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An Evaluation of Aerosol- and Liquid-Generated Silica Samples for Proficiency Analytical Testing

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Abstract

SRI International has prepared dynamically generated silica samples since 1980 for the National Institute of Occupational Safety and Health (NIOSH) and the American Industrial Hygiene Association (AIHA) Proficiency Analytical Testing (PAT) programs. Aerosol-generated samples were developed in 1980 to more closely approximate real world samples and to improve intrabatch precision. Liquid-generated samples may provide tighter control limits, and this method has been reexamined as the generation procedure of choice. Sample preparation procedures have also been investigated to minimize analytical uncertainty and, hence, obtain a true evaluation of the sampling error. Samples were analyzed by SRI, NIOSH, and the Wisconsin Occupational Health Laboratory, using X-ray diffraction or Fourier transform infrared spectrometry (FTIR). Results were plotted and statistically evaluated, then compared to the existing PAT interlaboratory database.

Keywords

proficiency analytical testing; Fourier transform infrared spectrometry (FTIR); X-ray diffraction (XRD); silica; aerosol-generation; liquid-generation

Introduction

Crystalline silica is found in many different industrial and mining occupations around the world. Inhalation of respirable crystalline silica has long been recognized as hazardous and

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can lead to silicosis and associated health effects. The International Agency for Research on Cancer (IARC) currently classifies crystalline silica as a group I human carcinogen [1]. Crystalline silica is found in several different forms, of which α -quartz is the most common and is the primary reference standard against which silica samples are measured.

SRI International has prepared dynamically generated silica samples since 1980 for the National Institute of Occupational Safety and Health (NIOSH) and American Industrial Hygiene Association (AIHA) Proficiency Analytical Testing (PAT) programs. Aerosol-generated samples were developed in 1980 to more closely approximate real world samples and to improve intrabatch precision. However, liquid-generated samples may provide tighter control limits, and this method may therefore be the generation procedure of choice.

Generally, silica analysis within the PAT program has had one of the highest interlaboratory relative standard deviations (RSD) compared with those for analysis of metals and organics [2]. The accuracy and precision of silica analysis has been problematic for several reasons. First, the results are reported from several different types of instruments: infrared (IR), X-ray diffraction (XRD), and ultraviolet-visible (UVVIS) spectrometers. Each of these methodologies has a different sample preparation procedure, which in itself leads to varying amounts of error, and each has inherent biases. Eller et al. [2] reported a wide range of materials and procedures used for calibration. All these differences, along with the normal range of analytical errors, result in a relatively large RSD for results reported to the PAT program, as reported by Eller et al. [2]. Various approaches have been used to reduce the variability in reporting, including the requirement to use National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1878a α -quartz or 1879a cristobalite, more frequent calibrations, and at least five calibration points within a calibration curve [2].

To investigate these issues, the methods of producing liquid- and aerosol-generated samples were reexamined, and sample preparation procedures were also investigated to minimize analytical uncertainty and, hence, obtain a true evaluation of the sampling error. To investigate these issues, samples were analyzed by SRI, NIOSH, and Wisconsin Occupational Health Laboratory (WOHL), using X-ray diffraction or Fourier transform IR spectrometry. Results were plotted and statistically evaluated, then compared to the existing PAT interlaboratory database, as reported by Eller et al. [2].

Methods

Liquid-Generation Method

Thirty-two polyvinyl chloride (PVC) filters (37-mm diameter, 5 μ pore size, Mine Safety Appliance, Inc., Pittsburgh, PA) and 14 DM-450 Metrical® (25-mm diameter, Gelman, Cortland, NY) filters were generated with MIN-U-SIL® 5 (U.S. Silica Company, Berkeley Springs, WV), using a liquid filtration procedure modified from the WOHL method WQ024.5.1. Changes were made in order to generate samples in bulk and spike larger amounts of solution to decrease errors, yet maintain solution homogeneity.

The following equipment was used:

37 mm, 5 μ PVC membrane filters (Mine Safety Appliance, Inc., Pittsburgh, PA; MSA filter, part # 625413)

DM-450 Metrical® (acrylonitrile copolymer, 25-mm diameter, Gelman, Cortland, NY)

SKC 37 mm Filter Funnel (SKC, Eighty Four, PA; Part No. 225-605)

NIST SRM 1878a—Respirable alpha quartz.

