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The Concentration of Cd, Cu, Fe. Ni, Pb, and Zn in Bituminous Coals from Mines with Differing Incidences of Coal Workers' Pneumoconiosis

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A detailed study of the analysis of Cd, Cu, Fe, Ni, Pb and Zn content in bituminous coals from Pennsylvania and Utah was made and a satisfactory procedure for their analysis is presented. The Cu, Fe, Ni, Pb and Zn content of coal from a Pennsylvania mine having a high incidence of Coal Workers' Pneumoconiosis (CWP) was found to be higher than a sample of coal from a Utah mine of low disease incidence. The cadmium content was found to be the same in both coals. The present investigation also deals with some observations concerning interferences associated with coal analysis using atomic absorption spectrophotometric methods. The significance of data with regard to the change in metal levels found in coal miners' lungs is discussed.

Introduction

THERE IS AN INCREASING NEED for the qualitative evaluation of environmental contaminants. Our work represents a continuing effort in this regard. We have undertaken an evaluation of coal dust as a contaminant of the miners' environment. The choice of mines from which coal samples were taken was based up an epidemiological study by Lainhart.[1] His studies demonstrated differences in occurrence of Coal Workers' Pneumoconiosis (CWP) in bituminous miners working in mines located in Appalachia, Illinois, Indiana and Utah.* Coals selected for this study were obtained from a mine in Pennsylvania with the highest incidene of CWP and from a mine in Utah having the lowest incidence.

Metal analyses of bituminous coal miners' lung tissue by Keenan,[2] Crable,[3,4] and Carlberg[5] have demonstrated higher than normal concentrations of iron, copper, lead, zinc and other metals. Since these abnormally high levels of metals could be involved in the etiology of CWP, our initial concern was to answer the following question: What are the differences in content of metals of interest found in coal from a mine of high incidence of CWP and a mine having a low incidence of CWP? Since there were no published concentration values for the metals in these coal samples and the unpublished data were conflicting, we attempted to accurately measure the concentrations of the various metals of interest using atomic absorption spectrophotometry. The data we have obtained suggest that there is a good correlation between the amount of metal in coal and the incidence of CWP.

Analytical Procedures

Apparatus

Atomic absorption spectrophotometer: Perkin-Elmer 303 with Sargent Model SRG recorder and a Perkin-Elmer Deuterium Lamp Continuous Source Compensation System.[7]

Plotter and Calculator: Wang 700 Series Advanced Programming Calculator with a

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Note added in proof: The results of this epidemiological study have been confirmed recently by Morgen et al.—Morgen, W. K. L., D. B. Burgress, G. Jackson, R. J. O'Brien, E. P. Pendergrass, R. B. Reger, and E. P. Shoub: The Prevalence of Coal Workers' Pneumoconiosis in U.S. Coal Mines. AMA Arch. Envirn. Health 27:221 (Oct. 1973).

program furnishing the equation for a fitted line determined by the least squares method at the 95% level of confidence and giving the confidence limits.

Glassware: All glassware was rendered metal free by soaking in 10% nitric acid for 24 hours and rinsing in deionized water.

Reagents

Acids: Dupont nitric acid, 70-71%, and Baker perchloric acid, 70-72%; both meet ACS specifications. The 10% nitric acid was made by dilution with deionized water.

Standard solutions of Cd, Cu, Fe, Ni, Pb and Zn: Standard solutions were made up from Fisher Certified Atomic Absorption Standards—1000 μg/ml. Dilutions were made with 10% nitric acid.

Orchard Leaves Standard: National Bureau of Standards Reference Material #1571.

Coal samples: Micronized coal samples were supplied by Mr. William Wagner of the National Institute for Occupational Safety and Health.

Preparation of Samples

Method of Additions, Wet-Ashing

Twelve 1.000 gm (0.100 gm for Fe determination in Pennsylvania coal) portions of micronized coal were weighed into separate 250-ml beakers. These were divided into groups of three. No additions were made to the first group. Increasing concentrations of metal, in 10% nitric acid, were added to the other three groups. Fifty ml of concentrated nitric acid and 10 ml of concentrated perchloric acid were added to each beaker and mixed well to wet all of the coal particles. A reagent blank was also prepared. Each beaker was covered with a watch glass and heated until the contents were reduced to a colorless solution, 1 ml in volume. If foaming or incomplete digestion occurred, an additional 10 ml of nitric acid was added and the solution again reduced to 1 ml. The final residue was heated with several mls of 10% nitric acid and transferred to a graduated centrifuge tube. Additional washings of the beaker with 10% nitric acid were also transferred to the tube and the final volume adjusted to 10 ml. After centrifugation the supernatants were transferred into polyethylene test tubes and capped for storage. Twelve 1.000 gm portions of NBS Orchard Leaves Standard were prepared by the same procedure.

