Applied Occupational and Environmental Hygiene

ISSN: 1047-322X (Print) 1521-0898 (Online) Journal homepage: https://www.tandfonline.com/loi/uaoh20

Evaluation of Direct-on-Filter Methods for the Determination of Respirable α-Quartz

Charles D. Lorberau , Thomas P. Carsey , Thomas J. Fischbach & Kevin J. Mulligan

To cite this article: Charles D. Lorberau , Thomas P. Carsey , Thomas J. Fischbach & Kevin J. Mulligan (1990) Evaluation of Direct-on-Filter Methods for the Determination of Respirable α-Quartz, Applied Occupational and Environmental Hygiene, 5:1, 27-35, DOI: 10.1080/1047322X.1990.10389584

To link to this article: https://doi.org/10.1080/1047322X.1990.10389584

Evaluation of Direct-on-Filter Methods for the Determination of Respirable α-Quartz

Charles D. Lorberau,[A] **Thomas P. Carsey,**[B] **Thomas J. Fischbach,**[A] **and Kevin J. Mulligan**[A]
[A]National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering, Cincinnati, Ohio; [B]National Oceanic and Atmospheric Administration, Miami, Florida

Two direct-on-filter methods for the determination of respirable α-quartz in air by X-ray powder diffraction (XRD) were compared with NIOSH Method 7500. The two direct-on-filter methods are direct-on-silver membrane filter and direct-on-mixed cellulose ester (MCE) filter with XRD analysis directly on the collection filter. Both the silver membrane and the mixed cellulose ester methods were subjected to a side-by-side comparison with NIOSH Method 7500 using a laboratory-generated atmosphere of mine dust. The comparison showed with 95 percent confidence that any single measurement by the direct-on-MCE method would produce a result within 25 percent on any single measurement of Method 7500 under the same experimental conditions over the range 200–1200 μg. The comparison also showed the direct-on-silver method would produce a result within 30 percent, with 95 percent confidence over the same range. There is some suggestion of a slight negative bias of the direct-on-silver method with respect to Method 7500 which may be due to difference in the particle size distribution between the mine dust of the collected samples and National Bureau of Standards Standard Reference Material 1878 (NBS SRM 1878) of the calibration samples.

Calibration curves were obtained from two different procedures. One curve was prepared by directly depositing α-quartz (NBS SRM 1878) aerosol directly on the filter, whereas the other curve was prepared by filtration of an isopropanol suspension of the same reference material on the filters. Although there was no difference in particle size distribution, there was a marked difference in the two curves. This dictates that samples must be referred to calibration curves which were prepared in an analogous manner. For the preparation of direct-on-filter calibration samples, a small aerosol generation system is presented. **Lorberau, C.D.; Carsey, T.P.; Fischbach, T.J.; Mulligan, K.J.: Evaluation of Direct-on-Filter Methods for the Determination of Respirable α-Quartz. Appl. Occup. Environ. Hyg. 5:27–35; 1990.**

Introduction

Silicosis due to quartz is a major occupational lung disease with an estimated 1.2 million individuals potentially exposed annually in the United States. Those affected include miners, crushing and grinding machine operators, brickmasons, and stonemasons.(1)

Quantitative analysis of filter samples containing respirable quartz performed by X-ray diffraction (XRD) is rapid, nondestructive, and can differentiate crystalline phases. Method 7500 of the *NIOSH Manual of Analytical Methods*(2) (hereafter referred to as Method 7500), which has been collaboratively tested(3) and is presently used in our laboratories, calls for the transfer of the collected dust from the polyvinyl chloride (PVC) collection filter and its redeposition onto a silver membrane filter. A sampling and analytical method which eliminates all sample work-up (i.e., in which the original filter sample is analyzed without modification) would give the advantages of reduced cost of analysis (due to reduced operator involvement and elimination of solvents used in the transfer step), higher sample throughput, and elimination of errors associated with transfer of dust. Direct quantitative analysis requires filter media amenable to X-ray powder diffraction analysis, a homogeneous dust deposition on the filter, and correction of the diffracted intensity for matrix X-ray absorption. The ideal filter material for a direct XRD analysis should have a low uniform X-ray background with no peaks interfering with those of the analyte, have a rugged construction for ease in handling, and have a high collection efficiency for the sampled dust. Sampling air for quartz using PVC filters, which have a high X-ray background, has been described by a number of researchers.(4–9) Collection on silver filters, which takes advantage of the low X-ray background of that material while allowing for absorption correction, has been used by a number of investigators.(10–13) Eight-tenth micrometer pore size, 37-mm diameter, mixed cellulose ester (MCE) filters have been suggested for use in routine respirable quartz monitoring.(14) Thirty-seven-millimeter diameter MCE filters have been employed in Mine Safety Appliance (MSA) respirable dust samplers; filter standards were prepared in a dust generation chamber.(15) Although MCE filters are used for metal analysis, they have not been widely used in XRD analysis because of their high X-ray background. Eight-tenth micrometer pore size polycarbonate filters were investigated for sampling because they had minimal X-ray absorption and a low X-ray background.(16) A recently suggested method involves sampling with polycarbonate or MCE filters which are placed over zinc plates for absorption correction.(17) However, polycarbonate filters have poorer collection efficiencies than other filters of comparable pore sizes and have poor retention of sampled dust.(18)

For the diffracted intensity of the irradiated area to be representative of the sample, the dust deposition on the filter must be uniform. A number of investigators(6,8,15,19) have reported that samples prepared under direct air deposition did not yield a uniformly distributed sample on the filter and deemed it necessary to redeposit the samples. A modified cyclone with 25-mm cassette and PVC filter was reported to give a homogeneous deposition.(5) It has also been noted that samples directly deposited onto filters from an aerosol that has fluctuating dust levels or that are sampled for a short time tend to give uneven dust distributions on filters as do samples prepared from the filtration of liquid suspensions.(6) This problem of nonhomogeneity of deposition was addressed by a "multiple exposures" approach, wherein the sample XRD intensities from four exposures of the sample were co-added. The sample is moved to cover the area of deposition without overlapping exposures. This technique, however, is not readily amenable to automation and therefore requires increased operator involvement over normal operation. Spinning of the sample has been recommended to average out inhomogeneities in sample deposition.(19,20)

