PART I. COAL MINE DUST

RECENT ADVANCES IN THE ANALYSIS OF RESPIRABLE COAL DUST FOR FREE SILICA, TRACE ELEMENTS, AND ORGANIC CONSTITUENTS

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INTRODUCTION

The occurrence of pneumoconiosis (black lung disease) in coal miners has prompted considerable study of the chemical agents that may be implicated. Miners who suffer from this malady undergo long-term accumulation of carbonaceous and other particles in the lungs. Cummins and Sladdin [1] believe respirable free silica to be implicated, possibly synergistically, with other respirable particles found in the lung; Morgan,[2] however, does not believe that silica is implicated.

ANALYSIS

The classes of material chosen for study in this paper are free silica (crystalline or amorphous SiO_2), elements (mainly trace metals), and organic compounds. Background information in each area will be briefly presented before discussing analytical advances.

Free Silica

A brief survey has been presented in a Bureau of Mine Publication [3] covering available and potentially feasible procedures for determining free silica in both coal and other types of respirable dust. Coal dust varies considerably in free silica content, with values ranging from 1–5% in most cases.

Analytical Methods

Although many analytical methods exist for determining silicon in solution, accurate determination of crystalline or amorphous silicon dioxide is accomplished with some difficulty. It is important that the limitations of this analysis be emphasized, particularly with regard to the problem at hand, namely, analysis of respirable free silica in airborne coal dust collected on membrane filters by size-selective samplers.

In the usual case, broad size-range silica is available in minerals and is submitted for analysis in relatively large quantities. The method of choice is usually x-ray diffraction, using several hundred mg samples admixed with an internal standard. At least three major peaks are measured. Results are at best

semiquantitative and often misleading, since the sample must be thoroughly ground to reduce soft mineral interferences (such as muscovite) to a very low particle size. As a result, the silica in the sample is also ground to a smaller size range. For the more specialized analysis involving only a few mg of respirable coal dust collected on a filter, infrared analysis is preferable. The sample is removed from the filter by ultrasonic washing, ashed, and pelletized with potassium bromide for infrared scan in the 800 cm^{-1} region. This type of analysis is carried out routinely at the Bureau.

Analytical Limitations. Some of the difficulties of free silica analysis have been mentioned above. For respirable dust, some of the limitations are low silica content, usually considerably less than 5%; small sample size, generally less than 5 mg; and the presence of interferences such as specific clay minerals. The mainly organic matrix also cuts down transmission in the rock salt region of the spectrum. Past experience indicates that the free silica is of the alpha quartz form. Further investigation in coal would be worthwhile, however, since other forms of free silica have lower threshold limit values (TLV's) than alpha quartz.[4] Although the size distribution of respirable dust depends on the collection device used, results indicate that the samples are sufficiently reproducible for valid quantitative analysis of alpha quartz. Interferences by other materials in the ash have been considered minimal for analysis in the 800 cm^{-1} region. Refinements of the infrared technique will facilitate further examination of this assumption.

Direct Analysis on Membrane Filters. Recently, we have found that small, known quantities of alpha quartz deposited on low-ash membrane filters give well-defined and reproducible peaks with high transmittance of the filter matrix. Respirable coal dust spread on these filters also displays small alpha quartz peaks. Estimation of concentration appears feasible, based upon the pure alpha quartz filter standards.

Mechanical and Thermal Alteration. Liberti and Devitofrancesco [5] have shown that the infrared spectra of quartz is degraded by grinding and heating, in proportion to the severity of treatment. Destruction or partial destruction of the crystallinity on the surface of quartz particles has been indicated by electron micrographs. This finding may have significance in the analysis of silica in coal, as well as in the establishment of the physiological properties of this component.

Determination of Major and Trace Elements

Some major and trace elements may be of importance in producing the disease, either alone or synergistically with other materials. It is difficult to guess which elements are critical. It may thus be worthwhile to consider the elements found in coal and also those found in miners' and nonminers' lungs. In TABLE 1, prepared by using values given in a West Virginia Geological Survey publication,[6] are shown the elements found in the ash from West Virginia coals, analyzed by emission spectrography.

