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Publisher: Taylor & Francis

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Applied Occupational and Environmental Hygiene

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/uaoh20>

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Version of record first published: 30 Nov 2010

To cite this article: Dhimiter Bello, M. Abbas Virji, Andrew J. Kalil & Susan R. Woskie (2002): Quantification of Respirable, Thoracic, and Inhalable Quartz Exposures by FT-IR in Personal Impactor Samples from Construction Sites, Applied Occupational and Environmental Hygiene, 17:8, 580-590

To link to this article: <http://dx.doi.org/10.1080/10473220290095853>

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Quantification of Respirable, Thoracic, and Inhalable Quartz Exposures by FT-IR in Personal Impactor Samples from Construction Sites

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The classification of quartz as a group I human carcinogen by the International Agency for Research on Cancer (IARC) highlights the need to develop a method to assess quartz exposures in the thoracic and inhalable particle size fractions to supplement the current method for the respirable size fraction. Heavy and highway construction operations can produce high respirable quartz exposures, but inhalable and thoracic exposures have not previously been well characterized. These larger particle size fractions may well contribute to the elevated cancers of the buccal cavity, throat, and GI tract in occupational cohorts of construction workers. A description is provided of the application of FT-IR for quartz analysis of personal cascade impactor air samples collected from highway construction sites. Separate calibration curves were generated for each stage of the four-stage personal impactor by using the impactor to sample quartz dust (Min-U-Sil 5 and Min-U-Sil 30) in an aerosol-generating loop. In addition, three separate calibration curves were generated using filters spiked with bulk Min-U-Sil 5, Min-U-Sil 30, and SRM 1878a (a respirable standard from NIST). The results showed that bulk Min-U-Sil 5 and SRM 1878a calibrations were identical and accurately estimated the respirable quartz fraction. Bulk Min-U-Sil 30 underestimated quartz in stages 1, 2, and 3 by 46 percent, 38 percent, and 18 percent, respectively. Using a respirable standard (bulk Min-U-Sil 5 or SRM 1878a) to quantify the larger particle sizes underestimated quartz in stages 1, 2, and 3 by 73 percent, 72 percent, and 63 percent, respectively. Until a standard reference material for quartz is developed for the larger particle sizes, the method described here, with some modifications, can be used to provide estimates of these biologically relevant particle size fractions. The results of this study also reaffirmed the need to collect narrow ranges of particle size in order to minimize quantification errors, since the FT-IR and XRD instrumental response is particle size-dependent.

Keywords Construction, Exposure Assessment, Fourier Transform Infrared Spectrophotometry (FT-IR), Min-U-Sil, Personal Impactor, Quartz, Respirable, Thoracic, Inhalable, Silica, Size-Selective Sampling

The research presented here was conducted as part of a surveillance and intervention study of quartz exposures of construction workers in heavy and highway construction on the Boston Central Artery Tunnel (CA/T) project. 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 such as the mechanical disruption of cured concrete or rocks during concrete demolition or finish work (through drilling, grinding, crushing), the movement of soil or clay for excavation, and the mixing of construction materials that contain quartz. During these activities, large quantities of quartz-containing dust in a wide range of particle sizes may be released into the environment, potentially exposing construction workers operating the equipment as well as other workers and bystanders.

Construction is one of the largest industries in the United States. Frequent violations of the Occupational Safety and Health Administration's (OSHA) permissible exposure limit (PEL) for respirable quartz have been documented.^(1,2) Our early work in highway construction also found high exposures to respirable quartz, especially in powered tool operations such as cutting, drilling, or chipping concrete, and jack hammering.^(3,4)

Quartz has been classified as a carcinogen by the International Agency for Research on Cancer (IARC) and the National Toxicology Program (NTP).^(5,6) However, controversy still surrounds the issue of the causal pathway among silica, silicosis, and lung cancer.^(7–10) A number of studies of construction workers working in jobs with exposure to crystalline silica and/or construction dust have reported increased risk of cancers of the gastrointestinal (GI) tract (buccal cavity, colon, stomach, pharynx).^(11–16)

However, none of these epidemiological studies of construction workers utilized silica exposure data in their analysis.

Exposures to thoracic and inhalable quartz are the size fractions more likely to be associated with diseases in the upper parts of the respiratory system and in the digestive organs. Yet there is very little data on quartz exposures for these size fractions. An earlier study reported exposure levels of agricultural workers to respirable and inhalable quartz during various operations using cyclones and IOM samplers.⁽¹⁷⁾ Samples were analyzed for quartz by X-ray diffraction (XRD) using NIOSH method 7500, which requires the use of a respirable standard reference material to quantify quartz. Another study used a high volume multiple stage cascade impactor to characterize particle size distribution of dust and crystalline silica in Ontario gold mines.⁽¹⁸⁾ The study used dispersive infrared (IR) spectroscopy and a (respirable) standard reference material with median diameter of 2–3 μm to quantify quartz in all size fractions.

Although these studies represent an important step in expanding the exposure assessments for quartz, the analytical method used for the larger particle size fractions would have introduced errors in the exposure estimates. However, standard reference material for the larger particle sizes was not available then or now. The purpose of this article is to propose some improvements in an attempt to quantify the thoracic and inhalable size fractions of quartz. Due to the potential carcinogenicity of quartz, OSHA's Silica Special Emphasis Program (SEP) and the proposal to revise the OSHA silica standard, we believe that efforts to develop particle size-selective standards for quartz exposures should be a priority.

