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#### ABSTRACT

Complete chemical analyses of 25 coals, primarily from Illinois, have been made in the laboratories of the Illinois State Geological Survey. Trace elements determined were antimony, arsenic, beryllium, boron, bromine, cadmium, chromium, cobalt, copper, fluorine, gallium, germanium, lead, manganese, molybdenum, nickel, mercury, phosphorus, selenium, tin, vanadium, zinc, and zirconium. Major and minor elements determined were aluminum, calcium, chlorine, iron, magnesium, potassium, silicon, sulfur, and titanium. Procedures for the analytical methods used—neutron activation, optical emission, atomic absorption, X-ray fluorescence, and ionselective electrode—are given in detail.

Wherever possible, accuracy was evaluated by comparing results obtained by the various methods with results from splits of the same coal samples. Further comparison were made by analyzing whole coal and its lowand high-temperature ashes, thus permitting a thorough evaluation of traceelement losses resulting from volatilization during sample preparation. Results of the various analytical procedures in general compared favorably, although exceptions are noted, e.g., vanadium and fluorine. Certain techniques have been chosen as preferred methods for determining specific elements because they are more accurate, their precision is superior, or they take less time for analysis.

The investigation is continuing, and many additional coal samples will be analyzed. Statistical analysis of available data suggests that most trace elements in coal are present in quantities that approximate the composition of the earth's continental crust and that those elements normally related to one another in other geological environments are also related in the coals studied.

#### INTRODUCTION

In recent years, society has become increasingly aware of the problems that may arise in the environment from concentrations of elements normally present in only trace amounts. Coal combustion, along with other means of producing energy, is under scrutiny as a potential source of pollution from volatile trace elements. Coal has become suspect because of the general knowledge that a variety of trace elements, some of which are toxic to plant and animal life in other chemical combinations, occur in coal (Goldschmidt, 1935, 1937). It has therefore become imperative to develop accurate and reliable data on the amount of these elements present in coal, their distribution and mode of occurrence, and their volatility during combustion of the coal. Only with the development of a sufficiently large fund of such data will the general public and the agencies with the responsibility of protecting the environment be in a position to reach intelligent conclusions concerning utilization of coal.

Numerous investigations have been conducted on the chemical constitution of coal ash, and these are amply summarized in several relatively recent review articles (Francis, 1961; Ode, 1963; Nicholls, 1968; and Watt, 1968), which deal in part with trace elements. However, research on trace elements has not been extensive because they occur in such small amounts that their determination is both costly and difficult.

Previous investigations of the concentrations of trace elements in coal have been based on analysis of high-temperature coal ash (Zubovic, Stadnichenko, and Sheffey, 1961, 1964, 1966, 1967; Abernethy, Peterson, and Gibson, 1969), which measures the oxides of the elements in the altered mineral matter. Although such investigations, are valuable for estimating concentrations of refractory constituents or elements of low volatility, they do not reliably measure total amounts of volatile trace elements in whole coal. In this study we have determined not only the amounts of the trace elements present in the coals but also their volatility when the coals were ashed at both conventional high temperatures (up to  $850^{\circ}$  C) and low temperatures (<150° C).

This report discusses the chemical analytical techniques developed for determination of many of the trace elements in coal, compares the results obtained by two or more analytical methods for the same element, and compares the determinations for a single element on samples prepared at different ashing temperatures. As a result of such cross-checking, a high degree of confidence can be placed on the "recommended" or "best" values reported.

Analyses of 25 coals are reported for the following trace elements: antimony, arsenic, beryllium, boron, bromine, cadmium, chromium, cobalt, copper, fluorine, gallium, germanium, lead, manganese, molybdenum, nickel, mercury, phosphorus, selenium, tin, vanadium, zinc, and zirconium. In addition, the major and minor elements (aluminum, calcium, chlorine, iron, magnesium, potassium, silicon, sulfur, and titanium) were determined.

The investigation of potentially volatile trace elements in coals is continuing at the Illinois State Geological Survey, and future publications will include results of many more chemical analyses, a more complete statistical handling of those data than is possible at this time, and a detailed analysis of the geological factors that control the distribution of the trace elements in coal. A series of prepared coal samples may be analyzed for their trace element content, to determine which elements can be removed from coals by coal cleaning techniques.

#### Acknowledgment

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#### COAL SAMPLE COLLECTION AND PREPARATION

## Type and Source of Samples

Chemical analyses of 25 coal samples were made for this study. Twentytwo of the samples were composite face channel samples collected in the coal mines by Illinois State Geological Survey personnel. Each face channel sample was cut by hand with a pick and represented the full height of the coal seam, excluding only mineral bands, partings, or nodules over three-eighths of an inch thick. This procedure follows a long standing practice at the Illinois State Geological Survey and is based on a technique described by Holmes (1911). Three face channel samples generally were collected in each mine, but in some mines only two could be collected. The face channel samples were crushed to pass a oneeighth-inch screen and then combined into a composite sample, riffled to the desired quantity.

The coal sample is comminuted further to 20 mesh (740  $\mu$ m), 100 mesh (149  $\mu$ m), or finer, depending on the analytical technique to be applied. In

all cases, the sample is subdivided into aliquots by riffle sample splitters or by quartering the sample. The parts are thus representative of the original coal sample.

Of the three coal samples that were not face channel samples, one (C-15944) was a drill core of the DeKoven Coal Member and was treated much like a face channel sample (omitting mineral bands in excess of three-eighths of an inch); sample C-17096 represents the production from a mine in Utah and was provided by the coal company; and sample C-18009, the National Bureau of Standards (NBS) sample SRM-1630, is a combination of several West Virginia coals.

## Low-Temperature Ashing (LTA)

A sample preparation technique variously identified as electronic low-temperature ashing, radio-frequency ashing, or oxygen-plasma ashing, was used in this study. The coal is ashed in commercially available devices, either the LFE Corporation Model LTA600 or the International Plasma Corporation Model 1101. Within these instruments, oxygen is passed through a high energy electromagnetic field produced by a radio-frequency oscillator. The oscillator tube operates on a frequency of 13.56 Mhz, in compliance with Federal Communication Commission requirements for scientific and medical equipment (Gleit, 1963).

As the oxygen is passed through the radio-frequency field, a discharge takes place. The activated gas plasma "is ... a mixture of atomic and ionic species as well as electronically and vibrationally excited states" (Gleit, 1963). The activated oxygen passes over the coal sample, and oxidation of the organic matter takes place at relatively low temperatures. The electronics involved are discussed in articles by the developers of this instrumental technique (Gleit, 1963; Gleit and Holland, 1962).

Coal to be ashed in this system is ground to pass 20 mesh, and approximately 50 grams (g) is placed in Pyrex boats and dried in a vacuum desiccator prior to being put into the ashing chamber. The ashing takes place at a pressure of 1 to 3 torr with an oxygen flow rate of 50 to 100 ml per minute. The plasma temperature may be varied by changing the radio-frequency power level. At a radio-frequency power of 100 watts the plasma temperature is approximately  $70^{\circ}$  C. Higher temperatures are reached in the ashing chambers due to the exothermic oxidative reaction between the activated gases and the coal. Ashing temperature, monitored with a Raynger model LTX-28 infrared remote thermometer, was not allowed to exceed 150° C in this study. Prior to analysis, the resulting low-temperature ash samples are hand ground in an agate mortar and, depending on the analytical method used, dried at 110° C or in a vacuum oven.

The effects of low-temperature ashing and of the oxidizing gas stream upon pure minerals and upon minerals in coal have been discussed in earlier papers (Gluskoter, 1965, 1967; Rao and Gluskoter, 1973). No oxidation of minerals in the coal has been reported, and the only changes observed are those to be expected at a temperature of 150° C and a pressure of 1 torr. Therefore, the major mineral constitutents of coals-pyrite, kaolinite, illite, quartz and calcite-are considered to be unaffected by the radio-frequency ashing.

Most trace elements contained in the coal in inorganic combination are not volatilized during low-temperature ashing, and many elements thought to be present in organic combination also remain in the low-temperature ash. The loss or retention of various elements during low-temperature ashing is discussed later in this report.

Samples prepared by low-temperature ashing can have several important advantages for analysis compared to whole coal: (1) no chemicals (such as are required for wet-washing whole coal) need be added during preparation because only high-purity oxygen is introduced, under a partial vacuum; (2) trace elements in the ash generally are preconcentrated to 10 or more times their amount in whole coal; and (3) subsequent analytical treatment is greatly simplified.

Low-temperature ashing also provides samples superior to those prepared in a muffle furnace at  $450^{\circ}$  to  $500^{\circ}$  C. The LTA technique minimizes or eliminates losses of trace elements by volatilization.

Certain trace elements, however, are at least partially lost during low-temperature ashing, which would preclude its use for those elements. Whole coal would then be analyzed directly or combusted under various controlled conditions.

#### Trace Element Volatility

## Low-Temperature Coal Ash

Because conventional high-temperature ashing in a muffle furnace results in possible losses of such trace elements as Hg, Se, Sb, and As, lowtemperature ashing in an oxygen atmosphere was investigated as a means of oxidizing organic matter without volatilizing the trace elements.

The volatility of each trace element during low-temperature plasma oxidation was studied by one of the following procedures:

1) Volatile combustion products, collected in cold traps (-78° C) in the vacuum train of the low-temperature asher, are analyzed.

2) Whole coal that has been subjected to neutron irradiation is ashed and the volatile radio-isotopes that have been collected in the cold trap of the asher are detected.

3) Results obtained from the analysis of whole coal for a particular trace element are compared with results for that element in a low-temperature ash prepared from the same coal to determine if significant losses occur during the ashing process. This procedure was also used to evaluate loss of trace elements by volatilization from coal samples ashed at 450° C.

Low-temperature ash: elements lost	Low-temperature a elements retaine	sh: High-temperature ash: d elements retained†
Hg (up to 90%)	Ga Cu*	Be
Br (~100%)	Se Pb*	Ge
Sb (up to 50%)	Aš Cd*	Мо
F (untested,	Zn* V*	В
probably 100%)	Ni* Mn*	
	Co* Cr*	

TABLE 1-VOLATILITY OF TRACE ELEMENTS IN COAL

\* Also retained in coal ash prepared at  $450^{\circ}$  C.

 $\pm$  No significant losses observed in coal ash prepared at 300  $^{\rm O}$  to 700  $^{\rm O}$  C.

Although our studies are incomplete, table 1 summarizes the results obtained thus far. The study of trace element volatility dictated the method to be used for the analysis. Determinations of Sb, Br, Hg, and F had to be carried out on whole coal; Ga, Se, and As could be determined in low-temperature plasma coal ash; and the remaining elements could be determined in hightemperature coal ash. Certain types of prepared samples are better suited to one particular analytical technique than to others.

## High-Temperature Coal Ash (HTA)

As high-temperature coal ash ( $450^{\circ}$  to  $500^{\circ}$  C) is more easily prepared than low-temperature coal ash, trace elements found to be retained in quantity in coal ash prepared at high temperatures are derived by conventional high-temperature coal ashing if whole coal cannot be conveniently analyzed. Low-temperature ash also has proved to be unsatisfactory for determination of the less volatile trace elements by optical emission spectroscopy because the ash sample contains chemical compounds (high-temperature ash is composed of elemental oxides) that behave erratically in the DC arc. These compounds also make comparison standards for low-temperature ash exceedingly difficult to prepare. Because high-temperature ash has the advantage of being composed of elemental oxides, ash prepared from -100 mesh coal and ashed in a muffle furnace at  $450^{\circ}$  to  $500^{\circ}$  C is used for both optical emission methods employed in this study. The ashing procedure is continued until all carbonaceous material is oxidized. Prior to analysis, the coal ash is ground in an agate or mullite mortar and dried at  $110^{\circ}$  C.

During the high-temperature ashing studies, the type of crucible in which the coal was ashed affected the apparent B concentration in the coal. No other trace elements were found to react in this manner. New porcelain crucibles seem to withdraw boron from the coal by some unknown mechanism (table 2), resulting in a lower apparent B concentration. The extraction is more efficient at the lower temperatures. Above  $600^{\circ}$  C, possible volatilization of B occurs. When coal samples are ashed in fused silica crucibles, the

observed moisture-free B concentrations are slightly higher than the results derived from the  $600^{\circ}$  C ash prepared in new porcelain and are essentially the same in  $300^{\circ}$  and  $600^{\circ}$  C ashes of both coals (table 2). Samples ashed in old porcelain crucibles exhibit the highest B concentrations in moisture-free coal, with the  $600^{\circ}$  C ash having a lower concentration than the  $300^{\circ}$  C ash. This may indicate contamination from B residues in the old porcelain crucibles.

Fused silica crucibles seem to give best results in coal ashing, and 500° C seems to be the optimum temperature.

## METHODS OF ANALYSIS

During the initial 12 months of this investigation, at least 10 chemists devoted nearly full time to the development and application of analytical methods for the determination of trace, minor, and major elements in whole coal and coal ash. Only minor modifications were needed to adapt many existing procedures to coal or coal ash determinations, but other methods required major changes or new approaches.

Accuracy and precision were emphasized relative to the speed of analysis. Where possible, results obtained from one procedure were critically compared with those of another, and refinements were made where necessary. The process has been slow because no standards for the trace element composition of coal are as yet available. Round-robin testing for the standardization of multiple trace element concentrations in coal is now being sponsored jointly by the U. S. Environmental Protection Agency and the National Bureau of Standards. The American Society for Testing and Materials, Committee D-5 on Coal and Coke, also has a new program for the standardization of methods for determining trace elements in coal. The Illinois State Geological Survey is participating in both studies.

