

**Before the Occupational Safety and Health Administration
United States Department of Labor**

**Comments of Cardno ChemRisk on OSHA's Discussion of the
Adequacy of Sampling and Analytical Methods for Measuring
Respirable Crystalline Silica at Exposure Levels of 25 and 50 $\mu\text{g}/\text{m}^3$
Docket No. OSHA-2010-0034, 78 Fed. Reg. 56274 (September 12, 2013)**

February 7, 2014

These Comments of Cardno ChemRisk, LLC were prepared at the request of the American Chemistry Council Crystalline Silica Panel, which has supported the work financially.

In the Notice of Proposed Rulemaking (NPRM) to adopt a standard for Occupational Exposure to Crystalline Silica, 78 Fed. Reg. 56274 (September 12, 2013), and in the associated Preliminary Economic Analysis (PEA), OSHA presents its justification for why the analytical methods for respirable crystalline silica (RCS) are adequate to accurately measure exposures at the proposed permissible exposure limit (PEL) of 50 $\mu\text{g}/\text{m}^3$ and at an action level of 25 $\mu\text{g}/\text{m}^3$. The overall justification is misguided and inaccurate because it fails to adequately characterize the various sources of sampling and analytical error associated with the sampling and analysis methods used for respirable crystalline silica. In addition, there is one instance of a calculation error in OSHA's analysis that mistakenly leads the Agency to conclude that precision is as good at lower silica loadings as at higher ones. The result is that OSHA has not made a supportable showing that RCS exposures can be accurately measured with acceptable precision at the concentrations of the proposed PEL and action level. The existence of sampling and analytical methods that can accurately and precisely measure respirable crystalline silica at the proposed PEL is the first step in determining the technological feasibility of the rule. If the sampling and analytical methods do not meet the necessary standards of accuracy and precision, then it is impractical to accurately determine the effectiveness of the engineering controls to meet the proposed PEL. According to NIOSH (1995), the necessary standard of accuracy and precision that a sampling and analytical method should meet is to give a result that is within $\pm 25\%$ of the true concentrations at a 95% confidence level. At exposure levels of 25 and 50 $\mu\text{g}/\text{m}^3$, that standard cannot be met.

The central premise of the feasibility determination in the proposed rule is that the current X-ray Diffraction (XRD) and Infra-red (IR) analytical methods are adequate to accurately measure

concentrations at or below the proposed action level of 25 $\mu\text{g}/\text{m}^3$ and the proposed PEL of 50 $\mu\text{g}/\text{m}^3$. OSHA discusses this issue in section VIII.D.1 of the preamble to the proposed rule, 78 Fed. Reg. at 56353-56354, and at greater length in Chapter IV of the PEA. The preamble summarizes several reasons that supposedly lend support to the feasibility of accurate measurement at the proposed PEL of 50 $\mu\text{g}/\text{m}^3$; a more detailed explanation of those reasons is presented in the PEA (pages IV-13 to IV-48).

The main statements made by the OSHA in the preamble regarding the feasibility determination are as follows:

- There are several commercially available personal sampling cyclones that can be operated at flow rates that conform to the ISO/CEN particle size selection criteria with an acceptable level of bias.
- These cyclones are capable of allowing a sufficient quantity of quartz to be collected from atmospheric concentrations as low as 25 $\mu\text{g}/\text{m}^3$ to exceed the limit of quantification for the OSHA ID-142 analytical method, provided that a sample duration is at least 4 hours.
- The XRD and IR methods are both sufficiently sensitive to quantify levels of quartz and cristobalite that would be collected in air samples taken from concentrations at the proposed PEL and action level.
- At filter loadings corresponding to the proposed PEL, the precision and the sampling and analytical error (SAE) for quartz are ± 17 percent and ± 14 percent, respectively. These results indicate that employers can have confidence in sampling results for the purpose of assessing compliance with the PEL and identifying when additional engineering and work practice controls and/or respiratory protection are needed.
- The method is sufficiently sensitive and precise to allow employers to distinguish between operations that have sufficient dust control to comply with the PEL and those that do not.
- Based on OSHA's analysis of PAT data, most laboratories achieve good agreement in results for samples having filter loads just above 40 μg quartz (49–70 μg).

- At filter loadings corresponding to the proposed action level, the precision and SAE of the method for quartz are ± 19 and ± 16 percent, respectively. These results show that Method ID-142 can achieve a sufficient degree of precision for the purpose of identifying those operations where routine exposure monitoring should be conducted.
- There are no available data that describe the total variability seen between laboratories at filter loadings in the range of 20 μg crystalline silica since the lowest filter loading used in PAT samples is about 50 μg .
- It is technologically feasible to reliably measure exposures of workers at the proposed PEL of 50 $\mu\text{g}/\text{m}^3$ and action level of 25 $\mu\text{g}/\text{m}^3$.

