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Since 1982 standard calibration materials recommended for respirable crystalline silica analysis by the Mine Safety and Health Administration (MSHA) P7 Infrared Method and the National Institute for Occupational Safety and Health (NIOSH) X-ray Diffraction (XRD) Analytical Method 7500 have undergone minor changes in size distribution. However, a critical assumption has been made that the crystalline silica in ambient mine atmosphere respirable dust samples has also remained essentially unchanged in particle size distribution. Therefore, this work compared recent particle size distributions of underground coal mine dust and the silica component of these dusts with estimated aerodynamic particle size distributions of calibration standard materials MIN-U-SIL 5, Berkeley 5, and SRM 1878 used by two crystalline silica analysis techniques. Dust impactor sampling data for various locations in 13 underground coal mines were analyzed for the respirable mass median aerodynamic diameters. The data suggest that the MSHA P7 method will underestimate the silica content of the sample by at most 7.4% in the median size range 0.9 to 3.6 μm, and that it is unlikely one would obtain any significant error in the MSHA P7 method analysis when the method uses Berkeley 5, MIN-U-SIL 5, or SRM 1878 as a calibration standard material. The results suggest that the NIOSH Analytical Method 7500 would be more appropriate for a dust sample that is representative of the total (no cyclone classifier) rather than the respirable airborne dust, particularly because the mass fraction in the size range below 4 μm is usually a small percentage of the total airborne dust mass. However, NIOSH Analytical Method 7500 is likely to underestimate the silica content of an airborne respirable dust sample by only 5 to 10%. The results of this study also suggest that any changes that may have occurred in the median respirable size of airborne coal mine dust are not significant enough to cause any appreciable error in the current methods used for respirable crystalline silica analysis.

Keywords: P7, silica, size distributions, XRD

Crystalline silica (referred to hereafter as silica) dust has long been recognized as an occupational health hazard to the respiratory system,(1–6) responsible for the insidious disease known as silicosis. In underground mining this silica dust is created from several sources that generally include, but are not limited to, cutting, drilling, or milling of rock material. For coal mining this rock material may be found as an inherent constituent of the coal, although this is usually not a significant source of silica. The majority of the silica is found in the immediate overlaying or underlying rock strata, which are frequently removed during the coal mining process. Also, significant rock inclusions known as partings occur within the coal seam itself and must be removed with the coal. Surface mining operations can also produce significant quantities of airborne respirable silica due to the amount of overburden that must be removed.

Monitoring the miner respirable coal mine dust exposure for compliance with federal regulations(7) is mandatory to protect the health of miners. For all coal mines, if the silica content of the dust sample is measured to be 5% or less, the respirable dust standard is 2.0 mg/m³. If the silica content exceeds 5%, the respirable dust standard is reduced according to the formula 10÷ % silica.(8) For metal and nonmetal mines, defined as all noncoal producing mines, the standard for respirable dust that contains silica (>1%) is calculated according to the formula 10 ÷ (% silica + 2). However, there is no technique available for the direct measurement of respirable silica dust concentration or size distribution in the mining environment. The only means to estimate the respirable silica dust concentration is to perform an analysis of the respirable dust sample collected, which may contain both coal and silica dust as well as other minerals.

Currently, the two fundamental techniques used for routine estimation of the silica content of a respirable dust sample are X-ray diffraction (XRD) and infrared (IR) absorption analysis. The techniques recommended by the National Institute for Occupational Safety and Health (NIOSH) are Method 7603 (crystalline silica in coal mine dust by IR) and Method 7500 (crystalline silica by XRD).(9) For determination of the silica content of respirable coal mine dust samples, the Mine Safety and Health Administration (MSHA) employs the MSHA P7 Infrared Method,(10,11) hereafter referred to as P7. The MSHA and NIOSH IR methods are similar but with some differences noted in the sample preparation. Airborne dust samples from metal and nonmetal mines are analyzed by MSHA using the NIOSH Method 7500.

