

**DISCUSSION OF THE SERIOUS INACCURACIES IN THE
EXISTING CRYSTALLINE SILICA INDUSTRIAL
HYGIENE TEST METHODS AND RESULTS**

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INTRODUCTION

All the existing industrial hygiene test methods have not proven to be capable of accurately measuring crystalline silica at concentrations at or below the current PEL of 100 $\mu\text{g}/\text{M}^3$. The Reform OSHA Coalition comments to the SBREFA process (11/25/03) discussed the relative inaccuracy of the various NIOSH methods used to measure silica, including crystalline forms of silica: quartz, cristobolite, and tridymite, which are the forms of silica that are implicated in the onset of silicosis. They correctly pointed out that even for very recent NIOSH Proficiency Analytical Testing (PAT) studies (2003) the percent Relative Standard Deviation (RSD) for the silica tests was far higher than for other analytes such as organics and metals, and it does not usually meet the NIOSH definition of accuracy even at the current 100 $\mu\text{g}/\text{M}^3$ OSHA PEL. They showed that for several PAT rounds, the RSD for silica was typically in the 15-17% range overall, while the RSD for metals was typically only 3-6%. The importance of these RSD values cannot be overstated. The acceptability criteria for the PAT samples are typically set at +/- 3 times the RSD—that is, if the compiled results from a PAT sample exhibit a 17% RSD, that **sample has an acceptance range of +/- 51%** around the mean of the laboratory results for any given PAT sample. Such an acceptance range is simply not suitable for compliance or enforcement testing and for making decisions to install adequate engineering controls. Many sources report that the PAT RSD values run even higher for lower concentration samples, often exceeding 20%.

A brief examination of the differences between the various methods accepted for silica analysis, and the differences between the PAT samples and actual real matrix samples convincingly demonstrates that if anything, the Reform OSHA Coalition comments as to the methods' inadequacies are much understated. The PAT samples are idealized laboratory generated test samples, with background matrices that do not match samples generated from most industries, particularly those industries involved in the manufacture or handling of building materials where

lots of clay (brick) and concrete products are used. The precision for all of the analytical methods gets much worse at lower concentration levels—levels in the 50 to 75 $\mu\text{g}/\text{M}^3$ concentration range where OSHA is now considering proposing new PEL limits. The PAT samples are rarely even prepared at these low concentration levels after accounting for the typical eight hour air sample size. There are several articles written concerning the inaccuracy of the crystalline silica tests used in the industrial hygiene field, some of which are cited below.

To help demonstrate the problems that this can cause, the following example is presented. For an IH silica sample with a “true value” of 75 $\mu\text{g}/\text{M}^3$ and an RSD of 20% (as in the PAT results), the margin of error range for labs whose results are deemed acceptable under the PAT criterion extends from 30 all the way up to 120 $\mu\text{g}/\text{M}^3$. If the new PEL were 75 $\mu\text{g}/\text{M}^3$ (equal to this sample), then many actual test results could range up to 120 $\mu\text{g}/\text{M}^3$ even if the actual exposure level were only 75 $\mu\text{g}/\text{M}^3$, giving a false conclusion of significant noncompliance. Also, many actual test results could range down to 30 $\mu\text{g}/\text{M}^3$ giving a false impression of being significantly in compliance. (If the true value is 100 $\mu\text{g}/\text{M}^3$ (the current PEL) the large margin of error given a 20% RSD extends from 40 $\mu\text{g}/\text{M}^3$ to 160 $\mu\text{g}/\text{M}^3$.) To further visually demonstrate this, most people realize that when driving on the interstate with a 75 mph speed limit, motorists are unlikely to be given a speeding ticket unless they exceed the speed limit by more than 5 or even 10 mph. This is because most troopers prefer to be outside the margin of error of their radar gun, which is much better than silica tests, so this would not be an issue in court. If the radar gun were as inaccurate as the silica tests, it is the equivalent of a state trooper waiting until your measured speed is **120 mph** or more in a 75 mph zone before pulling you over, because he knows that anything less is within the margin of error of his inaccurate radar gun!