Minimum sample requirements for quartz XRD analysis are determined by the limit of detection for quartz and the percentage of quartz in the respirable dust. Corrections due to matrix X-ray absorption are needed for accurate quantitative analysis, especially at higher loadings. Corrections are made by either obtaining the ratio of the response of the analyte to the response of an internal standard (a method not readily amenable to a direct analysis method) or by using the attenuation of the diffraction line of the silver filter substrate(10–12) to arrive at a determination of the matrix X-ray absorption coefficient. Another approach is to sample with a filter having a low X-ray absorption which can be placed over a silver filter(16) or zinc plate(17) for XRD analysis. This removes the problem of shadowing of the analyte particle whereby the metal substrate shields particles that are inside the pore structure of the filter (i.e., below the filter surface) from the full intensity of the incident X-ray beam.(4) The absorption correction procedure used places an additional stringent requirement on the background diffraction pattern: the filter and matrix diffraction lines can not interfere with the diffraction line of the metal substrate.

This article describes the comparison of two direct-on-filter methods for respirable quartz determination for which the filter may be analyzed by XRD without processing. The filters used in this study, in addition to the aforementioned characteristics, needed to have good retention of the sampled dust so as to be easily handled without loss of dust. This led to the use of silver membrane and MCE filters. The experimental design chosen allowed for statistical comparison of the test method to the X-ray powder diffraction method for respirable α-quartz presently used in our laboratory, i.e., Method 7500.

Experimental Section

Aerosol Generation and Sample Collection

The test material was a mineral ore dust containing approximately 59 percent α-quartz which was obtained from a uranium–vanadium mine in Colorado. The dust was placed in a freezer mill and ground for 10 minutes at liquid nitrogen temperatures. The material was then suspended in isopropanol, wet sieved to a nominal diameter of less than 53 μm, and dried overnight at 110°C. This material could then be used to generate an aerosol which would challenge the cyclone samplers used in the methods.

Test atmospheres were produced in the Large Inorganic Sampling Assembly (LISA) which has been described.(21) The fluidized bed aerosol generator (Model 3400, Thermo Science Inc., Minneapolis, Minnesota) of the LISA was charged with the prepared mine dust and was operated at a chain speed of 40 with an air flow through the fluidized bed of 30 L/min.

The aerosol which formed in the fluidized bed was passed through a ^{210}Po neutralizing section and, upon entering the sampling chamber, was mixed with clean dilution air of about 165 L/min. This diluted aerosol passed through a flow straightener on its way to the sampling region. After an equilibration interval of 30 minutes, an aerosol with a respirable concentration ranging from 3.7 mg/m^3 to 14.2 mg/m^3 was produced. Nine samplers were placed at fixed, evenly spaced locations across this sampling region.

An earlier investigation of the LISA(21) indicated that it had a high degree of aerosol homogeneity. The study revealed an overall pooled coefficient of variation between sampler positions of less than 3 percent. Although statistically significant differences were found between the positions, the maximum difference was less than 6 percent.

Samplers for Method 7500 consisted of a two-piece 37-mm cassette (P/N M000-037-A0, Millipore Corporation, Bedford, Massachusetts) connected to a Dorr-Oliver 10-mm nylon cyclone in a holder assembly (P/N 456243, Mine Safety Appliances, Pittsburgh, Pennsylvania). The cassette contained a 5-μm pore size PVC filter (P/N FWSB, MSA) and a cellulose backup pad (P/N AP1002500, Millipore Corp.). Flow rates to all sampler assemblies were controlled by individual flow limiting orifices at 1.78 (±0.03) L/min. All samplers were connected to the same vacuum manifold.

The direct-on-filter methods employed the same nylon cyclone and holder assembly with a smaller filter cassette (25-mm, P/N 322575, Nuclepore Filtration Products, Pleasanton, California). The 25-mm cassette contained a backup pad (P/N AP1002500, Millipore Corp.) and either a 25-mm diameter, 0.45 μm pore size silver filter (P/N AG4502500, Millipore Corp.) or a 0.8-μm pore size MCE filter (P/N AAWP, Millipore Corp.).

Since the combination of the cyclone with this smaller cassette would not fit snugly in the existing holder, some minor modifications were made. The upper cassette grip of the holder was removed and a 0.25-inch grommet was placed over the exit port of the cassette. Although this allowed the bracket to firmly grip the sampler, the nipple of the cassette did not protrude far enough beyond the bracket for the tubing from the vacuum line to be slipped over it. This problem was circumvented by using Luer® connectors to attach the vacuum tubing.

While these adaptations produced a sampler which was adequate for this study, the device is not robust enough for field applications. A better solution would be to reduce the "throw" of the bracket by raising the position of the knurled locking screw by 0.25 inch and shortening the length of the sliding arm by a similar amount.

Although previous work had shown that the performance of the cyclones was rugged with respect to minor leaks, this factor was removed from consideration by leak testing each sampler prior to use by means of equipment which has been described.(22) Samplers which lost vacuum at a rate of no more than 5 percent per minute at a vacuum of 37 torr were considered acceptable.

Each experimental run consisted of a comparison of NIOSH Method 7500 to one of the methods under test at either a low load or a high load of collected material. The target loading was defined by choosing a sampling time (at 1.78 L/min) of either 30 minutes or 2 hours. Following sample collection, the filters were removed for analysis and the flow rates through the critical orifices were determined with a bubble flowmeter. During subsequent handling, the samples were not inverted at any time. The total sample loading never exceeded two milligrams.

Occasionally, there was visual evidence of a failure of the sampling procedure. This took the form of the penetration of dust to the backup pad. These samples were discarded. Four such failures occurred during the evaluation of the direct-on-silver method while only one took place during the assessment of the direct-on-MCE method.

Runs were conducted in pairs at the same target loading level. Initially, five of the nine positions within the LISA were randomly assigned to one method while four of the positions were assigned to the other. At the conclusion of sample collection, the assignments of sampler positions were interchanged and the run was repeated. The random assignment of sampler positions was done independently for each pair of runs. In this manner, data were collected for each method at all sampler positions.