The results of both XRD and IR techniques have long been recognized to be dependent of particle size.(12–15) However, these techniques are considered reasonably accurate if the silica particle size distribution of the sample approximates the size distribution of the calibration material for the methods and the XRD intensity peak area is used instead of intensity peak height.(9) The criteria under which Methods 7603, 7500, and P7 were developed and implemented were closely scrutinized and impose strict limits on sample requirements and analysis protocol. Methods 7500 and P7 were recommended for silica determination of coal mine dust samples in 1982. At that time the product MIN-U-SIL 5 (U.S. Silica Co., Berkeley, W. Va.) was recommended(9) as the standard calibration material, based on this material's particle size distribution closely matching the silica particles found in respirable dust samples from ambient underground mine atmospheres.(16)

Since 1982 the recommended standard calibration materials have undergone relatively minor changes in size distribution. However, a critical assumption has been made that the silica in ambient mine atmosphere respirable dust samples has also remained essentially unchanged in particle size distribution. This may not be true in some situations because the mining industry has undergone many changes in mining technology, production, and dust control methods. For example, at the time of P7 development and implementation only a small percentage of continuous mining machines in coal mines were equipped with flooded bed scrubbers to collect the dust generated during mining. It is well documented that scrubbers are very efficient in capturing ambient dust particles down to 2 μm aerodynamic diameter.(17,18) Also among the changes in mining technology is a significant increase in the power delivered by mining machinery. Because mining frequently involves cutting the much harder rock material, which is usually the major source of silica, it is possible that there has been a change in the amount of milling or grinding and an increase in the actual breakage of this rock material due to these more powerful machines. It would appear reasonable to suspect that some change could occur in the median size of the airborne respirable silica compared with the early 1980s when the MIN-U-SIL 5 material was chosen as the best representation of airborne respirable coal mine silica dust.(16)

The objective of this work, therefore, was to compare particle size distributions of respirable underground coal mine dust with estimated aerodynamic particle size distributions of calibration standard materials MIN-U-SIL 5, Berkeley 5 (U.S. Silca Co.), and SRM 1878 by two silica analysis techniques. This was accomplished by evaluating the particle size dependency of the MSHA P7 method and the NIOSH XRD method on size fractions of MIN-U-SIL 10. MIN-U-SIL 10 was chosen to provide a broad size range so that four size fractions could be obtained as described under the Materials section.

MATERIALS, METHODS, AND ANALYSIS

Materials

The work was carried out on size fractions of MIN-U-SIL 10 silica (reported by the manufacturer to be 99.5% pure). Although the true crystalline purity is not known, the results presented will show that the purity most likely is quite high. The samples were prepared by size-fractionating MIN-U-SIL 10 material in a Bahco (H.W. Dietert Co., Detroit, Mich.) particle separator. This centrifuge separator allowed the extraction of four arbitrary size fraction groups with aerodynamic equivalent diameter (median d_{AED}) less than 9.95 μm. Each silica size fraction was originally collected and stored in a separate glass jar for subsequent analysis. Two samples from each size fraction were submitted for replicate P7 and size distribution analyses, respectively. XRD analyses were performed on the P7 deposits only and not on an independent sample. For P7 analyses, samples were prepared from suspensions of approximately 30 mg of silica dispersed in 1 liter of isopropyl alcohol (IPA).

Calibration material used for P7 was Berkeley 5 silica, which has the same manufacturer specifications as MIN-U-SIL 5 but which is produced at a different plant, according to the manufacturer. Calibration material for XRD was SRM 1878 produced from MIN-U-SIL 5 by the former National Bureau of Standards and distinct from the currently available and recommended SRM 1878a, prepared by the National Institute for Standards and Technology. It is noted that quantifying personal exposure to crystalline silica could be questioned regarding the actual crystalline purity of Berkeley 5, MIN-U-SIL 5, and SRM 1878. SRM 1878 has a certified purity of only 95.5% ±1.1 wt. percent crystalline α quartz, as compared with 100.00% ± 0.21 wt. percent crystalline α quartz for SRM 1878a. Edmonds et al(19) published data indicating that the MIN-U-SIL 10 material used for this study does not contain a significant amount of amorphous material in the 1–2 μm size range.