ANALYTICAL ISSUES

At the root of the problem in developing thoracic and inhalable quartz standards is the fact that the analytical response of quartz for XRD and IR spectroscopy is particle size-dependent. Bhaskar et al. (1994) studied the influence of particle size of quartz (Min-U-Sil 5 and 30) on the instrument response for Fourier-Transform IR (FT-IR) and XRD in the particle size range of 1.53–19.89 μm mass median diameters (MMD).⁽¹⁹⁾ Calibration curves of instrument response for FT-IR and XRD versus quartz load were then developed for each well-characterized particle size range. Their analyses showed that FT-IR has a maximum response for particles with a median diameter <3.42 μm (at the 798 cm^{-1} peak). This response is about 2.5 times stronger than that for an equal mass of particles with a median diameter of 10.56 μm , and about 11 times stronger than particles with a median diameter of 19.89 μm . The particle size dependency of FT-IR response is strongest for particles in the respirable and thoracic range (1 to 15 μm). Although the inhalable fraction contains particles up to 100 μm , extrapolation from the work by Bhaskar et al.⁽¹⁹⁾ suggests that instrument response may not vary as much for larger particles >20 μm . Their work further suggests that for an accurate quantification of quartz, the particle size distribution of the standard material used should

match the particle sizes of the sample collected after sample preparation.

The analytical response of quartz for XRD is also particle size-dependent, although the effect is in the opposite direction. Whereas the instrumental response for FT-IR increases with decreasing particle size, for XRD the response increases with increasing particle size.

At present, only a respirable quartz standard reference material (SRM 1878a) is available from the National Institute of Standards and Technology (NIST).⁽²⁰⁾ Ideally, standard reference materials for larger particle size fractions should be developed to facilitate the quantification of thoracic and inhalable fractions.

From a sampling standpoint, it would be desirable to use a validated thoracic or inhalable sampler. However, these samplers collect such a wide range of particle sizes that it would be difficult to accurately quantify such samples. We believe that the next best approach is to collect samples using an impactor to fraction the quartz into narrow size fractions so that changes in instrument response across these particle size ranges are minimal, and then use a commercial quartz material to generate standards whose particle size fraction matches the impactor samples.

As an alternative, this article also investigated the use of SRM 1878a, bulk Min-U-Sil 5, and Min-U-Sil 30 as direct standards for the quantification of the impactor stages. Finally, we report the results of personal exposures to the inhalable and thoracic size fractions of quartz by construction phases.

METHOD

Sample Collection

Personal breathing zone air samples, with a duration of approximately six hours, were collected on construction workers on the Boston Central Artery/Tunnel project (CA/T).⁽²¹⁾ A Marple four-stage personal impactor sampler with inlet cowl and visor (Model 294; Graseby Anderson Smyrna, Atlanta) operated at 2 liters per minute (L/min) was used for sample collection. For the impactor samples, Mylar filters were used for the upper four stages, and a PVC filter was used for the final stage. Apiezon-L grease coating (Supelco, Bellefonte, PA) was applied to the Mylar filters. The coating solution was prepared by mixing 20 percent Apiezon-L grease with 80 percent toluene by weight.⁽²²⁾ Approximately 1–2 mg of the coating was sprayed on the filters using an artist's air brush set at 5–10 psi. No interference was observed at the major quartz peak (798 cm^{-1}) from the apiezone coating.

The impactor samplers collected dust in the particle size range of >20 μm (stage 1), between 20 and 15 μm (stage 2), between 15 and 9.8 μm (stage 3), between 9.8 and 3.5 μm (stage 5A), and <3.5 μm (final filter F). Corrections for impactor inlet efficiency and interstage particle losses were made using the manufacturer's recommended method.⁽²³⁾ The method of Simpson's rule in a tabular-graphical procedure was used to estimate the three size fractions—inhalable, thoracic, and respirable from the impactor stages.⁽²⁴⁾ Appendix A contains the correction factor,

particle size range, midpoint and fraction of each stage used to estimate the respirable, thoracic, and inhalable particulate mass concentrations.

To test the performance of the impactor sampler and the algorithm used to estimate the respirable dust fraction, a set of 47 paired personal impactor samplers and BGI-4 (BGI Company, Waltham, MA) respirable cyclones were collected. The BGI-4 respirable cyclone was operated at 2.2 L/min and loaded with a 5 μm PVC filter (SKC, Eighty Four, PA). The samplers were operated by separate personal pumps and were positioned on the breathing zone of the worker, with the impactor on the right side. Filters were analyzed gravimetrically, and a paired t-test was performed on the respirable cyclone and the calculated respirable fraction from the impactor data.

Sample Analysis

The filters for each stage of the impactor sampler were first analyzed gravimetrically and then for quartz using FT-IR.⁽²⁵⁾ Originally, the impactor stages were combined to ensure quartz levels above the limit of quantification and to reduce the number of samples to be analyzed. Stage 1 was analyzed separately and contained dust in the particle size of $>20 \mu\text{m}$, stages 2 and 3 were combined and contained dust in the particle size range of 20–9.8 μm , and stage 5A was combined with the final filter F and contained dust in the particle size of $<9.8 \mu\text{m}$.

Filters were ashed and KBr pellets (13 mm or 5mm) were prepared and analyzed by Nicolet-Magna 550 FT-IR (Nicolet Instrument Corp., Madison, WI). The details of this method are described in a previous paper.⁽²⁵⁾ Briefly, two spectra of 64 scans each were collected and averaged. Spectra were deconvoluted using an enhancement factor of 1.5 and bandwidth of 10, except for stage 1 of samples and standard pellets, and Min-U-Sil 30 standard pellets, for which an enhancement factor of 1.5 and bandwidth of 16 was used. Quartz was quantified at its major peak at 798 cm^{-1} . The weaker absorbance at 696 cm^{-1} was also measured for comparison purposes. The method limit of detection (LOD) for the impactor stages was determined from seven nondetectable samples that contained the filter and the sample matrix, and was 1.5 μg for the combined stages 5A and F, 3 μg for the combined stages 2 and 3, and 4 μg for stage 1.

Impactor Stage-Specific Calibrations

The purity of Min-U-Sil 5 was previously investigated by examining the calibration curves for Min-U-Sil 5 compared to SRM 1878a.⁽²⁵⁾ Both these materials had identical calibration curves, suggesting that Min-U-Sil 5 obtained for this work was of acceptable quality. At present, there are no means of investigating the purity of Min-U-Sil 30, since a standard reference material for larger particles is not available.