		Туре	of crucible	and sample	number			
	<u>New por</u>	celain	Fused	silica	Used porcelain			
Temperature	C <b>-1</b> 6317	<u>c-16030</u>	<u>C-16317</u>	<u>c-16030</u>	<u>C-16317</u>	<u>C-16030</u>		
(°C)	(ppm B)	(ppm B)	(ppm B)	(ppm B)	(ppm B)	(ppm B)		
300	62	23	137	62	176	67		
400	90	31			ו			
500	104	34						
600	119	46	134	54	157	61		
700	106	40		94a				

TABLE 2---EFFECT OF CRUCIBLE TYPE ON BORON CONCENTRATION IN COAL ASH (calculated to moisture-free coal basis)\*

\* Study by G. B. Dreher. Results obtained by optical emission direct-reading spectrometry.

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In the present investigation, six independent instrumental methods were used to analyze whole coal and coal ashes. Considerable overlap occurs in the elements determined by each method. As the investigation progresses, the procedures that prove most precise, accurate, and convenient to use will be selected for routine analysis.

The various analytical methods were developed by the following personnel in the Survey's Section of Analytical Chemistry: X-ray fluorescence (X-RF) by John K. Kuhn, atomic absorption (AA) by Peter C. Lindahl, optical emission-direct reading (OE-DR) by Gary B. Dreher, optical emission-photographic (OE-P) by John A. Schleicher, neutron activation analysis (NAA) by Joyce Kennedy Frost, Patricia M. Santoliquido, and R. R. Ruch, and ion selective electrode (ISE) by Josephus Thomas, Jr.

## X-Ray Fluorescence Analysis of Whole Coal and Coal Ash

X-ray fluorescence determinations were made on whole coal for As, Br, Pb, Zn, Cu, Ni, P, Cl, S, V, Mg, K, Ca, Fe, Ti, Al, and Si and on coal ash for Ni, P, V, Mg, K, Ca, Fe, Ti, Al, and Si. A Phillips vacuum spectrometer equipped with a Mark I solid-state electronic panel was used for all analyses.

A chromium target X-ray tube was employed; however, subsequent investigations will be made with a tungsten target tube, which will very probably increase the number of elements determined. Goniometer and other instrument settings used for the analyses are listed in table 3. The preparation procedure follows.

#### Low-Temperature and High-Temperature Coal Ash

Coal ash is composed entirely of mineral matter, as opposed to whole coal, which comprises mainly carbon, hydrogen, oxygen, nitrogen, and sulfur along with the mineral matter. As such the ash creates matrix problems best handled by the dilution technique described by Rose, Adler, and Flanagan (1962) and used extensively for geological samples.

Low-temperature ash was dried in a vacuum oven and high-temperature ash was dried at 105° C in air. Ashes must be stored in a desiccator because some absorb relatively large quantities of water in a very few minutes. From the dried sample, 125 mg was weighed into a graphite crucible containing 1.0000 g of lithium tetraborate. A depression made in the tetraborate prior to addition of the sample prevented its contact with the crucible wall. Next, 125 mg of lanthanum oxide was added as a heavy-element absorber, and the contents of the crucible were'mixed with a glass rod as thoroughly as is possible without scraping the crucible wall or bottom. The mixture was fused in a furnace for 15 minutes at 1000° C, removed, covered with a second crucible, and allowed to cool to room temperature. The resulting fused pellet was then weighed alone to determine fusion loss and placed in the grinding vial of a No. 6 Wig-L-Bug with 2 percent by weight of Somar mix (a commercial mixture used as a grinding and plasticizing agent). The sample was ground for 3 minutes, transferred to a die, and pressed at 40,000 psi. Samples were then exposed to the X-rays and the various elements determined in the usual fashion.

						Pulse anal	height yzer
Element	X-ray	20 angle	Background 20	Crystal	Vacuum	Base	window
Si	KL & KL	108.01	111.01	EDDT	yes	7	17
Al	$KL^{2}_{2} \& KL^{2}_{2}$	142,44	145。95	EDDT	yes	5	12
Ti	$KL^{2} \& KL^{2}$	86.12	89.12	LiF	no	5	18
Fe	$KL^{2} \& KL^{2}$	57.51	60.51	LiF	no	5	25
Ca	$KL^2$ $Z$	44.85	47.95	EDDT	yes	14	30
К	KL & KL	50.32	53.90	EDDT	yes	14	21
Mg	KL <sub>23</sub>	136.69	139.69	ADP	yes	. 4	8
v	KL <sup>2</sup> & KL	76.93	80.93	Lif	no	5	16
S	KL <sup>2</sup> & KL <sup>2</sup>	75.24	78.38	EDDT	yes	12	18
Cl	KL <sup>2</sup> 2	64.94	67.94	EDDT	yes	11	19
Р	KL_ & KL	110.99	113.99	Ge	yes	9	15
Ni	KL <sup>2</sup> & KL <sup>2</sup>	48.66	50.36	LiF	yes	10	27
Cu	$KL_2^2 \& KL_2^2$	45.02	49.67	LiF	yes	11	28
Zn	KL <sub>2</sub> & KL <sub>2</sub>	41.79	44.25	LiF	yes	10	22
Pb	L <sub>3</sub> N <sub>5</sub> & L <sub>2</sub> M <sub>4</sub>	28.24	31.24	LiF	yes	22	28
Br	KL & KL	29.97	35.12	LiF	yes	25	23
As	$\operatorname{KL}_{3}^{2} \& \operatorname{KL}_{2}^{2}$	34.00	37.00	Lif	yes	24	23

TABLE 3-X-RAY FLUORESCENCE SETTINGS FOR THE ANALYSIS OF COAL AND COAL ASH

When backed with an appropriate material, the pressed disk was at least semipermanent and could be used to give quantitative determinations for major and minor elements.

## Whole Coal

Coal is a heterogeneous mixture composed primarily of organic compounds. Inorganic constituents such as pyrite (iron and sulfur) rarely fall short of 0.2 percent or exceed 5.0 percent of bituminous and higher rank coals. Other elements vary much less and, while matrix effects cannot be assumed to be absent, it is apparent that in most cases they are small and corrections for them are easily made.

To form the coal disk that is subjected to the X-rays, 2.0000 g of air-dried coal were placed in the grinding vial of a No. 6 Wig-L-Bug along with 10 percent by weight of Somar mix. The mixture was gound for 3 minutes, transferred to a die and, with a suitable backing, pressed into a disk at a pressure of 40,000 psi. The coal disk was dried in vacuum to prevent losses that could occur in a drying oven. Determinations on all elements except iron, titanium, and vanadium were performed in vacuum to avoid X-ray scattering due to adsorbed water on the surface of the whole coal disk.

Standards were prepared from chemically analyzed coals by the same procedure. Determinations were made in order of descending potential volatility. Some interferences, primarily from iron, do occur and must be dealt with individually for each trace element affected. One method for making such corrections is to observe and adjust the effect of adding different amounts of iron to a coal of known composition on the count rate of each element.

The concentration of an element in a sample of unknown composition is calculated by using a concentration/count "factor," which is the ratio of the background-corrected count rate for a given element (table 3, 2  $\theta$  angular settings) to the concentration of the element in chemically analyzed standards. This ratio is defined by the slope of the calibration curve obtained from a plot of the count rate for each element in the standards vs. the element's respective concentration. The concentration of any element in a sample being analyzed is the product of its "factor" multiplied by the count rate.

## X-Ray Fluorescence Study of the Effects of Different Whole Coal Particles

A set of whole coal samples was tested to determine the effect of particle size upon the precision of measurement. Samples of coal that were

Element	-60 mesh	-100 mesh	-200 mesh	-325 mesh	-400 mesh	Extra- fine mesh	Concen- tration unit
Fe	0.03	0.01	0,00	0.01	0.01	0.00	%
V	1.3	2.9	1.7	2.4	0.6	0.4	ppm
Ti	0.01	0,01	0.02	0.02	0.01	0.01	%
Al	0.03	0.08	0.03	0.02	0.04	0.01	%
Si	0.07	0.01	0,05	0.01	0.02	0.03	%
K	0.004	0.003	0.005	0,002	0.002	0.001	%
Ca	0.015	0.017	0.023	0.018	0.005	0.004	%
S	0.02	0.02	0.02	0.01	0.00	0.02	%
Cl	0.001	0.003	0.002	0.004	0.001	0.003	%
Р	1.3	1.6	2.1	1.3	1.0	1.0	ppm
Mg	0.012	0.012	0.010	0.011	0.005	0.005	%
Ni	1.9	<b>1.</b> 7	3.2	2.9	0.9	0.8	ppm
Cu	4.8	0.8	0.2	0.1	0.1	0.1	ppm
Zn	8.5	1.0	0.5	1.3	0.2	0.2	ppm
Pb	2.8	1.9	2.0	0.4	0.8	0.9	ppm
As	3.0	1.4	1.9	0.0	0.3	0.6	ppm
Br	0.8	0.4	0.5	0.4	0.3	0.2	ppm

## TABLE 4-ABSOLUTE DIFFERENCES BETWEEN DUPLICATE ANALYSES OF WHOLE COAL SIZE FRACTIONS

sequentially ground to pass through 60, 100, 200, 325, 400 and "extra fine" mesh sieves were used. From these size fractions duplicate disks were pressed for analysis, as has been described.

Table 4 shows the absolute differences in concentrations, expressed in percentage or parts per million, between duplicate coal samples. The data show that replication was satisfactory for most determinations made on whole coal splits ground to pass at least a -100 mesh sieve. This is generally true for Br and As, and also for Zn and Fe where concentrations are low. Other elements (e.g., V, Ca, Ni, and Pb) will yield more precise values if the samples are ground to -325 mesh. Further grinding, while increasing precision in some cases, is probably unwarranted because of variations encountered in field samples of coal. Although these size criteria were tested only in X-ray fluorescence determinations, they are probably valid for any procedure employing whole coal samples of 1 or 2 grams.

## Comparative Analyses

Table 5 compares whole coal analyses made by X-ray fluorescence with those on coal ash samples analyzed by the British Coal Utilization Research Association (Dixon et al., 1964). The results show the X-ray method

	BCUI	RA #4	BCUI	BCURA #5		RA #7	BCUI	RA #10	BCURA	slag	Av.	
Oxide	X-RF	Lit.*	X-RF	Lit.*	X-RF	Lit.*	X-RF	Lit.*	<u>X-RF</u>	Lit.*	diff.	
Si02	53.28	53.41	29.27	29.43	20.01	20.37	44.03	44.49	51.45	51.58	0.25	
Ti0 <sub>2</sub>	1.65	1.70	0.65	0.70	0.26	0.34	1.18	1.19	0.96	0.96	0.04	
A1203	34.11	33.88	19.73	19.82	10.03	10.33	29.93	30.02	28.20	28.45	0.19	
Fe203	5.83	5.76	39.02	39.24	62.16	62.31	13.56	13.82	6.27	5.99	0.17	
MgO	0.66	0.71	1.18	1.29	0.58	0.63	2.05	2.00	2.33	2.26	0.06	
CaO	0.73	0.77	2.47	2.54	2.31	2.30	1.24	1.29	7.89	7.91	0.04	
К <sub>2</sub> 0	2.45	2.38	1.94	1.95	1.38	1.39	3.68	3.71	2.84	2.81	0.03	
P205	0.48	0.41	0.14	0.14	0.17	0 <b>.1</b> 5	0.77	0.77	0.09	0.05	0.03	

## TABLE 5---COMPARISON OF ISGS X-RAY FLUORESCENCE ANALYSES OF WHOLE COAL WITH BCURA\* ANALYSES (in percent)

\* British Coal Utilization Research Association (Dixon et al., 1964).

to be accurate for the oxides listed. Comparisons, made later in tables ll and 13, also indicate that whole coal X-ray fluorescence determinations are generally in good agreement with those obtained by other methods and that analyses of whole coal compare very favorably with those of coal ash when the results are converted to a whole coal basis from the percentage of ash in the coal.

Because analyses performed by optical emission and atomic absorption methods are made on high- and low-temperature ash, small variations from the results obtained on whole coal samples by X-ray fluorescence are to be expected. For Zn and As (table 11), variations are larger at high concentrations. This may be due to sample particle size, as X-ray fluorescence analyses were made on coal samples ground to pass a -60 mesh sieve. Further studies are now being done to solve this problem and eliminate it if possible.

#### Precision

Estimates of relative standard deviation ( $l \sigma$ ) for the X-ray fluorescence analyses of whole coal are:

Si	0.35%	S	0.5%
Ti	1.9	Cl	4.2
Al	0.9	Ni	8.4
Fe	1.2	Cu	4.0
Mg	3.3	Zn	3.8
Ca	0.1	Pb	1.9
K	0.7	As	1.8
Р	1.6	Br	2.0
V	1.3		

#### Optical Emission Spectrometric Analysis of High-Temperature Coal Ash

Trace quantities of ll elements can be determined simultaneously and rapidly in high-temperature coal ash samples containing 10 to 30 percent Fe as  $Fe_2O_3$  with a Jarrell-Ash Model 750 direct-reading emission spectrometer, with Fe (2483.27 Å) as a variable internal standard. As little as 20 mg of coal ash sample will suffice for quadruplicate analyses. The elements determined by this method are B, Pb, Cu, Co, Ni, Be, Cr, V, Sn, Mo, and Ge.