Particle Sizing

Size distribution based on spherical equivalent diameter (d_{SED}) was performed by an independent laboratory. The size-classified bulk powder silica samples were prepared for size distribution analysis using two different methods. The first method dispersed the powder in IPA to achieve a suspension concentration of approximately 700 mg/L, which was stirred for 5 min, sonicated in a 200-W ultrasonic bath for 10 min, and then restirred. The second method used the low concentration suspensions produced for P7 analysis, which were in the range of 31 to 38 mg/L. To examine possible sizing variations due to suspension concentration, the silica sample material in the largest size fraction was analyzed for size over a suspension range of 45 to 714 mg/L. This was achieved by subsequent dilutions of the 714 mg/L suspension. Analysis of all samples was performed on a Horiba LA-920 (Horiba Instruments, Irvine, Calif.) particle size analyzer, which classified the particles into 68 size intervals below $d_{SED}=200$ µm. For each sample the median d_{SED} was calculated.

Two groups of size distribution data were also obtained. Group 1 consists of 83 underground samples from locations on 13 continuous mining and longwall mining operations. The underground data was obtained with Marple 298 personal sampling impactors (Thermo Andersen, Smyrna, Ga.), each equipped with the standard inlet cowl. The impactor stages 1 through 6 (20 through 1.55 µm cut point sizes) were used with the particles sizes less than 1.55 µm collected on the final filter, omitting stages 7 and 8. Although the current accepted definition of respirable dust recommended for industrial hygiene practice is the ACGIH/CEN/ISO (American Conference of Governmental Industrial Hygienists/Comité Européen de Normalisation/International Organization for Standardization) convention, these samples were analyzed for the respirable fraction according to the former ACGIH definition and the resulting median d_{AED} values.(20,21,22) There are several reasons for this choice. First, the U.S. coal mining industry is regulated by MSHA for respirable dust using the 10-mm nylon cyclone operated at 2.0 L/min as a particulate size classifier. When the 10 mm nylon cyclone is operated at the recommended flow rate of 1.7 L/min, the agreement with the ACGIH/CEN/ISO convention is improved but still possesses a steeper slope in the penetration characteristic. Therefore, this device does not correspond to the ACGIH/CEN/ISO convention at either flow rate. Second, the current ACGIH/CEN/ISO convention was not in effect at the time MIN-U-SIL 5 was recommended as the standard calibration material, based on this material's particle size distribution closely matching the silica particles found in respirable dust samples from ambient underground coal mine atmospheres.

Group 2 size distribution data consists of 29 samples from intake and return air locations on underground continuous mining sections as well as from rock material fed to a double roll crusher in a laboratory wind tunnel. These samples were also collected with Sierra 298 personal sampling impactors, each equipped with the standard inlet cowl. However, stages 7 and 8 were used to provide cut points from 0.1 to 0.93 µm.

Analysis

Two measures of individual particle size were used in this study. These are the spherical equivalent diameter (d_{SED}) reported by the particle size analyzer and the mass equivalent aerodynamic diameter (d_{AED}), measured by an aerosol impactor. Because d_{AED} is chosen as the relevant measure of particle size for aerosols sampled by aerodynamic properties, it is necessary to establish a reasonably accurate means to convert values of d_{SED} measured for the size fractions obtained from MIN-U-SIL 10. As a reasonable approximation the following method was used.

