8.5 ± 4%	10.43 ± 3%	10.6 ± 3%	9.89 ± 3%	0.51 ± 7%	0.50 ± 9%	0.44 ± 8%
Se	1.49 ± 7%	1.60 ± 7%	1.34 ± 7%	2.3 ± 28%	2.5 ± 18%	2.60 ± 11%	1.03 ± 10%	1.16 ± 10%	1.03 ± 8%
Br	15.7 ± 8%	15.5 ± 8%	15.5 ± 8%	50. ± 8%	50. ± 8%	49. ± 8%	1.14 ± 5%	1.06 ± 5%	1.05 ± 5%
Rb	9.0 ± 16%	7.2 ± 16%	7.1 ± 16%	<6.	<6.	<3.	<2.	1.00 ± 22%	0.95 ± 25%
Sr	58. ± 12%	61. ± 22%	65. ± 19%	97. ± 23%	116. ± 7%	101. ± 11%	71. ± 7%	68. ± 8%	70. ± 8%
Sb	0.239 ± 6%	0.240 ± 5%	0.221 ± 6%	0.625 ± 4%	0.458 ± 4%	0.535 ± 4%	0.118 ± 7%	0.098 ± 9%	0.106 ± 8%
Cs	0.737 ± 4%	0.69 ± 9%	0.67 ± 8%	0.256 ± 5%	0.283 ± 7%	0.247 ± 11%	0.123 ± 6%	0.148 ± 6%	0.119 ± 11%
Ba	44. ± 13%	51. ± 11%	44. ± 12%	197. ± 5%	203. ± 5%	193. ± 4%	35.7 ± 8%	38.1 ± 8%	47. ± 7%
La	6.19 ± 3%	6.15 ± 3%	6.11 ± 3%	6.78 ± 3%	6.77 ± 3%	6.73 ± 3%	3.41 ± 3%	3.27 ± 3%	3.24 ± 3%
Ce	11.5 ± 3%	11.5 ± 5%	11.1 ± 3%	11.6 ± 3%	11.8 ± 3%	11.5 ± 3%	4.88 ± 3%	4.67 ± 3%	4.84 ± 3%
Nd	<12.	<8	<10.	<18.	<16.	<14.	<3.	2.5 ± 16%	1.6 ± 26%
Sm	1.100 ± 2%	1.09 ± 2%	1.09 ± 2%	1.23 ± 2%	1.21 ± 2%	1.21 ± 2%	0.517 ± 3%	0.500 ± 3%	0.507 ± 3%
Eu	0.221 ± 4%	0.214 ± 4%	0.208 ± 6%	0.243 ± 4%	0.241 ± 4%	0.218 ± 10%	0.100 ± 6%	0.098 ± 5%	0.098 ± 4%
Tb	0.133 ± 5%	0.131 ± 10%	0.132 ± 8%	0.158 ± 6%	0.173 ± 4%	0.169 ± 4%	0.065 ± 5%	0.054 ± 5%	0.054 ± 5%
Yb	0.478 ± 5%	0.463 ± 5%	0.468 ± 5%	0.555 ± 5%	0.56 ± 10%	0.545 ± 5%	0.204 ± 7%	0.198 ± 15%	0.21 ± 18%
Lu	0.121 ± 6%	0.117 ± 10%	0.120 ± 5%	0.132 ± 5%	0.142 ± 5%	0.132 ± 5%	0.036 ± 9%	0.026 ± 11%	0.029 ± 7%
Hf	0.518 ± 4%	0.49 ± 8%	0.500 ± 4%	0.441 ± 6%	0.429 ± 4%	0.444 ± 4%	0.478 ± 3%	0.499 ± 5%	0.458 ± 3%
Ta	0.168 ± 5%	0.163 ± 5%	0.165 ± 5%	0.117 ± 12%	0.108 ± 8%	0.123 ± 6%	0.060 ± 7%	0.065 ± 7%	0.061 ± 6%
W	0.79 ± 6%	0.80 ± 8%	0.76 ± 8%	0.84 ± 7%	0.91 ± 8%	0.77 ± 8%	0.42 ± 10%	0.40 ± 11%	0.38 ± 9%
Th	1.53 ± 3%	1.46 ± 3%	1.44 ± 3%	1.19 ± 3%	1.12 ± 8%	1.17 ± 3%	0.609 ± 3%	0.614 ± 3%	0.622 ± 3%
U	0.36 ± 13%	0.37 ± 10%	0.45 ± 11%	0.47 ± 16%	0.51 ± 13%	0.55 ± 13%	0.76 ± 8%	0.70 ± 8%	0.76 ± 9%

Table 2. (Continued)

Sample:	WV PC-7-1	WV PC-7-2	WV PC-7-3	ND PC-8-1	ND PC-8-2	ND PC-8-3
Na	460. ± 10%	351. ± 3%	352. ± 2%	5400. ± 2%	5330 ± 3%	5150. ± 2%
K	5170. ± 3%	4970. ± 6%	5000. ± 4%	280. ± 28%	<400	300. ± 16%
Sc	7.69 ± 1%	7.54 ± 1%	7.61 ± 1%	0.846 ± 2%	0.828 ± 2%	0.865 ± 3%
Cr	36.2 ± 1%	35.6 ± 2%	35.7 ± 2%	2.23 ± 5%	2.16 ± 5%	2.33 ± 5%
Fe	4040. ± 3%	3840. ± 2%	4080. ± 2%	5530. ± 2%	5290. ± 2%	5630. ± 4%
Co	7.65 ± 2%	7.91 ± 2%	7.72 ± 3%	0.771 ± 3%	0.761 ± 3%	0.802 ± 3%
Ni	13.0 ± 20%	18. ± 20%	13.1 ± 19%	<6.	<3.	<3.
Zn	14.0 ± 4%	12.5 ± 4%	14.0 ± 4%	5.71 ± 5%	5.5 ± 7%	5.86 ± 5%
As	5.8 ± 12%	5.29 ± 3%	7.40 ± 3%	2.67 ± 4%	2.61 ± 4%	2.61 ± 4%
Se	5.3 ± 7%	5.54 ± 5%	5.5 ± 6%	0.51 ± 18%	0.61 ± 15%	0.63 ± 14%
Br	16.9 ± 2%	16.9 ± 3%	16.9 ± 3%	1.49 ± 6%	1.34 ± 6%	1.43 ± 6%
Rb	29.8 ± 3%	28.5 ± 3%	31.2 ± 4%	0.36 ± 30%	0.99 ± 26%	<1.
Sr	60. ± 11%	73. ± 19%	58. ± 17%	628. ± 4%	580. ± 9%	583. ± 5%
Sb	0.521 ± 2%	0.540 ± 3%	0.502 ± 4%	0.148 ± 7%	0.155 ± 8%	0.158 ± 9%
Cs	1.88 ± 2%	1.87 ± 2%	1.84 ± 3%	0.072 ± 10%	0.097 ± 23%	0.089 ± 9%
Ba	166. ± 11%	116. ± 5%	116. ± 6%	699. ± 4%	660. ± 4%	671. ± 3%
La	21.7 ± 2%	21.6 ± 2%	21.3 ± 2%	2.79 ± 3%	2.84 ± 3%	2.84 ± 3%
Ce	36.0 ± 2%	35.2 ± 3%	36.1 ± 2%	4.34 ± 3%	4.33 ± 3%	4.68 ± 5%
Nd	12.4 ± 8%	11.0 ± 7%	12.4 ± 9%	<3.	2.1 ± 25%	2.5 ± 22%
Sm	3.56 ± 2%	3.50 ± 2%	3.51 ± 2%	0.420 ± 3%	0.419 ± 3%	0.388 ± 3%
Eu	0.674 ± 2%	0.651 ± 2%	0.697 ± 4%	0.079 ± 4%	0.077 ± 4%	0.087 ± 4%
Tb	0.408 ± 2%	0.390 ± 2%	0.402 ± 3%	0.052 ± 9%	0.052 ± 15%	0.063 ± 7%
Yb	1.69 ± 3%	1.61 ± 7%	1.52 ± 5%	0.317 ± 9%	0.298 ± 10%	0.245 ± 6%
Lu	0.202 ± 3%	0.194 ± 5%	0.191 ± 6%	0.039 ± 13%	0.035 ± 9%	0.035 ± 8%
Hf	1.88 ± 2%	1.80 ± 2%	1.80 ± 2%	0.342 ± 4%	0.341 ± 3%	0.340 ± 4%
Ta	0.675 ± 2%	0.617 ± 3%	0.630 ± 5%	0.095 ± 6%	0.088 ± 5%	0.095 ± 5%
W	1.33 ± 7%	1.19 ± 8%	2.53 ± 4%	0.38 ± 17%	0.25 ± 31%	0.43 ± 13%
Th	6.49 ± 2%	6.26 ± 3%	6.49 ± 3%	1.057 ± 2%	1.027 ± 2%	1.113 ± 2%
U	1.67 ± 5%	1.60 ± 7%	1.64 ± 8%	0.52 ± 16%	0.46 ± 1%	<0.2

The half-lives, gamma-ray lines, detection limits and potential interferences for the indicator radionuclides of the elements determined in this study are given in Table 3. Errors reported in Table 2 were generally less than 10% except for Ni, Rb, and Nd, where the concentration was near or below the detection limit for all samples. Errors were also greater than 10% for Ba in UF PC-1, U in PITT PC-4, POC PC-5, and ND PC-8, and Yb in UT PC-6 (Table 2). Errors reported for K are variable even at the same concentration because it has the shortest half-life of the elements determined in this study and the detection limit varies by nearly an order of magnitude during the two-day counting cycle for the entire sample set.

Table 3. Long-lived (>10h) radionuclides (Table modified from Palmer and Baedecker, 1989)

Element	Indicator Radionuclide	Half-life	Preferred gamma Y-energy	Limit of Determination µg/g except % as indicated	Potential Spectral Interferences Radio-nuclide	Energy	Radio-nuclide	Energy
Na	^{24}Na	15.0 h	1368.9	10				
			2753.9					
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	50	^{182}Ta	1289.1		
			1291.5	75				
Co	^{60}Co	5.3 yr	1173.2	0.2				
			1332.5					
Ni	^{58}Co	71.3 d	810.8	0.55	^{152}Eu	810.8		
Zn	^{65}Zn	245 d	1115.4	1	^{160}Tb	1115.1		
As	^{76}As	26.4 h	559.0	0.1				
Se	^{75}Se	120.0 d	264.6	1	^{182}Ta	264.1		
Br	^{82}Br	35.4 h	554.3	0.5				
			776.5	0.5				
Rb	^{86}Rb	18.7 d	1076.8	5				
Sr	^{85}Sr	64.0 d	514.0	50				
Sb	^{122}Sb	67.2 h	564.0	0.05				
	^{124}Sb	60.0 d	1691.0	0.1				
Cs	^{134}Cs	2.1 yr	795.8	0.1				
Ba	^{171}Ba	12.0 d	476.3	50				
La	^{140}La	40.2 h	1596.6	0.02				
			487.0	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	0.04				
			1408.1	0.01				
Tb	^{160}Tb	72.1 d	298.6	0.05	^{233}Pa	299.9		
			1178.1	0.1				
Yb	^{175}Yb	101.0 h	396.1	0.1	^{147}Nd	398.2	^{233}Pa	398.2
			282.6	0.2				
Lu	^{177}Lu	6.7 d	208.4	0.01	^{239}Np	209.7		
Hf	^{181}Hf	42.5 d	482.2	0.1				
			133.1	0.05				
Ta	^{182}Ta	115.1 d	1221.3	0.02				
			1189.2	0.03				
W	^{187}W	24.0 h	479.5	0.1				
			685.7	0.1	^{147}Nd	685.9		
Th	^{233}Pa	27.0 d	311.9	0.1				
U	^{239}Np	2.3 d	277.6	0.5				

The concentrations reported for Ni, in WY PC-2 and UT PC-6, and for Rb, in UT PC-6 and ND PC-8, Table 2 are actually below the detection limits given in Table 3 because the values in Table 3 are determined for a "typical" coal matrix. The detection limits for individual coal samples may vary because of variations in the concentrations of the most sensitive elements that dominate the gamma-ray spectrum and to variations in the intensities of spectral interferences. The percent correction of each spectral interference for all premium coals are given in Table 4. Generally only a small correction is needed for most elements, however, some elements, such as Ni, Se, and Sm in some samples, require changes larger than 10%. In addition to corrections made due to spectral interferences, Ba and the light rare earth elements (La, Ce, Nd, and Sm) were corrected for interference due to neutron-induced fission of ^{235}U. Table 5 shows the percent correction for Ba and the light rare earth elements La, Ce, Nd, and Sm. The fission correction factors in μg of element per μg of U for Ce, Nd, and Sm are also given. However, corrections for Ba and La are time dependent and therefore vary during the counting of the samples. The concentration of Ba, Ba_{corr}, (corrected for the time dependent fission correction factor) was calculated using the formula reported by Palmer and Baedecker (1989):

$$Ba_{corr} = Ba_{meas} - 2.9Ue^{0.0402t}$$

and the concentration of La, La_{corr}, (corrected for the time dependent fission correction factor) was calculated using:

$$La_{corr} = La_{meas} - 0.002723Ue^{0.3592t}$$

where t= time after bombardment in days, Ba_{meas} and La_{meas} are the uncorrected Ba and La concentrations and U is the concentration of uranium. The constant 0.002723 in the La equation is calculated assuming a ^{235}U cross section of 580 barns which agrees with the experimental data within ±1%. The half-lives for ^{131}Ba and ^{239}Np (U) and ^{140}La were taken from Table 3. The half life of ^{140}Ba, which decays to the measured ^{140}La, was assumed to be 12.8 days. The fission correction factors are generally quite small except for Ba and Ce in IL PC-3 which are about 16 and 8 percent respectively, and for Ba and Nd in UT PC-6 which have correction factors as high as 9 and 7 percent, respectively.

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Table 4. Percent corrections made for spectral interferences on counts with the lowest errors. (--- indicates no correction was made; <0.1 indicates an extremely small correction was made).

	Cr	Fe	Ni	Zn	Se	Ce	Sm	Yb	Lu	W
Interfering Radio-nuclide(s)	^{177}Lu ^{147}Nd	^{182}Ta	^{152}Eu	^{160}Tb	^{182}Ta	^{154}Eu	^{239}Np	^{147}Nd ^{233}Pa	^{239}Np	^{147}Nd
UF PC-1-1	2.1	<0.1	8.9	3.5	12.7	---	4.3	1.0	4.1	---
UF PC-1-2	2.7	<0.1	11.1	3.7	14.7	0.3	4.7	---	3.3	---
UF PC-1-3	2.2	<0.1	11.4	2.7	16.1	0.3	4.5	---	1.2	1.3
WY PC-2-1	5.3	0.1	15.5	2.8	14.0	0.5	5.4	1.3	4.8	---
WY PC-2-2	4.6	0.2	13.3	2.7	13.2	0.4	5.0	---	5.1	---
WY PC-2-3	4.5	0.2	13.9	2.5	12.0	---	5.7	---	6.1	---
IL PC-3-1	1.0	<0.1	3.8	0.2	8.1	---	26.9	1.4	---	0.8
IL PC-3-2	1.3	<0.1	5.1	0.2	8.4	---	26.2	1.4	---	0.8
IL PC-3-3	1.3	<0.1	4.6	0.2	5.9	---	26.8	1.7	---	---
PITT PC-4-1	2.2	<0.1	9.3	4.0	14.2	0.5	3.7	1.2	4.6	---
PITT PC-4-2	2.3	<0.1	7.5	4.4	12.2	0.6	3.8	---	2.8	1.2
PITT PC-4-3	0.6	<0.1	6.6	3.5	16.2	---	4.2	---	4.1	---
POC PC-5-1	4.4	0.1	9.3	6.6	8.1	---	3.4	0.9	3.2	---
POC PC-5-2	2.0	---	10.4	6.6	6.6	0.4	4.2	---	3.1	---
POC PC-5-3	1.0	---	10.4	5.3	8.6	0.4	3.9	0.8	3.1	---
UT PC-6-1	0.3	0.1	13.5	2.9	9.9	---	9.5	0.4	2.6	---
UT PC-6-2	2.3	0.1	10.3	1.7	11.7	---	9.3	0.6	1.3	2.2
UT PC-6-3	1.4	0.1	12.3	1.9	11.2	---	10.1	0.3	---	---
WV PC-7-1	1.4	0.4	15.1	6.1	14.2	0.3	3.6	0.6	---	2.6
WV PC-7-2	1.5	0.5	13.4	6.1	13.8	0.3	3.6	0.6	---	2.1
WV PC-7-3	1.6	0.5	16.0	6.6	12.4	0.3	2.0	0.6	---	0.7
ND PC-8-1	4.3	<0.1	10.0	2.5	26.9	---	8.0	0.4	---	---
ND PC-8-2	4.4	0.1	9.5	2.0	25.2	---	8.2	0.5	---	---
ND PC-8-3	4.5	<0.1	9.3	2.5	15.5	---	13.2	0.5	---	---

Note: No corrections were required for spectral interference of the ^{160}Tb by the ^{233}Pa line in any of these samples

Table 5. Percent corrections made for fission product interferences. (--- indicates no correction was made; <0.1 indicates a correction of less than 0.1 percent was made).