Our comments on OSHA's statements in the preamble, as elaborated in more detail in the PEA, are summarized below. More detailed discussion of these comments follows in the subsequent sections.

- While the reported limit of quantification for the various analytical methods for respirable crystalline silica is 10 μg , which is below the estimated mass associated with an 8 hour sample at either the action level of 25 $\mu\text{g}/\text{m}^3$ (20 μg) or the proposed PEL of 50 $\mu\text{g}/\text{m}^3$ (41 μg), the actual reported limits of detection may be higher due to the presence of materials that interfere with the analysis.
- The sampling and analytical error (SAE) as defined by OSHA in the PEA is not an appropriate measure of sampling and analytical variability because it is based on a one-sided confidence limit and not a two-sided confidence limit. Precision, as defined in the PEA, is a more appropriate metric because it is a two-sided measure of sampling and analytical error.
- OSHA's statement that the sampling and analytical error (SAE) for quartz concentrations at the proposed PEL of 50 $\mu\text{g}/\text{m}^3$ is $\pm 14\%$ and the precision is $\pm 17\%$ is incorrect because this estimated SAE and precision are based on an incomplete characterization of the sampling and analytical errors associated with the available sampling and analytical methods. If additional sources of sampling and analytical error are included, the SAE

estimated at the proposed PEL can range from $\pm 31\%$ to $\pm 54\%$ and the precision can range from $\pm 37\%$ to $\pm 65\%$.

- For the same reasons, OSHA's statement that the SAE for quartz concentrations at the proposed action level of $25 \mu\text{g}/\text{m}^3$ is $\pm 16\%$ and the precision is $\pm 19\%$ is incorrect. If additional sources of sampling and analytical error are included, the SAE estimate at the proposed action level can range from $\pm 31\%$ to $\pm 62\%$ and the precision can range from $\pm 37\%$ to $\pm 74\%$.
- Due to a miscalculation, OSHA incorrectly states that most laboratories achieve good agreement in results for samples with filter loads just above $40 \mu\text{g}$ quartz.
- While OSHA states that the AIHA IH Proficiency Analytical Testing (PAT) program data cannot be used to characterize intra-laboratory variability, past data from the program for respirable crystalline silica have been used in this manner and these analyses have been published in the peer-reviewed literature.
- While high flow rate samplers, such as the BGI GK 2.69 are available and can collect a greater amount of silica than the low flow rate samplers that are currently used, the accuracy and precision associated with these samplers has not been evaluated and cannot be assumed to be acceptable at exposure levels of $50 \mu\text{g}/\text{m}^3$ and below.

1. The actual reported limits of detection may be higher than the stated limits of quantification for the various XRD and IR analytical methods due to the presence of interferences.

While the limits of quantification (LOQ) for the various XRD and IR methods range from 5 to $10 \mu\text{g}$, these LOQs are based on ideal conditions where substances that interfere with the analysis are not present. Quantification in the presence of interferences increases the potential error because additional measurements have to be made to compensate for changes to the background under the measurement peak or changes to the peak profile because of coinciding peaks (Stacey, 2007).

In most industrial settings, materials that interfere with the analysis of quartz and cristobalite are often present. For XRD methods, the presence of mica, feldspar, and other clay minerals will interfere with the quartz peak and degrade the detection limit significantly as well as affect the quantification accuracy for most analyses. In addition, the presence of iron will also decrease the ability of XRD methods to detect silica (Stacey, 2007). For IR methods, silicates and other minerals can interfere and affect the accuracy of the analysis. The range of reported detection limits in Eller et al. (1999a) of 5 to 50 µg reflects some of the variability associated with different matrices but is limited because it is based on data from the IH PAT program and not actual air samples collected from an industrial setting.

2. **The sampling and analytical error (SAE) as defined by OSHA in the PEA is not an appropriate measure of sampling and analysis variability because it is based on a one-sided confidence limit and not a two-sided confidence limit. Precision, as defined in the PEA, is a more appropriate measure because it is a two-sided measure of variability and uncertainty.**
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On page IV-34 of the PEA, OSHA defines the sampling and analytical error (SAE) as a one-sided 95% confidence limit:

$$SAE = 1.645 \times \sqrt{CV_1^2 + CV_2^2}$$

Where CV_1 is the analytical error and CV_2 is the sampling error. While not defined, the value 1.645 is the standard normal distribution value for a probability of 5% (100% - 95%) (Freund and Walpole, 1987). However, the NIOSH (1995) definition of an acceptable accuracy and precision is $\pm 25\%$ at a 95% confidence, which indicates the need for a two-sided confidence limit. In addition, it is clear that any measure of sampling and analysis error should be two-sided, that is, the measured concentration of silica may be either an underestimate or an overestimate of a true concentration of silica for any given environment.