According to Baron and Willeke,(23) it is possible to estimate d_{AED} from the d_{SED} by using the equation

$$d_{AED} = \Psi\left[\frac{\rho_P C_c(d_{SED})}{\chi C_c(d_{AED})}\right]^{1/2} \times d_{SED} \qquad \textbf{(1)}$$

where

ρ_p = material density
$C_c(d_{SED})$ = Cunningham slip correction factor for the chosen spherical diameter
$C_c(d_{AED})$ = Cunningham slip correction factor for the chosen aerodynamic diameter
χ = particle shape factor
Ψ = instrument calibration factor

$C_c(d_{SED})$ and $C_c(d_{AED})$ are determined using the equation

$$C_c = 1 + K_n\,[\alpha + \beta\,\exp(\gamma/K_n)] \qquad \textbf{(2)}$$

where

$K_n = 2\lambda/d_{SED}$, the Knudsen number
$\lambda = .0665$ µm, the air molecular mean free path(24)
$\alpha = 1.142$
$\beta = 0.558$
$\gamma = 0.999$ (Allen and Raabe)(25)

and are chosen for solid particles.

In the present work, gravimetric measurement of the median d_{AED} using an inertial impactor for the individual size fractions obtained from MIN-U-SIL 10 was not possible because insufficient material was available. However, measurement of median d_{AED} and median d_{SED} for the whole product of MIN-U-SIL 10 was performed. Using this method a calibration factor Ψ_{10} was obtained for the particle sizing instrument used to determine the median d_{SED} values. The approximation is made that the value of Ψ_{10}, obtained for the median size of the distribution, is applicable to particles of that size and the individual size fraction distributions of MIN-U-SIL 10 having median sizes $(d_{AED})_i$ and $(d_{SED})_i$. Therefore,

$$(d_{AED})_i = \Psi_{10}\left[\frac{\rho_P C_c(d_{SED})_i}{\chi_{average} C_c(d_{AED})_i}\right]^{1/2} \times (d_{SED})_i \qquad \textbf{(3)}$$

where the subscript "10" references the material MIN-U-SIL 10.

The values of $C_c(d_{AED})$ were determined by successive approximation using the initial assumption that $C_c(d_{SED})=C_c(d_{AED})$ in Equation 3. The first approximation values of $C_c(d_{AED})$ and d_{AED} were substituted into Equation 3 to obtain second approximation values. A third approximation provided no change in d_{AED} to two decimal places. Two values of the shape factor χ were used in computing an estimated range for $(d_{AED})_i$. Davies(26) reported a range of $1.36<\chi<1.82$ for silica dust particles, and these values were used in the calculations. Each size reported in the present work represents the average of sizes calculated from Equation 3 using the extreme values of χ. It is assumed that this same approximation can reasonably be applied to the various size fractions obtained from MIN-U-SIL 10 for estimation of the median d_{AED} in this study. For either shape factor, computation shows that Ψ varies by about 1% over the size range used in this work.

Analytically, an approximate value of the calibration factor Ψ_{10} is obtained by combining Equations 2 and 3, yielding

$$\Psi_{10} = \frac{(d_{AED})_{10}}{\Phi \times (d_{SED})_{10}}, \qquad \textbf{(4)}$$

where $\Phi \equiv$ the square root term in Equation 3 with $i = 10$, and requiring $(d_{AED})_{10}$, calculated from measurement of $(d_{SED})_{10}$, to be equal to $(d_{AED})_{10}$ measured by an acceptable gravimetric technique. In practical application, this was achieved by setting the relative index of refraction for silica dispersed in IPA so that the independently measured values of $(d_{AED})_{10}$ agreed.

Prepared laboratory samples of size-classified bulk powder were analyzed for silica content by (1) P7 at the NIOSH Pittsburgh

TABLE I. Calibration Material Median Size Data

Calibration Materials	d_{SED}[A] µm	d_{AED}[B] µm
MIN-U-SIL 5[C]	1.70[F]	2.23
Berkeley-5[D]	1.61	2.12
SRM 1878[E]	1.70	2.23

[A] Spherical equivalent diameter.
[B] Aerodynamic equivalent diameter.
[C] 1982 recommended calibration standard.
[D] Calibration material used for P7 analysis in this work.
[E] Calibration material used for XRD Method 7500 analysis in this work.
[F] Value reported by manufacturer using sedimentation method.