It is difficult to select materials that may be associated with the development of pneumoconiosis. One of the first studies on elements found in miners' lungs was reported by Crable and coworkers.[7] In TABLE 2 of their paper, concentrations of the elements found in miners' lungs (M) are compared with those of normal lungs (N). The 17 elements tabulated are not the only ones capable of determination by updated procedures. When the ratio, M/N (see TABLE 2 of

TABLE 1

ELEMENTS FOUND IN WEST VIRGINIA COALS

Element	Concentration Range % (in ash)	Element	Concentration Range % (in ash)
Li	0.005 – 1.00	Co	0.005–0.1
Na	0.3 –10.0	Cr	0.01 –0.05
K	0.4 – 4.0	Cu	0.006–0.50
Rb	0.03 – 0.1	Ga	0.005–0.10
Ca	0.1 –35.0	Ge	0.005–0.25
Sr	0.1 – 1.0	Hg	0.008–0.06
Ba	0.05 – 5.00	La	0.035–0.10
Mg	0.1 – 2.0	Mn	0.004–1.0
Al	5.0 –50.0	Mo	0.006–0.15
Si	3.0 –80.0	Ni	0.006–0.50
Fe	1.0 –80.0	P	0.2 –8.0
Ti	0.2 – 6.0	Pb	0.15 –0.20
Ag	0.0005– 0.02	Sb	0.005–0.03
As	0.7 – 0.3	Sn	0.01 –0.20
B	0.02 – 6.0	V	0.01 –0.15
Be	0.0005– 0.1	W	0.01 –0.05
Bi	0.004 – 0.01	Zn	0.05 –0.24
Cd	0.007 – 0.05	Zr	0.009–0.09

TABLE 2

COMPARISON OF LEVELS OF ELEMENTS IN MINERS' LUNGS WITH NORMAL LUNGS

Element	Mean Concentration (μg per dried lung)		Ratio
	Miner's Lung (M)	Normal Lung (N)	
Al	9535	205	47
Ba	283	2.5	113
Be	4.0	—	—
B	7.7	0.28	27.5
Cr	11.6	3.02	3.8
Ge	1.1	—	—
Fe	1595	2410	0.66
Pb	23.7	13.9	1.7
Mg	98.8	495	0.20
Mn	8.1	4.38	1.8
Ni	37.0	20.2	1.9
Ag	1.1	0.01	110
Sn	20.0	23.13	0.87
Ti	215	50.1	4.3
V	45.2	1.73	26

this paper) is plotted against average concentration for each element found in West Virginia coals (TABLE 1), poor correlation is observed. It remains to be seen whether such a relationship occurs in the case of collected respirable dust. The correlation of element levels, either in respirable dust or in miners' lungs, with high and low incidence of pneumoconiosis may prove to be of greater importance. Such a correlation would, of course, apply to silica and organic materials as well.

Analytical Methods for Elements

Several techniques are in use or under development in-house at the Bureau of Mines. They are atomic absorption, polarography, ring oven, ultraviolet-visual spectrophotometry, spark-source mass spectrometry, and emission spectrometry. Analysis by neutron activation and x-ray fluorescence may be carried on outside the Bureau.

Atomic Absorption. Atomic absorption has been the mainstay of our initial efforts, even though it lacks sensitivity for several elements. Samples consist of bulk coal ground and sized to 10 micrometers (μm), sized settled coal mine dust (float dust), and respirable dust collected on membrane filters by size-selective samplers. The filters are subjected to ultrasonic washing to remove the dust, and composite samples ranging in weight from 10 to 50 mg are prepared for analysis.

The coal dust is brought into solution either by alkaline fusion with lithium tetraborate [8] or by acid digestion, using fuming nitric acid followed by hydrofluoric acid to dissolve silica and silicates. This latter procedure, developed in our laboratory, involves the use of a teflon-lined bomb. Both a conventional aspirator burner and a flameless graphite furnace are used with Perkin-Elmer* Model 403 and 303 spectrophotometers.

The elements determined thus far with sensitivities as low as 0.01% of the weight of coal are: Li, Be, Na, Mg, Al, Si, Ca, K, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Ag, Cd, Ba, Pb, and Bi. Most of these elements were found in the coal dust by atomic absorption. When the coal is dissolved and spiked by very small, known amounts of elements, they are recovered quantitatively in almost all cases. Elements that are difficult to analyze by conventional atomic absorption, such as boron, will be determined by other means.

