

X-Ray Fluorescence Analysis of Whole Coal

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X-ray fluorescence analysis proved to be rapid, simple, and reasonably accurate for determining the concentration of 21 minor and trace elements in whole coal. Development of the method was facilitated by the availability of a set of samples that had been analyzed during the investigation of over 100 coals for trace and minor elements by optical emission spectroscopy, atomic absorption spectroscopy, neutron activation, and wet chemical techniques. Although major elements in coal, carbon, hydrogen, oxygen, and nitrogen, cannot be analyzed by x-ray fluorescence, most other elements at levels greater than a few parts per million are readily determined. Tables present data supporting the conclusion that x-ray fluorescence may be the best method for analyzing large numbers of coal samples.

Recent interest in the trace element content of coal has increased the need for rapid and accurate analytical methods for their determination. Because x-ray fluorescence analysis has demonstrated its usefulness in determining major, minor, and trace elements in numerous other types of materials, it was felt that this method could be extended to trace element determinations in whole coal. In the past, such analyses were seriously hampered by the lack of standard samples. However, research being conducted in our laboratories under the sponsorship of the U. S. Environmental Protection Agency produced a large number of coal samples for which trace elements had been determined by two or more independent analytical procedures, for example, optical emission, neutron activation, atomic absorption, and wet chemical methods. These coals were used as standards to develop an x-ray fluorescence method that would determine many trace and minor elements in pressed whole coal samples.

The instrument used in this project was a Phillips manual vacuum x-ray fluorescence spectrometer. All analyses were made in the Analytical Chemistry Laboratories of the Illinois State Geological Survey.

Preliminary Investigation of Major and Minor Elements in Whole Coal and Coal Ash

Two different types of materials, coal ash and whole coal, were analyzed, and sample preparation was varied accordingly.

Whole coal was ground with a binder (10 wt %) and pressed into a disk, which was used as the analytical sample. The binder was a commercial product, Somar Mix, and the sample was ground in a No. 6 Wig-L-Bug for 3 min. Pellets 1½ in. in diameter were then formed at 40,000 psi in a die designed for that purpose. Sample preparation techniques are given in detail in a previous publication (1).

Two g of coal made a disk that was infinitely thick, *i.e.*, no x-rays penetrated the sample, for soft x-rays emitted by light elements such as magnesium, silicon, aluminum, and calcium. However, for elements heavier than bromine, the sample weight had to be increased to attain infinite sample thickness.

The use of x-ray fluorescence was originally intended to obtain information about the major element matrix of coal ashes that were to be analyzed for trace elements by optical emission spectroscopy. Both low-temperature (<150°C) and high-temperature (450°C) coal ashes, prepared as described by Ruch *et al.* (1), were analyzed, and the method of Rose *et al.* (2) was adapted to determine the major and minor elements (Si, Ti, Al, Fe, Mg, Ca, K, and V). The instrumental parameters used for these elements are given in Table I.

To assess the validity of this procedure, a series of coal ashes analyzed by the British Coal Utilization Research Association (BCURA) were again analyzed with the two types of ash prepared in our laboratories. Calibrations for these analyses were prepared from U. S. Geological Survey and National Bureau of Standards rock standards, 1B, G1, W1, and Nos. 78, 79, 88. The values determined for the BCURA coal ashes agreed excellently with results obtained at BCURA by Dixon *et al.* (3). Standard deviations were calculated for the duplicate coal ash determinations: Si—0.07%, Ti—0.01%, Al—0.06%, Fe—0.05%, Mg—0.02%, Ca—0.03%, K—0.01%, P—0.01%, and V—1.3 ppm. These deviations are comparable with Class A wet silicate analyses and indicate a high degree of precision.

