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How reliable are crystalline silica dust concentration measurements?

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ABSTRACT

To determine how reliably commercial laboratories measure crystalline silica concentrations corresponding to OSHA's proposed limits, 105 filters were prepared with known masses of 20, 40, and 80 μg of respirable quartz corresponding to airborne silica concentrations of 25, 50, and 100 $\mu g/m^3$ and were submitted, in a blind test, to qualified commercial laboratories over a nine month period. Under these test conditions, the reported results indicated a lack of accuracy and precision needed to reliably inform regulatory compliance decisions. This was true even for filters containing only silica, without an interfering matrix. For 36 filters loaded with 20 or more micrograms of silica, the laboratories reported non-detected levels of silica. Inter-laboratory variability in this performance test program was so high that the reported results could not be used to reliably discriminate among filters prepared to reflect 8-h exposures to respirable quartz concentrations of 25, 50 and 100 $\mu g/m^3$. Moreover, even in intra-laboratory performance, there was so much variability in the reported results that 2-fold variations in exposure concentrations could not be reliably distinguished. Part of the variability and underreporting may result from the sample preparation process. The results of this study suggest that current laboratory methods and practices cannot necessarily be depended on, with high confidence, to support proposed regulatory standards with reliable data.

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1. Background

Silica is a very abundant mineral compound, found most often in crystalline form as quartz in sands, soils, rocks, dust, and air around the world and in many industry processes. Crystalline silica occurs when the oxygen and silicon molecules are arranged in a lattice. (WHO IARC, 2012) Workers in mining, construction, and manufacturing settings are exposed to silica dust (e.g., sand and dusts) and sufficiently prolonged inhalation exposure, to sufficiently high concentrations of crystalline silica dust, can cause adverse health effects including silicosis, a lung disease (NIOSH, 2004). Studies beginning in the 1980s also suggested that crystalline silica under some conditions might be carcinogenic (or co-carcinogenic), perhaps acting as a lung irritant and causing chronic inflammation of the lung (Borm et al., 2011) As a result of those findings, the Occupational Safety and Health Administration (OSHA) regulates crystalline silica exposure as a health hazard (20 CFR 1910.1000, Table Z-3).

1.1. *What is the regulatory history of silica?*

In 1971, OSHA first promulgated a permissible exposure limit (PEL) for respirable crystalline silica (RCS) working under an authority to expedite PELs for air contaminants and based upon the recommendation of the American Conference of Governmental Industrial Hygienists (ACGIH) (NIOSH, 1978). The limit was not substantially changed when OSHA issued its Air Contaminants final rule for general industry in 1989, which sought to simplify exposure calculations. In 1992, the Air Contaminants final rule was vacated by the U.S. Court of Appeals for the Eleventh Circuit returning the PEL for RCS to its original form.

In 1994, OSHA formally recognized RCS regulation as a priority and in 1996 made further efforts to both enforce the PELs and to provide better education on the hazards of overexposure to crystalline silica. Finding it had made little progress in these areas, OSHA endeavored to adopt a comprehensive silica standard. After

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significant efforts and input from other agencies, on August 12, 2013, OSHA proposed a new occupational health standard for respirable crystalline silica (RCS), or respirable quartz, which proposes to reduce the PEL by half in general industry and even more in the construction industry (OSHA, 2013). The proposal would also require medical surveillance of employees, increase hazard training, establish new protection procedures, and revise exposure monitoring.

In addition to establishing PELs, OSHA also promulgated in 1983 the Hazard Communication Standard (HCS) which mandates recognition and awareness promotion of health hazards in the workplace. (OSHA, 1983) A substance is a hazard for purposes of HCS if there is significant evidence based on one or more appropriate scientific studies that exposed employees may suffer acute or chronic health effects as a result of the exposure. Silica sand, or crystalline silica, meets these conditions, as inhaling high concentrations for long periods can harm the lungs. Likewise, the HCS includes substances that are classified as hazardous by sources such as the International Agency for Research on Cancer (IARC), OSHA, ACGIH, the National Institute for Occupational Safety and Health (NIOSH), and the National Toxicology Program (NTP), often based on a consensus opinion of selected experts.

The IARC evaluates chemicals and cancer risks and publishes a list of substances tiered by judged carcinogenicity. IARC began evaluating substances in 1967 and in 1987 found crystalline silica to be a Group 2A – probably carcinogenic to humans, in the opinions of those involved – substance, distinguishing it from amorphous silica for which there was inadequate evidence of carcinogenicity. In 1996, IARC reclassified occupational exposure to crystalline silica in the form of quartz or cristobalite as a Group 1 carcinogen, meaning that the IARC found in the literature evidence that it considered sufficient to establish carcinogenicity to humans, although others have noted that the mechanisms of carcinogenicity probably involve inflammation-mediated damage that only occurs when exposures are relatively (perhaps unrealistically) high (Borm et al., 2011). Amorphous silica, however, remains in Group 3. In proposing to reduce the PEL and action level, OSHA relies on studies which suggest that there would be a significant health and economic benefit from doing so. Industry argues that current data do not support the conclusion that the proposed reduction will cause such benefits. Industry members have also raised the question of whether current methods are capable of effectively monitoring compliance and detecting violations at the proposed lower levels. This paper reports on a study designed to test the reliability of commercial laboratories in assessing compliance with the proposed exposure limits under real-world conditions.

The current PEL for RCS is equivalent to 100 $\mu g/m^3$ averaged over an 8-h sampling period. OSHA's August 12, 2013 proposal (OSHA, 2013) would lower the PEL by a factor of 2, from 100 to 50 $\mu g/m^3$ (consistent with recommendations from NIOSH) and possibly set an action level of 25 $\mu g/m^3$ at which various ancillary requirements of the standard would be triggered. Commercial laboratories will analyze the majority of the RCS samples collected during exposure monitoring of silica-exposed workers.

