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Infrared Analysis of Respirable Coal Mine Dust for Quartz: Thirty Five Years

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ABSTRACT: The Mine Safety and Health Administration (MSHA) analyzes respirable coal mine dust samples for quartz content using infrared spectrometry. Samples are low-temperature ashed in an oxygen plasma, suspended in alcohol, and redeposited onto a vinyl/acrylic copolymer filter for analysis using a Fourier transform infrared spectrometer. The on-filter infrared method was developed by the United States Bureau of Mines and collaboratively tested by Stanford Research Institute (SRI) under contract to the National Institute for Occupational Safety and Health. The results of the collaborative study were published in 1983. Although much work has been performed since then to improve the precision of the method, details of those improvements have not always been published. Standard methods often do not discuss analytical theory and the preliminary steps necessary to achieve precise results. This paper gives a brief background of the changes that have been made in the procedures used for the analysis of respirable coal mine dust samples for quartz and discusses the current procedures used by MSHA to analyze such samples. Factors affecting the analysis such as optimization of the deposit size of the ashed sample, the importance of centering the sample in the infrared beam, baseline selection points, and peak measurement techniques as well as the quality assurance procedure and the precision of the analysis are discussed.

KEYWORDS: quartz, silica, coal mine dust, infrared analysis

Introduction

Exposure to crystalline silica (the form of crystalline silica found in coal mining is quartz) can cause silicosis, a disease characterized by fibrosis of lung tissue. The Federal Coal Mine Health and Safety Act of 1969 (1969 Act) provides for the protection of the health and safety of persons working in the coal mining industry. Under the 1969 Act, if the "…concentration of respirable dust in the mine atmosphere of any working place contains more than 5 per centum quartz, the Secretary of Health, Education and Welfare shall prescribe an appropriate formula for determining the applicable respirable dust standard…" [1]. The respirable dust is measured with an MRE[2] or equivalent instrument. The 1969 Act established the interim allowable average respirable dust concentration at 3.0 milligrams per cubic meter (mg/m^3) when the quartz content was 5% or less. That level statutorily reduced to 2.0 mg/m^3 in 1973. When the quartz content exceeds 5 percent, the concentration of respirable coal mine dust to which a miner may be exposed is calculated by the formula 10 divided by the percentage of quartz (10 ÷ % quartz). [2]

In order to calculate the quartz percentage, the mass of quartz in a sample must be determined. The Agency has used infrared (IR) spectroscopy for the analysis of quartz content in coal mine dust since the inception of the 1969 Act. While about 2 500 quartz analyses were performed in 1971, approximately 13 000 analyses were conducted in 2003. Modifications have

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[2] MRE instrument means the gravimetric dust sampler with four channel horizontal elutriator developed by the Mining Research Establishment of the National Coal Board, London, England

been made to the standard procedure in order to improve the precision of the analysis and to decrease the time required to analyze each sample.

Background

The U.S. Bureau of Mines (USBM), Department of the Interior, enforced the provisions of the 1969 Act. In order to obtain sufficient mass to analyze for quartz, the respirable dust from as many as 10 sample filters might be combined. The composite sample was ashed in a muffle furnace to remove the coal dust fraction. The remaining ash was mixed with potassium bromide (KBr), pressed into a pellet and analyzed using infrared spectroscopy (Standard Method No. A7). [3]

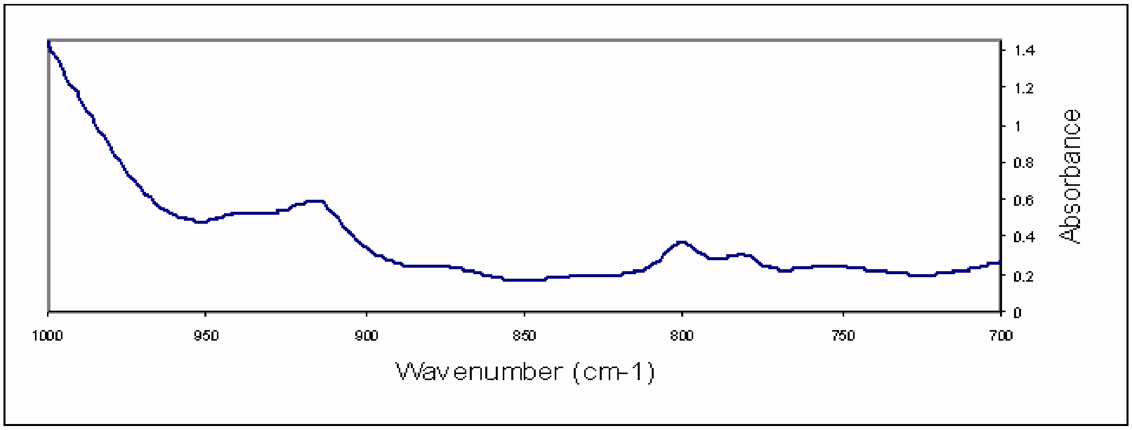
In 1973, a new agency in the Department of the Interior, the Mining Enforcement and Safety Administration (MESA), was created and given the authority to enforce the provisions of the 1969 Act. MESA continued to analyze samples for quartz using the standard analysis method A7.

