# SILICA

## SAMPLING AND ANALYTICAL CONCERNS

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# EXECUTIVE SUMMARY

According to the Occupational Safety and Health Administration (OSHA), one aspect of determining whether a proposed permissible exposure limit (PEL) is feasible is whether exposures at that level "can be reliably measured for purposes of the OSHA compliance programs."[1] If a PEL were established at a level that cannot be reliably and reproducibly measured, OSHA observes, "measurements taken by employers and by OSHA would provide an uncertain basis for determining whether employers have fulfilled their compliance duties."[2]

The objective of this Report is to discuss the problems involved in sampling and analyzing crystalline silica at respirable airborne concentrations of 0.1 mg/m$^3$ or below and to evaluate the precision and accuracy of sampling and analytical methodologies at those low airborne concentrations. The concentrations of particular interest are those between 0.025 mg/m$^3$ (which presumably would be the action level for a potential PEL of 0.05 mg/m$^3$) and 0.075 mg/m$^3$ (which probably is the highest PEL value OSHA would consider if it decides to reduce the PEL for crystalline silica at all). What we want to know is whether crystalline silica concentrations in that range can be measured reliably and reproducibly.

"Sampling and analysis of crystalline silica," as Steven Edwards of OSHA's Salt Lake Technical Center points out, "present unique problems to the industrial hygienist."[3] This Report discusses some of these problems and concludes that current sampling and analytical methodologies do not provide a basis for reliably and reproducibly measuring airborne silica concentrations below 0.1 mg/m$^3$. The following are among the principal points made in this Report.

- The only "validated method" OSHA has identified for analyzing quartz and cristobalite is OSHA Method ID-142, which uses X-ray Diffraction (XRD). OSHA ID-142 references a Precision and Accuracy Validation Range of 50-160 µg quartz per sample. (OSHA ID-142 does not list a precision and accuracy validation range for cristobalite.)

  *Based on the recommended air volume of 816 L for an 8-hour sample collected at the recommended flow rate of 1.7 L/min, 50-160 µg quartz per sample represents an air concentration range of 0.061 mg/m$^3$ - 0.196 mg/m$^3$. While this may be an appropriate range to consider when evaluating method performance for the current quartz PEL of roughly 0.1 mg/m$^3$, the entire range is above the values that OSHA appears to be considering for a new action level and PEL (i.e., 0.025 mg/m$^3$ – 0.05 mg/m$^3$).*

- OSHA's Inorganic Methods Protocol states that a validated method must have a pooled $CV_1$ of 0.07 or less for data in the range of 0.5 x the PEL to 2 x the PEL.[4]

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[1] See 53 Fed. Reg. 35610, 35618, 35619 (September 14, 1988) (lowest feasible short term excursion limit); see also 59 Fed. Reg. 40964, 40968 (August 10, 1994).

[2] 59 Fed. Reg. 40964, 40969 (August 10, 1994).

[3] Edwards, S.L., Crystalline Silica: Sampling and Analytical Issues. The Synergist, December 2000, p. 11.

[4] Occupational Safety and Health Administration, Salt Lake Technical Center, Inorganic Methods Evaluation Protocol, www.osha-slc/methods/imeprotocol/index.html, § 2.2.

> *OSHA ID-142 references a $CV_1$ of 0.106 for loadings in the range of 50 µg to 160 µg of quartz. Thus, OSHA ID-142 does not appear to be acceptable even for the current PEL, let alone for a PEL of 0.05 mg/m$^3$, where the $CV_1$ presumably would be higher than 0.106.*

- OSHA's Inorganic Methods Protocol states that the quantitative detection limit for an analytical method should be less than 0.1 times the PEL (or the mass equivalent of the PEL).[5] Assuming an air flow of 1.7 L/min (collecting an air volume of 816 Liters over 8 hours) and several alternative PEL values, the required quantitative detection limits would be as follows:

**Table 1**
**Quantitative Detection Limit For Quartz**
**Required for Alternative PELs**

| Alternative PEL Values | 0.1 x PEL | Required Detection Limit (µg quartz) |
|---|---|---|
| 0.1 mg/m$^3$ | 0.01 mg/m$^3$ | 8.16 |
| 0.075 mg/m$^3$ | 0.0075 mg/m$^3$ | 6.12 |
| 0.050 mg/m$^3$ | 0.0050 mg/m$^3$ | 4.08 |
| 0.025 mg/m$^3$ | 0.0025 mg/m$^3$ | 2.04 |

> *OSHA ID-142 lists a quantitative detection limit of 10 micrograms for quartz. That value is higher than any of the required detection limits for the alternative PEL values shown in the foregoing table. It is more than twice as high as the detection limit that would be required for a PEL of 0.05 mg/m$^3$ and more than four times as high as the detection limit that would be required for an action level of 0.025 mg/m$^3$. OSHA ID-142 lists a quantitative detection limit for cristobalite of 30 micrograms. Thus, for cristobalite, the discrepancy between the reported detection limit and the detection limit that would be required for the alternative PEL values is even greater than in the case of quartz. Of course, the discrepancy would be greater still if the PEL for cristobalite were reduced to a level that is 50% of a reduced PEL for quartz.*

- To ensure that a PEL is not below the "lowest level feasibly measured," OSHA allows for a combined sampling and analytical error (SAE) of ± 25% at the 95% confidence level.

> *OSHA Method ID-142 claims to have an Overall Analytical Error of ±26% for quartz loadings in the range of 50 to 160 µg quartz. This value assumes a mean bias of 5.2% and apparently is based on unpublished quality control data compiled at OSHA's Salt Lake Technical Center from December 1986 to September 1988. [However, it does not include sampling error. If one uses a 5% sampling error (the value assumed by NIOSH), the SAE for OSHA Method ID-142 would be ±30.2%, based on intra-laboratory analytical variance and using the methodology set forth in OSHA's Inorganic Methods*

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[5] Id. § 6.2.

> *Protocol.*[6] *The 5% sampling error value used by NIOSH, however, has not been substantiated, and previous studies indicate a sampling and cyclone error of 17%.*[7] *Assuming a 17% sampling error, the SAE for OSHA Method ID-142 would be ±46.1%. In either case, the SAE exceeds the ±25% level that OSHA states is necessary to ensure that a PEL can be feasibly measured.] The Overall Analytical Error of ±26% reflects sampling error only to the extent that samplers were used to collect dust from the generating system in the sampling and analysis experiment. Even so, this SAE exceeds the ±25% level that OSHA states is necessary to ensure that a PEL can be feasibly measured. Moreover, this SAE value is for quartz loadings in the range of 50 to 160 μg, which corresponds to an air concentration range of roughly 0.5 – 2 x a PEL of 0.1 mg/m*$^3$*. For a PEL of 0.05 mg/m*$^3$*, the relevant range of quartz loadings would be about 50% lower, and the SAE values presumably would be higher.*

- OSHA uses respirable dust collection criteria having a 50% cut point ($D_{50}$) of 3.5 micrometers mass median aerodynamic diameter. This reflects the collection profile of the 10 mm Dorr-Oliver sampler. As noted at page 19 below, if OSHA switched to an SKC cyclone with a $D_{50}$ cut point of 4.0 micrometers, there would be an increase in collection efficiency of 15-18%.

> *Depending on the particle size of the respirable dust samples, this could result in an automatic lowering of the existing standard without changing the existing PEL. This also would throw into question the relevance of all previous silica sampling and analytical results reflecting use of the Dorr-Oliver sampler (or an equivalent particle count conversion); yet the vast bulk of silica epidemiological studies are based on Dorr-Oliver equivalent sampling.*

- The American Industrial Hygiene Association (AIHA) sponsors the only round robin testing program for silica. This program is referred to as the Proficiency Analytical Testing or PAT Program. At its peak in 1984, 134 laboratories participated in the PAT program for silica. By December 2000, the number had fallen to 76. Recent PAT data (Rounds 124-139) indicate that a total of 80 labs participate in the PAT Program for silica. Only 56 of the participating laboratories are accredited. Of these, only 41 are located in the U.S. and accept silica samples from third parties on a "fee basis."

> *Accredited labs perform silica analyses with better precision and accuracy than non-accredited labs in the PAT Program. Yet, a relatively small number of accredited labs accept silica samples for analysis from third parties. This would create problems if OSHA were to require extensive and frequently repeated silica monitoring.*

- NIOSH's goal for analyses of silica under the PAT Program is a Relative Standard Deviation (RSD) of <15%.[8]

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[6] Occupational Safety and Health Administration**,** Salt Lake Technical Center, Inorganic Methods Evaluation Protocol, www.osha-slc/methods/imeprotocol/index.html.

[7] Anderson, C.C. Collaborative Tests of Two Methods for Determining Free Silica In Airborne Dust (NIOSH, October 1983), pp. 24, 26.

[8] Eller, P., *et al*. Silica Method Modifications for Improved Interlaboratory Precision. The Synergist, November 1999, p. 23.

> *The RSD for silica in PAT Rounds 71-138 ranges from 15.3% to 45.4%. For the more recent subset of these PAT rounds (Rounds 98-138), the range was from 15.3% to 37%. Even in Rounds 130-133, the range of RSDs was 16% to 33%.*[9] *The PAT silica sample weight range is 50-175 μg/filter. At a flow rate of 1.7 L/min, this represents a working range for airborne concentrations of 0.061 mg/m*$^3$*- 0.214 mg/m*$^3$*. So, even for silica samples that are above the concentration range that would be relevant to a PEL of 0.05 mg/m*$^3$*, PAT Program results consistently show RSDs that are well above the level NIOSH considers acceptable.*

- NIOSH researchers analyzed silica data from PAT Rounds 101-132 (1990-1998). The most common XRD method used by participating labs was NIOSH Method 7500. Based on an analysis of reported measurements by the reference labs, the NIOSH researchers found that the overall intra-laboratory CV for XRD methods in these rounds was 0.165, while for Infrared Spectroscopy (IR) methods it was 0.166.[10] These CV values are based solely on analytical variance; they do not reflect sampling error, since the participating labs received pre-loaded filters from the generating lab.

> *Assuming a 5% sampling error, and applying the formulas used by NIOSH to calculate method performance, the "Overall Precision" of XRD based on these data would be 17.2% and the "Accuracy" would be ±34%. The comparable values for IR would be 17.3% and ±34%.*[11] *These are well above the values that OSHA would deem to reflect reliable and reproducible measurements of crystalline silica.*

- In their analysis of silica data from PAT Rounds 101-132 (1990-1998), the NIOSH researchers found that all estimates of intra- and inter-laboratory variability tended to rise at low sample loadings, with the range of 60-80 μg silica per sample being a significant cut point.[12]

> *At a flow rate of 1.7 L/min, 60-80 μg silica is equivalent to 8-hour exposure to a silica concentration of 0.074 mg/m*$^3$ *- 0.098 mg/m*$^3$*. Thus, the NIOSH analysis indicates there would be a significant increase in measurement variability if the PEL were reduced from 0.1 mg/m*$^3$ *to 0.05 mg/m*$^3$*.*

- An analysis of silica data from PAT Rounds 124-139 shows that the RSD is lower for XRD methods than for IR when all the reported results (including outliers) are considered. However, when outliers are excluded from this data set, the opposite is true. The analysis also shows that when outliers are excluded, the RSDs for both IR and XRD are higher at filter loadings in the range of 50-100 μg silica than at filter loadings in the range of 101-150 μg

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[9] Id.

[10] Eller, P., *et al*. Proficiency Analytical Testing (PAT) Silica Variability, 1990-1998. AIHA Journal. 60:533-539 (1999) at 537.

[11] The formulas used by NIOSH are described in a letter dated September 9, 1999 to Robert E. Glenn from David Bartley and Martin Abell of NIOSH. A copy of that letter is attached to this Report as Appendix 1.