Overall, each method comparison consisted of two sets of paired runs at each nominal loading level.

Sample Preparation

Samples taken in accord with Method 7500 were redeposited by dissolving the PVC filters in tetrahydrofuran (high purity grade, Burdick and Jackson, Muskegon, Michigan) and filtering the suspension through 25-mm silver filters. Then, these samples were placed in sample holders for analysis.

Material which had been collected on silver filters was analyzed without sample preparation. The filters were simply removed from the cassettes and placed directly into XRD sample holders.

When a MCE filter was used as the collection filter, it was removed from the cassette and glued to a 25-mm silver filter using a photographic mounting adhesive (Scotch® Spray Mount, P/N 6094, 3M Corp., St. Paul, Minnesota) prior to XRD analysis. This improved the integrity of the mounting and provided a metal substrate for matrix absorption corrections.

X-Ray Analysis

X-ray diffraction analysis was performed on a Philips Model 3720 diffractometer (Philips Electronics, Mahwah, New Jersey) equipped with theta-compensating slits and a graphite monochromator. Copper K(α) radiation was generated at 40-kV and 35-mA. The receiving slit width was 1°. All samples were spun during analysis by means of a Philips Model PW1780/10 sample spinner which was attached to the goniometer.

Quartz was determined from the peak area of the diffraction line at 26.66 °2θ (d = 0.334 nm). Data was taken using a step scan of 0.002 °2θ/sec. A reference specimen of Arkansas stone was evaluated every two samples. In this case, the quartz diffraction line was scanned 10 times more quickly to provide a rapid index of the intensity of the X-ray beam. The value of the most recent reference run was used to normalize the sample intensity and, thereby, adjust for fluctuations in the output of the X-ray tube. Matrix X-ray absorption was corrected by means of the observed attenuation of the silver diffraction line at 38.12 °2θ.(23,24)

Details of the procedures are contained in NIOSH Method 7500.(2)

Standardization and Calibration

The quartz which was used as a reference material for these studies was obtained from the National Bureau of Standards as Standard Reference Material 1878 (NBS SRM 1878). It consists of α-quartz which has been certified with respect to crystalline phase purity as 95.5 ($\pm$1.1) wt percent. The equivalent spherical diameters for 95 percent of the mass of the material have been determined by sedimentation measurements to lie in the range 0.33–5.0 μm.

For Method 7500, aliquots of an isopropanol suspension of α-quartz were filtered through silver filters. Calibration standards were prepared in triplicate at each of three different aliquot volumes from two different suspension concentrations. This produced a total of 18 calibration samples at 6 levels of quartz content between 0.200 mg and 1.30 mg.

Calibration standards for the direct-on-filter methods were made by depositing an aerosol of α-quartz (NBS SRM 1878) onto preweighed filters through the use of a small aerosol generation system. Sample loading levels were controlled by varying the period of aerosol sampling. The calibration samples were removed from the cassettes and then equilibrated and reweighed in a room which was tightly controlled with respect to humidity and temperature. Although weight stability of MCE filters is a concern, since they are hygroscopic, one group of researchers(25) noted that weight gains by MCE filters are readily reversible and that equilibrium is reached in about 60 seconds.

The small aerosol generation system is a modification of a system described by the Health and Safety Executives (HSE) Occupational Hygiene Laboratory.(9) It consists of a "batch-mode" fluidized bed affixed to a plexiglass cylinder in which six cyclones are symmetrically arranged (see Figure 1).

The batch-mode fluidized bed consisted of a 2.54-cm i.d. galvanized pipe with 325-mesh stainless steel wire cloth epoxyed to its base. This was charged with about 38 g of 100-μm diameter bronze beads (P/N 1502574, Thermo Systems Inc., St. Paul, Minnesota) which had been mixed with approximately 0.1 g of NBS SRM 1878. To fluidize the bed, clean dry house air entered at the bottom of the bed at 130–200 kPa. The fluidized bed was connected to the sampling chamber by means of 48 cm of aluminum pipe, which could be opened to allow for additional material to be introduced. To neutralize the aerosol, a ^{210}Po neutralizer section, identical to that used with the LISA system, was placed on the upper section of the aluminum pipe.

The sampling chamber was constructed from a plexiglass cylinder (9.5 cm i.d.). Six Dorr-Oliver 10-mm cyclones were glued to the stainless steel lid in a symmetrical pattern. Additional support for the cyclones was provided by an aluminum plate with guide holes, which was located inside the chamber. A metal coupler assembly (P/N 457392, MSA) and a 25-mm cassette loaded with an appropriate (silver membrane or MCE) preweighed filter were mounted above each cyclone vortex finder. Ventilation for the chamber was provided by an exhaust pipe which was flush with the inner surface of the lid.

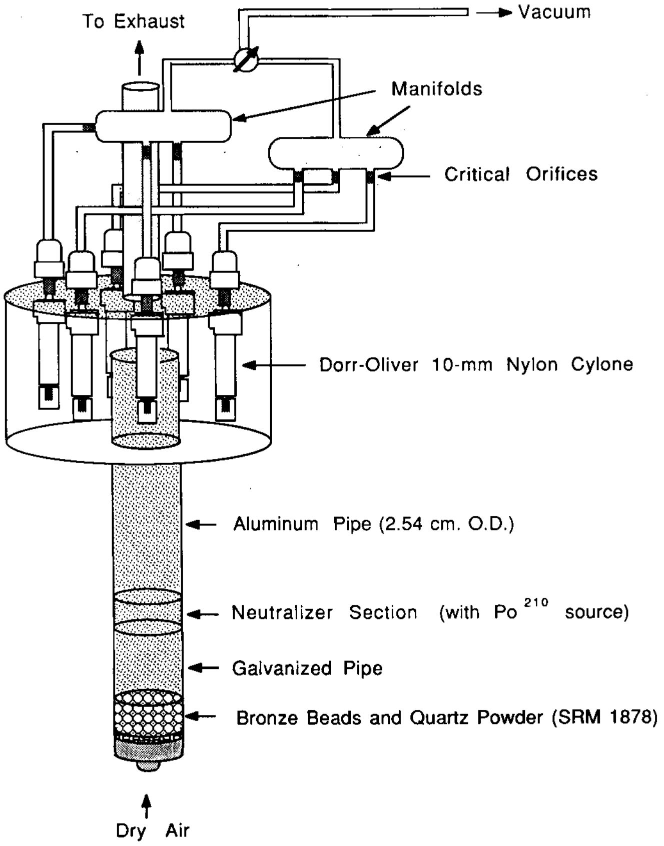

FIGURE 1. Schematic diagram of the bench scale aerosol generation and sampling system. The drawing is not to scale.