The following discussion briefly examines reasons why the Industrial Hygiene (IH) silica testing is barely accurate enough to determine compliance even at the current OSHA PEL except in cases of obvious substantial exceedances and shows that the current methods are incapable of accurately determining compliance at proposed PELs that are 25 to 50% lower.

ISSUE: Actual samples are far more complex than PAT samples, with more varied matrices and more varied filter loadings.

The PAT samples within each round must of necessity be uniform and accurate in both silica content and in the nature of the matrix. Otherwise results could not be comparable among the

labs. However, these requirements limit the capacity of these samples to accurately reproduce the multitude of sample matrices from the many different industrial materials that contain silica.

NIOSH produces silica PAT rounds with four different background matrices: coal mine dust (CMD), talc, calcite, and a mixed matrix of CMD and talc; all of these are relatively low in crystalline silica, but talc will contain high amounts of silicates, which are an interference in all methods. Crystalline calcite, if not removed, will also interfere with some of the methods. All of the PAT filters are then spiked with different amounts of a pure standard reference silica suspension solution, usually containing quartz or cristobalite.

Although the above may represent a good faith effort at generating matrix-similar PAT samples, it does not begin to encompass all the real world possibilities. First, the real samples from the construction industry alone include many clay content materials including different types of brick and ceramic material, concrete dust, as well as different rock cuttings and grindings, none of which are similar to the basic background materials used in the PAT samples. In addition, the PAT samples necessarily contain uniform background loadings, onto which pure reference silica material has been spiked. In real world samples, the silica is contained in the background materials at varying percentages, and the filter loading of material can vary greatly.

The differences in materials collected, and the uneven loading of the materials on the real world filters can cause interference removal or compensation steps in the methods to become less effective. One example is the removal of silicates from either bulk or settled dust samples, and also for air samples when using NIOSH Method 7601 (the visible colorimetric method).

Another example is the removal of the interfering calcite in Method 7500 only in samples where it is known to be present at 20% or greater. (Calcite may cause silica loss when filters are ashed in a muffle furnace.) This could create variability between samples treated to remove calcite (with 25% HCl) vs. those that were not treated, yet likely still contain some calcite (a common mineral). All of this greatly increases the variability of results from real world samples in comparison to the far more controlled PAT samples.

ISSUE: Interferences to all the methods are present in real samples and difficult to remove, requiring many additional sample handling procedures that are highly technique-oriented.

There are an exceptional number of interferences to the silica tests, most of which are not present in the PAT samples. Most of these interferences can result in false positive results. Many of

these require additional procedures to remove the interferences, or else the use of alternative analytical techniques, such as the use of less sensitive secondary silica response peaks, reducing analytical reliability and increasing the detection limits. These are listed for the three main NIOSH Methods below.

- **NIOSH Method 7500-X-ray Diffraction**—Interferences include barite, micas (muscovite, biotite), potash, feldspars (microcline, plagioclase), montmorillonite, sillimanite (both common clays), zircon, graphite, iron carbide, clinoferrosillite, wollastonite, sanidine, leucite, orthoclase, and lead sulfide. In addition, the forms of aluminum phosphate, if present, are virtually indistinguishable from the three forms of crystalline silica. Calcite interferes with the muffle furnace filter ashing, and the presence of elements such as iron (common in brick material) can result in appreciable X-ray fluorescence which leads to high background intensity. A diffracted-beam monochromator will minimize this last problem. The method recommends: “If interferences with the primary silica peak are present, **use a less sensitive peak**. When overlaps are not severe, a smaller receiving slit or chromium radiation may be used; however, a new calibration curve will be necessary.”
- **NIOSH Method 7601-Visible Spectrophotometric**—This method is the least reproducible, and has the most interference problems. It cannot distinguish between the three crystalline silica polymorphs, and in fact will give a positive response to all silicates and amorphous silica if these are not removed. A controlled phosphoric acid digestion (at exactly 240 deg C, for exactly 8 minutes) is used in an attempt to solubilize and remove silicates without also solubilizing silica. However, as the method points out, different silicates have differing solubility under these conditions, and this procedure is even less effective in removing amorphous silica. Any silicates or silica remaining in the sample after this treatment are a direct positive interference. Phosphate ion complexes are also interferences to this method. This method is extremely dependent on analyst technique, likely resulting in the high interlab variability observed.
- **NIOSH Method 7602-Infrared Method**—“Quartz and cristobalite can be determined in each other's presence by the use of less sensitive bands at 695 cm⁻¹ (quartz) and 625 cm⁻¹ (cristobalite). Tridymite can only be determined in the absence of the other two