[12] Eller, P., *et al*. Proficiency Analytical Testing (PAT) Silica Variability, 1990-1998. AIHA Journal. 60:533-539 (1999) at 536-537.

silica; and, for both IR and XRD, the highest RSDs are found when silica loadings are at the lowest level (in the range of 50-69 μg).

> *For PAT Rounds 124-139, the average RSD with outliers excluded was 24.6 for XRD methods and 21.1 for IR. For silica loadings in the range of 50 μg-69 μg (the range that is most relevant to measurements of air concentrations at a level of 0.05 mg/m$^3$), the average RSD with outliers excluded was 27.8 for XRD methods and 22.7 for IR. These RSD values reflect only analytical variability, since PAT Program participants are provided with pre-loaded filters. These high RSDs—and the performance data that OSHA provides for Method ID-142—suggest that current sampling and analytical methodologies do not provide a basis for reliably and reproducibly measuring airborne silica concentrations below 0.1 mg/m$^3$.*

- The average cost for a silica analysis using XRD is $75/sample, with an average turn-around time of 5 working days. The cost of a new X-Ray unit (including automatic sampler) is approximately $150,000.

> *Analytical methods for silica, particularly XRD, are complex, time-consuming and expensive.*

- NIOSH reported that in PAT Round 133 (April 1998), 12 different reference materials were used by the participating labs to prepare calibration curves.

> *NIST SRM 1878 is now available in very limited supply. The cost is $350 for five grams. As of October 2000, comprehensive comparisons among previous standards had not been published. Thus, it is not known how analyses made using NIST SRM 1878 for calibration purposes compare to analyses made using previous reference materials.*

- OSHA ID-142 and NIOSH 7500 require that samples be deposited on a silver membrane filter prior to X-Ray analysis. The silver absorption line is used to evaluate potential penetration of the sample into the pores of the filter and potential decreases in sensitivity due to sample-self-absorption of X-Rays.

> *In May 2000, the only manufacturer of silver membrane filters in the U.S. (Omega Specialty Filters) curtailed manufacturing. Other manufacturers are in the process of evaluating the feasibility of producing silver membrane filters. OSHA has reported that existing filters must be carefully examined because of poor quality control and pore size problems. If the silver membrane filter issue cannot be resolved quickly, the continued viability of both OSHA Method ID-142 and NIOSH Method 7500 would be thrown into question. NIOSH reportedly is considering a switch to a gold-impregnated membrane filter. If such a switch were made, the existing methods would have to be revalidated with use of the new filter.*

# BACKGROUND

According to OSHA, one aspect of determining whether a proposed exposure limit is feasible is whether exposures at that level "can be reliably measured for purposes of the OSHA compliance programs."[13] If a PEL were established at a level that cannot be reliably and reproducibly measured, OSHA observes, "measurements taken by employers and by OSHA would provide an uncertain basis for determining whether employers have fulfilled their compliance duties."[14]

To determine whether an exposure limit can be measured reliably for compliance and enforcement purposes, OSHA calculates what it refers to as the "lowest reliable limit of quantitation" for the OSHA Reference Method, taking into account both sampling and analytical error.[15] OSHA refers to this as the "lowest level feasibly measured" or the "lowest reliable level of detection."[16] To ensure that a PEL is not below the "lowest level feasibly measured," OSHA allows for a combined sampling and analytical error (SAE) of ± 25% at the 95% confidence level.[17] To satisfy the ±25% criterion, the 95% upper confidence limit on the true coefficient of variation ($CV_t$) for the test method at the concentration (or mass loading) of interest should be no greater than 0.128, *i.e.*, the Relative Standard Deviation (RSD) should be no greater than 12.8%.[18] The "overall precision" of the test method (presumably including an allowance for sampling error) should meet this criterion.[19]

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[13] See Amendment to Standard for Occupational Exposure to Asbestos, 53 Fed. Reg. 35610, 35618 (September 14, 1988).

[14] 59 Fed. Reg. 40964, 40969 (August 10, 1994).

[15] See 53 Fed. Reg. at 35618.

[16] See 53 Fed. Reg. at 35619.

[17] See 53 Fed. Reg. at 35619. Similarly, MSHA claims to apply the "NIOSH Accuracy Criterion [which] requires that measurements come within 25 percent of the corresponding true dust concentration at least 95 percent of the time." 65 Fed. Reg. 42068, 42090 (July 7, 2000).

[18] See Saltzman, B., Variability and Bias in the Analysis of Industrial Hygiene Samples. AIHA Journal. 46(3):134-141 (1985) at 141. MSHA makes the same point, stating that for an unbiased method, the NIOSH Accuracy Criterion requires that "the 'true' CV is no more than 0.128 (12.8 percent)"—or that "there be 95-percent confidence that measurements by the method will come within 25 percent of the true concentration 95 percent of the time." 65 Fed. Reg. 42068, 42091 (July 7, 2000).

[19] See 53 Fed. Reg. at 35619.

Sampling and analysis for crystalline silica are complicated and "present unique problems to the industrial hygienist."[20] There are numerous and significant sources of potential error. These include problems involving:

- sampling pump calibration
- cyclone calibration
- cyclone leakage
- filter cassette leakage
- total dust sampling as opposed to respirable dust sampling
- flow rates mandated by cyclone manufacturer
- cyclone particle size distribution
- cyclone contamination
- shipping contamination
- dust weighings
- sample loading
- balance calibration
- interferences
- differences in calibration standards
- particle size of calibration standards
- linear range of calibration standards
- frequency of calibration
- lower limit of quantitation
- sample preparation
- sample transfer
- silver membrane filters-production problems
- calculations

Given this range of problems, it is not surprising that the precision and accuracy of sampling and analytical methods for silica leave much to be desired, a point that has long been recognized in the industrial hygiene community.[21]

The objective of this Report is to discuss the problems involved in sampling and analyzing crystalline silica at respirable airborne concentrations of 0.1 mg/m$^3$ or below and to evaluate the precision and accuracy of sampling and analytical methodologies at those low airborne concentrations. The concentrations of particular interest are those between 0.025 mg/m$^3$ (which presumably would be the action level for a potential PEL of 0.05 mg/m$^3$) and 0.075 mg/m$^3$ (which probably is the highest PEL value OSHA would consider if it decides to reduce the PEL

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[20] Edwards, S.L., Crystalline Silica: Sampling and Analytical Issues. The Synergist. (December 2000), p. 12.

[21] See Anderson, C.C. Collaborative Tests of Two Methods for Determining Free Silica In Airborne Dust (NIOSH, October 1983); Occupational Safety and Health Administration: 1997 OSHA Cyber-conference: Sampling and Analysis of Crystalline Silica p.3; Eller, P., *et al.* Proficiency Analytical Testing (PAT) Silica Variability, 1990-1998. AIHA Journal. 60:533-539 (1999) at 536-537; Edwards, S.L., Crystalline Silica: Sampling and Analytical Issues. The Synergist, December 2000, pp. 11-13; Hall, T., The Need for an Accurate Silica Sampling and Analysis System (University of Oklahoma 19__).

for crystalline silica at all). The question is whether crystalline silica concentrations in that range can be measured reliably and reproducibly. This Report concludes that reliable and reproducible measurements in that low range of respirable silica concentrations are not feasible using current sampling and analytical methods.

# ANALYTICAL METHODS

## A. Principal Analytical Methods for Crystalline Silica

Occupational exposure levels for silica are measured by taking breathing zone samples using a pre-weighed filter and cyclone, and then analyzing the collected sample for free crystalline silica. The three most common analytical methods used for silica analysis are:

1. X-Ray Diffraction (XRD);
2. Infrared Spectroscopy (IR); and
3. Colorimetric.

Recognized analytical methods in the United States include:

- OSHA ID-142 (XRD)[22]
- NIOSH 7500 (XRD)[23]
- NIOSH 7602 (IR)[24]
- NIOSH 7603 (IR Coal Dust)[25]
- MSHA P-7 (IR Coal Dust)[26]
- NIOSH 7601 (Colorimetric)[27]

Although it is the most expensive, XRD is OSHA's "preferred method . . . because it can distinguish and quantitate the different polymorphs of free silica in a [sic] widest range of industrial dust matrices" and because it "is more accurate and offers better sensitivity than

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[22] Occupational Safety and Health Administration Analytical Laboratory: OSHA Manual of Analytical Methods (OSHA Method ID-142) Salt Lake City, UT. 1981 (Revised December 1996).

[23] National Institute for Occupational Safety and Health**:** NIOSH Manual of Analytical Methods, 4th edition (Method 7500 Silica, Crystalline by XRD), Issue 3:1998.

[24] National Institute for Occupational Safety and Health: NIOSH Manual of Analytical Methods, 4th edition (Method 7602 Silica, Crystalline by IR) Issue 2: 1994.

[25] National Institute for Occupational Safety and Health: NIOSH Manual of Analytical Methods, 4th edition (Method 7603, Silica, Crystalline in coal mine dust by IR) Issue 2: 1994.

[26] Mine Safety and Health Administration: Infrared Determination of Quartz in Respirable Coal Mine Dust (Method P-7) Revised 1994.

[27] National Institute for Occupational Safety and Health: NIOSH Manual of Analytical Methods, 4th edition (Method 7601, Silica, Crystalline by VIS) Issue 2, 1994.

previous methods of analysis."[28] XRD is the method OSHA uses for compliance purposes and apparently is the one OSHA plans to specify as the benchmark method in a new Crystalline Silica Standard. Consequently, this Report will focus on the accuracy and precision of XRD. At the same time, since IR methods are commonly used as well, and since relevant PAT Program data are available, this Report also will consider precision data for IR.

OSHA describes XRD and IR this way:[29]

> "X-ray Diffraction (XRD): The most common method is based on the diffraction of X-rays off the repeating layers of atoms in the crystalline structure. XRD is the most general but most expensive method. Because alternate analytical peaks are available, XRD is the method used by OSHA at the Salt Lake Technical Center (compliance) and at the Wisconsin State Lab (consultation). It is also used by MSHA for Metal and Non-metal Mining samples."
>
> "Infrared Spectroscopy (IR): The next most common method (currently a close second in popularity) is based on the absorption of infrared light of frequencies that correspond to characteristic vibrations of the tetrahedral $SiO_4$ structural units. . . . Compared to XRD, IR is a less expensive method choice when interferences are known and can be compensated for. The IR method is used by MSHA for Coal Mining samples."

Some of the advantages and disadvantages of these two methods are as follows.

<u>XRD Analysis</u>: In OSHA's view, XRD is "more accurate and offers better sensitivity" than other methods.[30] It can differentiate between Quartz, Cristobalite and Tridymite and is least prone to interference.[31] Analysts must be trained to recognize potential interferences and observe peak shifting or broadening. By comparing the primary and secondary absorption lines, effects from interferences can be minimized or eliminated. Alterations to the digestion system also can be employed to eliminate interferences. If interferences are present at the primary peak, the sample can be identified and quantitated using the secondary peak. However, there is a decrease in sensitivity if the secondary or tertiary lines of quartz are used to quantitate. OSHA has not published the effect of quantitation on the secondary peak or the lower limit of quantitation based on the secondary peak.

Because of the nature of X-ray diffraction, the particle size of the sample can greatly affect the quantitation of silica, so knowing the particle size distribution is very important. XRD is more sensitive to larger size particles (gives larger signals for larger particles) than to smaller particles;

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[28] OSHA Method ID-142, §§ 1.1.1 & 1.3.5.

[29] 1997 OSHA Cyber-conference: Sampling and Analysis of Crystalline Silica, p.3.

[30] OSHA Method ID-142, § 1.3.5.