Separate calibration curves were generated for each of the four stages and the final filter of the impactor by sampling in an aerosol generation loop. Min-U-Sil 5 was used for stages 5A and F, whereas Min-U-Sil 30 was used for all other stages. Min-U-Sil 5 has a respirable particle size range with cumulative

count distribution (98%) $<5 \mu\text{m}$ Stokes equivalent spherical diameter,⁽²⁶⁾ corresponding to aerodynamic equivalent diameter of 8 μm . Min-U-Sil 30 has a wider range of particle sizes with cumulative count distribution (98%) $<30 \mu\text{m}$ Stokes equivalent spherical diameter,⁽²⁷⁾ corresponding to aerodynamic equivalent diameter of 49 μm .

The aerosol generation loop was configured as a closed horizontal settling chamber with a 1 ft^2 area. A HEPA filter was in-line on the return side of the fan. The calibration impactors, without the cowl and visor, were positioned inside the aerosol-settling chamber with the inlets parallel to the flow of air. The aerosol was introduced into the ductwork directly before the settling chamber. Generally, the samples were in the chamber for 10 minutes. Air flow inside of the settling chamber was set at 50 fpm, close to the inlet velocity of the impactor to allow for isokinetic sampling of the aerosol. The air velocity in the settling chamber was verified using a hot wire anemometer (TSI VelociCalc, St. Paul, MN) by spanning the chamber and calculating the average velocity. The Wright Dust Feeder II (BGI, Inc., Waltham, MA) was used to generate the aerosol. Quartz (as Min-U-Sil 5 or 30) was packed, in small amounts at a time, into the dust chamber of the feeder using a hydraulic press at 4000 psig, and misting the cake between the pressings to ensure consistency by preventing the powder cake from breaking up. Air flow into the feeder was set at about 25 Lpm. Speed of the feeder was set at 0.050 rpm with some variation to allow for creating a higher or a lower Min-U-Sil concentration in the sampling chamber.

The quartz load on filters was determined gravimetrically. The filters were then treated in a similar manner as samples. Separate calibration curves, with an average of six data points, were generated for each stage of the impactor and the final filter. The amount of quartz collected on the impactor substrates ranged from 29–132 μg on stage F, 17–141 μg on stage 5A, 16–181 μg on stage 3, 34–229 μg on stage 2, and 22–330 μg on stage 1.

Estimating Quartz on Individual Impactor Stages

When field samples were analyzed, the individual impactor stage calibration curves were applied to each sample impactor stage. However, most of the impactor stages were combined before processing, initially to increase the amount of quartz in the KBr pellet, and later to minimize the sample processing time. In these cases the FT-IR absorbance for the combined stages needed to be partitioned so that the absorbance on each stage could be estimated and the stage-specific calibration curve applied. The combined absorbance was partitioned between the two stages based on the fraction of dust collected on the individual stage. This approach assumes that the fraction of dust and quartz on each stage was equal. For example, absorbance for stage 2 was obtained by partitioning the absorbance of combined stages 2 and 3 based on the fraction of dust on stage 2 as follows:

$$\text{Abs. Stage 2} = \text{Abs. Stages 2 and 3 combined} \times \frac{\text{Dust mass on Stage 2}}{\text{Dust mass on (Stage 2 + Stage 3)}} \quad [1]$$

To assess the validity of this assumption the distribution of dust and quartz across impactor stages was evaluated for a subset of 11 impactor samples for which quartz analysis was performed on individual stages. To estimate the error in quantification resulting from the above procedure, absorbance of the individual stages were summed together corresponding to filters that were added together, that is, stages 2 and 3, and stages 5A and F. The summed absorbances were then partitioned as described above based on the fraction of dust on the individual stages, which were then quantified using stage-specific calibrations. Regression analyses were performed on these data to investigate the relationship between the amount of quartz collected on the individual stages (direct approach) and the amount of quartz estimated for the stage based on the algorithm (indirect approach). A paired t-test was also performed on the quartz load on each stage as measured by the direct approach and as obtained by the indirect approach.

Alternative Bulk Material Calibrations

As an alternative to single-stage calibrations generated in the aerosol chamber, three separate calibration curves were generated using SRM 1878a, bulk Min-U-Sil 5, and Min-U-Sil 30 spiked on filters. The primary purpose of generating these bulk calibration curves was to investigate the possibility of using them as a surrogate for size-selective standards that could be directly used to quantify the impactor stages. This approach would be much easier and more widely applicable than generating standards using the aerosol loop. Standard pellets were prepared by spiking 37-mm PVC filters with bulk SRM 1878a, Min-U-Sil 5, or Min-U-Sil 30, weighed using a microbalance (Cahn C-30, Cahn Instruments Inc., Cerritos, CA). The spiked filters were then ashed and pelletized following the process previously described.⁽²⁵⁾ Standard pellets (5-mm) were prepared in the quartz mass range of 4–126 μg for SRM 1878a calibration curve, 3–130 μg for Min-U-Sil 5 calibration curve, and 3–250 μg for Min-U-Sil 30 calibration curve. The SRM 1878a calibration curve was applied to all of the impactor stages as one alternative approach. As a second approach, the Min-U-Sil 5 calibration curve was applied to individual stages 5A and F of the impactor samples (particles $<10 \mu\text{m}$), while Min-U-Sil 30 calibration curve was applied to individual stages 1, 2, and 3 (particles $>10 \mu\text{m}$).