		^{131}Ba	^{140}La	^{141}Ce	^{147}Nd	^{153}Sm
Apparent concentration of element in µg/g per µg/g of U		*	*	0.27	0.17	0.00008
UF	PC-1-1	6.6	0.1	1.2	0.7**	<0.1
UF	PC-1-2	4.3	0.1	1.2	0.8**	<0.1
UF	PC-1-3	3.7	0.1	1.2	0.4	<0.1
WY	PC-2-1	0.6	0.1	1.6	0.7**	<0.1
WY	PC-2-2	0.6	0.2	1.5	0.8**	<0.1
WY	PC-2-3	0.6	0.2	1.5	1.0**	<0.1
IL	PC-3-1	17.2	0.9	8.6	6.8**	<0.1
IL	PC-3-2	15.6	1.0	8.0	7.0**	<0.1
IL	PC-3-3	16.0	1.2	8.1	6.4**	<0.1
PITT	PC-4-1	3.4	0.1	0.8	0.6**	<0.1
PITT	PC-4-2	2.6	0.1	0.9	0.8**	<0.1
PITT	PC-4-3	4.5	0.1	1.1	0.6**	<0.1
POC	PC-5-1	0.9	0.1	1.1	0.4**	<0.1
POC	PC-5-2	0.9	0.1	1.2	0.5**	<0.1
POC	PC-5-3	1.0	0.2	1.3	0.6**	<0.1
UT	PC-6-1	9.1	0.4	4.0	4.0**	<0.1
UT	PC-6-2	5.8	0.5	3.8	4.4	<0.1
UT	PC-6-3	5.9	0.3	4.0	7.0	<0.1
WV	PC-7-1	2.8	0.1	1.3	2.2	<0.1
WV	PC-7-2	4.3	0.2	1.2	2.5	<0.1
WV	PC-7-3	4.9	0.1	1.2	2.2	<0.1
ND	PC-8-1	0.2	0.4	3.1	2.9**	<0.1
ND	PC-8-2	0.2	0.3	2.9	3.7	<0.1
ND	PC-8-3	---	---	---	---	---

* Apparent concentration of element in µg/g per µg/g of U is time dependent.

** Correction made on upper limit value.

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CHAPTER G

The Determination of Selected Elements in Whole Coal and in Coal Ash from the Eight Argonne Premium Coal Samples by Atomic Absorption Spectrometry, Atomic Emission Spectrometry, and Ion-selective Electrode

by Michael W. Doughten and Judy R. Gillison

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The Chemical Analysis of Argonne Premium Coal Samples

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The Determination of Selected Elements in Whole Coal and in Coal Ash from the Eight Argonne Premium Coal Samples by Atomic Absorption Spectrometry, Atomic Emission Spectrometry, and Ion-selective Electrode

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ABSTRACT

Methods for the determination of twenty-four elements in whole coal and coal ash by inductively coupled argon plasma-atomic emission spectrometry, flame, graphite furnace, and cold vapor atomic absorption spectrometry, and by ion selective electrode are described. Coal ashes were analyzed in triplicate to determine the precision of the methods. Results of the analyses of NBS standard reference materials 1633, 1633a, 1632a, and 1635 are reported. Accuracy of the methods is determined by comparison of the analysis of standard reference materials to their certified values as well as to other values in the literature.

INTRODUCTION

Procedures are described and results are presented for the determination of twenty-two elements in the coal ashes and elements in whole coal fractions from eight Argonne Premium Coal Samples by inductively coupled argon plasma-atomic emission spectrometry (ICAP-AES), atomic absorption spectrometry (AAS), and ion selective electrode (ISE). Results of the analyses of two standard reference materials from the National Institute of Standards and Technology (formerly the National Bureau of Standards, NBS), SRM 1633and SRM 1633a (coal fly ashes), are included for ICAP-AES and AAS analyses and compared with their certified values as well as with other values reported in the literature. Cadmium and lead are determined by graphite furnace atomic absorption spectrometry (GFAAS); cobalt and lithium are determined by flame atomic absorption spectrometry (FAAS). All other elements are determined by inductively coupled argon plasma-atomic emission spectrometry (ICAP-AES).

Fluorine is determined as fluoride by ISE and mercury is determined by cold vapor AAS on the whole coals. Results of the analyses of NBS SRM 1632a and an "in house" standard (24D) are included for cold vapor AAS analysis. Results of analysis of NBS 1635 are included for ISE analysis. The precision of all methods is determined from the standard deviation of replicate analyses.

SAMPLE PREPARATION

The raw coal samples are first ashed by weighing 70 g of coal into a previously weighed porcelain crucible. The crucible is placed in an electric furnace which is slowly heated to 200°C. After 1.5 hours at 200°C the temperature is increased to 350°C and is held at that temperature for 2 hours. The temperature is then increased to 525°C and maintained for about 36 hours. After cooling for 1-2 hours the weight of the ash is determined by subtracting the weight of the crucible from the weight of the crucible plus ash. Ash content is reported as percent ash and is calculated by:

$$\text{Percent ash} = \frac{\text{(weight ash)}}{\text{(weight coal)}} \text{ X } 100$$

Sample solutions for analysis by ICAP-AES and AAS are prepared by weighing 100 mg of the coal ash and placing it in a 75-mL Teflon screw cap bomb, then adding 7 mL of concentrated nitric acid. The bomb is capped and heated on a hotplate overnight at 200°C. After cooling, the bomb is uncapped and 2 mL of concentrated nitric acid, 2 mL of concentrated perchloric acid, and 10 mL of hydrofluoric acid are added. All acids used are reagent grade. The bomb is then recapped and again heated on a hotplate at 200°C for 4 hours. The bomb is uncapped and the sample evaporated to dryness. The sample is allowed to cool and 10 mL of 2N hydrochloric acid is added. The bomb is recapped once again. The sample is gently heated until the solution is clear and the dissolution is complete. The solution is then transferred to a 15-mL polyethylene tube. Using this digestion procedure the concentration of the coal ash in solution is 1 percent.

SAMPLE ANALYSIS

The determinations of barium, beryllium, chromium, copper, manganese, nickel, strontium, vanadium, yttrium, zinc, potassium, phosphorous, and titanium are made directly on this solution by ICAP-AES using a Jarrel-Ash model 1160 Atomcomp ICP system. Cobalt and lithium are determined on this solution by flame AAS using a Perkin-Elmer model 5000 atomic absorption spectrometer. A deuterium arc lamp background corrector is used for cobalt. Lithium requires no background correction. Concentrations for cobalt and lithium are calculated from a calibration curve (absorbance vs. concentration (μg/g)) established by analyzing a set of cobalt and lithium standard solutions. The sample solution is diluted 1 to 10 with 2N hydrochloric acid and analyzed for sodium and magnesium by ICAP-AES. Cadmium is determined on this solution using a Perkin-Elmer atomic absorption spectrometer with a graphite furnace assembly (model HGA 500) and a Zeeman background correction system. Lead is determined on this solution using a Perkin-Elmer model 603 atomic absorption spectrometer with a graphite furnace assembly (model HGA 2100) and a deuterium arc lamp background correction system. A 2% solution of $NH_4H_2PO_4$ (see Table 1) is used as a matrix modifier for both cadmium and lead. Concentrations for cadmium and lead are calculated from a calibration curve (absorbance vs. concentration (μg/g)) established from analyzing a set of cadmium and lead standard solutions. This diluted solution is further diluted to 1 to 100 with 2N hydrochloric acid and analyzed for aluminum, calcium, and iron by ICAP-AES.

Table 1. Graphite Furnace AAS Operating Conditions.

	Cd	Pb
Wavelength (nm)	228.8	283.3
Bandpass (nm)	0.7	0.7
Source Lamp	Hollow Cathode	Hollow Cathode
Graphite Tube	uncoated	uncoated
Sample Size	20 μL	10 μL
Matrix Modifier ($NH_4H_2PO_4$)	10 μL	10 μL
Drying Temperature	110°C	110°C
Drying Time -ramp	10 sec	0 sec
-hold	30 sec	30 sec
Charring Temperature	250°C	950°C
Charring Time -ramp	5 sec	0 sec
-hold	25 sec	20 sec
Atomizing Temperature	2300°C	2700°C
Atomizing Time -ramp	0 sec	0 sec
-hold	5 sec	5 sec
Background Correction	Zeeman	Deuterium
Calibration Standard		
Concentration Range	0-4 ng/mL	0-0.2 μg/mL
Lower Limit	0.2 ng/mL	0.01 μg/mL

All calibration solutions for AAS and AES are made in 2N hydrochloric acid. Instrumental operating parameters for GFAAS and FAAS are listed in Tables 1 and 2. ICAP-AES wavelengths and concentration ranges are listed in Table 3. Data for trace and major element analyses are listed in Tables 4 and 5.

Table 2. Flame AAS Operating Conditions.

	Co	Li
Wavelength (nm)	240.7	670.8
Bandpass (nm)	0.7	0.4
Source Lamp	Hollow Cathode	Hollow Cathode
Background Correction	Deuterium	none
Calibration Standards		
Concentration Range	0-5 μg/mL	0-2 μg/mL
Lower Limit	0.1 μg/mL	0.1 μg/mL

Flame is fuel lean air-acetylene.

Table 3. ICAP-AES Wavelengths, Calibration Ranges, and Detection Limits

Element	Wavelength (nm)	Calibration Range[a]	Limit of Detection
Al	308.2	0- 20 μg/mL	0.5 μg/mL
Ba	455.4	0- 20 μg/mL	0.5 μg/mL
Be	313.0	0- 1 μg/mL	0.1 μg/mL
Ca	317.9	0- 10 μg/mL	0.5 μg/mL
Fe	259.9	0- 20 μg/mL	0.5 μg/mL
K	766.5	0-200 μg/mL	10 μg/mL
Mg	280.2	0- 10 μg/mL	0.5 μg/mL
Mn	257.6	0- 10 μg/mL	0.5 μg/mL
Na	589.0	0- 10 μg/mL	0.5 μg/mL
Ni	231.6	0- 1 μg/mL	0.1 μg/mL
P	214.9	0- 50 μg/mL	1 μg/mL
Sr	407.7	0- 5 μg/mL	0.1 μg/mL
Ti	334.9	0-100 μg/mL	1 μg/mL
V	292.4	0- 1 μg/mL	0.1 μg/mL
Zn	213.8	0- 1 μg/mL	0.1 μg/mL

[a] calibration standard concentration range

Table 4. Trace Element Concentrations in Argonne Premium Coal Sample Coal Ashes ($\mu g/g$).

Coal Ash	Ba	Be	Cd	Co	Cr	Cu	Li	Mn	Ni	Pb	Sr	V	Y	Zn
UF - PC-1-1	400	11	0.53	38	150	140	110	300	110	58	440	190	69	140
UF - PC-1-2	410	11	0.51	38	140	140	110	310	100	55	450	190	69	140
UF - PC-1-3	420	11	0.54	35	150	140	110	300	110	51	430	190	68	150
WY - PC-2-1	180	3.1	1.1	19	73	140	48	240	58	37	1800	160	46	120
WY - PC-2-2	180	2.8	1.1	19	75	140	49	250	55	35	1700	160	44	120
WY - PC-2-3	170	2.9	1.1	19	71	150	48	220	61	32	1800	160	44	120
IL - PC-3-1	420	4.8	3.7	26	190	65	48	470	110	42	180	200	26	1000
IL - PC-3-2	540	4.6	4.0	28	200	64	49	480	120	39	180	200	26	1100
IL - PC-3-3	540	4.6	3.5	26	190	64	48	470	110	39	180	190	26	1200
PITT-PC-4-1	460	8.3	0.64	26	160	60	95	200	99	32	700	160	47	89
PITT-PC-4-2	450	8.3	0.63	28	150	58	93	190	90	32	700	160	46	81
PITT-PC-4-3	430	8.5	0.68	26	140	60	94	190	88	32	680	160	46	84
POC- PC-5-1	310	15	1.6	71	180	220	110	300	130	48	1600	200	120	73
POC- PC-5-2	310	15	1.4	71	160	220	110	300	120	45	1600	200	130	77
POC- PC-5-3	310	15	1.4	71	180	220	110	300	130	45	1600	200	110	74
UT - PC-6-1	690	2.8	1.3	18	110	84	110	88	73	34	1300	86	45	140
UT - PC-6-2	660	2.7	1.3	18	99	82	110	88	71	34	1300	87	46	130
WV - PC-7-1	610	9.7	0.40	40	210	100	150	80	81	63	250	220	55	65
WV - PC-7-2	630	9.8	0.37	43	210	100	150	78	82	61	240	230	54	66
WV - PC-7-3	680	10.	0.44	42	200	100	150	77	82	63	260	220	57	63
ND - PC-8-1	4500	1.9	0.50	<10	27	59	28	840	15	16	5400	37	20	54
ND - PC-8-2	4100	1.8	0.46	<10	26	37	28	830	15	16	5300	36	19	49
ND - PC-8-3	4700	---	0.48	<10	24	52	30	850	12	16	5300	38	---	47

Table 5. Major Element Concentrations in Argonne Premium Coal Sample Coal Ashes (Percent)

Coal Ash	Al	Ca	Fe	K	Mg	Na	P	Ti
UF - PC-1-1	11.9	3.31	13.8	2.10	0.61	0.24	0.056	0.58
UF - PC-1-2	11.9	3.30	14.0	2.10	0.61	0.24	0.059	0.59
UF - PC-1-3	11.8	3.28	13.6	2.10	0.61	0.24	0.061	0.58
WY - PC-2-1	8.18	14.2	4.21	0.33	2.83	1.40	0.31	0.66
WY - PC-2-2	8.21	13.6	4.46	0.33	2.78	1.37	0.29	0.66
WY - PC-2-3	8.26	14.3	4.28	0.31	2.81	1.40	0.30	0.65
IL - PC-3-1	7.75	5.82	16.8	1.20	0.47	0.60	0.036	0.43
IL - PC-3-2	7.70	5.96	16.4	1.20	0.48	0.61	0.037	0.43
IL - PC-3-3	7.72	6.00	17.2	1.20	0.47	0.58	0.037	0.42
PITT-PC-4-1	10.8	2.29	14.6	1.20	0.41	0.35	0.12	0.62
PITT-PC-4-2	10.9	2.23	14.3	1.20	0.41	0.35	0.12	0.61
PITT-PC-4-3	10.8	2.21	14.2	1.20	0.40	0.34	0.12	0.60
POC - PC-5-1	10.4	8.75	9.67	0.51	1.06	1.57	0.042	0.72
POC - PC-5-2	10.4	8.53	9.52	0.53	1.04	1.57	0.041	0.72
POC - PC-5-3	10.3	8.53	9.50	0.53	1.04	1.54	0.040	0.72
UT - PC-6-1	7.56	9.07	6.16	0.30	0.64	2.75	0.020	0.50
UT - PC-6-2	7.50	8.70	6.09	0.30	0.65	2.70	0.021	0.49
WV - PC-7-1	16.1	0.29	2.04	2.52	0.48	0.17	0.046	1.34
WV - PC-7-2	16.4	0.30	1.96	2.58	0.49	0.18	0.045	1.34
WV - PC-7-3	16.3	0.30	1.95	2.55	0.49	0.18	0.038	1.34
ND - PC-8-1	4.17	16.0	4.91	0.13	4.16	4.84	0.13	0.21
ND - PC-8-2	4.22	16.1	4.95	0.16	4.16	4.89	0.13	0.20
ND - PC-8-2	4.25	16.5	5.05	0.15	4.26	5.00	0.13	0.21

Mercury is determined on the raw coal sample using the cold vapor AAS method of Aruscavage and Moore (1989). All acids used are reagent grade. Sample solutions for cold vapor AAS analysis are prepared by weighing 100 mg of the whole coal and placing it into a 25-mL Teflon screw cap vial. After adding 5 mL of concentrated nitric acid and 5 mL of concentrated perchloric acid to the sample the vial is capped and heated on a hotplate at 150°C for 20 minutes. The vial is then uncapped and heated until about 3 mL of the solution remains (about 3 hours). After adding 1 mL of concentrated nitric acid to the hot solution the vial is filled to 25 mL with distilled water. The vial is then recapped until the solution is analyzed. This solution is added to a 125-mL gas washing bottle and distilled water is added to the 100 mL mark. Mercury is reduced by adding 3 mL of a 10 percent (w/v) $SnCl_2$ solution and capping the flask. Nitrogen is bubbled through the solution for three minutes. The evolved mercury is collected onto gold beads located in the center of the coils of an induction furnace. Activation of the furnace releases the mercury which is measured by cold vapor AAS at a wavelength of 253.652 nm. A Spectrometrics model HG-4 mercury analyzer was used in this study. Samples are compared against a calibration curve (absorbance vs. concentration (ng)) established from analyzing mercury standards with a range of 0 - 50 ng.