The Mine Safety and Health Administration (MSHA) was created within the Department of Labor by The Federal Mine Safety and Health Act of 1977, which amended the 1969 Act. MSHA continued to use the (KBr) infrared method to analyze respirable coal mine dust samples for quartz. Beginning in the late 70's, MSHA worked with the USBM to develop an improved method for analyzing a single respirable coal mine dust sample for quartz content using infrared spectroscopy.

IR analysis is used because of its speed and lower cost compared to x-ray diffraction, the other widely accepted analytical method. Although IR spectroscopy can not be used easily to quantitate the other forms (polymorphs) of crystalline silica (cristobalite and tridymite), these polymorphs are not found in respirable coal mine dust. With the exception of kaolinite, minerals that interfere with the analysis for quartz have not been found in respirable coal mine dust.

Infrared spectroscopy utilizes the principle that the atoms within a molecule continuously vibrate at frequencies that are characteristic of the particular molecule. When a sample is placed in a beam of infrared radiation, the sample will absorb some of the radiation, i.e.: when the frequency of the impinging radiation is the same as the natural vibrational frequency of a molecule in the sample. Individual vibrations within a molecule can be influenced by other vibrations within the molecule, making the IR spectra of a compound unique. Infrared spectra are presented as the amount of radiation transmitted through the sample (% transmittance) or absorbed by the sample (absorbance) versus the wavelength of the infrared radiation (micrometers, µm) or the wavenumber of the radiation (the reciprocal of the wavelength, cm^{-1}). The magnitude of the absorbance band is proportional to the quantity of the material (or molecule) absorbing the infrared energy, making quantitative analysis possible. MSHA quantifies quartz using the absorbance band at 800 cm^{-1}. A typical infrared spectrum of ashed respirable coal mine dust is shown (Figure 1).

FIG. 1- IR spectrum of ashed respirable coal mine dust



In 1981, MSHA modified the method used to analyze respirable coal mine dust samples for quartz. The modified method consisted of low-temperature ashing of individual samples in an oxygen plasma, suspending the ash in isopropanol using ultrasonic energy and then depositing the ash onto a DM™ [3] vinyl/acrylic copolymer membrane filter using an aluminum filtering funnel. The funnels had an opening approximately 10 mm in diameter. The sample filter was placed in a PetriSlide™ [4] holder and allowed to dry. For analysis, the sample filter was placed onto a steel plate with a center hole that was the same diameter as the sample deposit. Before the plate was placed in the infrared instrument, the filter was secured to the plate with a magnet.

The work performed by the USBM and MSHA confirmed that the characteristics of the reference material used to calibrate the infrared instruments was important to obtaining accurate results. Min-U-Sil® 5, a pure quartz material which closely matched the particle size distribution of the quartz found in ashed respirable coal mine dust, was chosen as the calibration material. The revised method, P7, (dated March 1982) did not include correcting the quartz measurement for interference by kaolinite. It was reported that kaolinite was unaltered in the low temperature ashing process and no interference was produced. [4]

The on-filter IR method was collaboratively tested by Stanford Research Institute (SRI) under contract with the National Institute for Occupational Safety and Health (NIOSH) and the USBM. A report of the results was published in October 1983. [5] This report stated that amorphous meta-kaolin is produced when kaolinite is heated at 500 °C to 900 °C. Below this temperature, kaolinite remains structurally unaltered and, therefore, would interfere with the quartz analysis. Thus, low temperature ashing of coal mine dust samples in an oxygen plasma asher would require a correction to the absorbance of quartz for the interference due to kaolinite.

In November 1983, the former National Bureau of Standards (NBS), now the National Institute of Standards and Technology (NIST), issued a standard quartz reference material, SRM 1878. This reference material was prepared from Min-U-Sil 5®[5]. MSHA compared this

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[3] DM-450, Pall Corporation, Gelman Sciences

[4] Millipore Corporation

[5] U.S. Silica Company

reference material to the Min-U-Sil® 5 that was used for instrument calibration and found no difference in instrument response.

The draft method published in the SRI report listed approximate baselines of 820 cm^{-1} to 670 cm^{-1} for the 800 cm^{-1} quartz absorbance band and 960 cm^{-1} to 860 cm^{-1} for the 915 cm^{-1} kaolinite absorbance band. The kaolinite measurement proved to be somewhat of a challenge. SRI reported that "…there is a good deal of scatter in the data, due undoubtedly to the difficulty in drawing an appropriate baseline under the 915 cm^{-1} peak…the correction curve is not well defined, the effect is not too severe if we do not try to measure a small amount of silica in the presence of a high loading of kaolinite."

