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Methods used by the United States National Institute for Occupational Safety and Health to monitor crystalline silica

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The National Institute for Occupational Safety and Health (NIOSH) in the United States has four methods for monitoring the concentration of crystalline silica dust. They all employ a cyclone for size-selective sampling in the field, but differ primarily in that the laboratory measurement is based on either infrared spectroscopy, X-ray diffraction, or colorimetry. The limits of detection for these methods are similar, but their accuracy is poor, particularly at low filter loadings near the current recommended exposure limit (50 $\mu g \cdot m^{-3}$). Advances in analytical instrumentation have improved measurement precision. Correction techniques to account for X-ray absorption in samples loaded with nonsilica dust have eliminated one source of bias. Direct analysis on collection filters is a convenient technique that should decrease sample manipulation errors, but it has not been shown to improve precision or accuracy significantly.

Key terms dust analysis, exposure limit, infrared spectroscopy, size selective sampling, X-ray diffraction.

Over the last 25 years researchers at the National Institute for Occupational Safety and Health (NIOSH) in the United States have developed and evaluated methods for measuring worker exposure to airborne crystalline silica. The methods are typically described by the instrumental techniques, because they all rely on the same sample collection procedures. Breathing-zone samples are collected using a 10-mm Dorr-Oliver nylon cyclone to remove nonrespirable particles and a polyvinyl chloride (PVC) filter to retain the respirable dust. In the laboratory, all the methods use ashing or chemical dissolution to remove the PVC filter from the collected dust, but final preparation differs for each technique.

The third edition of the *NIOSH Manual of Analytical Methods* contains four methods determining crystalline silica polymorphs (quartz, cristobalite, or tridymite) (1). The approaches are based on three instrumental techniques: colorimetry (COL) (method 7601), X-ray powder diffraction (XRD) (method 7500) and infrared spectroscopy (IR) (methods 7602 and 7603). Each procedure is described below.

Historically, the earliest procedure was the colorimetric method, in which silicates and amorphous silica are dissolved in phosphoric acid, leaving only crystalline silica behind. After washing, the remaining silica is dissolved in hydrofluoric acid. The dissolved silica is reacted with molybdic acid to give a characteristic silicomolybdate blue color, which is measured by visible absorption spectrometry (colorimetry). The advantage of the colorimetric method is the low start-up cost. The disadvantages include the nonspecificity of the phosphoric acid dissolution step and the inability of the method to distinguish the different silica polymorphs.

The X-ray diffraction method involves ashing or dissolution of the filter, suspension of the silica dust in isopropanol, deposition of the dust on a silver filter, and analysis of the contents of this filter by XRD. Ashing is done either in a muffle furnace or a low temperature asher, while dissolution of the PVC filter is done with tetrohydrofuran (THF). Samples can be analyzed for different polymorphs by scanning different diffraction lines characteristic of each polymorph. Although the XRD methods are costly, they are relatively straightforward and less prone to mineral interferences than other methods.

The IR methods also require ashing of the filter and either redeposition of the dust onto an IR-transparent filter (DM 450, Gelman, Ann Arbor, Michigan, United States) from isopropanol suspension (method 7603) or mixing of the dust with potassium bromide and pressing of the mixture into a pellet (method 7602). Samples can be analyzed for different polymorphs by scanning absorption bands characteristic of each. The absorbance bands of the polymorphs significantly overlap, making determinations of mixtures problematic, especially if there are absorbance bands from the matrix present. The IR startup cost is intermediate (dispersive instruments) to high (FT-IR, FT = fourier transform). Sensitivity is slightly better than for the other two methods, but interferences (particularly from silicates) can be a problem.

The goal of NIOSH researchers over the years has been to improve the accuracy of airborne silica determinations. Because

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there were no totally new approaches that might accomplish this goal, efforts consisted primarily of refining existing methods and evaluating their performance. The limit of detection is approximately 5 $\mu g \cdot sample^{-1}$ for each of these methods, but their accuracy is poor, particularly at low filter loadings ($\leq 30 \mu g \cdot sample^{-1}$) typically collected when workplace concentrations of airborne silica approach the current NIOSH recommended exposure limit (REL) of 50 $\mu g \cdot m^{-3}$. The problem is exacerbated when silica is present as more than one polymorph.