Utility of Bulk Calibrations in Quantifying Samples

To investigate performance of the bulk SRM 1878a, Min-U-Sil 5, and Min-U-Sil 30 calibration curves in quantifying quartz compared to the single-stage aerosol calibrations generated in the aerosol chamber, each field sample was quantified three times—once using the stage specific calibration curves ($\text{Quartz}_{\text{stage standard}}$), and twice using the bulk calibration curves ($\text{Quartz}_{\text{bulk standard}}$) (once using SRM 1878a and once using Min-U-Sil 5/Min-U-Sil 30). Descriptive statistics and the percent difference were calculated to compare the two alternative quantification approaches to the method of using the

stage-specific calibration curves. The percent difference for each stage and for the respirable, thoracic, and inhalable fractions was calculated as:

$$\% \text{Difference} = 100 \times \frac{\text{Quartz}_{\text{stage standard}} - \text{Quartz}_{\text{bulk standard}}}{\text{Quartz}_{\text{stage standard}}} \quad [2]$$

where:

$\text{Quartz}_{\text{stage standard}}$ = Quartz estimated from aerosol generated single-stage calibration

$\text{Quartz}_{\text{bulk standard}}$ = Quartz estimated from bulk SRM 1878a or Min-U-Sil spike calibration

To improve the performance of the bulk calibration approaches, the mean percent difference ($\% \text{Difference}$) between the quartz mass estimated by the single-stage and bulk calibrations for each stage was then used as a correction factor for the bulk SRM 1878a and Min-U-Sil calibrations. The respirable, thoracic, and inhalable exposures were re-estimated for the samples using the correction factors.

Quartz Quantification for Construction Phases

Quartz was quantified using the individual stage-specific calibrations for the different construction phases (Appendix B). Descriptive statistics were then calculated for quartz collected on the impactor stages and in the respirable, thoracic, and inhalable size fractions for these phases. Exposures were then re-estimated using the bulk SRM 1878a and Min-U-Sil calibrations in conjunction with correction factors and the percent difference ($\% \text{Difference}$) was calculated as described above.

RESULTS

A total of 174 personal impactor samples were used for the analyses by construction phases. The number of samples reported here is different from that reported elsewhere⁽²¹⁾ since in that analysis, the 1 and 2 stage impactor samples, impactor samples analyzed by XRD or with silicone coating, and cyclone samples were also used but are excluded from the present analysis. The number of impactor stages available for the analyses by stages ranged from 157 to 181.

FT-IR Response Across Stages

The particle size dependence of quartz response for FT-IR is apparent from the calibration curves and their regression coefficients (Figure 1). FT-IR response for quartz decreases considerably (almost fourfold) from stage F to stage 1. Responses for stages 5A and F are comparable, but decrease rapidly between stage 5A and stages 3 to 1.

Algorithm Validation

To validate the algorithm used to extract the biologically relevant fractions from the impactor sampler, a paired t-test was used to evaluate the agreement in the amount of respirable dust

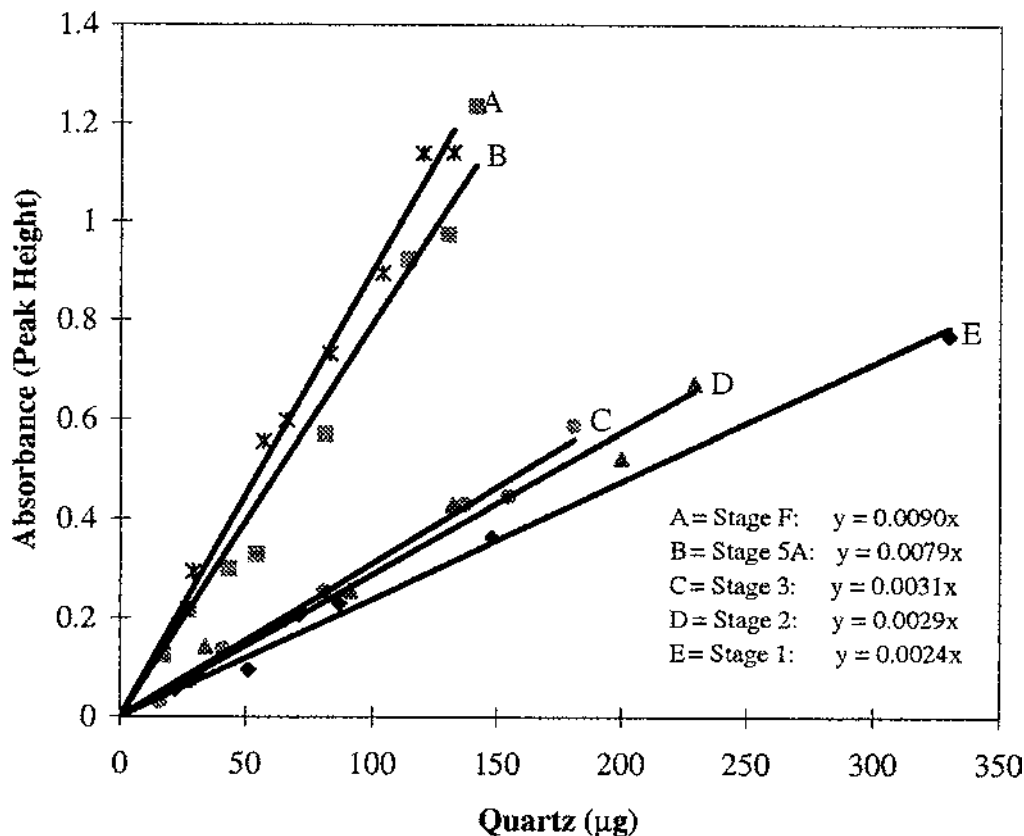


FIGURE 1

Calibration curves for the individual personal impactor stages.

between the respirable cyclone and the impactor estimate. The paired t-test on the log-transformed respirable fractions was not significant ($t = 1.46$, $Pr > t = 0.1518$), indicating that no significant difference existed between the cyclone and impactor respirable dust estimates. The respirable dust concentrations from the 47 paired samples gave geometric mean (GM) of 0.365 mg/m^3 (geometric standard deviation, $GSD = 2.9$) for the respirable cyclone, and $GM = 0.313 \text{ mg/m}^3$ ($GSD = 3.5$) for the impactors. The mean difference on the untransformed scale was 0.006 mg/m^3 (standard deviation, $SD = 0.344$), with the cyclone dust estimate being larger than the impactor estimate.

