OCCURRENCE AND DISTRIBUTION OF TRACE ELEMENTS IN COAL

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Chemical analyses for nearly 60 elements are reported for 70 whole coal samples, 34 separate fractions of five laboratory-prepared (washed) coals, and 40 bench samples from five different seams of Illinois coal. These data supplement the previously reported (1) analyses for 33 elements made for 101 whole coals. Analytical procedures used in this study are listed in Table 1. The application of instrumental neutron activation analysis has been primarily responsible for the increase in the number of elements reported. Two or more methods were used to assign a best value to many elements.

TABLE 1. Analytical Procedures Used in Coal Analyses

Procedure	Type of sample	Element
Instrumental neutron activation analysis (INAA)	Whole coal	Na*, K*, Rb, Cs, Sr*, Ba, Ga, In, As, Sb, Se, Cl*, Br*, I, Sc, V*, Cr*, Mn*, Co*, Fe*, Ni*, Zn*, Mo*, Ag*, Hf, Ta, W, La, Ce, Sm, Eu, Tb, Dy, Yb, Lu, Th, U
Neutron activation analysis-radiochemical separation (NAA-RC)	Whole coal Low-temperature ash (150°C)	Hg Te†
X-ray fluorescence - wave-length dispersion (XRF)	Whole coal	Na*, K*, Mg, Ca, Al, Si, S, P, Cl*, Br*, Ti, Ni*, Zn*, Fe*
Atomic absorption (AA)	Low-temperature ash (150°C)	Ni*, Cu*, Zn*, Cd*, Pb*, Tl†, Li†
Optical emission-direct reader (OED)	High-temperature ash (500°C)	Be, Sr*, B, Ge*, V*, Cr*, Co*, Cd*, Ni*, Cu*, Zn*, Zr*, Mo*
Optical emission-photographic (OEP)	High-temperature ash (500°C)	Ge*, Pb*, V*, Cr*, Co*, Ni*, Cu*, Mn*, Zn*, Zr*, Mo*, Ag*, Sn†
Ion-selective electrode (ISE)	Whole coal	F

*Elements for which two or more analytical procedures have been applied.
†Elements for which further methods of analysis are being developed.

This paper concentrates on data for 70 coal samples, of which 31 are from the Illinois Basin which includes parts of Indiana, Illinois, and western Kentucky. Fourteen samples are from Eastern states, 22 from Western states, and 3 from Iowa. Cumulative data for the 171 samples analyzed during this and the prior study are reported elsewhere (2).

Table 2 summarizes the analyses for the 70 whole coal samples. For calculation of the mean values, the "less-than" (below limit of detectability) values were considered real values. The number of samples that had "less-than" values is noted in the table. Individual distribution plots for each element are included in the final report (2). The data can be grouped into similar types of distribution, which is more useful than considering a range of values. Elements such as Zn, Ba, As, and Cd showed wide ranges and skewed distributions, which may be explained by the occurrence of discrete mineral phases in the coal mineral matter. Elements associated with the organic material of the coal may show moderate ranges or normal distributions. For the highly dispersed elements, such as the rare earths, moderate ranges and normal distributions are also observed.

TABLE 2. Preliminary Analytical Data For 70 Coal Samples*

Element	Mean	Min	Max	Element	Mean	Min	Max
Al	1.21%	0.31%	3.1%	P	112	16	1500
Sb	1.1	0.01	7.7	K	0.16%	0.01%	0.68%
As	15	0.3	116	Rb	19	<1	63
Ba (1)†	240	20	1600	Se	2.6	0.4	8.1
Be (7)	1.3	<0.1	3.8	Si	2.13%	0.38%	6.30%
B	88	5	<240	Ag	0.03	0.01	0.08
Br	5.2	0.5	27	Na	780	100	6000
Cd (54)	0.44	<0.1	9.3	Sr	126	13	550
Ca	0.96%	0.01%	3.3%	Ta	0.18	1.1	1.5
Cs	1.3	0.04	6.2	Th	2.6	0.6	9
Cl	0.09%	0.01%	0.8%	Sn (57)	0.67	<0.2	11
Cr	20	2.4	52	Ti	0.06%	0.02%	0.16%
Co	3.9	0.6	13	W (1)	0.8	<0.2	4.2
Cu	14	3	92	U (4)	1.5	<0.3	6.1
F	81	19	147	V	25	4.8	90
Ga	3.7	0.8	11	Zn (2)	51	<0.3	645
Ge (15)	3.3	<0.1	18	Zr	35	12	88
Hf	0.8	0.1	2.2	Ce	16	3	46
In (16)	0.16	<0.01	0.6	Dy	1.2	0.3	3.5
I (21)	1.2	<1	14	Eu	0.32	0.07	0.9
Fe	1.46%	0.3%	3.7%	La	8	1.8	23
Pb (17)	8.3	<0.7	79	Lu (10)	0.12	<0.1	0.4
Mg	0.09%	0.03%	0.39%	Sm	1.4	0.3	4.3
Mn	52	1.4	303	Sc	3.0	0.5	9.3
Hg (1)	0.15	<0.05	0.6	Tb	0.3	0.06	0.7
Mo (7)	5.4	<0.1	23	Yb	0.58	0.1	1.5
Ni	13	1.5	51				

*All values in ppm unless otherwise noted.
†( ) indicates number of samples below the limit of detectability.