Sampler improvements

The performance of the Dorr-Oliver 10-mm nylon cyclone has been studied by numerous investigators (2—6). Early efforts to alleviate sampling errors focused on eliminating sampling pump fluctuations (2). The development of flow-controlled sampling pumps mitigated this source of variability. Experimental work has shown that the 10-mm nylon cyclone closely meets the international respirable cut-size of 4.0 when operated at $1.7\ l \cdot min^{-1}$ (5).

The 10-mm cyclone was examined relative to potential leaks in the sampling train (6), and only major leaks were found to affect its performance. The O-ring at the cyclone's vortex finder was determined to be the most problematic, and a simple field test was proposed as a guide to the integrity of the O-rings: (i) the sampler is complete (no O-rings missing), (ii) the lower adapter O-ring can hold tightly onto a cyclone including the metal clip, (iii) the upper adapter O-ring can similarly hold a cassette, and (iv) the frame O-ring can similarly hold a cassette. Assembled cyclone samplers that met these simple tests were not found to have leaks that resulted in measurable losses in the sampled masses.

Instrumental improvements

Instrumental advances have resulted in improved methods for determining silica. FT-IR instruments have increased optical throughput over dispersive instruments, which only pass a fraction of the total power through to the sample. The lack of slits and absorbing optics further improves the optical throughput of the FT-IR instruments. In addition, the wavelength accuracy of the FT-IR instruments allows for a better subtraction of background (matrix) components and improved accuracy in the resultant spectra. This allows for a more precise IR determination of the silica polymorphs present in the sample.

Sample spinners on X-ray powder diffractometers allow for more crystallites to be properly oriented relative to the detector. The result is an average of the crystallites per unit of irradiated area and a reduction in the error due to the nonuniform deposition of particles on the filter surface, and, therefore, there is also better precision in the diffracted intensity of samples.

Examination of analytical procedure changes

A technique to correct for X-ray microabsorption by the sample matrix in XRD analysis was proposed by Leroux et al (7). The procedure, which was incorporated into method 7500, involves monitoring the attenuation of the diffraction line of the silver filter to arrive at a determination of the matrix X-ray absorption coefficient. The procedure mostly impacts heavily loaded filters where absorption of the diffracted intensity of silica by the matrix is highest.

The elimination of sample preparation steps by analysis directly on the collection filter has been proposed for XRD (8, 9) and IR (10). These "direct-on-filter" techniques would be convenient and would theoretically decrease errors due to sample manipulation. Therefore, on-filter methods were investigated for both XRD and IR analytical techniques (11, 12).

For XRD, direct-on-filter methods were examined with both silver and mixed cellulose ester (MCE) collection filters (11). While the direct-on-MCE filter technique was found to be within 25% of that of method 7500, the direct-on-silver filter technique was only within 30% of the same method. Standard samples prepared from liquid suspension were not found to be equivalent to those obtained by aerosol deposition, which would necessitate the preparation of aerosol deposited standards for direct-on-filter methods (11). The preparation of standards at very low sample loadings (such as ambient silica concentrations) would be extremely difficult due to weighing errors and would hinder any effort to implement a direct-on-filter XRD method.