## Construction of Calibration Curves

Eight standard samples were prepared by adding various amounts of a synthetic rock standard (1000 ppm of each of the elements to be determined) to U. S. Geological Survey standard granite G-2 (adjusted to a  $SiO_2:AI_2O_3$  ratio of 3:1 by addition of 379 mg of spectroscopically pure  $AI_2O_3$  to 0.50000 g of G-2). The preparation and resulting concentrations are summarized in table 6. A ninth standard sample was later prepared to increase the range of the boron calibration curve. To 0.50000 g of G-2 and 379 mg of  $AI_2O_3$ , 6.32 mg of  $Na_2B_4O_7\cdot10H_2O$  was added to attain a boron concentration of 1319 ppm.

The final mixtures for all standard and coal ash samples included 40 mg of standard or coal ash, 10 mg of spectroscopically pure  $Ba(NO_3)_2$ , and 150 mg of SP-2X graphite powder. They were combined in a plastic vial half an inch in diameter by 1 inch high that contained two plastic balls an eighth of an inch in diameter. One mixture was prepared for each of the nine standards. The small amount of  $Ba(NO_3)_2$  was added to improve the arcing characteristics and the reproducibility of results from replicate analyses. Higher amounts of  $Ba(NO_3)_2$  (up to 120 mg in 200 mg total mixture, 40 mg of sample) decreased reproducibility.

The amount of  $Fe_2O_3$  present in the high-temperature ash samples had a significant effect on the volatilization of the trace metals from the

Weight of synthetic standard (mg) added to 0.5 mg									6.32 mg of Na <sub>2</sub> B <sub>4</sub> 0 <sub>7</sub>
G-2 + 379 mg <sup>Al</sup> 2 <sup>0</sup> 3	0.00	1.00	4.04	9.19	19.79	54.45	133.22	535.89	10H <sub>2</sub> 0
Element	Parts per million								
В	1.86	2.84	5.78	10.7	20.5	50.2	106	264	1320
Pb	26.7	28.5	33.9	43.0	61.2	116	220	512	
Cu	9•95	11.8	17.3	26.6	45.1	101	206	5 04	
Co	4.55	6.40	12.0	21.3	39.9	96.0	202	501	
Ni	5•95	7.79	13.4	22.6	41.2	97.3	203	5 02	
Be	2.23	4.08	9.67	19.0	37.6	94.0	200	500	
Cr	8.37	10.2	15.8	25.0	43.6	99.5	205	503	
V	34.4	36.2	41.6	50.6	68.7	123	226	516	
Sn	0.93	2.78	8.37	17.7	36.4	92.8	199	500	
Мо	1.12	2.97	8.57	17.9	36.6	92.9	199	500	
Ge	0.66	2.51	8.11	17.5	36.1	92.5	199	499	

TABLE 6-CONCENTRATIONS IN STANDARD MATERIALS OF G-2 BASE IN 3:1 SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> MATRIX + 1000 ppm SYNTHETIC STANDARD

electrode during arcing, necessitating construction of a series of calibration curves for the Fe range of 10 to 30 percent (as  $Fe_2O_3$ ) in the sample. Five calibration curves were drawn for each of the 11 trace elements to be determined, with 5 percent increments of total  $Fe_2O_3$  in the undiluted standards, beginning with 10 percent  $Fe_2O_3$ .

Each standard sample mixture for which a calibration curve series was drawn consisted of standard material and  $Fe_2O_3$  totalling 40 mg. Because standard granite contains natural iron, an adjustment between standard sample and added  $Fe_2O_3$  was made for each sample mixture to produce 40 mg containing the desired final concentration of  $Fe_2O_3$ . This procedure was followed for each of the five sets of calibration curves.

## Internal Standardization

Because an iron line was used as the variable internal standard, the precise concentration of iron in each coal ash sample was determined by X-ray fluorescence analysis of the whole coal. A response curve for the Fe 2483.27 Å internal standard line was drawn. Six coal ash samples with known different  $Fe_2O_3$  concentrations were arced under identical conditions, and the relative intensity values of the Fe internal standard line were read from the standardized instrument readout meter. The data (relative intensity vs.  $Fe_2O_3$  concentration) were plotted on log-log graph paper. The response curve was confirmed by arcing the standard samples that contained added  $Fe_2O_3$ . The standardized relative intensity shown on the response curve for Fe 2483 Å was set on the readout meter by varying a gain adjustment for each sample arced.

## Standard Conditions

The electrodes used were a thin-walled crater electrode (with an outside diameter of one-eighth of an inch and a crater one-fourth of an inch deep; National L-3979, or equivalent) as the sample anode, and a pointed counter electrode (one-eighth of an inch in diameter; National L-4036, or equivalent). The analytical gap of 6 mm was surrounded by a 10 SCFH flow of gas 80 percent argon and 20 percent oxygen, operated at a short-circuit current of 15 amperes d.c. for 65 seconds burning a sample charge of 15 mg. The proportions in the sample mixture were 4:1:15 (sample:Ba(NO<sub>3</sub>)<sub>2</sub>:graphite powder) for standard and coal ash samples.

The wavelengths of the analytical lines used are listed in table 7.

Element	Analytical wavelength (Å)	Average relative standard deviation (%)	Range of relative standard deviation (%)
В	2496.8 (second order)	5.2	1.0 - 13
Pb	2833.07	8.6	3.8 - 14
Cu	3273.96	7.5	2.9 - 20
Co	3453.50	4.8	1.1 - 19
Ni	3414.76	4.7	2.4 - 11.2
Be	2348.61	3.6	1.2 - 8.6
Cr	4254.35	4.0	1.09.1
v	3185.40	6.6	2.8 - 11
Sn	3034.12	22	10 - 73
Мо	3170.35	6.3	2.6 - 22
Ge	2651.18	16	3.0 - 42

TABLE 7-ANALYTICAL WAVELENGTHS AND RELATIVE STANDARD DEVIATIONS FOR THE DETERMINATION OF TRACE ELEMENTS IN HIGH-TEMPERATURE COAL ASH BY DIRECT-READING SPECTROMETRY

## Comparative Analyses

The results, which are calculated back to a whole coal basis, are generally in agreement with results obtained by other methods of analysis atomic absorption spectrometry, X-ray fluorescence spectrometry and photographic optical emission spectroscopy (table 11). The atomic absorption method uses a low-temperature coal ash, the X-ray fluorescence method uses raw coal, and the optical emission spectrographic method uses high-temperature coal ash. Table 7 lists the average relative standard deviations and their ranges for each element. Most of the coal ash samples contain tin in concentrations less than the detection limit, making the relative standard deviations for tin of little value. Because the analytical line for germanium is weak, a small change in the number of germanium atoms emitting at that wavelength in the arc during the arcing period produces a relatively large change in line intensity. Germanium concentrations found in the coal ash samples have often been near the detection limit, and when that is true a small change in relative line intensity also produces a relatively large change in the corresponding observed concentration.

## Optical Emission Spectrographic Analysis of High-Temperature Coal Ash

Samples of coal ash ignited to 500° C were analyzed by the photographic method of emission spectrography with a Jarrell-Ash 3.4 m Ebert grating spectrograph. The elements so determined were: B, Mn, Cr, Ge, Pb, Be, Mo, V, Cu, Zn, Zr, Co, and Ni. Analyses of Ag and Bi were attempted but could not be detected.

#### Construction of Calibration Curves

Because of the high concentrations of many trace elements in coal ash and the inability of the photographic plate to record accurately the large amount of light emitted, a 6 percent neutral filter was inserted in the light path of the spectrograph to attenuate the emitted light. Synthetic standards containing 1, 10, 50, 100, 250, 500, and 1000 ppm of the elements to be determined were prepared (from commercially available mixtures) in a base matrix having a 3:1 silica-to-alumina ratio. To these standards was added 10 percent  $Fe_2O_3$ , so that the final concentration of elements to be determined was 0.9, 9, 45, 90, 225, 450, and 900 ppm.

The first two standards were too low in concentration to be measured. Ten mg of the higher concentration standards was mixed in replicate with 10 mg of graphite and arced to completion plus 10 seconds (about 150 seconds). The transmissions of the attenuated lines, as recorded on an 8 x 10 inch Eastman Spectrum Analysis #1 photographic plate, were measured on a densitometer-comparator, and the values converted to their Seidel values.

The Seidel values were plotted against concentration on semi-log paper and the resultant curves transferred to a calculating board. After attenuation, the background was barely dense enough to overcome emulsion inertia, so no background corrections were made.

#### Standard Conditions

The sample electrodes used were graphite (ASTM No. S-13); the counter-electrodes were one-eighth-inch tapered rods rounded to a radius of one-thirty-second of an inch at the tip. Current used was 11 amps true at 220 volts. The electrode spacing was 4 mm, and the analytical gap was surrounded by a 14 SCFH laminar flow of 80 percent argon and 20 percent oxygen. The photographic plates were developed in Eastman D-19 developer for 3.0 minutes, shortstopped in 11 percent acetic acid for 30 seconds, and fixed for 4 minutes in Eastman Fixer. The plates were washed in running tap water for 20 minutes, rinsed in deionized water, and dried. Wavelengths of analytical lines used are given in table 8.

Ag and Bi were sought, but in no case was a Bi line observed. In a number of ash samples an extremely faint Ag line was seen, but the amount present was too small to be measured accurately. In addition, many samples contained high Zn concentrations outside the analysis limitations of this photographic method.

Analytical wavelength (Å)	Relative standard deviation (%)
2497.7	12
2576.1	19
2677.2	23
2651.2	16
2833.1	9
3067.7	
3130.4	14
3170.4	22
3184.0	30
3247.5	18
3280.7	
3345.0	
3392.0	37
3405 <b>.1</b>	25
34 <b>1</b> 4.8	24
	Analytical wavelength (Å) 2497.7 2576.1 2677.2 2651.2 2833.1 3067.7 3130.4 3170.4 3184.0 3247.5 3280.7 3345.0 3392.0 3405.1 3414.8

## TABLE 8---ANALYTICAL WAVELENGTHS AND RELATIVE STANDARD DEVIATIONS FOR THE DETERMINATION OF TRACE ELEMENTS IN HIGH-TEMPERATURE COAL ASH BY PHOTOGRAPHIC OPTICAL EMISSION

#### Comparative Analyses

Although the precision values (table 8) indicate a relatively high error for the method, averages of replications showed generally good agreement with other methods of analysis when all values were calculated to the whole coal basis (table 11). This was particularly true when the concentrations were in the lower ranges—25 ppm or less. However, at or near 100 ppm, agreement with other methods was poor. The particularly poor precision obtained for V and Zr is unexplained.

## Atomic Absorption Analysis of Coal Ash

Atomic absorption methods for the determination of Cd, Cu, Ni, Pb, and Zn in both low- and high-temperature coal ash have been extensively investigated. Both types of coal ash samples can be readily analyzed by atomic absorption spectrophotometry when an acid digestion bomb is used for sample treatment.

Atomic absorption measurements were made using a Beckman Model 1301 Atomic Absorption Accessory with a Beckman DB-G Grating Spectrophotometer. Measurements were recorded on a Beckman Model 1005 Linear-Log Ten-Inch Potentiometric Recorder, which was coupled with a Beckman 73490 Scale Expander. A Beckman 100410 Autolam Burner was used with an air-acetylene flame. Standard, single element, hollow cathode lamps were used.

The digestion bomb technique for the decomposition of silicates (Bernas, 1968) and aluminosilicates (Buckley and Cranston, 1971) was modified and found applicable to the decomposition of low- and high-temperature coal ash samples.

## Reagents and Construction of Calibration Curves

All reagents used were ACS certified reagent grade chemicals. Standard stock solutions were prepared from high-purity metals. A standard stock solution of each element—Cd, Cu, Ni, Pb, and Zn—was prepared to give a metal ion concentration of 100 ppm. Calibration standards prepared from diluted stock solutions containing 1.4 percent V/v aqua regia, 1 percent V/v HF, and 1 percent W/v H<sub>3</sub>BO<sub>3</sub> were made up, so that the standards matched the sample solutions obtained by the decomposition method.

## Sample Decomposition Procedure

The decomposition of low-temperature and high-temperature coal ash was carried out in a Parr 4745 acid digestion bomb.

Approximately 0.1 g of a low- or high-temperature coal ash-previously ground in an agate or mullite mortar and dried at  $110^{\circ}$  C for several hourswas transferred to the Teflon cup of the decomposition vessel. The low-temperature ash sample was treated with 1.0 ml of concentrated HCl and then heated to dryness on a steam table. The HCl treatment was omitted for high-temperature ash samples. Both types of samples were then wetted with 0.7 ml of aqua regia (1:3:1 HNO<sub>3</sub>-HCl-H<sub>2</sub>O), 0.5 ml of HF was added, and the acid digestion bomb was closed. The bomb was heated at 100 to 110° C for 2 hours. After it had cooled to ambient temperature, the bomb was disassembled and the decomposed sample treated with 10 ml of a H<sub>3</sub>BO<sub>3</sub> solution (0.05 g per ml) to complex the HF. The dissolved sample was transferred to a 50 ml pyrex volumetric flask, diluted to volume with deionized water, and placed in a polyethylene bottle for storage.