Fluorine is determined in the whole coal sample using the ion-selective electrode method of Kirschenbaum (1989). Sample solutions for ISE analysis are prepared by weighing 250 mg of the coal sample and placing it in a 35-mL zirconium crucible, adding 1 mL of isopropanol to wet the sample. Then 1 mL of an MgO-$Mg(NO_3)_2$ solution (30 g MgO and 53 g $Mg(NO_3)_2$ in 500 mL distilled water) is added and the sample is dried in an oven at 110°C for 30 minutes. The sample is ashed in an electric furnace using the following sequence: 200°C for 30 minutes, 300°C for 30 minutes, 400°C for 90 minutes, and 500°C for 135 minutes. The sample is cooled to room temperature and 3 g of NaOH pellets are added. The sample is fused over a Meeker burner for 2 minutes. The sample is cooled and 25 mL of distilled water is added. The sample is then placed on a steam bath for 35 minutes to leach the fusion cake. The solution is transferred to a 100-mL polyethylene beaker and then filtered through a 9 mm Whatman #40 filter paper into a 100 mL-volumetric flask. The filter paper is washed with a 1% (w/v) NaOH solution. The solution is diluted to 100 mL with distilled water. A 10 mL aliquot of the sample solution and ten mL of a 1 M ammonium citrate solution are pipetted into a 100-mL polyethylene beaker. The sample is then stirred. The fluorine concentration of this solution is measured using an ion-selective electrode and an Orion Research model EA920 Ionalyzer. The concentration is calculated by comparing the potential of the sample to a calibration curve (potential (mV) vs. concentration (μg/mL)), on semi-logarithmic graph paper, established from analyzing fluoride standards with a range of 0.01 to 1.0 μg/mL.

DISCUSSION

SRM's 1633 and 1633a are used as control standards for each determination with the exception of mercury where NBS coal SRM 1632a and a U.S. Geological Survey "in-house" coal standard (24D) are used and fluorine where NBS coal SRM 1635 is used. Instrumental operating parameters and the lower limits of detection for AAS and ICAP-AES are shown in Tables 1-3. The lower limits of detection for fluorine and mercury are 20 μg/g (0.002 %), and 0.005 μg/g, respectively. Each Premium Coal Sample is run in triplicate (labeled 1, 2, and 3) with the exception of UT-PC-6 which is run in duplicate due to a lack of available sample. Data for these analyses are shown in Tables 4-6. The replicate analyses show the precision of the methods used. The relative percent standard deviation is generally about ±5%. Comparison of the analyses of these control standards with NBS certified values (Cali, 1975; Uriano, 1979), AAS values (Kane, 1989), and with values determined by instrumental neutron activation analysis (Ondov and others, 1975; Rowe and Steiness, 1977) shows the accuracy of the methods (Tables 7 and 8). Sample IL-PC-3 showed a wide concentration range for barium (420 - 540 μg/g). This could be due to sampling error or incomplete digestion of barite that may be present in the sample. Beryllium values by ICP are corrected for vanadium and titanium interferences and zinc values by ICP are corrected for interferences by manganese, iron, and vanadium. Interference corrections vary depending on the instrument operating conditions used and should be determined before the start of the analysis.

Aruscavage (1989) reported mercury values for NBS-1632a and USGS-24D as 0.11 μg/g ± 0.01 and 0.40 μg/g ± 0.02 respectively. Comparison of that data with data from this study (Table 8) shows good agreement. NBS 1635 has not been well characterized for fluorine, on which Gladney (1987), reports 3 values of 20, 63 and 77 μg/g. The value of 80 μg/g reported in this study seems to fit in well with the upper range of Gladney's reported values. Replicate analyses show the precision of both of these methods. The percent relative standard deviation is generally about ±10%.

Table 6. Fluorine and Mercury Concentrations and Percent Ash in Argonne Premium Coals

Coal	F (%)	Hg (μg/g)	Ash (%)
UF - PC-1-1	0.031	0.010	13.5
UF - PC-1-2	0.031	0.010	
UF - PC-1-3	0.031	0.009	
WY - PC-2-1	0.024	<0.005	8.5
WY - PC-2-2	0.025	<0.005	
WY - PC-2-3	0.020	<0.005	
IL - PC-3-1	0.027	<0.005	16.2
IL - PC-3-2	0.025	<0.005	
IL - PC-3-3	0.028	<0.005	
PITT-PC-4-1	0.024	<0.005	9.2
PITT-PC-4-2	0.020	<0.005	
PITT-PC-4-3	0.020	<0.005	
POC - PC-5-1	0.013	<0.005	5.3
POC - PC-5-2	0.010	<0.005	
POC - PC-5-3	0.010	<0.005	
UT - PC-6-1	0.007	<0.005	4.6
UT - PC-6-2	0.006	<0.005	
UT - PC-6-3	0.007	<0.005	
WV - PC-7-1	0.020	0.050	19.4
WV - PC-7-2	0.020	0.050	
WV - PC-7-3	0.010	0.050	
ND - PC-8-1	0.005	<0.005	9.5
ND - PC-8-2	0.005	<0.005	
ND - PC-8-2	0.004	<0.005	

Standard Coal	F %	Hg (μg/g)
USGS 24 D	-	0.37
NBS 1632a	-	0.10
NBS 1635	0.008	-

Table 7. Analysis of NBS Standard Reference Material 1633

Element	Method	This Work	Cali (NBS)	Gladney, and others	Kane	Ondov, and others	Rowe and Steiness
Ba (µg/g)	ICP	2700	---	2665 ± 160	---	2700 ± 200	2540
Be	ICP	11	---	12.1 ± 1.0	---	---	---
Cd	GFAA	1.5	1.45 ± .06	1.47 ± .15	1.56 ± .26	---	---
Co	FAA	41	(38)	40 ± 3	---	41.5 ± 1.2	40.3 ± .4
Cr	ICP	130	131 ± 2	127 ± 10	---	127 ± 6	129.2 ± 2.7
Cu	ICP	130	128 ± 5	129 ± 7	130 ± 6	---	115 ± 8
Li	FAA	160	---	170 ± 80	170 ± 13	---	---
Mn	ICP	510	493 ± 7	494 ± 20	496 ± 34	496 ± 19	488 ± 14
Ni	ICP	94	98 ± 7	98 ± 6	---	98 ± 9	69 ± 7
Pb	GFAA	70	70 ± 4	72 ± 6	67 ± 4	75 ± 5	---
Sr	ICP	1400	1430 ± 60	1380 ± 100	---	1700 ± 300	1430 ± 60
V	ICP	220	214 ± 8	224 ± 24	---	235 ± 13	237 ± 20
Y	ICP	66	---	64 ± 4	---	62 ± 10	---
Zn	ICP	210	210 ± 20	211 ± 11	210 ± 10	216 ± 25	201 ± 6
Al (%)	ICP	11.9	---	12.6 ± .6	---	12.7 ± .5	12.35 ± .25
Ca	ICP	4.58	---	4.65 ± .34	---	4.7 ± .6	4.69 ± .14
Fe	ICP	6.05	---	6.16 ± .27	---	6.2 ± .3	6.2 ± .05
K	ICP	1.80	(1.72)	1.69 ± .09	---	1.61 ± .15	1.80 ± .13
Mg	ICP	1.33	(1.98)	1.5 ± .3	1.17 ± .049	1.8 ± .4	1.78 ± .2
Na	ICP	0.31	0.307	0.313 ± .02	0.295 ± .023	0.32 ± .04	0.283 ± .014
P	ICP	0.12	---	0.101 ± .018	---	---	---
Ti	ICP	0.77	---	0.71 ± .05	---	0.74 ± .03	0.70 ± .03

Table 8. Analysis of NBS Standard Reference Material 1633A

Element	Method	This Work	Uriano (NBS)	Gladney, and others	Kane
Ba (μg/g)	ICP	1400	(1500)	1420 ± 100	---
Be	ICP	12	(12)	12.8 ± .6	---
Cd	GFAA	0.94	1.0 ± .15	1.12 ± .17	0.98 ± .08
Co	FAA	46	(46)	43 ± 3	---
Cr	ICP	190	196 ± 6	194 ± 7	---
Cu	ICP	110	118 ± 3	120 ± 4	114 ± 7
Li	FAA	170	---	165 ± 50	184 ± 14
Mn	ICP	180	179 ± 8	188 ± 15	160 ± 12
Ni	ICP	130	127 ± 4	124 ± 13	---
Pb	GFAA	71	72.4 ± .4	72 ± 4	62 ± 4
Sr	ICP	850	830 ± 30	810 ± 40	---
V	ICP	290	297 ± 6	294 ± 18	---
Y	ICP	87	---	82 ± 6	---
Zn	ICP	210	220 ± 10	226 ± 22	211 ± 11
Al (%)	ICP	14.0	14.3 ± 1.0	14.4 ± .7	---
Ca	ICP	1.14	1.11 ± .01	1.14 ± .06	---
Fe	ICP	9.18	9.40 ± .1	9.37 ± .23	---
K	ICP	1.95	1.88 ± .06	1.88 ± .05	---
Mg	ICP	0.44	0.455 ± .01	0.457 ± .045	0.436 ± .005
Na	ICP	0.17	0.17 ± .01	0.173 ± .011	0.158 ± .014
P	ICP	0.18	---	0.169 ± .024	---
Ti	ICP	0.92	(0.8)	0.823 ± .034	---

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CHAPTER H

Carbon, Hydrogen, and Nitrogen Analyses of Eight Argonne Premium Coal Samples

By Carol J. Skeen and Zoe A. Brown

U.S. GEOLOGICAL SURVEY OPEN-FILE REPORT 91-638

The Chemical Analysis of Argonne Premium Coal Samples

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Carbon, Hydrogen, and Nitrogen Analyses of Eight Argonne Premium Coal Samples

by Carol J. Skeen and Zoe A. Brown

ABSTRACT

The carbon, hydrogen, and nitrogen content of eight premium coals were determined by using the Perkin-Elmer 240B Elemental Analyzer. Precision for the analysis of these samples is within the accepted 0.1% relative standard deviation. The carbon content ranged from 56% to 86%; the hydrogen content ranged from 3.7% to 5.6%; and the nitrogen content ranged from 0.93% to 2.2%. Since these ranges are typical for coals, the NBS 1635 SRM was chosen as the control standard to evaluate the accuracy of the method.

INTRODUCTION

Analysis of a substance for carbon, hydrogen and nitrogen generally requires drastic treatment of the material in order to convert the elements into a form readily determined by routine analytical techniques. A common way to convert the carbon, hydrogen, and nitrogen to gaseous products is to carry out an oxidation in a quartz combustion tube through which is forced a stream of carrier gas. The stream transports the volatile products to the part of the apparatus where they can be separated for measurement.

The combustion train is packed with silver compounds to remove the halogen and sulfur compounds which interfere with the determination of carbon dioxide and water. Before reaching the combustion train, the helium and oxygen flow through scrubbers packed with colorcarb and anhydron to remove extraneous contaminants.

The Perkin-Elmer 240B elemental analyzer gives excellent results for finely ground, dry materials, especially materials high in organic matter, with following concentration ranges: 0.1%-100% for carbon, 0.01%-12% for hydrogen, and 0.10%-18% for nitrogen.

ANALYTICAL TECHNIQUE

Standard operating procedures for use of the Perkin-Elmer 240B and a revised statistical computer program (Abramowitz, 1964) were implemented in the analysis of the premium coals. The instrument was calibrated by oxidizing three samplings of standard acetanilide, all of approximately the same weight (1.0 to 1.3 mg). The furnace temperatures were 950 °C for the combustion tube and 650 °C for the reduction tube. The sample weights used were between 1.0 mg and 1.3 mg.

The NBS 1635 Coal SRM was analyzed as a control standard at the same time as the last three premium coals. These results along with the NBS SRM values (1975) and Gladney's (1987) analytical values are given in Table 1.

Table 1. Concentration in % for Carbon, Hydrogen and Nitrogen for NBS 1635.

	This Study	NBS (1975)	Gladney, and others (1987)
C%	63.0	62.2 ± 1.8	62.6
H%	3.98	3.96 ± 0.03	4.07
N%	1.5	1.0 ± 0.1	1.26

RESULTS AND DISCUSSION

A recent study was made to ascertain the detection limits of this method (Filby, 1985). By diluting pure acetanilide with ultra-pure silica to prepare three analytical standards (1) 7.1% C, 0.67% H, and 1.04% N, (2) 0.71% C, 0.067% H, and 0.104% N, (3) 0.071% C, 0.0067% H, and 0.010% N, and by using acetanilide undiluted (71.07% C, 6.71% H, and 10.36% N), the lowest detection limits were calculated to be 0.1% C, 0.01% H, and 0.10%N. The experiment using various sampling weights also validated that the analytical curves were linear from the detection limit to the highest standard.

The results of these coal analyses were compared to the published data for the Argonne Premium Coal Sample Program (Vorres, 1990) for C, H, N determined on dried whole coals. The values were in good agreement with all the coals except for the carbon values for the subbituminous (WY) and the lignite (ND). To verify the accuracy of this paper's results, these two samples were repeated with special attention given to proper drying of the samples before analysis. The carbon values, 61% for WY and 57% for ND, are in agreement with the initial analyses. Table 2 shows the results for the replicate analyses of these coals, the repeats, and Vorres' published data.

The differences between the results from Argonne National Laboratories and the data reported in this paper could be due to oxidation of these two coals. Argonne went to great lengths to seal these coals in an oxygen-free environment. Since analysis in the U.S.G.S. laboratories was not done immediately after the ampoules were opened, it is likely that the subbituminous and the lignite oxidized. Bituminous coals are characteristically more stable.

The precision of this method is within the 0.1% relative standard deviation which is well within the accepted deviation for this type of analysis. The analysis of NBS 1635 indicates that the accuracy is also excellent.

Table 2. Concentration in % for Carbon, Hydrogen and Nitrogen in Argonne Premium Coals.

Coal Samples		C (WT.%) This Study	C (WT.%) Vorres	H (WT.%) This Study	H (WT.%) Vorres	N (WT.%) This Study	N (WT.%) Vorres
UF	PC-1-1	77		4.6		2.2	
UF	PC-1-2	76		4.7		1.8	
UF	PC-1-3	---		---		---	
UF	AVG	76.5	74.23	4.65	4.08	2.0	1.35
WY	PC-2-1	60		4.4		1.2	
WY	PC-2-2	60		4.6		1.2	
WY	PC-2-3	---		---		---	
WY	AVG	60	68.43	4.5	4.88	1.2	1.02
WY	Repeat	61					
IL	PC-3-1	64		4.5		1.6	
IL	PC-3-2	65		4.5		1.8	
IL	PC-3-3	---		---		---	
IL	AVG	64.5	65.65	4.5	4.23	1.7	1.16
PITT	PC-4-1	74		5.0		2.2	
PITT	PC-4-2	75		5.0		2.0	
PITT	PC-4-3	---		---		---	
PITT	AVG	74.5	75.50	5.0	4.83	2.1	1.49
POC	PC-5-1	86		4.4		1.9	
POC	PC-5-2	86		4.3		2.0	
POC	PC-5-3	---		---		---	
POC	AVG	86	86.71	4.35	4.23	1.95	1.27
UT	PC-6-1	72		5.5		1.6	
UT	PC-6-2	74		5.5		1.8	
UT	PC-6-3	74		5.6		1.4	
UT	AVG	73.33	76.89	5.53	5.49	1.6	1.50
WV	PC-7-1	64		4.3		1.3	
WV	PC-7-2	65		4.3		1.4	
WV	PC-7-3	66		4.2		1.4	
WV	AVG	65	66.20	4.27	4.21	1.37	1.25
ND	PC-8-1	56		3.8		1.2	
ND	PC-8-2	57		3.7		1.0	
ND	PC-8-3	57		3.7		0.93	
ND	AVG	56.67	65.85	3.73	4.36	1.04	1.04
ND	Repeat	57					

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CHAPTER I

Compilation of Multi-Technique Analyses of Eight Argonne Premium Coal Samples for 33 Elements

by Curtis A. Palmer

U.S. GEOLOGICAL SURVEY OPEN-FILE REPORT 91-638

The Chemical Analysis of Argonne Premium Coal Samples

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APPENDIX

Compilation of Multi-Technique Analyses of Eight Argonne Premium Coal Samples for 33 Elements

by Curtis A. Palmer

Eight Argonne Premium Coal Samples were analyzed by the Branch of Geochemistry of the United States Geological Survey. The concentrations of 33 elements were determined by two or more techniques on each sample. The analyses were performed by X-ray fluorescence spectroscopy, instrumental neutron activation analysis, inductively coupled argon plasma atomic emission spectroscopy, atomic absorption spectrometry, and direct current arc spectrography. All data are compiled on a whole coal basis for ease of comparison. The ash values are also included so that data can be converted to an ash basis if desired.

INTRODUCTION

Although the eight Argonne Premium Coal Samples analyzed in this study are not classified as "reference standards" they are extremely important because of the care that has been taken in collection, preparation and storage. A detailed description of the background information for these samples has been reported by Vorres (1990). However, these samples have not been widely analyzed for trace elements. The analytical laboratories of the Branch of Geochemistry at the U.S. Geological Survey analyzed these samples to further characterize them and to provide a foundation for a trace-element data base.