On page IV-35 of the PEA, OSHA defines the precision in Table IV.B-6 using the following equation:

$$Precision = 1.96 \times \sqrt{CV_1^2 + CV_2^2}$$

This is the more appropriate measure of error because 1.96 is the standard normal distribution value for a probability of 2.5% (100% - 97.5%), which is the appropriate value for a two-sided 95% confidence limit (Freund and Walpole, 1987).

In the preamble of the proposed rule, 78 Fed. Reg. at 56354, OSHA uses the SAE and not the precision when making statements to the effect that the existing sampling and analysis methods are sufficiently sensitive and precise; however, this is not appropriate because the SAE is only a one-sided metric of sampling and analysis error. Instead, these statements should be made using the precision as defined in the PEA.

3. **OSHA's estimated SAE and precision for quartz concentrations at the proposed PEL of 50 $\mu\text{g}/\text{m}^3$ of $\pm 14\%$ and $\pm 17\%$, respectively, are incorrect because they are based on an incomplete characterization of the sampling and analytical errors. OSHA's estimated SAE and precision for quartz concentrations at the proposed action level of 25 $\mu\text{g}/\text{m}^3$ of $\pm 16\%$ and $\pm 19\%$, respectively, are incorrect for the same reasons.**

In the preamble to the NPRM, OSHA states that at filter loadings corresponding to the proposed PEL, the precision and SAE for quartz are ± 17 percent and ± 14 percent, respectively, and concludes that these results indicate that employers can have confidence in sampling results for the purpose of assessing compliance with the PEL and identifying when additional engineering and work practice controls and/or respiratory protection are needed. In addition, OSHA states that at filter loadings corresponding to the proposed action level, the precision and SAE for quartz are ± 19 percent and ± 16 percent, respectively, and concludes that Method ID-142 can achieve a sufficient degree of precision to identify operations where routine exposure monitoring is needed. According to the preamble, the basis for these statements is an evaluation of the precision of OSHA Method ID-142 at 20 and 40 μg loadings that was performed at the OSHA Salt Lake Technical Center (SLTC). The implication from the summary in the preamble is that this evaluation was a high quality study that thoroughly evaluated the precision of the method. However, based on the description of the study in Chapter IV of the PEA this is not the case.

According to the description in the PEA, this study consisted of the analysis of 10 replicate filters that were prepared with quartz loadings of 21.0 and 40.6 μg using NIST standard

reference materials (OSHA, 2013). These filters were then analyzed using Method ID-142 and the relative standard deviation (RSD), accuracy, precision, and SAE were calculated based on the results of these analyses.

In the PEA, OSHA defines the SAE and precision as functions of the analytical error characterized by the coefficient of variation associated with the analytical method (CV_1) and sampling error characterized by the coefficient of variation associated with the sampling method (CV_2). In the PEA, OSHA defines CV_1 as the RSD associated with the SLTC's evaluation of the 10 replicate samples for each loading (Table IV.B-6 of the PEA) and CV_2 as 5.0%, the error associated with pump flow rate variability. However, these estimates of CV_1 and CV_2 provide an incomplete description of the analytical and sampling error associated with the sampling and analysis of respirable crystalline silica at the proposed PEL.

First, OSHA's characterization of the sampling error using 5% to account for variability in sampling pump flow rates accounts for only a portion of the potential sampling error. Sampling error can occur from multiple sources other than just pump flow rate variability, including:

- Variability in the performance of different cyclones (Gautam and Sreenath, 1997; Gorner et al., 2001; Verpaele and Jouret, 2012);
- Performance of the cyclone with different dust particle sizes for a single dust species, with different dust species, and with a real world multispecies environment (Gautam and Sreenath, 1997; Vincent, 2007; Kulkarni et al., 2011; Verpaele and Jouret, 2012);
- Effect of loading/cleaning on cyclone performance (Lodge, 1988; Vincent, 2007), and;
- Effect of the electrostatic properties of dust (Lodge, 1988; Vincent, 2007).