Such samples typically are collected to assess workplace exposures with respect to a benchmark such as the PEL or an action level. It is of great practical interest, therefore, to assess the accuracy, precision, and reliability of analytical results that might be expected from commercial laboratories for filters with quartz dust loadings corresponding to RCS exposure concentrations of 100, 50 and 25 $\mu g/m^3$. These determine the rates of false positive and false negative errors and ultimately the efficacy of the proposed standard as a tool to reduce risk.

To help with this assessment, the American Chemistry Council Crystalline Silica Panel (ACC) sponsored an RCS performance testing program. Filters containing three different loadings of respirable quartz dust were sent over a period of several months, to five different commercial AIHA-accredited laboratories for analysis. The design of the program and the results of the analyses are described below, along with a statistical assessment of the findings.

2. Materials and methods

ACC contracted with RJ Lee Group (Monroeville, PA) to prepare polyvinyl chloride (PVC) filters containing different levels of respirable quartz dust loadings for analysis in a blinded testing program. The filters were sent to five AIHA-accredited commercial laboratories that perform analyses of RCS using x-ray powder diffraction (XRD) methodology. The program was blinded in the sense that the labs were not informed that they were participating in a performance testing program. The filters were submitted with standard chain-of-custody forms as if they were collected during ordinary workplace monitoring of crystalline silica exposures by commercial customers.

The testing program included three replicate rounds of testing over a period of months, so that precision and accuracy could be assessed on an intra-laboratory as well as an inter-laboratory basis (Hicks, 1993). For each round, three loading levels of respirable quartz (the "reference levels") were deposited onto new PVC filters by the RJ Lee Group. These loadings were the masses of respirable quartz that would be collected during 8-h monitoring at a sampling rate of 1.7 lpm when concentrations of respirable quartz dust in air were 25, 50, and 100 $\mu g/m^3$. The resulting reference levels (masses) of quartz dust on the filters were 20, 40 and 80 μg of quartz, respectively.

To assess the impact of other mineral interferences on reported lab results, filters for each reference level of RCS were to be prepared with three different matrices: (1) silica only (Min-U-Sil 5 (U.S. Silica Corp., Frederick, MD); (2) silica mixed with respirable kaolin; and (3) silica mixed with respirable soda-feldspar (SRM 99a; NIST). In addition, a blank filter was submitted to each lab with each round. Thus, in each replicate round, each of the five labs received 10 filters: 3 pure silica samples, 3 silica/feldspar samples, 3 silica/kaolin samples, and 1 blank filter – for a total of 150 samples (10 filters × 5 labs × 3 rounds).

2.1. Sample generation

The filters were prepared by weighing the minerals, suspending them, and then filtering the suspension onto new filters. To ensure that the mineral samples used were the respirable fraction, the oversize material in each sample was removed using sedimentation. A portion of the mineral was suspended in pH neutral, distilled water, agitated, and poured into a volumetric cylinder. The suspension was allowed to settle over a distance of 10 cm for 75 min before the remaining supernatant was siphoned and filtered. Each material was dried in a low-temperature oven overnight before being used to prepare the test filters.

To prepare the test samples, PVC filters (0.8 μm pore) were preconditioned in an oven at approximately 30 °C. Each filter was assigned a three digit tracking number and pre-weighed on a Mettler Toledo MX5 Microbalance (readability down to 1 μg). The test material was then tapped into a small, clean pan tared on the micro-balance. The contents of the pan were then carefully transferred to a beaker and the pan was rinsed well with isopropyl alcohol. The pre-weighed PVC filter was placed on the vacuum filtration system and topped with a funnel. The pre-made solution was poured onto the filter, the filter was allowed to air dry, and was then removed from the filtration set up. Filters were stored in a desiccator so they did not pick up moisture from the air until postweights were taken. Filters were post-weighed for record-keeping purposes.

2.2. Sample generation validation

Two prepared cassettes of each targeted loading were analyzed by RJ Lee Group using the NIOSH 7500 method (NIOSH, 2003) to confirm that accurate silica measurement is feasible. NIOSH 7500 is an external standard method for testing abundance of crystalline silica by XRD: the lab obtains a pure standard of each mineral, and then makes a set of standards of varying concentrations which it x-rays. This provides the lab with a series of data with varying peak intensities to which any unknown sample's peak intensities can then be related to determine concentration of each mineral present. X-ray absorption must be taken into account because varying thicknesses of material on the silver filter will vary the intensity of the peaks. This is corrected for by running blanks along with the standards.

Fig. 1 shows 6 calibration standards and a blank overlaid on the sample plot. These standards were created by weighing out the known concentrations and depositing the material onto silver filters. This data is zoomed in to 19–28°2θ to show the detail at the locations of the primary and secondary quartz peaks. As seen here, the standard with the highest concentration has the greatest intensity and with decreasing concentration, there is decreasing intensity down to the blank. The smallest concentration that can be seen, or the limit of detection, is 5 μg.

Initially, RJ Lee Group attempted to deposit the respirable dust by liquid filtration (quartz with or without feldspar or kaolin) onto PVC filters with a 5 μm pore size. The mass of respirable dust to be deposited on each filter was weighed to within ±1 μg of the target value. The respirable dust masses were suspended in 2-propanol and deposited onto 5 μm PVC filters by vacuum aspiration. After deposition, the prepared filter was then ashed and deposited onto silver membrane, as is routinely done in the preparation of standards and samples using the NIOSH 7500 method. The XRD spectrum acquired and mass estimated using the calibration curves is shown in Fig. 1. The XRD analysis showed that only about 47% ± 15% of the mass deposited on the 5um filters was retained, perhaps due to loss through the pores, as the Min-U-Sil 5 median particle size is 1.7 μm. To overcome this difficulty, RJ Lee Group switched to PVC filters with 0.8 μm pores, depositing the minerals suspended in 2-