## Atomic Absorption Spectrophotometric Procedure

The following analytical wavelengths were used: 228.8 nm (Cd), 324.7 nm (Cu), 232.0 nm (Ni), 283.3 nm (Pb), and 213.9 nm (Zn). Samples analyzed for Cd also were re-aspirated at a nonabsorbing wavelength, 227.6 nm, for background correction. Cation standards for Cu, Ni, and Zn ranging from 0.1 to 1.0 ppm were used. Lead standards ranging from 0.1 to 5.0 ppm and cadmium standards ranging from 0.01 to 0.5 ppm were prepared. In determinations of all elements except Zn, the sample being analyzed required no further dilution; for Zn an additional dilution might be necessary. Metal ion concentrations in the samples were calculated by interpolation from a calibration curve of absorbance vs. concentration. A new calibration curve was constructed for each set of analyses.

## Comparative Analyses

Results obtained by atomic absorption spectrophotometry for Cd, Cu, Pb, and Ni concentrations, expressed on the whole coal basis, agreed well with results obtained by the other analytical methods used in this study. Atomic absorption results for low- and high-temperature ashes prepared from the same coal sample also compared well when expressed on the whole coal basis. These favorable comparisons indicated that the trace elements involved were not volatilized when these coals are ashed at  $450^{\circ}$  to  $500^{\circ}$  C.

The determination of Zn in the coals and coal ashes studied presented a unique sampling problem. In a majority of the samples analyzed the results of the various analytical methods agreed well, as did results of the low- and high-temperature coal ashes analyzed by atomic absorption spectrophotometry. However, in a few samples, marked variations in zinc results were observed. The zinc content of these coals was attributed primarily to the presence of discrete particles of sphalerite (ZnS), which could contribute to the nonhomogeneity of a coal sample and thus result in significant variations in zinc concentrations. The degree of coal grinding required to achieve representative samples is being studied further, and decreased sample particle size may improve agreement of the methods of analysis.

Estimates of average relative standard deviation elements determined by atomic absorption spectrophotometry are as follows: Cd (23 values)  $\pm$  10.5 percent, Cu (40 values)  $\pm$  5.0 percent, Ni (40 values)  $\pm$  5.1 percent, Pb (39 values)  $\pm$  5.7 percent, Zn (39 values)  $\pm$  5.7 percent.

## Neutron Activation

Radiochemical separations performed on low-temperature coal ash were used for the determination of Se, As, Ga, Zn, and Cd. Analyses on whole coal were used to determine Hg, Sb, and Br, which are totally or partially volatilized during low-temperature coal oxidation. Mn was determined by instrumental neutron activation analysis.

All irradiations were made in the University of Illinois Advanced TRIGA reactor, with a thermal neutron flux of  $1.4 \times 10^{12}$  neutrons cm<sup>-2</sup> sec<sup>-1</sup>. During irradiation the samples and standards were rotated at 1 rpm to insure equal neutron flux.

The containers used for the samples and standards in the irradiations were two-fifths-dram polyethylene snap-cap vials that had previously been cleaned with deionized water and acetone.

The  $\gamma$ -ray counting system consisted of a 3 in. by 3 in. sodium iodide detector connected to a Nuclear-Chicago 400 channel analyzer.

Chemical yields were obtained for each sample to determine losses during radiochemical separations.

## Determination of Se in Low-Temperature Coal Ash

Each sample (about 200 mg) of low-temperature coal ash was accurately weighed into a polyethylene vial. The samples and a sealed polyethylene vial containing a comparative standard of 1 mg Se per ml solution (prepared by dissolving spectrograde Se metal in nitric and hydrochloric acids) were irradiated for 2 or 3 hours and allowed to decay for 3 days.

Each sample was quantitatively transferred to a 100-cc round-bottomed distillation flask and 20 ml of concentrated HCl, 5 ml of concentrated HNO<sub>3</sub>, 5 ml of concentrated HClO<sub>4</sub>, and 3 ml of Se carrier (containing 10 mg Se per ml) were added. The mixture was refluxed overnight.

The mixture was then distilled down to a volume of about 10 ml in an air stream and the distillate collected in 20 ml of distilled water in a flask in an ice bath. Ten ml of concentrated HCl and 12 ml of concentrated HBr were added to the distilling flask and distilled. Second portions of HCl and HBr were added and the distillation was repeated. To the combined distillate 7 ml of 6 percent sulfurous acid was added to precipitate red amorphous Se, which was allowed to settle.

The supernatant liquid was decanted through a Teflon-coated filtering apparatus containing a weighed filter paper. Hot water was then added to the Se in the beaker to convert it to gray metallic Se, which was filtered, washed with more hot water and acetone, air-dried for 2 hours, weighed, and then mounted on cardboard.

The Se comparative standard was diluted 1:100, and 1 ml (10  $\mu$ g of Se) was transferred to a flask containing 3 ml of selenium carrier, distilled, and precipitated in the same manner as the samples. Radiochemical yields of the samples and standard are quantitative.

The samples and standard were counted for the activity of the 0.121 and 0.136 MeV gamma rays of  $^{75}$ Se, which has a half-life of 120 days. These two gamma rays gave a single photopeak with the 3 in. by 3 in. sodium iodide detector and 400 channel analyzer.

The Se concentration of the low-temperature coal ash samples was calculated and, by using the percentage of low-temperature ash in the coal, converted to ppm of Se in whole coal. The relative standard deviation of a measurement is normally better than  $\pm$  10 percent. Analysis of the National Bureau of Standards SRM-1630 for Se gave the result 2.0  $\pm$  0.13 ppm, which compares favorably with the provisional value of 2.1 ppm established by the NBS.

## Determination of As in Low-Temperature Ash

Each sample (about 200 mg) of low-temperature coal ash was accurately weighed into a two-fifths-dram polyethylene vial. The samples and a sealed polyethylene vial containing a comparative standard of 10 mg As per ml (prepared by dissolving sodium arsenite in water and hydrogen peroxide) were irradiated for 2 hours and allowed to decay overnight. Each sample was quantitatively transferred to a l00-cc round-bottomed distillation flask, with the addition of 20 ml of concentrated HCl, 5 ml of concentrated HNO<sub>3</sub>, 5 ml of concentrated HClO<sub>4</sub>, and 3 ml of As carrier (containing l0 mg As per ml) and refluxed overnight.

The mixture was distilled down to a 10-ml volume in an air stream and the distillate collected in 30 ml of distilled water. Ten ml of concentrated HCl and 12 ml of concentrated HBr were added to the distillation flask and distilled. Second portions of HCl and HBr were added, and the distillation repeated. To the combined distillate 5 g of sodium hypophosphite was added and the mixture was heated to just below the boiling point for 2 to 3 hours until the solution cleared and the black As metal precipitate was completely digested. The As precipitate was suction-filtered onto a weighed filter paper, washed with distilled water and acetone, air-dried, weighed, and mounted on cardboard.

The As standard was diluted 1:250 with dilute HCl and a 1-ml aliquot (40  $\mu$ g of As) was transferred to a flask containing 3 ml of As carrier, distilled, and precipitated in the same manner as the samples. Radiochemical yields of the sample and standard were quantitative.

The samples and standard were counted for the activity of the 0.559 MeV  $\gamma$ -ray photopeak of 26.5 hr  $^{76}$ As.

The As concentration of the low-temperature coal ash samples was calculated and converted to a basis of ppm in whole coal from the percentage of low-temperature ash in the coal. The maximum relative standard deviation of a measurement is 12 percent.

## Determination of Ga in Low-Temperature Coal Ash

Oven-dried samples (100 mg) were weighed into two-fifths-dram snapcap polyethylene vials, heat-sealed, and irradiated for 2 hours along with standard solutions prepared from pure Ga metal.

Ga (6 mg) and Zn (30 mg) carriers were added to the irradiated ash sample, which was then fused with NaOH in a nickel crucible. (A tracer study showed that no gallium is lost during fusion.) When the fusion melt was dissolved in distilled water (25-50 ml), a mixed sulfide precipitate formed. The solution was filtered, and the pH was adjusted to 8 with HCl to precipitate  $Zn(OH)_2$ , which carries the Ga. The hydroxide precipitate was collected and dissolved in 8M HCl (15 ml), and Ga was extracted from the resulting solution with isopropyl ether (15 ml). Ga was then back-extracted from the organic fraction with distilled water (15 ml). Extraction and back-extraction were repeated twice, and the combined distilled water fractions were counted. Some  $^{76}$ As follows the Ga, but there was no interference with the 0.832 MeV photopeak of 14-hr  $^{72}$ Ga. Radiochemical yields were determined by re-irradiation and were within the  $^{46}$ -74 percent range.

The possibility that  $^{72}$ Ga might be produced during irradiation by a (n,p) reaction with  $^{72}$ Ge, as well as by the (n, $\gamma$ ) reaction with  $^{71}$ Ga, was investigated. Two milligrams of pure Ge metal were irradiated along with samples of coal ash in a regular run and subsequently counted. No radiochemical separation was needed for the Ge metal, as there is no spectral interference between Ge and Ga. Less than 0.02 micrograms of "apparent" Ga was produced in

Ge metal. Therefore, for every part of Ge in coal ash, the contribution to  $^{72}$ Ga is less than  $10^{-5}$ .

The average relative standard deviation of the technique was estimated to be  $\pm 8$  percent.

## Determination of Zn and Cd in Low-Temperature Coal Ash

Oven-dried LTA samples (100 mg) were weighed into two-fifths-dram snap-cap polyethylene vials, heat-sealed, and irradiated for 2 hours along with standard solutions prepared from pure Zn metal and pure Cl metal.

Zn (10 mg) and Cd (4 mg) carriers were added to the irradiated ash sample, which was then fused with NaOH (2 g) in a nickel crucible. (A tracer study showed that no Zn or Cd is lost during fusion.) The fusion melt was dissolved in 50 ml of distilled water, and then 25 ml of 8M HCl was added so that the resulting solution was 2M in HCl. The solution was then loaded onto a Dowex 1 x 8 (100 to 200 mesh) anion exchange column (6 g resin) that has been pre-equilibrated with 2 M HCl (30 ml). After the column had been rinsed with 2M HCl (20 ml), the Zn and Cd were eluted with distilled water (60 ml) in the same fraction. Zn was determined immediately by the 0.438 MeV photopeak of 13.8 hr <sup>69m</sup>Zn. For Cd, a decay period (one week from the time of irradiation) was allowed so that 13.8 hr<sup>69m</sup>Zn would completely decay and the  $239_{\text{Np}}$  Compton edge would diminish; then the 0.523 MeV photopeak of 54 hr  $115_{\text{Cd}}$ was used. Radiochemical yields were determined by re-irradiation and were in the 80 to 95 percent range for Zn and quantitative for Cd. The average relative standard deviation was  $\pm$  25 percent for Zn and better than  $\pm$  10 percent for Cd.

## Determination of Hg in Whole Coal

From 0.6 to 1.0 gram of coal (hand ground to 20 mesh and air-dried) was accurately weighed into a two-fifths-dram polyethylene snap-cap vial. Hand grinding of coal samples to only 20 mesh was used to avoid excessive heating and possible loss of volatile elements. A 1.0 ml aliquot of a 10.3 mg per ml standard solution of Hg<sup>++</sup> (as nitrate) was sealed in a similar polyethylene vial. Samples and standard were simultaneously irradiated for 2 hours. One day was allowed for the preferential decay of shorter-lived radioisotopes (such as  $^{24}$ Na,  $^{31}$ Si,  $^{56}$ Mn) to facilitate handling of the samples.

Each sample was mixed 1-to-1 with 60-mesh Norton Alundum RR  $(Al_2O_3)$ , transferred to a 4-inch porcelain boat (Fisher Combax, size A), and covered with Alundum. The boat, previously impregnated with 2-mg Hg<sup>++</sup> carrier (as nitrate), was placed in a 1-inch-diameter Vycor tube and the contents then combusted slowly with a Bunsen burner ( $\sim 500^{\circ}-600^{\circ}$  C), with an oxygen flow through the tube of about 50 to 75 ml per minute. The gaseous and volatilized products were bubbled through two consecutive 100 ml vacuum traps, each containing 20 ml of a 3.25 pH sodium acetate-acetic acid buffer solution (Hinkle, Leong, and Ward, 1966), 40 ml of saturated bromine water, and 30 mg Hg<sup>++</sup> (as nitrate). The combustion process required about 1 hour to insure controlled, thorough burning and efficient transfer to the traps. (NOTE: Sample should be burned very gradually, as there is danger of violent explosion.) Approximately 250 ml of 2M HCl was used to wash the glassware, including the Vycor tube, thoroughly and was then combined with the trap solutions.

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The resulting solution ( $\sim$  450 ml) was then passed through a column l cm in diameter that contained 3.5 ml of Dowex 2 in the chloride form. After radioactive interferences were eluted with 40 ml water and 40 ml of 2M HCl, the resin was transferred to a 100-ml polystyrene bottle, allowed to settle uniformly, and then counted for  $^{197}{\rm Hg}$  (t<sup>1</sup>/<sub>2</sub> = 65 hours, 77 keV gamma ray).

A 0.10-ml aliquot of the irradiated standard was diluted to 100 ml with 2M  $HNO_3$ . One ml of the diluted solution was immediately pipetted into a porcelain boat (already impregnated with 2 mg inactive  $Hg^{++}$ ) and allowed to dry. About l g of inactive coal was mixed with Alundum, put into the boat, covered with Alundum, and burned in the same manner as the irradiated samples.