Because of these encouraging results and previous work on brown coals by Sweatman *et al.* (4) and Kiss (5), which indicated that major and minor elements could be determined in whole coal, a series of 25 coals was prepared for x-ray fluorescence analysis. For each coal, a low-temperature ash, a high-temperature ash, and the whole coal itself

Table I. Spectrometer Parameters ($K\alpha$ x-ray)

Element	2θ Angle	Back- ground 2θ	Crystal	X-Ray Tube	PHA Volts	
					Base	Window
Si	108.01	111.01	EDDT	Cr	7	17
Al	142.42	145.95	EDDT	Cr	5	17
Ti	86.12	89.12	LiF	Cr ^a	5	18
Fe	57.51	60.51	LiF	Cr ^a	5	25
Ca	44.85	47.95	EDDT	Cr	14	30
K	50.32	53.90	EDDT	Cr	14	21
Mg	136.69	139.69	ADP	Cr	4	8
V	76.93	80.93	LiF	Cr ^a	5	16
S	75.24	78.38	EDDT	Cr	12	18
Cl	64.94	67.94	EDDT	Cr	11	19
P	110.99	113.99	Ge	Cr	9	15
Ni	48.66	50.36	LiF	Cr ^a	10	27
Cu	45.02	49.67	LiF	Cr ^a	11	28
Zn	41.79	44.25	LiF	Cr ^a	10	22
Pb ^b	28.24	31.24	LiF	Cr ^a	22	28
Br	29.97	35.12	LiF	Cr ^a	25	23
As	34.00	37.00	LiF	Cr ^a	24	23
Co	52.79	53.79	LiF	W	13	16
Mn	62.97	63.97	LiF	W	8	12
Mo	20.33	19.83	LiF	W	36	40
		20.83				
Cr	69.35	68.53	LiF	W	7	15

^a A tungsten tube is used on these elements when already in place.

^b $L\beta_1$ x-ray.

were prepared by the indicated procedures. When all values were converted to the whole coal basis, the agreement among the three types of coal materials was excellent (Table II), indicating that the simpler and more rapid whole coal technique is acceptable for determining major and minor elements.

Determination of Trace Elements in Whole Coal

Trace element determinations on whole coal have been severely handicapped by the lack of analyzed standards. Because of this it was necessary to prepare calibration curves from samples analyzed in our laboratories by independent methods. The accuracy of the x-ray fluorescence method is, therefore, dependent on the accuracy of the methods used to analyze the calibrating standards. It was too difficult to prepare standards by uniformly adding known quantities of trace elements to ground whole coal.

The light coal matrix of carbon, hydrogen, and oxygen and the relatively slight variation of heavier trace elements permit their determination with minimum interferences. The same whole coal procedures previously

Table II. Mean Absolute Variation Between Values Determined From 25 Raw Coals and Their Ashes

<i>Element</i>	<i>Mean Difference (%)</i>	<i>Maximum Difference (%)</i>
Si	0.10	0.24
Al	0.08	0.12
Ti	0.012	0.030
Fe	0.10	0.17
Ca	0.04	0.12
K	0.02	0.04
P	0.002	0.005
Mg	0.010	0.015

described were used, and the trace and minor elements, P, V, Cr, Mn, Co, Ni, Cu, Zn, As, Br, Mo, and Pb, were determined directly in 50 whole-coals.

The accuracy of the x-ray fluorescence method was evaluated by calculating, from the 50 whole coals analyzed, the mean variation of each element from its mean concentration, determined by the other independent methods previously mentioned and listed in Table III. Detection

Table III. Comparative Accuracy for Whole Coal and Limits of Detection Based on 50 Samples

<i>Element</i>	<i>Accuracy</i>	<i>Limit of Detection</i>
	per cent	per cent
Al	±0.08	0.012
Si	±0.10	0.016
S	±0.04	0.003
Cl	±0.01	0.0015
K	±0.02	0.003
Ca	±0.04	0.0005
Mg	±0.010	0.015
Fe	±0.10	0.005
	ppm	ppm
Ti	±6.3	7.5
V	±3.1	2.5
Ni	±1.9	3.5
Cu	±2.5	1.0
Zn	±23.0	2.0
As	±4.3	3.2
Pb	±7.7	1.8
Br	±1.0	0.5
P	±15.0	15.0
Co	±1.3	2.5
Mn	±3.4	4.5
Cr	±2.1	1.5
Mo	±5.2	5.0

limits, three standard deviations above background, for each element also are given in Table III.