MIN-U-SIL® 5 (U.S. Silica Company, Berkeley Springs, WV)

2-Propanol (IPA), HPLC grade

Variable pipette, 200–1000 μ L (Gilson Microman positive displacement pipette)

500 mL graduated cylinder

1000 mL beaker

1000 mL sidearm flask

100 mL beaker

Corning stir plate and bar

Infrared drying lamp

Cole-Palmer 4710 probe sonicator.

The samples were prepared as follows. Approximately 20 mg of MIN-U-SIL® 5 was weighed out, its weight was recorded, and the material was quantitatively transferred to a 100 mL beaker, using isopropanol (IPA). Approximately 50 mL of IPA was added to the beaker, and the mixture was sonicated. The solution was added quantitatively to the graduated cylinder, and the volume brought to 400 mL with IPA. The solution was transferred to a 1000 mL beaker on a stir plate with the bar spinning at the lowest possible speed. The graduated cylinder was rinsed twice with two 50 mL aliquots of IPA, and the rinsate was transferred to the beaker. A filter prewetted with IPA was placed on the filtering apparatus attached to the 1000 mL sidearm flask. After pipetting and dispensing several times to ensure that the pipette was wetted with solution, a known amount of standard solution was pipetted into the filtering flask (1–5 mL) and suction filtered; i.e., 1 mL = ~40 μ g quartz, 3 mL = ~120 μ g quartz, and 5 mL = ~200 μ g quartz. The filter was removed and allowed to dry completely, and the sample was then placed on clean aluminum foil under an IR lamp. Samples were tested for quartz, and the recovery of quartz was determined.

Air-Generation Method

Aerosol-generated samples were prepared using the SRI dynamic dust chamber and collection system. Atmospheres of silica and various matrixes (talc, coal mine dust, and calcite) are created by several connected pieces of equipment and then released into the chambers, where they are collected on filter air monitoring cassettes. A full description of this system is provided in NIOSH Publication No. 83-124 [3].

Analytical Approach

Several approaches were used to demonstrate the variability within the air- and liquid-generated samples and to test the variance with and without direct analysis of the samples. To obtain results typical of the variability of the reported PAT results, collaborators using different analysis techniques were given samples to analyze (see Table 1). The most prevalent analysis method is NIOSH 7500 [4], an XRD method that both NIOSH and WOHL used for quantification of the test samples. SRI uses Fourier transform infrared (FTIR) method 7603 [4] for sample analysis. The sum of the NIOSH, WOHL, and SRI results were designed to approximate the weighted average of the PAT reference values.

Two direct analysis methods were examined to minimize the sample preparation contribution to the overall error. For these sets of experiments, silica was collected on 37 mm PVC and 25 mm DM-450 filters and placed directly in the FTIR beam for analysis without the typical ashing and redeposition.

The FTIR analysis was done using NIOSH Method 7603. Liquid—or air-generated samples were manufactured using MIN-U-SIL® 5, then ashed in a muffle furnace at 600 °C for 2 h before being redeposited on an IR transparent DM-450 Metrice® filter from an IPA suspension. All sets of sample results were evaluated by comparison to a standard curve generated using NIST SRM 1878a. NIOSH Method 7500 for XRD analysis follows a similar ashing procedure, but the ash is redeposited from an IPA suspension on a silver filter before analysis. Sample filters analyzed without sample preparation (direct analysis) were placed directly in the FTIR light stream for analysis.