Most quantitative techniques used for elemental analyses of geologic samples offer high levels of precision and accuracy for selected elements in certain types of samples over specific ranges of concentrations, but all analytical techniques have certain characteristic limitations. For example, matrix induced spectral interferences can result in incorrect determinations of trace elements. Even if properly corrected, these interferences may lead to reduced sensitivity or precision for a given element. Generally, the concentrations of elements determined by another technique on the same matrix will not be affected by the same interferences.

A multi-technique approach for major and trace element analysis was taken to provide the high degree of reliability desired to characterize these materials. Because not all laboratories have all techniques available, this information may also be useful in evaluating data from a single technique for coal analysis. Semi-quantitative analytical techniques, while not offering the precision or accuracy of the quantitative techniques, rapidly provide a large volume of data. Some of that data are not easily obtainable by other quantitative methods, but the data can be useful in the overall characterization of these materials.

The purpose of this paper is to summarize the results of the multi-technique analyses of the Argonne Premium Coals and to discuss some discrepancies in the data. Each of the eight Premium Coal Samples has been analyzed in triplicate for 58 elements. However, only 33 elements were determined by more than one technique. Although up to 6 different techniques were used for some elements, there are not enough data to recommend values for these coals using common criteria for establishing such values (Kane and others, 1990). Therefore, all the results determined by different procedures for each element are presented so that comparisons of the data can be easily made. A detailed analysis of every discrepancy in the data is beyond the scope of this paper.

SAMPLES AND TECHNIQUES

Three splits of each of the Argonne Premium Coal Samples were analyzed using multiple techniques. A description of the samples and the sample identification protocol have been described earlier in this volume (Palmer, 1991a).

Better analytical data would probably be obtained by analyzing solid samples of the whole coal, thus avoiding problems caused by volatilization of elements during ashing or incomplete sample dissolution. The procedures used for determining element concentrations on the whole coal are discussed in this volume by Palmer (1991b) for instrumental neutron activation analysis (INAA), by Evans and others (1991) for wavelength dispersive (WDXRF) and energy dispersive (EDXRF) X-ray fluorescence spectrometry, and by Fletcher and Skeen (1991) for direct current atomic optical emission spectrography (DCAES). Although the sensitivity of INAA was acceptable for most of the 28 elements determined (Palmer, 1991b), the sensitivities of the other whole coal procedures were marginal for many elements. Therefore, coal ash procedures were also used for WDXRF, EDXRF (Evans and others, 1991) and DCAES (Skeen and others, 1991) to increase sensitivities because of low concentrations of some trace elements.

In addition to WDXRF, EDXRF and DCAES ash procedures mentioned above, techniques which require a dissolution of coal ash are discussed in detail by Doughten and Gillison (1991) in this volume. These techniques include inductively coupled argon plasma-atomic emission spectrometry (ICAP-AES), flame (FAAS) and graphite-furnace (GFAAS) atomic absorption analysis.

For procedures which required ashing, all samples were ashed at 525°C to prevent volatilization of Pb, Cd, and other moderately volatile trace elements. The ash contents were determined on the same splits used for the analyses. These ash contents were used to recalculate data determined on the ash to a whole coal basis. The 525°C ash contents are not directly comparable to those determined by ASTM ash procedures (750°C).

RESULTS AND DISCUSSION

Direct comparison of results presented in previous papers in this volume is difficult because data are presented in three different forms depending on the analytical technique used and the material analyzed. Concentrations are reported on an ash basis for some procedures, on a whole coal basis for some procedures, and on an oxide basis for major elements determined by WDXRF and DCAES. To facilitate a direct comparison of the data, the ash data have been recalculated to whole coal values and converted to an element basis for those elements reported on an oxide basis. The entire recalculated data set for all splits can be found in Appendix 1 (Table A1). The number of significant figures given in the original papers has been maintained in the converted values.

A careful examination of Appendix 1 shows that analytical procedures can be classified into two categories: Highly precise (HP) procedures which generally have relative standard deviation of less than 5%, and procedures which are less precise (LP) and have poorer precision. In this study the two DCAES procedures (ash and whole coal) and the EDXRF whole coal procedure were classified as LP procedures; INAA, ICAP-AES, and the other X-ray procedures were classified as HP procedures. It should be noted that no procedures had the same precision for all elements in all samples. For the designated high precision techniques most determinations were of high precision, but, as expected, determinations near the detection limit for some samples had poorer precision. LP procedures generally had lower precision for all samples and elements.

Statistical approaches are useful for large data sets, however they often do not provide the detail which is useful in evaluating individual problems in the data. The evaluation of the data in this publication remains difficult due to the large quantity of data presented (the 14 pages of Appendix 1) even though the individual samples were only analyzed in triplicate. A summary of the data is given in Tables 1 and 2. Table 1 presents the method averages of the major element data determined on each of the three splits of the eight Argonne Premium Coal Samples. Table 2 is a similar table for the trace element data.

Agreement between techniques can be graphically presented by plotting the concentrations of all elements determined by one technique versus all corresponding concentrations by a second technique and comparing it to a theoretical line with 0 intercept and a slope of 1. Figure 1, for example, shows the comparison of INAA and ICAP-AES data from Table 2 for all elements which the two techniques have in common. There is relatively little scatter (excellent agreement) in most of the data, therefore the few problems with the data are easily recognizable. The most obvious discrepancy in the data is that the Ba concentration determined by ICAP-AES is more than an order of magnitude smaller in WY PC-2 and POC PC-5 than the concentration determined by INAA.

Table 1. Average concentrations of major elements in weight percent based on triplicate analyses except values in brackets are averages of 2 analyses and numbers in parentheses are based on only one analysis. Complete data set is given in Appendix 1. Material analyzed: (A)=ash (C)=whole coal.

Sample Technique	UF PC-1	WY PC-2	IL PC-3	PITT PC-4	POC PC-5	UT PC-6	WV PC-7	ND PC-8
Si								
DCAES(A)	3.1	1.4	3.6	2.7	0.95	0.86	5.2	0.60
DCAES(C)	3.3	0.77	3.3	2.3	0.88	---	---	---
WDXRF(A)	[2.67]	[1.24]	[3.04]	[1.96]	[0.804]	(0.893)	(4.90)	(0.768)
Al								
WDXRF(A)	[1.54]	[0.672]	[1.21]	[0.981]	[0.548]	(0.370)	(3.17)	(0.45)
ICAP-AES(A)	1.60	0.699	1.25	1.00	0.549	[0.347]	3.16	0.400
DCAES(A)	2.4	0.53	2.0	2.1	0.71	0.32	3.9	0.23
DCAES(C)	2.0	0.48	2.0	1.7	0.85	---	---	---
Fe								
INAA(C)	1.78	0.366	2.67	1.35	0.509	0.317	0.397	0.547
WDXRF(A)	[1.93]	[0.33]	[2.70]	[1.44]	[0.52]	(0.29)	(0.37)	(0.45)
ICAP-AES(A)	1.86	0.367	2.72	1.32	0.507	[0.282]	0.385	0.472
DCAES(A)	1.6	0.27	2.4	1.9	0.50	0.24	0.40	0.37
DCAES(C)	2.3	0.29	2.3	1.3	0.69	---	---	---
Mg								
WDXRF(A)	[0.079]	[0.26]	[0.09]	[0.03]	[0.067]	(0.048)	(0.08)	(0.42)
ICAP-AES(A)	0.082	0.239	0.077	0.038	0.0548	[0.030]	0.094	0.398
DCAES(A)	0.15	0.37	0.12	0.073	0.11	0.041	0.097	0.51
DCAES(C)	0.099	0.20	0.098	0.048	0.077	---	---	---
Ca								
WDXRF(A)	[0.40]	[1.12]	[0.90]	[0.20]	[0.443]	(0.401)	(0.06)	(1.54)
ICAP-AES(A)	0.445	1.19	0.96	0.206	0.456	[0.409]	0.058	1.54
DCAES(A)	0.64	1.2	1.6	0.41	0.58	0.29	0.078	1.3
DCAES(C)	0.58	1.0	1.7	0.29	0.80	---	---	---
Na								
INAA(C)	0.0341	0.115	0.102	0.0343	0.0782	0.146	0.0388	0.529
ICAP-AES(A)	0.032	0.119	0.097	0.032	0.0826	[0.126]	0.034	0.466
WDXRF(A)	[0.03]	[0.092]	[0.11]	[0.03]	[0.071]	(0.13)	(0.05)	(0.50)
DCAES(A)	0.045	0.13	0.15	0.036	0.13	0.072	0.036	(0.25)
K								
INAA(C)	0.227	0.0292	0.195	0.110	0.029	[0.022]	0.506	[0.029]
WDXRF(A)	[0.27]	[0.03]	[0.20]	[0.11]	[0.03]	(0.02)	(0.46)	(0.03)
ICAP-AES(A)	0.283	0.028	0.194	0.110	0.028	[0.014]	0.495	0.014
DCAES(A)	0.30	0.033	0.26	0.13	0.036	0.017	0.36	0.037
Ti								
WDXRF(A)	0.080	[0.051]	[0.07]	[0.059]	[0.040]	(0.02)	(0.24)	(0.02)
ICAP-AES(A)	0.079	0.056	0.070	0.056	0.038	[0.023]	0.260	0.020
DCAES(A)	0.053	0.036	0.066	0.057	0.028	0.019	0.18	0.018
DCAES(C)	0.10	0.044	0.092	0.091	0.082	---	---	---
P								
WDXRF(C)	---	0.03	---	0.009	---	---	---	0.02
WDXRF(A)	[0.006]	[0.03]	[0.004]	[0.010]	[0.002]	(0.001)	(0.007)	(0.02)
ICAP-AES(A)	0.0079	0.025	0.0059	0.011	0.0022	[0.00094]	0.0084	0.012
DCAES(A)	---	0.026	---	---	---	(0.00074)	(0.017)	0.011
Mn								
WDXRF(A)	---	---	---	---	---	---	---	(0.007)
ICAP-AES(A)	0.0041	0.0020	0.0076	0.0018	0.0016	[0.00041]	0.0015	0.0080
DCAES(A)	0.0055	0.0033	0.0011	0.0036	0.0024	0.00061	0.0020	0.010
DCAES(C)	0.0053	0.0013	0.0016	0.0020	0.0019	---	---	---

Table 2. Average concentrations of trace elements in micrograms per gram based on triplicate analyses except bracketed values are averages of 2 analyses and numbers in parentheses are based on only one analysis. Complete data set is given in Appendix 1. Material analyzed: (A)=ash (C)=whole coal.

Sample Technique	UF PC-1	WY PC-2	IL PC-3	PITT PC-4	POC PC-5	UT PC-6	WV PC-7	ND PC-8
Be								
ICAP-AES(A)	1.5	0.25	0.76	0.77	0.80	[0.13]	1.9	[0.18]
DCAES(A)	1.4	0.14	0.97	1.2	0.67	0.20	3.0	0.28
Sc								
INAA(C)	4.06	1.68	2.59	2.57	1.79	0.813	7.62	0.846
DCAES(A)	2.1	1.3	2.6	1.9	1.3	0.69	6.4	0.90
V								
ICAP-AES(A)	26	14	32	15	11	[4.0]	44	3.5
DCAES(A)	16	9.0	24	13	7.1	3.7	32	3.6
DCAES(C)	41	[14]	52	24	18	---	---	---
Cr								
INAA(C)	20.3	6.1	33.1	14.8	9.1	5.3	35.8	2.23
EDXRF(A)	26.0	8.2	43.2	17.9	12.3	---	45.9	2.6
ICAP-AES(A)	20	6.2	31	14	9.2	[4.8]	40	2.4
EDXRF(C)	19	[4]	35	8	5	---	49	---
DCAES(A)	19	5.7	38	19	8.8	4.8	39	2.4
DCAES(C)	32	7	52	24	16	---	---	---
Co								
INAA(C)	5.33	1.68	4.39	2.62	4.07	1.00	7.74	0.778
FAAS(A)	5.0	1.6	4.3	2.4	3.8	[0.83]	8.1	---
DCAES(A)	3.5	1.3	3.7	2.6	2.6	0.64	6.3	0.55
DCAES(C)	5.0	---	---	---	5.0	---	---	---
Ni								
INAA(C)	14.5	4.9	21.0	[10.3]	8.6	[3.4]	15.4	---
EDXRF(A)	14	3.9	18	9.3	7.91	---	17	1.9
ICAP-AES(A)	14	4.9	18	8.5	6.7	[3.3]	16	1.3
EDXRF(C)	23	8	32	13	11	5	18	6
DCAES(A)	14	5.2	22	13	6.5	4.0	21	1.8
DCAES(C)	25	---	33	12	[11]	---	---	---
Cu								
EDXRF(A)	20.4	12.9	9.6	6.2	12.5	---	23.6	3.3
ICAP-AES(A)	19	12	10	5.5	12	[3.8]	19	4.7
EDXRF(C)	18	17	14	10	17	8	31	9
DCAES(A)	17	13	11	6.5	19	2.9	16	4.9
DCAES(C)	18	7	9	6	19	---	---	---
Zn								
INAA(C)	19.7	11.3	220	9.1	6.4	6.4	13.5	5.69
EDXRF(A)	20.5	10.6	107	8.4	4.8	---	12	5.4
ICAP-AES(A)	19	10	180	7.8	4.0	[6.2]	13	4.8
EDXRF(C)	33	25	140	15	14	---	10	5
DCAES(C)	33	---	280	27	---	---	---	---
Ga								
DCAES(A)	6.2	2.4	4.7	4.7	2.3	1.2	12	1.7
DCAES(C)	10	3	7	5	4	---	---	---
Ge								
DCAES(A)	3.6	---	8.9	1.2	0.46	---	[1.1]	---
DCAES(C)	4	---	9	(3.0)	---	---	---	---
As								
INAA(C)	17.1	3.6	4.7	8.42	10.3	0.48	6.2	2.63
DCAES(A)	30	---	---	17	15	---	---	---

Table 2 (continued)

Sample Technique	UF PC-1	WY PC-2	IL PC-3	PITT PC-4	POC PC-5	UT PC-6	WV PC-7	ND PC-8
Rb								
INAA(C)	19.5	---	16	7.7	---	[1.02]	29.7	[0.93]
EDXRF(A)	21.2	3.5	15	9.1	2.3	---	43.6	---
EDXRF(C)	21	13	20	8	5	3	42	4
Sr								
INAA(C)	49	252	39	61	105	70	60	590
EDXRF(A)	60	260	29.9	68	110	---	78.0	640
ICAP-AES(A)	59	150	29	64	85	[60]	49	500
EDXRF(C)	62	294	33	63	85	63	86	780
DCAES(A)	63	220	40	91	110	89	70	630
Y								
EDXRF(A)	10	3.6	4.1	4.9	6.89	---	21.2	---
ICAP-AES(A)	9.3	3.8	4.2	4.3	6.2	2.0	11	[1.8]
EDXRF(C)	---	---	---	---	---	(2)	19	---
DCAES(A)	4.7	3.0	4.7	3.1	4.6	1.8	9.1	2.4
Zr								
EDXRF(A)	27.3	22.7	22.3	20.5	16.9	---	80.5	6.5
EDXRF(C)	23	19	23	17	10	18	103	18
DCAES(A)	11	17	17	12	12	11	34	13
DCAES(C)	33	---	21	24	30	---	----	---
Nb								
EDXRF(A)	2.5	1.0	[2.1]	1.9	0.85	---	8.3	---
EDXRF(C)	---	---	---	---	---	---	[13]	---
DCAES(A)	1.7	1.4	2.5	1.8	1.1	0.51	3.6	0.58
Ba								
INAA(C)	61	310	94	47	198	36	133	680
EDXRF(A)	52	270	74.5	35.7	180	---	110	460
EDXRF(C)	60	410	121	30	140	29	210	1030
ICAP-AES(A)	55	15	81	41	16	31	120	420
DCAES(A)	41	320	60	38	210	36	130	580
DCAES(C)	81	250	120	66	450	---	---	---
La								
INAA(C)	10.1	5.35	6.10	6.15	6.76	3.31	21.5	2.82
EDXRF(A)	8.2	---	---	[4.4]	2.2	---	17	---
EDXRF(C)	16	6	15	9	5	10	16	8
DCAES(A)	6.9	6.1	9.3	5.8	7.2	2.9	14	3.7
Ce								
INAA(C)	18.3	9.4	12.6	11.3	11.6	4.81	35.8	4.45
EDXRF(A)	17.0	[5.2]	7.2	9.0	7.6	---	29.9	---
EDXRF(C)	40	25	40	17	10	15	55	19
DCAES(A)	(10)	9	(28)	---	12	6.9	26	---
Nd								
INAA(C)	(8.0)	---	---	---	---	[2.0]	11.7	[2.3]
DCAES(A)	8	---	(6.5)	3.9	6.0	(2.9)	19	---
Sm								
INAA(C)	1.97	0.978	1.20	1.09	1.22	0.508	3.52	0.41
DCAES(A)	---	---	---	---	0.76	0.37	[1.7]	(0.47)
Yb								
INAA(C)	0.88	0.42	0.52	0.470	0.555	0.20	1.61	0.287
DCAES(A)	0.84	0.29	0.61	0.54	0.45	0.21	1.5	0.20
Pb								
GFAAS(A)	7.4	2.9	6.5	2.9	2.4	[1.6]	12	1.5
DCAES(A)	10	3.4	14	7.3	11	1.9	16	2.6
DCAES(C)	8	---	8	4	5	---	---	---