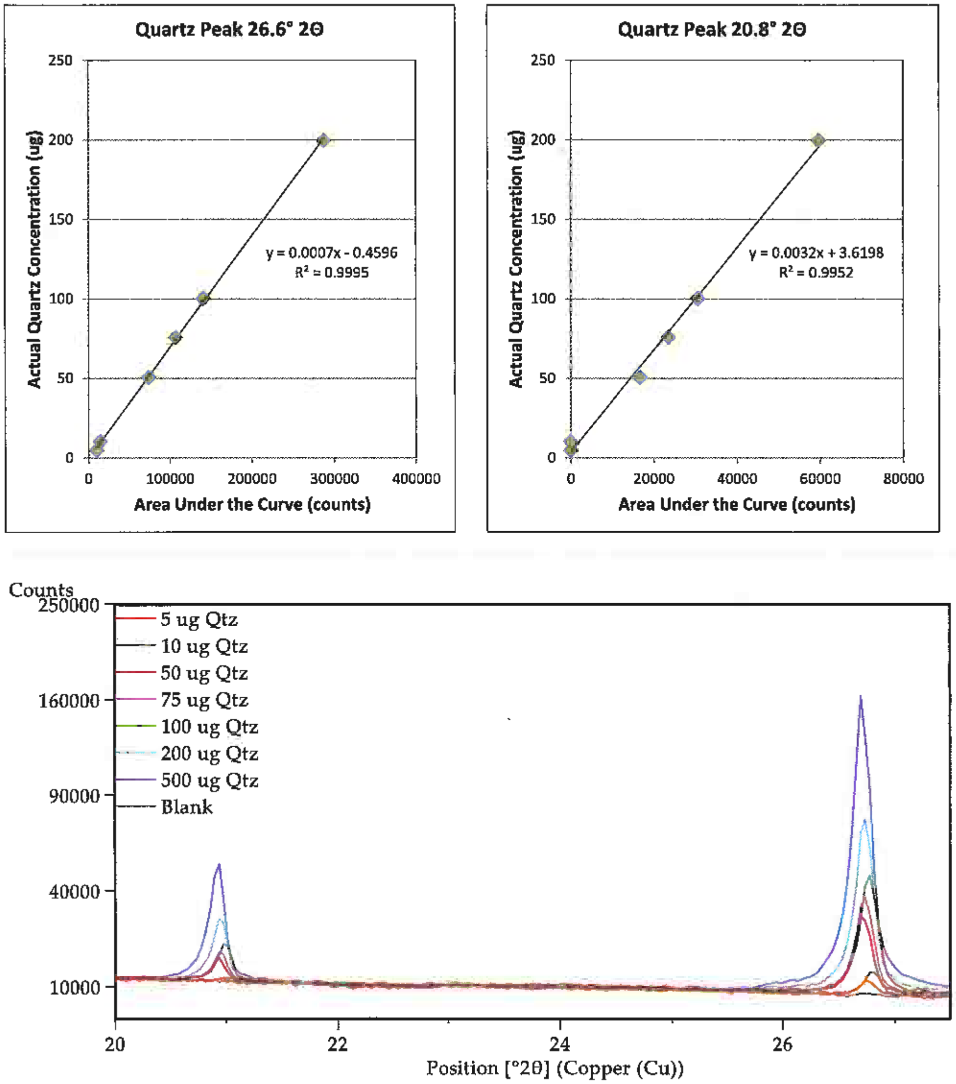

Fig. 1. Graphs showing the calibration curves (top) and x-ray diffraction scans for the silica calibration standards (bottom) used in these studies.

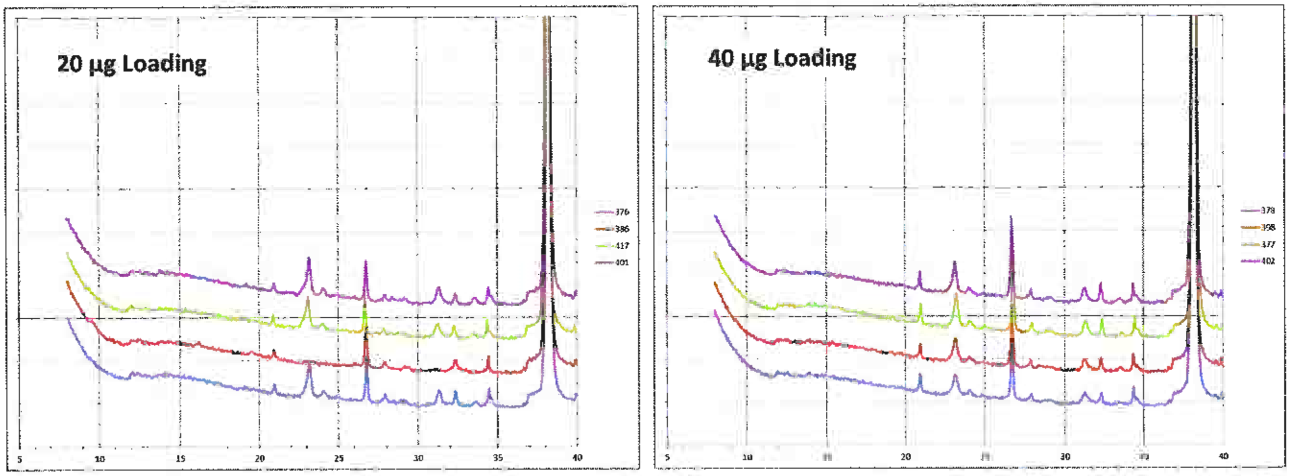

Fig. 2. X-ray diffraction scans of prepared samples showing the uniformity of the scans for the recovery of the deposited silica. There was a 93% recovery for the 20 µg loading and a 96% recovery for the 40 µg loading. The primary silica peak is at 26.66 °2θ and the secondary peak is at 20.85 °2θ.

propanol by vacuum aspiration. The recoveries after deposition onto 0.8 µm filters averaged 93% ± 8%, using the NIOSH 7500 method with low temperature ashing as the means of filter preparation, Fig. 2.