A direct examination of the distribution of dust and silica mass across the stages for a subset of 11 samples showed it to

be variable (Table I). While there was some agreement between the two distributions for some samples/stages, for others the distributions varied greatly. However, a paired t-test performed to investigate the difference between the amount of quartz collected on the individual stages (direct approach) and the amount of quartz estimated for the stage based on the algorithm (indirect approach) was not significant over all the comparisons ($t = 0.241$ and $Pr > t = 0.81$), as well as by impactor stages.

Plots of quartz measured by the direct and indirect approaches for the impactor stages 2 to F that undergo combination are presented in Figure 2, along with the results of the regression of the indirect approach against the direct approach. The regression coefficients for these plots indicate the error introduced using the

TABLE I

Distribution of dust and quartz mass (average and percent) across impactor stages

Impactor stages	Average dust mass mg (SD)	Fraction of total dust % (SD)	Average quartz mass μg (SD)	Fraction of total quartz % (SD)
Stage 1	3.907 (3.140)	0.38 (0.077)	368 (105)	0.49 (0.063)
Stage 2	1.045 (0.886)	0.31 (0.080)	80 (103)	0.44 (0.199)
Stage 3	0.871 (0.972)	0.23 (0.069)	32 (54)	0.17 (0.069)
Stage 5A	1.036 (1.305)	0.25 (0.081)	20 (33)	0.13 (0.076)
Stage F	0.500 (0.448)	0.14 (0.062)	9 (9)	0.17 (0.161)

*A subset of $n = 11$ impactor samples.

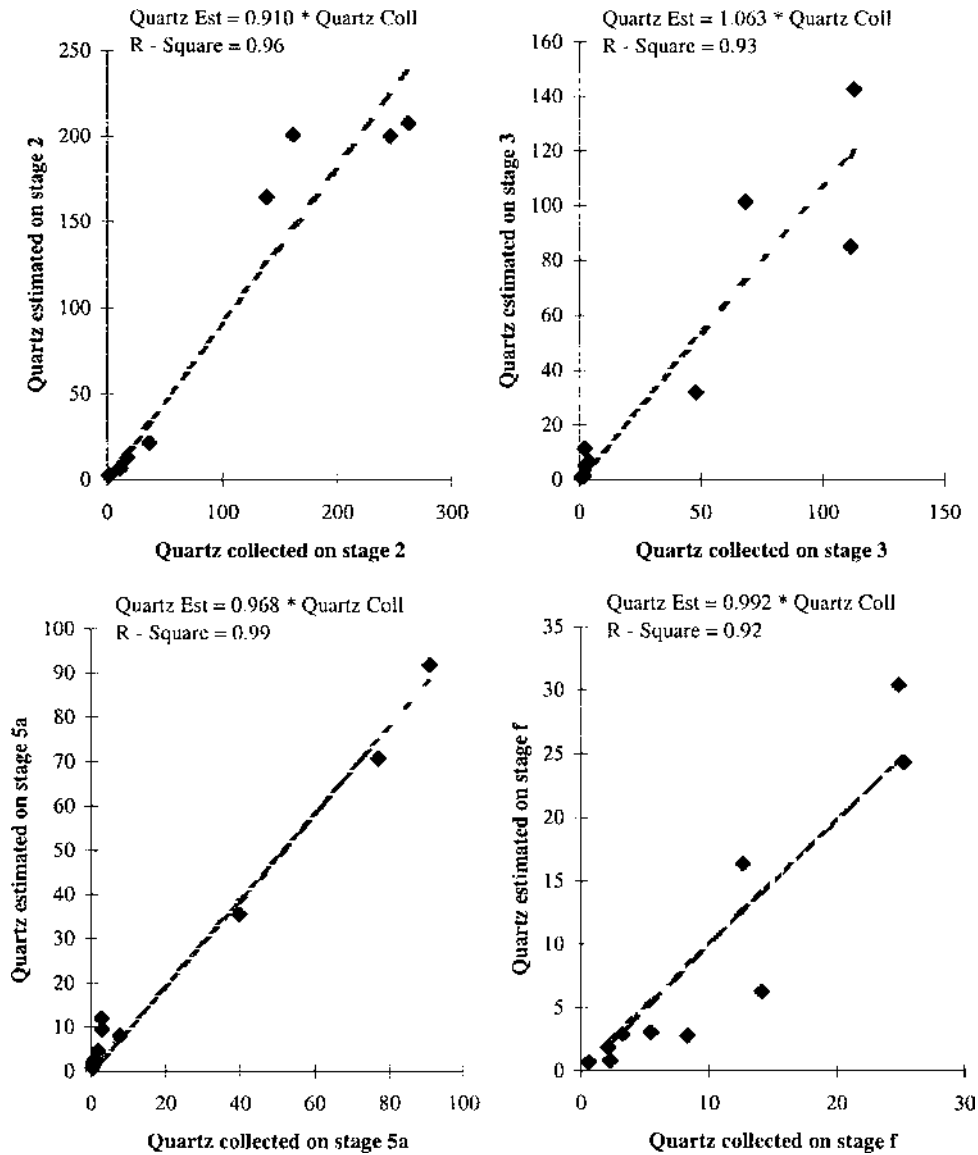


FIGURE 2

Quartz quantified by the direct (collected) and indirect (estimated) approaches for the impactor stages.

indirect approach (partitioning the absorbances of the combined stages based on the distribution of dust on the stages) is dependent on particle size, and is generally <10 percent. Although these errors are not great, improvements in the method⁽²⁵⁾ that reduced the LOD now make it feasible to analyze all stages separately. This approach will improve accuracy but increases analytical time and cost.