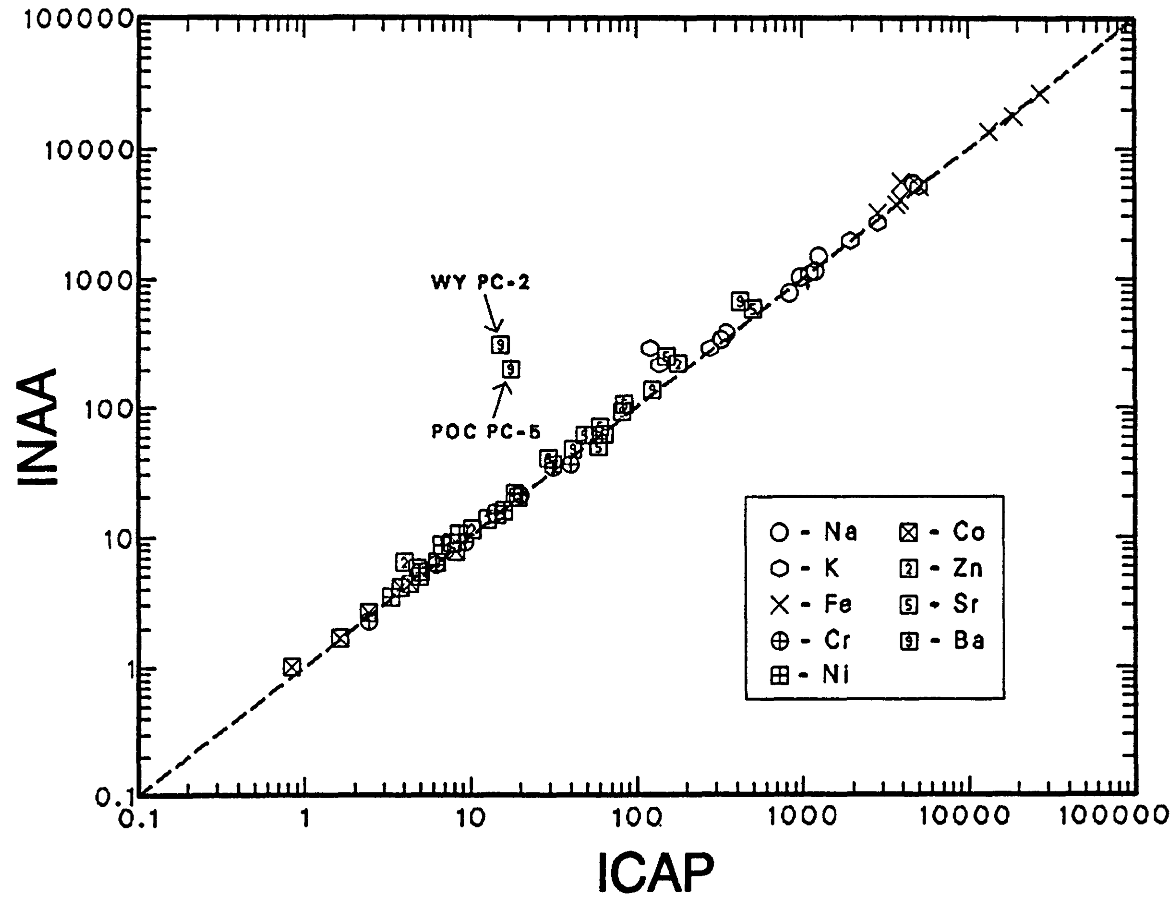

Figure 1. A comparison of average concentrations of all elements determined by both inductively coupled argon plasma-atomic emission spectroscopy (ICAP-AES) on the ash and instrumental neutron activation analysis (INAA) determined on the whole coal. All data determined on the ash are converted to a whole coal basis. Dashed line is the line of perfect agreement.

All of the data for Ba determined by the six different techniques are shown in Figure 2 by plotting Ba determined by all techniques other than EDXRF on the whole coal versus Ba determined by EDXRF. Although there is clearly scatter among techniques, ICAP-AES data for PC-2 and PC-5 are clearly off the correlation line. The disagreement of ICAP-AES with all other techniques suggests that Ba is concentrated in a species, probably $BaSO_4$, which is not being dissolved by the ICAP-AES acid dissolution procedures. Both of these coals contain enough sulfate sulfur (Vorres, 1989) to account for all barium being $BaSO_4$ in the original coal. However, solubility studies of these coals by Finkelman and others (1990) show that Ba in these two samples is soluble in ammonium acetate and is therefore readily exchangeable. This suggests that $BaSO_4$ is not in the original samples of WY PC-2 and POC PC-5 and that if it is formed in the ashing process it is probable that the determination of Ba using a dissolution of the whole coal or by a fusion of the ash would have produced ICAP-AES values closer to those of other techniques. Further work is needed confirm this.

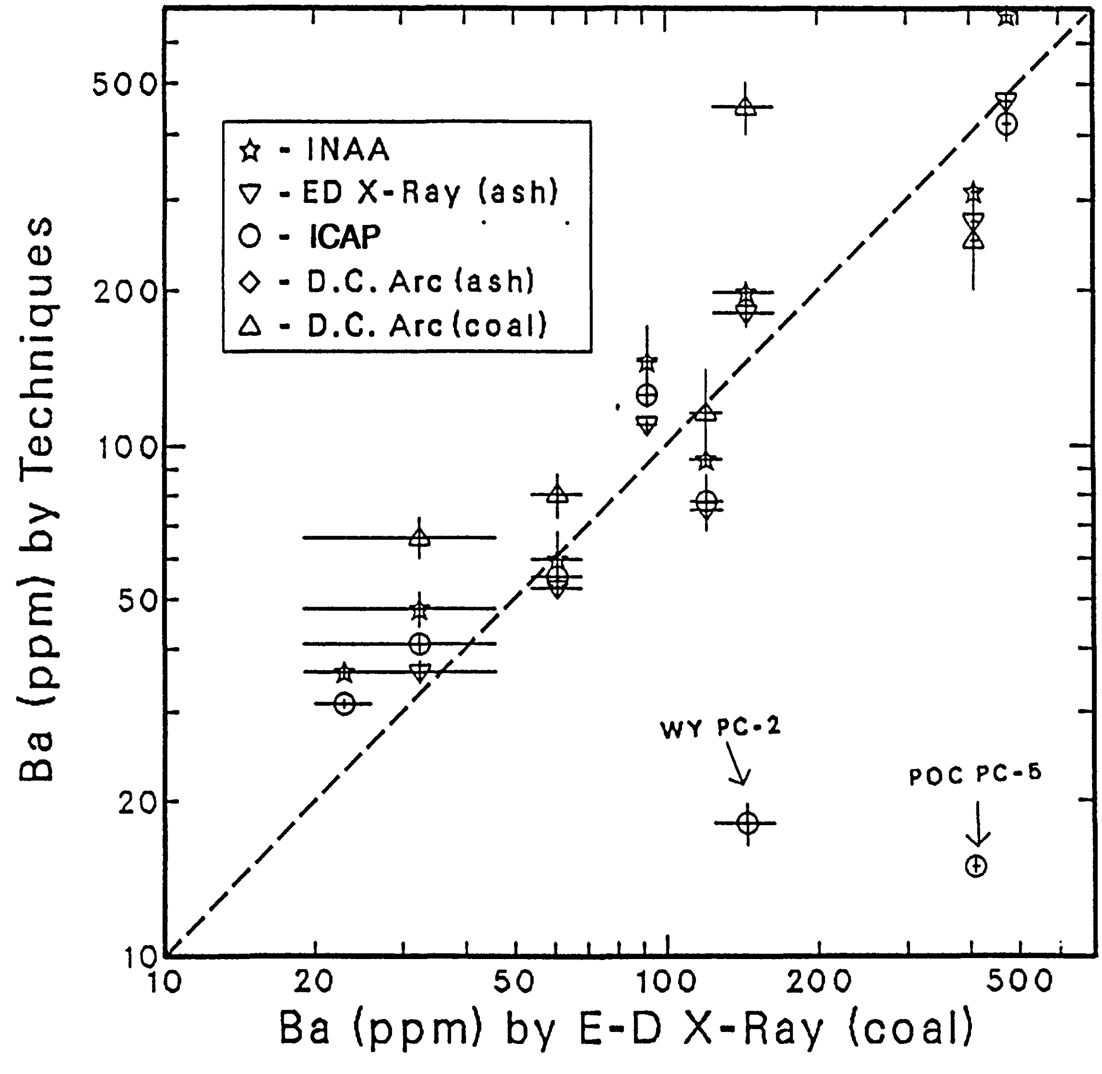

Figure 2. The comparison of average concencentrations of Ba determined by EDXRF on the whole coal with average concentrations of Ba determined by other techniques. All plotted data are determined on, or converted to, a whole coal basis. The dashed line is the line of perfect agreement. Bars are indicative of the range.

Another approach to analyzing the data is to define the agreement between techniques in a useful non-statistical manner and then discuss individual cases of disagreement. In a practical sense, for major elements (Table 1), procedures are said to be in "good agreement" with one another if individual values are within ± 5% of the mean of the HP procedures and do not disagree by more than 0.5% absolute. For trace elements (Table 2), "good agreement" is defined as ±10% of the mean. "Usable agreement" is four times the uncertainty of "good agreement" or ±20% for the majors and 40% for the traces. Procedures which do not meet the "usable agreement" criteria were not included in determining the mean except when there were only two procedures.

A summary of the agreement for major elements (Table 1) is given in Table 3. Data for elements by specific techniques were classified as in "overall good agreement" with the mean of the HP procedures if at least half of the individual samples were in good agreement using the above criteria and no samples had "poor agreement"; "overall usable agreement" if half or more of the samples determined were in "good" or "usable agreement" and not classified as in "good agreement"; and "overall poor agreement" for all others except where the technique was the only HP technique in which case agreement can not be calculated and was used instead of the mean of the HP techniques to assess the agreement of the LP techniques. All HP techniques listed in Table 3 were in "overall good agreement" except for Al, Na and Mn determined by WDXRF on the ash, and K determined by ICAP-AES, which were classified as having "overall usable agreement", and Si which was determined by only one HP technique (WDXRF on the ash). In contrast, all LP techniques had "overall poor" or "overall usable agreement."

For elements which are traditionally considered major elements (Table 1) but whose concentrations were less than 0.1% in all or some samples trace element criteria were applied for those samples. This included P and Mn for all samples and Mg, Na, K, and Ti (see Table 3) for four or more samples. It should be noted that the ±5% criterion for "good agreement" is better than expected for some HP techniques for some samples as concentrations approach the detection limit, for example, counting errors of as high as 28% are reported for K by INAA (Palmer, 1991b). The criterion of 20% required for "usable agreement" is much smaller than the inherent precision for many of the LP techniques. For example, Skeen and others report errors of +50% or -33% because of the nature of standard curves for each of the elements. It is not surprising, therefore, that not all HP techniques have "good agreement" for all samples and that most LP techniques have "poor agreement" for most samples. Most of these disagreements were within ±50% of the HP mean concentrations and scatter in inter-technique comparison plots simply demonstrate the poorer precision of the LP techniques. A complete discussion of the precision of all values in this study is beyond the scope of this paper but an indication of the precision can be obtained by examining Appendix 1.

Table 3. Agreement between techniques for major elements using data from Table 1 and criteria described in text. The following abbreviations were used under exceptions: 1=UF PC-1; 2=WY PC-2; 3=IL PC-3; 4=PITT PC-4; 5=POC PC-5; 6=UT PC-6; 7=WV PC-7; 8=ND PC-8; g=good agreement; u=usable agreement; p=poor agreement; x=only upper limits found; t=agreement calculated using trace element criterion because of low concentration in sample; equal sign indicates there are no other high precision values. The mean of these values was used for comparison in evaluating low precision values. Sample numbers in parentheses are samples where only single determinations are available.

Element	Exceptions to major Elements	HP Techniques	Overall Agreement	Exceptions	LP Techniques	Overall Agreement	Exceptions
Si		WDXRF(A)	----	1-8=	DCAES(A)	usable	2,6g;4,8p
					DCAES(C)	poor	3,4u;6-8x
Al		WDXRF(A)	usable	1-7g;(8)p	DCAES(A)	poor	8g,6u
		ICAP-AES(A)	good	8=	DCAES(C)	poor	1,3,6-8x
Fe		INAA(C)	good	8=	DCAES(A)	usable	5,7g
		WDXRF(A)	good	2,4,7,(8)u	DCAES(C)	poor	3,4u;6-8x
		ICAP-AES(A)	good	6,8u			
Mg	1,3-7t	WDXRF(A)	good	4,6,(7)u	DCAES(A)	poor	7g;3,6u
		ICAP-AES(A)	good	4,6u;7=	DCAES(C)	usable	2p;6-8x
Ca	7t	WDXRF(A)	good	2-7g;(8)u	DCAES(A)	poor	1g;7,8u
		ICAP-AES(A)	good	1,8u	DCAES(C)	poor	2u;6-8x
Na	1,4,5,7t	INAA(C)	good	1,4,6,8u	DCAES(A)	usable	7g;3,5,6,8p
		ICAP-AES(A)	good	3,5,6,8u			
		WDXRF(A)	usable	1,6,8g;2u			
K	2,5,6,8t	INAA(C)	good		DCAES(A)	usable	3,7p
		WDXRF(A)	good	7u			
		ICAP-AES(A)	usable	1-5,7g;6,8p			
Ti	1-6,8t	WDXRF(A)	good	(6),(7)u	DCAES(A)	usable	3,4,8g;1,2,7p
		ICAP-AES(A)	good	6,7=	DCAES(C)	usable	4,5p;6-8x
P	1-8t	WDXRF(C)	usable	2,4g;1,3,5-7x	DCAES(A)	usable	2g;8p;1,3-7x
		WDXRF(A)	good	1,3,8u			
		ICAP-AES(A)	good	1,3,8u			
Mn	1-8t	WDXRF(A)	usable	8g;1-7x	DCAES(A)	usable	7g;2-4,6p
		ICAP-AES(A)	good	1-7=	DCAES(C)	usable	2,3p;6-8x

Table 4 summarizes the agreement of trace elements reported in Table 2. All agreements were evaluated using trace element criteria discussed above and summary classifications similar to Table 3. HP procedures generally had "good agreement" and LP procedures generally had "usable" or "poor agreement".

There are some exceptions to the "agreement" classifications given in Table 4. For example, Cr determined by EDXRF on the ash had only "usable agreement" in 6 of the eight samples. Although Zn determined by the same technique had "good agreement" in 5 samples, the concentration of Zn in IL PC-3 was only slightly greater than one half of the Zn values determined by INAA and ICAP-AES for that sample. Barium had only "overall usable agreement" because of the "poor agreement" in WY PC-2 and POC PC-5 probably caused by incomplete dissolution as discussed earlier. The "usable" classification of Sr determined by ICAP-AES because of the low value of Sr in WY PC-2 may also be related to incomplete dissolution. The "usable" (instead of "good") agreement by all HP techniques for La and Ce are probably the result of the La and Ce concentrations being near the detection limits of EDXRF which result in much poorer precision (See Appendix 1) and probably accuracy for these elements by this technique. INAA has long been a standard method for determining trace quantities of rare-earth elements and is probably accurate for La and Ce. DCAES on the ash, an LP technique had "good agreement" for Cr and Ba although in both cases three samples had "usable agreement."

The exact cause of many of these discrepancies is not known at this time. Overall, however, the data are generally useful and should provide an excellent base for further study.

CONCLUSIONS

A multi-technique approach is the best method to differentiate "good" values from "poor" values caused by spectral interferences, volatilization due to ashing or incomplete sample dissolution. Interferences for a given element usually differ for each technique. Losses caused by volatilization can be determined by comparing data from whole coal procedures and ash procedures. Insolubility problems can be identified by comparing techniques not requiring dissolution with those techniques requiring dissolution.

Although this paper does not recommend values for each element, it does provide reliable data for many trace elements. More importantly it points out the uncertainties in attempting to obtain reliable data from a single technique for coals of widely differing matrices, such as those in this study, and provides a basis for determining some of the uncertainties of the techniques used in this study. This paper should aid in the evaluation of data determined by different techniques.

Table 4. Agreement between techniques for trace elements using data from Table 1 and criteria described in text. The following abbreviations were used under exceptions: 1=UF PC-1; 2=WY PC-2; 3=IL PC-3; 4=PITT PC-4; 5=POC PC-5; 6=UT PC-6; 7=WV PC-7; 8=ND PC-8; g=good agreement; u=usable agreement; p=poor agreement; x=only upper limits found; t=agreement calculated using trace element criterion because of low concentration in sample; equal sign indicates there are no other high precision values. The mean of these values was used for comparison in evaluating low precision values. Sample numbers in parentheses are samples where only single determinations are available.

