ANALYSIS OF RESPIRABLE COAL MINE DUST SAMPLES BY INFRARED SPECTROSCOPY

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ABSTRACT

To control the health hazard associated with quartz in the United States coal mining industry, Federal regulation requires that whenever the quartz content of the respirable dust in the coal mine environment exceeds five percent, the applicable respirable dust standard be reduced. This regulation, which is applicable for both surface and underground mining operations, has been in force since the promulgation of the Federal Coal Mine Health and Safety Act in 1969. To enforce this regulation, the Mine Safety and Health Administration (MSHA) analyzes approximately 6,000 respirable coal mine dust samples per year for quartz content. The quartz content of these samples is determined using an infrared spectroscopic method.

This paper presents an overview of MSHA's quartz enforcement program, the analytical method used for quartz determination and efforts underway to enhance the sensitivity of the method.

INTRODUCTION

At the time of promulgation of the Coal Mine Health and Safety Act of 1969, the Congress of the United States of America stipulated that a limit be placed on the allowable quantity of quartz to which miners would be exposed. The requirement for this limit was based on work performed in the 1930's and 1940's[1,2] which showed that the presence of quartz increased the health hazard associated with exposure to coal dust. Based on this data, the United States Bureau of Mines in 1948 established a dust exposure limit when the dust in the environment was found to contain more than five percent quartz. The limit at that time, determined by multiplying the dust particle concentration by the percent quartz, was not to exceed five million particles per cubic foot of air.

When the United States Congress promulgated the Coal Mine Health and Safety Act in 1969, they directed that a formula be developed for lowering the applicable respirable dust standard when the quartz content of the dust to which miners are exposed is greater than five percent. Such a formula was developed on March 10, 1971, and was included in Parts 70.101, 71.101 and 90.101 of Title 30 of the Code of Federal Regulations. According to the formula, the applicable dust standard (mg/m^3) is determined by dividing the percent quartz into the number 10 (i.e., standard = 10/% quartz). This formula was continued under the Federal Mine Safety and Health Act of 1977 which amended the 1969 Act.

To enforce this standard, the quartz content of respirable coal mine dust samples is determined by the use of infrared absorption spectrophotometry. Three common methods available for the analysis of crystalline silica are the use of X-ray diffraction, visible absorption spectrophotometry and infrared absorption spectrophotometry. The advantage of using the infrared method over the others for the analysis of coal mine dust samples is that the sensitivity is greater than either that of the X-ray Diffraction Method[3] or the visible absorption spectrophotometric method, also referred to as the Talvitie method.[4,5] In addition, the X-ray method, although able to differentiate between different forms of free silica (quartz, cristobalite and tridymite), is affected by several compounds which have diffraction peaks that interfere with the major peak for quartz. The Talvitie method, which cannot distinguish between the crystalline forms, requires extensive sample preparation using various corrosive acids and is a time consuming procedure.

Since cristobalite, tridymite and amorphous silica, all of which would cause an interference in the infrared analysis for quartz, have not been detected in coal mine dust,[3] the infrared method is ideal for the determination of quartz in coal mine dust samples. From 1970 through 1980, quartz analysis was conducted by MSHA using a high temperature ashing (800°C) technique and the subsequent pelletizing of the ash with potassium bromide (KBr). This procedure required a sample mass of one to four milligrams, thus requiring the compositing (combining) of a number of samples from various coal mine operations to obtain a sample of sufficient weight for analysis.[6] In 1981, the method was upgraded to the current method which is known as the Low Temperature Ashing (LTA) Method. This LTA method allows for the analysis of individual coal mine dust samples containing from 0.5 to 2.5 mg of dust. The method, developed by the Bureau of Mines, has been ruggedized and evaluated.[3]

From 1970 through December of 1985, enforcement of the quartz standard in the United States was determined solely from the analysis of a single sample or composited samples collected by Federal mine inspectors. In December of 1985,

MSHA's enforcement policy was revised so that the quartz content of the dust in the environment is based on a number of samples (up to three) collected over a period of several months and includes samples collected by the coal mine operators.