Evaluation of Bulk Calibrations

Application of the bulk calibrations (see Figure 3) to quantify quartz on stages 1, 2, and 3 resulted in a significant underestimation of quartz on these stages compared to using the aerosol generated calibration curves for the stages (Table II). Quantification of the respirable fraction using SRM 1878a calibration com-

pared to using the aerosol generated single-stage calibrations resulted in less than $1 \mu\text{g}$ difference (6% error). The thoracic and inhalable fractions, however, are underestimated substantially (an average of 40% and 64%, respectively) when using the SRM 1878a calibration curve compared to using the aerosol generated single-stage calibration curves. The bulk Min-U-Sil 5/Min-U-Sil 30 calibration curves perform better than the SRM 1878a but still underestimate the thoracic and inhalable fractions by 19 percent and 35 percent, respectively. The reason for this underestimation is the presence of a large percentage of the respirable particles in the bulk Min-U-Sil materials, despite a particle size range similar to the corresponding impactor stages.^(26,27) Thus, Min-U-Sil 30 has a much higher content of the respirable particles compared to what is collected by

TABLE II
Differences in the quantification of quartz using separate stage calibration curves versus bulk Min-U-Sil 5 and 30 or SRM 1878a calibration curves

Impactor stages	N	^A Min-U-Sil	^B Min-U-Sil	^A SRM	^B SRM
		mean error (μg)	mean error (%)	mean error (μg)	mean error (%)
1	157	235	46	398	73
2	177	74	38	160	71
3	177	6	18	56	63
5A	181	5	14	5	14
F	181	<1	2	<1	2
Particle size fraction					
Respirable	176	<1	5	<1	6
Thoracic	176	14	19	40	40
Inhalable	176	175	35	352	64

^AQuartz quantified using aerosol sampling stage-specific calibrations (μg)—quartz quantified using bulk Min-U-Sil 5 and 30 or SRM 1878a calibrations (μg).

^BDifference as percent fraction of quartz quantified using stage-specific calibrations, Eq. (2).

the impactor on stages 1 to 3, even though particle size range matches with these fractions.

In an attempt to improve quantification using the bulk calibrations (Min-U-Sil and SRM 1878a), factors to adjust quartz exposures were chosen based on the mean percent difference between the bulk calibrations and the aerosol generated single-stage calibration reported in Table II. The resulting correction factors for Min-U-Sil were 1.46 for stage 1, 1.38 for stage 2, and 1.18 for stage 3. To evaluate the utility of these generic correction factors, each sample was quantified twice, once using calibration curves from the bulk Min-U-Sil 5 and 30 spikes

adjusted by the correction factors, and once using aerosol generated stage-specific calibration curves. The mean percent difference calculated as the difference between quartz quantified by the aerosol generated single-stage calibration and quartz quantified using the bulk Min-U-Sil calibration in conjunction with correction factors is reported for each construction phase (Table III). The results show that the mean percent difference between using the single-stage calibrations and the Min-U-Sil calibrations ranged from 3 to 26 percent for the inhalable concentrations, and from -8 to 17 percent for the thoracic concentrations for the various construction phases (Table III). With the

TABLE III
Differences in quartz quantification using bulk Min-U-Sil 5 and 30 or SRM 1878a as the standard material for calibration in conjunction with correction factors from Table II compared to using separate single-stage calibrations

Construction phase	N	Min-U-Sil 5 and 30 (% error)		SRM 1878a (% error)	
		Thoracic	Inhalable	Thoracic	Inhalable
Build road	15	-2	8	17	43
Build supported excavation	25	6	16	18	44
Caisson work	16	17	26	29	51
Cut and cover	3	16	24	22	45
General contract infrastructure	17	9	18	20	47
Jet grouting	16	5	11	21	40
Roadway demolition	16	2	8	9	33
Slurry wall	31	1	9	13	37
Tunnel finish	6	10	18	15	40
Utility relocation	26	-8	3	10	39
Vertical building construction	3	11	9	9	18

exception of two construction phases, the predicted exposures using the correction factors on average underestimated the thoracic and inhalable concentrations.

A similar approach was used to investigate the use of SRM 1878a calibration curve with correction factors for estimating quartz exposures in the thoracic and inhalable size ranges. The correction factors used from Table II were 1.73 for stage 1, 1.72 for stage 2, and 1.63 for stage 3. The results from Table III show that, compared to the use of single-stage calibrations, the use of SRM 1878a underestimated the inhalable concentration by 18–51 percent, and the thoracic by 9–29 percent in the various construction phases (Table III).

Respirable, Thoracic, and Inhalable Exposures in Specific Construction Phases

Quartz concentrations, estimated using the single stage calibrations, are reported by construction phases in Table IV. From these data, it is clear that the highest quartz exposures in the construction industry are found in the larger particle size fractions (stages 1 and 2). As a result, the inhalable aerosol fraction exceeds the respirable aerosol fraction by an order of magnitude.

DISCUSSION

Given the evidence that quartz may be an upper airways or a GI tract carcinogen^(11–16) it is important that the exposure assessment methods to estimate the biologically relevant thoracic and inhalable particle size be developed. In this and a previous article, we present an approach to estimate quartz exposures in the respirable, thoracic, and inhalable size fractions. The utility of size-selective sampling for quartz can be seen from the exposure data for the construction phases sampled on the Boston CA/T highway construction project. Detailed analysis of the data from this project showed that, on average, thoracic quartz exposures were 4.5 times higher than respirable quartz and that inhalable exposures were 25.6 times higher than respirable exposures.⁽²¹⁾

The major challenge in characterizing quartz in the three biologically meaningful particle size fractions is the particle size dependency of quartz response for the two major analytical instruments used for its quantification, namely XRD and FT-IR. The impact of particle size on quantification of quartz is apparent when two samples contain the same mass of quartz but with different particle size distributions is analyzed. The sample with a predominance of smaller particles will have a larger IR absorbance than the sample with the predominance of larger

TABLE IV
Quartz exposure levels for construction phases by impactor stage and biologically relevant fractions