The inter-sampler variation associated with variability in different cyclone samplers of the same type has been quantified by Gautam and Sreenath (1997) and is also discussed in ASTM Method D4532-10, Standard Test Method for Respirable Dust in Workplace Atmospheres Using Cyclone Samplers. Gautam and Sreenath (1997) collected four replicate efficiency measurements with

eight Dorr-Oliver samplers and eight multi-inlet samplers. They estimated a value of 7.5% for the RSD for the Dorr-Oliver samplers and 5.3% for the multi-inlet samplers, for an average RSD of 6% due to inter-sampler variation. In addition, the uncertainty associated with using different types of samplers based on the same respirable particle size convention has also been quantified and is presented in ASTM Method D4532-10 as well. For this source of sampling error, it was conservatively estimated that using different types of samplers could lead to 5.0% variation in results.

The following equation can be used to estimate the sampling error (CV_2) due to pump flow rate variability, inter-sampler variability, and sampler type variability of 9.3%:

$$CV_2 = \sqrt{(5\%)^2 + (6\%)^2 + (5\%)^2} = \sqrt{25 + 36 + 25} = 9.3\%$$

Table 1 presents the estimates of CV_1 , SAE, and precision associated with different silica loadings, different data sets and alternative assumptions regarding CV_2 . The first two rows show the SAE and precision values presented by OSHA in the preamble and PEA for silica concentrations at the proposed action level and the proposed PEL using a CV_2 value of 5.0%. The next two rows show those same metrics using a corrected CV_2 value of 9.3%. As can be seen, if the estimate of CV_1 from the SLTC evaluation is used with the corrected CV_2 of 9.3%, the revised SAE and precision values at the proposed PEL are 19% and 23%, respectively. Similar comparisons of SAE and precision values using alternative CV_2 values of 5.0% and 9.3% are shown for a study conducted at the SLTC in 2010 and for AIHA IH PAT Rounds 156 to 180 at filter loadings less than 70 ug. The 2010 SLTC study and results from PAT rounds 156 to 180 are discussed in more detail later in these Comments.

Table 1. Calculation of Sampling and Analysis Error (SAE) and Precision at the Proposed Action Level and PEL Based on a More Complete Characterization of Sampling and Analysis Errors.

Data set	Loading (µg)	N	CV ₁	CV ₂	SAE	Precision
SLTC Table IV.B-6 at the proposed action level using CV ₂ = 5.0%	21.0	10	8.6%	5.0%	16%	19%
SLTC Table IV.B-6 at the proposed PEL using CV ₂ = 5.0%	40.6	10	7.3%	5.0%	15%	17%
SLTC Table IV.B-6 at the proposed action level using CV ₂ = 9.3%	21.0	10	8.6%	9.3%	21%	25%
SLTC Table IV.B-6 at the proposed PEL using CV ₂ = 9.3%	40.6	10	7.3%	9.3%	19%	23%
SLTC 2010 from OSHA docket at proposed action level using CV ₂ = 5.0%	20.3	10	16%	5.0%	28%	33%
SLTC 2010 from OSHA docket at proposed PEL using CV ₂ = 5.0%	40.75	10	13%	5.0%	23%	27%
SLTC 2010 from OSHA docket at proposed action level using CV ₂ = 9.3%	20.3	10	16%	9.3%	31%	36%
SLTC 2010 from OSHA docket at proposed PEL using CV ₂ = 9.3%	40.75	10	13%	9.3%	26%	31%
AIHA IH PAT Rounds 156 to 180 for loadings less than 70 ug using CV ₂ = 5.0%	40 to 70	23	18%	5.0%	31%	37%
AIHA IH PAT Rounds 156 to 180 for loadings less than 70 ug using CV ₂ = 9.3%	40 to 70	23	18%	9.3%	33%	40%

The use of the RSD from the SLTC evaluation to estimate CV₁ fails to account for several sources of analytical error, including:

- Effect of differences in particle sizes on the analysis of silica by XRD and IR methods (Bhaskar et al., 1994; Kauffer et al., 2002; Ferg et al., 2008; Stacey et al., 2009);
- Effect of potential interferences on the XRD and IR analysis methods (Eller et al., 1999b; Stacey, 2007);

- Effect of inter-laboratory differences in sample preparation, calibration standards, and implementation of the XRD and IR methods (NIOSH, 1995; Eller et al., 1999b; Stacey et al., 2003; Stacey, 2007; Stacey et al., 2009), and;
- Effect of intra-laboratory differences in sample preparation and analysis caused by differences between sample preparation methods, analysts and variability in analysis runs (NIOSH, 1995; Eller et al., 1999b; Stacey et al., 2003).