polymorphs; it is rarely encountered in industrial hygiene samples. Interfering silicates can be removed using a phosphoric acid cleanup procedure [2]. Cristobalite and tridymite interfere positively at the 800 cm⁻¹ peak, although they are rarely present in industrial hygiene samples. Kaolinite, a common component of coal, can interfere when RF plasma ashing is used to remove the collection filter, if it is present in sufficient quantity. A correction procedure is outlined in the method (steps 6 and 10). Calcite, at greater than 20% of the total dust loadings, can interfere by reacting with the quartz during muffle ashing. A procedure for its removal is given (step 3.b). Amorphous silica may interfere if present in large amounts. This interference can be minimized by accounting for its broad absorbance band when drawing the baseline.” (Note that this method is also dependent on the phosphoric acid digestion for silicate removal.)

ISSUE: The acceptability of at least three different types of analytical techniques serves only to increase the already high analytical variance for silica determinations shown by the PAT results. Alternatives within each method may also contribute to variability.

A 1999 article in the AIHA Journal (Eller et. al.) discusses the variability problems in the Proficiency Analytical Testing program for silica, focusing on PAT rounds during the years 1990-1998. The paper focused on these years, because prior years had several different firms preparing the PAT samples, and the background matrices used were irregular. Also, at one point in time prior to 1990, the PAT standard for crystalline silica used significantly larger particles than were used during 1990-1998. (The particle size has different effects for different methods.) During this time period, and continuing to the present day, the PAT tests have been better standardized, with all samples spiked using “min-u-sil 5” silica standard, and with each round having one of four background matrices (see above) rotated in a regular schedule. Some of the key information or findings in this paper are as follows:

- The main purpose of the paper focused on the much higher variability found in IH silica PAT testing vs. most other PAT parameters. The abstract states that historically (prior to the examined PAT period), the relative standard deviation from these tests had been around 25-30%, while the %RSD for metals and organic parameters is typically around 4-6%. During the period examined by this paper, improvement was noted in the RSD

data for silica, but the RSD remained much higher for silica for all of the methods than for most other IH analytical parameters.

- From Figure 1, it is evident that the relative number of labs using each of the three main methods had changed from 1972 to 1998. Up until 1977, the majority of PAT participating labs used the colorimetric method; after that time, X-ray diffraction became the most common method. By 1982, the IR method had also become more popular than the colorimetric method. In PAT round 132 from 1998, the last round reviewed, out of 78 labs, 50% used XRD, 38% used IR, and only 12% used the colorimetric procedure. It appears this test has become much less popular over the years. This trend has likely continued over the years since this study.
- The paper states that the colorimetric procedure had far greater variability than either the IR or XRD methods. The authors note that for the colorimetric test, %RSD fell from 35-40% in the first few rounds to less than 30% recently. During that time, the number of labs using the colorimetric procedure dropped by 50% (24% to 12%). The RSD remained constant, but still relatively high for the x-ray diffraction and IR methods, which dominated the statistics for the later PAT rounds. The decline in the use of the colorimetric method appeared to be one reason for the overall RSD improvement, and the improvement within the remaining labs appears to have been due to greater proficiency with that method in those laboratories that decided to keep it.
- The data cited in this paper showed that overall precision of PAT silica results depends on sample loadings (silica concentration), improving above loadings of 60-80 µg silica per sample. The observed interlaboratory variability (for low concentration samples) had not changed significantly over the last 8 years (1990-1998) and remain(ed) above $RSD = 20\%$.