Also among SRI's reported results was the description of the preparation of calibration standards by the slurry deposition technique. Following the collaborative study, NIOSH published an on-filter method (7602) for the analysis of quartz in respirable coal mine dust in 1984. MSHA also revised the P7 method in 1984, changing the procedure for the preparation of calibration samples to the slurry deposition technique, rather than the gravimetric procedure, and adding the kaolinite correction. By this time, glass funnels were being used for depositing the ashed samples. These processes have been reported previously. [6]

Much work has been performed by MSHA to make improvements to the on-filter method. In 1987, MSHA acquired a Fourier transform infrared spectrometer (FTIR). The only modification made to the P7 method was to add the change in instrumentation. The P7 method was modified in 1989 and these changes were reported in an agency informational report. [7]

In 1991, the size of the ashed sample deposit was reduced to 9 mm using funnels made of aluminum. If the infrared beam and the sample deposit are the same diameter (assuming that the beam and sample deposit are concentric), any variability caused by non-uniformity of the sample deposit would be minimized because the entire sample would be irradiated. The beam diameter at the focal point of the first FTIR instrument purchased by MSHA was 8 mm. By reducing the sample deposit from the 10 mm diameter to 9 mm, the amount of sample irradiated by the beam increased from approximately 65% to 80%, a substantial increase in the portion of sample exposed to the infrared beam. The steel plate for holding the sample filter has approximately a 10 mm diameter opening. When held up to light, the sample deposit could easily be centered over the opening. This modification was reported in 1992 [8] and the revised method was published in 1994.

MSHA continues to optimize the analysis of coal mine dust samples for quartz. In order to further enhance the analytical capability, a new FTIR was acquired and the method was modified in 1999. At this time, adjustments were made to the sample holder and funnel to optimize the placement of the sample in the FTIR. In addition, measurements were made using adjusted baseline points and peak area instead of peak height. This paper describes the effects of the selection of baseline points for net peak measurement, peak area versus peak height measurements, sample deposit size, sample placement and the quality assessment procedures used by MSHA.

Discussion

Ashed Sample Deposit – Size and Placement

Previously, discussions concerning the method for measuring quartz in respirable coal mine dust, including the report by SRI, did not discuss the methodology as it pertained to the infrared spectrometer or the possible effects due to differences in infrared instrumentation. There was no discussion on why the particular deposit diameter was used. The only mention of the importance of the size of the sample deposit was that it had to be the same diameter as the calibration standards. MSHA reported on the increase in the precision of the analysis due to improvements in the reproducibility of the funnels when new funnels were made from aluminum rather than glass [9], and the benefit of reducing the size of the deposit slightly, as previously mentioned. In addition to maintaining a high degree of precision between the deposit diameters of samples and calibration standards, optimization of the method requires determining the appropriate sample deposit size and placement in the infrared beam, which can vary with different instruments.

In 1998, MSHA acquired an FTIR which had a beam diameter of 13 mm, significantly larger than the 8 mm of the original FTIR. As mentioned above, the ideal is to expose as much of the sample as possible to the infrared beam. The reason is two-fold. First, instrument response is proportional to the amount of quartz. Increasing the amount of quartz that is exposed to the infrared beam increases the instrument response. That is, if the mass of quartz per unit volume of sample is the same and the instrument response is greater, the sensitivity of the analysis is increased and the detection limit of the method is reduced. Second, by irradiating more of the sample, non-homogeneity in the deposit is minimized.

The larger diameter beam would allow a larger sample deposit to be used. A larger sample deposit would eliminate the need for special handling of samples with excessive dust (since the deposit would adhere to the filter better) and would decrease the time required for filtering the ash onto the analysis filter. But because MSHA still planned on using the older FTIR instrument, it was not practical or cost effective to make new funnels and to use two different size sample deposits depending on which instrument would be used to analyze samples. Therefore, the decision was made to continue using the 9 mm sample deposits. Some important elements in the analysis that had not previously been evaluated became apparent while working with the 9 mm sample deposits in the 13 mm beam.

Comparisons between the two different instruments and duplicate analyses on the new instrument produced larger than expected variability. Investigation of the cause of the differences led to the discovery that the beam on the new instrument was not centered in the sample compartment. Even though the beam was much larger than the sample deposit, only a portion of the sample was being irradiated. The differences in the results were most likely due to the fact that only part of the sample was being irradiated in the new instrument and the sample deposit may not have been completely homogeneous. Also, the infrared beam was passing through the opening in the sample plate (10 mm) and around the 9 mm sample deposit. The 'stray light' was affecting the sample result, causing the instrument response to be non-linear, particularly for kaolinite.

The position of the sample deposit in the infrared beam and stray light reaching the detector were the two main concerns that needed to be addressed. For these reasons, new sample holders were designed for the new instrument. In addition to the optical issues, another factor that entered into the design of a new sample holder was the need to make sure that the sample did not move or slide (if the magnet slipped) while the holder was being placed in the instrument.