Limitations of the use of direct-on-filter methods in IR analysis include variations in filters, both within-lot (filter-to-filter) and within-filter (12). Of the filters examined, DM-450 filters were found to be the most consistent with up to 2.4% relative standard deviation (RSD) at 798 cm^{-1}, while DM-800 filters were similar at about 2.8% RSD. A weight-based subtraction of co-added spectra of the filter was found to give a flat base line at the 798—800 cm^{-1} analytical band. However, there were problems at the lower analytical wavelength (695 cm^{-1}) because of carbon monoxide absorbance. The problems were mitigated with a long (20-min) purge of the instrument with nitrogen, but they could not be totally compensated for because of the limited IR source power and detector response at the lower wave lengths. The major problem with direct-on-filter IR methods are absorbance bands of the matrix interfering with the bands employed in the analysis. The presence of 1 mg of coal dust, a broad band absorber, resulted in a negative bias of 7—10% in the determination of quartz at 50 and 200 µg (12). The presence of kaolinite at 100 µg resulted in errors of up to 20% in the quartz determinations, despite the absorbance of other interferences (coal dust) and knowledge of the mass of kaolinite present. The direct-on-filter IR approach was too vulnerable to interferences which might otherwise be removed by pretreatment (ashing) to be a useful approach for assessing exposure to silica.

Improvements in laboratory proficiency

In general, the precision and accuracy of airborne silica determinations have improved over the last 20 years, as shown by a statistical study (13) of the results reported by laboratories analyzing silica samples in rounds 30—101 of the proficiency analytical testing (PAT) program administered by the American Industrial Hygiene Association. Five laboratories participated in the first round of the PAT program in 1972, and participation grew to 130 laboratories before falling to 105 in round 101 in 1990 (figure 1). The objectives of the study were to determine bias between methods, the variability associated with the methods, and any changes in bias or variability due to numerous factors. Because there were so few laboratories participating before round 30 (1974), only data for later rounds were used for this study.

Several models were used to examine bias due to the analytical method and other factors; the conclusions drawn from the models were similar. The colorimetric method has given the lowest results, regardless of sample matrix or particle size, particularly at higher loadings (>100 µg). For sample loadings closer to

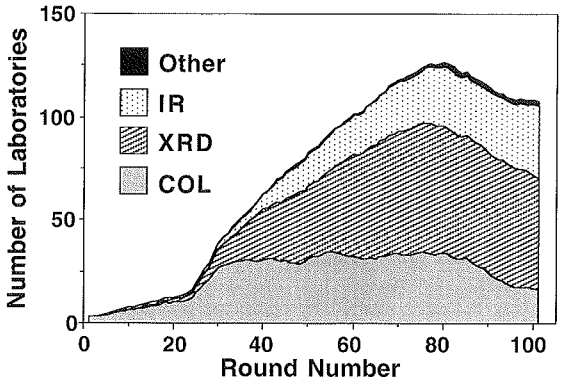

Figure 1. Cumulative number of laboratories using a particular method of silica analysis in the proficiency analytical testing (PAT) program. (IR = infrared spectroscopy, XRD = X-ray defraction, COL = colorimetry)

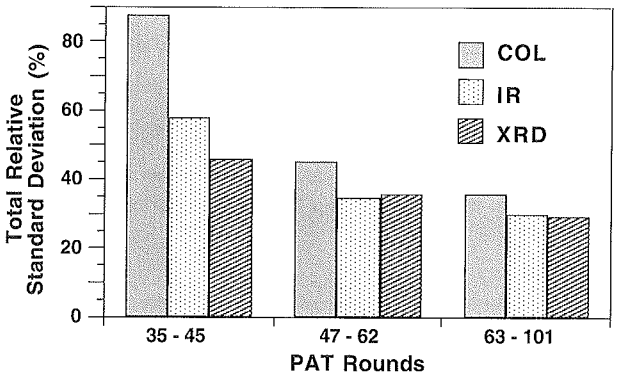

Figure 2. Total variability of silica methods in different periods in the proficiency analytical testing (PAT) program. (COL = colorimetry, IR = infrared spectroscopy, XRD = X-ray defraction)

what would be collected at the REL, however, the bias among methods has been negligible for the last 10 years (rounds 63—101). X-ray diffractometry results were biased higher than IR results during one period, but not in the following period. Between the two periods, the procedures and materials used to prepare PAT samples changed in numerous ways, but the switch to quartz dust with a smaller particle size is a likely explanation for the bias difference (14—16). Generally, silica sampling analyses have improved, and this improvement has taken place for all three of the methods. The colorimetric method has shown the poorest precision of the three methods (figure 2), but, unlike the differences in bias, the differences in precision have diminished considerably over time. The differences in method variability were consistent across the PAT sample matrices (coal dust, talc, calcite, and combinations thereof).