Flow rates of 1.78 L/min were established through each sampler by means of in-line critical orifices. (P/N XX50-000-00, Millipore Corp.), each of which was connected to the vacuum pump through one of two central manifolds.

This small aerosol generator is compact and rugged. It can be constructed from readily available materials without the involvement of skilled craftsmen such as a glassblower. Moreover, the calibration standard which is produced is size selected so as to lie within the respirable range.

Particle Size Determination

The particle size distribution was evaluated for calibration standards of NBS SRM 1878 which had been prepared by either filtration of a liquid suspension or through sampling of an aerosol. A quartz aerosol was generated and maintained in either the LISA or the bench scale aerosol generation system as described above. The total amount of material deposited on the filter was on the order of 1 μg.

For these studies, a polycarbonate filter (P/N 110605, Nuclepore Corp.) was used to collect the quartz since this filter has a smooth regular surface which offers a good background for scanning electron microscopy.

The distributions were obtained by means of an Hitachi Model S-570 scanning electron microscope with a Kevex Model 7000 energy dispersive X-ray spectrometer (Kevex Corporation, Scotts Valley, California) and LeMont Model DA-10 image analyzer (LeMont Scientific, State College, Pennsylvania).

Experimental Design

Each direct-on-filter method was individually compared to NIOSH Method 7500 in side-by-side sampling of the same atmosphere. The comparison of methods conformed to a randomized incomplete block experimental design with the following factors and levels: method (test and reference), filter load (high and low), run (two pairs at each load), and sampler position (nine). This required that 72 samples be collected for each method comparison.

Results and Discussion

Known amounts of α-quartz (NBS SRM 1878) were deposited on filters either from a suspension of quartz in isopropanol or through the sampling of a quartz aerosol. Calibration curves were obtained by plotting the integrated background corrected intensity across the quartz peak at 26.66 °2θ versus the amount of quartz deposited on the filter. Each value was corrected for matrix absorption.

The effective sampling area of the filter used for filtration of the liquid suspension (Method 7500) was 349 mm^2 whereas the area covered by the direct deposited aerosol

TABLE I. Comparison of Calibration Curves* for the Methods Under Test

Method	Slope (cnts/[μg/cm^2])	Intercept (cnts)	Std. Err. (cnts)
NIOSH 7500 (n = 18)	2.15 (0.03)	-13.3 (5.2)	14.3
AgM Direct (n = 10)	2.73 (0.05)	-22.2 (8.9)	15.7
MCE Direct (n = 18)	2.69 (0.09)	-5.21 (18.)	34.0
MCE Liquid (n = 18)	2.42 (0.04)	6.65 (9.0)	16.7

*The curves were generated using nonweighted linear least squares regression. The error which is assignable to the slope and to the intercept appears in parentheses within the body of the table.

was 394 mm^2. Since the X-ray beam examines only a portion of the filter (about 25%) at any given time, the quartz loading on each filter was changed to a flux by dividing by the sampling area to allow for comparison of the calibration curves. A comparison of the linear regression results obtained by using flux in place of the net amount of quartz is shown in Table I.

A comparison of the slopes indicates that the direct methods offer approximately a 25 percent enhancement in sensitivity over the liquid redeposition onto silver. This is in marked contrast to a previous study(26) in which no difference was observed in calibration curves which were obtained from Min-U-Sil 15 as either a liquid suspension or an aerosol. NBS SRM 1878 has a finer nominal particle size than Min-U-Sil 15. The effect which was observed may be due to penetration of the smaller particles into the silver filter whereupon they are shielded (or shadowed) from the X-ray beam.(15) This would imply that penetration of particulate matter into or through the filter is enhanced by isopropanol. A similar though much less dramatic effect is observed with the MCE filter. This filter type is much more transparent to the X-ray beam than silver.

It has been suggested that inertial impaction and electrostatic interaction deposits quartz aerosol on the surface of the filter whereas filtration of a liquid suspension, which relies on a screening mechanism, draws the material into the pores.(27)

The marked difference in slope dictates that samples must be referred to a calibration curve of the appropriate type.

Since it had been reported by a number of workers(15,23) that particle size can have a dramatic effect on the intensity of the diffracted X-ray, we examined the possibility that differences in the mode of preparation of the calibration standards (NBS SRM 1878) produced differences in the particle size distributions. Standards were prepared on polycarbonate filters. The particle size distribution on each was evaluated using scanning electron microscopy with automated image analysis. The results for samples obtained from the LISA system, the bench scale aerosol generation system, and through filtration of a suspension of quartz in isopropanol are presented as Figure 2. There are no apparent differences in the distributions.

For each comparison of a test method to NIOSH Method 7500, samples were collected at two nominal amounts of deposited material: high and low. The result of the X-ray analysis of each filter was translated into the concentration of the test atmosphere by means of 1) the calibration curve appropriate to the method, 2) the sampling time, and 3) the measured flow rate through the sampler. These results are presented in Table II and Table III.