QUARTZ ENFORCEMENT PROCEDURE

The rudiments of MSHA's current quartz enforcement program require the analysis of selected respirable dust samples collected by mine inspectors during the approval or verification of mine operators' dust control plans. Samples typically selected for analysis are those collected on the designated occupation (DO), that occupation in an underground mining operation that has the highest respirable dust exposure, the roof bolting (RB) operation in underground mining and designated work positions (DWP) in the surface coal mining industry. If the analysis of any of these samples shows that the quartz content is in excess of five percent, the mine operator is notified of the option of collecting a sample for analysis on the mine entity representative of the original sample which was in excess of five percent quartz. If the difference between the quartz percentage of the operator's sample and the quartz percentage of the MSHA sample is within plus or minus two percent, (e.g., MSHA value seven percent, operator value five to nine percent) the results of the two analyses are averaged and the respirable dust standard is set accordingly. If the quartz determination of the operator's optional sample differs from the MSHA sample by more than plus or minus two percent, the operator is given the option of collecting a second sample on the mine entity. Following analysis of the operator's second sample, the average quartz percentage is determined from the three samples (MSHA sample plus the two samples submitted by the operator). If the operator elects not to collect a sample or if the samples submitted have insufficient dust for analysis (less than 0.5 milligrams), the standard is adjusted based on the analysis of the MSHA sample. At six month intervals, any entity on a reduced standard is automatically reevaluated by analyzing for quartz one of the mine operator's samples submitted for dust compliance, provided there is sufficient weight gain on the sample. Analysis of MSHA inspector samples, mine operator optional samples and six month operator samples accounts for the analysis of approximately 6,000 samples per year.

ANALYTICAL METHOD

Analysis of respirable coal mine dust samples for quartz is conducted in a central laboratory located in Pittsburgh, Pennsylvania. The operation of this laboratory is a function of MSHA's Pittsburgh Health Technology Center. The analytical method used for the analysis employs the principle of infrared spectrophotometry. The current LTA method allows for the analysis of the quartz content of a sample with a mass of 0.5 milligrams or greater. The method has a detection limit of 10 micrograms of quartz and a precision of 13 to 22 percent for quartz masses ranging from 25 to 160 micrograms.[3]

Samples are collected with approved respirable coal mine dust sampling assemblies equipped with a quartz-free, ashable filter medium. Following weighing of the filter to determine sample mass, the filter medium is ashed in a low-temperature ashing system. This ashing system, shown in Figure 1, operates at a temperature of approximately 120°C and utilizes radio frequency energy to generate an oxygen plasma which destroys the filter matrix and the carbonaceous material present in the sample.

Following ashing, isopropyl alcohol is added to the residue. The residue is dispersed in the alcohol using an ultrasonic generator. The suspension is filtered onto one half of a Gelman DM-450 vinyl metricel filter. The filtering is accomplished by washing the sample through a specially constructed, glass filter funnel on a vacuum manifold system, shown on Figure 2. The funnel is designed to produce a 10 millimeter diameter deposit. Once filtration is complete, the filters containing the ashed deposits are dried on a slide warmer for approximately 20 minutes at a temperature of approximately 42°C.

Analysis for quartz is then conducted using a dispersive infrared spectrophotometer. The DM-450 filter half containing the ashed residue is mounted in a sample holder and placed in the sample beam of the infrared spectrophotometer. A blank DM-450 filter half which has been treated with alcohol and dried is similarly mounted in the reference beam of the instrument. Following appropriate parameter setting of the infrared instrument, the sample is scanned in the absorbance mode from 1,000 to 710 cm^{-1}. Quartz absorbs infrared energy in the 800 cm^{-1} region. The clay mineral kaolinite, which is also found in coal mine dust, also absorbs infrared energy in this region.[3] Its presence causes a slight overestimation of the quartz content. To correct for this overestimation, the absorption for kaolinite is measured at 915 cm^{-1}. Thus, measuring the absorbance of infrared energy by the sample from 1,000 to 710 cm^{-1} allows for the quantification of kaolinite at 915 cm^{-1} and the correction for its interference with quartz absorbance at 800 cm^{-1}.

Figure 3 shows a sample of an infrared scan of a typical coal mine dust sample. As illustrated on the figure, the peak intensities at 915 and 800 cm^{-1} are determined by measuring the height from established baselines to the peak maximums. The baselines are drawn from 950 to 890 cm^{-1} for the 915 cm^{-1} kaolinite band and from 810 to 760 cm^{-1} for the 800 cm^{-1} quartz-kaolinite band. The measured net peak heights are converted into absorbance units and the interference due to kaolinite is determined from a calibration curve of kaolinite absorbance at 915 cm^{-1} versus kaolinite absorbance at 800 cm^{-1}. The calculated absorbance for kaolinite at 800 cm^{-1} is subtracted from the measured absorbance at 800 cm^{-1} (quartz-kaolinite) to give the absorbance due to quartz. The amount of quartz is determined from a calibration curve of absorbance of quartz at 800 cm^{-1} versus mass of quartz.

For MSHA's quartz enforcement program, -5 μm Minusil, a commercial product of the Pennsylvania Glass Sand Company, Berkeley Springs, West Virginia, is used as the quartz standard.[7] Kaolinite used for the standard is Hydrite UF, supplied by the Georgia Kaolin Company, Elizabeth, New Jersey.