The relative errors for all elements determined are given in Table IV. For completeness, data on minor elements in whole coal also are included in the trace element tables. These data indicate the precision obtained for the x-ray fluorescence analysis on replicates of 15 samples of whole coal ground to -325 mesh.

Table IV. Deviation on -325 Mesh on 15 Samples of Whole Coal

<i>Element</i>	<i>Standard Deviation</i>	<i>Relative Deviation (%)</i>
	per cent	
Al	0.02	1.77
Si	0.05	1.96
S	0.01	0.532
Cl	0.003	1.13
K	0.004	2.26
Ca	0.005	1.65
Mg	0.002	3.88
Fe	0.02	1.26
	ppm	
Ti	4.16	0.564
V	1.58	3.84
Ni	1.12	4.29
Cu	0.75	3.92
Zn	3.61	1.37
As	0.94	2.49
Pb	1.53	2.29
Br	0.39	2.11
P	3.41	10.92
Co	0.43	4.79
Mn	4.14	7.53
Cr	1.14	4.35
Mo	3.11	23.9

X-Ray Matrix Corrections for Analysis of Whole Coal

Because of the lack of standards, variations in analyses made by other methods, and errors caused by coal sampling problems, it was difficult to evaluate the need for x-ray matrix corrections and to select the best method for applying them. However, corrections were necessary because some elements in whole coal such as iron, silicon, and sulfur may vary considerably. For these elements, corrections were applied indiscriminately to all samples, because it was impossible to determine the point at which matrix variations required a correction greater than the accuracy limits of the method. We elected to use the minimum number of corrections compatible with reasonably accurate results. Therefore,

the elements Mg, Al, Si, P, S, Cl, K, and Mo were left uncorrected. While these determinations probably could be improved (6), they were shown to be adequate for our purposes (Table II). The titanium and vanadium values were corrected by using the variations in the iron content of the whole coal.

The method used for correcting the other elements for matrix variations was proposed by Sweatman *et al.* (4). Total mass absorption was determined by measuring the attenuation of the radiation in question by a thin layer of the sample to be analyzed. The mass absorption coefficient M was calculated by $M = A/W (\ln Cs/Cx)$; where A = area of sample (cm^2), W = weight of sample (g), Cs = intensity of the standard (counts/sec), and Cx = intensity of the standard (counts/sec) attenuated by the thin layer coal elements determined. Using these coefficients, a corrected value was obtained for the elements determined, even when matrix variations were considerable. Great care was taken to press the coals to a uniform thickness so that the mass absorption coefficient was affected only by density (for which compensation was made) and matrix considerations.

Effect of Coal Particle Size on Analytical Precision of Trace Elements

Our results indicated that coals ground to -60 mesh failed to yield a consistently acceptable precision for most trace element determinations. Therefore, it was necessary to evaluate the errors associated with trace element determinations in coals ground to various particle sizes.

Nine coals, representing a range of trace element concentrations, were carefully ground to pass screens of various mesh sizes (Table V). Duplicate 2-g coal samples for each mesh size were weighed and then ground 3 min in a No. 6 Wig-L-Bug to further reduce particle size. The final grinding eliminated, as nearly as possible, any variation in the pressed coal disks, which were subsequently prepared for analysis (1). More than 1000 individual determinations were made in this study.

