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CHEMISTRY

TRACE METALS IN WYOMING COAL: THEIR ANALYSIS, CONCENTRATIONS, AND INTERRELATIONSHIPS

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The Teflon bomb and the flameless atomic absorption spectrophotometer (AAS) were used to analyze trace metals in Wyoming coal. The results were compared to a National Bureau of Standard (NBS) reference coal sample. The combined use of the Teflon bomb and flameless AAS appears to be a sensitive, accurate, and practical method for analyzing trace metals in coal. Most metallic concentrations in Wyoming coal samples do not appear to exceed the collected U.S. coal samples.

† † †

INTRODUCTION

In the future, more coal will be used as a domestic energy source, producing additional environmental problems and creating major changes in the American life style and economy. Consequently, rapid and accurate, though sensitive, analytical methods are needed for the analysis of trace metals in coal. Therefore, this study reports on the use of the flameless atomic absorption spectrophotometer and the Teflon bomb as analytical techniques for analyzing trace metals in Wyoming coal.

METHODS

The coal samples (supplied by G. B. Glass, Staff Coal Geologist, Box 3008, University Station, Laramie, Wyoming 82071) were pulverized by a ball mill to pass through a 325 mesh screen. Upon drying, 50 mg of pulverized coal were transferred to a 25 ml Parr (4745) Teflon-lined bomb, to

which 1.0 ml of Ultrex nitric acid (J. T. Baker Chemical Co.) was added. The bomb was placed in an oven at 150°C for six hours. After cooling, 0.1 ml of Ultrex hydrofluoric was added, and the digested sample was again heated at 150°C overnight. After cooling, 24 ml of distilled-deionized water and 50 mg of boric acid were added to the dissolved sample, which was stored in a one-ounce polyethylene container until analysis. Only new linear polyethylene containers were used as the storage vessels, and these were subjected, as were the ball mill and Teflon liners, to a thorough acid soaking and cleaning process. After the acid soaking and cleaning process, any container with a blank solution found to have a detectable background of zinc (the most contaminable metal under study) was discarded.

All elements, except sodium and potassium, were analyzed by flameless atomic absorption spectrometry (Perkin-Elmer Model 303 Spectrophotometer with background corrector and HGA-2000 graphite furnace), using the manufacturer's recommended settings. Sodium and potassium were analyzed by flame photometry (Beckman DU-2 spectrophotometer with flame attachment). Sodium was run at 589 nm, potassium at 768 nm, and a slit-width of 0.1 mm was used for both elements.

RESULTS AND DISCUSSION

Table I shows the concentration in ppm of eleven metallic elements in the twelve coal samples. Sample 12-74 is from the

TABLE I

Metal Concentrations in Wyoming Coal, ppm

Sample No.	County	Al	Na	K	Mn	Zn	Cu	Co	Pb	Cd	
5-74	Campbell	7,200	550	390	42	69	27	6.0	10.1	0.75	1
6-74	Campbell	3,800	1,300	250	18	20	16	5.5	6.7	0.20	0
29-74	Campbell	3,600	870	180	12	62	15	3.5	2.7	0.25	0
30-74	Campbell	4,000	820	210	41	24	29	3.9	3.0	0.28	0
32-74	Sheridan	4,900	1,870	470	15	29	22	4.0	2.3	0.45	1
33-74	Sheridan	3,300	1,970	290	43	36	16	3.7	1.7	0.89	0
9-74	Sweetwater	3,800	220	70	39	25	17	3.6	3.4	0.31	0
10-74	Sweetwater	7,500	370	270	39	51	26	3.9	8.9	0.46	0
8-74	Converse	8,600	160	660	113	70	15	4.4	8.8	0.43	0
37-74	Converse	19,700	250	2,500	11	12	26	2.9	9.9	0.35	1
38-74	Converse	7,600	160	450	79	25	22	3.2	4.2	0.38	0
	\bar{X}	6,700	780	520	41	38	21	4.1	5.6	0.43	0
	σ	4,720	670	680	31	21	5	0.9	3.3	0.21	0
12-74*	Carbon	3,200	120	350	31	26	16	3.8	3.0	0.25	0

*This is the only sample obtained from the Hanna Formation. The other samples are from the Ft. Union Formation.