[31] Edwards, S.L., Crystalline Silica: Sampling and Analytical Issues. <u>The Synergist</u>. (December 2000), p. 12.

by contrast, IR absorption is highest for small particles.[32] In performing an XRD analysis, the particle size of the sample must be closely matched to the particle size of the calibration standard, and it is absolutely imperative that samples be taken using a cyclone at the designated flow rate. It is helpful if a bulk of the material is submitted to the lab. This aids in identification of potential interferences and the ability to make adjustments in digestion or determination of the principal diffraction line used in quantitation.

"XRD instrumentation," as Steven Edwards of OSHA points out, "is expensive."[33] A new system including automatic sampler and spinner costs in excess of $150,000.00. Because of the expense involved with the instrumentation, labs will normally maintain only one X-Ray Diffractometer. Analysis time is lengthy. Samples must be scanned over a wide range to observe the ratio of the primary and secondary peaks, and each sample takes approximately 15-20 minutes of instrument time. Hence, the number of samples that can be processed in a day is limited.

IR Analysis: One major advantage of IR is that the necessary instrumentation is significantly less expensive than for XRD. The cost is approximately $40,000.00. Quantitation at low levels (10-20 µg) appears to be more precise for IR than for XRD—perhaps because, as noted above, IR is more sensitive to smaller particles, *i.e.*, absorption is highest for small particles. Though widely employed for quartz, IR generally is not used to identify or quantitate cristobalite or tridymite.

Interferences are more of a problem with IR than with XRD, although altering the digestion process can minimize certain interferences. Because coal mine dust is less prone to interferences, IR appears to be a viable method for the analysis of silica in coal mine dust. However, in a complex matrix, such as metal/non metal surface mines or iron and steel foundries, significant interferences cannot be resolved using IR.

## B. Evaluation of OSHA Method ID-142

The only "Validated Method" that OSHA has identified for crystalline silica (quartz and cristobalite) is OSHA Method ID-142, which employs X-ray Diffraction. OSHA has not validated an IR method for analysis of silica. Nor has NIOSH, except in the context of coal mine dust where interferences are minimal. Accordingly, the following method evaluation will focus on OSHA Method ID-142 as revised in December 1996. In evaluating Method ID-142, this Report will consider criteria established by the OSHA Salt Lake Technical Center (OSHA-SLTC) in its Inorganic Methods Evaluation Protocol.[34]

Among the recommendations and method performance statistics that OSHA provides for ID-142 are the following:

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[32] See Esche, C.A. & J.H. Groff, Proficiency Analytical Testing (PAT) Program: August 28, 1998. AIHA Journal. 60:123-125 (1999); Eller, P., *et al.* Proficiency Analytical Testing (PAT) Silica Variability, 1990-1998. AIHA Journal 60:533-539 (1999) at 534.

[33] Edwards, S.L., Crystalline Silica: Sampling and Analytical Issues. The Synergist. (December 2000), p. 12.

[34] Occupational Safety and Health Administration, Salt Lake Technical Center, Inorganic Methods Evaluation Protocol, www.osha-slc/methods/imeprotocol/index.html.

*OSHA ID-142*

| | |
|---|---|
| *Method Classification:* | *Validated Method* |
| *Recommended Sampling Rate:* | *1.7 L/min* |
| *Collection Device:* | *37-mm polyvinyl chloride filter preceded by a 10-mm nylon Dorr-Oliver cyclone used with a personal sampling pump.* |
| *Recommended Air Volume:* | *816 L* |
| *Detection Limits:* | |
| *Qualitative* | *5 μg quartz*<br>*10 μg cristobalite* |
| *Quantitative* | *10 μg quartz*<br>*30 μg cristobalite* |
| *Precision and Accuracy Validation Range* | |
| *Quartz* | |
| *50-160 μg quartz per sample* | |
| $CV_1$ | *0.106* |
| *Bias* | *5.2%* |
| *Overall Analytical Error* | *±26%* |

Several aspects of the foregoing performance data and recommendations warrant comment.

**First**, the method has been "validated" only for quartz in a range of 50-160 μg per sample. Thus, even assuming the "validation" is otherwise correct, it would apply only to a PEL of 0.1 mg/m$^3$ or greater, because at a recommended sampling rate of 1.7 L/min and a recommended air volume of 816 L, filter loadings of 50-160 μg of quartz correspond to air concentrations of 0.061 mg/m$^3$ - 0.196 mg/m$^3$—*i.e.*, roughly 0.5 to 2 times a PEL of 0.1 mg/m$^3$. The precision and accuracy of Method ID-142 have not been "validated" for a PEL lower than 0.1 mg/m$^3$ using the recommended collection device, sampling rate, and air volume. To evaluate precision and accuracy for air concentrations covering a range of 0.5 to 2 times a PEL of 0.05 mg/m$^3$, quartz loadings in the range of roughly 20-80 μg per sample would have to be measured, assuming the recommended air volume of 816 L is used.

**Second**, OSHA's Inorganic Methods Protocol says an analytical method must be capable of achieving a $CV_1$ value of 0.07 or less.[35] The $CV_1$ for Method ID-142 is 0.106, and thus exceeds the maximum value specified in OSHA's Inorganic Methods Protocol. Moreover, the $CV_1$ value of 0.07 or less is supposed to be achievable for data in the range of 0.5 x the PEL to 2 x the PEL. Thus, OSHA ID-142 does not appear to be acceptable even for the current PEL, let alone for a PEL of 0.05 mg/m$^3$, where the $CV_1$ presumably would be higher than 0.106. Furthermore, although OSHA has not identified the "true" coefficient of variation ($CV_t$) for sampling and analysis of Method ID-142, the fact that the $CV_1$ for analytical variability alone is 0.106 suggests

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[35] Occupational Safety and Health Administration, Salt Lake Technical Center, Inorganic Methods Evaluation Protocol, www.osha-slc/methods/imeprotocol/index.html, § 2.2.

that $CV_t$ is greater than 0.128, and thus does not satisfy the ±25% criterion at the 95% confidence limit.[36]

**Third**, OSHA's Inorganic Methods Protocol states that the quantitative detection limit for an analytical method should be less than 0.1 times the PEL (or the mass equivalent of the PEL).[37] At a recommended sampling rate of 1.7 L/min and a recommended air volume of 816 L, the required quantitative detection limits for several alternative PEL values would be as follows:

**Table 2**
**Quantitative Detection Limit For Quartz**
**Required for Alternative PELs**

| Alternative PEL Values | 0.1 x PEL | Required Detection Limit (µg quartz) |
|---|---|---|
| 0.1 mg/m$^3$ | 0.01 mg/m$^3$ | 8.16 |
| 0.075 mg/m$^3$ | 0.0075 mg/m$^3$ | 6.12 |
| 0.050 mg/m$^3$ | 0.0050 mg/m$^3$ | 4.08 |
| 0.025 mg/m$^3$ | 0.0025 mg/m$^3$ | 2.04 |

As noted above, the quantitative detection limit for quartz under Method ID-142 is 10 µg. This is higher than the detection limit of 8.16 µg that OSHA's Inorganic Methods Protocol indicates is required for a PEL of 0.1 mg/m$^3$, and more than twice as high as the detection limit of 4.08 µg that OSHA's Inorganic Methods Protocol indicates is required for a PEL of 0.05 mg/m$^3$. For cristobalite, of course, the situation is even worse, since the quantitative detection limit for cristobalite under Method ID-142 is 30 µg, three times higher than that for quartz.

**Fourth**, OSHA Method ID-142 claims to have an Overall Analytical Error of ±26% for quartz loadings in the range of 50 to 160 µg quartz. This value assumes a mean bias of 5.2% and apparently is based on unpublished quality control data compiled at OSHA's Salt Lake Technical Center from December 1986 to September 1988.[38] As we understand it, sampling error is included in this value only to the extent that samplers were used to collect quartz-containing dust from the generating system in the sampling and analysis experiment. Whether that reflects an adequate allowance for sampling error is questionable, since "the sample collection process is a major potential source of error," and NIOSH found a sample pump error of 17% in Collaborative Tests of its comparable XRD procedure, NIOSH Method 7500.[39] Even so, the Overall Analytical

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[36] See p. 6 & n. 18, *supra*.

[37] Occupational Safety and Health Administration**,** Salt Lake Technical Center, Inorganic Methods Evaluation Protocol, www.osha-slc/methods/imeprotocol/index.html, § 6.2.

[38] See OSHA Method ID-142, §§ 3.1, 8.13.

[39] Anderson, C.C. Collaborative Tests of Two Methods for Determining Free Silica In Airborne Dust (NIOSH, October 1983), pp. 3, 24, 26.

Error of ±26% exceeds the ±25% level that OSHA states is necessary to ensure that a PEL can be feasibly measured.[40] Moreover, this Overall Error value is for quartz loadings in the range of 50 to 160 μg, which corresponds roughly to an air concentration range of 0.5 x a PEL of 0.1 $mg/m^3$ to 2 x a PEL of 0.1 $mg/m^3$. As noted above, for a PEL of 0.05 $mg/m^3$, the relevant range of quartz loadings would be 20-80 μg, or about 50% lower than the range for which Method ID-142 was validated. The Overall Analytical Error for this lower range of quartz loadings presumably would be higher than the ±26% value referenced in Method ID-142 for quartz samples in the range of 50-160 μg.

**Fifth**, it is not a simple matter to overcome the shortcomings of Method ID-142 noted above by changing the recommended collection device, sampling rate, and air volume. These recommendations are designed to achieve the particle size selection criteria specified in 29 CFR § 1910.1000, Table Z-3, and those are the only particle size selection criteria for which Method ID-142 has been "validated." As pointed out in Method ID-142, one cannot simply adjust the flow rate of an alternative, higher volume sampler to achieve a 50% cut point for particles having a 3.5 μm aerodynamic diameter and assume that the other specified particle size cut points also will be achieved.[41] Currently, the Dorr-Oliver cyclone is the only one "that has the characteristic sampling efficiencies listed in 29 CFR 1910.1000 Z-3."[42] An alternative to the Dorr-Oliver cyclone would have to be "verified to achieve comparable selectivity at all five aerodynamic diameters listed in" OSHA's regulations.[43] As Steven Edwards of OSHA points out: "Incorrect conclusions about exposure hazards can occur if the wrong [particle size] classifier is used or if it is operated at the wrong flow rate."[44]

**Sixth**, OSHA Method ID-142 does not list a Precision and Accuracy Validation Range for Cristobalite, since the data on which the method performance statistics are based do not include measurements of cristobalite. OSHA has not shown that Method ID-142 would achieve the same precision and accuracy for cristobalite as for quartz.

## C. Analytical Problems

As NIOSH observes: "The analysis of crystalline silica is difficult, and there are numerous problems not found with other materials."[45] These include the following:

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[40] See 53 Fed. Reg. at 35619; Occupational Safety and Health Administration, Salt Lake Technical Center, Inorganic Methods Evaluation Protocol, www.osha-slc/methods/imeprotocol/index.html, § 3.2.

[41] OSHA Method ID-142, § 1.2.

[42] 1997 OSHA Cyber-conference- Sampling and Analysis of Crystalline Silica, FAQ #4.

[43] *Id.*

[44] Edwards, S.L., Crystalline Silica: Sampling and Analytical Issues. The Synergist. (December 2000), p. 12.

[45] Anderson, C.C. Collaborative Tests of Two Methods for Determining Free Silica In Airborne Dust (NIOSH, October 1983), p. 3.