Specifically, because only the XRD method was used, the SLTC evaluation fails to account for the analytical error associated with differences between the two methods, which has been identified in the scientific literature (Bhaskar et al., 1994; Eller et al., 1999b; Kauffer et al., 2002; Kauffer et al., 2005; Ferg et al., 2008). Because only one method was used, the RSD associated with the SLTC evaluation does not account for the variability associated with the analytical method or the differences in precision between the two methods that have been shown in the published literature (Eller et al., 1999b; Stacey et al., 2003; Bhaskar et al., 1994; Kauffer et al., 2005).

Second, the sample size of 10 samples per loading used in the evaluation is fairly small given that the results are being used to characterize the overall analytical error for two analysis methods that may be used by at least 57 laboratories based on the numbers from the IH PAT Round 180 results from testing done in 2009. Interestingly, the results of a similar evaluation of accuracy and precision performed by the SLTC in 2010 using twice as many samples per loading level are included in the OSHA docket (OSHA-2010-0034-1670) but not discussed in the NPRM or PEA. While the documentation for this study is limited, it appears to include the analysis of two sets of ten samples of cristobalite and two sets of ten samples of quartz by the XRD method at loadings of around 20 and 40 μg , with one set analyzed using a Rigaku XRD system and one using a PanAnalytical XRD system. The RSD and associated accuracy and precision values were estimated for each set of 10 in the same manner as in the SLTC evaluation that is presented in the PEA.

Based on what is in the docket, the estimates of CV_1 for this study are much higher than those from the SLTC evaluation presented in the PEA. For quartz, the estimate of CV_1 was 16.1% based on the first analytical line of the 10 samples at 20 μg analyzed using the Rigaku XRD system and was 12.8% for the 10 samples at 40 μg . For the PanAnalytical XRD system, the estimate of CV_1 was 21.6% for the 10 samples at 20 μg and was 13.4% for the 10 samples at 40 μg . However, based on the documentation provided, OSHA did not consider the PanAnalytical XRD system to be ready for compliance sampling; therefore, the values for CV_1 associated with that system may be not appropriate for use in estimating the SAE or precision, so they are not considered further in these Comments.

Table 1 presents the estimates for SAE and precision associated with the CV_1 estimates from this study for the two quartz loadings analyzed by the Rigaku XRD system. For the 20 μg loading, the SAE and precision values range from 28% – 31% and from 33% – 36%, respectively, depending on the value of CV_2 that is used. For the 40 μg loading, the SAE and precision values range from 23% – 26% and from 27% – 31%, respectively, depending on the value of CV_2 . These precision estimates are higher than those presented in the PEA from the smaller SLTC evaluation in March 2013, with the precision at 20 μg being 14% higher and the precision at 40 μg being 10% higher when a CV_2 value of 5.0% is used. These data indicate that the estimated precision at SLTC could be much higher than the values estimated using the 10 samples per loading discussed in the PEA and well above the $\pm 25\%$ level considered to be acceptable for a sampling and analysis method (NIOSH, 1995).

Third, the SLTC evaluation included only one laboratory, so the RSD values do not account for inter-laboratory variability, which has also been identified as a major contributor to sampling and analysis error and has been characterized in the published literature (Eller et al., 1999b; Stacey et al., 2003). The SLTC used a specific method for sample preparation, digestion by THF, and a specific XRD method, while many laboratories use different preparation methods and different analytical methods. The SLTC evaluation, by using only the THF digestion method, does not address sample preparation error, a component of inter-laboratory variability, associated with preparation methods in which the PVC filters are ashed in a muffle furnace or low temperature

plasma asher. It is expected that most AIHA accredited laboratories use a muffle furnace to prepare the filters for analysis.

Finally, the SLTC used pure silica standards that were directly deposited onto a series of PVC filters, digested by THF, and re-deposited onto silver membranes. No attempt was made to account for the existence of potential interferences by using alternate sample matrices. The AIHA IH PAT program evaluates potential interferences by rotating the matrix for the test samples for each round in the program between pure silica, silica in calcite, silica in talc, and silica in talc with coal mine dust. The variability associated with silica being in different matrices can have a significant impact on the analytical error and precision as demonstrated in the Eller et al. (1999b) analysis of the IH PAT data from 1990 to 1998. Also, by not attempting to account for potential interferences, the SLTC evaluation was not consistent with the NIOSH (1995) guidelines for assessing the accuracy and precision of a sampling and analysis method.