Statistical evaluation of the data was conducted using the General Linear Models Analysis of Variance package (PROC GLM) of the Statistical Analysis System (SAS Institute, Inc., Gary, North Carolina). Preliminary analysis indicated the need for transformation of the data since the observed standard deviation increased as the value of the

TABLE II. Comparison of Direct-on-Silver Method to NIOSH Method 7500 Quartz concentration[A] (mg/m^3)

Run	Nominal Load[B] (μg)	Direct-on-Silver Filter Method	NIOSH Method 7500	Percent[C] Difference
1	553 (High)	2.44 (0.13)	2.59 (0.05)	-5.8
2	901 (High)	3.92 (0.13)	4.22 (0.19)	-7.1
3	300 (Low)	5.28 (0.07)	5.61 (0.47)	-5.9
4	352 (Low)	6.07 (0.27)	6.60 (0.28)	-8.0
5	233 (Low)	4.92 (0.18)	4.37 (0.26)	+13.
6	242 (Low)	5.12 (0.20)	4.53 (0.20)	+13.
7	1110 (High)	4.96 (0.19)	5.21 (0.13)	-4.8
8	1090 (High)	4.86 (0.19)	5.09 (0.10)	-4.5
Pooled Coefficient of Variation		0.037	0.035	

[A] These values represent the average concentration of the aerosol as determined by the method indicated. The standard deviation is shown in parentheses for the four or five experimental values which constitute each average.

[B] The nominal load is calculated from the average value of the aerosol concentration which was obtained using NIOSH Method 7500 by multiplying by the flow rate and sampling time. For purposes of the ANOVA, the loads were classified as either high or low.

[C] The percent difference is defined as 100 times the difference between the test method and NIOSH Method 7500 divided by latter result.

TABLE III. Comparison of Direct-on-MCE Method to NIOSH Method 7500 Quartz Concentration[A] (mg/m^3)

Run	Nominal Load[B] (μg)	Direct-on-MCE Filter Method	NIOSH Method 7500	Percent[C] Difference
1	417 (Low)	7.92 (0.31)	7.81 (0.16)	+1.4
2	407 (Low)	7.91 (0.23)	7.63 (0.24)	+3.7
3	1000 (High)	4.77 (0.07)	4.69 (0.26)	+1.7
4	1100 (High)	5.08 (0.14)	5.16 (0.21)	-1.6
5	1060 (High)	4.75 (0.17)	4.96 (0.11)	-4.2
6	1150 (High)	5.15 (0.06)	5.38 (0.22)	-4.3
7	313 (Low)	6.37 (0.16)	5.86 (0.30)	+8.7
8	387 (Low)	7.49 (0.32)	7.25 (0.34)	+3.3
Pooled Coefficient of Variation		0.028	0.038	

[A] These values represent the average concentration of the aerosol as determined by the method indicated. The standard deviation is shown in parentheses for the four or five experimental values which constitute each average.

[B] The nominal load is calculated from the average value of the aerosol concentration which was obtained using NIOSH Method 7500 by multiplying by the flow rate and the sampling time. For purposes of the ANOVA, the loads were classified as either high or low.

[C] The percent difference is defined as 100 times the difference between the test method and NIOSH Method 7500 divided by latter result.

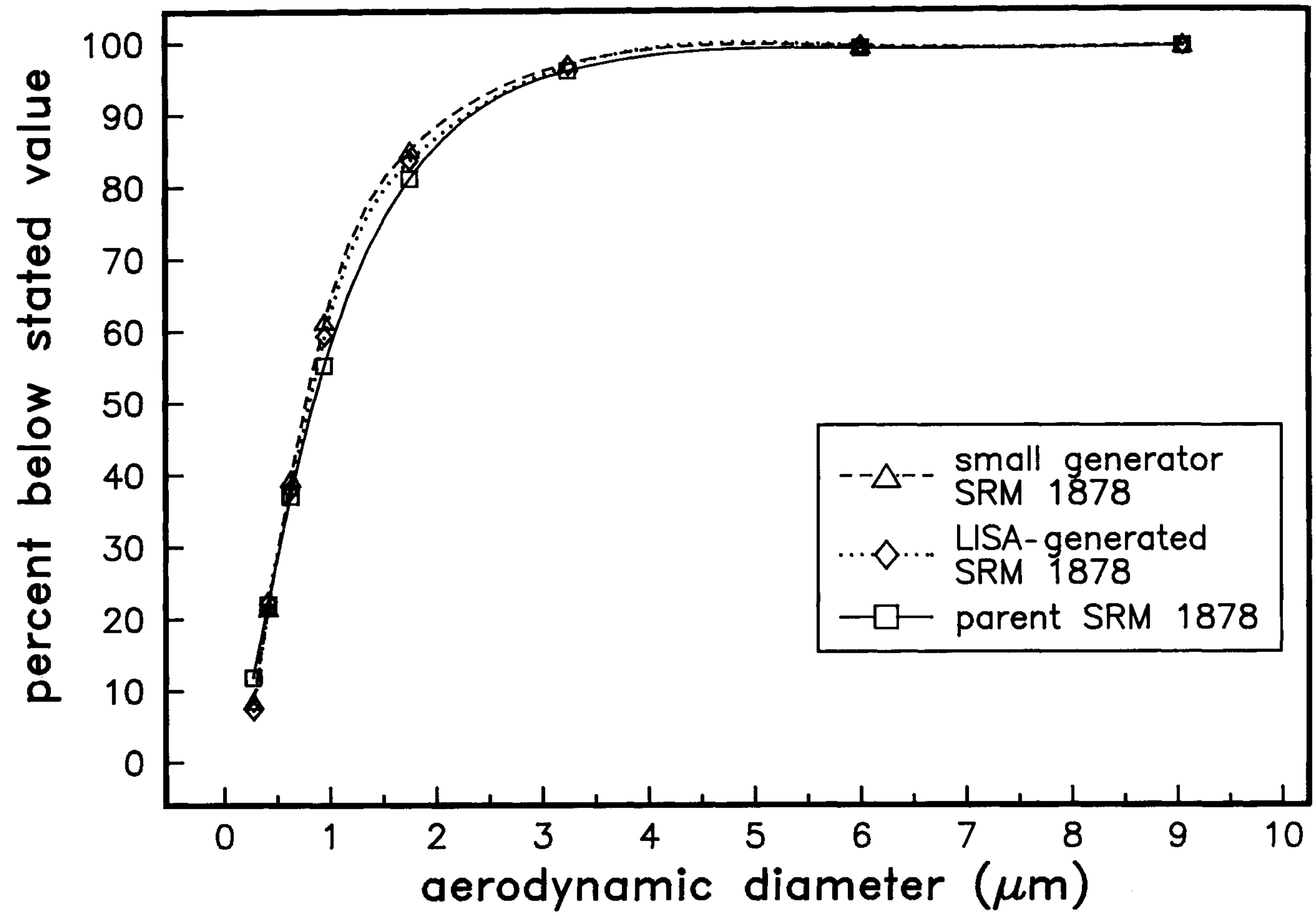

FIGURE 2. Particle size distributions (by count) of NBS SRM 1878 which has been deposited on polycarbonate filters through filtration of an isopropanol suspension or through the sampling of an aerosol from one of the generation systems.

mean increased. Therefore, prior to further work, the aerosol concentrations were transformed into logarithms to reduce this heterogeneity in variance with magnitude.[28] However, the resutls were not substantially affected by the transformation. The GLM ANOVA of each of the side-by-side comparisons of direct-on-filter analyses of quartz with Method 7500 is given in Table IV.