Interpolation, Wet-Ashing

The samples prepared for the method of additions but without added metal, were used for analysis by interpolation.

Interpolation, Dry-Ashing

Three 1.000 gm (0.100 gm for Fe determination in Pennsylvania coal) samples of coal were weighed into small fused quartz crucibles and placed in a muffle furnace at 425°C for 18 hours. After cooling, the ash of each sample was dampened with several drops of water. Then 2 ml of concentrated nitric acid was added, the crucible covered with a watch glass, and the solution evaporated to near dryness. Digestion was repeated with an additional 2 ml of acid. Final residues were suspended in 10% nitric acid and transferred to graduated centrifuge tubes where the final volumes were adjusted to 10 ml. After centrifugation the supernatants were poured into polyethylene tubes and capped for storage. Then 1.000 gm samples of NBS Orchard Leaves Standard were prepared in the same manner.

Standard Metal Solutions

Commercial metal standards in 10% nitric acid were diluted to various concentrations with 10% nitric acid to obtain a range which would include the concentration of metal in the samples. These solutions were transferred to 125-ml polyethylene bottles for storage.

Metal Recovery from Blanks

Quantities of metal in 10% nitric acid in amounts similar to those added to coal samples were placed in 250-ml beakers, three beakers per concentration level. Fifty ml of concentrated nitric acid and 10 ml of concentrated perchloric acid were added to each and the samples treated in the same manner as those in the wet-ashing procedure.

Metal Recovery from Samples

Samples prepared by adding metal to the coal for wet-ashing were also used in a recovery determination. Additions (μg) were as follows:

Utah: Cd – 0.2, 0.5, 1.0; Cu – 5, 10, 15; Fe – 1000, 2000, 3000; Ni – 50, 100, 150; Pb – 5, 10, 15; Zn – 5, 10, 15;

Pennsylvania: Cd – 0.2, 0.5, 1.0; Cu – 10, 20, 30; Fe – 1000, 2000, 3000; Ni – 200, 300, 400; Pb – 5, 10, 15; Zn – 10, 20, 30.

Interference Studies

Samples were analyzed with and without a deuterium arc lamp as a source of continuous radiation to check for non-specific absorption. In addition, samples were analyzed at non-absorbing wavelengths to determine if any broad band absorption existed. These wavelengths were 216 nm for Cd, 333 nm for Cu, 260.5 nm for Fe, 223 nm for Ni, 288 nm for Pb and 211 nm for Zn. To study the effect of the physical matrix on elemental absorption, samples were aspirated into the atomic absorption spectrophotometer and their rate of flow determined by measuring the average time required to aspirate 1 ml of sample.

Atomic Absorption Spectrophotometric Method

Appropriate dilutions of the final solutions were prepared with 10% nitric acid to place the elements of interest into the working range of the atomic absorption spectrophotometer. Samples were run at the following wavelengths: 228.8 nm (Cd), 324.7 (Cu), 248.3 nm (Fe), 232 nm (Ni), 283.3 nm (Pb) and 213.9 nm (Zn). The chart readout in percent absorption was converted to absorbance. For coal and Orchard Leaf samples these values were then plotted versus concentration of metal added. The x-intercept of the extrapolated regression line is the concentration of metal in the sample by the method of additions.

Percent absorption values for external standards were likewise converted to absorbance and plotted versus metal concentrations. The average absorbances of the dry-ashed and wet-ashed coal, and Orchard Leaf samples without additions were used in the equation of the external standard curve to solve for the concentration of metal in the unknown by interpolation.

The values for the recovery of metal from blanks were also obtained by interpolation using the external standard curve, but final concentrations were then computed as percentage of the amount originally added to the blank.

To compute percentage recovery of metal added to the samples, the average absorbance increase due to added metal was divided by the absorbance increase due to the same amount of metal in the standard solutions and multiplied by 100.

Results and Discussion

Concentrations of Cd, Cu, Fe, Ni, Pb and Zn in both coals obtained by the methods of additions and interpolation using wet and dry ashing techniques are presented in Table I. Comparing the amounts found in each coal, the Pennsylvania sample has a higher concentration of Cu, Fe, Ni, Pb and Zn; Cd is the same as that in Utah coal. Inspection of these data reveals that the concentrations of copper, lead and zinc were only two to three times higher, while the concentrations of iron and nickel were ten and five times higher in Pennsylvania coal as compared to Utah coal. These data are in good agreement with those reported by Nord and Bingham[7] for the analysis of similar Pennsylvania and Utah coal samples.

