Applied Occupational and Environmental Hygiene
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uaoh20

Analysis of Quartz by FT-IR in Air Samples of Construction Dust

M. Abbas Virji [a], Dhimiter Bello [a], Susan R. Woskie [a], X. Michael Liu [b] & Andrew J. Kalil [a]

[a] Department of Work Environment, University of Massachusetts, Lowell, Lowell, Massachusetts

[b] Global Scientific Affairs, Bausch & Lomb, Rochester, New York

Version of record first published: 30 Nov 2010

To cite this article: M. Abbas Virji, Dhimiter Bello, Susan R. Woskie, X. Michael Liu & Andrew J. Kalil (2002): Analysis of Quartz by FT-IR in Air Samples of Construction Dust, Applied Occupational and Environmental Hygiene, 17:3, 165-175

To link to this article: http://dx.doi.org/10.1080/10473220275343825 2

Applied Occupational and Environmental Hygiene
Volume 17(3): 165–175, 2002

1047-322X/02 $12.00 + .00

Analysis of Quartz by FT-IR in Air Samples of Construction Dust

M. Abbas Virji,[1] Dhimiter Bello,[1] Susan R. Woskie,[1] X. Michael Liu,[2] and Andrew J. Kalil[1]
[1]*Department of Work Environment, University of Massachusetts, Lowell, Lowell, Massachusetts;*
[2]*Global Scientific Affairs, Bausch & Lomb, Rochester, New York*

The construction industry is reported to have some of the highest exposures to silica-containing dust. With the designation of crystalline silica as a group I human carcinogen by the International Agency for Research on Cancer (IARC), there exists a need for an analytical method to accurately quantify low levels of quartz. A method is described that uses FT-IR for quartz analysis of personal air samples collected from heavy and highway construction sites using 4-stage personal impactors. Sample filters were ashed and 13-mm or 5-mm pellets were prepared. Absorbance spectra were collected using FT-IR at resolution of 1 cm^{-1} and 64 scans per spectrum. Two spectra were collected per sample using the appropriate background spectrum subtraction. Spectral manipulations such as Fourier self-deconvolution and derivatizations were performed to improve quantification. Peak height for quartz was measured at 798 cm^{-1} for quantitative analysis. The estimated limit of detection for the 5-mm pellets was 1.3 μg. Recoveries of Min-U-Sil 5 spikes showed an average of $\geq$ 94 percent for the two pellet types. The coefficient of variation of the 5-mm pellet was 9 percent at 6 μg quartz load, and 7 percent at 62 μg load. Interferences from clay, amorphous silica, concrete, calcite, and kaolinite were investigated, these being the more likely sources of interferences in construction environment. Spikes of mixtures of amorphous silica or kaolinite with Min-U-Sil 5 showed both contaminants introduced, on average, a positive error of < 5 μg with average recoveries of 106 percent and 111 percent, respectively. Spikes of mixtures of clay or concrete with Min-U-Sil 5 showed overall average recovery of 100 percent and 90 percent, respectively, after accounting for the presence of quartz in clay and concrete. This method can quantify low levels of quartz with reasonable accuracy in the face of common contaminants found in the construction industry.

Keywords Analytical Method, Crystalline Silica, Fourier Transform Infrared Spectrophotometry (FTIR), Heavy and Highway Construction, Min-U-Sil 5, Personal Impactor, Quartz, Size Selective Sampling

The widespread occupational exposures to crystalline silica and its associated health effects have long been recognized and are amply documented in the literature. It is estimated that nearly 700,000 construction workers in the United States may be exposed to crystalline silica during various operations.(1) Historically, exposure to respirable crystalline silica has been associated with the development of silicosis, bronchitis, and chronic obstructive airway diseases.(2) Crystalline silica is also designated a human lung carcinogen by the International Agency for Research on Cancer (IARC).(1) Based on their extensive review of epidemiological studies, IARC found sufficient evidence for the carcinogenicity of crystalline silica based on animal and human studies, and supported the finding that occupational exposures to crystalline silica resulted in an increased risk for lung cancer. While the debate over the causal pathway between silica, silicosis, and lung cancer continues in the scientific community,(3–5) the public health efforts to assess and reduce workers' exposures and their risk of silicosis or lung cancer need to continue. In addition to the pulmonary effects of crystalline silica, some studies have also found an association between exposure to crystalline silica, construction, or excavation dusts and cancers of the lung, throat, colon, or stomach.(6,7)

A study reviewing published literature on the risk of silicosis reports an excess risk in workers exposed to crystalline silica at 0.1 mg/m^3 for 45 years.(3) Based on the data and models reviewed, the study further suggests that even at an average exposure level of 0.05 mg/m^3 over 45 years, the risk among exposed workers of grade 1/1 and 1/0 silicosis would be 10–20 percent and 20–40 percent, respectively. Based on these results, a lowering of the respirable exposure limit to

0.01 mg/m^3 is proposed, with the ultimate goal of 0.001 mg/m^3, which would reduce the risk of grade 1/1 silicosis to $<$ 2 percent, and grade 1/0 silicosis to $<$ 5 percent. Reducing the exposure limits will only be effective if there is an accompanying improvement in the sampling and analytical method as well as the availability of control technology to reduce exposure levels. Based on these observations, there exists a need for the accurate quantification of low levels of crystalline silica (quartz), and for its quantification in the respirable, thoracic, and inhalable particle size fractions, especially for epidemiological studies of health effects.

Standard analytical methods available for the analysis of quartz in occupational and environmental samples include x-ray diffraction (XRD) and infrared (IR) spectroscopic methods. Since the early 1970s, both these methods have experienced increased application in the analysis of quartz, although only modest improvements in their precision, accuracy, and the detection limit have been documented.(8) Extensive comparisons of quartz analysis by XRD and FT-IR through the Proficiency Analytical Testing program (PAT) showed comparable detection limits, within- and between-lab variability, sample precision, and relative recovery.(9,10) Both methods had within-lab variability of 16–20 percent, between-lab variability of about 20 percent, and a mean recovery of 102 percent (range 84–117 percent).(10)

Conventional dispersive IR has limited applications in quartz analysis, especially in samples with complex matrix, due to its low sensitivity and insufficient resolution to separate interfering peaks from the target peaks. However, advances in Fourier Transform IR (FT-IR) and its reduced cost have made it an accessible and reliable tool for multipurpose analysis. FT-IR achieves higher sensitivity and accuracy than traditional IR as a result of high-speed repeated scans of each sample, greater optical throughput (which allows more energy to reach the detector), computerized data processing such as background subtraction, Fourier Self-Deconvolution, spectrum derivatization, increased accuracy in wavelength measurement, and library search of spectra.(11)

In this article, a method is described that uses FT-IR for the quantitative analysis of quartz in air samples from construction environments. The analytical method development is described as well as its experimental evaluation. The method evaluation addresses the important issues of spectral interferences, method precision, limit of detection of the method, and the particle size dependence of quartz analysis. The major strengths and the notable improvements of the method described are its ability to resolve potential interferences in the construction environment, its lower limit of detection and improved precision, and its application to particle size selective sampling methods (described elsewhere).(12) In a companion paper, an approach is presented for the quantification of respirable, thoracic, and inhalable quartz in personal samples collected using a four-stage cascade impactor.(12)

STUDY SITE

This method was developed to analyze air samples collected from construction workers on the Boston Central Artery/Tunnel Project (CA/T). This project, one of the largest and most complex highway construction projects in the United States, includes the construction of an underground highway, bridges, and tunnels through the center of Boston. In the course of construction, quartz exposures may occur during a number of activities. These activities include mechanical disruption of concrete or rocks (through drilling, grinding, crushing) during concrete demolition or finish work; movement of soil or clay for excavation; and mixing of construction materials that contain quartz, such as bentonite or fly ash for slurry wall construction or jet grouting for unstable soils. During these activities, large quantities of quartz-containing dust may be released into the environment, potentially exposing construction workers operating the equipment, as well as other workers and bystanders.