The over-all recovery of Hg in the process was  $67 \pm 15$  percent. The amount of Hg in a sample was calculated by comparing the height of the photopeak of the sample to that of the standard. The average relative standard deviation of the method was  $\pm$  20 percent and the detection limit was 0.01 ppm for l-gram samples and 2-hour irradiations.

Table 9 compares our values to preferred values derived from a U. S. Bureau of Mines round-robin study (Schlesinger and Schultz, 1972). The accuracy of this method is shown to be excellent.

Coal location	Best value (ppm)	ISGS (ppm)
Belmont Co., Ohio	0.15 ± 0.03	0.15, 0.17
Harrison Co., Ohio	0.41 ± 0.06	0.45, 0.46
Jefferson Co., Ohio	0:24 ± 0.04	0.23, 0.30
Kanawha Co., W. Virginia	$0.07 \pm 0.02$	0.09, 0.08
Washington Co., Pennsylvania	0.12 ± 0.04	0.13, 0.14
Clay Co., Indiana	0.07 ± 0.02	0.08, 0.11
Muhlenberg Co., Kentucky	0.19 ± 0.03	0.24, 0.23
Rosebud Co., Montana	0.061 ± 0.007	0.07, 0.06
Henry Co., Missouri	$0.16 \pm 0.06$	0.17, 0.18, 0.19
Montrose Co., Colorado	$0.05 \pm 0.01$	0.05, 0.05, 0.05
Navajo Co., Arizona	0.06 ± 0.01	0.05, 0.05, 0.07
NBS SRM-1630 (West Virginia)	0.13	0.14

TABLE 9-COMPARISON OF Hg VALUES WITH PUBLISHED DATA\*

\* Schlesinger and Schultz, 1972.

#### Determination of Sb in Whole Coal

From 0.6 to 1.0 g of coal was hand ground, weighed, and irradiated with a standard in a manner similar to that described in the Hg procedure.

The irradiated sample,  $\sim 100$  mg benzoic acid, and from 10 to 30 mg of accurately weighed Sb<sub>2</sub>O<sub>3</sub> carrier, were fired with 25 atmospheres of oxygen in a Parr bomb.

The contents of the bomb were rinsed into a beaker with concentrated HCl and digested on a hot plate for 1 hour. The mixture was filtered. The filter paper and contents were vigorously heated with 100 ml of 1M KOH and 4 ml 30 percent  $H_2O_2$  for 2 hours and then cooled and filtered.

The filtrates were combined, diluted to  $\sim 1000$  ml and  $\rm H_2S$  passed through. The sulfide precipitate was filtered, dissolved in 20 ml aqua regia and evaporated to dryness. The residue was treated with 1 g of NH\_2OH·HCl, dissolved in 2 ml of 4M HCl, and evaporated to dryness.

The residue was dissolved in 1 ml of 0.5M  $\rm NH_4SCN-2M$  HCl (Hamaguchi et al., 1969) and loaded on a Dowex 2 column ( $\sim 5$  ml in SCN<sup>-</sup> form). The column was then eluted with 15 ml of 0.5M  $\rm NH_4SCN-0.5M$  HCl (to remove As) and then 10 ml of 0.005M  $\rm NH_4SCN-0.5M$  HCl. The Sb fraction was eluted with 150 ml of 2N  $\rm H_2SO_4$ . Fifty milligrams of concentrated HCl was added to the eluate.

The solution was counted for  $^{122}$ Sb ( $t_2^1 = 2.8$  day, 0.56 MeV  $\gamma$ -ray). Radiochemical yields were determined by re-irradiation and ranged from 30 to 55 percent. The average relative standard deviation of the method was  $\pm$  20 percent.

#### Determination of Br in Whole Coal

From 0.6 to 1.0 g of coal (hand ground to 20 mesh and air-dried) was accurately weighed into a two-fifths-dram polyethylene snap-cap vial. A 1.0-ml standard (lll  $\mu$ g Br) of NH<sub>4</sub>Br was sealed in a similar vial. Samples and standards were simultaneously irradiated for 2 hours. About 1 day was allowed for the decay of shorter-lived radioisotopes.

Each sample was mixed 1 to 1 with 60-mesh Norton Alundum RR  $(Al_2O_3)$ and transferred to a 4-inch procelain boat. Twenty mg Br as a NH<sub>4</sub>Br solution was added to the boat and allowed to dry. The contents of the boat were then covered with Alundum. The boat was placed in a 1-inch Vycor tube and the contents combusted slowly with a Bunsen burner (~500°-600° C) in an oxygen-flow system, with the flow rate about 50 to 75 ml per minute. The gaseous and volatilized products were bubbled through two consecutive traps containing 3M NaOH or KOH. The first trap contained 200 ml and the second contained 80 ml. (NOTE: Sample should be burned very gradually, as there is danger of violent explosion.)

After combustion, all the glassware was washed with  $H_2O$  and the wash liquid combined with the alkali trap solutions. The combined solutions were counted for  $^{82}Br$  ( $t_2^1 = 36$  hours, 0.56 MeV  $\gamma$ -ray).

A 5-ml aliquot was re-irradiated for chemical yield determination, which varied from 49 to 77 percent. The average relative standard deviation was  $\pm$  10 percent.

## Instrumental Neutron Activation Analysis of Mn in Whole Coal

From 0.6 to 1.0 g of coal (hand ground to 20 mesh and air-dried) was accurately weighed into two-fifths-dram polyethylene snap-cap vials. A 1.0-ml solution containing a known amount of  $Mn^{+2}$  (from 100-200 µg) was heat-sealed into a similar vial. Samples and standard were simultaneously irradiated for only 15 minutes in a thermal neutron flux of about 0.7 x  $10^{12}$  neutrons cm<sup>-2</sup> sec<sup>-1</sup>.

After approximately 2 hours were allowed for the preferential decay of the shorter lived radioisotopes (e.g.,  $^{31}$ Si and  $^{38}$ Cl), the samples were transferred to unirradiated containers, counted, and compared with the standard for  $^{56}$ Mn ( $t_2^1$  = 2.6 hours, 0.84 MeV  $\gamma$ -ray).

The average relative standard deviation of this instrumental technique was  $\pm$  4 percent.

## Ion-Selective Electrode Method for Determination of F in Whole Coal

A 1-gram coal sample, ground to pass a 100-mesh screen, was mixed with about 0.25 g benzoic acid (primary standard) and placed in a fused quartz sample holder within a Parr combustion bomb that contained 5 ml of 1N NaOH. The bomb was pressurized to about 28 atmospheres and fired. At least 15 minutes were allowed to elapse before the bomb was depressurized. Three approximate 5-ml aliquots of distilled water were used to rinse the bomb contents into a 50-ml plastic beaker (plastic-ware was used from here on).

The beaker contents were magnetically stirred with a Teflon bar while the pH was adjusted to 5.2-5.5 with 0.5N H<sub>2</sub>SO<sub>4</sub>. (The initial pH before ajustment was about 7.0.) The beaker was then placed in a hot water bath for about 10 minutes, removed, and again stirred to drive off most of the dissolved CO<sub>2</sub>. Five ml of 1M sodium citrate-citric acid buffer (pH 6.3) containing 0.2M KNO<sub>3</sub> was added to the beaker contents. The total volume was adjusted to 50 ml with distilled water and cooled to room temperature. At this time, the potential was read. In some cases, about 10 minutes were required for equilibrium to be reached. The F concentration was calculated by the known addition method (1 ml of 0.01M F was added and the potential of the solution was again read).

The pH is quite critical for the initial potential reading. At 5.0 to 5.5, final results tended to be low because of F<sup>-</sup> complexing with H<sup>+</sup>. Above 6.5, final results were high because of interference by OH<sup>-</sup> or  $HCO_3^-$  at 1000 to 1 concentration over the F.

Various coal samples have been analyzed by this technique and, thus far, our F results are in only fair agreement with those determined by a distillation-colorimetric method at Stewart Laboratories, Knoxville, Tennessee (table 11). Five replications were made on a proposed National Bureau of Standards SRM coal and a concentration of  $80 \pm 4$  ppm F was determined. Additional checking of this method is planned.

#### Trace Element Detection Limits

Table 10 gives trace element detection limits for each method used. Whole coal detection limits are given for those methods used in the direct analysis of raw coal. However, it is not possible to give whole coal detection limits for analyzed coal ash, because the ash content of the coals directly affects the detection limit, as calculated to the whole coal. For the methods that require a coal ash, detection limits are given on the ash basis.

#### RESULTS FOR TRACE ELEMENTS

Results for 25 coals analyzed by the various methods are given in table 11. The table includes analyses for the different kinds of samples analyzed—whole coal, low-temperature ash (LTA), and high-temperature ash (HTA). Some coals have been analyzed by several methods by using more than one type of sample. All results are given so that comparisons may be made; concentrations in parts per million have been calculated to a single base, i.e., moisture-free whole coal. For some elements—Hg, Sb, Ga, and Se—only one analytical method was used. In such cases, considerable effort was made to be reasonably certain that accurate results were obtained (see discussion for individual trace elements).

Table 12 shows our interpretation of the best or "recommended" trace element values for each coal. When results of two or more methods are in good agreement, the mean of these is given as the "recommended" value. If discrepancies among results of the various methods exist, "recommended" values are those obtained by the method deemed to be most accurate. Because this investigation is continuing, these values may be altered as new data or refined methods become available.

#### DISCUSSION OF TRACE ELEMENTS

## Selenium (Se)

The neutron activation radiochemical separation technique for lowtemperature coal ash yielded precise values on replicate samples and, these, when calculated to the whole coal basis, compared very well (Se = 2.0 ppm) with the provisional value for SRM-1630 coal standard (Se = 2.1 ppm). Preliminary comparisons with the previously mentioned National Bureau of Standards—U. S. Environmental Protection Agency round-robin coal sample continue to indicate that the method is accurate. The recommended Se values given in table 12 were determined by this method.

## Gallium (Ga)

Results obtained for Ga by the radiochemical procedure developed for low-temperature coal ash check well with data given by Zubovic,

## TABLE 10-SUMMARY OF DETECTION LIMITS FOR METHODS USED IN THIS INVESTIGATION

		ppm i	ppm in whole coal			
Element	Atomic absorption	Neutron activation	Optical emission- photographic	Optical emission- spectrometric	Neutron activation	X-ray fluores- cence
Ag			4.0			
Al						300
As		1.2				2
В			25	2		
Be			1	1		
Br					1	1.5
Ca						12
Cđ	2.5	50				
Cl						36
Co			20	3		
Cr			45	1.5		
Cu	7.5		4	1.5		1.0
F	Detection li	mit for F by s	elective electro	ode ion = 10 ppm i	n whole coal.	
Fe						36
Ga		1				
Ge			40	1.5		
Hg					0.01	
K						9
Mg						25
Mn					2	
Mo			25	3		
Ni	20		7	1		3.5
P						20
Pb	20		30	5		2.5
S						72
Sb					0.1	
Sn				3		
Se		1.8				
Si						240
Ti						27
V			45	5		0.5
Zn	20		80			4
Zr			5			

Stadnichenko, and Sheffey (1964). Our average for Illinois coal is 3.6 ppm and Zubovic's average value is 4.1 ppm. Also the literature values for U. S. Geological Survey standard rock W-1 range from 16 to 20 ppm (Fleisher, 1969); our value is 21 ppm. Recommended values for Ga (table 12) were determined by this method.

## Mercury (Hg)

The radiochemical procedure previously developed (Ruch, Gluskoter, and Kennedy, 1971) checked well with the 1971 U. S. Bureau of Mines roundrobin study (table 9), and the values obtained by this method are being reported without further independent checks.

## Antimony (Sb)

To determine the accuracy of the neutron activation radiochemical procedure developed for whole coal, a coal sample was analyzed by an independent instrumental neutron activation technique for whole coal. Results obtained by the two methods compare favorably (8.9 ppm and 10 ppm, respectively). Several analyses of low-temperature coal ash for Sb determination by another radiochemical procedure were also in good agreement with those obtained by the whole coal radiochemical separation method described herein.

Volatilization studies of Sb showed that some of it was lost from one coal during low-temperature ashing. The radiochemical procedure for whole coal eliminates the possibility of unpredictable Sb losses. Recommended values obtained by this method are given in table 12.

## Manganese (Mn)

Mn results obtained by the instrumental neutron activation method compare well with values given for G-1, W-1, and other chemically analyzed rock samples, all of which were routinely analyzed along with whole coal samples. The value given for U.S.G.S. standard rock G-1 is 230 ppm Mn (Fleisher, 1969); our value is 239 ppm. For U.S.G.S. standard rock W-1, Fleisher's value is 1320 ppm Mn; ours is 1290 ppm. Other Mn values for coals, obtained by X-ray fluorescence and photographic optical emission methods, are a factor of 2 or 3 higher and have not been tabulated. These values are apparently subject to a high bias from background interferences. Therefore, the values obtained by the instrumental neutron activation method are recommended (table 12).

## Arsenic (As)

Two methods, neutron activation analysis of LTA and X-ray fluorescence analysis of whole coal, are used for the determination of As. Neutron activation results, calculated to the whole coal basis, compare well with X-ray fluorescence values at the higher concentrations. However, we feel that the latter method frequently exhibits a high bias for low As concentrations (see table 11 for comparisons). The recommended values for As (table 12) are those determined by this neutron activation method.