TABLE II. Summary Particle Sizing Replication Data for MIN-U-SIL 10 Size Fractions

	Particle Sizing Replication				
Sample Weight (mg)	Sizing Dilution (mg/L)	d_{SED}[A] Average (µm)	SD N = 3 (µm)	Pooled Average (µm)	d_{AED}[B] Average (µm)
0.304	700	7.63	0.015	7.63	9.95
0.304	700	7.52	0.022	7.52	9.81
0.333	700	7.49	0.014	7.49	9.77
0.333	33	6.90	0.019		
0.333	33	7.06	0.036		
0.333	33	7.02	0.026	6.99	9.12
0.333	33	6.82	0.004		
0.333	33	6.90	0.046		
0.333	33	6.90	0.022	6.87	8.96
0.302	700	4.03	0.004	4.03	5.27
0.300	700	3.93	0.002	3.93	5.14
0.328	700	4.11	0.003	4.11	5.37
0.328	33	4.16	0.006		
0.328	33	4.17	0.012		
0.328	33	4.05	0.010	4.13	5.40
0.328	33	4.04	0.004		
0.328	33	4.05	0.020		
0.328	33	4.07	0.009	4.05	5.29
0.310	700	1.99	0.002	1.99	2.61
0.303	700	2.08	0.003	2.08	2.73
0.310	700	2.06	0.001	2.06	2.70
0.383	38	2.12	0.002		
0.383	38	2.12	0.004		
0.383	38	2.12	0.003	2.12	2.78
0.383	38	2.02	0.003		
0.383	38	2.02	0.001		
0.383	38	2.07	0.006	2.04	2.68
0.307	700	1.24	0.002	1.24	1.64
0.308	700	1.25	0.001	1.25	1.65
0.307	700	1.22	0.001	1.22	1.61
0.307	31	1.26	0.001		
0.307	31	1.26	0.003		
0.307	31	1.24	0.001	1.25	1.65
0.307	31	1.24	0.004		
0.307	31	1.24	0.002		
0.307	31	1.23	0.003	1.24	1.64

[A] Spherical equivalent diameter.
[B] Aerodynamic equivalent diameter estimate based on average of particle shape factors 1.82 and 1.36.

Research Laboratory using a PerkinElmer (PerkinElmer, Shelton, Conn.) 1760X spectrometer and a newer PerkinElmer Spectum GX FTIR spectrometer, and (2) the NIOSH XRD method at an independent laboratory participating in the Proficiency Analytical Testing (PAT) program and accredited by the American Industrial Hygiene Association. The P7 and XRD methods used were performed according to the method protocol as specified by MSHA and NIOSH, respectively, with the exception that samples prepared for P7 analysis were from size-classified bulk powder, as described earlier, instead of from an airborne respirable dust sample. XRD samples were prepared from the same sample deposit on which P7 analysis had been performed by low-temperature ashing of the deposit and substrate, followed by redeposition on a silver membrane filter. Silica reported by XRD was based on intensity peak area, as required by Method 7500.

The testing proceeded with sample preparation and analysis performed in three distinct series of measurement. The first series was performed using a high-suspension concentration and the older Perkin-Elmer 1760X FTIR spectrometer for the four MIN-U-SIL 10 size fractions. The second and third series were performed at the low suspension concentrations with the newer PerkinElmer Spectum GX FTIR spectrometer.

Group 2 of the impactor samples was analyzed for silica by removing the dust collected on the individual stages and compositing into three groups. These groups consisted of impactor stages 1, 2, and 3 (21.3 to 9.8 µm); stages 4, 5, and 6 (6.0 to 1.55 µm), and stages 7, 8, and final (0.93 to 0.1 µm). Each composite was analyzed for silica according to the NIOSH XRD method at an independent accredited PAT laboratory.