POTENTIAL INTERFERENCES WITH QUARTZ ANALYSIS FROM CONSTRUCTION DUST

The dust matrix of air samples collected in the construction environment is generally very complicated. The matrix might contain appreciable levels of interfering minerals that may pose a serious challenge for quartz analysis, such as concrete, kaolinite, and clay. The major component of all the excavated material on the Boston CA/T highway construction project is the Boston blue clay, a marine sediment rich in minerals.(13) An XRD analysis of the Boston blue clay revealed the presence of feldspars (30%), mica (20%), kaolinite (20%), quartz (15%), and chlorite (8%).(13)

Quartz absorbs in two regions of interest for quantitative analysis: a doublet with its maxima at 798 cm^{-1} and 779 cm^{-1}, and a singlet at 696 cm^{-1}. The first peak of the doublet has the strongest absorbance and is commonly used for quartz analysis. The two polymorphs of quartz (tridymite and cristobalite) positively interfere with quartz analysis at the 798 cm^{-1} peak. Cristobalite can be identified in the presence of quartz by its secondary peaks, but tridymite can not be identified in the presence of quartz. However, these high-temperature polymorphs are rare in environments where they are not being created or processed.(14)

Portland cement, a commonly used construction material does not contain quantifiable levels of quartz or other minerals that, after ashing, might interfere with quartz analysis. Kaolinite, a major component of clay has its peaks at 940 cm^{-1}, 913 cm^{-1}, and 798 cm^{-1}, presenting a significant potential interferent for quartz analysis. However, the kaolinite spectrum changes after the sample is ashed (at 600°C) and resembles the spectrum for amorphous silica in the quartz quantification region (Figure 1). Amorphous silica can be identified by the broad and intense peak between 850 cm^{-1} and 770 cm^{-1} with a maximum at 800 cm^{-1}.

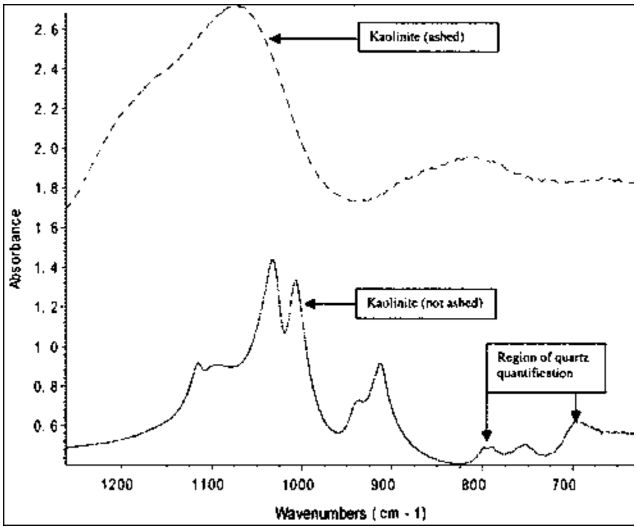

FIGURE 1
Absorbance spectra of a filter spiked with kaolinite and ashed at 600°C for two hours compared to unashed kaolinite showing the effects of ashing on the main peaks for kaolinite identification.

Its presence in a sample can potentially be a significant source of interference for quartz quantification at the 798 cm^{-1} peak, but not at the 696 cm^{-1} peak.

Generally, clays absorb in the region between 790 cm^{-1} to 620 cm^{-1} with prominent peaks at 787 cm^{-1}, 760 cm^{-1}, 745 cm^{-1}, 720 cm^{-1}, and 648 cm^{-1} (Figure 2). Clay bulk samples from the present study were analyzed by FT-IR and were found to contain quartz in the range of 5 to 6.5 percent, a dominant feldspar matrix (mainly albite), microcline, chlorite, meerschaum, and low levels of other unidentified compounds.(15,16) Wet concrete is made up of aggregate (crushed stone, gravel, sand) along with Portland cement, fly ash, and water. The formulations of concrete vary based on the use, but on the CA/T project, cured concrete contains quartz, alumina, lime, ferric oxide, and a variety of other components. Concrete bulk samples from the present study were analyzed by FT-IR and were found to contain an average of 3.1 percent quartz, a little lower than expected. However, published reports show that the quartz content of concrete can be variable depending on its formulation.(17) Both concrete and clay are potentially significant sources of interference in the region 830 cm^{-1} to 630 cm^{-1} for quartz quantification.

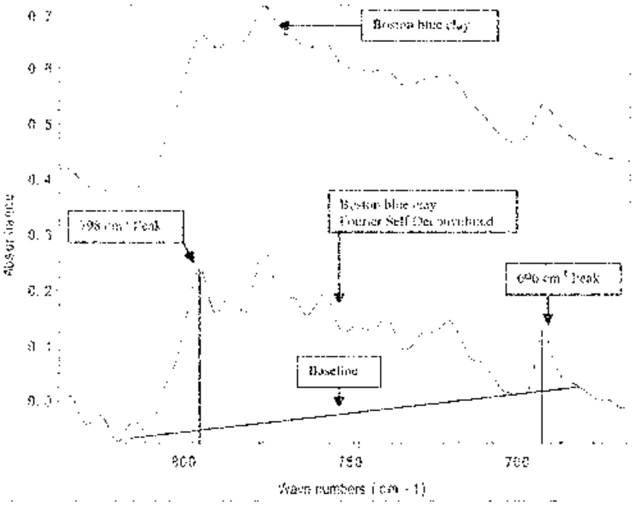

FIGURE 2
Spectra of Boston blue clay quantification and its Fourier self deconvolution (FSD) showing the effect of FSD in resolving adjacent peaks in the process of spectral quantification.