HP Element	Overall Techniques	Agreement	LP Exceptions	Overall Techniques	Agreement	Exceptions
Be	ICAP-AES(A)	----	1-8=	DCAES(A)	poor	1g;3u
Sc	INAA(C)	----	1-8=	DCAES(A)	usable	3,8g;1p
V	ICAP-AES(A)	----	1-8=	DCAES(A)	usable	6,8g;1,2,5p
				DCAES(C)	poor	2g;6-8x
Cr	INAA(C)	good	2,5,7u	EDXRF(C)	usable	1,3g;2,4,5p;6,8x
	EDXRF(A)	usable	8g;6x	DCAES(A)	good	2,4,5u
	ICAP-AES(A)	good	3u	DCAES(C)	poor	2g;6-8x
Co	INAA(C)	good	8=	DCAES(A)	poor	4g;2,7u
	FAAS(A)	good	8x	DCAES(C)	usable	1g;2-8x
Ni	INAA(C)	good	5u,8x	EDXRF(C)	poor	2,5u
	EDXRF(A)	good	2,8u;6x	DCAES(A)	usable	1g
	ICAP-AES(A)	good	5,8u	DCAES(C)	poor	4u;2,6-8x
Cu	EDXRF(A)	good	8u,6x	EDXRF(C)	poor	1g;2,5u
	ICAP-AES(A)	good	6=;8u	DCAES(A)	usable	2g;5,6p
				DCAES(C)	usable	1,3,4g;6-8x;2,5p
Zn	INAA(C)	good	5u	EDXRF(C)	poor	8g;3,7u
	EDXRF(A)	usable	1,2,4,7,8g;3p,6x	DCAES(C)	poor	3u;2,5-8x
	ICAP-AES(A)	good	5u			
Ga				DCAES(A)	usable	4g;6-8=
				DCAES(C)	usable	4g;6-8x
Ge				DCAES(A)	usable	1,3g;6-8=;4p
				DCAES(C)	usable	1,3g;6-8x;(4)p
As	INAA(C)	---	1-8=	DCAES(A)	poor	5u;2,3,6-8x
Rb	INAA(C)	good	6,8=;7u;2,5x	EDXRF(C)	usable	3g;2,5,6,8p
	EDXRF(A)	good	2,5=;7u;6,8x			
Sr	INAA(A)	good	3u	EDXRF(C)	usable	3,4,6g
	EDXRF(A)	good	7,8u;6x	DCAES(A)	usable	5g;4p
	ICAP-AES(A)	usable	1,4,6g;2p			
Y	EDXRF(A)	good	5,7u;6,8x	EDXRF(C)	usable	(2)g;7u;1-5,8x
	ICAP-AES(A)	good	6,8=;5,7u	DCAES(A)	usable	5,6g;1,4,7p
Zr	EDXRF(A)	---	1-5,7-8=;6x	EDXRF(C)	usable	3g;5,8p
				DCAES(A)	poor	2,3,6u
				DCAES(C)	usable	3g;2,6-8x
Nb	EDXRF(A)	---	1-5,7=;6,8x	EDXRF(C)	poor	1-6,8x
				DCAES(A)	usable	4g;6,8=;1,7p
Ba	INAA(C)	good	4,8u	EDXRF(C)	usable	1g;3,4,7,8p
	EDXRF(A)	good	3,4,8u;6x	DCAES(A)	good	1,3,5u
	ICAP-AES(A)	usable	1,3,4,6,7g;2,5p	DCAES(C)	poor	2,3u;6-8x
La	INAA(C)	usable	1g;2,3,6,8=;5p	EDXRF(C)	poor	2,5,7p
	EDXRF(A)	usable	1g;5p;2,3,6,8x	DCAES(A)	usable	4g;3,5p
Ce	INAA(C)	usable	1g;6,8=	EDXRF(C)	poor	5g
	EDXRF(A)	usable	1g;6,8x	DCAES(A)	usable	1,3,6p;4,8x
Nd	INAA(C)	---	1,6-8=	DCAES(A)	poor	1g;(3)-5=;8x
Sm	INAA(C)	---	1-8=	DCAES(A)	usable	5,7p;1-4x
Yb	INAA(C)	---	1-8=	DCAES(A)	usable	1,6,7g;8p
Pb	GFAAS(A)	---	1-8=	DCAES(A)	usable	3-5,8p
				DCAES(C)	usable	1g;5p;2,6-8x

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APPENDIX 1

Table A1. Comparison of the concentrations of 33 elements determined by multiple analytical techniques in eight Argonne Premium Coal Samples. The techniques include: inductively coupled argon plasma atomic emission spectroscopy (ICAP-AES), flame (FAAS) and graphite furnace (GFAAS) atomic absorption spectroscopy, direct current optical emission spectrography (DCAES), wavelength dispersive (WDXRF) and energy dispersive (EDXRF) X-ray fluorescence spectrometry, and instrumental neutron activation analysis (INAA). Original material analyzed: whole coal (WC) and ash (converted to a whole coal basis). The ash content was also reported. Concentrations orginally reported as an oxide were converted to an elemental basis for ease of comparison. Values in parentheses indicate only one value reported.

Element (units)	ASH (%)	Si (%)			Al (%)			
Technique Material	550° C	DCAES	DCAES	WDXRF	WDXRF	ICAP-AES	DCAES	DCAES
Analyzed Sample split or average	WC	WC	ASH	ASH	ASH	ASH	ASH	WC
UF PC-1-1	13.5	3.0	3.0	2.64	1.54	1.61	2.0	2.0
UF PC-1-2	13.5	4.0	3.0	2.69	1.54	1.61	2.6	2.0
UF PC-1-3	13.5	3.0	3.4	–	–	1.59	2.6	2.0
AVG PC-1	13.5	3.3	3.1	2.67	1.54	1.60	2.4	2.0
WY PC-2-1	8.5	0.80	1.3	1.23	0.675	0.695	0.42	0.47
WY PC-2-2	8.5	1.00	1.3	1.25	0.670	0.698	0.54	0.54
WY PC-2-3	8.5	0.52	1.5	–	–	0.705	0.61	0.44
AVG PC-2	8.5	0.77	1.4	1.24	0.672	0.699	0.53	0.48
IL PC-3-1	16.2	3.0	3.6	3.04	1.21	1.26	1.9	2.0
IL PC-3-2	16.2	4.0	3.2	3.04	1.20	1.25	1.9	2.0
IL PC-3-3	16.2	3.0	4.0	–	–	1.25	2.1	2.0
AVG PC-3	16.2	3.3	3.6	3.04	1.21	1.25	2.0	2.0
PITT PC-4-1	9.2	2.0	2.4	1.95	0.988	0.993	2.2	1.0
PITT PC-4-2	9.2	3.0	2.7	1.97	0.974	1.00	1.9	2.0
PITT PC-4-3	9.2	2.0	2.9	–	–	0.993	2.2	2.0
AVG PC-4	9.2	2.3	2.7	1.96	0.981	1.00	2.1	1.7
POC PC-5-1	5.3	0.83	0.95	0.810	0.550	0.551	0.64	0.80
POC PC-5-2	5.3	1.00	0.90	0.798	0.547	0.551	0.74	0.92
POC PC-5-3	5.3	0.80	1.00	–	–	0.546	0.74	0.84
AVG PC-5	5.3	0.88	0.95	0.804	0.548	0.549	0.71	0.85
UT PC-6-1	4.6	–	0.74	0.893	0.370	0.348	0.31	–
UT PC-6-2	–	–	0.92	–	–	0.345	0.32	–
UT PC-6-3	–	–	0.92	–	–	–	0.29	–
AVG PC-6	(4.6)	–	0.86	(0.893)	(0.370)	0.347	0.32	–
WV PC-7-1	19.4	–	4.3	4.90	3.17	3.13	3.3	–
WV PC-7-2	–	–	5.8	–	–	3.18	4.3	–
WV PC-7-3	–	–	5.4	–	–	3.16	4.1	–
AVG PC-7	(19.4)	–	5.2	(4.90)	(3.17)	3.16	3.9	–
ND PC-8-1	9.5	–	0.54	0.768	0.45	0.396	0.21	–
ND PC-8-2	–	–	0.63	–	–	0.401	0.28	–
ND PC-8-3	–	–	0.63	–	–	0.404	0.21	–
AVG PC-8	(9.5)	–	0.60	(0.768)	(0.45)	0.400	0.23	–

TABLE A1 (continued)

Element (units)	Fe (%)					Mg (%)			
Technique Material Analyzed Sample split or average	INAA WC	WDXRF ASH	ICAP-AES ASH	DCAES ASH	DCAES ASH	WDXRF ASH	AES ASH	DCAES ASH	DCAES WC
UF PC-1-1	1.75	1.98	1.86	1.6	2.0	0.079	0.082	0.13	0.097
UF PC-1-2	1.81	1.88	1.89	1.3	3.0	0.079	0.082	0.15	0.100
UF PC-1-3	1.79	–	1.84	1.7	2.0	–	0.081	0.16	0.100
AVG PC-1	1.78	1.93	1.86	1.6	2.0	0.079	0.082	0.15	0.099
WY PC-2-1	0.381	0.33	0.358	0.26	0.34	0.25	0.241	0.33	0.20
WY PC-2-2	0.379	0.32	0.379	0.26	0.33	0.27	0.236	0.39	0.20
WY PC-2-3	0.339	–	0.363	0.31	0.20	–	0.239	0.37	0.20
AVG PC-2	0.366	0.33	0.367	0.27	0.29	0.26	0.239	0.37	0.20
IL PC-3-1	2.66	2.71	2.72	2.3	2.0	0.09	0.076	0.11	0.096
IL PC-3-2	2.67	2.70	2.66	2.3	2.0	0.09	0.078	0.11	0.099
IL PC-3-3	2.68	–	2.79	2.6	3.0	–	0.076	0.12	0.100
AVG PC-3	2.67	2.70	2.72	2.4	2.3	0.09	0.077	0.12	0.098
PITT PC-4-1	1.36	1.45	1.34	1.7	1.0	0.04	0.038	0.065	0.045
PITT PC-4-2	1.34	1.43	1.32	1.8	1.0	0.03	0.038	0.064	0.048
PITT PC-4-3	1.33	–	1.31	2.0	2.0	–	0.038	0.089	0.052
AVG PC-4	1.35	1.44	1.32	1.9	1.3	0.03	0.038	0.073	0.048
POC PC-5-1	0.504	0.52	0.513	0.52	0.60	0.067	0.0562	0.10	0.079
POC PC-5-2	0.521	0.52	0.505	0.44	0.80	0.067	0.0551	0.11	0.074
POC PC-5-3	0.502	–	0.504	0.53	0.68	–	0.0551	0.11	0.079
AVG PC-5	0.509	0.52	0.507	0.50	0.69	0.067	0.0548	0.11	0.077
UT PC-6-1	0.327	0.29	0.284	0.21	–	0.048	0.030	0.043	–
UT PC-6-2	0.310	–	0.281	0.27	–	–	0.030	0.038	–
UT PC-6-3	0.315	–	–	0.23	–	–	–	0.041	–
AVG PC-6	0.317	(0.29)	0.282	0.24	–	(0.048)	0.030	0.041	–
WV PC-7-1	0.400	0.37	0.396	0.35	–	0.08	0.092	0.128	–
WV PC-7-2	0.384	–	0.381	0.45	–	–	0.095	0.084	–
WV PC-7-3	0.408	–	0.379	0.41	–	–	0.096	0.078	–
AVG PC-7	0.397	(0.37)	0.385	0.40	–	(0.08)	0.094	0.097	–
ND PC-8-1	0.553	0.45	0.466	0.35	–	0.42	0.395	0.52	–
ND PC-8-2	0.529	–	0.470	0.43	–	–	0.395	0.51	–
ND PC-8-3	0.560	–	0.480	0.33	–	–	0.405	0.51	–
AVG PC-8	0.547	(0.45)	0.472	0.37	–	(0.42)	0.398	0.51	–

TABLE A1 (continued)

Element (units)	Ca (%)				Na(%)			
Technique Material	WDXRF	ICAP-AES	DCAES	DCAES	INAA	ICAP-AES	WDXRF	DCAES
Analyzed Sample split or average	ASH	ASH	ASH	WC	WC	ASH	ASH	ASH
UF PC-1-1	0.40	0.447	0.69	0.57	0.0336	0.032	0.03	0.042
UF PC-1-2	0.40	0.445	0.59	0.54	0.0343	0.032	0.03	0.047
UF PC-1-3	–	0.443	0.63	0.63	0.0342	0.032	–	0.046
AVG PC-1	0.40	0.445	0.64	0.58	0.0341	0.032	0.03	0.045
WY PC-2-1	1.10	1.21	1.0	1.0	0.114	0.119	0.10	0.12
WY PC-2-2	1.15	1.16	1.3	1.0	0.117	0.119	0.083	0.16
WY PC-2-3	–	1.22	1.4	1.0	0.113	0.119	–	0.12
AVG PC-2	1.12	1.19	1.2	1.0	0.115	0.119	0.092	0.13
IL PC-3-1	0.90	0.943	1.6	2.0	0.103	0.097	0.13	0.16
IL PC-3-2	0.89	0.965	1.5	2.0	0.101	0.099	0.09	0.14
IL PC-3-3	–	0.972	1.8	1.0	0.103	0.094	–	0.15
AVG PC-3	0.90	0.960	1.6	1.7	0.102	0.097	0.11	0.15
PITT PC-4-1	0.20	0.211	0.46	0.24	0.0343	0.032	0.04	0.039
PITT PC-4-2	0.20	0.205	0.33	0.34	0.0342	0.032	0.03	0.033
PITT PC-4-3	–	0.203	0.43	0.28	0.0344	0.031	–	0.037
AVG PC-4	0.20	0.206	0.41	0.29	0.0343	0.032	0.03	0.036
POC PC-5-1	0.443	0.464	0.53	0.69	0.0797	0.832	0.073	0.13
POC PC-5-2	0.443	0.452	0.58	0.93	0.0773	0.0832	0.069	0.13
POC PC-5-3	–	0.452	0.64	0.79	0.0778	0.0816	–	0.13
AVG PC-5	0.443	0.456	0.58	0.80	0.0782	0.0826	0.071	0.13
UT PC-6-1	0.401	0.418	0.28	–	0.148	0.127	0.13	0.087
UT PC-6-2	–	0.401	0.29	–	0.147	0.124	–	0.064
UT PC-6-3	–	–	0.29	–	0.143	–	–	0.064
AVG PC-6	(0.401)	0.409	0.29	–	0.146	0.126	(0.13)	0.072
WV PC-7-1	0.06	0.057	0.078	–	0.0460	0.033	0.05	0.037
WV PC-7-2	–	0.058	0.060	–	0.0351	0.035	–	0.035
WV PC-7-3	–	0.058	0.095	–	0.0352	0.036	–	0.037
AVG PC-7	(0.06)	0.058	0.078	–	0.0388	0.034	(0.05)	0.036
ND PC-8-1	1.54	1.52	1.2	–	0.540	0.460	0.50	–
ND PC-8-2	–	1.53	1.3	–	0.533	0.464	–	0.25
ND PC-8-3	–	1.57	1.4	–	0.515	0.475	–	–
AVG PC-8	(1.54)	1.54	1.3	–	0.529	0.466	(0.50)	(0.25)

TABLE A1 (continued)