- Standards for calibration must have particle size distributions matching those of the samples.
- Standards must be prepared from suspensions rather than solutions. This requires considerable care and practice.
- There are several material transfer steps in the analysis—all creating the potential for sample loss.
- Polyvinyl Chloride (PVC) filters can contain significant amounts of quartz. Background levels of manufacturer and lot numbers must be checked.
- PVC filters may not be properly "degassed" after cleaning; consistent background levels for stable weight gains must be validated
- Filters must be environmentally conditioned before weighing and after sampling—a minimum of 4 hours is recommended.
- Pre-weighed filters must be carefully transferred to the appropriate cassette, and filter pre-weight must be properly recorded.
- Samples should be post-weighed on the same balance as the pre-weighed tare weight.
- Samples must be tightly sealed in the sampling cassette so that there is no leakage.
- Samples must be carefully transferred for final weighing so that all material on the filter remains intact.
- Samples cannot be overloaded with either total particulate or silica.
- Samples must be appropriately digested or chemically treated and then quantitatively transferred for final analysis.
- Silver membrane filters used in XRD analysis must be carefully inspected since there have been production problems with these filters.
- Appropriate calibration curves and spikes must accompany each set of samples.
- Calibration standards must match the particle size of the samples.
- XRD analysis requires that the samples be "spinning" in order to achieve sample homogeneity.
- The X-Ray diffraction pattern must be evaluated to determine the appropriate ratio of primary to secondary peak and also to observe any potential interferences at the primary or secondary peak.
- The sample reporting range must be within the calibration range—normally 10 micrograms to 200 micrograms.
- Final calculations must be checked for accuracy.
- The response of the X-Ray tube must be checked against a known standard.

## D. Interferences

In addition to the foregoing problems, "[m]any materials interfere in the analysis either by giving positive response for the silica measurement or by depressing the response"[46] The ability of the

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[46] Id. at 4.

sampling and analytical method to discriminate between the analyte in question and similar species is examined both at the sampling and the analytical level. Interferences normally are important when they either significantly diminish or increase the true amount of analyte present during collection or analysis.

Several documented compounds have been identified as potential interfering substances with either the primary or secondary quartz line using X-Ray Diffraction. These include:

Aluminum Phosphate
Biotite
Clinoferrosilite
Graphite
High albite
Iron Carbide
Lead chromate
Lead sulfate
Leucite
Microline
Muscovite
Orthoclase
Potassium Hydroxide
Sanidine
Sillimanite
Wollastonite
Zircon
Aluminum Phosphate
High albite
Microline

Although potential interferences have been well documented and can be either minimized or eliminated through altered digestion procedures or use of alternate X-ray lines, analysts are not always aware of potential interferences and may not compensate appropriately. Samples submitted to laboratories very seldom mention potential interferences.

The effects of utilizing alternate X-Ray lines and effects on sensitivity and the Limit of Detection have not been documented for the available methods.

The presence of Iron Oxide depresses both the Quartz peak and the Silver peak. Results indicate that samples with Iron Oxide present show an increase of error (not including pump) of approximately 5%.[47]

## E. Other Analytical Concerns

**Silver Membrane Filters**. In XRD analysis, after appropriate sample preparation, samples are transferred to a silver membrane filter which is placed in the instrument for analysis. The recent supplier of the silver membrane filters, Osmonics Corporation, has decided to discontinue the

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[47] Anderson, C.C. Collaborative Tests of Two Methods for Determining Free Silica In Airborne Dust (NIOSH, October 1983), p. 24.

manufacture of these filters. Although other manufacturers are in the process of evaluating production options, the availability of these filters is very questionable. In addition, several labs have noted quality control problems with the filters. Uncertainty regarding the continued availability of silver membrane filters poses serious questions about the ability to employ XRD methods beyond the very short term. NIOSH reportedly is considering a switch to a gold-impregnated membrane filter. If such a switch were made, the existing methods would have to be revalidated with use of the new filter.

**Limited Supply of NIST Standard Reference Materials**. NIOSH is in the process of working with NIST to obtain a large supply of SRM 1878a, but supply problems have not yet been resolved.

**Quantitation Limits**. There are no validated lower limits of quantitation for cristobalite and no validated lower limits of quantitation for quartz based on secondary peak.

# SAMPLING

As noted above, OSHA exposure limits are referenced to particle size selection criteria having a 50% cut point ($D_{50}$) at 3.5 micrometers as the respirable particulate standard. The Dorr-Oliver 10-mm nylon Cyclone collects dust that meets the OSHA criteria. Various other bodies (including ISO, CEN, and ACGIH) have adopted particle size selection guidelines for respirable particulates having a $D_{50}$ of 4 micrometers, and cyclones have been developed to reflect this new guideline. These include the SKC Aluminum Cyclone—for which an air flow rate of 2.5 L/min results in a collection efficiency curve that best matches the 4 micrometer $D_{50}$ definition of respirable particulate[48]—and the BGI Incorporated Cyclone—for which an air flow rate of 4.2 L/min results in a collection efficiency curve that best matches the 4 micrometer $D_{50}$ definition of respirable particulate.

## A. Cyclone Effects

Because they have a higher air flow rate than the Dorr-Oliver Cyclone, the SKC and BGI Cyclones will collect a greater volume of "respirable" dust in the same workplace atmosphere than the Dorr-Oliver Cyclone when sampling is conducted over the same period of time—though the particle size characteristics of the "respirable" dust will differ.

Table 3 below shows the concentration levels needed to collect a silica mass equal to the 10 microgram Limit of Quantitation for quartz based on use of the SKC Cyclone.

**Table 3**

| **$D_{50}$ 4 micrometers cut point<br>10 microgram LOQ Quartz<br>SKC Cyclone 2.5 L/min** | | |
|---|---|---|
| **Sampling Time** | **Total Air Volume (Liters)** | **Concentration mg/m$^3$** |
| 15 Minutes | 37.5 | 0.27 |
| 60 Minutes | 150 | 0.067 |
| 4 Hours | 600 | 0.017 |
| 8 Hours | 1,200 | 0.0083 |

Table 4 below shows the concentration levels needed to collect a silica mass equal to the 10 microgram Limit of Quantitation for quartz based on use of the BGI Cyclone.

**Table 4**

| **$D_{50}$ 4 micrometers cut point<br>10 microgram LOQ Quartz<br>BGI Cyclone 4.2 L/min** | | |
|---|---|---|
| **Sampling Time** | **Total Air Volume (Liters)** | **Concentration mg/m$^3$** |
| 15 Minutes | 63 | 0.159 |
| 60 Minutes | 252 | 0.040 |
| 4 Hours | 1008 | 0.0099 |
| 8 Hours | 2016 | 0.0050 |

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[48] See Harper, M., C.P. Fang, D.L. Bartley, B.S. Cohen: Calibration of the SKC Inc. Aluminum Cyclone For Operation in Accordance with ISO/CEN/ACGIH Respirable Aerosol Sampling Criteria. J. Aerosol Sci. 29: S347-S348 (1998).

Table 5 below shows the concentration levels needed to collect a silica mass equal to the 10 microgram Limit of Quantitation for quartz based on use of the three different Cyclones for a full shift (8-hour) monitoring sample.

**Table 5**

| **10 microgram LOQ Cyclone Comparison 8 Hour Sampling Time** | | |
|---|---|---|
| **Cyclone** | **Total Air Volume Liters** | **Concentration mg/m$^3$** |
| BGI | 2016 | 0.0050 |
| SKC | 1200 | 0.0083 |
| Dorr-Oliver | 816 | 0.012 |

As the foregoing illustrates, because of the difference in air flow rate, the BGI and SKC Cyclones will collect more "respirable" silica over any given time interval than the Dorr-Oliver Cyclone. But the "respirable" silica being collected is not the same, since the BGI and SKC Cyclones are designed to collect respirable dust with different particle size characteristics than the Dorr-Oliver Cyclone. And, as noted above, it is not simply a matter of a different $D_{50}$ cut point. The selectivity at all five aerodynamic diameters will differ and must be accounted for.[49] The greater the particle size at the $D_{50}$ cut point, the higher the measured dust concentration is likely to be in a typical (polydisperse) atmosphere.[50]

Furthermore, these other cyclones have a greater collection efficiency than the Dorr-Oliver Cyclone. A recent presentation at the American Industrial Hygiene Conference and Exposition, May 24, 2000, showed that the "SKC cyclones consistently yielded higher dust concentrations than those of the Dorr-Oliver cyclones at the low, moderate, and high dust level concentrations. The average Time Weighted Average Concentrations ( TWAC's) indicated by the SKC aluminum cyclones were 15%, 16%, and 18% higher than those of the Dorr-Oliver cyclones at the low, medium, and high dust concentration ranges, respectively."[51] This implies that a shift from Dorr-Oliver Cyclone sampling (with a 3.5 micrometer $D_{50}$ cut point) to sampling with a cyclone having a $D_{50}$ cut point of 4 micrometers would in effect lower the existing PEL by an estimated 15-20%. Such a change also would throw into question the health significance of the sampling results, since the hazards of exposure to crystalline silica have reflected Dorr-Oliver (or equivalent) sampling. In addition, of course, a change in samplers would require that OSHA Method ID-142, which has been "validated" for Dorr-Oliver sampling, be "validated" for the new sampler with its new particle size characteristics.

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[49] 1997 OSHA Cyber-conference- Sampling and Analysis of Crystalline Silica, FAQ #4.

[50] See Groves, W.A., R.M. Hanhe, S.P. Levine, M.A. Schork: A Field Comparison of Respirable Dust Samplers. Am. Ind. Hyg. Assoc. 55(8): 748-755 (1994).

[51] Breay, J. Comparison of the Dorr-Oliver 10 MM Nylon Cyclone with the SKC Aluminum Cyclone For Collecting Silica Containing Dust (1999 AIHCE).

Finally, if OSHA switched to a sampler with a higher air flow rate and greater dust collection efficiency, the amount of silica collected on the filter over eight hours in atmospheres where the respirable silica concentration exceeded 0.1 mg/m$^3$ would approach or exceed the linear calibration range for silica.

## B. Other Sampling Problems

Cassette Leakage is another potential source of error. NIOSH suggests that sampling error due to improperly sealed cassettes can account for an additional 25% sampling error. Samples are normally taken on a 5 micron PVC filter that has been equilibrated weighed on a microbalance and transferred to a cassette with a back-up pad. Improper closing of the cassette can result in cassette leakage.

Samples submitted to the laboratory for analysis **must** include information about the operation and potential interferences. This information enables the laboratory to evaluate the samples, alter digestion procedures, and maximize analysis parameters in an effort to minimize interferences.

An AIHA Accredited Consulting laboratory estimates that the number of samples submitted to the laboratory for silica analysis taken as <u>total</u> dust as opposed to <u>respirable</u> dust is approximately 15%. In addition approximately 20% of samples submitted using a cyclone are not taken at the cyclone manufacturers recommended flow rate.[52]

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[52] NATLSCO Laboratory, Sandra C. Wroblewski, Manager, Marketing and Methods Development.

# LABORATORIES

## A. Laboratory Selection Criteria

The following points should be considered in selecting a laboratory for analysis of crystalline silica:[53]

1. Is the Laboratory Accredited?
    - American Industrial Hygiene Association (AIHA)
    - Other
2. Does the Laboratory participate in a Round Robin Testing Program?
    - AIHA
    - Other
3. Is the laboratory rated Proficient in that program?
4. Request to see Proficiency Analytical Testing (PAT) results.
5. What instrument is used for analysis
    - X-Ray
    - IR
    - Colorimetric
6. What Method is used for analysis?
    - NIOSH Methods
        - 7500
        - 7601
        - 7602
        - 7603
    - OSHA Method
        - ID-142
7. Does the laboratory report
    - Quartz?
    - Cristobalite?
    - Tridymite?
8. What standards does the laboratory use to calibrate their instrument?
9. What is the normal range of the standards used to calibrate?
10. Does the laboratory make provisions for high sample loading?
11. Who is the supplier of their standards?
12. How often does the laboratory calibrate their instrument?