ANALYTICAL METHOD

The method described here was developed for the analysis of quartz in air samples collected from construction sites, and is a refinement of the National Institute for Occupational Safety and Health (NIOSH) Method 7602.(18) The major improvements arise from utilizing the advanced features of the FT-IR and from using the 5-mm pellets to concentrate the samples. The focus of this article is on developing and testing the analytical method, and creating calibration curves using Min-U-Sil 5 (U.S. Silica Company, Berkeley Springs, WV),(19) a commercially available, relatively pure form of quartz, and standard reference material for respirable α-quartz (SRM 1878a), prepared and certified by the National Institute of Standards and Technology (NIST).(20) In the companion paper, particle size–specific calibration curves are created for the quantification of inhalable, thoracic, and respirable fractions of quartz.(12)

Personal breathing zone air samples were collected on construction workers using a four-stage personal impactor sampler (Graseby Anderson, Atlanta, GA), details of which are provided elsewhere.(12,21) Collection of personal impactor samples permitted the estimation of quartz in the inhalable, thoracic, and respirable size fractions as defined by the American Conference of Governmental Industrial Hygienists (ACGIH®).(22) Briefly, Mylar filters sprayed with Apiezon-L grease (Supelco, Bellefonte, PA) were used for the upper four stages, and PVC filters were used for the final filter of the impactor. For quartz analysis, stage 5A and the final filter were combined, as were stages 2 and 3, with the objective of obtaining adequate mass in the combined stages to reach the limit of quantification. Stage 1 was analyzed separately.

Sample Preparation for the 13-mm and 5-mm Pellets

Samples were prepared according to the NIOSH method 7602 for crystalline silica by IR. Filters from impactor stages and the respirable cyclone were ashed in a muffle furnace for 2 hours at a temperature of 600°C to destroy organic material and simplify the matrix. A 13-mm pellet was prepared by adding 300 milligrams (300 ± 0.1 mg) of potassium bromide (KBr), dried overnight (110°C), to the ashed residue. The sample residue and KBr was thoroughly ground and mixed for approximately 2 minutes, transferred to a 13-mm evacuable pellet die, where it was vacuum pressed under 1 ton for 1 minute, then 8.2 tons for another minute. The finished pellet was then analyzed by Nicolet-Magna 550 FT-IR (Nicolet Instrument Corp., Madison, WI).

The 5-mm pellets were obtained by inserting into the 13-mm die a set of two paper rings with an outer diameter of 13-mm and an inner diameter of 5-mm. The sample residue was diluted with 20 ± 0.1 mg dried KBr and transferred to the 5-mm inner hole. The rest of the procedures were as described above for the 13-mm pellets.

FT-IR Setup

The FT-IR was set to absorbance mode, and the pellets were scanned from 2100 cm^{-1} to 600 cm^{-1} at a mirror velocity of 0.6329 mm s^{-1} and aperture of 64, using a KBr beam splitter and a DTGS detector. FT-IR spectra were obtained by averaging 64 scans at 1 cm^{-1} resolution with the Happ-Genzel apodization function, using autogain mode. Two spectra were collected per sample, rotating the pellet 180 degrees each time. If a discrepancy was detected between the two spectra, then two additional spectra were collected, giving a total of four spectra per sample. CO_2-free compressed air was used as purge gas to reduce interference near the 696 cm^{-1} peak region. The two- or four-sample spectra collected were averaged before quantification.

To ensure that the FTIR was operating optimally, the instrument stability and reproducibility was consistently evaluated through the following procedures:

1. The major FT-IR parameters were recorded and compared with previously recorded parameters.
2. The noise in the background pellet spectrum was measured and compared with previously recorded typical values.
3. Absorbances of three standard pellets were measured alternatively and were compared with previously recorded absorbances.

In case any of these tests failed to comply with the quality control criteria specified, a bench alignment was performed to bring them within the typical range.

Background Handling

Since there were different types and numbers of filters in the pellet samples, appropriate background subtraction was applied to each sample, reflecting the filter media and the number of filters combined in the pellet samples. The background spectra were obtained following the ashing and pelletization of the appropriate filters, processed as described above. These were then analyzed by FT-IR, which was set to collect 2000 scans per spectrum. Separate sets of background spectra were collected for the 13-mm and the 5-mm pellets.

Preparation of Standard Pellets and Calibration Curves

Standard pellets were prepared according to the NIOSH method 7602, by spiking 37-mm PVC filters with Min-U-Sil 5 or respirable α-quartz (SRM 1878a), weighed using a microbalance (Cahn C-30, Cahn Instruments Inc., Cerritos, CA). The spiked filters were then ashed and pelletized following the process described above. Two sets of calibration curves were prepared for the 5-mm and the 13-mm pellets using Min-U-Sil 5 and SRM 1878a. Standard pellets were prepared in the quartz mass range of 10 μg to 1000 μg for the 13-mm pellets, and 3 μg to 130 μg for the 5-mm pellets for Min-U-Sil 5 calibration curves. Calibration curves for SRM 1878a were prepared in the quartz mass range of 59 μg to 403 μg for the 13-mm pellets, and 4 μg to 126 μg for the 5-mm pellets. For all the calibration curves, the amount of quartz used was within the linear response range of quartz for FT-IR (ca. 1.0 absorbance units).

Quality Control

To check the method performance, 8 filters were spiked with known amounts of Min-U-Sil 5 in the range of 13 μg to 502 μg for the 13-mm pellets. Another 11 filters were spiked with Min-U-Sil 5 in the range of 14 μg to 121 μg for the 5-mm pellets. A set of 4 NIST-certified filters consisting of a mixture of respirable quartz and clay (SRM 2679a: quartz on filter media)(23) were also analyzed using the 13-mm pellet method. In addition, two sets of 7 filters were spiked with 6 μg or 62 μg of Min-U-Sil 5. These spiked samples were analyzed using the 5-mm pellet method to obtain method Coefficients of Variation (CV) for the low- and midrange of quartz loads.

Limit of Detection/Quantification (LOD/LOQ)

The instrument limit of detection (LOD) for the 13-mm and 5-mm pellets was calculated based on the RMS (root mean square) noise in the spectral region of 2050 cm^{-1} to 1950 cm^{-1}, where there is least interference from any compounds. The instrument LOD was defined as three times the RMS noise, while the instrument limit of quantification (LOQ) was established as 10 times the RMS noise.(11) The overall method LOD was determined by identifying seven samples (containing the filter and the sample matrix) near the estimated LOD. These were then quantified at 798 cm^{-1} and 696 cm^{-1}, and the standard deviation of the seven measurements was calculated. The overall method LOD was defined as 3.3 times the standard deviation of the seven measurements, and the overall method LOQ was defined as 10 times the standard deviation.(24) This method was applied to both the 13-mm and the 5-mm pellets.

Quantification

Quartz was quantified using the 798 cm^{-1} peak, while the 779 cm^{-1} peak could not be used due to interference from clay. The 696 cm^{-1} peak was only used for comparative purposes, and was rarely applied for quartz quantification because of its weak absorbance and the potential for interferences from clays and other minerals. Prior to quantification, each spectrum was examined for the presence of compounds that might interfere with the quartz peak, such as the polymorphs of quartz, clays, kaolinite, calcite, and amorphous silica.