An examination of the results for each test method and Method 7500 indicates that the concentration of the aerosol was subject to considerable variation among pairs and between runs within a pair. This reflects changes in the aerosol concentration of the generation system from day to day. The influence of position echoes a performance characteristic of the LISA which was discussed above.

When each test method is compared to the reference method, there is no net significant difference in the results over the range 200 to 1200 micrograms. However, this conclusion is misleading since the method differences vary among pairs more than can be accounted for by error. The pair-by-method interaction indicates that the difference between the methods varied from pair to pair. In the direct-on-silver method comparison, one pair even showed a reversal in method differences. A graphical representation of the effect is shown in Figure 3 and Figure 4. The line at 45° to the abscissa tracks a perfect correspondence between the two methods. Clearly, the effect is barely discernible in light of the nonsimultaneous 95 percent confidence intervals which are shown about each point.

An evaluation of the differences between the average results obtained using each test method and the reference method, Method 7500, showed that both test methods satisfy the accuracy standard[29] that they be within 25 percent of the reference value ninety-five percent of the time.

An additional statistical analysis was performed. Since

TABLE IV. Analysis of Variance of Aerosol Concentrations Determined by Each Method

	F-Test Significance Level	
Factor (d.f.)	Direct on Silver[A] and Method 7500	Direct on MCE[B] and Method 7500
Pair (3)	0.0001	0.0001
Run (Pair) (4)	0.0001	0.0001
Position (8)	0.0001	0.0001
Method (1)	0.0926	0.1436
Pair by Method Interaction (3)[C]	0.0001	0.0001

[A] The estimates for the mean square error (with 48 degrees of freedom) and coefficient of variation for the Direct-on-Silver method are 0.00198 and 2.92%, respectively.

[B] The estimates for the mean square error (with 51 degrees of freedom) and coefficient of variation for the Direct-on-MCE method are 0.00144 and 2.12%, respectively.

[C] All other interactions capable of being estimated were not found to be significant.

the relative bias of the direct-on-filter methods to Method 7500 was potentially different in each of the four pairs, to achieve a statement about accuracy holding with 95 percent confidence required that statements about the upper bounds of each of its two components—bias and precision (coefficient of variation)—hold with 97.5 percent confidence. The upper bound for bias had to hold simultaneously with 97.5 percent confidence for the pairs while a 97.5 percent confidence for the coefficient of variation for the pair with the worst relative bias was needed. For the direct-on-silver method, the upper bound for bias is slightly under 20 percent with 97.5 percent confidence. This value was used to enter the nomograph for combinations of total coefficient of variation and bias that meet the accuracy standard(29) to determine that the maximum of the upper bound for the coefficient of variation was 3 percent. In one case, the 97.5 percent upper bound for this coefficient was in excess of 5.3 percent. However, for the direct-on-MCE method, the upper bound for bias is slightly under 13 percent with 97.5 percent confidence. This value, when entered into the nomograph, indicated that the maximum of the upper bound for the coefficient of variation was 7 percent. The 97.5 percent upper bound for the largest coefficient of variation of the direct-on-MCE comparison was only slightly more than 4.6 percent.

This leads to the conclusion that, even under this much more stringent assessment of the extent of agreement between the two methods, the direct-on-MCE method will produce results within 25 percent of Method 7500 with 95 percent confidence over the range investigated. The direct-on-silver method does not fare quite as well; however, we can assert that it would produce results within 30 percent of Method 7500 with 95 percent confidence.

The marginal tendency for Method 7500 to overestimate the amount of quartz with respect to the direct-on-silver method may be due to the mismatch between the particle size distribution of the reference standard, NBS SRM 1878, and that of the mine dust aerosol. The mine dust has a larger nominal particle size than NBS SRM 1878 and, therefore, is less susceptible to the shadowing effect that was described in the dicussion of the calibration curves. It has been observed that the liquid transfer step of Method 7500 apparently leads to a greater degree of shadowing than if the material is deposited as an aerosol. It is proposed that these two effects interact to produce a greater difference between NBS SRM 1878 and mine dust when liquid transfer is a part of the experimental protocol than if the samples are deposited as aerosols. More shadowing would occur with the standard since it is the "smaller" material; therefore, a lower X-ray signal would be observed per unit weight of standard than would accurately map unit weight of quartz in the mine dust. Hence, the amount of mine