		Parts per million, moisture-free whole coal															
		F	F	Hg	Sb	Sb	Mn	Ga	Se	As	As	Br	Br	P	V	v	v
		Whole	Whole	Whole	Whole		Whole				Whole	Whole	Whole	Whole	Whole		
		coal	coal	coal	coal	LTA	coal	LTA	LTA	LTA	coal	coal	coal	coal	coal	HTA	HTA
Sample	Coal	Dist.															
no.	no.†	color.	ISE	NAA	NAA	NAA	NAA	NAA	NAA	NAA	X-RF	X-RF	NAA	X-RF	X-RF	OE-DR	0E-P
C <b>-1</b> 6030	6	107	58	0.14	1.0	0.3*	15	4.6	2.0	4.5	6	<b>1</b> 5	26	40	40	33	11*
C <b>-1</b> 6264	5	112	69	0.24	0.8	0.6*	21	4.3	1.5	9.6	10	14		110	32	24	12*
C-14970	6	105		0.14	0.3	0.2*	72	3.7	1.7	2.1	2	16		22	28	18	11*
C <b>-1</b> 4796	5	105	112	0.38	0.8	0.8*	43	6.0	1.7	28	30	22	18	320	46	36	22
C <b>-1</b> 6317	6	162	52	0.10	4.3		67	4.7	2.5	24	22	14		21	43	36	18*
C <b>-1</b> 5384	5	103		0.16	2.6		62	3.0	1.6	7.4	19	14	21	<10	48	59	35
C <b>-</b> 12062	6	105	51	0.52	1.4		87	3.6	3.1	8.3	21	17		7.7	35	37	
C <b>-</b> 15566	2	93	46	0.49	8.9	9.0*	90	7.5	1.2	93	90	10	6	29	21	10	
C <b>-1</b> 2495	5	65		0.09	0.6		90	1.9	1.3	5.5	<b>1</b> 9	12	11	21	26	13	
C-18009	West	123		0.14	0.6		6	1.1	2.0	19	22	29	29	17	34	13*	24
	Va.																
C <b>-</b> 15117	6	69		0.32	2.6		72	3.9	1.9	29	27	6		28	45	29	12*
C <b>-1</b> 5456	6	75	103	0.09	0.3		25	3.5	1.9	1.7	7.9	19		12	43	29	10*
C <b>-</b> 13895	6	101		0.17	0.3		54	3.3	1.9	2.1	<b>1</b> 5	<b>1</b> 5		<10	42	20	<b>1</b> 5
C <b>-</b> 15231	6	110		0.19	0.4		39	3.7	1.6	2.4	<5	13	11	28	35	34	31
c <b>-1</b> 4684	6	83	63	0.18	0.2		30	2.8	1.2	3.7	18	19		18	42	24	7.3*
C <b>-</b> 13464	6	103	59	0.21	1.1		69	3.0	2.3	4.3	11	<b>1</b> 5		48	42	76	33
C-14721	6	130	60	0.32	0.7		65	3.5	1.4	4.6	7.1	17		23	40	28	15
C <b>-</b> 15944	De-	94		0.37	1.2		10	3.6	3.0	37	66	17		<b>1</b> 44	37	30	41
	Kove	n															
C <b>-1</b> 4774	5	104	42	0.28	0.9		100	2.2	1.9	4.5	6.4	14	11	29	31	26	24
C-17001	5	83	44	0.50	2.5		22	2.0	3.3	9.4	22	16	<b>1</b> 9	48	42	> 52*	82
C <b>-1</b> 5402	4	134	49	0.19	2.7		28	2.6	2.4	18	40	11	7	24	38	37	18*
C <b>-</b> 17096	Utah	66	50	0.04	0.2		8	1.6	1.2	0.52	14	23		80	36 <b>*</b>	9.3	10
C <b>-</b> 16139	6	103		0.10	1.4		61	3.3	7.7	5.1	4	12		57	32	34	72*
C <b>-</b> 12831	6	69		0.23	0.3		28	4.5	1.3	4.3	33	<b>1</b> 7	17	29	36	20	37
C <b>-1</b> 5038	6	138	68	0.11	0.4		42	2.5	1.3	5.9	9	19	12	53	44	29	24

TABLE 11---TRACE ELEMENT CONCENTRATIONS IN WHOLE COAL AND COAL ASHES AS DETERMINED BY SEVERAL ANALYTICAL METHODS

		Be	Be	Cu	Cu	Cu	Cu	Cu	Ni	Ni	Ni	Ni	Ni	Ni	Ni	Zn	Zn	Zn	Zn
				Whole					Whole							Whole			
		HTA	HTA	coal	LTA	HTA	HTA	HTA	coal	LTA	LTA	HTA	HTA	HTA	HTĄ	coal	LTA	HTA	HTA
Sample	Coal																		
no.	no.†	OE-DR	0E-P	X-RF	AA	AA	OE –DR	OE-P	X-RF	X-RF	AA	AA	X-RF	0E-DR	OE-P	X-RF	AA	AA	OE -P
C-16030	6	2.4	3.0	19	18	17	17	7.8*	35		33	38		47	58*	1610	1611	1756	
C-16264	5	2.9	3.2	13	11	8	8	5.0	18		24	17		19	32*	143	166	182	
C <b>-1</b> 4970	6	1.5	1.6	17	14	12	11	4.2*	13		15	13		12	16	25	24	15	16
c <b>-</b> 14796	5	1.1	1.2	26	30	34	36	25	20		19	19		26	23	63	64	97	26*
C⊷16317	6	2.6	3.0	19	19	14	21	12	27	25	27	24	20	36	34	587*	2665	1671	
C <b>-1</b> 5384	5	0.9	1.6	16	12	8	9	5.4	18	20	16	15	21	16	19	47	34	34	29
C-12062	6	2.8		21	23		26		28		36			36		700	3099		
C <b>-</b> 15566	2	2.9			23		28				61			58			213		
C <b>-1</b> 2495	5	1.3		<b>1</b> 5	12		10		15		14			5.6*		26	18		
C-18009	West	1,2	0.8	48*			16		16		8	8		9•7	12	6.3	36	6	10
	Va.																		
C <b>-1</b> 5117	6	3.3	4.5	30*	13	16	20	7.5*	30	26	27	30	28	36	11*	65	121*	41	47
C <b>-1</b> 5456	6	1.1	1.6	18	10	10	12	2.9*	18	15	15	14	17	<b>1</b> 5	15	53	178	59	25
C <b>-1</b> 3895	6	1.2	1.8	<b>1</b> 5	11	10	13	7.0	<b>1</b> 5	13	14	13	13	11	14	46	30*	÷ 68	55
C-15231	6	0.9	0.8	20	12		12	14	20		15			21	12	75 <b>1</b>	297		
C-14684	6	0.7	1.0	16*	7	8	8.5	4.1*	16	14	12	12	10	14	12	45	31	39	18*
C-13464	6	1.4	2.3	19*	9	10	11	6.9	19	17	16	15	21	17	20	37	31	41	35
C-14721	6	1.5	1.2	18*	10	9	9.1	6.6	18	17	15	14	11	18	22	123	294	221	85
C-15944	De -	5.9	2.1	28	24		27	35	28		27			30	25	<b>1</b> 49	189		99
	Koven																		
C-14774	5	2.0	1.5	<b>1</b> 4	9		7.4	8.7	14		10			10	5.1*	1063	885		
C-17001	5	1.1	2.1	20*	8	7	8.6	5.8	20	21	18	16	13	15	19	68*	184	171	117
C <b>-</b> 15402	4	1.0	1.2	20	18	14	21	6.5*	20		15	16		17	11	53	54	54	28*
C-17096	Utah	0.5	0.2	12	8		13	8.5	12*		4			5	2.0	53*	13		7
C <b>-</b> 16139	6	1.1	0.9	30*	21		12	15	30		32			45	39	44	86		140
C-12831	6	2.1	0.7	19	9		4.3*	12	<b>1</b> 9		14			13	15	38	24		22
C-15038	6	1.3	0.7	35*	12		12	10	35		31			54	27	74	102		87

X-RF = X-ray fluorescence.

TABLE 11-Continued

\* Excluded from recommended value calculations. OE-DR = Optical emission-direct

is given.

+ All coals are from Illinois unless state

Dist. color. = Distillation-colorimetric method. reading.

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					9999 (J. <sup>1</sup> 99 <sup>9</sup> 1997) - Hand Hand (J. 1999) - Hand (J. 1997) - Hand (J.		Parts	per mi	llior	ı, moi	sture-f	ree who	ole coa	1		ananan an brideac	**************************************		allan yi Tiri tini orayo ya mu		
		Pb	Pb	Pb	Pb	Pb	Ge	Ge	Cr	Cr	Cr	Cr	В	Co	Co	Co	Cd	Cd	Cd	Cd	Cđ
		Whole														Whol	е				
		coal	LTA	HTA	HTA	HTA	HTA	HTA	LTA	HTA	HTA	HTA	HTA	HTA	HTA	coal	HTA	LTA	LTA	HTA	LTA
Sample	Coal																				
no,	no.†	X-RF	AA	AA	OE-DR	0E-P	0E-P	OE-DR	AA	AA	OE-DR	0E-P	OE-DR	OE-DR	0E-P	NAA	AA	AA	NAA	ASV	ASV
c-16030	6	59	58	62	46	53	6.8	8.1	21	29	17	35	34	17	11	8	3.6	3.2			
C <b>-1626</b> 4	5	58	61	60	43	58	11	19			14	19	139	2.0	14*	1.4	3.1	2.7		3.0*	2.4*
C <b>-1</b> 4970	6	15	10	8	4.7	<18*	<3.7	<0.9*	18	17	12	19	186	3.0	11*	1.7	≤0.3*	≤0.4			
c <b>-1</b> 4796	5	20	32	27	18	<b>1</b> 5		2.7	22	23	17	24	48	4.6	2.8		0.5	≤0.3			
C-16317	6	51	86	57	64	53	5.9*	20*	25	23	19	33	104	8.5	9.2	6.2	17	28	21*	18*	29*
a 1570h	-	. 0			- (				2		- 1.		40	3.8	13*	<1*	<b>≤</b> 0.3*	≤0.4			
0-15304	5	48	49	46	36	35	3.9	5.9			14	-13	v193	5.9				19	17*		28*
C=12062	6	43	38		44			12			18		115	23				0.9			
C-15500	2	104	220	ſ	∿226 ∠ -			<i>35</i>			4.4		164					< 0.6			
C-12495	5	76*	10		6.3			8.9	12		7.6	0.7	104		6 2		<0 1	<0.1			
0-10009	West	9	5		4.0	4.2	1.2	0.γ			6.7	9.0	4.0	2.4	0.2		<b>~0.1</b>				
0 10 110	va.	07*	• (7	- 00	210	175	10	10			10	10	155	1)(	1);		0.5	1.2			
	6	*رہ	165	100	249	125	12	12			10	19	155	2 0	14 73		<0.3*	<0.4			
0-15450 0 17805	0	25	12	. 10	5.0*	<1/"	~).)"	0.9			14	10	130	2.9	(・ノ 17米		<0 3*	<0.5			
0-15095	6	01*	7	11	(•2	~20"	<4.1 - 0	4.1			17	12	170	z 8	1 I			1.1			
0-15251	6	19*	9	• 0	· (• (	0.2	5.0	2.4			15	9.2	119	).0 // 0	+.1 5 /l		<0.2*	<0.3			
C <b>-</b> 14004	0	57*	14	18	11	10	<3.0	<0.7*			11	0.9	110	+.Z	10*		0.5	0.5			
C <b>-</b> 13464	б	60*	11	10	12	<20*	≪4.0	<1.0*			33	74	100	5.5 Ji o	13*		1 <u>µ</u>	1.8			
C-14721	6	14	14	13	12	<16*	4.1	2.1			13	19	122	Ψ.Ζ	I)"		7 ° -	1.0			
<b>C-</b> 15944	De-	106	197		>99*	258	5.4	6.7			1.3*	<b>1</b> 3*	38	9.3	19			≤0.4			
	Kover	n																			
C-14774	5	20	37		25	54*	13	11			9.4	6.6	141	2.7	2.7			7,1			
C-17001	5	84	70	67	46	59	60*	9.1*			20*	3.9	* 37	2.8	13*		1.8	1.2			
C <b>-1</b> 5402	4	93	95	109	112	87	117*	9.4*			12	16	43	4.4	13*		0.7	0.7			
C <b>-1</b> 7096	Utah	<b>1</b> 5*	6		5.1	3.7		1.0			6.6	<3.8*	* >84	1.2	0.9			<0.2			
C <b>-</b> 16139	6	23*	9		3.1	7.0	6.2	1.4			16	34	154	4.8	12*			0.9			
C-12831	6	22*	11		5.2	10		5.7			6.4	8.4	106	2.5	5.9			≦0.4			
C-15038	6	30*	18		8	14		1.0			14	9.8	117	12	19			0.8			

TABLE 11-Concluded

LTA = Low-temperature ash

AA = Atomic absorption.

HTA = High-temperature ash.

OE-DR = Optical emission-direct

† All coals are from Illinois unless state reading.

OE-P = Optical emission-photographic.

NAA = Neutron activation analysis. ASV = Anodic stripping voltammetry. \* Excluded from recommended value calculations.

X-RF = X-ray fluorescence.

is given.

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#### Bromine (Br)

Neutron activation and X-ray fluorescence results for Br in whole coal compare favorably (table 11). The X-ray fluorescence procedure is rapid, has good precision, and is the method of choice for the determination of Br in whole coal.