Polarography. Classical d.c. polarography has the capability of analysis in the 10^{-5} M range, falling short of the sensitivity required for trace elements. Stripping voltammetry, however, can readily provide sensitivities of 10^{-9} M and below, a very adequate level. We are in the process of obtaining analysis for elements such as the transition metals, most of which are present in coal at levels less than 0.1%. With modern instruments, good selectivity, as well as adequate sensitivity, can be obtained. The extreme sensitivity of this technique will make it possible to conduct analysis of elements that cannot be achieved by any other techniques.

Ring Oven. This technique has been relegated to the archives by many chemists. Philip West,[9] of Louisiana State University, however, has used this method for multi-element analysis of a large number of metals. Sensitivities of

* Use of brand names does not constitute endorsement by the Bureau of Mines.

1–100 ppm (in solution) are readily achieved with accuracies in the ± 10–20% range. We recently acquired a ring oven and have determined iron and several other elements with expected sensitivity. Elements that were analyzed or will be analyzed are: Al, Ba, Be, Bi, Co, Cu, Cr, Fe, Pb, Ni, Ag, Sr, Ti, Sn, and V. This list includes several elements that have poor sensitivity using atomic absorption, such as Ba, Bi, Cr, Sr, and Sn. Ti and V have low sensitivities but are often in relatively high concentration in coal. It is likely that the ring oven will serve best as a confirmatory technique.

Spectrophotometry. Ultraviolet-visible (UV-Vis) spectrophotometric analysis, usually employing colored complex ions, has long been one of the mainstays of the classical analytical chemist. Although reasonable sensitivity can be achieved in many cases, the wet-chemical procedures are often tedious and exacting. In most cases, only one metal can be determined at a time. Nevertheless, this type of analysis is useful for confirmatory backup determinations and for elements difficult to analyze by other techniques.

Many new procedures are being developed at the present time to achieve specificity and to bypass tedious separation often associated with classical UV-Vis spectrophotometry. For example, in the June 1971 issue of *Analytica Chemica Acta,* 11 of the 35 articles involve UV-Vis spectrophotometry or spectrofluorometry.

Spark Source Mass Spectrometry. Atomization of small samples in the spark discharge provides a means of simultaneous analysis of a great many elements. This method suffers from matrix interferences, much in the manner of optical emission spectrometry. Nevertheless, appropriate corrections can be made by computer techniques to yield semiquantitative results. With sufficient information regarding matrix and other interferences, quantitative results are obtainable for many elements.

At present, semiquantitative analysis of respirable size coal dust is obtained from an outside laboratory. A single spectrum will provide an analysis for over 55 elements, ranging in concentration from 0.06 to 10,000 ppm (in the coal ash). Major elements such as Al, Si, S, Ca, and Fe are off-scale and require dilution of sample solutions prior to analysis.

Emission Spectroscopy. Optical emission using a spark or arc source readily provides semiquantitative analysis of many elements in a single "burn." Through the use of modern gratings and direct-reading photomultipliers behind individual prepositioned slits, quantitative accuracy can be achieved. A 3.4 meter grating direct-reading Jarrel-Ash instrument has been installed at a Bureau laboratory. It is expected that this technique will become the mainstay for rapid sensitive routine analysis for trace elements. This method has a sensitivity at least one order of magnitude better than conventional atomic absorption. Based upon extensive experience in the metal industries, the present state of the art will permit better accuracy than that obtainable by its close relative, spark-source emission spectroscopy.

When our optical emission spectrometer is in operation, we plan to use several other techniques, such as atomic absorption and polarography, to establish accurate standard response curves for use in computerization of the output of the spectrograph.

X-Ray Fluorescence. X-ray fluorescence holds promise for confirmatory analysis, mainly of major elements in coal dust. Relative large samples, of the order of 500 mg, are required for many of the trace elements. Nevertheless, the simplicity and capability of nondestructive analysis may prove useful in

some instances. This type of analysis would be done on a fee-paid basis by outside service laboratories.