In connection with the mixed matrix filter preparation, RJ Lee Group initially loaded 10, 20 and 40 µg of quartz (and equivalent amounts of kaolin or feldspar) on the mixed matrix filters, rather than 20, 40, and 80 µg of quartz.[1] Additional filters were prepared for the 80 µg loading for the mixed matrix filters. The mixed matrix filters containing only 10 µg of quartz were excluded from the present analysis altogether, since there were no pure quartz filters at that level, and because for almost all of those filters (27/30), the labs reported that any quartz present was below the estimated limit of detection (which ranged from 5 µg to 12 µg for the various labs). That left 120 sample results for analysis.

2.3. Sample shipment

The prepared filters were placed in standard 2-piece 37-mm sampling cassettes with a unique identification code, and sealed in zip-lock plastic bags, which were boxed and shipped by commercial carrier to Sandler Occupational Medicine Associates (SOMA, Reston, VA). For each round of testing, once prepared, SOMA labeled and shipped the samples with its own sample identification numbers using a standard chain of custody form to each of the five commercial laboratories. These laboratories were not informed that they were participating in a performance testing program and did not know the reference levels of quartz on the various filters. They were asked to analyze the silica mass on each filter and report the results back to SOMA as their client.

2.4. Selection of laboratories

The selected labs met the following criteria: they accepted samples on a commercial basis; they performed silica analysis by XRD; and they had successfully completed the AIHA-LAP accreditation protocol, as revised in April, 2010. The labs were also located in several different regions of the country.

The test design required the use of five laboratories. The RCS analytical method (NIOSH 7500) sample preparation requirements can be satisfied using any of three methods: low temperature ashing, muffle furnace ashing, or filter dissolution. Of the five laboratories initially selected, three used a muffle furnace preparation and two filter dissolution. During the first round of testing, two laboratories reported difficulty preparing the filters for XRD analysis. These two labs used tetrahydrofuran (THF) as a filter-dissolving agent, and it appears that PVC filters with 0.8 µm pores may have interfered with the dissolution of the filters and no silica analyses could be obtained. By contrast, the three labs that used a muffle furnace to ash the filters before depositing the minerals onto silver membranes did not report any sample preparation problems. Accordingly, the two labs that used the THF process were replaced with labs that used a muffle furnace preparation. The resulting group of five AIHA-accredited labs employing the muffle furnace preparation procedure was used throughout the remainder of the test program.

2.5. Data analysis

The data were analyzed by comparing mean reported silica mass on filters from different reference concentrations and, conversely, by examining the distributions of reference concentrations in different quartiles of the reported silica mass distribution. Variability in reported silica mass for each reference concentration was compared within and among laboratories, using tree-based (CHAID-like) analysis implemented in KnowledgeSeeker™ (Angoss Software Corp., Toronto, Canada), a commercial classification tree and data mining software package to evaluate inter-laboratory differences. All other analyses and comparisons were performed using the Statistica 10.0 (StatSoft, Tulsa, OK) statistics environment.

3. Results and analysis

Appendix A provides the full data set and results for the 105 filters with quartz loadings at the 20, 40 and 80 µg reference levels and the 15 blanks. About a third (34%, 36/105) of the non-blank filters were reported by the laboratories to be below the detection limit even though they contained loadings above each laboratory's reported limit of detection. These false negatives were excluded from the following statistical data, resulting in an

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[1] 10, 20, 40 and 80 µg quartz were RJ Lee's target loading levels. For some of the filters, the actual loadings achieved were 1 µg higher or lower than the targeted value.

overestimation of precision and accuracy for the remaining data. As shown in the tables below, none of the laboratory means came within 30% of the reference values, indicating that the accuracy of the analyses was problematic even when the non-detect results were excluded.

3.1. Accuracy of laboratory results and ability to discriminate between higher and lower concentrations

In the following analysis, filters for which the silica mass was reported to be below the detection limit were excluded, thereby producing higher mean values (hence, better apparent accuracy) and smaller standard deviations (hence, better apparent precision) than would have been the case if these "non-detect" results had been included in the analysis with an assigned value of either 0 or one-half the detection limit.

Table 1 shows – for each reference level – the arithmetic mean of the reported silica mass and the standard deviation for all of the silica-only filters having a positive reported value. Fig. 3 plots these values for each reference level. The mean reported silica mass increased as the underlying reference level increased. The 95% confidence intervals (vertical bars) around the mean reported levels show that the reference level of 40 µg of silica had mean reported silica values greater than those from the 20 µg reference level and significantly less than those from the 80 µg reference level. However, none of the mean reported silica values for any of the three reference levels came within 30% of the applicable silica reference value: they are all significantly lower, indicating that the accuracy of the analyses was problematic even when the non-detects were excluded. Had they been included, the mean reported values would have fallen further below the respective reference levels, making the accuracy of the results even more problematic.

Table 2 shows – for the 20, 40 and 80 µg reference levels – the arithmetic mean of the reported silica mass and the standard deviation for all of the filters (mixed-matrix as well as silica-only) having a positive reported value (i.e., with non-detects excluded). Fig. 4 plots these values for each reference level. The results are similar to those in Fig. 3, which was limited to the silica-only filters. As in Fig. 3, the mean values would be lower (i.e., accuracy would deteriorate) and the standard deviations would be larger (i.e., precision would deteriorate) if the non-detect filters were included. The impact of excluding the non-detects could be significant, as 34% (36 out of 105) of the filters with positive reference level loadings of RCS were reported as non-detects, including 25 of 45 (56%) of the 20 µg reference level filters. Together, Figs. 3 and 4 indicate that the accuracy and precision of the reported results leave much to be desired at all three reference levels.

Table 3 presents data for all 71 filters with reported silica mass above the detection limits. The filters are sorted in order of increasing reported silica mass, from 5.1 µg to 66 µg. Among the 10 filters with the lowest reported silica mass above the detection limit, one came from the 0 µg reference level set. This is a false positive, in the sense that positive silica content is identified for a blank filter prepared without any silica. Six of the remaining nine filters with the lowest reported values came from the 20 µg reference level set and three from the 40 µg reference level set. For the ten filters with the highest reported silica loadings, eight (80%) are from the 80 µg reference level, one from the 0 µg reference level, and one from the 40 µg reference level (silica and kaolin matrix). For the top quartile (18 filters with the highest reported silica concentrations), almost half (8) are from the 40 µg reference level set, and one is from the 0 µg reference level set.