First, it was necessary to determine where the beam was located as it passed through the sample compartment of the instrument. Unless the laboratory has specialized equipment (the beam in infrared instruments can not be seen with the naked eye while the beam in near infrared instruments can), the instrument manufacturer should be utilized to assist the laboratory in determining the optimum set up for the particular instrument and sample deposit. After discussing the issue with the manufacturer, MSHA determined that good results could be achieved by approximating the location of the infrared beam and designing the sample holder so that the opening was centered in the infrared beam.

In order to determine the position of the infrared beam, a hole approximately 13 mm was cut in a piece of cardboard and it was moved around in the infrared beam while monitoring the amount of energy that reached the detector. The approximate center of the beam is located when the energy reaching the detector is the greatest. This location was marked on the cardboard which was then used as a template for making the steel plate that would be used for holding the sample filter.

The new instrument had a fixed Jacquinot–stop (J-stop) aperature. This aperature restricts the beam divergence as the infrared beam passes through the interferometer and therefore determines the beam diameter at the image focal position in the sample compartment. If the instrument is fitted with a variable J-stop aperature, the aperature can be reduced to its smallest diameter and the opening in the cardboard adjusted to coincide with the resulting beam diameter.

In addition to centering the opening in the sample plate in the beam, the opening should be smaller than the sample deposit, so that the beam can not pass around the sample deposit. A hole of approximately 8 mm in diameter was drilled in the steel plate. The steel holder acts as a mask to restrict the infrared beam diameter to 8 mm (slightly smaller than the sample deposit), thereby assuring that no stray light passed through the filter.

To facilitate centering of the sample deposit directly over the opening in the plate, and to keep the filter from slipping out of place, a recess to hold the sample filter was made in the plate. The recess is approximately 19 mm in diameter, the size of the DM-450 filter (Figure 2). The filter is placed in the recess and held in position with a magnet.

A funnel was designed that would center the ashed sample deposit on the analysis filter. A schematic diagram of the funnel is shown (Figure 3). The funnel bottom also has a very slight "lip," approximately 1 mm in depth which makes a tight seal when clamped against the filter. The lip is wide enough that it does not cut through the filter (Figure 4).

FIG. 2 – Steel sample filter holder

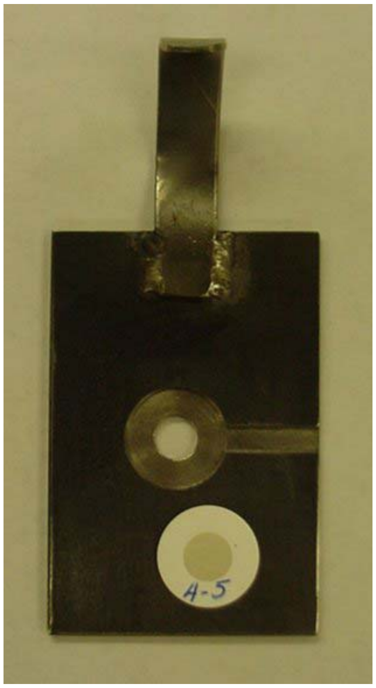


FIG. 3 – Schematic diagram of aluminum filtering funnel

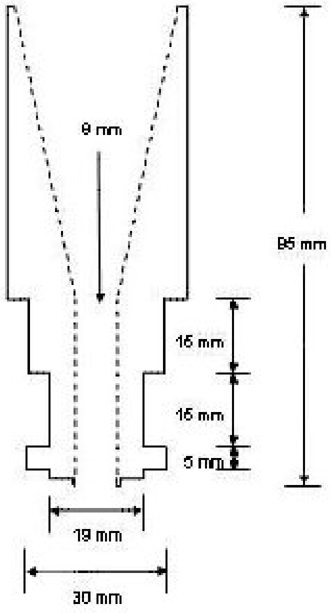
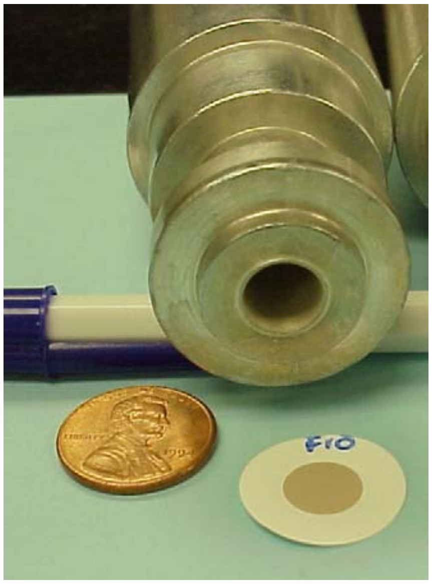