Comparison of the concentrations obtained by the two ashing techniques employed (Table I) points out that both gave

TABLE I
Metals in Utah and Pennsylvania Coals ($\mu g/gm$)*

	Wet-ashing, Additions	Wet-ashing, Interpolation	Dry-ashing, Interpolation	
Cd	0.40 (0.27–0.53)	0.23 (0.05–0.41)	0.38 (0.18–0.58)	Utah
	0.39 (0.32–0.46)	0.24 (0.06–0.42)	0.24 (0.06–0.42)	Penn.
Cu	9.9 (7.4–12.4)	7.6 (7.3–7.9)	5.9 (5.6–6.2)	Utah
	27.5 (25.7–29.3)	24.8 (20.7–28.9)	19.9 (15.0–24.0)	Penn.
Fe	3540 (3120–3960)	3180 (2763–3597)	1838 (1290–2386)	Utah
	31380 (29700–33060)	27880 (23470–32290)	12584 (11051–14117)	Penn.
Ni	220 (180–260)	140 (109–171)	96 (39–153)	Utah
	989 (945–1033)	595 (361–829)	587 (296–878)	Penn.
Pb	6.4 (5.2–7.6)	6.6 (5.6–7.6)	6.5 (5.5–7.5)	Utah
	15.3 (11.8–18.8)	13.5 12.7–14.3)	18.0 (16.8–19.2)	Penn.
Zn	9.4 (7.0–11.4)	10.4 (7.4–13.4)	9.2 (5.3–13.1)	Utah
	24.8 (19.2–30.4)	23.9 (19.4–28.1)	20.3 (15.3–25.3)	Penn.

*Mean and the range obtained at the 95% level of confidence.

similar results with the exception of Fe and Ni. The concentration of Fe was found to be lower when the samples were dry-ashed as compared to wet-ashing. The concentration of Ni was found to be lower in wet and dry ashed samples analyzed by interpolation as compared to the method of additions.

TABLE II
Average Percentage Recovery of Added Metals*

Element	Penn. Coal	Utah Coal	Blanks
Cd	88 (88)	83 (93)	98
Cu	114 (100)	83 (93)	99
Fe	96 (96)	96 (101)	101
Ni	64 (93)	83 (89)	103
Pb	83 (95)	92 (107)	100
Zn	86 (93)	105 (84)	100

*The values in parenthesis are the average percentage recoviers obtained when a second batch was analyzed.

Analysis of a different batch of the two coals gave the same relative differences in metal concentrations. The Pennsylvania coal contained more of each of the metals except cadmium; and the relative amount of each metal, except nickel, in the two coals was the same. In this second analysis the amount of nickel found by wet-ashing and using the method of additions was 176 $\mu g/gm$ for the Utah coal and 2900 $\mu g/gm$ for the Pennsylvania coal. The nickel found by wet-ashing and using the interpolation method was 113 $\mu g/gm$ for the Utah coal and 2770 $\mu g/gm$ for the Pennsylvania coal. These results point out the relative homogeneity of the micronized coal samples with regard to the content of Cd, Cu, Fe, Pb and Zn. Only the nickel in the Pennsylvania coal varied significantly.

Recovery studies suggest that the higher value may be the more correct one. The data presented in Table II show good recovery of metal in coal samples with the exception of Pennsylvania nickel. Recovery of nickel in this coal on re-analysis of a different batch of coal was 93% using the method of additions. Excellent recovery data have been obtained for aqueous standard blanks which are included in Table II. These recovery data compared to those obtained with the coal samples suggest that there may be a source of interference associated with this particular sample of coal.

Possible interferences associated with atomic absorption spectrophotometry have been evaluated. Light scatter and molecular absorption were evaluated with the deuterium lamp continuous-source compensation system.[8] No differences in absorptions were detected with this sytem compared to those obtained without it. Samples irradiated with non-absorbing wavelengths had negligible increases in absorption, further indicating that light scatter and molecular absorption interferences were absent. Physical differences in the matrices (viscosity, surface tension, etc.) of the solutions can also be a source of interference. Aspiration rates of sample solutions, standard metal solutions, and 10% nitric acid were the same, ruling out a matrix matching interference associated with the physical properties of the sample solutions. The possibility that the differences in nickel concentration observed for the two determinations are due to differences in chemical interference has not been ruled out. It may be that this type of interference associated with different amounts of silicate, known to be present in these coals, can account for the difference in concentration observed for nickel in the two determinations.