Hanna Formation; the remaining samples are from the Ft. Union Formation. The arithmetic means and standard deviations are shown for the Ft. Union coal samples. National Bureau of Standards (NBS) Reference Coal Standard No. 1632 served as the control for all metals tested except aluminum, sodium, and potassium. The NBS certified elements were manganese, zinc, lead, copper, thallium, and cadmium. The non-certified metals were cobalt and silver. The results in the study were based on a maximum deviation of 9 percent for any certified or non-certified element. The authors believe that sodium and potassium also fall within these limits, as flame photometry is well suited for these elements.

Little variation in trace metal concentrations is evident in the Ft. Union samples. Differences in metal concentrations among different samples are within a factor range of two to four. Manganese, however, exhibits the greatest concentration range of any element by one order of magnitude among the samples. The concentrations of all the elements are lower in the sample for the Hanna Formation (Carbon County), except

silver. Less than 0.5 ppm of thallium, the limit of detection was found in any sample.

For comparative purposes, data have been assembled Table II showing metal concentrations in collected U.S. coal samples (Bertine and Goldberg, 1971). Even though the comparative values are generalized, the data indicate that the Ft. Union coal samples contain lower concentrations of most elements, except copper, than that found in comparative United States coal. It is noteworthy that the Ft. Union coal contains considerably less lead than the comparative U.S. coal value.

In the interest of finding a relationship among metal concentrations, correlation coefficients have been computed between metal pairs in the Ft. Union samples, and are shown in Table III. Aluminum and potassium show the strongest positive correlation coefficient (0.96). Lead, considered a biologically toxic element, is positively correlated to all elements except sodium (-0.57). The grouping of the Ft. Union samples by county

TABLE II

Comparative Metal Concentrations in Coal, ppm

	Ft. Union	Collected U.S. Values*
Al	6700	10,000
Na	780	2,000
K	520	1,000
Mn	41	50
Zn	38	50
Cu	21	15
Co	4.1	5
Pb	5.6	25
Cd	0.43	not reported
Ag	0.5	0.5
Tl	< 0.5	not reported

*Bertine and Goldberg (1971)

in Table I reveals a clue as to the negative behavior of sodium. It shows that the concentrations of sodium exceed that of potassium in the coal samples from Campbell, Sheridan, and Sweetwater counties. On the other hand, the opposite trend is noted in the coal samples from Converse County, where potassium exceeds that of sodium, even by one order of magnitude in sample 37-74. Since this relationship is evident in this study, but anomalous to the general trend, additional coal samples may be needed to verify the preceding statement.

CONCLUSIONS

The combination of the Teflon acid digestion bomb and flameless atomic absorption spectrophotometer appears to be an accurate, sensitive, practical, and fairly rapid method of analyzing metals in coal. The application of this method can be extended to include many trace metals in coal. For the eleven metals tested, little variation in concentrations is evident in the Ft. Union coal. Furthermore, their concentrations do not appear to exceed the metal concentrations of collected United States coal samples.

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TABLE III

Correlation Coefficients (x100) of Metals in Ft. Union Coal

ppm in earth's crust*	Al	Na	K	Mn	Zn	Cu	Co	Pb	Cd	Ag
Al 81,300		-49	96	- 1	-19	39	-31	67	- 5	38
Na 28,300			-27	-44	-17	-23	16	-57	34	17
K 25,900				-16	-32	30	-36	50	- 6	40
Mn 950					40	-17	5	18	18	-35
Zn 70						-18	41	30	35	0
Cu 55							1	34	7	54
Co 25								38	22	24
Pb 13									5	31
Cd 0.2										30
Ag 0.07										

*Mason (1966)

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