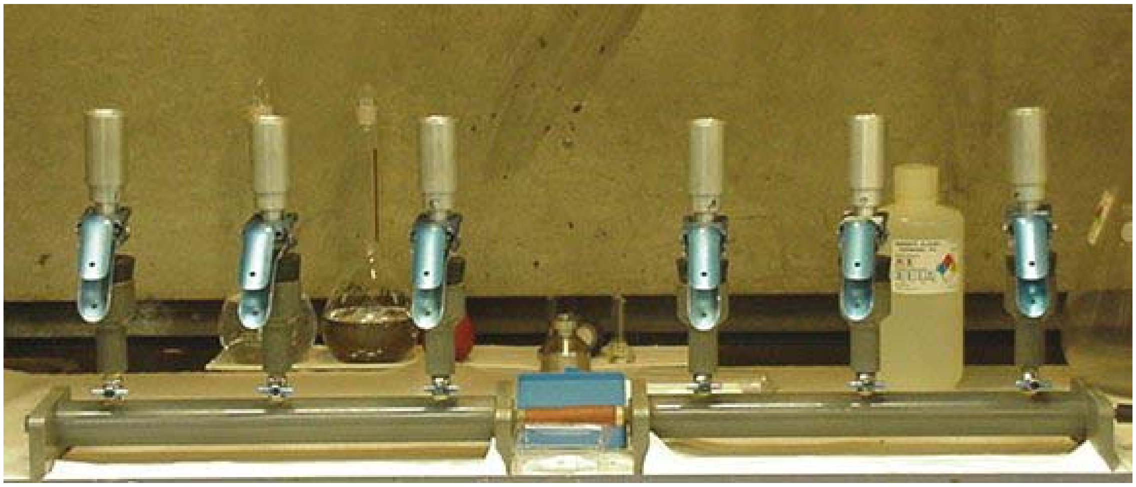
FIG. 4 – 'Lip' on aluminum funnel and ashed sample deposit



This funnel design also uses a centering ring which fits over the fritted glass support base (Figure 5). The centering ring holds and centers the filter onto the fritted base. The funnel bottom fits into the centering ring, centering the funnel on the filter. Rectangular cuts on both the sample holder and the centering ring allow easier access to the filter using forceps. This filter funnel system allows the analyst to quickly set up the filtration manifold (FIG. 6) for redepositing the ashed samples. For this particular design to work, the analysis filter manufacturer provides filters cut to a special diameter, 19 mm. This system could be redesigned to use 25 mm analysis filters, but the filters cost slightly more and the smaller filter size is adequate for the 9 mm sample deposit.

FIG. 5 – Centering ring on fritted glass support base

FIG. 6 – Filtration manifold



Another change that was made with the new FTIR was to eliminate the use of a sample shuttle and to use only one steel sample holder. The first FTIR was equipped with a sample shuttle which moved the sample filter and reference filter alternately into the beam in order to be scanned. Three steel sample holders were made: one for the reference filter, which was left in the instrument, and two for samples. While one sample was being scanned, the next sample was being placed on the second sample holder.

When the new FTIR was being tested before use, it was also noted that when the sample shuttle was moved, there was some variability in its positioning. Millimeter differences had a small but measurable effect on the sample result. Also, each sample holder plate was slightly different and could make a difference in sample results of a few micrograms. Therefore, MSHA decided to use only one plate for analyzing the reference filter and all samples.

Baseline points and peak measurement

The final changes which have been made involve the absorbance measurements of the peaks. It is important to keep in mind that the older dispersive instruments had strip chart recorders, which could only be read to a few wavenumbers. The wavenumbers used for peak and baseline locations vary somewhat due to the various IR instruments and recorders that were used to analyze samples. Analytical results obtained from computer controlled FTIR instruments used today are more reproducible than those from dispersive infrared instruments which used strip chart recorders.

Samples and standards are scanned on the infrared spectrometer between 1000 cm^{-1} and 700 cm^{-1}. Quartz appears as a doublet with peaks at approximately 800 cm^{-1} and 780 cm^{-1}. Kaolinite appears as a doublet in the region between 950 cm^{-1} and 900 cm^{-1} (Figure 7). In the draft method published in the SRI report, the baseline points suggested for measuring kaolinite were 960 and 860 cm^{-1}. In the revision of P7 dated 1984 (when measuring kaolinite was added), MSHA measured the kaolinite peak height from a baseline chosen at 950 cm^{-1} and 880 cm^{-1}. Quartz was measured from a baseline drawn between 810 cm^{-1} and 760 cm^{-1}. These baseline points were adjusted slightly over time, as different instruments were acquired. The 1994 version of P7 listed modified baseline points of 950 cm^{-1} and 895 cm^{-1} for kaolinite and 815 cm^{-1} and 770 cm^{-1} for quartz. Further investigation using FTIR and the added capabilities that the computer control provided led to changes in the baseline points that reduced the variability of the kaolinite measurement and prevented possible problems with the quartz measurement.

Three basic changes have been made that improved the precision of the kaolinite analysis. First, if dolomite is present in the sample, the dolomite peak causes a problem with the selection of a baseline point at 895 cm^{-1} (Figure 8). This was not obvious if a small amount of dolomite was present with a larger amount of calcite, but becomes obvious in samples with more dolomite and little or no calcite. To correct for the underestimation of kaolinite if dolomite was present, the baseline point was changed from 895 cm^{-1} to 900 cm^{-1}.