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[53] 1997 National Conference to Eliminate Silicosis, Laboratory Selection Criteria That Can Be Used To Select a Laboratory: , Harper, M. and Wroblewski, S.

13. Can the laboratory provide you with silica control charts?
14. What is the Lower Limit of Quantitation (LLQ) from the laboratory?
15. Can the laboratory document determination of the LLQ?
16. Does the laboratory keep maintenance records?
17. Does the laboratory provide sampling guidance?
18. Does the laboratory request information regarding the operation or the process?
19. Is the laboratory familiar with common interferences of their method?
20. How many years has the laboratory analyzed silica samples?
21. Does the laboratory differentiate between total and respirable dust?
22. Does the laboratory require a respirable dust sample for silica?
23. Does the laboratory provide sampling media?
24. Does the laboratory know the background levels of silica in the media?
25. Does the laboratory know and understand the silica formula and calculation?

## B. AIHA Laboratory Accreditation Program

At the present time, the American Industrial Hygiene Association (AIHA)[54] is the only organization in the United States that offers an Industrial Hygiene Laboratory Accreditation Program specifically designed for laboratories involved in analyzing samples to evaluate workplace exposure. Included in the AIHA program is the Proficiency Analytical Testing (PAT) Program that includes Silica samples.

The PAT Program is designed to assist a laboratory improve its analytical performance by providing samples on a quarterly basis, evaluating the results, and providing a report on how well the laboratory performed. In the same way, the PAT Program also tests the analytical competence of participating occupational health laboratories. Samples are generated by SRI International. Data analysis and distribution of reports are performed by NIOSH as permitted under a Cooperative Research and Development Agreement (CRADA) with AIHA.

Laboratories may participate in the AIHA PAT program without becoming accredited. If a laboratory analyzes samples taken from the workplace environment, then participation in the PAT Program can provide information to clients on laboratory performance.

Once a laboratory participates in the AIHA PAT Program, it may chose to become accredited in the Industrial Hygiene Laboratory Accreditation Program (IHLAP). The AIHA IHLAP is the largest program of its kind in the world and has been in operation since 1974. AIHA criteria for IHLAP accreditation include evaluation of the following:

- Personnel Qualification
- Participation in PAT Program and demonstrated proficiency

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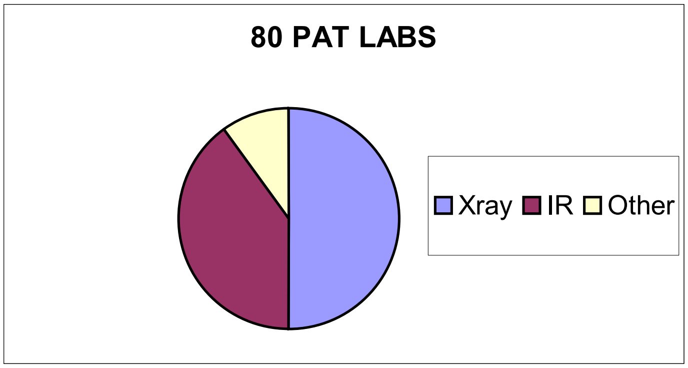
[54] American Industrial Hygiene Association (AIHA), 2700 Prosperity Ave., Suite 250, Fairfax, VA 22031. (703) 849-8888.

- Facilities
- Quality Control and Equipment
- Laboratory Records
- Methods of Analysis
- Site Visits

The number of PAT Program participants analyzing for silica reached a peak of 134 laboratories in 1984 (PAT Round 78), and has been declining since that time.[55] In December 2000, 76 labs participated in the PAT Program for silica.

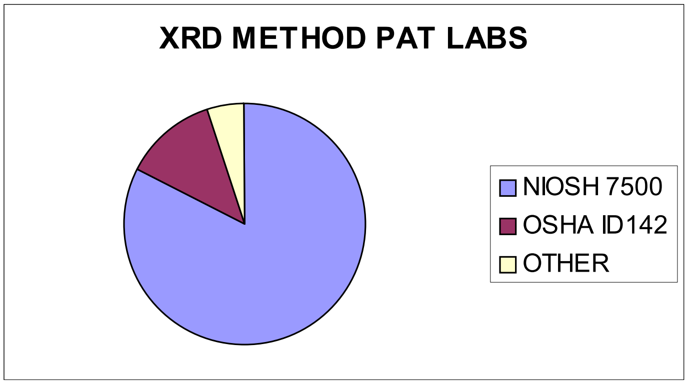
PAT Round 133 in April 1998 had a total of 82 laboratories participating in silica analysis. A NIOSH questionnaire to all participating laboratories in that round (80 responses) gave the following breakdown according to methodology.

## GRAPH 1



Graph 1 indicates that 50% of the labs in PAT Round 133 utilized XRD, 40% utilized IR and 10% utilized the colorimetric method.

## GRAPH 2



Graph 2 indicates that only 12.5% of the PAT labs used OSHA Method ID-142 in Round 133.

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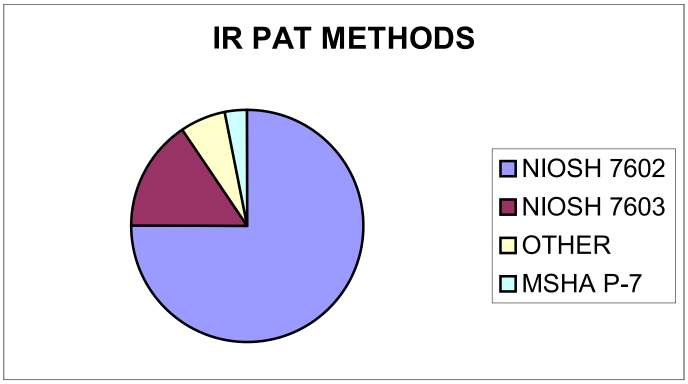
[55] Eller, P., *et al*. Proficiency Analytical Testing (PAT) Silica Variability, 1990-1998. AIHA Journal. 60:533-539 (1999).

# GRAPH 3



Graph 3, showing the various IR methods used by PAT laboratories, indicates that 19% of the laboratories utilized IR methods specific for Coal Mine Dust which would not be applicable to other complex environments such as metal/non-metal surface mines, or iron and steel foundries.

In the July 24, 2000 listing of AIHA accredited labs participating in Silica PAT testing, only 56 labs are listed. Of the 56 accredited labs, only 41 labs will accept samples on a consulting basis. The remaining 15 laboratories are either government-related labs or "in-house" labs that do not accept samples on a consulting basis, or labs outside the United States. Appendix 2 lists the AIHA Accredited Labs analyzing silica.

## C. AIHA Accredited Labs Telephone Poll

A Telephone poll of AIHA accredited labs in July 2000 indicates that the average turn-around time for silica samples analyzed by XRD is 5 working days. The cost range is $70.00-$80.00 including the respirable dust for XRD air samples. Bulk samples are usually $10.00 more per sample. Although most labs have received the new NIST Quartz Standard, few have implemented quantitation based on the NIST Standard.

AIHA has recognized the need to improve the Silica method. In February 2000, representatives from OSHA and NIOSH spoke to the AIHA Industrial Hygiene Site Visitors and discussed methods that could improve the analytical data. Site visitors were requested to incorporate these suggestions when performing site visits at accredited labs analyzing silica samples.

# ROUND ROBIN TESTING AND STATISTICS

## A. Background Information on the Proficiency Analytical Testing (PAT) Program

The American Industrial Hygiene Association (AIHA) provides a round robin testing program for:

Silica
Metals (Lead, Cadmium, Chromium, Zinc)
Asbestos
Solvents (Solid Sorbents and Passive Monitors)

Laboratories may choose to participate with respect to any or all analytes. Up until Round 134, Reference Values for individual analytes were based on average values reported by "Reference Labs." Reference Labs were accredited labs that did not have outliers in the four previous rounds. Outliers were defined as measurements falling outside three standard deviations ($3\sigma$) of the reference values. Since PAT Round 134, the Reference Value is the mean of the reported measurements from all participating labs all data, and acceptable performance is deemed to be a measurement that falls within $3\sigma$ of the mean.

A laboratory that successfully completes two PAT rounds may choose to become accredited. As of PAT Round 139, 80 laboratories participated in PAT Silica analyses, and 55 of those were accredited.

Silica samples are prepared by SRI on 37-mm PVC filters and distributed to participating laboratories. Samples are distributed quarterly and include 4 filters containing quartz and a blank filter. Samples are prepared using 5 micron Min-U-Sil. AA PAT rounds (except Round 130) include a matrix effect of either:

Calcite,
Talc,
Talc and Coal Mine Dust
Coal Mine Dust.

PAT samples do not include a matrix effect from Iron or Iron Oxide.

## B. Comparison of PAT Program Results for Silica, Asbestos and Lead

PAT data for silica are available from 1972. The normal range of filter loadings for silica samples in the PAT Program is 50 micrograms - 175 micrograms/filter.

Table 6 below summarizes the Relative Standard Deviation (RSD) values for the Silica data in PAT Rounds 71-138. It shows an improved RSD for silica in Rounds 98-138 as compared to Rounds 71-97. This directly corresponds to a decrease in the number of laboratories analyzing silica via the colorimetric method. The data indicate a range of RSDs for silica from a low of 15.3 to a high of 45.4.

**Table 6**
**PAT Data Silica**
**Relative Standard Deviation (RSD)**

| *ALL Rounds 71-138 DATA* | **RSD Silica** | *ROUND 71-97* | **RSD Silica** | *ROUND 98-138* | **RSD Silica** |
|---|---|---|---|---|---|
| MEAN | 22.2 | MEAN | 23.2 | MEAN | 21.7 |
| LOW | 15.3 | LOW | 16.7 | LOW | 15.3 |
| HIGH | 45.4 | HIGH | 45.4 | HIGH | 37.0 |

The foregoing data for silica can be compared to data for other analytes in the PAT program. For purposes of comparison, the author selected Asbestos (because of its high coefficient of variation which appears to rival silica data) and lead (because of the similarity of the permissible exposure limit). A copy of the complete data set is included in Appendix 3.

The analytical method for asbestos involves microscope counting and is subject to analyst interpretation. In order to improve the RSD for asbestos, OSHA mandated the use of NIOSH Method 7500. The more stringent method would be reflected in PAT data from Round 98 forward. Lead data include analyses performed by either Atomic Absorption (AA) or Inductively Coupled Plasma Emission (ICP).

Tables 7, 8, and 9 below summarize the PAT data for Silica, Asbestos, and Lead from PAT Rounds 71-138.