Construction phase	Impactor stage mean $\mu\text{g}/\text{m}^3$ (SD)					Particle size fraction mean $\mu\text{g}/\text{m}^3$ (SD)		
	1	2	3	5A	F	Respirable	Thoracic	Inhalable
Build road	326 (241)	142 (148)	52 (62)	19 (23)	8 (10)	10 (12)	53 (57)	294 (374)
Build supported excavation	480 (400)	175 (190)	85 (86)	39 (55)	21 (26)	26 (30)	100 (108)	520 (448)
Caisson work	369 (411)	75 (53)	36 (23)	6 (4)	8 (4)	8 (4)	35 (18)	317 (276)
Cut and cover	115 (4)	68 (26)	32 (11)	16 (12)	8 (4)	10 (5)	38 (17)	157 (37)
General contract infrastructure	215 (195)	60 (41)	31 (23)	11 (7)	7 (5)	8 (5)	32 (17)	196 (138)
Jet grouting	338 (757)	79 (86)	48 (58)	16 (25)	6 (5)	9 (8)	46 (49)	311 (504)
Roadway demolition	158 (121)	94 (66)	44 (39)	35 (48)	14 (15)	18 (21)	64 (68)	218 (173)
Slurry wall	314 (361)	139 (159)	42 (42)	16 (22)	12 (17)	13 (19)	49 (52)	247 (247)
Tunnel finish	386 (284)	327 (360)	147 (139)	74 (55)	68 (119)	72 (114)	203 (229)	680 (648)
Utility relocation	510 (884)	369 (851)	165 (384)	74 (168)	22 (50)	31 (69)	168 (359)	680 (1440)
Vertical building construction	75 (53)	42 (34)	29 (23)	32 (27)	9 (6)	13 (10)	46 (35)	129 (95)

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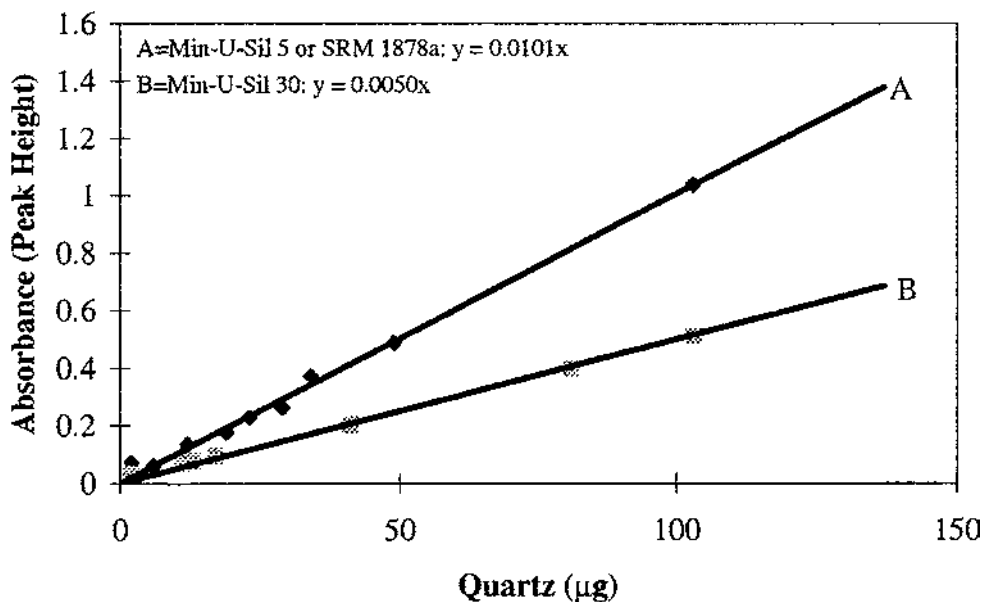


FIGURE 3

Calibration curves for bulk Min-U-Sil 5, Min-U-Sil 30, and SRM 1878a.

particles. If the same calibration is applied to the two samples, the amount of quartz in the sample containing larger particles will be underestimated. Since the larger particles are very common in the construction environment, use of an inappropriate (respirable) calibration curve will cause an underestimation of quartz levels for samples containing larger particles. Use of XRD analysis with a respirable calibration curve will result in overestimation of the quartz level for the same samples, because the particle size effect for XRD analysis is the reverse of the FT-IR.

The results of the present study clearly show the particle size dependence of quartz response for FT-IR. The response (slope of calibration curve) decreased by a factor of four from the final filter (stage F) to stage 1. These results are in agreement with the work of Bhaskar et al.⁽¹⁹⁾ who described the particle size dependence of quartz response for FT-IR and XRD. This emphasizes the need to collect narrow particle size range on a filter to minimize the quantification error, and brings forth the discussion on selecting the appropriate sampling device. The personal impactor is useful because it collects narrow particle size ranges. However, it also has several problems, including internal losses, limited entry of large particles into the inlet, potential for particle bounce and overload, and the need to use algorithms to estimate the inhalable, thoracic, and respirable fractions. The high flow impactors used by Verma et al.⁽¹⁸⁾ to estimate quartz exposure in the larger particle size fractions avoid any limit of detection issues present for personal impactors but have the drawback of being an area sampler. Samplers that directly collect the biologically relevant size fractions such as the thoracic cyclones, inhalable samplers, or other specialty samplers collect a wider range of particle sizes on the sampling media, making quantification less accurate. For these samplers, the mass of each particle size collected on the sampling media will also depend on the

particle size distribution in the air. Thus, a universal reference material for inhalable or thoracic samplers could still produce measurement errors.