For quantitative analysis, Fourier self-deconvolution was carried out in the region 840 cm^{-1} to 670 cm^{-1} using the Nicolet-Omnic v. 3.1 software package (Nicolet Instrument Corp., Madison, WI). For the standard pellets and mixture samples, as well as stage 5A and the final filter of the impactor samples, the bandwidth was set at 10 cm^{-1}, and the enhancement factor to 1.5. The bandwidth and enhancement factors for impactor samples and standard pellets for larger particle size were different and are reported elsewhere.(12) These settings provided adequate deconvolution of the spectrum as indicated by the absence of side lobes in the spectrum (Figure 2). The 798 cm^{-1} and 696 cm^{-1} peak heights were quantified by drawing a common baseline from approximately 820 cm^{-1} to 680 cm^{-1} and measuring the peak absorbances to 0.0001 absorbance units. For some samples where the baseline increased across the spectrum, two shorter baselines were drawn from 820 cm^{-1} to 755 cm^{-1} for the 798 cm^{-1} peak and from 702 cm^{-1} to 685 cm^{-1} for the 696 cm^{-1} peak. For a few noisy spectra for which the deconvolution parameters could not be set to the required values, smoothing was applied to diminish the noise, and then the spectra were deconvoluted. Smoothing has an effect similar to that of using a lower resolution. The degree of smoothing was kept at a minimum (less than 4 cm^{-1}) since a high degree of smoothing (above 7 cm^{-1}) can affect the peak height.(25)

For some spectra (especially at very low levels of quartz), the identification of quartz peaks or the baseline points was difficult even after deconvolution. In these cases, the original spectrum was differentiated to obtain the first and second derivatives. The second derivatives of the sample and the Min-U-Sil standard spectra were overlaid with the deconvoluted sample spectrum. Presence of quartz in the sample was verified when the maxima of the second derivatives of the sample spectrum and the Min-U-Sil standard spectrum were aligned (Figure 3). The maxima also identify the exact location of the quartz peaks at 798 cm^{-1} and 696 cm^{-1} in the deconvoluted sample spectrum for quantification. To improve the identification of the baseline points, the deconvoluted sample spectrum was overlaid with the first derivative of the original sample spectrum. The point at which the first derivative spectrum flattens at either shoulder of the 798 cm^{-1} and the 696 cm^{-1} peaks identifies the baseline points (Figure 4).

To verify sample quantification, the ratio of the 798 cm^{-1} to the 696 cm^{-1} peak for the samples was compared to the corresponding ratio for the standard pellets. The ratios for the standard pellets did not vary much due to the absence of spectral interference at the two peaks. When the sample ratio was out of range of the standard ratios, it was generally due to interferences at either the 798 cm^{-1} or the 696 cm^{-1} peaks of the sample. In these situations, the sample spectra were inspected with extra care to ensure that the quantification error was kept to a minimum. Although some studies have suggested the use of the ratio of the standard pellets to correct for interferences in the sample peaks or for particle size effects, such corrections were not considered in the present study.(25,26)

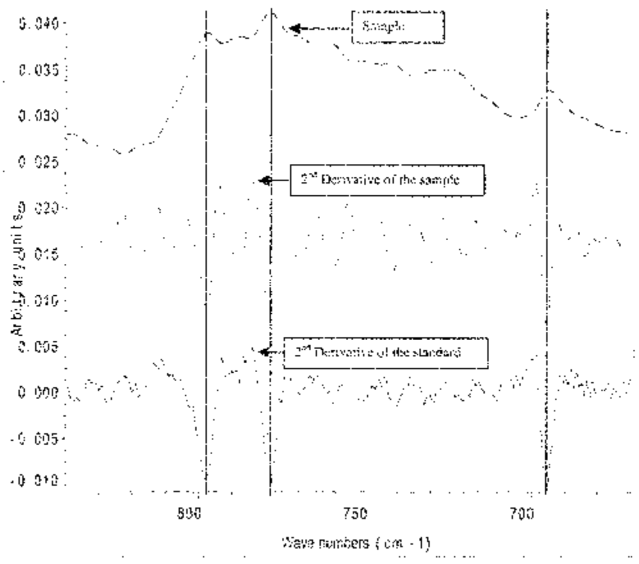

FIGURE 3

Spectra of a sample filter and the second derivatives of the sample and Min-U-Sil 5 standard showing agreement at the doublet at 798 cm^{-1}, 779 cm^{-1}, and at 696 cm^{-1}, which confirms the presence of quartz.

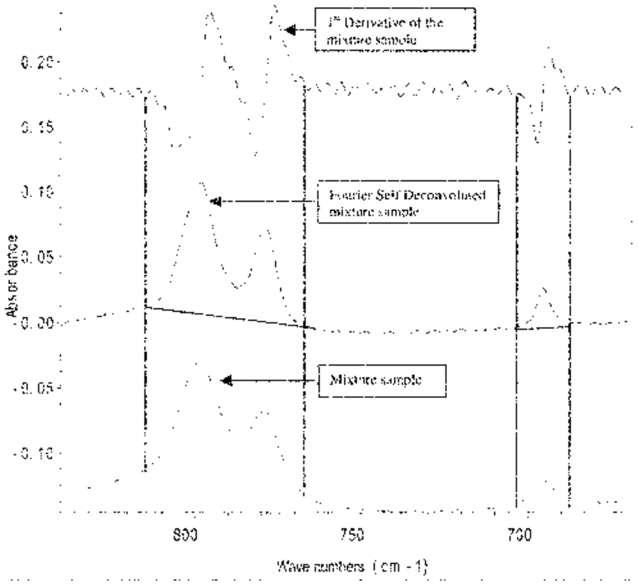

FIGURE 4

A sample spectrum and its first derivative showing the use of the first derivative to identify baseline points in samples.

Interference

In order to investigate the severity of interferences from contaminants with quartz analysis, sets of mixtures of Min-U-Sil 5 and the potential contaminants were spiked onto 37-mm PVC filters by accurately weighing the components of the mixture. The mixtures were created over a range of Min-U-Sil 5 and contaminant amounts, pelletized, and analyzed for quartz. Recoveries and bias in quantification were calculated for sets of mixtures and used to evaluate the accuracy of the method when applied to the common contaminants found in the construction environment.

Mixtures of amorphous silica and Min-U-Sil 5 were prepared in the range of 49 μg to 683 μg of amorphous silica and 9 μg to 77 μg of Min-U-Sil 5. Similarly, mixtures of kaolinite and Min-U-Sil 5 were prepared in the range of 46 μg to 672 μg of kaolinite and 5 μg to 96 μg of Min-U-Sil 5. A total of 17 amorphous silica mixture samples and 11 kaolinite mixture samples were each divided into four categories representing high and low levels of the contaminants and Min-U-Sil 5. Using the cut points of 30 μg for Min-U-Sil 5 and 200 μg for the contaminants, these mixture samples were divided into high and low Min-U-Sil 5 and the contaminant categories. Combinations of the contaminants and Min-U-Sil 5 were created in a manner to ensure approximately equal number of mixture samples in each of the quadrants. For these mixtures, average recoveries were calculated as the ratio of the amount of quartz quantified to the amount of quartz spiked onto the filter. The mean (bias) and range of the difference between the amount of quartz quantified and the amount of quartz spiked onto the filter were calculated.