Another source of data that could be used to characterize the analytical variability is the data available from the AIHA IH PAT program administered by IH professionals from AIHA and NIOSH over the last 30 years. This program serves as the standard for certification for silica analyses for all IH laboratories in the U.S. and many others around the world. For each round of the IH PAT program, samples are prepared with silica loadings embedded in different matrices on a rotating schedule and sent to the labs four times per year. The matrices are typical of what might exist in samples collected from industries that monitor silica exposures. These matrices include calcite, coal dust, talc dust, and a combination of coal and talc dust. Each laboratory analyzes the samples based on standard methods that can include XRD, IR, or colormetric methods, though very few labs have used the colormetric method to analyze PAT samples in recent years. Thus, the data associated with the IH PAT program can account for variability due to inter-laboratory differences, intra-laboratory differences over time, analytical method differences, and differences in sample matrices.

OSHA chose not to use the PAT data to estimate overall analytical error (CV_1) because it claimed that the PAT data were not suitable for characterizing precision and accuracy because of the high variability of the data across laboratories. However, the IH PAT data are well suited to characterize the analytical error for analysis of respirable crystalline silica because the program evaluates several of the sources of analytical error that the SLTC evaluation does not cover, specifically, variability due to inter-laboratory differences, analytical method differences, and differences in sample matrices. The data from the IH PAT program are inherently more variable than the data from the SLTC evaluation because of the additional sources of variability that are characterized by the IH PAT data. Compared to the SLTC evaluation, a CV_1 estimate from this data set would provide a better characterization of analytical error and results that are more representative of real world conditions.

One drawback to using the IH PAT program data to estimate CV_1 is that the lowest silica loading used in the program is typically around 40 μg , which corresponds to the proposed PEL. However, it has been demonstrated that the RSD increases with decreasing silica loading for the XRD and IR methods (Eller et al., 1999b; Stacey et al., 2003) so any estimate of RSD calculated from the lower end of the silica loadings used in the IH PAT data will be lower than the actual value that might be estimated for 40 μg samples and certainly for the 20 μg samples that correspond to the proposed action level.

The IH PAT data that are available to estimate the RSD associated with silica analyses in the OSHA docket are those from Rounds 156 to 180 because OSHA used different subsets of the IH PAT data in the PEA. Rounds 156 to 180 cover a time period from April 2004 to February 2010. Similar to what was done for other analyses of the IH PAT data by OSHA in the PEA, Cardno Chemrisk estimated the RSD in this data set for samples having silica loadings less than 70 μg . This included 23 of the 100 available samples. The CV_1 estimate was 18%. Using this estimate of CV_1 with either the original estimate of CV_2 of 5.0% or the corrected estimate of 9.3%, the SAE and precision values were estimated to range from 31% – 33% and from 37% – 40%, respectively (Table 1). These values are similar to the ranges that were estimated based on the SLTC 2010 data, which had SAE values that ranged from 23% – 31% and precision values that

ranged from 27% – 36%, depending on the loading level and CV_2 . The estimates of precision ranging from $\pm 37\%$ to $\pm 40\%$ are greater than the value of $\pm 25\%$ typically considered acceptable to demonstrate acceptable accuracy of a sampling and analysis method (NIOSH, 1995).

Another source of data that can be used to characterize the CV_1 and the overall SAE and precision are the results of a respirable crystalline silica round-robin performance testing program sponsored by the American Chemistry Council (ACC) Crystalline Silica Panel. Filters containing three different loadings of respirable quartz dust were sent over a period of several months to five different AIHA-accredited commercial laboratories for analysis as part of a blinded testing program. Each of the five laboratories uses the XRD method to analyze for crystalline silica. As part of the blinding process, the laboratories 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 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. For each round, three loading levels of respirable quartz (the “reference levels”) – 20, 40, and 80 μg – were deposited onto new PVC filters. These reference levels are the loadings associated with 8-hour samples of respirable quartz at concentrations of 25 $\mu\text{g}/\text{m}^3$ (the proposed action level), 50 $\mu\text{g}/\text{m}^3$ (the proposed PEL), and 100 $\mu\text{g}/\text{m}^3$ (the current PEL for general industry).