The second issue that was addressed was that kaolinite usually appears on the shoulder of a large absorbance band (due mostly to large quartz and kaolinte bands above 1000 cm^{-1}). The baseline has a steep slope which makes the peak height measurement at 915 cm^{-1} prone to variability. The computer control and software available with new instrumentation makes the calculation of peak area much easier than when strip chart recorders were used. By using area for the peak measurement instead of peak height, the precision of the kaolinite measurement was improved.

A third issue is the presence of a small absorbance peak in the DM filter media at approximately 950 cm^{-1} (Figure 9). If the reference filter and the sample filter are not an exact match (in thickness), this peak may be present in the sample scan, or may be over-corrected for in the sample scan. This can have an effect on the kaolinite measurement. By changing the baseline points to 930 cm^{-1} and 900 cm^{-1} the peak area is decreased but becomes more reproducable. The quartz peak measurement has also been changed to an area measurement to coincide with the kaolinite measurement.

FIG. 7 – IR spectra of quartz and kaolinite standards

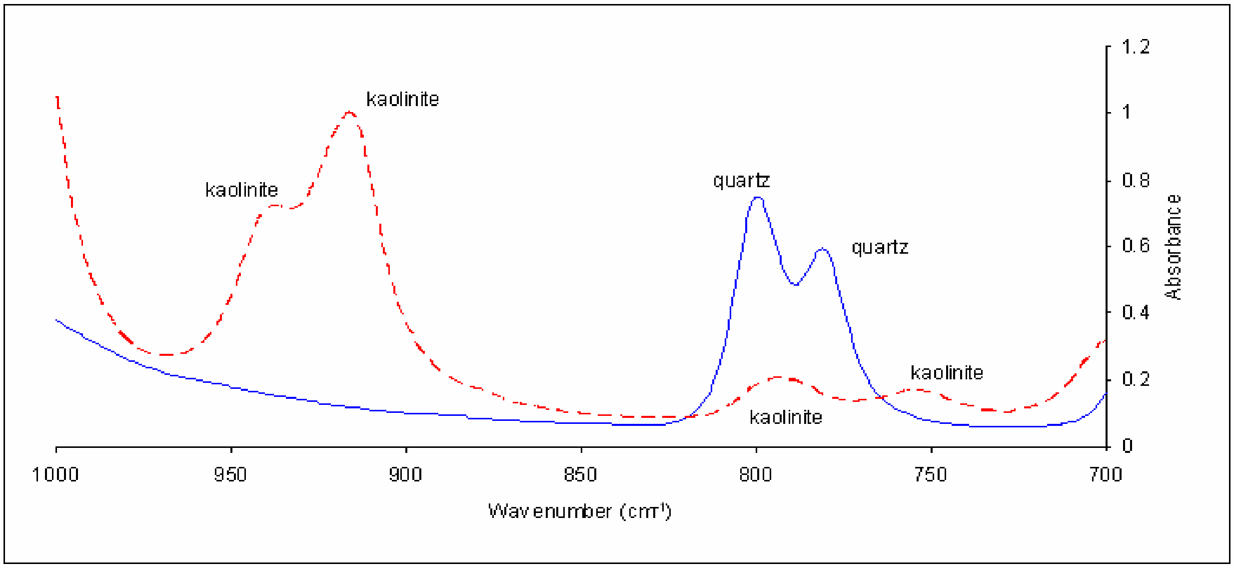


FIG. 8- IR scans of samples containing calcite, dolomite, and mixture of calcite and dolomite