Table 1
Mean reported silica mass (µg) and standard deviations for silica-only and blank filters having positive reported results.

Reference level (µg)	Number of data points, N	Lab results, µg	
		Mean	Standard deviation
0	2	28.85	32.74
20	7	13.36	5.21
40	12	22.93	11.22
80	12	46.91	18.31

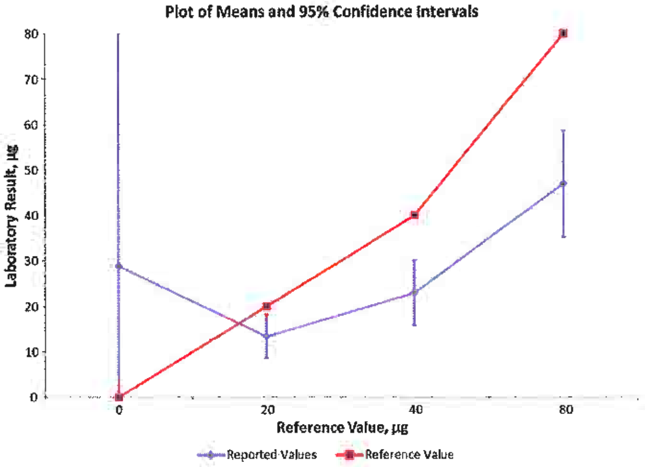

Fig. 3. Mean reported silica mass (µg, vertical axis) on silica-only and blank filters increased with reference masses of silica dust on filters (horizontal axis).

Table 2
Mean reported silica mass (µg) and standard deviations for all 20, 40 and 80 µg reference level filters having positive reported results.

Reference level (µg)	Number of data points, N	Lab results, µg	
		Mean	Standard deviation
20	20	13.33	4.50
40	37	25.04	9.08
80	12	46.91	18.31

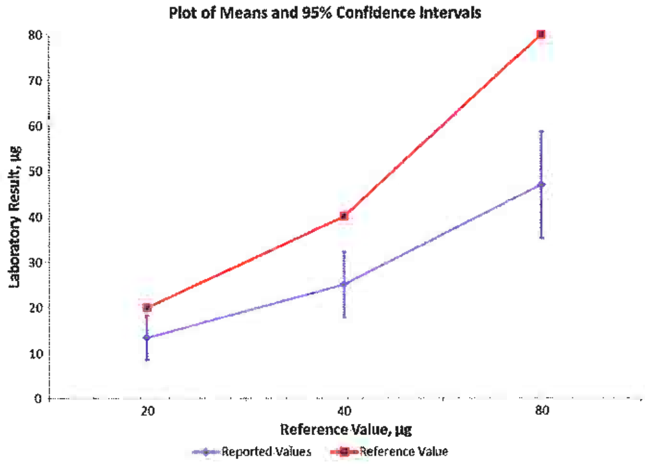

Fig. 4. Mean reported silica mass (µg, vertical axis) on non-blank filters with positive reported results increased with reference masses of silica dust on filters (horizontal axis).

Table 3
Filter data sorted by increasing reported silica mass (Only filters with reported silica content above the detection limit are shown.).

1 Filter loading reference level (μg Silica)	2 Matrix	3 Lab results (μg Silica)	4 Lab no.
40	Silica	5.1	4
20	Silica + Feldspar	5.4	5
20	Silica	5.7	4
0	Blank	5.7	5
40	Silica + Feldspar	5.7	4
20	Silica	6.8	4
40	Silica	7.8	4
20	Silica + Kaolin	8.6	4
20	Silica + Kaolin	11	5
20	Silica + Kaolin	11	3
20	Silica + Feldspar	12	3
20	Silica + Kaolin	12	2
80	Silica	13	1
20	Silica + Feldspar	13	3
20	Silica + Kaolin	14	2
20	Silica + Kaolin	14	5
20	Silica	14	3
40	Silica	14	5
20	Silica	14	2
20	Silica + Feldspar	14	2
40	Silica	14.2	4
40	Silica + Feldspar	14.7	4
40	Silica + Kaolin	15	2
20	Silica	16	3
40	Silica + Feldspar	16	5
20	Silica + Kaolin	17	2
20	Silica	18	2
20	Silica	19	2
20	Silica + Feldspar	19	2
40	Silica	20	3
40	Silica + Kaolin	21	3
40	Silica	21	5
40	Silica + Feldspar	21	3
20	Silica + Feldspar	22	2
40	Silica + Kaolin	22	1
40	Silica + Kaolin	22.8	4
40	Silica + Kaolin	24	3
40	Silica + Kaolin	24	3
80	Silica	24.6	4
40	Silica	25	3
80	Silica	26	5
40	Silica + Kaolin	26	5
40	Silica + Feldspar	27	5
40	Silica + Feldspar	27	3
40	Silica + Feldspar	27	5
40	Silica	27	2
40	Silica + Feldspar	28	3
40	Silica + Kaolin	28	1
40	Silica + Kaolin	29	5
40	Silica	31	3
40	Silica + Feldspar	31	2
40	Silica + Kaolin	31.1	4
40	Silica + Feldspar	32	2
40	Silica + Kaolin	32	2
40	Silica + Kaolin	33	1
40	Silica + Kaolin	33	5
40	Silica	35	2
40	Silica	35	5
80	Silica	39	5
40	Silica	40	2
40	Silica + Feldspar	40	2
40	Silica + Kaolin	41	2
80	Silica	42.5	4
80	Silica	43.8	4
0	Blank	52	2
80	Silica	55	3
80	Silica	60	3
80	Silica	64	2
80	Silica	64	2
80	Silica	65	5
80	Silica	66	3

