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Analysis of Free Silica in Respirable Dust

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ANALYSIS OF FREE SILICA IN RESPIRABLE DUST

by

Robert W. Freedman[1]

ABSTRACT

The Bureau of Mines investigated methods of analysis of free silica in respirable dust, including both work done at the Bureau of Mines and work done elsewhere. The review covers both coal dust and noncoal dust, taking into account both existing and proposed chemical and spectroscopic procedures.

INTRODUCTION

Silicosis is a form of pneumoconiosis (9),[2] as is "black lung" disease. The latter malady typically affects coal miners and is characterized by long-term accumulation of carbonaceous particles in the lungs, possibly brought on synergistically by the presence of free silica (4). Other authorities state that the prevalence of black lung disease bears no relation to the silica content of the coal mines (11). This Bureau of Mines paper reviews the state of the art of analyzing for free silica in respirable dust in both coal and noncoal mines.

A medical distinction is made between the various forms of free silica because of differences in toxicity (1). An excellent tabulation of pulmonary responses to mineral dusts is given in table 12.2 of Johnstone and Miller (10). The present survey makes no attempt to cover the full range of toxic industrial dusts but is limited to analysis of free silica in the respirable range. We have arbitrarily defined the respirable particle size as 0.1 to 5 micrometers (μm). Almost all the dust that collects in the lungs is within this range, although a very small proportion in the 5- to 10-micrometer range is also respirable.

A variety of methods are available for the determination of free silica in mine dusts. Chemical methods depend upon dissolving silicates and other materials, leaving free silica relatively unattacked. Phosphoric, fluosilicic, and fluoboric acids have been used, but attack quartz significantly in the

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[2] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

smaller size ranges. Durkin (5) discusses several methods including differential thermal (DTA), petrographic, and X-ray diffraction analysis procedures. Edwards (6) compares X-ray diffraction with chemical and microscopic methods. As pointed out in these publications, DTA suffers from lack of sensitivity and specificity, while both petrographic and microscopic examination require very skilled operators and have limited precision. X-ray diffraction is a promising technique. Infrared spectroscopy was applied by Tuddenham and Lyon (13) to the 5,000 to 650 cm^{-1} region with a critical examination of the effects of particle size, and Bureau of Mines investigators at Morgantown, W. Va., employed infrared spectroscopy out to the 200 cm^{-1} region in a quantitative analysis of various minerals in coal (7). The specificity of these spectra offer some hope of extending the use of this technique to noncoal samples.

The present survey provides perspective and defines limits for further Bureau of Mines research, and should aid others doing similar work. At present, the Analytical Research Group of the Bureau's Pittsburgh Mining and Safety Research Center is engaged in two free-silica programs. These cover free silica in respirable coal mine dust and free silica in respirable noncoal mine dust. Separate programs are essential because of significant differences in the types of free silica and in the types of interfering materials present in each type of dust.

LIMITATIONS OF ANALYSIS

Analysis of free silica in mine dust depends upon the type of dust, the interfering materials, the amount of sample available, and the time per analysis permitted, as determined by the number of samples submitted. The strong dependence of most spectrometric methods upon particle size is also an important limitation.

Types of Free Silica and Interfering Materials

In coal mines, free silica exists mainly in the form of crystalline quartz. The respirable dust in the mine is contaminated, to a great extent, by rock dust (calcium carbonate or calcium magnesium carbonate), and to a lesser extent by clay minerals from rock and slate. The coal particles themselves contain major amounts of organic matter and about 10 percent of inorganic ash-producing substances. The interferences in molecular spectroscopy of quartz result from spectral peak overlap by specific minerals in crystalline form, such as muscovite, and the broad band absorption effects of massive levels of carbon and inorganic materials. Interferences are of greatest importance at low levels of quartz (less than 2 percent). Current methods demand ashing of the sample in order to remove organic matter and to concentrate the quartz.

Noncoal mine dust contains free silica mainly in the form of crystalline quartz and crystalline cristobalite. Tridymite, another crystalline form of silica, and cryptocrystalline or submicroscopic minerals such as chert, flint, and agate are found in lower concentrations. Amorphous free silica occurs as opal and diatomaceous earth. The proportions of these components are, of course, dependent upon the material mined. Because of the complexity of these samples, routine analysis has thus far been limited to bulk samples using X-ray diffraction.

Sampling Limitations

Analysis for free silica is limited in sensitivity and precision by the small amounts of sample available as collected by size-selective personal respirable dust samplers. In most cases, less than 5 mg of respirable dust is collected on each 37-mm membrane filter. In addition, dust composition varies drastically with location in the mine. For instance, two samples taken only a few inches apart cannot be considered duplicates. This renders method development by comparative methods difficult, especially since the dust is deposited nonuniformly on each filter.