The filters for each reference level were prepared with three different matrices: silica only; silica mixed with respirable kaolin; and silica mixed with respirable soda-feldspar. The latter matrices simulate what may actually be present in the air samples collected in an industrial setting. In addition, a blank filter was sent to each lab in each round. Thus, in each replicate round, each of the five laboratories received 10 filters: 3 pure silica samples (one at each of the three reference levels), 3 silica/feldspar samples (one at each of the three reference levels), 3 silica/kaolin samples (one at each of the three reference levels), and 1 blank filter – for a total of 150 samples

(10 filters x 5 labs x 3 rounds). As noted, the filters were sent to each laboratory in such a way that the laboratories believed they were analyzing actual air samples collected by a commercial customer, rather than samples distributed as part of a laboratory performance evaluation. This use of blinding eliminates any bias that might be created if the analyst were aware that the samples are part of a performance and/or laboratory proficiency testing program. In this respect, the ACC-sponsored round-robin study differs from both the SLTC studies relied on by OSHA and from the IH PAT program, where the analysts understood that performance testing was involved.

An analysis of variance (ANOVA) of the round-robin data indicated that there were significant differences with respect to results at the different loading levels. Because of this, the RSD was calculated for all of the data at 20 and 40 μg loadings, respectively, and separate estimates of the SAE and precision were calculated. These estimates are presented in Table 2. The estimate of CV_1 at a loading of 20 μg was 37%, and the SAE and precision values ranged from 61% – 62% and from 72% – 74%, respectively, depending on whether a value of 5.0% or 9.3% was used for CV_2 . At a loading of 40 μg , the estimate of CV_1 was 32%, and the SAE and precision values ranged from 53% – 54% and from 63% – 65%, respectively, depending on the value assumed for CV_2 . These estimates of precision are substantially higher than those estimated using the March 2013 SLTC evaluation, the SLTC 2010 evaluation, and the IH PAT data.

What makes the estimates of precision from this study more realistic is that the samples were not part of a laboratory evaluation in which the analysts knew they were participating. Instead these samples were sent to the laboratory as actual air samples and treated the same as any other air sample that the laboratory would receive and analyze for respirable crystalline silica. Because of the blinding, there is no chance for biases caused by the laboratory assigning the samples to the best analyst, or performing a higher level of QA/QC than is normally conducted, or taking special care with the analysis in order to ensure that the results would not be deemed unacceptable in a proficiency evaluation.

Table 2. Calculation of Sampling and Analysis Error (SAE) and Precision at the Proposed Action Level and PEL Based on the ACC Round Robin Study Data.

Data set	Loading (µg)	N	CV ₁	CV ₂	SAE	Precision
ACC Round Robin Study at proposed action level using CV ₂ = 5.0%	20	45	37%	5.0%	61%	72%
ACC Round Robin Study at proposed PEL using CV ₂ = 5.0%	40	45	32%	5.0%	53%	63%
ACC Round Robin Study at proposed action level using CV ₂ = 9.3%	20	45	37%	9.3%	62%	74%
ACC Round Robin Study at proposed PEL using CV ₂ = 9.3%	40	45	32%	9.3%	54%	65%

4. **Due to a miscalculation, OSHA incorrectly states that most laboratories achieve good agreement in results for samples with filter loadings just above 40 µg quartz.**

In the preamble to the proposed rule, OSHA states that most laboratories achieve good agreement in results for samples having filter loads just above 40 µg quartz (49–70 µg). This statement is based on an analysis of the number of laboratories that had sample results that were within ±25% of the reference values in the AIHA IH PAT program for Rounds 156 to 165. It is unclear why OSHA limited its analysis to the data from these rounds, which are not the most recent. Whatever the reason, Table IV.B-9 of the PEA presents the percentage of laboratories reporting values within ±25% of the reference value in these PAT rounds. OSHA states that for all reference values the laboratories achieve good agreement because 80% were within ±25% of the reference value. In addition, OSHA states that for reference values less than 70 µg, 81% of the laboratories were within 25%. However, a recalculation of the results shown on Table IV.B-9 indicates that the actual percentage of the labs within ±25% of the reference value for reference values less than 70 µg is not 81% but 73%, while for reference values above 70 µg, 83% of the

labs were within $\pm 25\%$ of the reference value – thus demonstrating that precision deteriorates at lower silica loadings.

5. Past data from the AIHA IH PAT program for respirable crystalline silica have been used to characterize method differences and intra-laboratory variability, and these analyses have been published in the peer-reviewed literature.