- In a technical exchange involving many of the same authors in “The Synergist” (an AIHA monthly magazine) from November 1999, follow-up questionnaires were submitted to laboratories that participated in PAT round 133, and the recovery was evaluated for the IR and X-ray diffraction (XRD) methods for PAT rounds 130-133. Using relative recovery (vs. the all-lab average mean) as a measure, there were significant differences between these two methods. XRD relative recovery was 0.96, with an SD of 0.17, while IR relative recovery was 1.13, with an SD = 0.47. This limited data could indicate a high bias in the IR method, and also shows that these two methods continued to have precision problems.
- A brief review of PAT rounds from later years continues to show that the RSD remains high for silica. URS intends to perform a more complete study of more recent PAT data as a future addendum to this report.

ISSUE: The PAT data from the 1999 Eller report demonstrates that the lower the concentration, the poorer the precision, which means that the methods accepted by OSHA and NIOSH are not capable of accurately measuring a PEL that would be lower than the current 100 $\mu\text{g}/\text{M}^3$.

As indicated from the above findings, the precision for all silica methods, even using the controlled laboratory generated samples used in the PAT certification testing program, deteriorates at values below 80 $\mu\text{g}/\text{sample}$, with significant deterioration below 60 $\mu\text{g}/\text{sample}$. This was true for all three methods. In addition, there is evidence that both the IR and colorimetric methods have high bias at lower sample concentrations. This is extremely relevant if OSHA lowers the current PEL from 100 $\mu\text{g}/\text{M}^3$ to 75 or even 50 $\mu\text{g}/\text{M}^3$ as an 8 hour, time weighted average. The current PAT samples are mostly spiked at values that greatly exceed the current OSHA PEL of 100 $\mu\text{g}/\text{M}^3$, which roughly equals an 80 μg sample if taken for a full eight hours, as indicated above. For most PAT rounds, the great majority of silica values exceed 80 $\mu\text{g}/\text{sample}$, ranging as high as 185 μg , far in excess of the current OSHA PEL. A quick URS review of the data from PAT rounds 144-180 (years 2001-2010) reveals that only ten PAT

samples out of 148 (6.8%) were less than 60 μg (roughly equal to a possible PEL of 75 $\mu\text{g}/\text{M}^3$), and only one out of 148 (0.7%) was at a level roughly equivalent to 50 $\mu\text{g}/\text{M}^3$. Not one single PAT sample over this ten year period was actually *lower* than a potential 50 $\mu\text{g}/\text{M}^3$ PEL after accounting for the sampling volume. **This conclusively demonstrates that the RSDs measured from current PAT testing, even as high as they are, are not indicative of method performance at the concentration levels OSHA may propose for a new PEL.**

One issue that results from actual IH field samples is that most IH samples taken for silica do not sample a full cubic meter of air within one eight hour shift. The sampling apparatus flow rate required to capture respirable dust with a Dorr-Oliver Cyclone is 1.7 liter per minute, which is fixed by the physical requirements of the front cyclone used to separate the respirable dust fraction. There are 480 minutes in an eight hour shift, so only 816 liters, or 0.816 cubic meters of air maximum can be collected during a single eight hour shift. This means that a sample filter containing 80 μg of silica is already equivalent to 98 $\mu\text{g}/\text{M}^3$ (80/0.816), which is essentially at the current OSHA PEL. A 60 μg sample, the level at which precision “significantly” deteriorates, equals 73.5 $\mu\text{g}/\text{M}^3$. While occasionally some samples are taken for 480 minutes or longer, many of the OSHA and NIOSH sampling events involve sample time significantly less than that, typically 420 to 460 minutes. A 60 μg sample that ran for 420 minutes equals 84 $\mu\text{g}/\text{M}^3$, which is already well above a potential PEL of 50 $\mu\text{g}/\text{M}^3$.