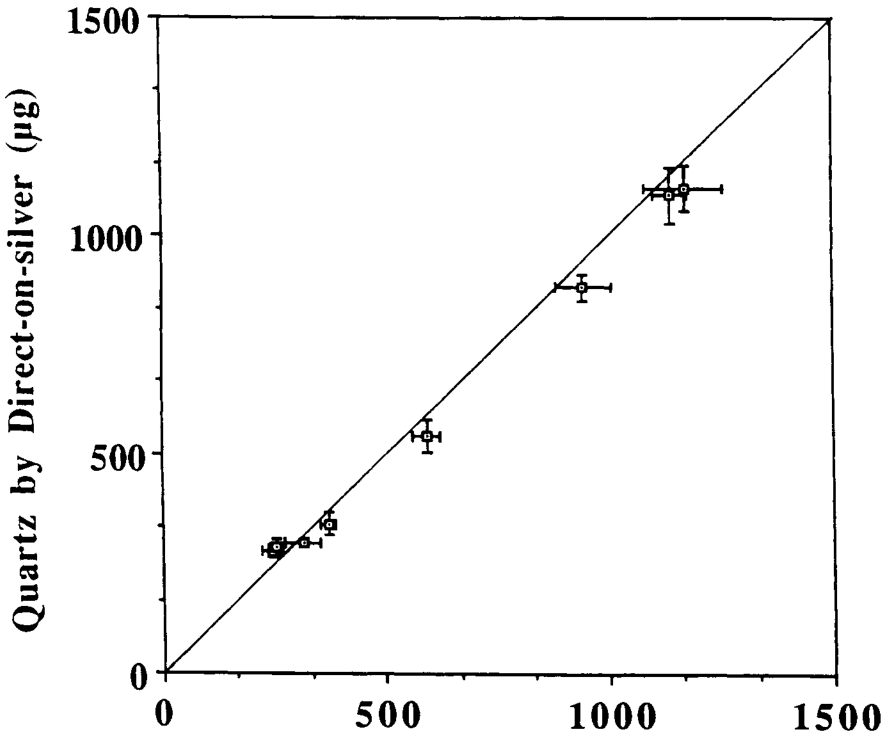

FIGURE 3. Plot of the amount of quartz as determined by the direct-on-silver filter method against the amount of quartz as determined by NIOSH Method 7500. The diagonal represents a 1:1 correspondence of the two techniques, 95% confidence limits are shown about each point. Each point is the average of four (or five) experimental points.

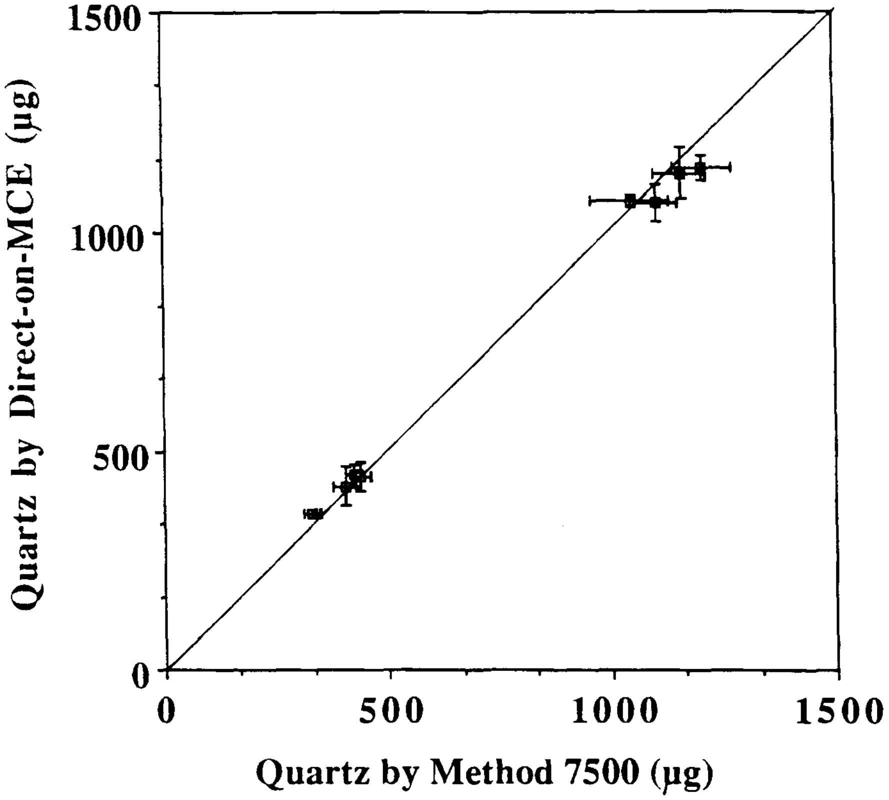

FIGURE 4. Plot of the amount of quartz as determined by the direct-on-MCE filter method against the amount of quartz as determined by NIOSH Method 7500. The diagonal represents a 1:1 correspondence of the two techniques, 95% confidence limits are shown about each point. Each point is the average of four (or five) experimental points.

dust which corresponds to an observed X-ray signal would be overestimated by the calibration curve. A similar effect should be observed in the comparison of direct-on-MCE with Method 7500, but it is masked if present by the way in which the points are grouped and the scatter in the results.

Conclusion

The direct-on-filter methods produced results that were similar to those which were obtained by the reference method, NIOSH Method 7500. This conclusion is in keeping with the results of a recent interlaboratory comparison program.(30) Statistical analysis showed that the direct-on-filter methods produce results which are equivalent to Method 7500 for the range investigated. Even under a more rigorous comparison, it can be asserted with 95 percent confidence that any single measurement by the direct-on-MCE method would produce a result within 25 percent of any single measurement by Method 7500 under the same experimental condition. With the direct-on-silver method, the results would fall within 30 percent. Moreover, direct-on-filter methods are attractive since they offer substantial savings in time and effort.

There appears to be a subtle bias between the direct-on-silver Method and Method 7500 which, we suggest, might be ascribed to a mismatch between the particle size distribution of the calibration material, NBS SRM 1878, and the mine dust which was used as a test aerosol. Under this explanation, the issue of which method is more accurate remains open to debate.

Regardless of the method, it is imperative to refer samples taken under a certain method to standard curves which are prepared in a similar manner. To this end, a small aerosol generation system has been described which can be constructed from readily available materials.

Minor modifications to the design of the commercially available cyclone/cassette holder which was used for this study are needed if this direct-on-filter method is to be used in the field.

Recommendations

Based on this laboratory study, both direct-on-filter methods were found to be equivalent to Method 7500 over the range 200 μg to 1.2 mg. It is imperative that the samples be referred to calibration curves which are prepared in a similar manner. Minor modifications to the design of the direct-on-filter sampler are needed prior to field evaluation or use.

References

1. National Institute for Occupational Safety and Health: Occupational Respiratory Diseases, pp. 219–237. J. Merchant, Ed. DHHS (NIOSH) Pub. No. 86-102. Cincinnati, OH (1986).
2. National Institute for Occupational Safety and Health: Method 7500-

Silica, Crystalline, Respirable. In: NIOSH Manual of Analytical Methods, 3rd ed. P. M. Eller, Ed. DHHS (NIOSH) Pub. 84–100. Cincinnati, OH (1984).