For the mixtures of clay and Min-U-Sil 5, the amount of clay varied from 288 μg to 2356 μg, while Min-U-Sil 5 ranged from 19 μg to 575 μg. For the mixtures of concrete and Min-U-Sil 5, the amount of concrete varied from 50 μg to 509 μg, while Min-U-Sil 5 ranged from 22 μg to 499 μg. Since both clay and concrete contain some amount of quartz, calculating the recoveries in the classic sense as the ratio of the amount of quartz quantified to the amount of quartz spiked is erroneous. Thus, the total recovery was computed as the ratio of the total amount of quartz quantified to the sum of the amount of quartz spiked onto the filter and the amount of quartz present in the contaminants (Equation [1]).

$$\text{Recovery}\,(\%) = 100 \times \left[\frac{\text{Total Quartz Quantified}\,(\mu\text{g})}{\text{Quartz Spiked}\,(\mu\text{g}) + [\text{Contaminant Spiked}\,(\mu\text{g}) \times \text{Quartz in Contaminant}\,(\%)]}\right] \qquad [1]$$

The amount of quartz in the contaminants was obtained by analyzing bulk samples of clay and concrete, and obtaining the average percentage of quartz they contained.

RESULTS

The initial method development and evaluation was performed using the 13-mm pellet method. When the method was modified to the 5-mm pellets, the evaluation of recoveries from NIST SRM 2679a samples and mixture samples of Min-U-Sil 5 and the contaminants was not repeated, but was supplemented with other quality control procedures such as the evaluation of method precision. Only the evaluation of the method LOD and LOQ, calibration curves using Min-U-Sil 5 and SRM1878a, and recoveries from spiked filters were repeated using the 5-mm pellets.

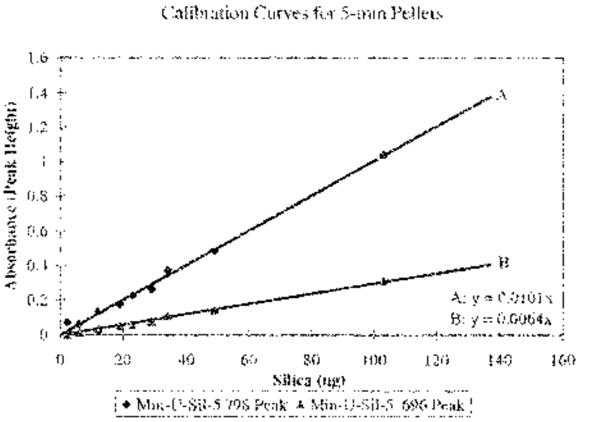

FIGURE 5

Calibration curves for 5-mm micro-pellets for the 798 cm^{-1} and 696 cm^{-1} peaks.

The instrument LOD and LOQ were 0.3 μg and 1 μg, respectively. The overall method LOD for the 13-mm and the 5-mm pellets were 3 μg and 1.3 μg, respectively, while the LOQ were 10 μg and 4 μg, respectively. The LOD value for the 5-mm pellets is substantially lower than what is generally reported in the literature and in NIOSH method 7206.[8,18] The low LOD for this method is attributed to the sample concentration in the 5-mm pellets, the superior signal-to-noise ratio of the FT-IR, and spectral enhancement due to Fourier self-deconvolution.

Quality Control

Calibration curves were obtained using Min-U-Sil 5 for the 5-mm as well as the 13-mm pellets for both the 798 cm^{-1} and the 696 cm^{-1} peaks (Figures 5 and 6). Calibration curves for the 13-mm as well as the 5-mm pellets for the 798 cm^{-1} peak were also created using SRM 1878a, which only became available towards the end of this study and yielded regression coefficients identical to those obtained using Min-U-Sil 5 (Table I). This finding points to the purity and acceptability of the present batch of bulk Min-U-Sil 5 used for these experiments.

The average recoveries from the spiked filters were 94 percent and 97 percent for the 798 cm^{-1} and 696 cm^{-1} peaks for the 13-mm pellet procedure, and 101 percent and 97 percent for the 798 cm^{-1} and the 696 cm^{-1} peaks for the 5-mm pellets

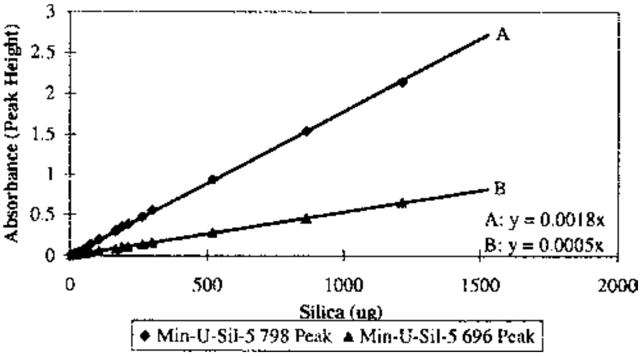

FIGURE 6

Calibration curves for 13-mm pellets for the 798 cm^{-1} and 696 cm^{-1} peaks.

(Table II). Furthermore, there was no concentration effect on the recoveries over the range of Min-U-Sil 5 spiked. Analysis of the set of four NIST-certified SRM 2679a filters using the 13-mm pellets showed the quantified amount was well within the range of acceptable concentrations for all the NIST samples (Table III).

The CV of the analytical method for the 5-mm pellets was 9 percent for the lower loading of 6 μg and 7 percent for the midrange loading of 62 μg for the 798 cm^{-1} peak. It is thought that these results are biased high due to the difficulty in generating identical replicates of quartz using the gravimetric method. However, NIOSH method 7602 recommends achieving a CV < 15 percent at 30 μg quartz for the method to be acceptable.(18)

Interferences

Quartz recoveries from mixtures of amorphous silica and Min-U-Sil 5 are shown in Table IV. The bias in the four categories of amorphous silica and Min-U-Sil 5 were all less than 5 μg, and the difference in the range of 0 μg to 11.4 μg. The average recovery of quartz from these mixture samples was 113 percent, with a range of 96 to 210 percent. The average recovery improved substantially to 106 percent (range 96–120 percent) after excluding one mixture sample that had an amorphous silica to Min-U-Sil 5 ratio of greater than 100 (683 μg amorphous silica and 6 μg Min-U-Sil 5). The recoveries for the 696 cm^{-1} peak were much better, with an average of 102 percent. This results from amorphous silica not absorbing near the region of the 696 cm^{-1} peak. A regression of the amount of quartz quantified using the 798 cm^{-1} peak to the amount spiked gave a regression coefficient of 1.08 with an $R^2 > 0.99$.

TABLE I

Regression coefficients for the 798 cm^{-1} peak calibrations for the 13-mm and the 5-mm pellet

Standards	^A^Particle size median (90th %)	13-mm pellet $^B\beta_1$	5-mm pellet $^B\beta_1$
Min-U-Sil 5	1.6 (~3.8) μm	0.00187	0.0101
SRM 1878a	1.6 (3.8) μm	0.00186	0.0100

^A^Equivalent spherical diameter.

^B^Regression Model: Absorbance = $\beta_1 \times$ Quartz Mass (μg) (after spectral deconvolution).