ISSUE: Silicon is the second most ubiquitous element on the planet, and is most often in the form of silica and silicates. Method, reagent, and sample handling blanks can be a serious problem.

With various forms of silica being so prevalent in the environment, and the interfering silicates even more prevalent, any plan to lower the OSHA PEL significantly should also take into account method blanks, as well as the more complex matrices found in real world samples. Blanks are not typically reported for PAT samples. However, Eller et al. report that the colorimetric test averages 20 μg per sample. Measurable blanks for XRD and IR are reported to be “infrequent”, but inconsistent, that is the contamination level is not the same within a particular lot of filters and/or reagents. The effects of variability in the blanks would be greatly amplified in samples with low concentrations, and might account for part of the poor precision seen in PAT samples below 80 μg . Blank information, as well as other detailed laboratory data

should be requested from the various NIOSH and OSHA site or enforcement visits cited in the docket. (The current reports in the docket contain no analytical information other than the reported results.)

CONCLUSIONS

All of the three basic accepted analytical methods for silica are inadequate to accurately measure potential PELs that are lower than the current $100 \mu\text{g}/\text{M}^3$ limit, based on the following reasons.

The silica analytical methods have very poor precision compared to other IH analyses, often exceeding 20% RSD in PAT rounds. This precision already presents problems at the current PEL of $100 \mu\text{g}/\text{M}^3$, but the problem is greatly amplified with all the analytical methods when measuring down to these proposed lower levels. Several papers investigating problems with the silica analytical methods indicate that precision and accuracy for these methods drop off dramatically at concentration levels much higher than a proposed PEL concentration of $50 \mu\text{g}/\text{M}^3$, with RSD values often exceeding 30%. Ninety-three percent of the PAT sample spike values since 1999 have exceeded a potential PEL of $75 \mu\text{g}/\text{M}^3$, and >99% exceed a potential $50 \mu\text{g}/\text{M}^3$ PEL. Therefore, statistical data generated from the PAT samples taken as a whole is simply inadequate to describe the accuracy and precision at the lower concentration levels in these potential PELs. Several papers from NIOSH find that very significant deterioration in both precision and accuracy occurs at these lower concentration levels. The colorimetric procedure is especially inadequate. It normally has much higher imprecision than the other analyses, and also a high bias in samples below the current PEL (but above the lower OSHA potentially proposed PELs). There is also evidence of high bias in the IR PAT samples.

Although the PAT samples use a series of four different background matrices, these backgrounds are tightly controlled among the samples within a PAT round, and the materials do not match the dusts generated from most industrial or construction activities, either in the type of material or the quantity of material present on the sample filters.

The new potential OSHA PELs do not take into account silica present on analytical blanks. Blanks often found in the colorimetric procedure at least, are unacceptably high in comparison to

the new limits. Since blank data is not reported with the PAT samples, there could be issues with the other methods as well.

All three analytical procedures require extensive interference removal in real world samples. Most of the known interferences for the methods are positive interferences causing high bias in real world samples that is not manifested in the PAT samples. The interference removal techniques are imperfect, and involve much additional sample handling, or analysis at less than optimum and/or less sensitive analytical conditions. All of these techniques cause higher detection limits, greater sample contamination, and a greater reduction of precision and accuracy that is not reflected in the statistics for the PAT samples.

Other quality control issues not discussed in this document are related to sampling methods. The issues with sampling may have an even greater impact than the poor laboratory test methods.

Prior to OSHA seriously considering any lowering of the crystalline silica PEL, adequate test procedures need to be developed and proven accurate over time at the concentration level of any new PEL. Not doing so will only result in large numbers of facilities being falsely and haphazardly identified as being out of compliance with the new PEL.