In Chapter IV of the PEA, OSHA states that the IH PAT data were not suitable for characterizing the method differences and intra-laboratory variability because PAT sample preparation errors may contribute to the analytical error and because the reference value is based on either the average of a subset of laboratories or all of the laboratories reporting for the round, depending on the round being evaluated. However, the IH PAT data have been used to evaluate the accuracy and precision of the respirable crystalline silica method in two separate studies that have been published in the peer-reviewed literature, Shulman et al. (1992) and Eller et al. (1999b). Both papers evaluated the accuracy and precision of the different analytical methods (XRD, IR, and colorimetric), as well as inter-laboratory and intra-laboratory differences in precision of the analytical methods based on different time periods of the PAT program. Thus, members of the scientific community have considered PAT program data to be suitable and useful for evaluating the precision of analytical methods for crystalline silica. Moreover, in 1995, OSHA scientists, Madsen et al. used the IH PAT data for silica that was current at the time of the paper to discuss the imprecision associated with silica analyses (Madsen et al., 1995). While OSHA now contends that these data are not useful for the purpose of evaluating the accuracy and precision of sampling and analytical methods, it apparently took a different position in the past.

6. While high flow rate samplers, such as the BGI GK 2.69 are available and can collect a higher amount of silica than the low flow rate samplers that are currently used, the accuracy and precision associated with these samplers has not been evaluated.

On page IV-43 of the PEA, OSHA states that a higher flow rate device such as the BGI GK 2.69 (with a recommended flow rate of 4.2 L/min) can collect more than 10 μg of dust for a 1 hour

sample at the proposed PEL. The implication of this statement is that even if the accuracy and precision of the sampling and analysis of respirable crystalline silica does not meet the standard of $\pm 25\%$ at a 95% confidence level when silica filter loadings are 40 μg and below, there are samplers that are capable of collecting a greater amount of silica at the same air concentration due to the increased sampler flow rate. However, there are several limitations to using the high flow samplers.

First, the accuracy and precision of the high flow rate samplers for measuring respirable crystalline silica have not been evaluated. While the performance of these samplers for collecting respirable particulates and quartz has been evaluated relative to the low flow samplers in several studies (Gorner et al., 2001; Lee et al., 2010; Lee et al., 2012), these studies have focused on the sampling efficiencies of the respective samplers relative to the ISO/CEN particle size convention and on how the amount of mass the individual high flow samplers collect compared to the low flow samplers. None of these studies evaluated the accuracy and precision of the samplers using the methods recommended in NIOSH (1995) for sampling and analytical method development.

Second, the need to evaluate the accuracy and precision of these methods is important because, studies by Lee et al. (2010; 2012) indicate that the high flow rate samplers tend to collect a higher proportion of larger size particles than the lower flow rate samplers currently used. Lee et al. (2010) found that the BGI GK 2.69 high flow sampler had a large bias for particles with a large MMAD. The sampling efficiency for this sampler at 10 μm was 9.9% compared to the expected efficiency of 1% for the ISO/CEN standard. This indicates that the BGI GK 2.69 sampler will tend to collect a higher proportion of large particles. In general, all three high flow samplers evaluated by Lee et al. (2010) tended to have a substantial bias towards collecting more respirable particulates than the low flow samplers, collecting between 12% to 31% more mass than the low flow samplers.

Lee et al. (2012) compared three high flow samplers with two low flow samplers using two types of coal dust. For this study, they evaluated both respirable particulates and analyzed the samples for quartz using both XRD and IR methods. Similar to the previous study (Lee et al., 2010), they found that the high flow samplers tended to collect a greater mass of respirable particles, between 2.3% to 18.7% more compared to the lower flow rate 10 mm Dorr Oliver sampler. While the high flow samplers collected more quartz mass than the low flow samplers, the standard deviations associated with the mass ratios and net mass ratios were high, indicating a potential increase in sampling and analysis error (Lee et al., 2012). However, Lee et al. (2012) did not discuss differences in accuracy and precision between the sampler types.

Because respirable silica in occupational settings tends to have a greater proportion of smaller particle sizes, while the high flow samplers tend to oversample larger size particles compared to the low flow rate samplers, it seems likely that the high flow samplers will collect a greater proportion of non-silica particles that can interfere with the analysis of respirable crystalline silica using the XRD or IR methods. In addition, the standard deviations of the mass ratios calculated by Lee et al. (2012) for the performance of high and low flow samplers analyzing coal dust suggest that there may be substantial differences in the sampling error associated with the high flow samplers compared to the low flow samplers. A further consideration is that the use of a high flow sampler likely would necessitate use of a pump with higher flow rates than those currently used by most industrial hygienists and dust samplers – particularly if the industrial hygienist is collecting full shift samples at a sampling rate of 4.2 L/min versus the current rate of 1.7 L/min for the Dorr-Oliver sampler.

For these reasons, before recommending the use of high flow samplers, OSHA would have to develop a much better understanding of the accuracy and precision of these samplers under real world conditions using particles that may be found in the workplace.

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