## Vanadium (V)

Vanadium determinations made by X-ray fluorescence analysis of whole coal and by both direct-reading and photographic optical emission analysis of high-temperature ash exhibit a wide scatter. We believe X-ray fluorescence results are high and photographic optical emission results low. Our provisional recommended values, expressed as concentrations in whole coal, are the means of selected values determined by all three methods. Very high or low results were deleted (see table 11 for all results and table 12 for our recommended values).

## Copper (Cu)

X-ray fluorescence, atomic absorption, and direct-reading and photographic optical emission results compare well for Cu in whole coal, although X-ray fluorescence values tend to be high and those for photographic optical emission low (table 11). The recommended Cu values, in most cases, are the means of atomic absorption results for low-temperature ash and direct-reading optical emission results for high-temperature ash (table 12). Cu concentrations are given on the whole coal basis calculated from the percentage of lowor high-temperature ash in the coal.

## Nickel (Ni)

X-ray fluorescence, atomic absorption, direct-reading and photographic optical emission results for Ni agree very well when all values are calculated to the whole coal basis (table 11). The recommended values (table 12) are means of results from all of these methods.

## Zinc (Zn)

X-ray fluorescence, atomic absorption, and photographic optical emission all yield acceptable results for Zn when all values are given on the whole coal basis. Photographic optical emission values tend to be slightly lower than those of other methods. Mean values of the consistent data, deleting abnormally high or low values, are recommended (tables 11 and 12). As previously mentioned, inconsistent results for high levels of Zn (like those for Pb) are associated with localized mineralization and sample inhomogeneity (see also the discussion of the scanning electron microscope). Finer grinding of coal samples might improve agreement.

## Lead (Pb)

X-ray fluorescence, atomic absorption, and photographic and directreading optical emission results for Pb are in good agreement, although the

TABLE 12-RECOMMENDED

			· · · · · · · · · · · · · · · · · · ·	Pa	rts per	millic	on, mo	istur	e-free	whole o	oal		
		F	F	Hg	Sb	Mn	Ga	Se	As	Be	Cu	Ni	Zn
		Whole	Whole	Whole	Whole	Whole							
		coal	coal	coal	coal	coal	LTA	LTA	LTA				
Sample	Coal	Dist.								Rec.	Rec.	Rec.	Rec.
no.	no.*	color	ISE	NAA	NAA	NAA	NAA	NAA	NAA	value	value	value	value
C <b>-</b> 16030	6	107	58	0.14	1.0	15	4.6	2.0	4.5	2.7	18	38	1659
C <b>-</b> 16264	-5	112	69	0.24	0.8	81	4.3	1.5	9.6	3.0	9	20	164
C-14970	6	105		0.14	0.3	72	3.7	1.7	2.1	1.6	14	14	20
C <b>-1</b> 4796	5	105	112	0.38	0.8	43	6.0	1.7	28	1.1	31	21	75
C <b>-</b> 16317	6	162	52	0.10	4.3	67	4.7	2.5	24	2.8	17	27	1978†
C <b>-</b> 15384	5	103		0.16	2.6	62	3.0	1.6	7.4	1.2	10	18	36
C-12062	6	105	51	0.52	1.4	87	3.6	3.1	8.3	2.8	23	33	1900
C <b>-</b> 15566	2	93	46	0.49	8.9	90	7.5	1.2	93	2.9	25	60	213
C <b>-</b> 12495	5	65		0.09	0.6	90	1.9	1.3	5.5	1.3	12	14	22
C <b>-</b> 18009	West	123		0.14	0.6	6	1.1	2.0	19	1.0	16	11	7
	Va.												
C-15117	6	69		0.32	2.6	72	3.9	1.9	29	3.9	16	30	51
C <b>-</b> 15456	6	75	103	0.09	0.3	25	3.5	1.9	1.7	1.4	13	15	
C <b>-</b> 13895	6	101		0.17	0.3	54	3.3	1.9	2.1	1.5	11	14	56
C-15231	6	110		0.19	0.4	39	3.7	1.6	2.4	0.9	15	17	524
C <b>-1</b> 4684	6	83	63	0.18	0.2	30	2.8	1.2	3.7	0.9	8	13	38
C <b>-1</b> 3464	6	103	59	0.21	1.1	69	3.0	2.3	4.3	1.8	9	18	36
C-14721	6	130	60	0.32	0.7	65	3.5	1.4	4.6	1.4	9	16	213
C <b>-</b> 15944	De-	94		0.37	1.2	10	3.6	3.0	37	4.0	29	28	169
	Kove	n											
C-14774	5	104	42	0.28	0.9	100	2.2	1.9	4.5	1.7	9	11	974
C-17001	5	83	44	0.50	2.5	22	2.0	3.3	9.4	1.6	7	17	157
C <b>-</b> 15402	4	134	49	0.19	2.7	28	2.6	2.4	18	1.1	18	16	54
C-17096	Utah	66	50	0.04	0.2	8	1.6	1.2	0.52	0.4	10	4	10
C <b>-</b> 16139	6	103		0.10	1.4	61	3.3	7.7	5.1	1.0	19	36	90
C-12831	6	69		0.23	0.3	28	4.5	1.3	4.3	1.4	13	15	28
C <b>-</b> 15038	6	138	68	0.11	0.4	42	2.5	1.3	5.9	1.0	11	31	88

LTA = Low-temperature ash.

NAA = Neutron activation analysis.

Rec. value = Recommended value.

\* All coals are from Illinois except where state is given. ISE = Ion selective electrode.

+ Value includes 1600 ppm by NAA.

direct X-ray fluorescence analysis of whole coal tends to give higher results than the other methods, which require coal ash for analysis. Recommended values are means of all the data after deletion of abnormally high and low values (tables 11 and 12).

## Germanium (Ge)

Photographic and direct-reading optical emission results for Ge in high-temperature coal ash are in good agreement. Recommended values, with

TRACE ELEMENT VALUES

				Parts	s per m	illion,	moistu	re-free	whole o	oal			
		Pb	Ge	Cr	Co	Cd	V	Br	Р	Zr	Sn	Mo	В
							·	Whole	Whole				
Sample	Coal	Rec.	Rec.	Rec.	Rec.	Rec.	Rec.	coal	coal	HTA	HTA	HTA	HTA
no.	no.*	value	value	value	value	value	value	X-RF	X-RF	OE-P	OE -DR	OE-DR	OE - DR
C-16030	6	55	7	25	12.	3.4	36	15	40	39	<2.0	19	34
C-16261	5	56	15.	16	2	2.9	28	14	110	52	<1.8	5.1	139
C-14070	5	) 0		16	3	<04	23	16	22	30	<1.8	6.4	186
C-14706	5	22	2.7	22	у Ц	0.4	35	22	320	>100	4.2	3.4	48
C-16317	6	62	-•1	25	7	22	39	14	21	20	<4.2	- 9.3	104
0 15784	E	lız	F	11	11		17	14	<10	133	2 5	9.4	40
$C_{-12062}$	5	サノ	12	18	+ 6	10	36	17	7.7	1))	22	11 (	v 193
0-12002	2	187	35	. <u>10</u> Ц	23		15	10	29		<1.8	6.2	115
С-12405	5	8	20	10	0.8	<0.6	20	12	21		51	5.6	164
$C_{-1} = 18000$	Wost	6	1	8	6	< 0.1	29	29	17	21	5.5	1.6	4.6
0-10009	Va	0	± .	0	0		-)	- /	- (				
C-15117	6	184	12	19	14	0.8	37	6	28	36	1.9	6.4	155
C-15465	6	15	0.9	-> 15	- 5	≤0.4	36	19	12	45	<4.1	13	156
C = 13895	6	8	<b>≤</b> 4	12	2	<0.5	17	15	<10	65	4.7	8.0	132
C = 15231	6	8	4	11	_ Ц	1.1	33	13	28	28	<4.3	8.8	179
c-14684	6	12	<3	10	5	<0.3	38	19	18	40	1.9	3.4	82
0.13/16/1	6	11	- 11	55	6	0.5	50	15	48	103	2.0	11	110
C 1/1721	6	13	~+	16	ш	1.6	34	17	23	83	<1.6	4.1	122
C-150UU	De	187	6	1,0		<0.4	36	17	144	31	2.1	3.2	38
0-1)944	Kove	n 107	Ū		11	<b>_</b> •••	20	- 1		2-			-
C <b>-</b> 14774	5	27	12	8	3	7.1	27	14	29	22	<4.3	7.3	141
C-17001	5	65		-	3	1.6	62	16	48	70	6.7	14	37
	1	-		- 11	1	0 7	70		21	22	~1.8	1)(	113
0-15402	4	99	-	14	4	0.7	21	11	24 80	22 7)	< 2 /1	14 1/1	>8µ
0-17096	utan C	1 5 6	⊥ ۱	(	1 E	NU.2	10	رے 12	57	(+	<u 8<="" td=""><td>工。十 1旦</td><td>154</td></u>	工。十 1旦	154
0-10139	o C	0	4	27 7	• "	- 0.9	2) 21	17	20	<b>5</b> 2	<7 8	11	106
0-12031	6	0	6 1	1	4	<b>S</b> 0.4	) I 20	+ ( 10	27 57	55	<3 K	тт Ц 7	117
0-15038	6	13	1	12	15	0.0	52	19	<i></i>	00	~).0	+• (	T T (

HTA = High-temperature ash.

X-RF = X-ray fluorescence.

OE-P = Optical emission-photographic.

OE-DR = Optical emission-direct reading.

where state is given. Rec. value = Recommended value.

\* All coals are from Illinois except

certain exceptions noted (tables 11 and 12), are mean values of whole coal concentrations determined by both methods.

## Chromium (Cr)

Atomic absorption results for Cr agree well with those obtained by both optical emission methods. Recommended values, calculated to the whole coal basis, are the means of results from all three methods (tables 11 and 12).

## Cobalt (Co)

Good agreement for cobalt determined in coal ash was obtained using three analytical methods—photographic and direct-reading optical emission and neutron activation—although photographic optical emission values tend to be high for samples that have low concentrations. Recommended values are the mean concentrations, expressed on the whole coal basis, as determined by the three methods. Certain exclusions are noted (tables 11 and 12).

## Cadmium (Cd)

Cadmium determinations of low-temperature coal ash samples made by using atomic absorption and neutron activation methods are in good agreement. Determinations by the University of Illinois Environmental Analytical Laboratory performed by an anodic-stripping procedure agree very well with atomic absorption determinations of Cd in coal ash. Our recommended values (tables 11, 12), calculated to the whole coal basis, are those determined by atomic absorption.

## Beryllium (Be)

Direct reading and photographic optical emission methods give comparable results for Be in high-temperature coal ash. The recommended whole coal values (table 12) are an average of results from both methods.

## Fluorine (F)

Fluorine determinations were performed by Stewart Laboratories, Knoxville, Tennessee, and by the Illinois State Geological Survey. The results of the Stewart Laboratories distillation-colorimetric method do not check well with those performed in our laboratories by the ion selective electrode procedure. Both values are reported; however, no recommended value is given for F. Several independent checks are now underway to clarify the inconsistencies.

Phosphorus (P), Boron (B), Zirconium (Zr), Molybdenum (Mo), and Tin (Sn)

Each of these elements has been determined by a single method only and no confirmation of the values is available at this time. Phosphorus is being determined by X-ray fluorescence analysis of whole coal; B, Zr, Mo, and Sn are being determined in coal ash by optical emission spectroscopy.

## RESULTS FOR MAJOR AND MINOR CONSTITUENTS

Table 13 gives, in percent, X-ray fluorescence values on the moisture-free whole coal basis for Si, Ti, Al, Fe, Ca, K, Mg, S, and Cl; gravimetric values are given for the percentage of ash in coal (low- and high-temperature). Most elemental concentrations have been determined in both whole coal and samples of low- and high-temperature ash prepared from splits of the coal sample. Table 13 shows that there is good agreement among results obtained for the three different coal sample preparation techniques when all values are expressed as concentrations in whole coal. In addition, the X-ray fluorescence results for S and Cl agree well with the corresponding values obtained by wet-chemical (ASTM) methods. For all major and minor constituents except S and Cl, determinations made on the whole coal are preferred.

## IDENTIFICATION OF MINERAL PHASES CONTAINING TRACE ELEMENTS

During the past few years several investigations concerned with the origin, distribution, and mode of occurrence of mineral matter in Illinois coals have been published, and several of them (Gluskoter, 1967; Gluskoter, Pierard, and Pfefferkorn, 1970; Gluskoter and Ruch, 1971; and Rao and Gluskoter, 1973) apply directly to the present study.

We expect that certain of the trace elements determined to be present in coal by chemical analyses occur in discrete mineral phases. The identification of those minerals is an important first step in preventing the heavy metals they contain from reaching the environment, if that proves necessary. It also provides a basis for interpreting analytical discrepancies. The first step in identifying minerals in the low-temperature ash of coals is generally an X-ray diffraction analysis, but the technique is not sufficiently sensitive to identify very small quantities of a mineral. However, by using a scanning electron microscope (SEM) and the nondispersive X-ray analytical equipment that is an accessory to the SEM, many of the minerals can be identified.

Sphalerite (ZnS) has been identified as the host mineral for Cd and Zn in the low-temperature ash of five different coal samples. Chemical analyses of three of these samples are included in this report (C-16030, C-12062, and C-15566); their cadmium content ranges from 0.9 ppm to 19 ppm and their zinc content ranges from 213 ppm to 1900 ppm. The sphalerite has been found in relatively large, discrete grains (pl. 1). As the specific gravity of sphalerite is greater than 4, the mineral might be removed if the coal is washed (separated by specific gravity techniques).