Addendum

Follow-up Examination of PAT Data from Rounds 144 to 180 (Dates 2001 through January, 2010)

As referenced in the previous report on the IH silica analytical PAT program, URS has further examined FOIA data from the OSHA laboratory participation in the NIOSH industrial hygiene PAT program for the silica test. These rounds administered quarterly consisted of 148 different filter samples from January of 2001 through January 2010. For each round, all participating labs would receive a set of four different samples. The number of participating labs for each round ranged from 57 to 74, with an overall gradual decrease in the number of labs over time. The decrease in laboratories so far does not appear to have impacted the precision of the analytical results. The overall percent RSD for this period was 16.7%, still very high compared to other analytical procedures. The *average* range for acceptable percent recovery (vs. the mean or reference value) for samples in these groups was still 50-150%. However, during this period there appear to have been two changes to the rules governing the data calculations that serve to lower the percent RSD obtained and tighten the acceptance limits. (These procedural changes are not typically discussed in the results reports issued to the laboratories, which is what was furnished by OSHA in the FOIA request.) Such actions by the test administrator (NIOSH) might be fully justified based on the data, especially if there are consistently a few laboratories that are outliers distorting the data. The reports we have do not indicate the individual lab results even by a redacted lab ID, so URS cannot determine this. However, these changes for these PAT rounds do make historical comparison to the data discussed in the 1999 Eller paper cited more difficult. The first data calculation change is quite obvious. Starting with PAT Round 159, it is apparent that a limit of 20% has been applied by NIOSH as a maximum RSD. Prior to this round, many samples would exceed 20% RSD, and values greater than 20% were routinely reported. From this round onward, the maximum RSD found is exactly 20.0%, and this exact 20.0% value appeared 18 times out of a total of 86 samples in the subsequent rounds. This was probably instituted to tighten the limits, and thereby isolate “outlier” laboratories, which are discussed in the “Synergist” paper cited in the above report. However, this does complicate comparisons to

older data, to determine whether there is any ongoing improvement in either the test or laboratory performance.

The second possible data change seems to occur around PAT round 172, but is less obvious. This round coincides with a distinct drop in percent RSD that is coupled with a significant increase in unacceptable results from the laboratories. Generally, the acceptance limits for each sample in each round are determined by the pool of laboratory results submitted for that sample. However, severe outlier results can have undue influence on the calculation of these limits. In typical statistical practice, a consistent set of screening mechanisms is used to determine whether to eliminate data points as gross outliers, and not include them in the acceptance limit calculation. However, the NIOSH administrators may have decided to either tighten or add to these outlier procedures to narrow the limits. The following table shows the data changes before and after Round 172:

	%RSD	Percent Acceptance Limits	Percent Unacceptable Results
Prior to Round 172	17.5%	47.5 to 152.5%	4.52%
Round 172 and Later	14.04%	57.9 to 142.1%	7.23%

Note that the increase in unacceptable results mirrors the tightening of the acceptance limits. This suggests that at least some of the unacceptable lab results that may have been used in the past are no longer being included in the calculation of the more recent limits.

It was the intention of URS to compare these later PAT results to the results discussed in the 1999 Eller report, especially as it related to lower concentration samples. However, the implementation of a 20% limit on the RSD, possibly coupled with other data processing changes has made this comparison difficult. A truly valid comparison can only be made if URS can obtain the original statistical data for the PAT rounds Round 159, when the first of these adjustments was initiated. However, the data do suggest that any slightly lower percent RSD

values from these later rounds is more an artifact of changes in data handling than overall improvement in the laboratory results.

Because of these difficulties, URS compared the RSD of the low concentration samples to the higher concentrations only within these PAT rounds. Lower concentrations of silica still do appear to have higher RSD values, but this effect is no doubt masked by the maximum 20% RSD that was applied to most of the samples in these PAT rounds. The RSD for low concentration samples is likely much higher than is evident here. The following table shows the RSD broken down by silica concentration on the filter, and a conversion to ug/M³ based on a maximum sample size using the current sampling system.