Results

Liquid-Generated 37 mm PVC Filters, Indirect Analysis

Collaborative test samples were analyzed by SRI, NIOSH, and WOHL using XRD or FTIR. NIOSH and WOHL each received a set of duplicate blind samples and reported the values back to SRI, and SRI also analyzed a set of duplicates for data analysis. Results were plotted and evaluated for the overall RSD of all samples, precision of duplicates, and accuracy. Figure 1 shows the XRD results from NIOSH (line C) and WOHL (line B) along with the FTIR results from SRI (line A). Eller et al. [2], in their analysis summary of PAT laboratories, reported a low bias for XRD and a high bias for FTIR. The results in Fig. 1 suggest a similar pattern, especially at lower concentrations. There is almost a 70 % difference between values reported in this experiment at the lowest level analyzed. The negative slope of line A shows a larger high bias at lower concentrations and approaches unity near the higher end of the analytical range. Both upward sloping lines (B and C) have nearly identical slopes; this pattern indicates a possible instrumental bias from XRD analysis. Convergence of the slopes at approximately 140 µg indicates good agreement between the methodologies only in the portion of the tested analytical range between 55 and 145 µg. The RSDs for the reported analytical results are 12 % for SRI, 10 % for WOHL, and 14 % for NIOSH. These results are illustrated in Fig. 2. The overall accuracy for all three labs was 89 %, with an intralaboratory RSD of 20.1 %, which is comparable to results for a

single round in the PAT program. The results are also similar to the overall PAT interlaboratory RSD (the last column on the right) reported for all laboratories.

Liquid-Generated 37 mm PVC Filters, Direct Analysis by FTIR

The results of direct analysis of liquid-generated samples by FTIR were compared to the mean values reported from SRI, NIOSH, and WOHL. The objective of this comparison was to determine whether it was possible to compare the FTIR direct analysis results with the collaborators' results. Only one set of the collaborative liquid-generated samples was analyzed by this method. The accuracy values were low over-all, possibly because of the low concentrations of silica on the filters combined with the low absorption reading of the NIST 1878a analytical calibration on the 37 mm PVC filters. Table 2 provides the results of this comparison.

Liquid-Generated 25 mm DM-450 Metrical® Filters, Direct FTIR Analysis

DM-450 Metrical® filters have low IR absorbance and are typically used as a substrate for ashed and redeposited silica samples collected on PVC filters. The sample results are presented in Table 3. Both the high accuracy (103 %) and overall precision (6.1 % RSD) of measurement for this set of samples suggest ideal analytical conditions and generation. The lack of background and a higher concentration of silica on the filters allowed for good FTIR spectral analysis. The pooled replicate RSD value of 3.15 % is a good indicator of the true precision of this generation method without the confounding error from redepositing the samples.

Air-Generated 25 mm DM-450 Metrical® Filters, Direct Analysis by FTIR

Direct analysis samples were generated by air sampling on 25 mm Gelman DM-450 Metrical® filters and analyzed by FTIR. Open-faced polystyrene cassettes were placed in the dust generation chamber and sampled an atmosphere of silica and background matrix prepared for PAT round 155. The sample nomenclature (see Table 4) designates the various ports used in the collection of these samples in the dust chamber. The overall RSD of 9.0 % is within the expected range, which is wide primarily because of the background matrix.

Air-Generated 37 mm PVC Filters, Direct Analysis for Accuracy and Precision

Three sets of PAT samples from previous testing rounds were used to generate accuracy and precision data for this type of analysis. The samples were chosen for their various backgrounds and concentrations. PAT Sample 142-2 has a light talc/coal mine dust background, Sample 147-2 has a heavy coal mine dust background, and Sample 148-3 has a calcite background. When the samples were analyzed, the spectrometer baseline varied greatly depending on the interference, and the recovery results are high, probably because background matrixes added to the signal during FTIR analysis. The 9.5 % pooled RSD value for the three sets is within the expected range and close to the 9 % found in the 25 mm samples taken from the generation and collection system.

Conclusions

The values for the liquid-generated and aerosol-generated PAT interlaboratory RSDs were similar [2], and the RSD values for the direct analyses of samples of both generation types were relatively low. These results suggest that the primary cause of high interlaboratory RSD values is laboratory analytical error created by ashing and redeposition of the sample. Regardless of background matrix or filter type, both liquid- and aerosol-generated samples analyzed indirectly using FTIR Method 7603 had higher RSDs compared with those for the respective direct samples. Even though the dust chamber-generated air samples were all treated with a background matrix, overall precision was better when samples were analyzed directly by FTIR.