Another sampling limitation is the time permitted for each analysis. Because of the relatively large number of samples expected, possibly as many as 100 per day, analysis must be carried out using a rapid instrumental technique. Also, because of time limitations, it is desirable that the sample be analyzed directly on the collection filter, but this is very difficult and it may be necessary to remove the dust in order to concentrate it or even to composite several samples to achieve sufficient sensitivity.

Effect of Particle Size

Absorbance varies strongly with particle size, in both infrared and X-ray diffraction analysis. The size distribution within samples of respirable dust collected with a given type of size-selective sampler varies in a predictable way. However, simulation of actual samples by grinding known materials such as analyzed coal is almost impossible. This renders preparation of reliable standards difficult. Another problem is that within the respirable range, narrow size cuts may differ greatly in composition. Also, in any analytical technique, the grinding of the sample to reduce the size and peak intensity of soft materials (which interfere with silica) can produce dubious results, since silica itself is ground to some extent in the process. Another very disturbing fact is that the particle size of minerals taken from miners' lungs was found by Crable and coworkers (3) to range from 0.08 to 0.58 µm with a geometric mean of 0.22 µm. This is considerably smaller than the size range under consideration in the analytical studies discussed in this paper.

METHODS FOR ANALYSIS OF FREE SILICA

Of the methods mentioned previously for analysis of mine dust, X-ray diffraction and infrared spectroscopy offer the most immediate promise of success for both coal and noncoal respirable dust samples. Laser Raman and other techniques may be of future interest.

Coal Mine Dust Analysis

Bulk samples of settled coal dust can be analyzed by X-ray diffraction; the size range is very broad, and only a small weight fraction is in the respirable size range. The analysis of respirable dust collected on membrane filters is carried out routinely by infrared analysis only.

X-Ray Diffraction

Analysis of respirable coal mine dust has occasionally been carried out in this laboratory using an in-house X-ray diffraction procedure. A cobalt target and external standard silicon disk were employed. Samples of as little as 1 mg were collected on membrane filters and analyzed.

Subsequent research has cast considerable doubt upon the validity of results obtained by this procedure. The sample must be removed from the filter, wetted with methanol, and ground. This minimizes interference of relatively soft muscovite which has a strong diffraction peak at a d value of 3.36 A that interferes with the d 3.34 A quartz peak used. In the grinding process, it is inevitable that some quartz is reduced in size and brought into the respirable range, thus destroying the significance of the analysis from a physiological standpoint. Another difficulty results from the presence of an organic matrix consisting of high-molecular-weight compounds which provide a substantial X-ray background level and considerably reduce the signal-to-noise ratio.

A somewhat more promising approach is provided by Schliephake for routine determination of quartz in coal (12). The article mentions the significance of particles with a diameter of less than 5 µm, but describes the samples, collected on filters, as float dust weighing 20 to 200 mg. Float dust contains a large proportion of particles considerably greater in diameter than 5 µm. In addition, recognition of interference by inorganic materials such as illite, kaolinite, chlorite, calcite, siderite, dolomite, pyrite, and feldspar is mentioned. For this reason, ashing the coal at 800° C is recommended to provide about 6 mg of ash for a good analysis. These sample requirements cannot be met using the approved sampling procedures provided for in the U.S. Coal Mine Health and Safety Act of 1969.

Infrared Spectroscopy

Analysis for quartz in respirable coal mine dust collected on membrane filters is carried out routinely by the Bureau's Pittsburgh Field Health Group. The original infrared method used soon proved to be highly inaccurate because of interference by the organic matrix. Only relatively high concentrations of quartz could be determined reliably. The method was modified by combining a microashing procedure using 1- to 5-mg coal dust with an infrared pelletizing technique involving admixture of the ash with potassium bromide and scanning to obtain the 12.52-µm peak. Results appear adequate. However, certain assumptions are made, such as the absence of significant amounts of clay minerals and other forms of silica. Particle size distribution in the respirable range is also assumed to be fairly reproducible. The resistance to change of quartz crystals when subjected to high temperatures is also assumed. The sensitivity of the method (to about 8 µg of quartz) is a decided advantage.

As previously mentioned, Bureau investigators at Morgantown, W. Va. (7) devoted their attention to minerals occurring in coal. Low-temperature ashing was employed to destroy organic matter and to concentrate the mineral fraction with a minimum of change of crystal form. Although this technique is desirable from an investigative standpoint, the lengthy ashing procedure renders this approach impractical for rapid routine analysis.