One method used to show trends in environmental and geological data is the calculation of enrichment factors, or Clarke values. The ratio is calculated from the concentration of a given element compared to its average abundance in the earth's crust. Elements having a Clarke value greater than 10 are considered highly enriched; those with values less than 0.1 are considered depleted. Table 3 groups the data into four general categories. Only Se shows high enrichment, a condition that was also observed by Ruch et al. (1). Boron, which was shown to be organically combined (1), is only slightly enriched. The depletion of seven elements, largely those associated with crustal rocks, is probably due to dilution by organic matter. The slight enrichment of 9 elements may be due in part to

organic combination of these elements in the coal matrix to their concentration in sulfide minerals, or to uncertainties in the crustal averages used.

TABLE 3. Average Enrichments* in 70 Coals

Elements <0.1	Depleted	Na, Mg, Mn, K, Si, P, Ti
Elements 0.1-2	No trend	Al, Ca, Fe, V, Sn, Cu, Co, Ni, Be, Cr, Sr, Zr, Pb, Zn, Ga, Hg, F, U, Ba, Ce, In, La, Lu, Ag, Rb, Cs, Sc, Sm, Tb, Dy, Yb, Th, W, Eu, Hf
Elements 2.0-10	Slightly enriched	B, As, I, Cl, Sb, Mo, Cd, Ge, Br
Elements >10.0	Highly enriched	Se

*Crustal averages used are from Taylor (3).

Two additional methods are being used to establish the presence of trace elements in coal. Specific gravity separations, which had been made on 4 coals in the previous study (1) were conducted on five coals in this study. Washability curves show some elements (e.g., Ge, B, Be) are associated with the organic phase, some (e.g., Zn, Cd, As) are present in the mineral phase, while other elements demonstrated mixed associations. An acid extraction procedure for preferential dissolution of mineral matter is being used on 25 whole coals to determine the quantity of each element closely associated with the organic fraction of the coal.

The vertical distribution of trace elements was studied in five coal seams from the Illinois Basin. Representative curves are shown for Tb, Br, Sb, and Ge in four different bench sets (Figs. 1-4). A few elements, notably Ge, appear to be concentrated in the upper and lower coal bench samples. Elements such as Tb and Br often show relatively flat distributions. Further work on this phase of the project is being continued to make significant trends more obvious.

Our program is designed to characterize the nature and association of elements within the coal matrix and to approximate the range of concentrations of elements occurring in coal.

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REFERENCES

(1) Ruch, R. R., H. J. Gluskoter, and N. F. Shimp, Occurrence and distribution of potentially volatile trace elements in coal: Illinois State Geological Survey Environmental Geology Note 72, 1974, 96 pp.

(2) Final Report EPA Contract 68-02-1472, 1976.

(3) Taylor, S. R., Abundances of chemical elements in the continental crust: Geochimic et Cosmochimica Acta, v. 28, pp. 1280-1281, 1964.

BENCH SAMPLE DISTRIBUTIONS

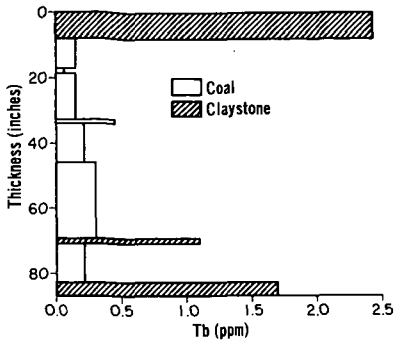

Fig. 1

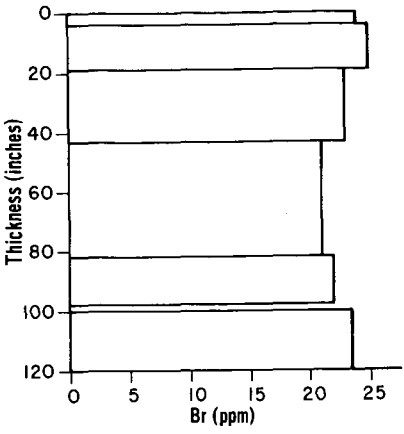

Fig. 2

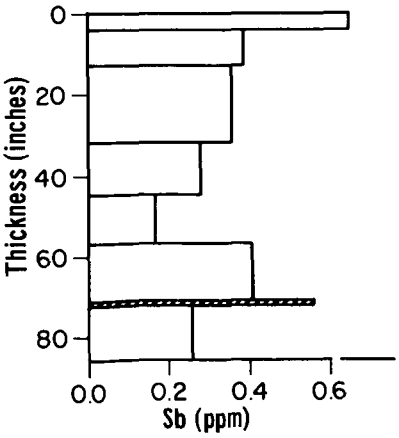

Fig. 3

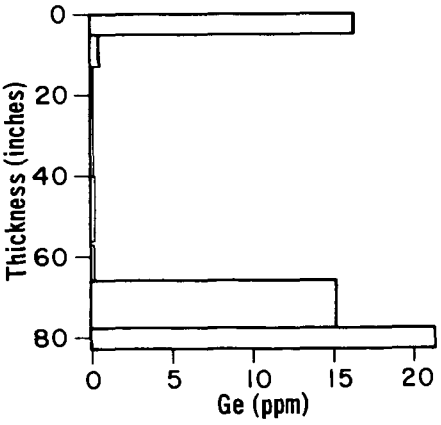

Fig. 4