The 25 mm DM-450 filters produced better results overall than the 37 mm PVC filters regardless of the generation or analysis method. Several factors probably account for this difference. The absorption on the 37 mm PVC filters is very low (much larger surface area), which produced a very low absorbing calibration curve. This low absorption creates larger variability in measuring peak height for quantification. Also, the IR transparent DM-450 filter itself produces a cleaner background than PVC filters, which helps in correctly measuring the baseline and interferences. The liquid generation method does not appear to create any biases that would add to the overall interlaboratory RSD. It could thus be used as a bulk generation method if proper modifications are made to incorporate a multiple filter manifold system and add background matrixes. Direct collection and analysis of aerosol-generated silica on 25 mm DM-450 filters is a viable method for monitoring the quality control of proficiency testing sample production.

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FIG. 1. XRD results from NIOSH (line C) and WOHL (line B) along with the FTIR results from SRI (line A).

FIG. 2.
RSDs for the reported analytical results.

TABLE 1

Summary of all liquid- and aerosol-generated sample sets, media, and analytical methods.

Analysis Type	Air-Generation Samples	Liquid-Generation Samples
Indirect	37 mm PVC filters (FTIR) ^a	37 mm PVC filters (FTIR & XRD) ^b
Direct	25 mm DM-450 filters (FTIR) ^c	25 mm DM-450 filters (FTIR) ^e 37 mm
	37 mm PVC filters (FTIR) ^d	PVC filters (FTIR) ^f

^a Samples collected in aerosol chamber with matrix background.

^b Six sets of samples, four sets analyzed by XRD and two sets by FTIR.

^c One set of four samples collected in aerosol chamber with matrix background.

^d PAT samples with matrix background analyzed in three sets of replicates

^e Seven sets of replicate samples at various concentrations collected on 25 mm liquid-generation manifold with no background.

^f One set of the eight liquid-generated sets with no background matrix.

TABLE 2

Results of direct FTIR analysis of liquid-generated 37 mm PVC filters.

Sample Code	Mean Absorbance	Conc. (μg)	Theoretical Value (μg)	Percent Recovery
14149-38-8	0.0070	46.4	57.1	81.3
14149-38-20	0.0187	119.5	142.7	83.8
14149-38-28	0.0101	65.7	85.6	76.7
14149-38-32	0.0137	88.0	114.1	77.1
			Mean Recovery	79.7
			RSD	4.3

TABLE 3

Results of FTIR analysis of liquid-generated 25 mm DM-450 Metrical® filters.

Sample Code	Mean Absorbance	Conc. (μg)	Theoretical Value (μg)	Percent Recovery
14238-38-33	0.0339	54.2	57.1	94.9
14238-38-34	0.0348	56.1	57.1	98.2
14238-38-35	0.0527	92.2	85.6	107.7
14238-38-36	0.0533	93.5	85.6	109.2
14238-38-37	0.0641	115.2	114.1	100.9
14238-38-38	0.0694	126.0	114.1	110.4
14238-38-39	0.0754	138.2	142.7	96.8
14238-38-40	0.0765	140.3	142.7	98.3
14238-38-41	0.1004	188.7	171.2	110.2
14238-38-42	0.1006	189.0	171.2	110.4
14238-38-43	0.1186	225.4	199.8	112.8
14238-38-44	0.1104	208.8	199.8	104.5
14238-38-45	0.1296	247.6	228.3	108.5
14238-38-46	0.1247	237.6	228.3	104.1
			Mean Recovery	103.0
			RSD	6.1

TABLE 4Results of direct FTIR analysis of air-generated DM-450 Metrice[®] filters with background matrix.

Sample Code	Mean Absorbance	Conc. (μg)	PAT Reference Value (μg)	Percent Recovery
I-D-5	0.0399	66.3	70.1	94.5
II-D-5	0.0434	73.4	70.1	104.8
III-D-5	0.0448	76.2	70.1	108.7
IV-D-5	0.0381	62.6	70.1	89.3
			Mean	99.3
			RSD	9.0

TABLE 5

Direct FTIR analysis of PAT aerosol-generated samples.

Sample Code	Mean Absorbance	Conc. (μg)	PAT Reference Value (μg)	Percent Recovery
PAT 142-2	0.0097	63.4	48	132
PAT 142-2 REP	0.0098	63.8	48	133
PAT 147-2	0.0254	160.7	118.3	136
PAT 147-2 REP	0.0214	136.3	118.3	115
PAT 148-3	0.0235	149.3	104.1	143
PAT 148-3 REP	0.0278	176.0	104.1	169
			pooled RSD	9.5