3. Anderson, C.C.: Collaborative Tests of Two Methods for Determining Free Silica in Airborne Dust. DHHS (NIOSH) Pub. 83–124. Cincinnati,. OH (1983).
4. Henslee, W.W.; Guerra, R.E.: Direct Quantitative Determination of Silica by X-ray Diffraction on PVC Membrane Filters. Adv. X-ray Anal. 20:139 (1977).
5. Edmonds, J.W.; Henslee, W.W.; Guerra, R.E.: Particle Size Effects in the Determination of Respirable α-Quartz by X-ray Diffraction. Anal. Chem. 49:2196 (1977).
6. Chung, F.: Imaging and Analysis of Airborne Dust for Silica. Environ. Sci. Technol. 12:1208 (1978).
7. Davis, B.L.; Johnson, L.R.: On the Use of Various Filter Substrates for Quantitative Particulate Analysis by X-ray Diffraction. Atmos. Environ. 16:273 (1982).
8. Illinois Institute of Technology Research Institute: Preliminary Evaluation of Direct Free Silica Analysis on PVC Membranes by X-ray Diffraction. Final Report Task 8 Phase 2 Prepared for NIOSH, Contract No. 210-81-7108. Chicago, IL (1983).
9. Health and Safety Executive: Quartz in Respirable Airborne Dusts, Method MDHS 51. Occupational Medicine and Hygiene Laboratory, U.K. (1986).
10. Leroux, J.; Powers, C.: Direct X-ray Diffraction Quantitative Analysis of Quartz in Industrial Dust Films Deposited on Silver Membrane Filters. Staub Reinhalt. Luft 29:26 (1969).
11. Knight, G.; Stefanich, W.; Ireland, G.: Laboratory Calibration of a Technique for Determination of Respirable Quartz in Mine Air. Am. Ind. Hyg. Assoc. J. 33:469 (1972).
12. Knight, G.: CAMPEDS—A Dust Sampling and Assessment System for Use in Hard Rock Mines. Ann. Occup. Hyg. 30:139 (1986).
13. Altree-Williams, S.: Quantitative X-ray Diffractometry on Milligram Samples Prepared on Silver Filters. Anal. Chem. 49:429 (1977).
14. Tossavainen, A.: Determination of Quartz on Membrane Filters by X-ray Diffraction. Scand. J. Work Environ. Health 5:379 (1979).
15. Allen, G.; Samimi, B.; Ziskind, M.; Weill, H.: X-ray Diffraction Determination of α-Quartz in Respirable and Total Dust Samples from Sand-Blasting Operations. Am. Ind. Hyg. Assoc. J. 35:711 (1974).
16. Altree-Williams, S.; Lee, J.; Mezin, N.: Quantitative X-ray Diffractometry on Respirable Dust Collected on Nuclepore Filters. Ann. Occup. Hyg. 20:109 (1977).
17. Kohyama, N.: A New X-ray Diffraction Method for the Quantitative Analysis of Free Silica in the Airborne Dust in Working Environment. Ind. Health 23:221 (1985).
18. Lippmann, M.: Sampling Aerosols by Filtration. In: Air Sampling Instruments for the Evaluation of Atmospheric Contaminants, 6th ed., Chap. F. P.J. Lioy and M.J.Y. Lioy, Eds. American Conference of Governmental Industrial Hygienists, Cincinnati, OH (1983).
19. Bumsted, H.E.: Determination of Alpha-Quartz in the Respirable Portion of Airborne Particulates by X-ray Diffraction. Am. Ind. Hyg. Assoc. J. 34:150 (1973).
20. Suortti, P.; Jennings, L.D.: Accuracy of Structure Factors from X-ray Powder Intensity Measurements. Acta Cryst. A 33:1012 (1977).
21. Carsey, T.: LISA: A New Aerosol Generation System for Sampler Evaluation. Am. Ind. Hyg. Assoc. J. 48:710 (1987).
22. Carsey, T.; Shulman, S.; Lorberau, C.: An Investigation of the Performance of the 10-mm Nylon Cyclone. Appl. Ind. Hyg. 2:47 (1987).
23. Abell, M.T.; Dollberg, D.D.; Crable, J.V.: Quantitative Analysis of Dust Samples from Occupational Environments Using Computer-Automated X-ray Diffraction. Adv. X-ray Anal. 24:37 (1981).
24. Kohyama, N.: Quantitative X-ray Diffraction Analysis for Airborne Asbestos Dust in Industrial Environment; 1. Application of X-ray Absorption Correction Method. Ind. Health 18:69 (1980).
25. Charell, P.R.; Hawley, R.E.: Characteristics of Water Adsorption on Air Sampling Filters. Am. Ind. Hyg. Assoc. J. 42:353 (1981).
26. Anderson, D.W.; Gebhardt, R.F.; Trader, C.W.; Dobson, L.A.: Improved Quantitative X-ray Diffraction Determination of Respirable Free Silica. In: Proceedings of a Roundtable Discussion on Thermal Analysis Techniques. DHEW (NIOSH) 76–173. Cincinnati, OH (1976).
27. Knight, G.: Comments in Proceedings of a Roundtable Discussion on Analytical Techniques for Quartz, p. 67. American Conference of Governmental Industrial Hygienists, Cincinnati, OH (1973).
28. Box, G.E.P.; Hunter, W.G.; Hunter, J.S.: Statistics for Experimenters. John Wiley and Sons, New York (1978).
29. Busch, K.; Taylor, D.G.: Statistical Protocol for the NIOSH Validation Tests. In: Chemical Hazards in the Workplace: Measurement and Control. G. Choudhary, Ed. ACS Symp. Ser. 149. American Chemical Society, Washington, DC (1981).
30. Knight, G.: Interlaboratory Crosscheck of Quartz Analysis on Mine Airborne Dust Samples. Am. Ind. Hyg. Assoc. J. 45:655 (1984).

Received 9/14/88; review decision 1/23/89; revision 5/11/89; accepted 8/3/89