**Table7**
**PAT Rounds 71-138**
**RSD (%) Silica, Asbestos, Lead**

| | **RSD Silica** | **RSD Asbestos** | **RSD Lead** |
|---|---|---|---|
| MEAN | 22.21 | 24.75 | 4.30 |
| LOW | 15.3 | 12.9 | 2.7 |
| HIGH | 45.4 | 44.7 | 7.80 |

**Table 8**
**PAT Rounds 71-97**
**RSD (%) Silica, Asbestos, Lead**

| | **RSD Silica** | **RSD Asbestos** | **RSD Lead** |
|---|---|---|---|
| MEAN | 23.22 | 29.90 | 4.60 |
| LOW | 16.70 | 18.30 | 2.70 |
| HIGH | 45.4 | 44.7 | 7.80 |

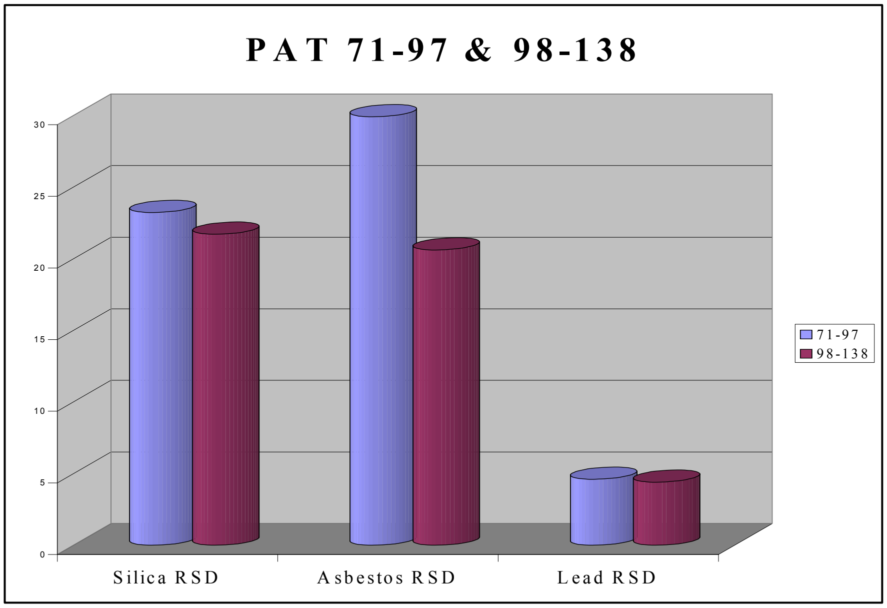
**Table 9**
**PAT Rounds 98-138**
**RSD (%) Silica, Asbestos, Lead**

| | **RSD Silica** | **RSD Asbestos** | **RSD Lead** |
|---|---|---|---|
| MEAN | 21.68 | 20.6 | 4.2 |
| LOW | 15.3 | 12.9 | 3 |
| HIGH | 37 | 42.3 | 6.5 |

As can be seen, the RSD for asbestos improved from 29.9 (Rounds 71-97) to 20.6 (Rounds 98-138). This represents an overall improvement of 31%. During the same time period, the RSD for lead improved by 8.7%, and the RSD for silica improved by 6.6%. Moreover, the RSD for silica is roughly five times higher than the RSD for lead, even though the PEL that OSHA is considering for silica (0.05 mg/m$^3$) is the same as the PEL for lead.[56]

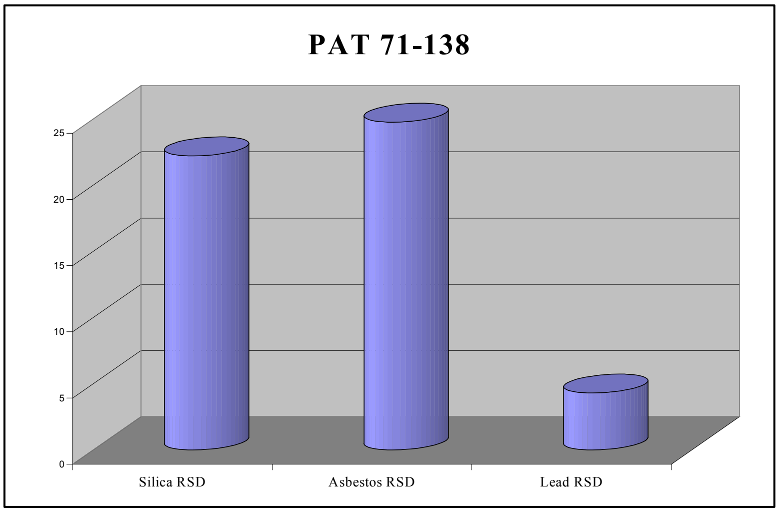
Graph 4 below presents a pictorial view of the changes in PAT RSDs for silica, asbestos and lead, comparing PAT Rounds 71-97 to Rounds 98-138.

**GRAPH 4**



Graph 5 below summarizes the mean RSDs in PAT Rounds 71-138 for Silica, Asbestos and Lead.

**GRAPH 5**



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[56] See 29 CFR § 1910.1025.

## C. NIOSH Report on PAT Data for Silica

In 1999, NIOSH researchers analyzed silica data from PAT Rounds 101-132 (1990-1998). Based on an analysis of reported measurements by the reference labs,[57] the NIOSH researchers found that the overall intra-laboratory CV for XRD methods in these rounds was 0.165 (or an RSD of 16.5%), while for IR methods it was 0.166 (or an RSD of 16.6%).[58] For the reference labs as a group (without differentiation as to method), the mean CV was 0.229 (or an RSD of 22.9%). These CV values are based solely on analytical variance; they do not reflect sampling error, since the participating labs received pre-loaded filters from the generating laboratory, SRI. Assuming a 5% sampling error, and applying the formulas used by NIOSH to calculate method performance, the "Overall Precision" of XRD based on these data would be 17.2% and the "Accuracy" would be ±34%.[59] The comparable values for IR would be 17.3% and ±34%. These are well above the values that OSHA would deem to reflect reliable and reproducible measurements of crystalline silica.

The NIOSH researchers found that the inter-laboratory CV for XRD methods in these rounds was 0.249 (or an RSD of 24.9%), while for IR methods it was 0.253 (or an RSD of 25.3%).[60]

Finally, the NIOSH researchers found that all estimates of intra- and inter-laboratory variability in these rounds tended to rise at low sample loadings—with the range of 60-80 μg silica per sample being a significant cut point.[61] At a flow rate of 1.7 L/min (the recommended flow rate for OSHA Method ID-142), 60-80 μg silica on a filter is equivalent to 8-hour exposure to a silica concentration of 0.074 $mg/m^3$ - 0.098 $mg/m^3$. Thus, the NIOSH analysis indicates there would be a significant increase in measurement variability if the PEL were reduced from 0.1 $mg/m^3$ to 0.05 $mg/m^3$.

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[57] AIHA defines reference labs as accredited labs that participate in all analytes for the PAT program and were rated Proficient for each of them in the previous two PAT rounds.

[58] Eller, P., *et al*. Proficiency Analytical Testing (PAT) Silica Variability, 1990-1998. AIHA Journal. 60:533-539 (1999) at 537. The most common XRD method used by participating labs was NIOSH Method 7500.

[59] The formulas used by NIOSH are described in a letter dated September 9, 1999 to Robert E. Glenn from David Bartley and Martin Abell of NIOSH. A copy of that letter is attached to this Report as Appendix 1.

[60] See Eller, P., *et al*. Proficiency Analytical Testing (PAT) Silica Variability, 1990-1998. AIHA Journal. 60:533-539 (1999) at 537, Table III..

[61] *Id*. at 536-537.

## D. Independent Evaluation of Silica Data from PAT Rounds 124-139

An independent evaluation of PAT data was undertaken by the author in order to:

1) Evaluate IR and XRD data in detail—with separate analyses of data that include outliers as defined by AIHA and data that exclude such outliers;[62] and
2) Compare IR data vs. XRD data vs. reference laboratory data.[63]

Table 10 below shows the mean values of reported data from PAT Rounds 124-139 broken out as follows:

1. *RL*= Data reported by the Reference Labs as defined by AIHA regardless of method;
2. *IR All* = IR data including AIHA defined outliers;
3. *IR NO*= IR data excluding AIHA defined outliers;
4. *XRD All* = XRD data including AIHA defined outliers; and
5. *XRD NO* = XRD data excluding AIHA defined outliers.

**Table 10**

| Pat ID | Milligrams Silica Reported—Mean Value | | | | |
|---|---|---|---|---|---|
| | RL | IR All | IR NO | XRD All | XRD NO |
| 124-1 | 0.1043 | 0.1046 | 0.1065 | 0.1051 | 0.1051 |
| 124-2 | 0.1472 | 0.1575 | 0.1575 | 0.144 | 0.144 |
| 124-3 | 0.0753 | 0.0742 | 0.0742 | 0.0722 | 0.0736 |
| 124-4 | 0.095 | 0.0875 | 0.0875 | 0.0997 | 0.0997 |
| 125-1 | 0.1018 | 0.0995 | 0.102 | 0.1098 | 0.1064 |
| 125-2 | 0.0676 | 0.0676 | 0.0692 | 0.0671 | 0.0671 |
| 125-3 | 0.1013 | 0.1002 | 0.1001 | 0.0977 | 0.0994 |
| 125-4 | 0.0566 | 0.0547 | 0.0547 | 0.0553 | 0.0553 |
| 126-1 | 0.0824 | 0.1154 | 0.082 | 0.0776 | 0.0776 |
| 126-2 | 0.1038 | 0.1308 | 0.1049 | 0.0899 | 0.0899 |
| 126-3 | 0.0876 | 0.1186 | 0.0886 | 0.0844 | 0.0844 |
| 126-4 | 0.1406 | 0.1864 | 0.1408 | 0.143 | 0.143 |
| 127-1 | 0.09 | 0.0875 | 0.0878 | 0.0886 | 0.0871 |
| 127-2 | 0.0606 | 0.0554 | 0.0518 | 0.0623 | 0.0623 |
| 127-3 | 0.1736 | 0.1691 | 0.1695 | 0.1791 | 0.1753 |
| 127-4 | 0.0806 | 0.0767 | 0.0767 | 0.0790 | 0.0774 |
| 128-1 | 0.1093 | 0.1118 | 0.1145 | 0.1118 | 0.1118 |
| 128-2 | 0.0733 | 0.0741 | 0.0741 | 0.0739 | 0.0739 |
| 128-3 | 0.0575 | 0.0574 | 0.0586 | 0.0574 | 0.0574 |

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[62] AIHA defines outliers as data that are more than 3 standard deviations from the mean value.

[63] Reference labs were used in all PAT rounds through 132. They included accredited labs that had no outliers in the previous two PAT rounds. The mean value of all participating labs was used as the reference value in PAT rounds 133-139.