In the absence of a standard reference material (SRM), the use of bulk Min-U-Sil calibrations for the quantification of thoracic and inhalable quartz exposures is an appealing alternative. It would eliminate the need for creating aerosol-generated stage-specific calibrations, as done in this article. However, the use of SRM 1878a as a calibration material for thoracic and inhalable samples produced errors of 40 and 64 percent, respectively (Table II). These data suggest that studies that have used a respirable standard reference material to quantify the larger particle size of quartz using the IR technique have significantly underestimated the amount of quartz present in the larger particle size fractions. Although the use of Min-U-Sil 5 and 30 provided some improvement (errors of 19% and 35% for thoracic and inhalable samples), the use of bulk calibrations alone will only provide a rough approximation of the quartz exposures in the larger particle size fractions.

Data from Table III show that the use of correction factors with the bulk Min-U-Sil calibration curves provides some improvement in the prediction of each size fraction for the construction phases. However, the mean percent errors for the inhalable and thoracic fractions were still 12 percent and 3 percent, respectively, for Min-U-Sil calibrations with correction factors, and 41 percent and 16 percent for SRM 1878a calibration with correction factors over all the construction phases. Since the correction factors were derived from our data set with its own unique particle size and sample concentration distributions it is unlikely that these correction factors would be transferable to another data set. Also, these factors are applicable only to the IR technique. For these reasons, the use of bulk Min-U-Sil,

even with correction factors, has a limited range-finding use in estimating thoracic and inhalable exposures. Separate stage-specific calibrations and sample analysis are a more accurate way of quantifying thoracic and inhalable exposures, albeit a very laborious one.

Study Limitations

Despite our efforts to minimize the overall error in quantification of quartz in the thoracic and inhalable fraction, we are aware of the limitations inherent in the design of this study. The major errors originate from several sources: 1) sampling errors related to the use of personal impactors and the extraction of the biological fractions; 2) errors associated with combining stages together; 3) errors due to the lack of standard reference material for the larger particle sizes; 4) errors due to the difference in the particle size distributions of the sample and the standard material; and 5) a lack of certainty on the purity of Min-U-Sil 30.

CONCLUSION

The method described in this article enables quantification of inhalable and thoracic quartz exposures when a personal four-stage cascade impactor is used for sample collection. Despite the limitations described above, we believe the exposure assessment strategy and the analytical method described in this article provide reasonable estimates of quartz exposures to the inhalable, thoracic, and respirable fractions. This approach to quantifying quartz in the larger particle size fraction is the first step toward a more standardized exposure assessment and analysis method for quartz.

ACKNOWLEDGMENTS

This study was funded by NIOSH through a cooperative agreement with the Center to Protect Workers Rights (CPWR) (#60/CCU317202-01). The authors thank and acknowledge Michael McCawley for sharing his experience and thoughts on size-selective quartz sampling, Michael Ellenbecker for his assistance with the aerosol generation loop, and James Platner from CPWR for encouraging us in these endeavors. Also, thanks to the contractors, construction workers, and local unions who participated in the sampling and to students and staff who assisted in data collection and analysis including Nicole Blute, Cathy Greenspan, Dana Hanson, Bernie Mizula, Mary Sobolefski, Heather Lyons, Todd Burnham, X. Michael Liu, Michael Landadio, and Jeffrey Vardis.

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APPENDIX A

The tabular-graphical procedure was used to calculate the size-selective fractions from impactor data. The major advantage of this procedure is that no underlying distribution of the data need be assumed. First, the mass on each impactor stage is corrected for entry and internal losses. Then, for each

size-selective fraction the portion of each stage contributing to the fraction is determined using Simpson's rule. This calculation uses the size-selective fraction for the upper and lower range and midpoint of particle sizes collected on a stage.

Stage	Cutpoint (μm) ^A	Inlet and internal correction	Range (μm) ^A	Midpoint (μm) ^A	Respirable fraction	Thoracic fraction	Inhalable fraction
1	21.1	0.52	21.1-42	31.55	0	0.01	0.58
2	15	0.61	15.0-21.1	18.05	0	0.096	0.677
3	9.8	0.78	9.8-15.0	12.3	0.005	0.338	0.617
5A	3.5	0.875	3.5-9.8	7.4	0.152	0.711	0.74
F	0	0.9	0-3.5	1.75	0.895	0.951	0.951

^A Aerodynamic mass median diameter.

APPENDIX B

Build Road—Refers the construction of either elevated highway or surface roads. For elevated highway, the road bed usually is constructed using reinforced concrete.

Build Supported Excavation—The operations related to the installation of the bracing (struts and wales) and removal of the earth for any large excavation (building, tunnel, etc).

Caisson Work—Operations related to the placement of caissons for foundation support.

Cut and Cover—In this type of construction, an initial excavation (cut) is completed. The walls of the excavation may become a future tunnel's walls. Further construction involves building the top (cover). Cut and cover tunnel construction may be contrasted with immersed tube or bored (tunnel jacking) construction.

General Contract Infrastructure—Any site-related activities not directly associated with the actual contract objectives. Instead this revolves around housekeeping on site, traffic control, and the cleaning of the vehicular traffic leaving the site.

Jet Grouting—Refers operations related to this technique of injecting grout to change the characteristics of soil to make it amenable to further construction activities. Also a straight cement-water mix may be used.

Roadway Demolition—Removal of the old reinforced concrete structures, steel, and asphalt to make room for new road construction.

Slurry Wall—All operations related to the construction of underground reinforced concrete walls with slurry used to stabilize the soil during excavation. Typically, slurry walls become the outer walls of cut and cover or building excavations, but can also be used in specialized applications like elevator shafts.

Tunnel Finish—All operations related to finishing the tunnel after the basic tunnel structure has been completed.

Utility Relocation—The installation of new utility lines (gas, electric, water, sewer, and communications) to upgrade/replace the old lines or as part of new construction. Typically a shallow trench is dug with an excavator, the pipe laid, encased in concrete, and backfilled. A variant of this basic description is pipejacking: A jacking pit (a deep excavation with shoring using sheet piles or lagging) is used as the base for a tunneling type operation that does not disturb the surface.

Vertical Building Construction—Any of the activities involved in the building or renovation of the systems or structures that make a building habitable.