Table V gives the combined means of the differences between duplicate trace element determinations for each coal particle size analyzed. Both the means of the absolute differences (in ppm) and the means of

Table V. Mean Error for All Elements at Various Coal Particle Sizes

<i>Mesh Size (M)</i>	<i>ppm</i>	<i>Error of Mean Element Concentration (%)</i>
-60	± 3.05	8.47
-100	± 2.11	6.38
-200	± 1.26	4.28
-325	± 1.12	2.62
-400	± 1.02	1.56
<400	± 0.93	1.40

the relative differences (absolute difference expressed as a percentage of the concentration) are given. The results show a progressive improvement in precision with decreasing coal particle size.

The ranges of relative differences between duplicate analyses for several trace elements, each in three mesh sizes, are given in Table VI. With the exception of bromine, the ranges are narrower for the -200 and -325 sizes than they are for the -60-mesh coal.

Table VI. Range of Relative Errors for Three Particle Sizes of Whole Coal (%)

<i>Element</i>	<i>-60 Mesh</i>	<i>-200 Mesh</i>	<i>-325 Mesh</i>
V	0.0—10.0	0.3— 5.0	0.3—4.0
P	2.0—18.0	2.0—10.0	1.5—7.5
Ni	1.5—25.0	0.0—20.0	1.5—8.0
Cu	0.8—20.0	0.2— 1.0	0.2—1.0
Zn	1.2—25.0	1.2—12.0	0.1—6.5
Pb	0.4—23.0	1.2— 9.5	0.4—5.0
As	0.1— 6.0	0.1— 4.0	0.0—1.5
Br	0.0— 4.0	0.0— 3.5	0.0—3.0

Progressive reduction in coal particle size from -60 to -400 mesh improved the precision for all elements except bromine. The combined mean relative error for all elements was reduced below 5% for coal ground to -200 mesh.

These data indicate that, for most purposes, acceptable precision can be obtained when -200-mesh coal samples are used. Further improvement is achieved by grinding the samples to -325 mesh, but this is unnecessary except for analyses that are to be used as standard values or for other special purposes. Variations in the original field sampling of coal would probably negate any improvements in precision that might be gained from grinding below -325 mesh. Although this study applies directly to x-ray fluorescence analysis of whole coal, it should also apply to any method in which a limited sample (~3 g or less) is taken for analysis.

Discussion and Conclusions

Results of analysis of whole coal samples by x-ray fluorescence agreed well with values determined by several other independent methods (Table IV). Subsequent analyses of more than 100 coals have supported this conclusion, and the figures will be published in a forthcoming *Environmental Geology Note* by the Illinois State Geological Survey. Some variations among the methods occurred when concentrations of trace elements were high, especially for the more coarsely ground coals. Be-

cause this was true with the other methods investigated, as well as with the x-ray fluorescence method, we felt the variations resulted from sampling errors caused by discrete mineral particles, such as pyrite and sphalerite, in whole coal. Geologists at the Illinois State Geological Survey have confirmed the presence of these discrete particles with the scanning electron microscope.

It is apparent from Table IV that trace elements determined by the x-ray fluorescence method are limited to those occurring in whole coals at concentrations of at least a few parts per million. Elements such as selenium, mercury, and antimony, which are generally present in whole coal at levels below 1 ppm, cannot be determined by this method. The major elements in coal, hydrogen, carbon, oxygen, and nitrogen, cannot be determined by x-ray fluorescence, but this should not inhibit the use of the method for trace and minor element determinations.

Our results indicate that x-ray fluorescence is highly useful for rapid and reasonably accurate analyses of whole coal for trace elements. Because of the speed and simplicity of the method, it is highly adaptable to large-scale surveys of coal resources. A suite of 24 samples can be analyzed for 21 elements in 3 days by manual instrumentation. While this simple procedure can not be used to determine certain elements, the time-saving factor over other methods (40 or 50 to 1 in the case of bromine by neutron activation) without loss of accuracy may well make x-ray fluorescence the method of choice for many elements. Improved equipment, such as nondispersive systems and automation, could extend the application of x-ray analysis to a dominant position for determining trace elements in whole coal.

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RECEIVED January 21, 1974