RESULTS AND DISCUSSION

Particle Sizing

The median value $(d_{AED})_{10}$ for MIN-U-SIL 10 was determined to be 3.83 µm from an average of four measurements using Marple Model 298 9-stage personal sampling impactors. The size distribution of the respirable fraction of the dust was determined from the impactor data and ACGIH definitions.(20–22) The appropriate median value $(d_{SED})_{10}$ was determined to be 2.97 µm on the Horiba LA-920 particle size analyzer. Using $(d_{SED})_{10}=2.97$ µm in Equation 3 yielded $(d_{AED})_{10}=3.89$ µm, good agreement with the value obtained from the gravimetric determination.

Table I summarizes median size data for three materials used for calibration of the P7 and the XRD methods. The median d_{SED} value of 1.70 µm for MIN-U-SIL 5 is that reported by the manufacturer. The median d_{SED} values for Berkeley 5 (1.61 µm) and SRM 1878 (1.70 µm) were measured by the same technique as used for the analysis of the MIN-U-SIL 10 size fractions. These values are reported to show the relatively small differences in median size between the original calibration material, MIN-U-SIL 5, and two other standard materials used for instrument calibration during these tests. Calculated values of median d_{AED} for the calibration materials listed in Table I are reported, assuming that the same shape factors reported by Davies are reasonable approximations for these silica products.

Table II summarizes the fractionated MIN-U-SIL 10 particle size analysis results. The size fractions are categorized by suspension concentration as well as median d_{SED}. Size values also have been expressed in terms of the median d_{AED} as previously described. The coefficient of variation for repeatability for all median d_{SED} reported in Table II was less than 0.5%, based on three replicate measurements.

The effect of particle sizing suspension concentration was also investigated. A series of suspension concentrations using the largest size fraction were generated. Beginning with an initial silica/

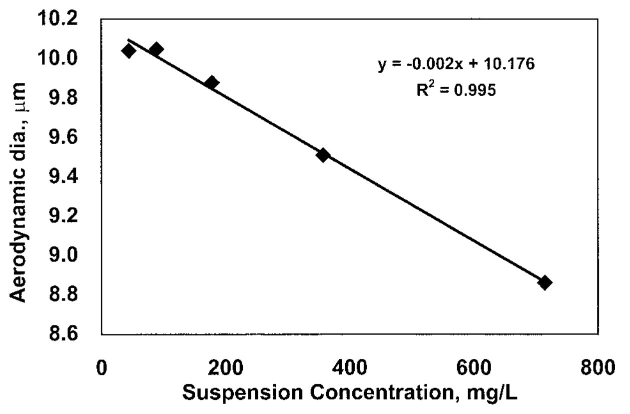

FIGURE 1. Suspension concentration effect on the reported median aerodynamic sizes

IPA concentration of 714 mg/L, four successive factor-of-two dilutions were prepared. Figure 1 shows the results, which indicate a significant bias in the particle sizing due to sample concentration. It is not known whether this bias is due to an inherent suspension concentration dependency in the LA 920 sizing instrument or sample preparation for the dilution tests. However, one would intuitively suspect that, assuming no bias in sample preparation such as differential particle settling, the LA 920 would produce a positive size versus suspension concentration relationship on a purely statistical basis. This would occur due to too few of the larger particles being present in the suspension for proper measurement, resulting in an underestimation of particle size at the lower dilution concentrations. Therefore, the demonstrated bias may be in sample preparation.