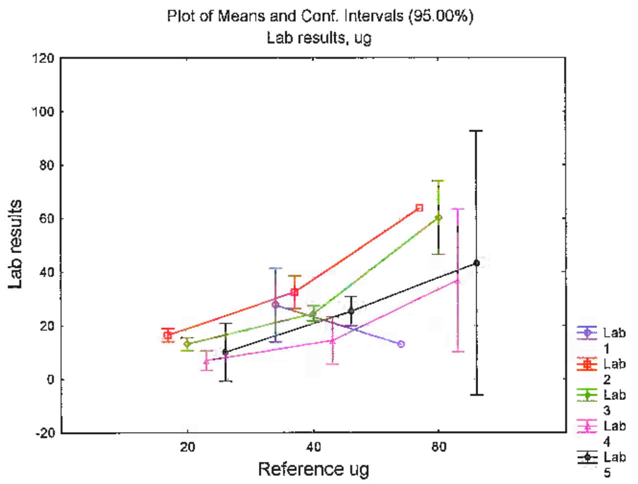

Fig. 5. Individual laboratories differ systematically in reported silica mass at the respective reference levels (data with non-detects removed).

These data indicate that the silica mass reported by the labs does not sharply discriminate among different reference levels of actual silica loadings. For example, a reported silica mass in the highest quartile (all of which would be from the 80 μg reference level set if there were perfect agreement between higher reference levels and higher reported silica mass) has about a 50% (9/18) chance of coming from the 40 or 0 μg reference level sets. Conversely, a reported silica mass in the lowest quartile has some chance (about 1/18) of being a false positive and a greater probability (about 4/18, or 22%) of coming from the 40 μg reference level set. Thus, if one wished to identify a threshold for reported silica mass above which one could be confident (e.g., with 95% statistical confidence) that the reported level exceeds some true level – say, 60 μg – these data indicate that such a level of confidence could not be achieved under the conditions of this performance testing protocol.[2] Indeed, among the top 10% of filters (12 out of 120) reported as having the greatest crystalline silica loads, 25% (3 of the 12) come from the 40 μg reference level set, and one is a false positive (a blank with 0 silica load) – indicating that under the conditions of this testing protocol, the laboratory results were not sufficiently accurate to reliably distinguish between concentrations that differ by a factor of 2 (i.e., 80 μg v. 40 μg).

3.2. Variability among laboratories

Fig. 5 shows the relation between reference levels and reported silica mass for individual laboratories (with non-detects removed).[3] The results from some laboratories (e.g., lab 2) indicate a higher silica loading than others (e.g., lab 4), for every reference level. A filter with a given load of silica particles could easily yield a reported silica mass that varied by a factor of approximately two, depending on which labs provided the analyses. This finding suggests that inter-laboratory variability alone would make it impossible to reliably discriminate among RCS exposure concentrations that differ by a factor of about 2, consistent with the values in Table 3. In addition, within individual laboratories, there was substantial overlap among the 95% confidence intervals around mean reported silica mass values for different reference levels. Thus, variability of reported results within individual laboratories was such that reference levels of 20, 40, and 80 μg could not be distinguished reliably from each other.

Fig. 6 presents an interaction tree, showing in more detail how estimated mean silica mass ("avg") (and their sample standard deviations, "std") depend on specific laboratories. For all non-zero reference levels, the reported silica mass on filters depended significantly on the laboratory that performed the analysis. Laboratory 2 systematically reported silica mass levels about twice that of laboratory 4, for both the 20 and the 40 μg reference levels. These wide ranges indicate that two-fold differences in reference levels could not reliably be distinguished using the reported laboratory results.

Table 4 shows that different labs have quite different coefficients of variation (ratios of standard deviations to means) for their reported results. Moreover, with the possible exception of Lab 3, the high CV values shown in Table 4 suggest that intra-laboratory precision in these analyses of silica dust is poor – with relative standard deviations ranging from 20% to 66% at the various reference levels.

4. Discussion

The objective of the study was to determine if commercial laboratories, in a blind study, could accurately determine the crystalline silica content of filters at concentrations corresponding to OSHA's current and proposed PEL's and action levels. These filter loadings were the masses of respirable quartz that would be collected during 8-h monitoring at a sampling rate of 1.7 lpm when concentrations of respirable quartz dust in air are 25, 50, and 100 $\mu g/m^3$. The resulting reference levels (masses) of quartz dust on the filters were 20, 40 and 80 μg of quartz, respectively, which correspond to the current PEL, proposed PEL, and proposed action limit.

The results demonstrate that inter- and intra-laboratory variability was high. The five commercial laboratories tested could not reliably distinguish between the different reference levels; laboratories did not achieve the conventional 95% statistical confidence level for an analytical method. In some cases, variability was so high that a 2-fold variation in exposure could not be distinguished.

The results were unexpected. The laboratories participating in the blind study are all AIHA certified, which means they participate in the AIHA PAT program. The PAT program sends out samples on a quarterly basis, where one might argue that a variability and bias such as shown here should have been detected. Several mitigating factors may be involved. The PAT program samples are designated as such when the laboratory receives them and there is a significant possibility that a "white hat" syndrome exists, i.e. the process performs better when being observed. The AIHA sample performance loadings are evaluated on a consensus basis, which would tend to reduce the effects of the bias seen in this study. This study used known loadings and each laboratory analyzed the sample loading multiple times over the course of the study so an inter-laboratory variability can be derived, which is not possible in the AIHA program.

The potential for particle loss during shipping as a contributor was raised as a possible concern. RJLG prepared an additional set of

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[2] OSHA standards typically require that employers use a method of monitoring and analysis that has an accuracy of plus or minus 25 percent (±25%) with a confidence level of 95 percent for measurements at airborne concentrations at or above the PEL. See, e.g., 29 CFR § 1910.1028(e) (6) (±25% for Benzene); 29 CFR § 1910.1026(d) (5) (±25% for concentrations at or above the action level for Hexavalent Chromium).