Similar results were obtained from the mixtures of kaolinite and Min-U-Sil 5 (Table V). The bias in the four categories of kaolinite and Min-U-Sil 5 ranged from 2 μg to 6 μg. The difference between the amount of Min-U-Sil 5 quantified to the amount of Min-U-Sil 5 spiked for all the mixture samples ranged from 0.1 μg to 10.3 μg. The average recovery of quartz for the 798 cm^{-1} peak from these mixture samples was 125 percent, with a range of 102–272 percent. The average recovery and the range improved significantly to 111 percent (range 102–121 percent) after excluding one mixture sample that had a kaolinite to Min-U-Sil 5 ratio of greater than 100 (672 μg kaolinite and 6 μg Min-U-Sil 5). The average recoveries for the 696 cm^{-1} peak with and without the outlier were 112 percent and 105 percent, respectively. A regression of the amount of quartz quantified to the amount spiked gave a regression coefficient of 1.09 with an $R^2 > 0.99$.

The average recovery over a range of mixtures of Min-U-Sil 5 and clay was 100 percent for the 798 cm^{-1}, with a range of 95–106 percent after accounting for the quartz content in clay. The average recovery for the 696 cm^{-1} peak was also 100 percent, with a range of 95–106 percent. The amount of quartz quantified using the 798 cm^{-1} peak matched well with the amount of quartz spiked as indicated by the regression coefficient of 1.004 and $R^2 > 0.99$ for that comparison (Figure 7).

The average recovery over a range of mixtures of Min-U-Sil 5 and concrete was 90 percent, with a range of 83–100 percent for the 798 cm^{-1} peak after accounting for the quartz content in concrete. The average recovery for the 696 cm^{-1} peak was 95 percent, with a range of 82–107 percent. A comparison of the amount of quartz quantified using the 798 cm^{-1} peak to the amount of quartz spiked across a range of concentrations showed a good relationship, with a regression coefficient of 0.94 and $R^2 > 0.99$ (Figure 7). The lower recoveries for quartz in these mixtures may be due to the heterogeneity and the high variability of quartz in concrete bulk samples.

NIOSH method 7602 cautions that calcite may interfere with quartz analysis at loads >20 percent of the total dust by reacting with quartz during ashing. Since materials used in concrete contain carbonates, the impact of calcite on quartz analysis was examined. In fact, carbonates are rarely seen in our samples, nor do they cause spectral interference with quartz analysis.

DISCUSSION

FT-IR offers a number of opportunities for spectral collection and manipulation and has great potential for the accurate quantification of low levels of quartz.(28) These features, which are discussed in the introduction, enhance peak identification and allow quartz quantification at low levels. Also important is the option to vary pellet size, which allows the degree of sample

TABLE II

Average recovery of filters spiked with Min-U-Sil 5 for the 798 cm^{-1} and the 696 cm^{-1} peaks using 13-mm and 5-mm pellets

Pellet type	N	Min-U-Sil-5 spikes range (μg)	% Recovery 798 cm^{-1} peak mean (range)	% Recovery 696 cm^{-1} peak mean (range)
13-mm Pellets	8	13–998	94 (87–101)	97 (90–104)
5-mm Pellets	11	14–121	101 (89–112)	97 (77–122)

concentration to be optimized for each application. The use of smaller pellets was first reported in the early 1970s, although the original version produced even smaller pellets (3 mm), and required microscope accessories, thus making it less feasible for routine work.[26] The use of the 5-mm pellets as described here requires attention to strict quantitative methods, but is easily applied.

The method described here is for the analysis of quartz in impactor samples using FT-IR. Results of the experimental evaluation of the method shows it to be sensitive, precise, and capable of handling the major sources of spectral interferences encountered in the construction environment. This method evaluation procedure is the first step toward a more standardized exposure assessment and analysis method for size selective sampling and analysis for quartz. A formal method evaluation procedure such as that described by NIOSH in its *Guidelines for Air Sampling and Analytical Method Development and Evaluation* is the next step if this method is to have broader and regular application in the analysis of quartz.[29] In the meantime, the present method evaluations show that it will serve well during the transition period to a more standard method.

The evaluation of the method sensitivity shows it to be capable of detecting quartz as low as 1.3 μg per sample using the 5-mm pellets. The LOD achieved with this method is substantially lower than the commonly accepted LOD for IR method, which is generally in the range of 5–10 μg.[14,30] However, studies have reported LODs that approach the LOD achieved by the present method. A study using FT-IR for the direct on-filter analysis of quartz reported an LOD of 2.9 μg for the 798 cm^{-1} peak.[31] Comparable LODs of 1 μg have also been reported in studies using the XRD method for quartz analysis.[8,14] The high method sensitivity permits the monitoring of low levels of quartz from occupational and environmental settings, and facilitates the discussion on lowering the respirable quartz exposure limit to make it more consistent with its designation as a lung carcinogen.

This method has improved precision in quantifying quartz. The CV of the method ranged from 7–9 percent for the quartz loading of 62 μg and 6 μg, respectively, representing the low- to midrange of filter loading. For PAT data, the CV was estimated from 13 replicates of 4 samples, and was found to be 14 percent (range: 4.6–23.7%).[10] Moreover, recoveries from filters spiked with quartz in the range of 14–121 μg were 89–112 percent, with a mean of 101 percent. In comparison, the filter loading for the quality control studies of PAT samples ranged from 38–173 μg, with average recovery of 102 (range: 84–117%).[10] The present method shows improved quality control and equivalent recoveries from filters spiked with quartz.

Generally, recoveries from mixtures of Min-U-Sil 5 and the various matrices studied were good. The present work shows that interference from amorphous silica and kaolinite is not significant. The bias in quantification from the mixture samples of amorphous silica and kaolinite were typically < 5 μg. Clearly, the effect of amorphous silica on quartz quantification using the 798 cm^{-1} can't be eliminated with the present method, but can be minimized and verified by comparing with the 696 cm^{-1} peak. Nevertheless, in the present study, amorphous silica was found in only a few samples where fly ash was a significant contaminant, accounting for a small percentage of samples (less than 3%).

TABLE III

Analysis of NIST-certified filters spiked with a mixture of respirable quartz and clay at the 798 cm^{-1} and 696 cm^{-1} peaks

NIST standard (SRM 2679a)		13-mm Pellet	
n	Certified amount of quartz (μg)	Quantified (μg) 798 cm^{-1} peak	Quantified (μg) 696 cm^{-1} peak
1	≤ 2	Not detected	Not detected
1	27.4–34.2	29.9	30.4
1	76.1–84.3	80.0	82.0
1	194.0–211.4	201.7	206.0

TABLE IV

Recoveries of quartz from filters spiked with mixtures of amorphous silica and Min-U-Sil 5 for the 13-mm pellets

Mixtures [A]bias and range	Min-U-Sil 5 high (>30 μg)	Min-U-Sil 5 low (≤ 30 μg)
Amorphous silica High (>200 μg)	N = 5 Bias = 4.3 μg Range = 0.3–11.4 μg	N = 4 Bias = 3.7 μg Range = 0–6.6 μg
Amorphous silica Low (≤ 200 μg)	N = 4 Bias = 4.2 μg Range = 1.0–8.8 μg	N = 4 Bias = 0.32 μg Range = 0–1.6 μg

[A] Bias = [Quartz quantified (μg) − Quartz spiked (μg)]/N.