The contribution of within-laboratory variability to the total was of interest; therefore "duplicates" were chosen from rounds that included two samples for which the median results were within 20 µg, as long as each result was greater than 40 µg. The within laboratory variability computed from these data are shown in figure 3, which is similar in appearance to the total variability in figure 2. The within laboratory variability for the colorimetric method was statistically significantly higher than that of the IR method in each of the periods shown in figure 3, and higher than that of the XRD method in the earlier periods, but not in the most recent period.

Precision estimates from other studies were compared with those from this study to learn more about sources of variability. As shown in a collaborative study of silica methods (17), interlaboratory variation remains high (8—14%) even when laboratories employ the same procedures.

Recent developments

All silica methods have relied on the 10-mm nylon cyclone and assembled filter cassette for sample collection. The cyclone, being nonconductive, has been subject to effects of electrostatic charge, as has been described earlier (18, 19). Another design, which is made of (conducting) metal, has been recently evaluated: the Higgens-Dewell (HD) cyclone (5). Experimental work has shown that the HD cyclone closely meets the international respirable cutsize of 4.0 when operated at 2.2 l · min^{-1} (5). This higher sampling rate results in a nominally higher sample load than the 10-mm

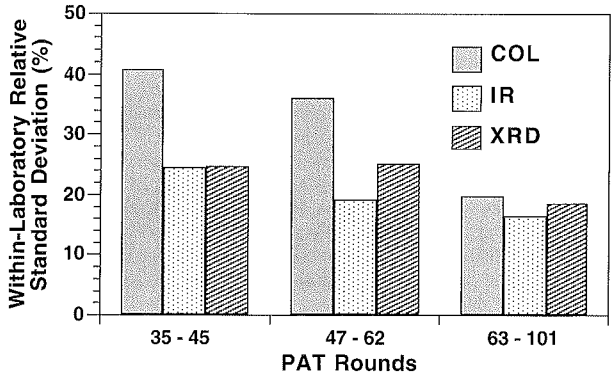

Figure 3. Within laboratory variability of silica methods in different periods in the proficiency analytical testing (PAT) program. (COL = colorimetry, IR = infrared spectroscopy, XRD = X-ray defraction)

nylon cyclone; 53 µg of quartz would be collected when sampled for 8 h at the REL of 0.05 mg · m^{-3} (versus 41 µg of quartz for the nylon cyclone). The HD cyclone is being added as an alternative to the 10-mm nylon cyclone for crystalline silica methods in the fourth edition of the *NIOSH Manual of Analytical Methods*.

Some improvements have been suggested to XRD instrumentation by other researchers (20). High-power X-ray tubes with a rotating anode, capable of about 35 kW versus 2—5 kW for a conventional tube, have been suggested to improve the diffracted intensity. The tubes are very expensive, over USD 100 000 each, and their performance gains have yet to be evaluated. A modification of the XRD goniometer that would allow the sample to be rocked during analysis would allow the diffracted line of more crystallites to be aligned to the detector, but it has yet to be evaluated and is not available commercially. This modification resulted in modest gains (limits of detection to 1 µg · sample^{-1}) but required data collection times of 5—6 h for a single line. Overall, the suggested improvements seem to offer minimal gains that are offset by substantially extra expense and time and result in decreased throughput.

Concluding remarks

In summary, modest improvements in precision and accuracy have been documented for NIOSH sampling methods, presumably as a result of the incremental refinements of the analytical procedures

used by laboratories. Unfortunately, radically new techniques that will allow accurate determinations at significantly lower levels are not anticipated.

Disclaimer

Mention of a company or product name does not constitute endorsement by the US Centers for Disease Control and Prevention.

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