[3] Of the 21 non-blank filters it analyzed, Lab 1 reported only four values above the detection limit (3 for the 40 μg reference level and 1 for the 80 μg reference level); hence, the plot for Lab 1 has no data point for the 20 μg reference level and no confidence limits for the 80 μg reference level.

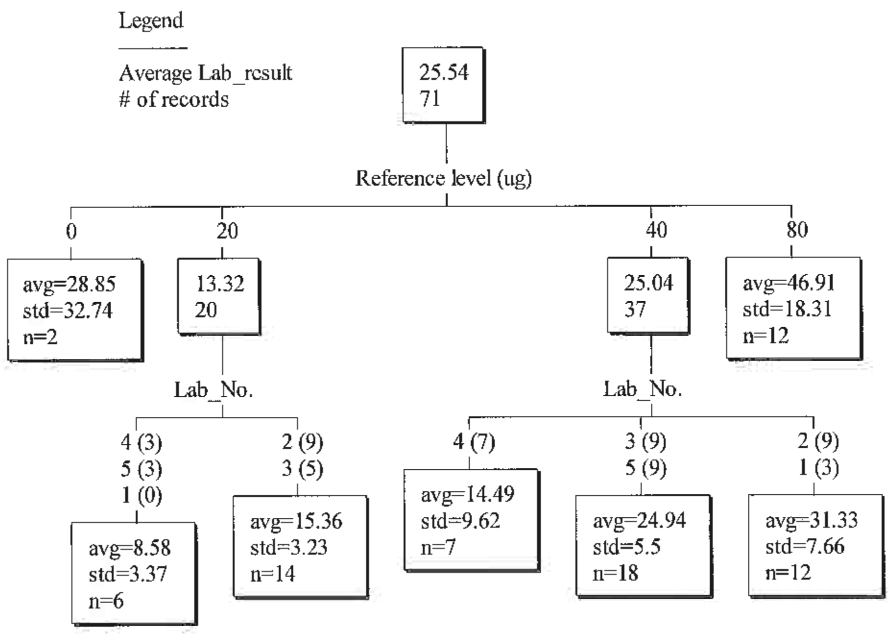

Fig. 6. Estimated silica mass varied with the laboratory that performed the analysis.

filters and sent them to SOMA who returned them to RJLG for analysis as routine blind samples. The results were then returned to SOMA. Subsequently the samples were decoded and the results analyzed. This data is summarized in a companion paper, but show that RJLG had recovered 93 ± 5% of the original loadings vs 92% ± 4% for a parallel set of samples that were retained in-house and analyzed. These results indicate that potential particle loss during shipping was not a significant factor in the results reported by the five commercial laboratories.

The results of this study were summarized at the recent OSHA hearings (Bailey, 2014). During the course of testimony, questions were raised about the validity of the results. The results were challenged because RJ Lee Group itself was not accredited by an independent agency to produce reference standards. However, production of internal standards for XRD analysis is a routine part of every laboratory's operation. Indeed, the production of standards is required by the NIOSH 7500 method. Secondly, during method development it was demonstrated that the recovery was better than 90% for all loadings, compared to the roughly 50% recovery by the laboratories in the study. The apparent biases across AIHA-accredited laboratories, and the differing variances observed in the analysis of the data, cannot be explained by RJ Lee Groups' certification status.

5. Conclusion

The results of these tests suggests that commercial laboratories, using existing laboratory methods, cannot reliably determine the crystalline silica content of filters that have a silica loading corresponding to the mass of silica collected in eight-hour sampling at

Table 4
Coefficients of variation (CV) are higher for some labs (e.g., 5) than others (e.g., 3), for all reference levels.

1 Lab no.	2 Filter loading reference level (μg Silica)	3 Mean lab results (μg Silica)	4 N = Number of data points	5 Standard deviation	6 CV
1	0	–	0	–	–
1	20	–	0	–	–
1	40	27.67	3	5.51	0.20
1	80	13.00	1	0.00	0.00
2	0	52.00	1	0.00	0.00
2	20	16.56	9	3.24	0.20
2	40	32.56	9	8.14	0.25
2	80	64.00	2	0.00	0.00
3	0	–	0	–	–
3	20	13.20	5	1.92	0.15
3	40	24.56	9	3.64	0.15
3	80	60.33	3	5.51	0.09
4	0	–	0	–	–
4	20	7.03	3	1.46	0.21
4	40	14.49	7	9.62	0.66
4	80	36.97	3	10.73	0.29
5	0	5.70	1	0.00	0.00
5	20	10.13	3	4.37	0.43
5	40	25.33	9	7.12	0.28
5	80	43.33	3	0.46	0.46

airborne concentrations corresponding to OSHA's proposed PEL and action levels. The study suggests that data reported by commercial laboratories may underestimate the silica concentrations, resulting in a false sense of compliance in situations where overexposures may be occurring. The study has larger implications however. It indicates that the AIHA PAT program, as currently structured, is not adequate for certifying laboratories at the proposed PEL and action levels. The relatively small size of the study is recognized and we highly recommend that OSHA conduct a blind study of a similar nature including all laboratories certified to perform the NIOSH 7500 method. In addition, employers might want to consider submitting blind and duplicate samples on a random regular basis to ensure the laboratory they use is producing a quality result.

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Transparency document

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Appendix A

Appendix A provides the full data set and results for the 105 filters with quartz loadings at the 20, 40 and 80 µg reference levels and the 15 blanks. In Appendix A:

- Column 1 ("Filter No.") shows an assigned number for the particular filter.
- Column 2 ("Filter Loading Reference Level (µg Silica)") shows the reference level (in micrograms of quartz) on the filter.
- Column 3 ("Matrix") indicates whether the filter contained pure quartz or quartz plus kaolin or feldspar.
- Column 4 (Lab results (µg Silica)") shows the quantity of crystalline silica (in micrograms) reported by the lab that analyzed the filter. All of the laboratories had minimum detection levels below which silica mass could not be reliably quantified. These detection limits varied among the labs. Where a lab reported the silica mass as being below its detection limit, the notation "0" appears in Column 4.
- Column 5 ("Lab No.") identifies the laboratory that analyzed the filter. The laboratories are identified here by arbitrarily assigned numbers from 1 to 5.
- Column 6 ("Round No.") indicates which of the three rounds of testing the filter was in.