A coal sample from Colorado (C-17097) that has a relatively high phosphorus content was studied in an attempt to identify the mineral phase containing the phosphorus. A distinct mineral phase containing Ca in addition to P was found in the low-temperature ash of this coal (pl. 1). Apatite (generally carbonate-fluorapatite) has been reported associated with coals, and it is reasonable to assume that the mineral we have observed is apatite.

A separate phase containing lead has also been observed in the very fine fraction (less than  $74 \mu m$ ) of the low-temperature ash of a sample of the DeKoven Coal Member (C-15944). However, because of the nature of the X-radiation of Pb, S, O, and C, we have not been able to identify the mineral observed, although galena (PbS) would reasonably be expected.

#### SUMMARY AND GEOCHEMICAL IMPLICATIONS

Although some inconsistencies exist in data obtained by different methods, over-all agreement of analytical results is highly satisfactory.

							Percer	nt of mo	isture-f	ree whol	e coal					
			Si			Ti			Al			Fe		Ca		
Sample no.	Coal no.*	LTA†	HT A ‡	Whole coal	LTA	HTA	Whole coal	LTA	HT A	Whole coal	LTA	HTA	Whole coal	LTA	HTA	Whole coal
C-16030	6	2.46	2.48	2.47	.070	.070	.070	1.22	1.23	1.23	1.83	1.99	1.91	.16	.16	.21
C <b>-1</b> 6264	5	2.20	2.01	1.92	.050	.050	.050	•96	• 93	.92	1.94	2.01	2.05	.68	.75	.56
C <b>-</b> 14970	6	2.04	1.92	1.89	.050	.050	.050	1.08	• 99	1.00	1.66	1.83	1.72	. 92	.85	.80
C <b>-</b> 14796	5	2.23	2.06	2.08	.070	.064	.080	1.44	1.37	1.38	.79	.73	.89	.49	.42	.46
C <b>-</b> 16317	6	2.48	2.24	2.48	.066	.064	.066	1.25	1.18	1.12	1.55	1.44	1.57	•77	.76	•730
C <b>-</b> 15384 C <b>-</b> 12062	5 6	2.63	2.53	2.56 2.18	.055	.057	.056	• 95	1.01	1.04	2.55	2.62	2.69	•56	.61	.608
C-15566	2	. 75		- 88	020		025	30		1.29	2 88		2 81	80		.010
C-12495	5	• 12		2.24	. 02 0		040	• 7 9		.+)	2.00		2.01	.00		• 92
C = 18009	West			.72			018			• (20			2.05			.000
0-10009	Va.			• [ 2			.040			•52			1.04		-	.072
C-15117	6	1.95	2.00	2.17	.059	.066	.066	1.23	1.26	1.31	2.64	2.61	2.72	.87	.72	.761
C <b>-</b> 15456	6	2.79	2.53	2.70	.066	.064	.072	1.27	1.18	1.38	1.36	1.48	1.43	•55	.60	.674
C <b>-</b> 13895	6	2.81	2.61	2.77	.072	.064	.060	1.35	1.17	1.29	2.88	2.91	2.94	.437	.400	.502
C <b>-</b> 15231	6			2.87			.058			1.36		-	1.83	•		.898
C <b>-</b> 14684	6	1.98	1.97	2.10	• 056	.053	.065	• 99	1.04	1.11	1.59	1.62	1.72	.49	.45	•543
C <b>-</b> 13464	6	2.54	2.49	2.65	.057	.059	.054	1.08	1.11	1.18	2.22	2.39	2.34	.50	.56	.504
C-14721	6	1.79	1.96	2.00	.054	.054	.061	<b>*</b> 98	1.00	1.04	1.69	1.73	1.75	.66	.66	.663
C <b>-</b> 15944	De-			2.04			.072			1.28			2.19			.135
	Koven															
C-14774	5			2.68			.052			1.00			1.71			1.31
C-17001	5	2.03	1.90	2.08	. 05 0	.050	.059	.88	.82	.86	2.65	2.70	2.76	•77	•73	.823
C <b>-</b> 15402	4	1.91	1.92	2.04	.041	.043	.050	•76	•79	.84	2.45	2.59	2.42	.68	.61	.671
C <b>-</b> 17096	Utah			1.99			.060			•718			.48			.928
C-16139	6			2.95			.056			1.33			1.78			.713
C-12831	6			2.45			•059			1.20			1.50			.930
C-15038	6			2.65			.070			1.20			1.22			. 684

## TABLE 13-MAJOR AND MINOR CONSTITUENTS IN WHOLE COAL AND COAL ASHES AS DETERMINED BY X-RAY FLUORESCENCE

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1

					Pe	rcent o	f moistu	re-free	whole co	al			
			K			Mg		C L	3	C	1		
Sample no.	Coal no.*	LTA	HTA	Whole coal	LTA	НТА	Whole coal	ASTM <u></u>	X-RF	ASTM	X-RF	% Ash LTA	% Ash HTA
C <b>-</b> 16030	6	.20	.20	.20	.050	.050	<b>.</b> 050	3.25	3.20	.18	.18	14.26	12.11
C <b>-</b> 16264	5	.16	.17	. 15	.020	025	.038	4.52	4.47	.01	.01	15.88	11.85
C-14970	6	.14	.12	.13	.020	.030	.029	4.25	4.13	.10	.14	15.63	12.19
C-14796	5	.27	.26	.27	.046	.054	.056	1.34	1.44	.02	.03	12.63	10.16
C-16317	6	.162	.165	.168	.054	.045	.048	3.25	3.22	.02	.016	17.90	11.94
C <b>-</b> 15384	5	1.88	1.83	.173	.148	.101	.110	3.74	3.63	.19	.23	16.47	13.28
C-12062	6			.142			.041	3.46	3.55	. 03	.03	17.56	11.20
C <b>-</b> 15566	2	.050		.059	.017		.014	4.79	4.70	.03	.01	14.05	11.96
C <b>-</b> 12495	. 5			.100			.042	4.35	4.47	.12	.13	23.53	12.79
C-18009	West			.078			.020					4.22	3.83
	Va.												
C <b>-</b> 15117	6	.133	.157	.157	.047	.036	.046	3.83	3.74	.03	.01	15.27	12.76
C-15456	6	.206	.192	.197	.045	.041	.048	3.35	3.26	.01	.01	15.37	11.66
C-13895	6	.167	. 153	.148	.52	.050	.045	4.57	4.55	.02	.04	18.68	13.52
C-15231	6			.171			.067	4.21	4.12	.10	.14	15.46	12.24
c-14684	6	.137	.145	.148	.021	.023	.018	2.55	2.46	.40	.42	12.32	9.95
C-13464	6	.166	.170	.166	.063	.067	.065	4.05	4.08	•35	.33	17.60	13.41
C-14721	6	.137	. 153	.147	.040	.037	.033	3.32	3.24	.02	.02	13.78	10.64
C <b>-</b> 15944	De 🗕			.177			.040	3.37	2.48	.28	.31	14.59	9•94
	Koven							- (0		00	00	10 71	10 74
C <b>-</b> 14774	5			.141			.046	3.68	3.74	.02	.02	10.51	12.94
C-17001	5	.145	.142	.140	.023	.018	.019	3.53	3.49	.26	•21	16.00	11.74
C <b>-</b> 15402	4	.150	.178	.189	.007	.005	.009	4.15	4.23	.14	.16	15,90	11,88
C-17096	Utah			.022			.026	•71	, 68	.03	.03	7.79	6.73
C-16139	6			.162			.061	4.18	4.01	.19	.22	18.94	13.60
C-12831	6			<b>.</b> 159			.044	2.65	2.70	.25	.28	14.30	10.72
C <b>-</b> 15038	6			.210			.044	1.41	1.32	.09	.11	13.37	10.24

TABLE 13-Concluded

\* All coals are from Illinois unless

+ HTA = High=temperature ash.

state is given.

\$ ASTM = American Society for Testing and Materials standard method for sulfur and chlorine (D271-70).

+ LTA = Low-temperature ash.

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Pl. 1 - Scanning electron photomicrographs of host minerals of some trace elements in coal. Above: Sphalerite (ZnS) in low-temperature ash of Herrin (No. 6) Coal (sample C-16030). Below: Apatite (calcium phosphate) in low-temperature ash of coal from Colorado (sample C-17097). Further improvements in methods for determining V and F will certainly result from studies now underway, and additional coal analyses will permit statistical treatment of data, which will be reported in a later publication.

Of the methods used in this investigation, all have exhibited applications of special merit. X-ray fluorescence proved to be much more useful for the analysis of whole coal than expected, and this was especially true for certain of the trace elements. It is an exceedingly useful tool because both trace and major constituents can be determined in a single pressed coal disk. The usual matrix effects associated with X-ray fluorescence analysis are virtually absent and are easily corrected in the whole coal light matrix (H, S, C, O, and N). However, a lack of analyzed coal standards is still a serious handicap for this method.

Neutron activation with radiochemical separations, although slower than other methods, has proved to be extremely sensitive for the volatile trace elements most difficult to determine—Se, As, Ga, Hg, Sb, Cd, and Br. The neutron activation instrumental method has proved to be the most rapid and accurate of the methods used in this study for determining Mn.

Atomic absorption is a suitable method for determining Cd, Zn, Pb, Ni, and Cu in solutions of coal ash. With careful attention to operating detail and background, the method has been found to be virtually interferencefree.

The method described for optical emission direct-reading spectrometry of high-temperature coal ash is unsurpassed for speed of analysis. Although months were required for calibration, it is one of the most useful instrumental methods of analysis used during the course of this investigation. We anticipate the addition of new elements (Cd, for example) to those now being determined.

Table 14 gives the mean values and the standard deviations for all major, minor, and trace constituents determined for the Illinois coals analyzed. These data represent only a quarter of the total coal samples that are to be analyzed in the current investigation of the occurrence and distribution of potentially volatile trace elements in coal. Preliminary statistical analyses of these values have provided the bases for several observations concerning the geochemical relations of the concentrations of the trace elements.

Several geochemists have attempted to determine the abundance of chemical elements in the earth's crust; Clarke and Washington (1924) were among the first to do so. The term "clarke" is defined as the average percentage of an element in the earth's crust. Only three of the trace elements in coals shown on table 14 have mean values that are an order of magnitude greater or smaller than the clarke of those elements. Manganese (mean 54.4 ppm, clarke 950 ppm) and phosphorous (mean 53 ppm, clarke 1050 ppm) are depleted in coal, whereas boron (mean 113 ppm, clarke 10 ppm) is enriched in coal. Clarke values used here are from Taylor (1964). All other trace elements are present in amounts that approximate (i.e., same order of magnitude) their abundances in the earth's crust.

Further statistical analyses of the values determined for each element (correlation of data of one element with that of every other element) demonstrate the following geochemical associations:

Constituent	No. of samplest	Mean value (pom)	Standard
		( 55 )	
As	23	14.	20.0
В	23	113.	52.0
Be	23	1.9	0.9
Br	. 23	15.	3.5
Cd	<b></b> ‡	<b>~ +</b>	<b></b> ‡
Co	23	6.	5.
Cr	21	17.	10.
Cu	23	15.	6.
Ga	23	3.6	1.3
Ge	+	₩ # <sup>‡</sup>	
Hg	23	0.24	0.14
Mn	23	54.	27.
Mo	23	8.6	4.2
Ni	23	23.	11.
P	21	53.	69.
Ръ	23	49.	59.
Se	23	2.2	1.3
Sb	23	1.6	1.9
V	23	34.	10.
Zn	22	342.	548.
Zr	18	52.	30.
		Mean value	
		(percent)	
Si	23	2.30	•45
Al	23	1.11	2.38
Ca	23	0.679	0.246
Cl	23	0.14	0.12
K	23	0.161	0.040
Mg	23	0.044	0.021
Ti	23	0.059	0.012
Ash	23	11.8	<b>1</b> .5
Organic S	22	0.67	0.56
Sulfate S	22	0.88	0.15
Pyritic S	22	1.97	0.67
Nonpyritic Fe	22	0.36	0.29
Ash, pyrite free	22	8.2	1.7

TABLE 14-MEAN ANALYTICAL VALUES FOR ALL ILLINOIS COALS ANALYZED\* (on moisture-free whole coal basis)

\* National Bureau of Standards coal SRM-1630 and a Utah coal were not included in the calculations.

+ Number of samples included in the statistical analysis.

+ Owing to the relatively large number of Cd and Ge determinations that were equal to or below the limit of detection, mean values and standard deviations for these elements were not calculated at this time. 1. A good positive correlation is present between Zn and Cd. Zn is present, at least in part, as ZnS (sphalerite), and Cd would be expected to substitute for Zn in this mineral.

2. A group of elements, most of which are commonly found in nature as sulfides (the chalcophile elements), are positively correlated with each other—As, Sb, Hg, Pb, Ni, Cu, Co. Gallium and Be are also positively correlated with the chalcophile elements.

3. Data on those elements in coal ash that generally form silicates in natural environments (the lithophile elements) also are related by positive correlation coefficients. These elements, Si, Al, Ti, and K, occur in coal in clay minerals and in quartz.

4. A positive correlation exists between Ca and Mn. Manganese commonly substitutes for Ca in calcite  $(CaCO_3)$ .

Additional relations have been suggested by our preliminary statistical analyses, but much more detailed analysis and interpretation will be made and reported following completion of the chemical analyses of the entire suite of 100 coal samples.

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