Silica Concentration Range, ug/filter	Approximate Equivalent in ug/M³ based on current normal size sample and a full 8 hours of sampling	Average Percent RSD
<60	<75	18.3%
>60, <80	>75, <100	17.5%
>80	>100	16.2%

As to the OSHA laboratory itself, (lab ID number 101575 in the PAT program), URS calculated the average of the absolute value of the OSHA lab’s “Z score”, which was 0.97. The “Z score” for a reported sample result is the number of standard deviations that result is away from the laboratory mean. Z scores greater than 3 deviations from the mean are generally unacceptable. Raw “Z scores” can be positive or negative, depending on whether the result is above or below the mean value, however, the larger the absolute value of the score, the more inaccurate or imprecise the result. Based on normal distribution, an average “Z score” is around 0.6-0.7. The OSHA average Z-score of 0.97 is slightly worse than average on that scale. However, the OSHA lab was above average in avoiding unacceptable results, which affects a laboratory’s accreditation as proficient for an analytical test. Out of 148 samples submitted, OSHA was outside acceptance limits for only 2 samples, or 1.3%. This was well below the overall lab rate

of about 5% unacceptable results. Both missed samples were in Round 173, which was after URS believes limits were tightened. Overall, the OSHA lab is an average performing laboratory in the PAT program, and therefore does not support the supposition that laboratories experienced in IH silica analysis can perform far better than average in the IH PAT program.

Finally, URS is aware that there are modifications to the sampling procedures and devices being discussed that would enable larger samples of respirable dust to be taken. These would necessarily involve larger pre-filter cyclones capable of a faster respirable sampling rate and larger volume sampling pumps. However, simply taking larger samples alone does not fix the analytical problems, unless there are also corresponding changes made to the analytical procedures, and unless and until the analytical method is validated at any new PEL concentration level based on the larger samples. This is true for the following reasons:

1. The size of the samples taken must be increased dramatically, especially since most samples are taken for shorter than eight hours of working time due to practical considerations. Based on a full eight hours of sampling at the currently allowed sampling rate (a maximum sample), there was only one PAT sample out of 148 that equaled 50 ug/M^3 , and only 11 samples that were equal to or less than 75 ug/M^3 for PAT rounds 144 through 180. Furthermore, there were 103 out of 148 samples that exceeded 100 ug/M^3 (with only 45 below 100). Therefore, the current PAT program is already skewed too high even for the current 100 ug/M^3 OSHA PEL. Ideally, a QA program should be centered around a compliance limit, with approximately equal spike values above and below the regulatory limit. Lowering the PAT spiking concentrations does not appear to be an option, since the precision of the analyses will deteriorate further. Therefore the sample size must be increased at least 2.5 to 3 times the current maximum to “center” the PAT samples around a new 50 ug/M^3 PEL.
2. The problem is not solved simply by raising the sample volume three-fold. The silica test is very sensitive to interfering materials in the sample. To our knowledge, the silica analyses are the only IH PAT samples that must include a variable background matrix (i.e. currently, calcite, talc, coal mine dust (CMD) and a combined talc/CMD backgrounds are used on a rotating basis in each PAT round). The biggest weaknesses of

the NIOSH silica methods are the procedures that remove the many interfering compounds from the samples prior to measurement. Sampling three times as much air through a filter would dramatically increase the amount of background interferences captured on each filter. It is entirely possible that the silica analysis could be so adversely affected that the method would be no more capable of accurate and precise measurement at the 50 ug/M³ concentration levels than it is now. The entire analytical method would require re-validation, using PAT samples with background matrices in proportionately higher (2.5-3 fold) concentrations, to verify that the method was capable of removing the much greater amounts of interferences present, while still preventing a further erosion of method precision (which is already very poor).

The conclusion is that while larger sampling may be possible, it would be a mistake to assume that a simple three-fold increase in sample size would automatically mean that the range of accurate measurements in these tests will also automatically be lowered by a factor of three. Around the PEL concentration level, it is simply not sufficient to merely have a detection limit (which by definition is below any quantifiable limit) lower than the PEL; the method must also be demonstrated as capable of sufficient accuracy and precision to enforce a regulatory limit. Even at the current 100 ug/M³ PEL, the current silica methods are marginal in this regard at best. Making radical changes in sample size affects all aspects of these already marginal analytical methods, and needs to be fully validated at the concentration levels of any proposed new PEL.