Filter no.	Filter loading reference level (µg silica)	Matrix	Lab results (µg silica)	Lab no.	Round no.
1	20	Silica	0	1	1
2	40	Silica	0	1	1
3	80	Silica	13	1	1
4	20	Silica + Kaolin	0	1	1
5	40	Silica + Kaolin	33	1	1
6	20	Silica + Feldspar	0	1	1
7	40	Silica + Feldspar	0	1	1
8	0	Blank	0	1	1
9	20	Silica	19	2	1
10	40	Silica	35	2	1
11	80	Silica	0	2	1
12	20	Silica + Kaolin	14	2	1
13	40	Silica + Kaolin	41	2	1
14	20	Silica + Feldspar	22	2	1
15	40	Silica + Feldspar	32	2	1
16	0	Blank	52	2	1
17	20	Silica	0	5	1
18	40	Silica	35	5	1
19	80	Silica	65	5	1
20	20	Silica + Kaolin	11	5	1
21	40	Silica + Kaolin	33	5	1
22	20	Silica + Feldspar	0	5	1
23	40	Silica + Feldspar	27	5	1
24	0	Blank	0	5	1
25	20	Silica	16	3	1
26	40	Silica	25	3	1
27	80	Silica	66	3	1
28	20	Silica + Kaolin	0	3	1
29	40	Silica + Kaolin	21	3	1
30	20	Silica + Feldspar	13	3	1
31	40	Silica + Feldspar	27	3	1
32	0	Blank	0	3	1
33	20	Silica	6.8	4	1
34	40	Silica	5.1	4	1
35	80	Silica	43.8	4	1
36	20	Silica + Kaolin	0	4	1
37	40	Silica + Kaolin	0	4	1
38	20	Silica + Feldspar	0	4	1
39	40	Silica + Feldspar	0	4	1
40	0	Blank	0	4	1
41	20	Silica	0	5	2

(*continued*)

Filter no.	Filter loading reference level (μg silica)	Matrix	Lab results (μg silica)	Lab no.	Round no.
42	40	Silica	21	5	2
43	80	Silica	39	5	2
44	20	Silica + Kaolin	14	5	2
45	40	Silica + Kaolin	29	5	2
46	20	Silica + Feldspar	5.4	5	2
47	40	Silica + Feldspar	16	5	2
48	0	Blank	0	5	2
49	20	Silica	0	1	2
50	40	Silica	0	1	2
51	80	Silica	0	1	2
52	20	Silica + Kaolin	0	1	2
53	40	Silica + Kaolin	22	1	2
54	20	Silica + Feldspar	0	1	2
55	40	Silica + Feldspar	0	1	2
56	0	Blank	0	1	2
57	20	Silica	18	2	2
58	40	Silica	40	2	2
59	80	Silica	64	2	2
60	20	Silica + Kaolin	17	2	2
61	40	Silica + Kaolin	32	2	2
62	20	Silica + Feldspar	19	2	2
63	40	Silica + Feldspar	40	2	2
64	0	Blank	0	2	2
65	20	Silica	5.7	4	2
66	40	Silica	14.2	4	2
67	80	Silica	42.5	4	2
68	20	Silica + Kaolin	8.6	4	2
69	40	Silica + Kaolin	31.1	4	2
70	20	Silica + Feldspar	0	4	2
71	40	Silica + Feldspar	14.7	4	2
72	0	Blank	0	4	2
73	20	Silica	14	3	2
74	40	Silica	31	3	2
75	80	Silica	60	3	2
76	20	Silica + Kaolin	11	3	2
77	40	Silica + Kaolin	24	3	2
78	20	Silica + Feldspar	12	3	2
79	40	Silica + Feldspar	28	3	2
80	0	Blank	0	3	2
81	20	Silica	0	5	3
82	40	Silica	14	5	3
83	80	Silica	26	5	3
84	20	Silica + Kaolin	0	5	3
85	40	Silica + Kaolin	26	5	3
86	20	Silica + Feldspar	0	5	3
87	40	Silica + Feldspar	27	5	3
88	0	Blank	5.7	5	3
89	20	Silica	0	1	3
90	40	Silica	0	1	3
91	80	Silica	0	1	3
92	20	Silica + Kaolin	0	1	3
93	40	Silica + Kaolin	28	1	3
94	20	Silica + Feldspar	0	1	3
95	40	Silica + Feldspar	0	1	3
96	0	Blank	0	1	3
97	20	Silica	14	2	3
98	40	Silica	27	2	3
99	80	Silica	64	2	3
100	20	Silica + Kaolin	12	2	3
101	40	Silica + Kaolin	15	2	3
102	20	Silica + Feldspar	14	2	3
103	40	Silica + Feldspar	31	2	3
104	0	Blank	0	2	3
105	20	Silica	0	4	3
106	40	Silica	7.8	4	3
107	80	Silica	24.6	4	3
108	20	Silica + Kaolin	0	4	3
109	40	Silica + Kaolin	22.8	4	3
110	20	Silica + Feldspar	0	4	3
111	40	Silica + Feldspar	5.7	4	3
112	0	Blank	0	4	3
113	20	Silica	0	3	3
114	40	Silica	20	3	3
115	80	Silica	55	3	3

(*continued on next page*)

(*continued*)

Filter no.	Filter loading reference level (μg silica)	Matrix	Lab results (μg silica)	Lab no.	Round no.
116	20	Silica + Kaolin	0	3	3
117	40	Silica + Kaolin	24	3	3
118	20	Silica + Feldspar	0	3	3
119	40	Silica + Feldspar	21	3	3
120	0	Blank	0	3	3

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