The decreased values for Fe and Ni, obtained by dry-ashing, may be attributed to a loss during combustion. These elements readily form volatile carbonyls and may be lost in this form.

To evaluate the accuracy of the analytical results obtained for the coal samples, National Bureau of Standards Reference Material #1571, Orchard Leaves, was analyzed. The results presented in Table III supported the validity of the coal data. The concentrations obtained for copper, iron, lead and zinc agree with those reported by the NBS. The values obtained for nickel and cadmium are consistently high but close to the suggested value. These data were obtained repeatedly using both ashing technique and analyzing by the methods of additions and interpolation.

In conclusion, it is important to point out that our data correlate with the observations of others who have analyzed bituminous coal miners' lung tissue for various metals. In our study of metal content of coal from mines with high and low disease incidence, we have found higher concentrations of metals in the coal from the mine with higher disease incidence. While others have shown that bituminous coal miners' lungs contain elevated amounts of metals compared to normal adults, Keenan *et al.*[2] have analyzed lung tissue and hilar lymph nodes of West Virginia bituminous coal miners and report an increase in copper, iron, lead and nickel compared to concentrations normally found in adult lung tissue. Crable *et al.*[3] have demonstrated an increase in mineral content of West Virginia bituminous coal miners' lungs compared to that found in British studies of anthracite coal miners. The Crable study also demonstrated that West Virginia bituminous miners' lungs contained elevated amounts of copper, lead and nickel com-

TABLE III
Metals in Orchard Leaves Standard (μg/gm)

	Wet-Ashing		Dry-Ashing	Reference Values Provisionally Certified by NBS
Element	Addition	Interpolation	Interpolation	
Cd	0.45	0.48	0.55	0.11±0.02
	(0.32–0.58)†	(0.25–0.71)	(0.06–1.02)	
Cu	12.6	13.8	12.0	12±1
	(10.0–15.2)	(11.0–15.6)	(10.9–13.1)	
Fe	265	260	261	270*
	(258–272)	(254–266)	(255–267)	
Ni	3.0	4.5	2.9	1.3±.2
	(2.4–3.6)	(4.2–4.8)	(2.1–3.7)	
Pb	52.1	48.6	42.9	44*
	(49.4–64.8)	(45.3–51.9)	(36.6–49.2)	
Zn	29.3	24.2	28.0	25±3
	(24.6–34.0)	(20.9–27.5)	(25.5–30.5)	

†Ranges obtained at their 95% level of confidence.
*Not certified but reported by NBS as acid soluble.

pared to normal. In their continuing studies of West Virginia miners, Crable *et al.*[4] demonstrated that lung tissue from another group of bituminous miners contained more copper, iron, nickel and zinc but less lead than normals. Carlberg *et al.*[5] have reported an elevation of nickel, copper, zinc, lead and iron in lung tissue as well as pulmonary hilar lymph nodes of West Virginia bituminous coal miners. Recently, Bergman *et al.*[9] have suggested that the amount of iron in simple pneumoconiosis lungs is related to their mineral and coal contents and to "years underground." Abnormally high amounts of iron-containing material are found in pneumoconiotic lungs; the quantity of this material is related to the coal and mineral contents of the lungs and is probably due to the deposition of hemosiderin. Hence, there seems to be a direct relationship between the amounts of these metals in coal and the amount found in the coal miners' lungs and hilar lymph nodes. In our study, the amount of these metals in the two coal samples correlate with the incidence of coal workers' pneumoconiosis. It is suggested that the metal content of coal may play some role in the etiology of this disease. The possibility that there are organic components in these coal samples, that may also be involved in the etiology of CWP, is being investigated in our laboratories.

Summary

Our data consistently demonstrate that the Pennsylvania coal samples contain more copper, iron, nickel, lead and zinc than the Utah sample. The cadmium content was the same in both coals. The concentration of iron and nickel are much greater in the Pennsylvania coal than the Utah coal.

Light scatter, non-specific molecular absorption, matrix matching interferences and losses in preparation have been eliminated as possible interferences. Losses during combustion have been demonstrated for iron and nickel. The existence of a chemical interference is suggested as a possible source of apparent concentration variation in the analysis of coal for metals.

The relative concentrations of the metals we have found in the two coals correlates with the disease incidence found in the miners working in the mines from which the coal samples were taken.

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