| Pat ID | Milligrams Silica Reported—Mean Value | | | | |
|---|---|---|---|---|---|
| | RL | IR All | IR NO | XRD All | XRD NO |
| 128-4 | 0.1531 | 0.1570 | 0.1570 | 0.1525 | 0.1525 |
| 129-1 | 0.1047 | 0.1054 | 0.1054 | 0.1018 | 0.1018 |
| 129-2 | 0.1329 | 0.1417 | 0.1417 | 0.1326 | 0.1326 |
| 129-3 | 0.0584 | 0.0583 | 0.0583 | 0.0561 | 0.0561 |
| 129-4 | 0.0840 | 0.0863 | 0.0863 | 0.0818 | 0.0839 |
| 130-1 | 0.1399 | 0.1661 | 0.1546 | 0.1347 | 0.1371 |
| 130-2 | 0.0933 | 0.1026 | 0.1038 | 0.0845 | 0.0845 |
| 130-3 | 0.0568 | 0.0623 | 0.0643 | 0.0519 | 0.0519 |
| 130-4 | 0.1039 | 0.2183 | 0.1181 | 0.0997 | 0.0972 |
| 131-1 | 0.0502 | 0.0540 | 0.0469 | 0.0471 | 0.0445 |
| 131-2 | 0.0750 | 0.0801 | 0.0787 | 0.0701 | 0.0701 |
| 131-3 | 0.1064 | 0.1022 | 0.1059 | 0.1200 | 0.0983 |
| 131-4 | 0.1106 | 0.1147 | 0.1175 | 0.1078 | 0.1078 |
| 132-1 | 0.0638 | 0.0647 | 0.0670 | 0.0613 | 0.0595 |
| 132-2 | 0.0896 | 0.0904 | 0.0973 | 0.0886 | 0.0886 |
| 132-3 | 0.1179 | 0.1211 | 0.1201 | 0.1193 | 0.1146 |
| 132-4 | 0.0683 | 0.0663 | 0.0710 | 0.0677 | 0.0666 |
| 133-1 | 0.0588 | 0.0605 | 0.0605 | 0.0566 | 0.0541 |
| 133-2 | 0.0865 | 0.0885 | 0.0871 | 0.0828 | 0.0807 |
| 133-3 | 0.0917 | 0.1235 | 0.0981 | 0.0896 | 0.0824 |
| 133-4 | 0.1236 | 0.1243 | 0.1243 | 0.1202 | 0.1183 |
| 134-1 | 0.0663 | 0.0652 | 0.0652 | 0.0681 | 0.0656 |
| 134-2 | 0.0876 | 0.0891 | 0.0891 | 0.0918 | 0.0861 |
| 134-3 | 0.1160 | 0.1206 | 0.1206 | 0.1170 | 0.1119 |
| 134-4 | 0.1152 | 0.1210 | 0.1210 | 0.1215 | 0.1111 |
| 135-1 | 0.0880 | 0.0913 | 0.0898 | 0.0878 | 0.0852 |
| 135-2 | 0.0645 | 0.0650 | 0.0650 | 0.0653 | 0.0614 |
| 135-3 | 0.0915 | 0.0976 | 0.0962 | 0.0898 | 0.0876 |
| 135-4 | 0.0803 | 0.0834 | 0.0813 | 0.0807 | 0.0753 |
| 136-1 | 0.0709 | 0.0666 | 0.0691 | 0.0720 | 0.0704 |
| 136-2 | 0.0814 | 0.0816 | 0.0781 | 0.0810 | 0.0802 |
| 136-3 | 0.1227 | 0.1140 | 0.1140 | 0.1338 | 0.1299 |
| 136-4 | 0.1452 | 0.1418 | 0.1418 | 0.1501 | 0.1505 |
| 137-1 | 0.1026 | 0.1072 | 0.1055 | 0.1003 | 0.1022 |
| 137-2 | 0.0583 | 0.0622 | 0.0638 | 0.0542 | 0.0531 |
| 137-3 | 0.0881 | 0.0901 | 0.0901 | 0.0871 | 0.0871 |
| 137-4 | 0.0977 | 0.1104 | 0.1040 | 0.0900 | 0.0895 |
| 138-1 | 0.0601 | 0.0666 | 0.0638 | 0.0569 | 0.0566 |
| 138-2 | 0.0860 | 0.0963 | 0.0963 | 0.0798 | 0.0812 |
| 138-3 | 0.1147 | 0.1194 | 0.1194 | 0.1195 | 0.1192 |
| 138-4 | 0.1038 | 0.1192 | 0.1170 | 0.0998 | 0.0995 |
| 139-1 | 0.1185 | 0.1327 | 0.1267 | 0.1155 | 0.1155 |
| 139-2 | 0.1036 | 0.1166 | 0.1126 | 0.0987 | 0.0987 |
| 139-3 | 0.0695 | 0.0721 | 0.0721 | 0.0681 | 0.0685 |
| 139-4 | 0.0849 | 0.0867 | 0.0856 | 0.0853 | 0.0853 |

Table 11 below shows the Relative Standard Deviations of data from PAT Rounds 124-139 broken out in the same way as the mean values in Table 10. (Note: Outliers are data that are more than 3 standard deviations from the mean value. In the case of both IR and XRD, approximately 3% of the data were eliminated based on the above definition of an outlier.)

**Table 11**

| PAT Round | Mean Reference Lab Values (mg) | RSD (%) | | | | |
|---|---|---|---|---|---|---|
| | | RL | IR NO | XRD NO | XR All | IR All |
| 124-1 | 0.1043 | 21.0 | 20.2 | 24.1 | 24.1 | 23.0 |
| 124-2 | 0.1472 | 20.5 | 18.0 | 22.3 | 22.3 | 18.0 |
| 124-3 | 0.0753 | 22.7 | 24.3 | 24.6 | 27.1 | 24.3 |
| 124-4 | 0.0950 | 24.6 | 27.7 | 21.3 | 21.3 | 27.7 |
| 125-1 | 0.1018 | 20.5 | 24.4 | 22.1 | 25.6 | 27.7 |
| 125-2 | 0.0676 | 21.4 | 20.7 | 23.0 | 23.0 | 24.8 |
| 125-3 | 0.1013 | 20.2 | 21.5 | 19.7 | 22.4 | 26.6 |
| 125-4 | 0.0566 | 24.8 | 29.3 | 26.4 | 26.4 | 29.3 |
| 126-1 | 0.0824 | 23.9 | 22.9 | 23.9 | 23.9 | 206.4 |
| 126-2 | 0.1038 | 28.1 | 21.7 | 27.1 | 27.1 | 121.0 |
| 126-3 | 0.0876 | 20.1 | 17.7 | 27.8 | 27.8 | 162.0 |
| 126-4 | 0.1406 | 28.1 | 27.1 | 23.8 | 23.8 | 157.0 |
| 127-1 | 0.0900 | 20.0 | 24.2 | 21.4 | 23.5 | 33.5 |
| 127-2 | 0.0606 | 27.6 | 31.9 | 28.7 | 28.7 | 35.5 |
| 127-3 | 0.1736 | 22.1 | 19.8 | 23.8 | 27.2 | 30.4 |
| 127-4 | 0.0806 | 23.5 | 22.3 | 31.8 | 34.3 | 32.7 |
| 128-1 | 0.1093 | 19.6 | 17.9 | 20.3 | 20.3 | 22.1 |
| 128-2 | 0.0733 | 20.1 | 16.0 | 21.2 | 21.2 | 16.0 |
| 128-3 | 0.0575 | 19.6 | 19.0 | 25.1 | 25.1 | 21.8 |
| 128-4 | 0.1531 | 23.7 | 22.0 | 22.9 | 22.9 | 22.0 |
| 129-1 | 0.1047 | 23.8 | 22.0 | 24.9 | 24.9 | 22.0 |
| 129-2 | 0.1329 | 24.8 | 23.1 | 26.4 | 26.4 | 23.1 |
| 129-3 | 0.0584 | 25.8 | 27.5 | 31.9 | 31.9 | 27.7 |
| 129-4 | 0.0840 | 23.1 | 21.3 | 24.6 | 29.2 | 21.3 |
| 130-1 | 0.1399 | 19.3 | 15.7 | 21.6 | 24.2 | 52.8 |
| 130-2 | 0.0933 | 20.9 | 17.2 | 21.1 | 21.1 | 24.4 |
| 130-3 | 0.0568 | 23.1 | 17.4 | 27.1 | 27.1 | 23.9 |
| 130-4 | 0.1039 | 21.8 | 18.0 | 21.6 | 25.6 | 471.0 |
| 131-1 | 0.0502 | 33.3 | 32.3 | 35.7 | 48.9 | 88.8 |
| 131-2 | 0.0750 | 21.7 | 27.8 | 23.5 | 23.5 | 35.6 |
| 131-3 | 0.1064 | 19.5 | 23.0 | 21.7 | 136.3 | 30.2 |
| 131-4 | 0.1106 | 21.4 | 21.8 | 27.4 | 27.4 | 25.2 |
| 132-1 | 0.0638 | 18.7 | 19.8 | 26.3 | 31.1 | 29.8 |
| 132-2 | 0.0896 | 17.0 | 23.4 | 22.4 | 22.4 | 29.1 |
| 132-3 | 0.1179 | 15.9 | 21.5 | 18.7 | 24.4 | 32.1 |

| PAT Round | Mean Reference Lab Values (mg) | RSD (%) | | | | |
|---|---|---|---|---|---|---|
| | | RL | IR NO | XRD NO | XR All | IR All |
| 132-4 | 0.0683 | 18.3 | 23.0 | 24.3 | 25.9 | 35.0 |
| 133-1 | 0.0588 | 19.1 | 15.9 | 23.0 | 28.5 | 15.9 |
| 133-2 | 0.0865 | 17.2 | 19.0 | 24.3 | 29.5 | 20.9 |
| 133-3 | 0.0917 | 16.9 | 13.6 | 22.1 | 57.2 | 142.0 |
| 133-4 | 0.1236 | 15.8 | 19.9 | 21.5 | 23.5 | 19.9 |
| 134-1 | 0.0663 | 18.4 | 19.8 | 27.1 | 43.8 | 19.8 |
| 134-2 | 0.0876 | 17.1 | 14.7 | 18.2 | 33.8 | 14.7 |
| 134-3 | 0.1160 | 16.0 | 18.0 | 21.0 | 29.2 | 18.0 |
| 134-4 | 0.1152 | 16.0 | 17.9 | 18.9 | 47.3 | 17.9 |
| 135-1 | 0.0880 | 17.1 | 22.7 | 28.4 | 38.7 | 24.1 |
| 135-2 | 0.0645 | 18.6 | 23.4 | 34.8 | 45.0 | 23.4 |
| 135-3 | 0.0915 | 16.9 | 20.4 | 25.3 | 35.7 | 21.7 |
| 135-4 | 0.0803 | 17.5 | 22.8 | 23.6 | 47.9 | 25.6 |
| 136-1 | 0.0709 | 18.1 | 22.5 | 23.1 | 26.8 | 26.7 |
| 136-2 | 0.0814 | 17.4 | 23.5 | 28.1 | 33.6 | 28.6 |
| 136-3 | 0.1227 | 15.8 | 19.3 | 25.9 | 31.7 | 19.3 |
| 136-4 | 0.1452 | 15.3 | 15.1 | 20.2 | 23.8 | 15.1 |
| 137-1 | 0.1026 | 16.4 | 22.3 | 22.4 | 25.0 | 22.5 |
| 137-2 | 0.0583 | 19.2 | 20.4 | 26.8 | 27.7 | 23.8 |
| 137-3 | 0.0881 | 17.1 | 20.0 | 24.1 | 26.8 | 20.0 |
| 137-4 | 0.0977 | 16.6 | 25.7 | 23.8 | 32.5 | 29.8 |
| 138-1 | 0.0601 | 19.0 | 17.8 | 25.6 | 30.0 | 24.5 |
| 138-2 | 0.0860 | 17.2 | 16.4 | 18.4 | 21.0 | 16.4 |
| 138-3 | 0.1147 | 16.0 | 15.2 | 24.1 | 28.3 | 15.2 |
| 138-4 | 0.1038 | 16.4 | 18.6 | 28.4 | 34.9 | 20.7 |
| 139-1 | 0.1185 | 15.9 | 18.9 | 29.2 | 29.2 | 24.6 |
| 139-2 | 0.1036 | 16.4 | 18.3 | 29.6 | 29.6 | 21.3 |
| 139-3 | 0.0695 | 18.2 | 22.8 | 31.5 | 40.0 | 22.6 |
| 139-4 | 0.0849 | 17.2 | 25.0 | 25.6 | 25.6 | 33.2 |

Table 12 below shows the average RSDs for PAT Rounds 124-139 broken out in the same way as in Tables 10 and 11. Not surprisingly, the RSDs for the Reference Labs and for IR and XRD with outliers excluded are significantly better than the RSDs for IR and XRD with outliers included. IR All Data has the highest RSD. (A review of individual PAT rounds shows that Round 130-4 has an RSD for IR of 471%.) Reference Labs show the lowest RSD.

**Table 12**

| Average Relative Standard Deviation (%) | | | | | |
|---|---|---|---|---|---|
| **PAT Rounds 124-139** | **Reference Labs** | **IR All Data** | **IR No Outliers** | **XRD All Data** | **XRD No Outliers** |
| | 20.0 | 43.2 | 21.1 | 30.9 | 24.6 |

Graph 6 below is a pictorial representation of the data in Table 12.