Element (units)	K (%)				Ti (%)			
Technique Material Analyzed Sample split or average	INAA WC	WDXRF ASH	ICAP-AES ASH	DES WC	WDXRF ASH	ICAP-AES ASH	WDXRF ASH	DCAES ASH
UF PC-1-1	0.264	0.26	0.283	0.31	0.078	0.078	0.061	0.10
UF PC-1-2	0.262	0.28	0.283	0.28	0.082	0.080	0.039	0.10
UF PC-1-3	0.280	–	0.283	0.30	–	0.078	0.059	0.10
AVG PC-1	0.227	0.27	0.283	0.30	0.080	0.079	0.053	0.10
WY PC-2-1	0.0268	0.03	0.028	0.031	0.051	0.056	0.030	0.050
WY PC-2-2	0.0335	0.03	0.028	0.037	0.052	0.056	0.037	0.050
WY PC-2-3	0.0272	–	0.026	0.031	–	0.055	0.041	0.038
AVG PC-2	0.0292	0.03	0.028	0.033	0.051	0.056	0.036	0.044
IL PC-3-1	0.199	0.21	0.194	0.24	0.07	0.070	0.062	0.089
IL PC-3-2	0.186	0.20	0.194	0.26	0.07	0.070	0.065	0.100
IL PC-3-3	0.199	–	0.194	0.28	–	0.070	0.073	0.086
AVG PC-3	0.195	0.20	0.194	0.26	0.07	0.070	0.066	0.092
PITT PC-4-1	0.109	0.11	0.110	0.13	0.059	0.057	0.059	0.086
PITT PC-4-2	0.112	0.11	0.110	0.12	0.060	0.056	0.052	0.090
PITT PC-4-3	0.109	–	0.110	0.14	–	0.055	0.059	0.097
AVG PC-4	0.110	0.11	0.110	0.13	0.059	0.056	0.057	0.091
POC PC-5-1	0.0284	0.03	0.027	0.034	0.040	0.038	0.028	0.084
POC PC-5-2	0.026	0.03	0.028	0.033	0.039	0.038	0.025	0.084
POC PC-5-3	0.033	–	0.028	0.039	–	0.037	0.031	0.078
AVG PC-5	0.029	0.03	0.028	0.036	0.040	0.038	0.028	0.082
UT PC-6-1	0.018	0.02	0.014	0.022	0.02	0.023	0.018	–
UT PC-6-2	< 0.025	–	0.014	0.014	–	0.023	0.020	–
UT PC-6-3	0.025	–	–	0.017	–	–	0.018	–
AVG PC-6	0.022	(0.02)	0.014	0.017	(0.02)	0.023	0.019	–
WV PC-7-1	0.517	0.46	0.489	0.39	0.24	0.260	0.18	–
WV PC-7-2	0.500	–	0.501	0.33	–	0.260	0.18	–
WV PC-7-3	0.500	–	0.495	0.35	–	0.260	0.17	–
AVG PC-7	0.506	(0.46)	0.495	0.36	(0.24)	0.260	0.18	–
ND PC-8-1	0.028	0.03	0.012	0.038	0.02	0.020	0.017	–
ND PC-8-2	< 0.040	–	0.016	0.033	–	0.019	0.017	–
ND PC-8-3	0.030	–	0.015	0.039	–	0.020	0.019	–
AVG PC-8	0.029	(0.03)	0.014	0.037	(0.02)	0.020	0.018	–

TABLE A1 (continued)

Element (units)	P(%)				Mn (%)			
Technique Material Analyzed Sample split or average	WDXRF WC	WDXRF ASH	ICAP-AES ASH	DCAES ASH	WDXRF ASH	ICAP-AES ASH	DCAES ASH	DCAES WC
UF PC-1-1	< 0.005	0.005	0.0076	< 0.0092	< 0.01	0.0041	0.0055	0.0053
UF PC-1-2	< 0.005	0.006	0.0080	< 0.0092	< 0.01	0.0042	0.0051	0.0059
UF PC-1-3	< 0.005	–	0.0082	< 0.0092	–	0.0041	0.0058	0.0048
AVG PC-1	–	0.006	0.0079	–	–	0.0041	0.0055	0.0053
WY PC-2-1	0.03	0.03	0.026	0.020	< 0.007	0.0020	0.0042	0.0010
WY PC-2-2	0.02	0.03	0.024	0.026	< 0.007	0.0021	0.0027	0.0016
WY PC-2-3	0.03	–	0.026	0.033	–	0.0019	0.0031	0.0014
AVG PC-2	0.03	0.03	0.025	0.026	–	0.0020	0.0033	0.0013
IL PC-3-1	< 0.005	0.004	0.0058	< 0.011	< 0.01	0.0076	0.011	0.015
IL PC-3-2	< 0.005	0.004	0.0060	< 0.011	< 0.01	0.0076	0.010	0.015
IL PC-3-3	< 0.005	–	0.0060	< 0.011	–	0.0076	0.011	0.017
AVG PC-3	–	0.004	0.0059	–	–	0.0076	0.011	0.016
PITT PC-4-1	0.009	0.010	0.011	< 0.0063	< 0.007	0.0018	0.0030	0.0016
PITT PC-4-2	0.009	0.010	0.011	< 0.0063	< 0.007	0.0017	0.0038	0.0028
PITT PC-4-3	0.009	–	0.011	< 0.0063	–	0.0017	0.0039	0.0018
AVG PC-4	0.009	0.010	0.011	–	–	0.0018	0.0036	0.0020
POC PC-5-1	< 0.005	0.002	0.0022	< 0.0036	< 0.004	0.0016	0.0024	0.0016
POC PC-5-2	< 0.005	0.002	0.0022	< 0.0036	< 0.004	0.0016	0.0023	0.0024
POC PC-5-3	< 0.005	–	0.0021	< 0.0036	–	0.0016	0.0026	0.0017
AVG PC-5	–	0.002	0.0022	–	–	0.0016	0.0024	0.0019
UT PC-6-1	< 0.005	0.001	0.00092	< 0.0031	< 0.004	0.00041	0.00064	–
UT PC-6-2	< 0.005	–	0.00097	< 0.0031	–	0.00041	0.00046	–
UT PC-6-3	< 0.005	–	–	0.00074	–	–	0.00074	–
AVG PC-6	–	(0.001)	0.00094	(0.00074)	–	0.00041	0.00061	–
WV PC-7-1	< 0.005	0.007	0.0089	0.017	< 0.015	0.0016	0.0018	–
WV PC-7-2	< 0.005	–	0.0087	< 0.013	–	0.0015	0.0023	–
WV PC-7-3	< 0.005	–	0.0074	< 0.013	–	0.0015	0.0019	–
AVG PC-7	–	(0.007)	0.0084	(0.017)	–	0.0015	0.0020	–
ND PC-8-1	0.02	0.02	0.012	0.012	0.007	0.0080	0.010	–
ND PC-8-2	0.02	–	0.012	0.010	–	0.0079	0.010	–
ND PC-8-3	0.02	–	0.012	0.0093	–	0.0081	0.010	–
AVG PC-8	0.02	(0.02)	0.012	0.011	(0.007)	0.0080	0.010	–

TABLE A1 (continued)

Element (units)	Be (µg/g)		Sc (µg/g)		V (µg/g)		
Technique	ICAP-AES	DCAES	INAA	DS	ICAP-AES	DS	DS
Material Analyzed	ASH	ASH	WC	ASH	ASH	ASH	WC
Sample split or average							
UF PC-1-1	1.5	1.5	4.04	2.6	26	18	38
UF PC-1-2	1.5	1.2	4.01	1.5	26	13	45
UF PC-1-3	1.5	1.5	4.14	2.2	26	17	41
AVG PC-1	1.5	1.4	4.06	2.1	26	16	41
WY PC-2-1	0.26	0.14	1.67	1.0	14	7.3	10
WY PC-2-2	0.24	0.14	1.69	1.4	14	9.3	14
WY PC-2-3	0.25	0.15	1.66	1.5	14	10.	17
AVG PC-2	0.25	0.14	1.68	1.3	14	9.0	14
IL PC-3-1	0.78	0.89	2.55	2.5	32	23	52
IL PC-3-2	0.75	0.96	2.57	2.6	32	23	59
IL PC-3-3	0.75	1.1	2.64	2.8	31	26	44
AVG PC-3	0.76	0.97	2.59	2.6	32	24	52
PITT PC-4-1	0.76	1.1	2.61	1.8	15	12	20
PITT PC-4-2	0.76	1.2	2.56	1.7	15	12	25
PITT PC-4-3	0.78	1.2	2.55	2.0	15	14	27
AVG PC-4	0.77	1.2	2.57	1.9	15	13	24
POC PC-5-1	0.80	0.74	1.80	1.3	11	6.9	16
POC PC-5-2	0.80	0.58	1.79	1.3	11	6.4	21
POC PC-5-3	0.80	0.69	1.77	1.5	11	7.9	18
AVG PC-5	0.80	0.67	1.79	1.3	11	7.1	18
UT PC-6-1	0.13	0.15	0.832	0.74	4.0	3.8	–
UT PC-6-2	0.12	0.24	0.801	0.69	4.0	3.6	–
UT PC-6-3	–	0.20	0.805	0.64	–	3.6	–
AVG PC-6	0.13	0.20	0.813	0.69	4.0	3.7	–
WV PC-7-1	1.9	2.9	7.69	7.0	43	31	–
WV PC-7-2	1.9	3.1	7.56	6.0	45	35	–
WV PC-7-3	1.9	3.1	7.61	6.2	43	29	–
AVG PC-7	1.9	3.0	7.62	6.4	44	32	–
ND PC-8-1	0.18	0.27	0.846	0.87	3.5	3.6	–
ND PC-8-2	0.17	0.33	0.827	0.86	3.4	3.6	–
ND PC-8-3	–	0.23	0.865	0.95	3.6	3.5	–
AVG PC-8	0.18	0.28	0.846	0.90	3.5	3.6	–

TABLE A1 (continued)

Element (units)	Cr (μg/g)						Co (μg/g)			
Technique Material	INAA	EDXRF	ICAP-AES	EDXRF	DCAES	DCAES	INAA	FAAS	DCAES	DCAES
Analyzed Sample split or average	WC	ASH	ASH	WC	ASH	WC	WC	ASH	ASH	WC
UF PC-1-1	20.4	25.1	20	15	22	32	5.27	5.1	3.8	5.0
UF PC-1-2	20.3	26.5	19	23	17	38	5.41	5.1	3.0	5.0
UF PC-1-3	20.4	26.5	20	19	19	26	5.32	4.7	3.9	5.0
AVG PC-1	20.3	26.0	20	19	19	32	5.33	5.0	3.5	5.0
WY PC-2-1	5.7	7.3	6.2	3	4.8	8.0	1.66	1.6	1.0	< 5.0
WY PC-2-2	6.22	8.2	6.4	5	6.3	6.0	1.73	1.6	1.4	< 5.0
WY PC-2-3	6.23	9.18	6.0	–	5.9	8.0	1.65	1.6	1.4	< 5.0
AVG PC-2	6.1	8.2	6.2	4	5.7	7	1.68	1.6	1.3	–
IL PC-3-1	33.7	42.9	29	29	36	54	4.22	4.2	3.6	< 5.0
IL PC-3-2	32.5	42.9	32	36	36	57	4.42	4.5	3.4	< 5.0
IL PC-3-3	33.2	43.7	31	41	42	47	4.53	4.2	4.2	< 5.0
AVG PC-3	33.1	43.2	31	35	38	52	4.39	4.3	3.7	–
PITT PC-4-1	15.0	18.4	15	6	20	23	2.65	2.4	2.8	< 5.0
PITT PC-4-2	15.0	17.5	14	10	17	27	2.61	2.6	2.3	< 5.0
PITT PC-4-3	14.5	17.9	13	9	20	21	2.61	2.4	2.8	< 5.0
AVG PC-4	14.8	17.9	14	8	19	24	2.62	2.4	2.6	–
POC PC-5-1	9.3	12.5	9.5	5	9.0	17	4.09	3.8	2.4	5.0
POC PC-5-2	9.06	11.9	8.5	7	8.0	17	4.13	3.8	2.3	5.0
POC PC-5-3	8.85	12.5	9.5	4	9.5	14	3.98	3.8	3.0	5.0
AVG PC-5	9.1	12.3	9.2	5	8.8	16	4.07	3.8	2.6	5.0
UT PC-6-1	5.20	–	5.1	< 10	5.1	–	1.01	0.83	0.69	–
UT PC-6-2	5.00	–	4.6	< 10	3.9	–	0.99	0.83	0.60	–
UT PC-6-3	5.62	–	–	< 10	5.5	–	1.00	–	0.64	–
AVG PC-6	5.3	–	4.8	–	4.8	–	1.00	0.83	0.64	–
WV PC-7-1	36.2	46.2	41	50	43	–	7.65	7.8	7.0	–
WV PC-7-2	35.6	45.4	41	48	35	–	7.86	8.4	5.8	–
WV PC-7-3	35.7	46.0	39	48	41	–	7.72	8.2	6.0	–
AVG PC-7	35.8	45.9	40	49	39	–	7.74	8.1	6.3	–
ND PC-8-1	2.20	2.5	2.6	< 10	2.4	–	0.771	< 1	0.54	–
ND PC-8-2	2.20	2.7	2.5	< 10	2.4	–	0.761	< 1	0.57	–
ND PC-8-3	2.30	2.8	2.3	< 10	2.5	–	0.802	< 1	0.54	–
AVG PC-8	2.23	2.6	2.4	–	2.4	–	0.778	–	0.55	–

TABLE A1 (continued)

Element (units)	Ni (μg/g)						Cu (μg/g)				
Technique Material Analyzed Sample split or average	INAA WC	EDXRF ASH	ICAP-AES ASH	EDXRF WC	DCAES ASH	DCAES WC	EDXRF ASH	ICAP-AES ASH	EDXRF WC	DCAES ASH	DCAES WC
UF PC-1-1	15.9	14.0	15	27	14	22	19.7	19	20	17	20
UF PC-1-2	13.2	15.9	14	22	13	29	20.5	19	18	16	18
UF PC-1-3	14.3	11	15	21	14	24	21.3	19	17	19	16
AVG PC-1	14.5	14	14	23	14	25	20.4	19	18	17	18
WY PC-2-1	4.4	4.3	4.9	9	4.8	< 10	12.1	12	18	11	5.0
WY PC-2-2	5.4	3.9	4.7	7	5.4	< 10	13.4	12	17	14	10
WY PC-2-3	5.0	3.7	5.2	8	5.4	< 10	13.1	13	17	14	6.0
AVG PC-2	4.9	3.9	4.9	8	5.2	–	12.9	12	17	13	7
IL PC-3-1	24.2	14	18	33	21	28	11	10	15	13	9.0
IL PC-3-2	17.8	20	19	30	19	35	9.4	10	13	11	10
IL PC-3-3	21.0	19	18	33	24	37	8.7	10	15	9.4	9.0
AVG PC-3	21.0	18	18	32	22	33	9.6	10	14	11	9
PITT PC-4-1	9.4	9.0	9.1	17	14	13	6.4	5.5	10	5.3	5.0
PITT PC-4-2	11.3	8.8	8.3	11	12	14	6.1	5.3	9	8.2	6.0
PITT PC-4-3	< 12	10.3	8.1	15	13	11	6.1	5.5	10	6.1	7.0
AVG PC-4	10.3	9.3	8.5	14	13	12	6.2	5.5	10	6.5	6
POC PC-5-1	9.2	7.00	6.9	11	6.4	11	12.7	12	16	22	18
POC PC-5-2	8.5	7.74	6.4	9	5.8	11	13.0	12	16	15	13
POC PC-5-3	8.2	8.0	6.9	12	7.4	< 10	11.9	12	19	20	27
AVG PC-5	8.6	7.91	6.7	11	6.5	11	12.5	12	17	19	19
UT PC-6-1	< 3	–	3.4	5	3.9	–	–	3.9	8	3.2	–
UT PC-6-2	3.2	–	3.3	5	4.1	–	–	3.8	8	2.4	–
UT PC-6-3	3.7	–	–	5	4.0	–	–	–	8	3.0	–
AVG PC-6	3.4	–	3.3	5	4.0	–	–	3.8	8	2.9	–
WV PC-7-1	14.0	18	16	17	23	–	25.2	19	30	17	–
WV PC-7-2	18.0	16	16	18	19	–	22.3	19	30	16	–
WV PC-7-3	14.3	17	16	19	21	–	23.3	19	32	13	–
AVG PC-7	15.4	17	16	18	21	–	23.6	19	31	16	–
ND PC-8-1	< 5	2.4	1.4	4	1.6	–	3.4	5.6	8	3.9	–
ND PC-8-2	< 3	1.6	1.4	10	1.6	–	3.3	3.5	10	3.8	–
ND PC-8-3	< 3	1.8	1.1	4	2.1	–	3.2	4.9	10	7.1	–
AVG PC-8	–	1.9	1.3	6	1.8	–	3.3	4.7	9	4.9	–

TABLE A1 (continued)

Element (units)	Zn (μg/g)					Ga (μg/g)		Ge (μg/g)	
Technique Material	INAA	EDXRF	ICAP-AES	EDXRF	DCAES	DCAES	DCAES	DCAES	DCAES
Analyzed Sample split or average	WC	ASH	ASH	WC	WC	ASH	WC	ASH	WC
UF PC-1-1	18.2	21.9	19	35	30	6.1	11	3.5	4.0
UF PC-1-2	17.0	19.2	19	32	30	6.3	11	3.4	4.0
UF PC-1-3	23.9	20.3	20	31	40	6.3	8.0	3.9	3.0
AVG PC-1	19.7	20.5	19	33	33	6.2	10	3.6	4
WY PC-2-1	11.0	9.7	10	26	< 20	2.2	4.0	< 0.4	< 2
WY PC-2-2	11.6	11.1	10	29	< 20	2.6	2.0	< 0.4	< 2
WY PC-2-3	11.2	11.1	10	21	< 20	2.5	3.0	< 0.4	< 2
AVG PC-2	11.3	10.6	10	25	–	2.4	3	–	–
IL PC-3-1	218	94	160	137	250	4.7	8.0	8.4	8.0
IL PC-3-2	243	112	180	105	260	4.4	5.0	8.4	7.0
IL PC-3-3	200	115	190	186	320	5.0	7.0	9.7	12
AVG PC-3	220	107	180	140	280	4.7	7	8.9	9
PITT PC-4-1	8.9	8.5	8.2	17	20	5.2	6.0	1.2	3.0
PITT PC-4-2	7.77	8.5	7.4	14	30	4.0	5.0	1.2	< 2
PITT PC-4-3	10.5	8.1	7.7	15	30	5.0	5.0	1.1	< 2
AVG PC-4	9.1	8.4	7.8	15	27	4.7	5	1.2	(3.0)
POC PC-5-1	5.7	4.3	3.9	14	< 20	2.2	4.0	0.46	< 2
POC PC-5-2	6.2	5.3	4.1	14	< 20	2.1	3.0	0.43	< 2
POC PC-5-3	7.3	4.7	3.9	15	< 20	2.5	4.0	0.49	< 2
AVG PC-5	6.4	4.8	4.0	14	–	2.3	4	0.46	–
UT PC-6-1	4.9	–	6.4	< 2	–	1.5	–	< 0.2	–
UT PC-6-2	7.4	–	6.0	< 2	–	0.9	–	< 0.2	–
UT PC-6-3	6.8	–	–	< 2	–	1.3	–	< 0.2	–
AVG PC-6	6.4	–	6.2	–	–	1.2	–	–	–
WV PC-7-1	14.0	12	13	9	–	13	–	1.1	–
WV PC-7-2	12.6	11	13	10	–	11	–	< 0.89	–
WV PC-7-3	14.0	12	12	10	–	11	–	1.2	–
AVG PC-7	13.5	12	13	10	–	12	–	1.1	–
ND PC-8-1	5.71	5.8	5.1	5	–	1.8	–	< 0.44	–
ND PC-8-2	5.51	5.1	4.7	4	–	1.5	–	< 0.44	–
ND PC-8-3	5.86	5.2	4.5	6	–	1.9	–	< 0.44	–
AVG PC-8	5.69	5.4	4.8	5	–	1.7	–	–	–