Neutron Activation. Neutron activation provides a promising backup capability for our other analytical procedures. Sensitivities for the wide range of elements capable of analysis range from poor to excellent. This technique is developing rapidly. Several laboratories, such as Gulf-Atomic, will do service work on a fee basis. The cost per sample is prohibitive for routine analysis, however.

The following sensitivities in μg are currently available: Al, 0.004; B, 1.1; Ba, 0.02; Be, 15; Bi, 1.0; Co, 0.01; Cr, 0.3; Cu, 0.002; Pb, 0.5; Mg, 0.5; Mn, 0.0001; Ni, 0.7; Ag, 0.004; Ti, 0.1; V, 0.002; Zn, 0.1; and Fe, 2.0.

Determination of Organic Compounds by High-Resolution Mass Spectrometry

The chemical nature of the organic constituents of respirable dust may affect the incidence of pneumoconiosis in coal miners. Warden [10] reported that the chemical composition and activity, as well as the solubility, of the particulates are important factors determining the reaction in lung tissues. In animal tests, Saffiotti and coworkers [11] have demonstrated that polynuclear aromatic compounds, such as those prevalent in coal dust, produce some of the most severe lung irritants when combined with inorganic material. Langer and Selikoff [12] have reported evidence that the chemical composition of asbestos fibers is altered when in contact with lung tissue. To assist with the medical aspects of the disease, it is therefore necessary to determine the composition of the organic as well as the inorganic material associated with coal dust.

Analysis

High resolution mass spectrometry is being used to determine the chemical composition of whole coal, respirable-size coal dust, and mine dust. High resolution mass spectrometry is unique in providing a precise mass from which a molecular formula can be derived. The basis of the high resolution technique is the ability of the instrument to resolve multiplets arising from components having the same nominal mass but differing in precise mass, and to make precise mass assignments corresponding to various combinations of elements. A very simple example of the use of this instrument is the series of multiplets resulting from a mixture of nitrogen, carbon monoxide, and ethylene, all having the same molecular weight (28), but differing in precise mass. Contributions from these three components would normally appear as a singlet, but under high resolution, three distinct peaks can be seen.

Although most of the high resolution data reported to date has dealt with studies of the structure of pure compounds, several investigations of complex hydrocarbon mixtures have been reported by the Pittsburgh Energy Research Center of the United States Bureau of Mines.[13-15] These investigations have primarily employed mixtures of polynuclear aromatic hydrocarbons derived from coal and airborne particulate matter. To illustrate the type of data obtained, some of the combinations of elements that have been detected at mass 184 are shown in FIGURE 1. It should be noted that the eight different combinations of elements occur within less than 1/10 atomic mass unit.

A major advantage of high resolution mass spectrometry for studies of organic materials in coal dust is that molecular formulas for literally hundreds of components in the dust can be obtained without prior separation of the sample. In the present investigation, high resolution mass spectra have been obtained for the organic material in coal particles in the respirable range (3.3–5.5 μm) separated from two coal dusts prepared in the laboratory. A limited number of mine dust samples have also been examined. Spectra were obtained by introducing the coal directly into the mass spectrometer and also by extracting with quinoline and pyridine. The extraction technique, utilizing ultrasonic irradiation, results in the removal of 70 to 80% of the organic material in many coals. The extraction technique has been successfully altered and scaled down to accommodate the few milligrams of each respirable mine dust available in most instances.

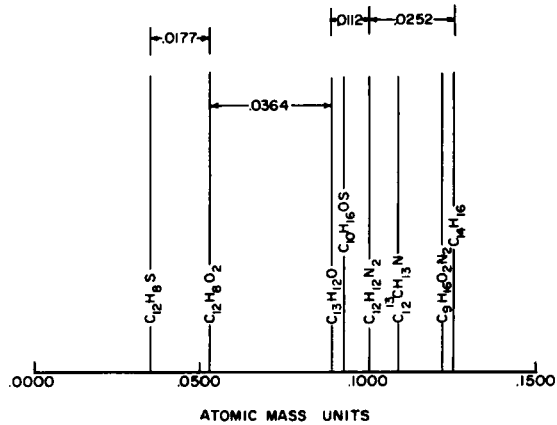

FIGURE 1. Relative positions of several atomic combinations of mass 184.