## GRAPH 6

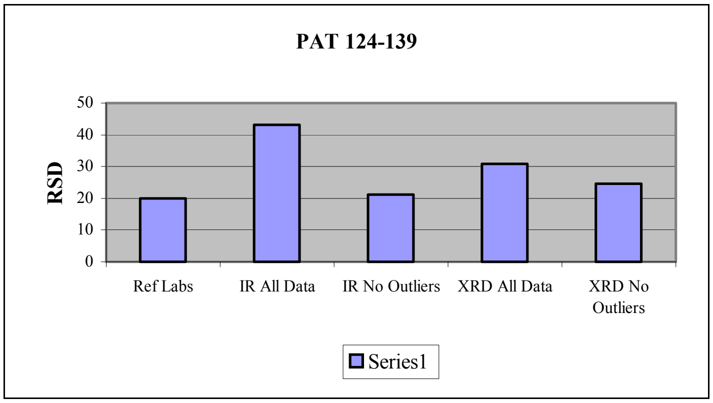


Table 13 below shows the RSDs for various silica concentration ranges summarized from PAT Rounds 124-139. Concentration ranges were bracketed at 20 microgram intervals, starting with the lowest reference value at 50 micrograms. The highest reference value in PAT Rounds 125-139 was 175 micrograms, and only one round encompassed this value. Therefore, the final range includes values between 150-175 micrograms.

**Table 13**

**PAT Rounds 124-139**
**Relative Standard Deviation (%)**

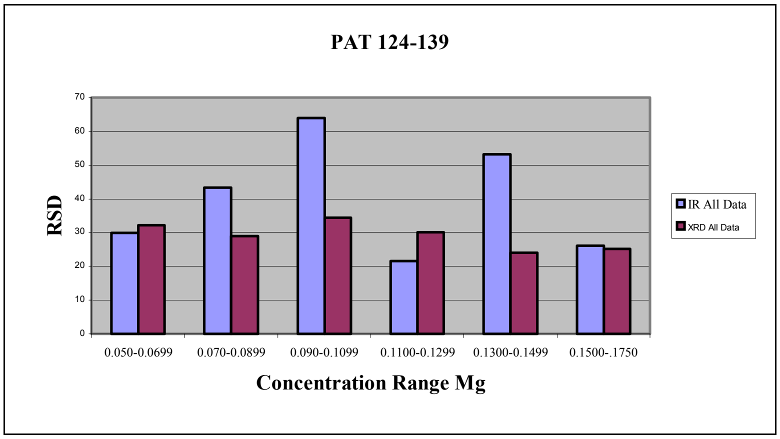
| Milligram Range | Reference Labs | IR All Data | IR No Outliers | XRD All Data | XRD No Outliers |
|---|---|---|---|---|---|
| 0.050-0.0699 | 21.7 | 29.8 | 22.7 | 32.2 | 27.8 |
| 0.070-0.0899 | 19.3 | 43.4 | 21.3 | 29.0 | 24.3 |
| 0.090-0.1099 | 20.0 | 64.0 | 21.0 | 34.5 | 23.3 |
| 0.110-0.1299 | 16.6 | 21.5 | 19.1 | 30.1 | 23.3 |
| 0.130-0.1499 | 21.6 | 53.2 | 19.8 | 24.1 | 22.9 |
| 0.150-0.1750 | 22.9 | 26.2 | 20.9 | 25.1 | 23.4 |

Analysis of data from Table 13 indicates the following:

1. With *outliers excluded*., the highest RSD for silica is at the lowest range of 50-70 micrograms in the case of both IR and XRD.
2. *IR All Data* (including outliers) has an RSD range from 21.5-64.0.
3. *XRD All Data* (including outliers) has an RSD range from 24.1-34.5.

Graph 7 below is a pictorial representation of the data in Table 13 for *IR All Data* and *XRD All Data* (*i.e.*, with Outliers included in both cases). For these data sets, IR shows the highest RSD. It occurs at a concentration level of 0.090-0.1099 milligrams.

## GRAPH 7



Graph 8 below is a pictorial representation of the data in Table 13 for *IR NO* and *XRD NO* (*i.e.*, with Outliers excluded in both cases). In these data sets, the RSDs for XRD are consistently higher than the RSDs for IR. The Highest RSD is for XRD in the 0.050-0.069 milligram range.

## Graph 8

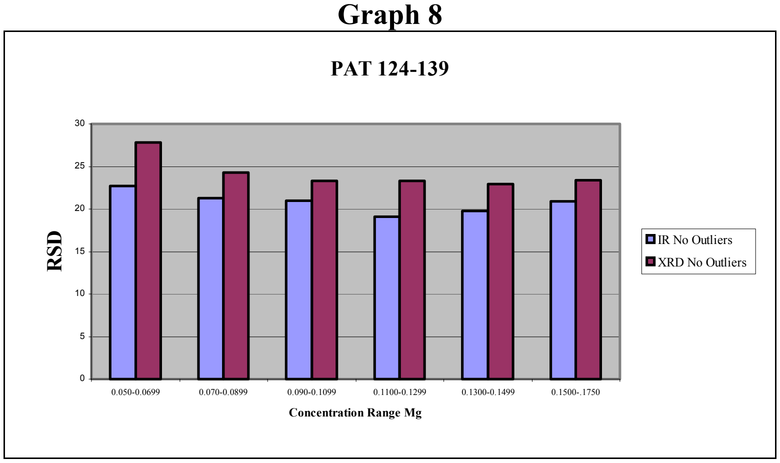


Table 14 below summarizes the PAT data in two different ranges: 0.050-0.100 milligrams and 0.101-0.150 milligrams. With outliers excluded, IR shows a lower RSD than XRD in both ranges. The reverse is true when outliers are included.

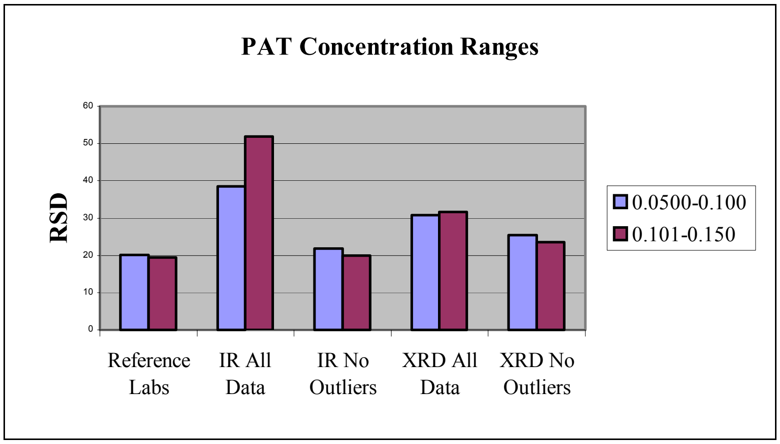
### Table 14

**PAT Rounds 124-139**
**Relative Standard Deviation (%)**

| Milligram Range | Reference Labs | IR All Data | IR No Outliers | XRD All Data | XRD No Outliers |
|---|---|---|---|---|---|
| 0.050-0.100 | 20.2 | 38.5 | 21.9 | 30.7 | 25.4 |
| 0.101-0.150 | 19.4 | 51.9 | 20.0 | 31.6 | 23.5 |

Graph 9 below is a pictorial representation of the data in Table 14.

## GRAPH 9



Graph 10 below is a plot of PAT Silica concentration ranges vs. RSD according to Methodology.

## GRAPH 10

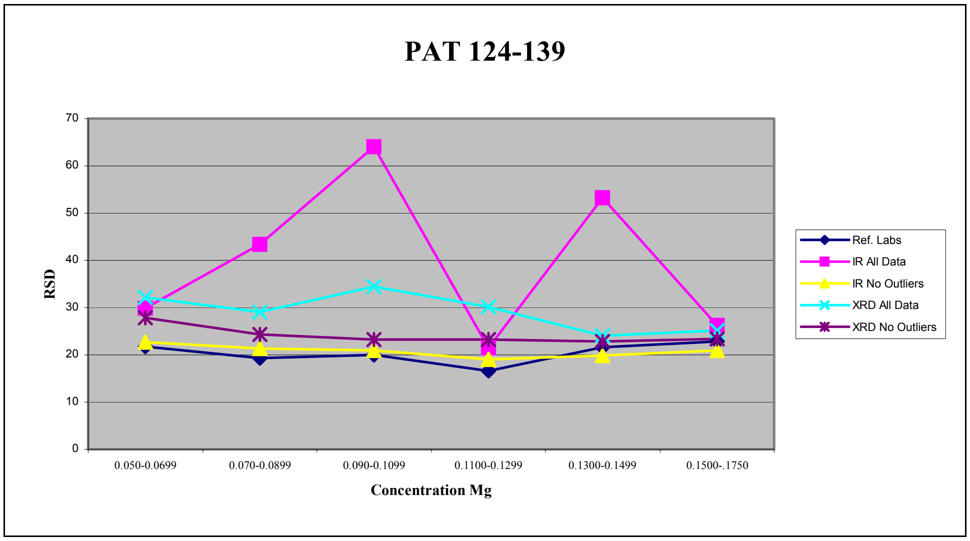


Table 15 below summarizes data from PAT Rounds 124-139 in the lowest concentration range of 0.050-0.060 milligrams (mean values), showing the acceptable upper and lower reporting ranges and the corresponding air concentration ranges based on eight-hour sampling at an air flow rate of 1.7 L/min (collecting a total of 816 Liters of air).

For example: In PAT Round 129-3, the Mean Reported Value was 0.0584 milligrams silica. Based on an acceptable reporting range of 3σ, the corresponding Lower Acceptable Reporting Limit would be 0.0133 mg and the Upper Acceptable Reporting Limit would be 0.1035. The Lower Acceptable and Upper Acceptable Reporting Limits are divided by 0.816 $m^3$ of air (816 Liters) to obtain the Acceptable Air Concentration Range. These data indicate that for a PEL of roughly 0.07 mg/m$^3$, a normal acceptable reporting range as determined under the PAT Program could vary from roughly 20% of the PEL to 180% of the PEL. For a PEL of 0.05 mg/m$^3$, the acceptable reporting range presumably would be even greater.

**Table 15**
**0.050-0.060 Milligram PAT Reference Values**
**Upper and Lower Limits of Acceptance**
**Corresponding Air Concentration Ranges for Silica**

| PAT Round | Mean PAT Value mg | Lower Acceptable Limit | Upper Acceptable Limit | Acceptable Air Concentration Range mg/m$^3$ |
|---|---|---|---|---|
| 131-1 | 0.0502 | 0.0200 | 0.1002 | 0.0245-0.123 |
| 125-4 | 0.0566 | 0.0144 | 0.0987 | 0.0176-0.121 |
| 130-3 | 0.0568 | 0.0175 | 0.0962 | 0.0214-0.118 |
| 128-3 | 0.0575 | 0.0236 | 0.0913 | 0.0289-0.112 |
| 137-2 | 0.0583 | 0.0248 | 0.0919 | 0.030-0.113 |
| 129-3 | 0.0584 | 0.0133 | 0.1035 | 0.016-0.127 |
| 133-1 | 0.0588 | 0.0251 | 0.0925 | 0.038-0.113 |

# CONCLUSION

The sampling and analysis of crystalline silica at respirable airborne concentrations of 0.1 mg/$m^3$ or below presents a number of challenging problems which become even more challenging as the concentrations of interest are reduced to levels of 0.05 mg/$m^3$ and below (reflecting a potential PEL of 0.05 mg/$m^3$ and an action level of 0.025 mg/$m^3$). In order to evaluate the precision and accuracy of sampling and analytical methodologies at those low airborne concentrations, this Report examined performance data for OSHA Method ID-142 and silica data from the AIHA PAT Program. The Report also considered the special problems and concerns associated with sampling and analysis for crystalline silica.

Based on the data and information presented in this Report, the author concludes that reliable and reproducible measurements of respirable silica—with acceptable precision and accuracy—are not feasible at airborne concentrations below 0.1 mg/$m^3$ using current sampling and analytical methods.

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