TABLE A1 (continued)

Element (units)	As (µg/g)		Rb (µg/g)			Sr (µg/g)				
Technique Material	INAA	DCAES	INAA	EDXRF	EDXRF	INAA	EDXRF	ICAP-AES	EDXRF	DCAES
Analyzed Sample	WC	ASH	WC	ASH	WC	WC	ASH	ASH	WC	ASH
split or average										
UF PC-1-1	16.6	31	19.4	21.6	23	56	59	59	61	66
UF PC-1-2	17.6	38	19.0	20.8	21	58	61	61	63	57
UF PC-1-3	17.1	22	20.0	21.3	20	33	61	58	61	66
AVG PC-1	17.1	30	19.5	21.2	21	49	60	59	62	63
WY PC-2-1	3.67	< 9	< 5	3.4	14	263	260	153	292	170
WY PC-2-2	3.23	< 9	< 5	3.4	14	248	260	145	300	240
WY PC-2-3	3.75	< 9	< 5	3.7	11	245	260	153	291	260
AVG PC-2	3.6	–	–	3.5	13	252	260	150	294	220
IL PC-3-1	4.46	< 16	15.5	15	22	42	30.5	29	33	40
IL PC-3-2	4.65	< 16	17.2	15	17	36	28.8	29	30	37
IL PC-3-3	4.90	< 16	14.6	15	21	40	30.5	29	35	44
AVG PC-3	4.7	–	16	15	20	39	29.9	29	33	40
PITT PC-4-1	8.44	19	9.0	9.38	8	58	70	64	59	88
PITT PC-4-2	8.30	17	7.2	8.6	8	61	68	64	61	83
PITT PC-4-3	8.50	15	7.1	9.20	8	65	65	63	69	100
AVG PC-4	8.42	17	7.7	9.1	8	61	68	64	63	91
POC PC-5-1	10.4	18	<6	2.6	5	97	110	85	86	110
POC PC-5-2	10.6	11	<6	2.1	4	116	110	85	77	100
POC PC-5-3	9.89	14	<3	2.2	5	101	110	85	93	120
AVG PC-5	10.3	15	–	2.3	5	105	110	85	85	110
UT PC-6-1	0.51	< 10.1	<2	–	3	71	–	60	58	83
UT PC-6-2	0.50	< 10.1	1.10	–	2	68	–	59	65	92
UT PC-6-3	0.44	< 10.1	0.95	–	3	70	–	–	66	92
AVG PC-6	0.48	–	1.02	–	3	70	–	60	63	89
WV PC-7-1	5.8	< 43	29.8	42.3	43	64	76.2	49	87	76
WV PC-7-2	5.30	< 43	28.5	45.0	43	59	78.0	47	87	62
WV PC-7-3	7.40	< 43	31.2	43.4	40	58	79.7	51	83	72
AVG PC-7	6.2	–	29.7	43.6	42	60	78.0	49	86	70
ND PC-8-1	2.67	< 21	0.86	–	4	638	640	510	800	590
ND PC-8-2	2.61	< 21	0.99	–	5	580	640	500	800	600
ND PC-8-3	2.61	< 21	<1	–	3	583	630	500	750	690
AVG PC-8	2.63	–	0.93	–	4	590	640	500	780	630

TABLE A1 (continued)

Element (units)	Y (μg/g)				Zr (μg/g)				Nb (μg/g)		
Technique Material Analyzed Sample split or average	EDXRF ASH	ICAP-AES ASH	EDXRF WC	DCAES ASH	EDXRF ASH	EDXRF WC	DCAES ASH	DCAES WC	EDXRF ASH	EDXRF WC	DCAES ASH
UF PC-1-1	10	9.3	–	6.2	27.7	24	13	36	2.7	–	1.6
UF PC-1-2	9.7	9.3	–	3.0	26.5	22	7.4	29	2.2	–	1.3
UF PC-1-3	11	9.2	–	4.9	27.7	24	12	34	2.7	–	2.0
AVG PC-1	10	9.3	–	4.7	27.3	23	11	33	2.5	–	1.7
WY PC-2-1	3.4	3.9	–	2.4	22.1	19	12	< 20	1.2	–	1.2
WY PC-2-2	3.6	3.7	–	3.1	23.4	21	17	< 20	1.0	–	1.3
WY PC-2-3	3.7	3.7	–	3.6	22.5	17	21	< 20	0.85	–	1.8
AVG PC-2	3.6	3.8	–	3.0	22.7	19	17	–	1.0	–	1.4
IL PC-3-1	4.9	4.2	–	4.4	23.7	24	14	22	1.9	–	1.9
IL PC-3-2	3.2	4.2	–	4.7	21.1	22	16	25	< 1.6	–	2.3
IL PC-3-3	4.2	4.2	–	5.2	22.0	24	23	16	2.3	–	3.2
AVG PC-3	4.1	4.2	–	4.7	22.3	23	17	21	2.1	–	2.5
PITT PC-4-1	5.1	4.3	–	2.8	20.7	15	10	23	2.0	–	1.7
PITT PC-4-2	5.1	4.2	–	3.3	21.2	17	15	21	1.8	–	2.0
PITT PC-4-3	4.4	4.2	–	3.0	19.8	18	11	28	1.8	–	1.7
AVG PC-4	4.9	4.3	–	3.1	20.5	17	12	24	1.9	–	1.8
POC PC-5-1	7.10	6.4	–	4.6	17.0	10	13	25	0.85	–	1.3
POC PC-5-2	6.68	6.4	–	4.3	16.7	8	11	34	0.85	–	0.74
POC PC-5-3	6.89	5.8	–	4.9	17.0	11	12	32	0.85	–	1.2
AVG PC-5	6.89	6.2	–	4.6	16.9	10	12	30	0.85	–	1.1
UT PC-6-1	–	1.8	2	1.9	–	20	12	–	–	< 10	0.46
UT PC-6-2	–	2.1	< 2	1.9	–	17	13	–	–	< 10	0.51
UT PC-6-3	–	–	< 2	1.6	–	16	9.2	–	–	< 10	0.55
AVG PC-6	–	2.0	(2)	1.8	–	18	11	–	–	–	0.51
WV PC-7-1	21.4	11	19	9.7	80.0	106	47	–	7.8	13	2.5
WV PC-7-2	19	11	20	10.0	79.8	102	29	–	8.3	< 10	3.7
WV PC-7-3	22.9	11	17	7.6	81.6	101	27	–	8.9	13	4.5
AVG PC-7	21.2	11	19	9.1	80.5	103	34	–	8.3	13	3.6
ND PC-8-1	–	1.9	< 2	2.3	6.5	20	12	–	< 1	< 10	0.63
ND PC-8-2	–	1.8	< 2	2.6	7.0	19	12	–	< 1	< 10	0.51
ND PC-8-3	–	–	< 2	2.4	4.5	17	13	–	< 1	< 10	0.61
AVG PC-8	–	1.8	–	2.4	6.5	18	13	–	–	–	0.58

TABLE A1 (continued)

Element (units)	Ba (μg/g)						La (μg/g)			
Technique Material	INAA	EDXRF	EDXRF	ICAP-AES	DCAES	DCAES	INAA	EDXRF	EDXRF	DCAES
Analyzed Sample	WC	ASH	WC	ASH	ASH	WC	WC	ASH	WC	ASH
split or average										
UF PC-1-1	52	51	54	54	40	88	10.0	7.0	31	8.6
UF PC-1-2	68	54.7	68	55	43	72	10.0	8.1	9	5.3
UF PC-1-3	63	50	59	57	39	84	10.3	9.5	9	6.7
AVG PC-1	61	52	60	55	41	81	10.1	8.2	16	6.9
WY PC-2-1	324	270	400	15	290	200	5.32	< 3	4	4.8
WY PC-2-2	318	280	410	15	310	260	5.34	< 3	4	6.5
WY PC-2-3	297	260	420	14	360	300	5.38	< 3	11	7.1
AVG PC-2	310	270	410	15	320	250	5.35	–	6	6.1
IL PC-3-1	94	75.3	112	68	51	140	6.11	< 5	16	8.7
IL PC-3-2	91	74.5	122	87	53	120	6.10	< 5	15	8.9
IL PC-3-3	96	73.7	129	87	76	92	6.09	< 5	15	10
AVG PC-3	94	74.5	121	81	60	120	6.10	–	15	9.3
PITT PC-4-1	44	34.0	46	42	36	66	6.19	< 3	23	5.5
PITT PC-4-2	51	37.7	22	41	34	72	6.15	4.6	1	6.1
PITT PC-4-3	44	35.4	19	39	45	60	6.11	4.2	2	5.7
AVG PC-4	47	35.7	30	41	38	66	6.15	4.4	9	5.8
POC PC-5-1	197	170	134	16	190	400	6.78	1.6	1	6.9
POC PC-5-2	203	190	124	16	190	460	6.77	2.6	4	6.9
POC PC-5-3	193	180	164	16	260	500	6.73	2.3	10	7.9
AVG PC-5	198	180	140	16	210	450	6.76	2.2	5	7.2
UT PC-6-1	36	–	28	32	34	–	3.41	–	9	3.0
UT PC-6-2	37	–	32	30	31	–	3.27	–	9	2.9
UT PC-6-3	36	–	28	–	41	–	3.24	–	11	2.9
AVG PC-6	36	–	29	31	36	–	3.31	–	10	2.9
WV PC-7-1	166	110	230	120	130	–	21.7	15	15	14
WV PC-7-2	116	112	202	120	140	–	21.6	18	18	14
WV PC-7-3	116	107	200	130	120	–	21.3	19	14	12
AVG PC-7	133	110	210	120	130	–	21.5	17	16	14
ND PC-8-1	700	480	1000	430	500	–	2.79	–	8	3.5
ND PC-8-2	660	470	1040	390	700	–	2.84	–	6	3.8
ND PC-8-3	670	450	1060	450	540	–	2.84	–	10	3.7
AVG PC-8	680	460	1030	420	580	–	2.82	–	8	3.7

TABLE A1 (continued)

Element (units)	Ce (μg/g)				Nd (μg/g)		Sm (μg/g)	
Technique Material	INAA	EDXRF	EDXRF	DCAES	INAA	DCAES	INAA	DCAES
Analyzed Sample	WC	ASH	WC	ASH	WC	ASH	WC	ASH
split or average								
UF PC-1-1	18.1	15.1	27	< 9	< 20	10	1.98	< 1.4
UF PC-1-2	18.2	18.4	46	10	< 18	< 4	1.94	< 1.4
UF PC-1-3	18.7	17.5	48	< 9	8.0	5.0	2.00	< 1.4
AVG PC-1	18.3	17.0	40	(10)	(8.0)	8	1.97	–
WY PC-2-1	9.0	6.1	18	6.3	< 13	< 6	0.968	< 0.8
WY PC-2-2	9.5	4.2	21	10	< 11	< 6	0.988	< 0.8
WY PC-2-3	9.6	< 3	35	9.3	< 9	< 6	0.977	< 0.8
AVG PC-2	9.4	5.2	25	9	–	–	0.978	–
IL PC-3-1	12.5	6.8	23	< 32	< 10	< 11	1.19	< 1.6
IL PC-3-2	12.5	8.4	39	< 32	< 8	< 11	1.18	< 1.6
IL PC-3-3	12.8	6.5	64	28	< 11	6.5	1.22	< 1.6
AVG PC-3	12.6	7.2	40	(28)	–	(6.5)	1.20	–
PITT PC-4-1	11.5	7.4	19	< 18	< 12	4.3	1.10	< 0.9
PITT PC-4-2	11.5	9.94	25	< 18	< 8	4.2	1.09	< 0.9
PITT PC-4-3	11.1	9.57	6	< 18	< 10	3.2	1.08	< 0.9
AVG PC-4	11.3	9.0	17	–	–	3.9	1.09	–
POC PC-5-1	11.6	5.30	4	12	< 18	5.3	1.23	0.74
POC PC-5-2	11.8	8.59	19	10	< 16	6.9	1.21	0.69
POC PC-5-3	11.5	8.90	8	14	< 14	5.8	1.21	0.85
AVG PC-5	11.6	7.6	10	12	–	6.0	1.22	0.76
UT PC-6-1	4.88	–	20	7.4	< 3	2.9	0.517	0.37
UT PC-6-2	4.67	–	13	7.4	2.5	< 7	0.500	0.38
UT PC-6-3	4.84	–	12	6.0	1.6	< 7	0.507	0.36
AVG PC-6	4.81	–	15	6.9	2.0	(2.9)	0.508	0.37
WV PC-7-1	36.0	28.2	64	25	12.4	19	3.56	1.7
WV PC-7-2	35.2	31.7	54	27	11.7	19	3.50	1.7
WV PC-7-3	36.1	29.9	48	25	12.4	18	3.51	< 0.6
AVG PC-7	35.8	29.9	55	26	11.7	19	3.52	1.7
ND PC-8-1	4.34	–	21	< 6	< 3	< 3	0.420	< 0.3
ND PC-8-2	4.33	–	19	< 6	2.1	< 3	0.419	< 0.3
ND PC-8-3	4.68	–	17	< 6	2.5	< 14	0.388	0.47
AVG PC-8	4.45	–	19	–	2.3	–	0.409	(0.47)

TABLE A1 (continued)

Element (units)	Yb (μg/g)		Pb (μg/g)		
Technique Material	INAA	DCAES	GFAAS	DCAES	DCAES
Analyzed Sample split or average	WC	ASH	ASH	ASH	WC
UF PC-1-1	0.91	0.84	7.8	10	8.0
UF PC-1-2	0.84	0.82	7.4	10	10
UF PC-1-3	0.90	0.86	6.9	11	6.0
AVG PC-1	0.88	0.84	7.4	10	8
WY PC-2-1	0.42	0.23	3.1	2.6	< 2
WY PC-2-2	0.44	0.30	3.0	4.1	< 2
WY PC-2-3	0.40	0.35	2.7	3.5	< 2
AVG PC-2	0.42	0.29	2.9	3.4	–
IL PC-3-1	0.51	0.57	6.8	14	9.0
IL PC-3-2	0.51	0.58	6.3	13	8.0
IL PC-3-3	0.55	0.68	6.3	14	6.0
AVG PC-3	0.52	0.61	6.5	14	8
PITT PC-4-1	0.478	0.63	2.9	7.3	4.0
PITT PC-4-2	0.463	0.51	2.9	6.9	3.0
PITT PC-4-3	0.468	0.48	2.9	7.7	5.0
AVG PC-4	0.470	0.54	2.9	7.3	4
POC PC-5-1	0.555	0.46	2.5	12	5.0
POC PC-5-2	0.565	0.47	2.4	8.5	4.0
POC PC-5-3	0.545	0.42	2.4	12	5.0
AVG PC-5	0.555	0.45	2.4	11	5
UT PC-6-1	0.204	0.22	1.6	2.1	–
UT PC-6-2	0.198	0.20	1.6	1.7	–
UT PC-6-3	0.21	0.21	–	2.0	–
AVG PC-6	0.20	0.21	1.6	1.9	–
WV PC-7-1	1.69	1.8	12	18	–
WV PC-7-2	1.61	1.4	12	16	–
WV PC-7-3	1.52	1.4	12	13	–
AVG PC-7	1.61	1.5	12	16	–
ND PC-8-1	0.317	0.22	1.5	2.7	–
ND PC-8-2	0.298	0.19	1.5	2.1	–
ND PC-8-3	0.245	0.20	1.5	3.0	–
AVG PC-8	0.287	0.20	1.5	2.6	–