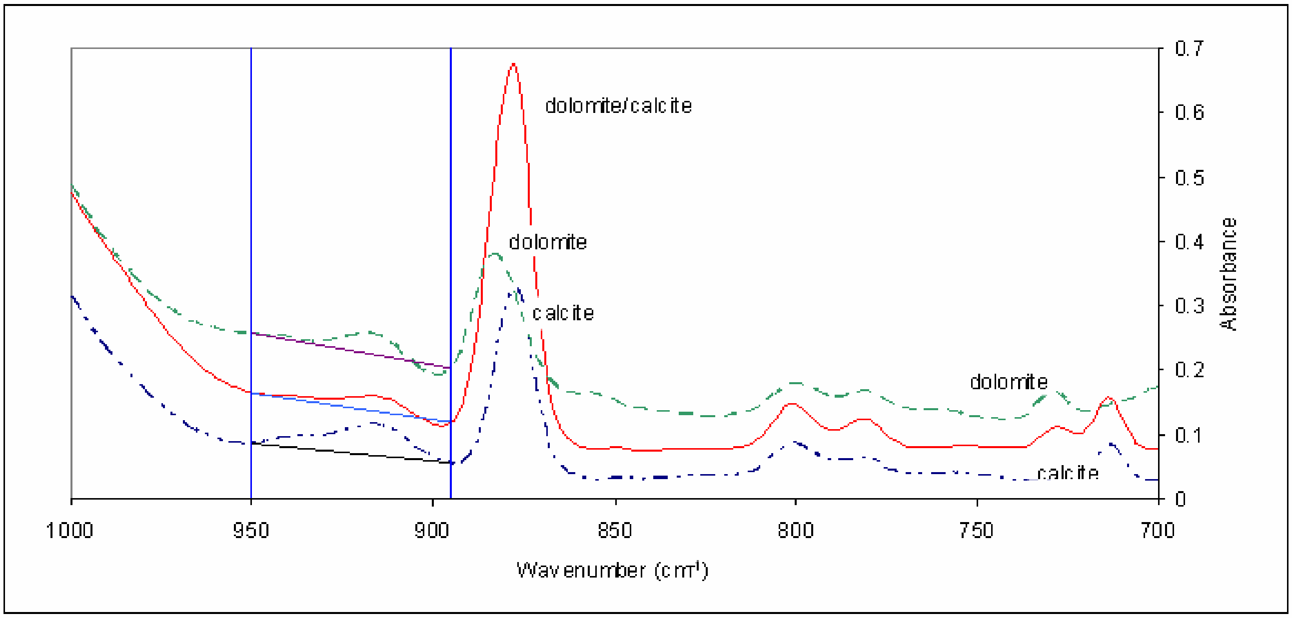
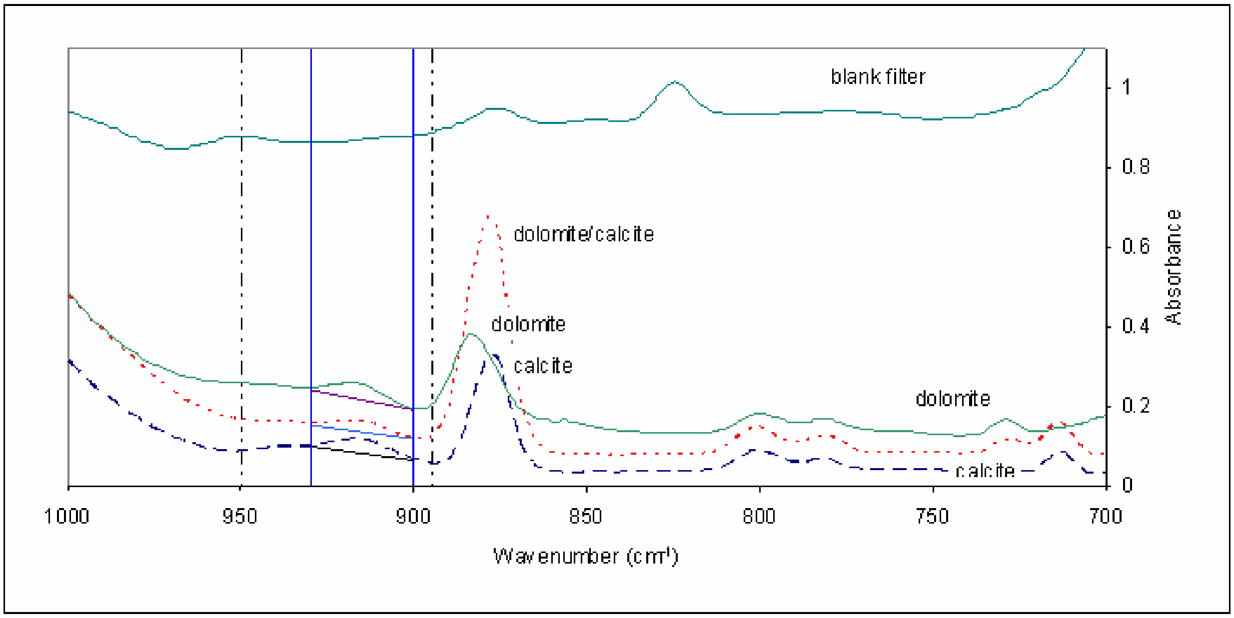


FIG. 9 – IR scans of ashed Respirable coal mine dust and DM blank filter



An anomaly can be caused by the presence of isopropanol on the filter. If the polystyrene PetriSlide dishes with the wet DM filters are placed on a slide warmer to dry with the lids on, even filters that appear to be dry may show alcohol peaks (Figure 10). It can take several minutes for these peaks to disappear once the filter is removed from the PetriSlide. The kaolinite measurement as well as the quartz measurement can be affected by the presence of these peaks. Holes can be drilled into the lid of a PetriSlide™ to allow the alcohol to evaporate or the lid can be left open until the sample is dry (Figure 11).