TABLE V

Recoveries of quartz from filters spiked with mixtures of kaolinite and Min-U-Sil 5 for the 13-mm pellets

Mixtures [A]bias and range	Min-U-Sil 5 high (>30 μg)	Min-U-Sil 5 low (≤30 μg)
Kaolinite	N = 3	N = 3
High (>200 μg)	Bias = 5.8 μg	Bias = 4.7 μg
	Range = 4.7–7.7 μg	Range = 0.7–10.3 μg
Kaolinite	N = 3	N = 2
Low (≤200 μg)	Bias = 4.9 μg	Bias = 2.0 μg
	Range = 3.2–7.4 μg	Range = 0.1–4.0 μg

[A] Bias = [Quartz quantified (μg) − Quartz spiked (μg)]/N.

Previous studies of the effect of matrix on quartz quantification using mixture samples have generally used higher amounts of quartz in the mixture samples (generally > 30 μg) and have reported a more severe effect from interference.(8,32) Negative bias of 6–10 percent in quantifying quartz has been reported in a study that evaluated mixture samples containing 1 mg of coal dust and quartz in the range of 50–200 μg.(8) The study further reports an error of 20 percent in quartz quantification due to the presence of 100 μg of kaolinite. Other studies have reported < 30 μg positive error introduced in the quantification of quartz due to unashed kaolinite.(26)

The most common and abundant source of contaminant (or sample matrix) is clay or concrete dust. The average recovery from clay mixtures was 100 percent, with a range of 95–106 percent. These results are very encouraging since clay is the most dominant matrix for samples collected from construction sites. Concrete is another dominant matrix for samples collected from construction sites, but generally gave low recoveries. Since both concrete and clay had very similar absorbance spectra, they were expected to have similar recoveries. The discrepancy in the recoveries could not have been entirely due to spectral interferences, but, instead, due mainly to the lack of certainty in the amount of quartz present in the concrete bulk sample used in these experiments. Specifically, since the concrete bulk sample was obtained by manually crushing concrete, a wide range of particle size of the material was generated. This range of particle size could easily have resulted in the observed range of quartz content of the concrete bulk sample.

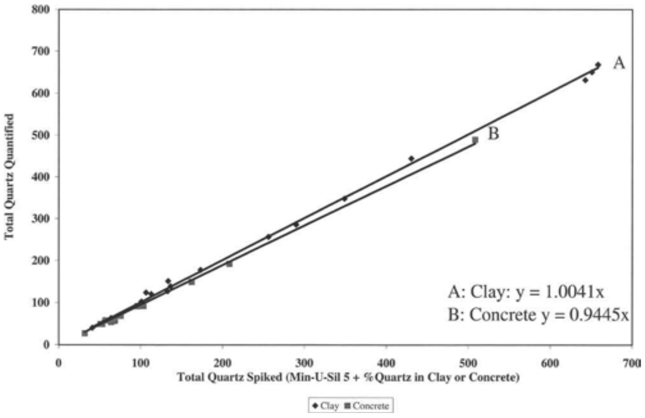

FIGURE 7

Quartz quantification in the presence of clay and concrete: Regression curves showing the amount of quartz spiked on filters versus the amount quantified in the presence of clay and concrete matrix.

The mixture samples used in evaluating this method included very low levels of Min-U-Sil 5 in mixtures with high contaminant to Min-U-Sil 5 ratio. This is a more rigorous evaluation of the method than has generally been carried out, but is necessary if the method is to have widespread application. The experimental evaluation of this method shows its suitability for its present application or its application in construction environments with similar exposures and background matrix. Further experimental evaluations and improvements are needed to apply this method to quantify quartz in other occupational or environmental settings.

Since particle size is known to effect IR absorbance, separate quartz calibration curves were developed to be used with the different particle sizes collected by the impactor sampler, and is reported in detail elsewhere.(12) In general, IR absorbance is greater for smaller particle sizes. The calibration curves prepared using Min-U-Sil 5 correspond to particles with a cumulative count distribution (98%) less than 8 μm aerodynamic equivalent diameter. The particle diameters were reported as Stokes equivalent spherical diameter, which were converted to aerodynamic equivalent diameter using equation (3.28) in Hinds (1982).(33) The range of particle sizes in the standard compared well with the range of particles collected by the sampler. For the respirable fraction of the personal impactor, the cumulative count distribution (ca. 98%) is 10 μm, while that for its corresponding Min-U-Sil 5 standard is 8 μm. Min-U-Sil 5 and SRM 1878a had similar particle size distributions with median particle size diameter around 1.6 μm.(19,20)

Purity of Min-U-Sil 5 was investigated by comparing its coefficient of calibration with that of SRM 1878a. Both these materials had identical coefficients of calibration suggesting that the batch of Min-U-Sil 5 was acceptably pure. The equivalence of FT-IR response for Min-U-Sil 5 and SRM 1878a has also been previously documented in literature.(34) The SRM 1878a is reported to be 100.00 percent(20) pure crystalline α-quartz, while Min-U-Sil 5 is 99.0 percent(19) pure crystalline α-quartz. Moreover, the particle size distributions of SRM 1878a and Min-U-Sil 5 are very similar over a range of particle size (< 1–10 μm), as observed by overlaying the size distributions of the two materials. These materials have identical median and 90th percentile values of 1.6 μm and 3.8 μm, respectively.(19,20)

Despite these agreements and Min-U-Sil 5 being one of the commonly used reference materials, there is some concern about using noncertified material for generating calibration curves. At the 1999 AIHCE conference in Toronto, a meeting was held to discuss silica reference materiall, during which NIOSH and other researchers cautioned against using Min-U-Sil 5 or other materials of uncertified origin due to impurities in them as well as high batch-to-batch variability. We acknowledge the necessity of using certified material in generating calibration curves. However, when certified reference material is not available as in the case of quartz in larger particle size (for estimating the thoracic and inhalable exposures), the present results show that Min-U-Sil can be used as an alternative reference material to generate calibration curves to quantify quartz. This issue is further discussed in the companion article.(12)

CONCLUSION

Application of the FT-IR for quartz analysis has advantages over the other methods that use IR. These advantages include a lower LOD, improved precision, and a minimization of interferences. Sample concentrations in 5-mm pellets can be easily implemented in any lab that uses normal KBr disc method without incurring significant extra expenses. The method can find applications in environmental and industrial hygiene surveys of quartz exposures, especially for low levels of quartz. Monitoring quartz exposure to particles in the thoracic and inhalable size ranges is an important advancement, and is further discussed in a companion article.(12) This method is able to estimate with reasonable accuracy quartz exposure of workers in the construction operations by using the 5-mm pellet method with FT-IR and the appropriate calibration curves for different particle sizes to analyze personal impactor samples. It is believed that this method will be useful for hazard surveillance and epidemiological studies, specifically for exposure surveillance of inhalable, thoracic, and respirable quartz exposures of construction workers.