Once the analysis and calculations are completed, the percent quartz in the coal mine dust sample is computed by using the

following equation:

$$\text{quartz (percent)} = \frac{\text{mass of quartz } (\mu g)}{\text{mass of coal mine respirable dust } (\mu g)} \times 100$$

The percent quartz determined for a coal mine dust sample is truncated to the whole percent value which is subsequently used in the formula for the determination of the reduced coal mine dust standard when the quartz percentage is in excess of five percent (reduced standard = 10/% quartz).

To insure the integrity of the quartz analyses performed, MSHA conducts an internal quality assurance program. This program consists of the analysis of three specially prepared samples, containing varying known quantities of quartz, with each group of 20 to 25 samples analyzed. The mass of quartz on each of the three quality control samples is unknown to the analysts. These samples undergo the same processing as the coal mine dust samples; i.e., ashing, deposition by filtration and IR scanning. The analysis of these samples is used to verify that the process is controlled, assuring the reliability of analytical results.

IMPROVEMENTS TO ANALYTICAL CAPABILITY

In an effort to improve the sensitivity of the present analytical technique, MSHA recently acquired a Fourier transform infrared spectrophotometer (FTIR). A FTIR operates differently than a dispersive infrared spectrophotometer. A FTIR employs an interferometer to obtain information about the transmission of infrared energy of all wavelengths (simultaneously) emitted by the source and passing through the sample, whereas a dispersive spectrophotometer uses a monochromotor and slit system to divide the infrared radiation into frequency elements. The interferometer of the FTIR contains a fixed mirror and a moving mirror, the position of which is determined by a helium-neon laser. The information obtained from a sample is digitally stored as signal intensity versus mirror displacement as shown in Figure 4. This is known as an interferogram. The instrument's computer then performs a Fourier transform of the interferogram to produce the desired absorbance versus frequency (in wave numbers) spectrum as shown in Figure 5.

The FTIR has many advantages over the dispersive instrument. Since there are no entrance or exit slits in the FTIR, a greater amount of energy reaches the detector, resulting in increased sensitivity. The laser tracking of the moving mirror results in greater precision of the wavelength measurement, permitting multiple scans to be averaged and thereby increase the signal to noise ratio of the absorbance spectrum. Precise duplication of the analytical frequencies and computer control of the calculations with the FTIR reduce the errors associated with the electromechanical components of the dispersive instruments and the necessary manual measurements of frequencies and peak intensities.

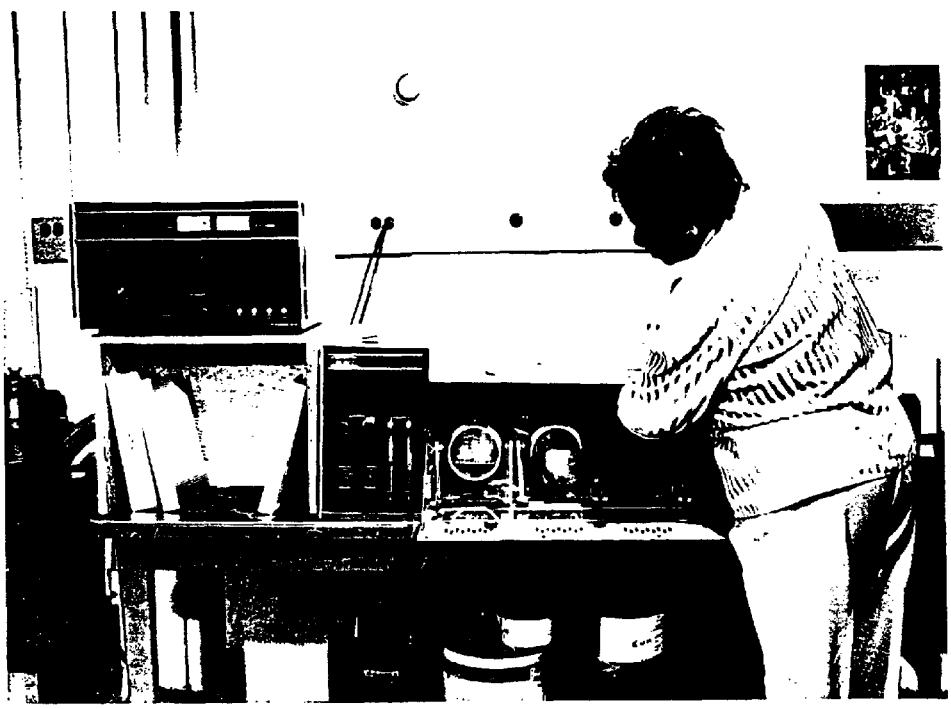

Figure 1. Low-Temperature ashing system.

Figure 2. Vacuum filtration of ashed samples.