Noncoal Mine Dust Analysis

Many of the principles involved in coal mine dust analysis apply to the analysis of the mine dust collected in noncoal mines; rock dust used for inerting coal dust layers against explosion can be similarly analyzed for free silica. Here routine analysis at the Bureau has been limited almost exclusively to bulk or settled dust which has a particle size range much greater than that of the respirable region. Practically all the analyses carried out in Bureau laboratories are by X-ray diffraction.

The samples are generally available in fairly large amounts, which is helpful. However, in order to cope with the many interferences, the samples are mixed with an internal standard and wet ground. Three separate peaks of the X-ray scan are used for calculation of quartz content.

As previously mentioned, the grinding procedure alters the quartz size range. In addition, it does not appear likely that the method could be scaled down sufficiently for use with the small respirable dust samples available on membrane filters.

Because of the many interferences, the use of infrared spectroscopy in the rock salt region is not considered promising for analysis of noncoal samples. As discussed later, the far infrared region may be more promising.

CURRENT AND PROJECTED ANALYTICAL RESEARCH

Two programs are in progress at the Bureau's Pittsburgh Mining and Safety Research Center involving the determination of free silica in respirable mine dust. The first program involves coal mine dust; it is entitled Rapid Analysis for Free Silica and Chemical Elements in Mine Dusts and deals with the coal mine health problem. Analysis of chemical elements has been included because of the possibility of synergistic activity or their individual effects as toxicants. The second program involves noncoal mine dust and is entitled Rapid Method for Determination of Free Silica in Respirable Noncoal Mine Dust. As mentioned previously, the programs involve somewhat different approaches because of the nature of the samples available.

Coal Mine Dust

A variety of analytical techniques are being applied to the low levels of respirable dust collected on 37-mm membrane filters in coal mines, and comparisons are being made with synthetic standards and mixtures thereof.

X-ray diffraction techniques applied to coal dust obtainable on individual filters have been found to be insufficiently sensitive with existing equipment. Ashing of the dust removed from filters has given promising results in terms of specificity and sensitivity.

Samples submitted to the Bureau's Energy Research Center at Morgantown, W. Va., for electron spectroscopic analysis have not provided conclusive results. In addition, samples submitted to two manufacturers of laser Raman spectrometers have given negative results owing to the combustibility of coal dust. No report on ashed samples has been forthcoming. However, some spectra have been obtained by Bureau personnel in collaboration with Mellon Institute (8).

Our standard infrared procedure appears to work well on ashed coal removed from the filter. However, the current rate of eight samples per day is far too slow. Plans are underway to speed up and improve this operation by the use of several pelletizing presses and by variation of scanning techniques. A more versatile instrument will be employed.

Attempts will be made, using newer X-ray diffraction equipment, to carry out direct analysis of coal dust, using the collection filters themselves in the X-ray beam. Equipment having high-intensity monochromatic X-ray diffraction systems is on order.

A technique described by Bradley (2) employing very thin samples may work for coal using the appropriate region of the response-deposition density curve, since absorption effects are minimized. In the event that it is necessary to ash the sample, studies of the effect of high-temperature ashing upon particle size will be undertaken. In both cases, a careful study of the effects of interfering materials will be made.

Noncoal Mine Dust

In this program the presence of other forms of free silica besides quartz presents a somewhat different set of problems. Other forms of silica can be present, as can mineral interferences.

Current X-ray procedures using dust collected on individual filters are too insensitive. Our in-house procedure for noncoal minerals requires relatively large amounts of sample and is tedious, and it is necessary to scan for three separate peaks to obtain sufficient selectivity. It is conceivable that the newly ordered X-ray diffractometer will overcome some of these difficulties. However, analysis for other forms of free silica such as cristobalite is important because of their higher relative concentrations and differences in toxic behavior as compared to quartz.

Infrared spectroscopy in the rock salt region (5,000-650 cm^{-1}) offers little hope in terms of specificity. The far infrared region is much more promising and will be studied. Quantitative analysis may be possible with coincident peaks by application of standard mathematical techniques. Even though organic matter may be absent, the ashing of samples may be useful for destroying carbonates and complex silicate crystals while leaving crystalline silica intact.

Laser Raman spectroscopy may be of value in analyzing ashed samples since peaks resulting from vibrations may be available which are infrared insensitive. The great sensitivity of laser Raman spectroscopy as compared to conventional infrared may be of definite value.

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