The current investigation includes the determination of the organic material in coal as a function of particle size down to the respirable range, studies of mine dust from seams of various rank, and investigations of samples collected in mines in geographic areas having both low and high incidence of pneumoconiosis. Retrieval of the mass spectral data by ADP methods, including molecular formulas for all organic compounds detected, is now in progress. Mass spectra of most samples studied to date indicate components with molecular weights up to at least 400. The general distribution of peaks for organic material extracted from coal particles in the respirable range (3.3–5.5 μm) is illustrated by the low resolution mass spectrum shown in FIGURE 2. The detailed information derived from a high resolution mass spectrum of organic material obtained from a mine dust is illustrated in TABLE 3; only a limited mass range is shown. "Fragment" as well as "molecular" peaks are obtained, but they can be sorted during final interpretation of the data.

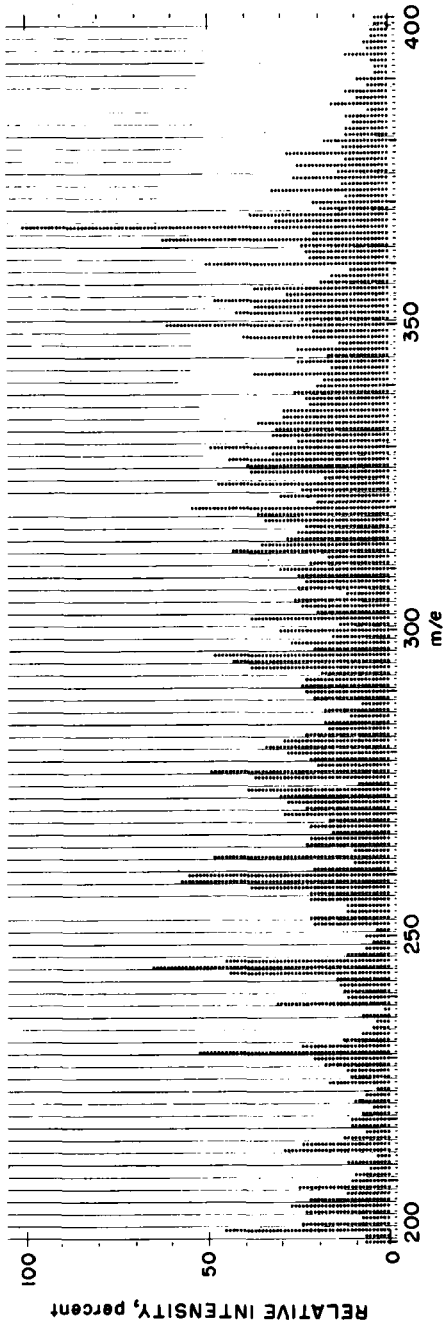

FIGURE 2. Partial mass spectrum of pyridine extract 3.3–5.5 μ Russelton Coal-computer plot.

TABLE 3

PARTIAL MASS SPECTRAL DATA FROM A RESPIRABLE MINE DUST; HVAB * COAL

Nominal	Mass Precise, amu			Empirical Formula		
	Measured	Theoretical	Δ	C	H	O
178	.0772	.0783	.0011	14	10	
	.1000	.0994	.0006	11	14	2
	.1718	.1721	.0003	13	22	
179	.0849	.0861	.0012	14	11	
	.1069	.1072	.0003	11	15	2
	.1781	.1800	.0019	13	23	
180	.0924	.0939	.0015	14	12	
	.1116	.1150	.0016	11	16	2
	.1860	.1878	.0018	13	24	
181	.0660	.0653	.0013	13	9	1
	.1017	.1017	0	14	13	
	.1957	.1956	.0001	13	25	
182	.0723	.0732	.0009	13	10	1
	.1069	.1095	.0026	14	14	
	.2006	.2034	.0028	13	26	

* HVAB = high volatile A-type bituminous.

SUMMARY

Analytical techniques currently in use and under development have been described for materials that may be involved in the development of coal workers' pneumoconiosis. The three classes of materials discussed were free silica, elements, and organic compounds. Emphasis has been upon newer techniques and modification of well-known means of conducting analysis.

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