FIG. 10 – IR scan of quartz standard with isopropanol peaks

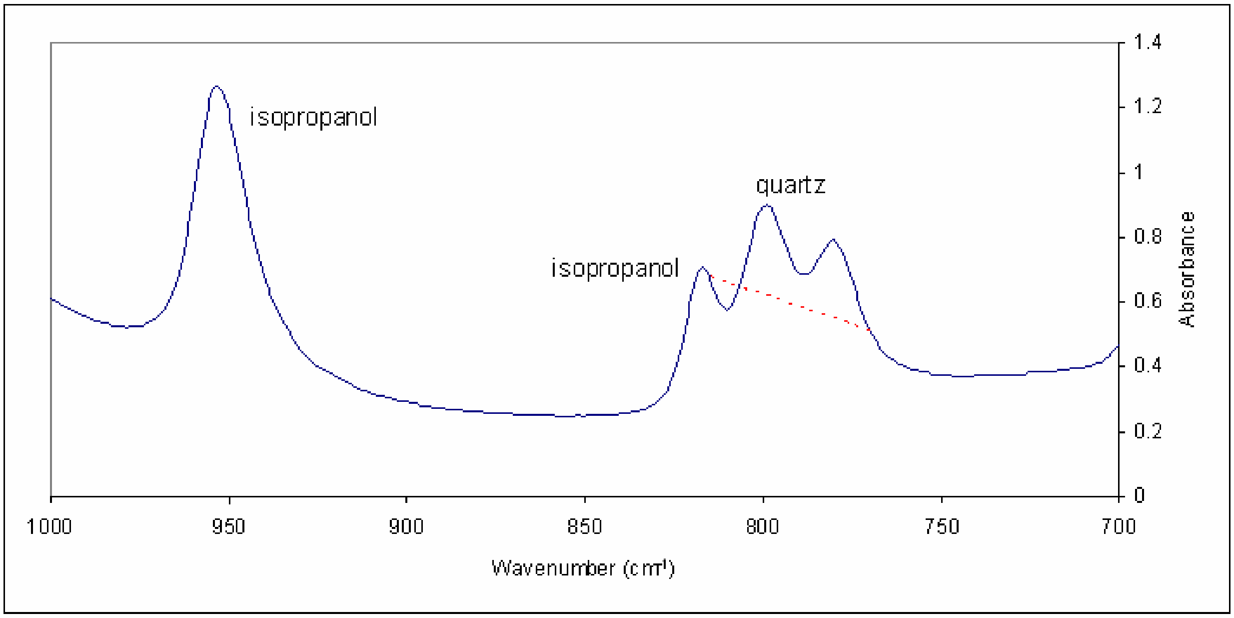


FIG. 11 – PetriSlide™ with holes

Reference Materials

Due to the limited availability of the SRM 1878 reference material, MSHA used Min-U-Sil® 5 for calibration. Although, the laboratory verified that there was no detectable difference in instrument response between the two materials, in 1999 when NIST made available the new quartz standard reference material, SRM 1878a, MSHA began using it rather than Min-U-Sil® 5 for instrument calibration. The FTIR instruments also need to be calibrated for kaolinite, but a standard reference material from NIST is not available. For the kaolinite calibration, MSHA uses Hydrite UF®[6], the kaolinite material used in the SRI collaborative study.

Quality assessment

Previously, the quality assessment process for the quartz analysis used three samples that were prepared in the same manner as calibration standards. In 1991, MSHA began to use respirable coal mine dust samples which had already been analyzed for quartz as quality assessment (QA) 'spiked' samples. This was described in 1992 [10]. In 1999, MSHA reduced the number of QA 'spiked' samples to two, and added the analysis of a laboratory blank and a field blank to each batch of field samples to be analyzed. In 2003, MSHA analyzed 1 106 ('spiked', not blanks) QA samples. The recovery on the re-analyzed 'spiked' QA samples can be used to calculate the precision of the analysis and the laboratory blanks can be used to calculate the method detection limit.

The precision, expressed as a coefficient of variation (CV) can be determined from equation (1):

$$CV^2 = (2/n)\ \Sigma\ [(x_{i2} - x_{i1}) / (x_{i2} + x_{i1})]^2 \qquad (1)$$

Where:

x_{i1} is the first value in the pair
x_{i2} is the second value in the pair
n is the total number of pairs

Using this equation, the precision estimated for the measurement of quartz mass for the first 295 pairs of QA samples for the year 2004 is 0.034.

A simplistic approach to calculating the method detection limit is to calculate the mean value measured for the laboratory blank analyses plus 3 standard deviations. [11,12]. The method detection limit using this approach using the most recent lab blank results for the year 2004 is 4 µg.

Summary

The analytical procedure used by MSHA to analyze respirable coal mine dust samples for quartz was first used to enforce the respirable coal mine dust provisions of the Coal Safety and Health Act of 1969. Since that time, the method has undergone developments that have provided enhanced capability, both by increasing the analytical precision and reducing the analysis time. Computer-controlled FTIR spectrometers have enabled data to be evaluated, such as peak area measurements, which previously was not practical. Questions which arose concerning the kaolinite correction during the collaborative testing of the method are now better understood. Maintaining a quality assessment program for the analysis and a having a thorough understanding of the precision that can be achieved is critical, both in determining whether or not the analysis is in a state of statistical control and also as a tool for evaluating changes to the method.

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