ACKNOWLEDGMENT

This study was funded by NIOSH through a cooperative agreement with the Center to Protect Workers Rights (CPWR) (#60/CCU317202-01). The authors thank Professor Richard Gore of the Department of Environmental, Earth and Atmospheric Sciences for his support in providing us with a number of mineral standards. We also acknowledge the contribution of Todd Burnham in performing the initial laboratory analysis of the samples.

REFERENCES

1. International Agency for Research on Cancer (IARC): IARC Monograph on the Evaluation of Carcinogenic Risks to Humans: Silica, Some Silicates, Coal Dust and Para-Aramid Fibrils: Volume 68. IARC, Lyon, France (1997).
2. American Thoracic Society: Adverse Effects of Crystalline Silica Exposure. Am J Resp Crit Care Med 155:761–765 (1997).
3. Greaves, I.A.: Not-So-Simple Silicosis: A Case of Public Health Action. Am J Indus Med 37:245–251 (2000).
4. Checkoway, H.; Franzblau, A.: Is Silicosis Required for Silica Associated Lung Cancer? Am J Indus Med 37:252–259 (2000).
5. Soutar, C.A.; Robertson, A.; Miller, B.G.; et al.: Epidemiological Evidence on the Carcinogenicity of Silica: Factors in Scientific Judgement. Ann Occup Hyg 44(1):3–14 (2000).
6. Siemiatycki, J.; Dewar, R.; Lakhani, R.; et al.: Cancer Risks Associated with 10 Inorganic Dusts: Results from a Case-Control Study in Montreal. Am J Indus Med 16:547–567 (1989).
7. Center to Protect Workers Rights (CPWR): Patterns of Death Among Construction Workers, California 1979–81, Report Number D-93. CPWR, Washington, DC (December 1993).
8. Lorbrau, C.D.; Abell, M.T.: Section 2. Silica Sampling, Industrial Hygiene and Modeling. Scand J Work Environ Health 21 suppl.(2):35–38 (1995).
9. Shulman, S.A.; Groff, J.H.; Abell M.T.: Performance of Laboratories Measuring Silica in the Proficiency Analytical Testing Program. Am Indus Hyg Assoc J 53(1):49–56 (1992).
10. Eller, P.E.; Feng, H.A.; Song, R.S.; et al.: Proficiency Analytical Testing (PAT) Silica Variability. Am Indus Hyg Assoc J 60:533–539 (1999).
11. Griffiths, P.R.; de Haseth, J.A.: Fourier Transform Infrared Spectroscopy. John Wiley and Sons, Inc., New York (1986).
12. Bello, D.; Virji, M.A.; Woskie, S.R.; et al.: Quantification of Respirable, Thoracic and Inhalable Quartz by FT-IR in Impactor Samples from Construction Sites. Applied Occupational and Environmental Hygiene, in press.
13. Camp Dresser and McKee Inc.: Environmental Consequences of Utilizing Boston Blue Clay in Landfill Closure: Final Report Subtask #8.2, Prepared for Massachusetts Department of Public Works, pp. 3–7 (1991).
14. Madsen, F.A.; Rose, M.C.; Cee, R.: Review of Quartz Analytical Methodologies: Present and Future Needs. Appl Occup Environ Hyg 10(2):991–1002 (1995).
15. Ferraro, J.R. (Ed.): The Sadtler Infrared Spectra Handbook of Minerals and Clays. Sadtler Research Labs. Inc., Philadelphia (1982).
16. Van der Marel, H.W.; Beutelspacher, H.: Atlas of IR Spectroscopy of Clay Minerals and Their Admixtures. Elsevier, Amsterdam (1976).
17. Lofgren, D.J.: Silica Exposures for Concrete Workers and Masons, Case Studies, D. Tharr, (Ed.). Appl Occup Environ Hyg 8(10):832–836 (1993).
18. National Institute of Occupational Safety and Health (NIOSH): Manual of Analytical Methods, 4th ed: Silica, Crystalline by IR Method 7602. NIOSH, Cincinnati, OH (1994).
19. U.S. Silica: Product Data Min-U-Sil-5. Berkeley Springs, WV (October 1998).
20. National Institute of Standards and Technology (NIST): Standard Reference Material 1878a, Respirable Alpha Quartz. NIST Certificate of Analysis. NIST, Washington, DC (August 1999).
21. Woskie, S.R.; Kalil, A.J.; Bello, D.; et al.: Exposures to Quartz, Diesel, Dust and Welding Fumes in Heavy and Highway Construction. American Industrial Health Association Journal, in press.
22. American Conference of Governmental Industrial Hygienists (ACGIH): Threshold Limit Values for Chemical Substances and Physical Agents. ACGIH, Cincinnati, OH (1998).
23. National Institute of Standards and Technology (NIST): Standard Reference Material 2679a, Quartz on Filter Media. National Bureau of Standards Certificate. NIST, Washington, DC (April 1997).

24. Skoog, D.A.; West, D.M.; Holler, F.J.: Fundamentals of Analytical Chemistry, Sixth ed., pp. 53–54. Saunders College Publishing, New York (1992).
25. Foster, R.D.; Walker, R.F.: Quantitative Determination of Crystalline Silica in Respirable-Size Dust Samples by Infrared Spectrophotometry. Analyst 109:1117–1127 (1984).
26. Dodgson, J.; Whittaker, W.: The Determination of Quartz in Respirable Dust Samples by Infrared Spectrophotometry-I: The Potassium Bromide Disc Method. Ann Occup Hyg 16:373–387 (1973).
27. Larsen, D.J.; von Doenhoff, L.J.; Crable, J.V.: The Quantitative Determination of Quartz in Coal Dust by Infrared Spectroscopy. Am Indus Hyg Assoc J 33:367–372 (1972).
28. Miles, W.J.: Issues and Controversy: The Measurement of Crystalline Silica; Review Papers on Analytical Methods. Am Indus Hyg Assoc J 60:396–402 (1999).
29. NIOSH: Guidelines for Air Sampling and Analytical Method Development and Evaluation. NIOSH DHHS Publication No. 95-117. NIOSH, Cincinnati, OH (1995).
30. Eller, P.M.; Key-Schwartz, R.J.; Song, R.; et al.: Silica Method Modifications for Improved Interlaboratory Precision. Technical Exchange. The Synergist, pp. 23–24 (November 1999).
31. Lorberau, C.: Investigation of the Determination of Respirable Quartz on Filter Media Using Fourier Transform Infrared Spectrophotometry. Appl Occup Environ Hyg 5(6):348–350 (1990).
32. Nieto, J.L.: Infrared Determination of Quartz, Kaolin, Corundum, Silicon Carbide and Orthoclase in Respirable Dust from Grinding Wheels. Analyst 103(2):128–133 (1978).
33. Hinds, W.C.: Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles. John Wiley and Sons Inc., New York (1982).
34. Verma, D.K.; Sebestyen, A.; Julian, J.A.; et al.: A Comparison of Two Methods of Sampling and Analysis for Free Crystalline Silica α-Quartz. Appl Occup Environ Hyg 7(11):758–763 (1992).