Table III summarizes the MIN-U-SIL 10 size fraction analysis results. The average reported mass and standard deviations were determined from triplicate P7 measurements of the sample. The average reported masses with no reported standard deviation are single measurements. Figure 2 shows the silica reported by P7 for

TABLE III. Summary Data for P7 Infrared and NIOSH 7500 XRD Methods for Silica on MIN-U-SIL 10 Size Fractions

	Silica P7 Replication					X-Ray: Peak Area Analysis Only			
d_{AED}[A] Average (µm)	Infrared Spectrometer	Reported Mass Avg. (mg)	SD N = 3 (mg)	Percentage Silica Average	Percentage Silica SD	Reported Mass (mg)	Reported Mass Avg. (mg)	Percentage Silica Average	Percentage Silica SD[B]
9.95	P-E 1760X	0.092	0.008	30.3	2.5	0.294	0.294	96.7	7.7[B]
9.81	P-E 1760X	0.094	0.001	30.9	0.3				
9.77	P-E 1760X	0.103	N/App[C]	30.9	N/App	0.372	0.372	111.7	8.9[B]
	P-E Spectrum GX	0.100	0.002			0.301			
	P-E Spectrum GX	0.097	0.004			0.357			
9.12	P-E Spectrum GX	0.096	0.004	29.4	1.1	0.327	0.328	98.6	8.4
	P-E Spectrum GX	0.070	0.004			0.333			
	P-E Spectrum GX	0.107	0.001			0.345			
8.96	P-E Spectrum GX	0.107	0.004	28.5	5.6	0.342	0.340	102.1	1.9
5.27	P-E 1760X	0.220	0.007	73.0	2.3				
5.14	P-E 1760X	0.226	0.005	75.2	1.7	0.308	0.308	102.7	8.2[B]
5.37	P-E 1760X	0.232	N/App	70.7	N/App	0.307	0.307	93.6	7.5[B]
	P-E Spectrum GX	0.206	0.006			0.285			
	P-E Spectrum GX	0.219	0.003			0.291			
5.40	P-E Spectrum GX	0.219	0.018	65.5	3.5	0.301	0.292	89.1	2.5
	P-E Spectrum GX	0.227	0.004			0.334			
	P-E Spectrum GX	0.215	0.011			0.313			
5.29	P-E Spectrum GX	0.225	0.012	67.8	3.1	0.291	0.313	95.3	6.6
2.61	P-E 1760X	0.304	0.006	98.2	1.9				
2.73	P-E 1760X	0.304	0.007	100.4	2.1				
2.70	P-E 1760X	0.310	N/App	100.0	N/App	0.307	0.307	99.0	7.9[B]
	P-E Spectrum GX	0.383	0.016			0.375			
	P-E Spectrum GX	0.383	0.009			0.351			
2.78	P-E Spectrum GX	0.371	0.019	98.9	3.8	0.334	0.353	92.3	5.4
	P-E Spectrum GX	0.375	0.008			0.360			
	P-E Spectrum GX	0.390	0.016			0.371			
2.68	P-E Spectrum GX	0.386	0.015	100.1	3.6	0.378	0.370	96.5	2.4
1.64	P-E 1760X	0.311	0.012	101.3	3.8	0.271	0.271	88.3	7.1[B]
1.65	P-E 1760X	0.316	0.006	102.7	1.8				
1.61	P-E 1760X	0.312	N/App	101.6	N/App	0.246	0.246	80.1	6.4[B]
	P-E Spectrum GX	0.317	0.008			0.261			
	P-E Spectrum GX	0.324	0.007			0.283			
1.65	P-E Spectrum GX	0.318	0.009	104.1	2.5	0.250	0.265	86.2	5.5
	P-E Spectrum GX	0.291	0.006			0.260			
	P-E Spectrum GX	0.294	0.017			0.273			
1.64	P-E Spectrum GX	0.336	0.004	100.0	7.7	0.254	0.262	85.5	3.2

[A] Aerodynamic equivalent diameter estimate based on average of particle shape factors 1.82 and 1.36.
[B] Based on the accepted value of 8% relative standard deviation (NIOSH, 1994).
[C] Not applicable; N = 1.

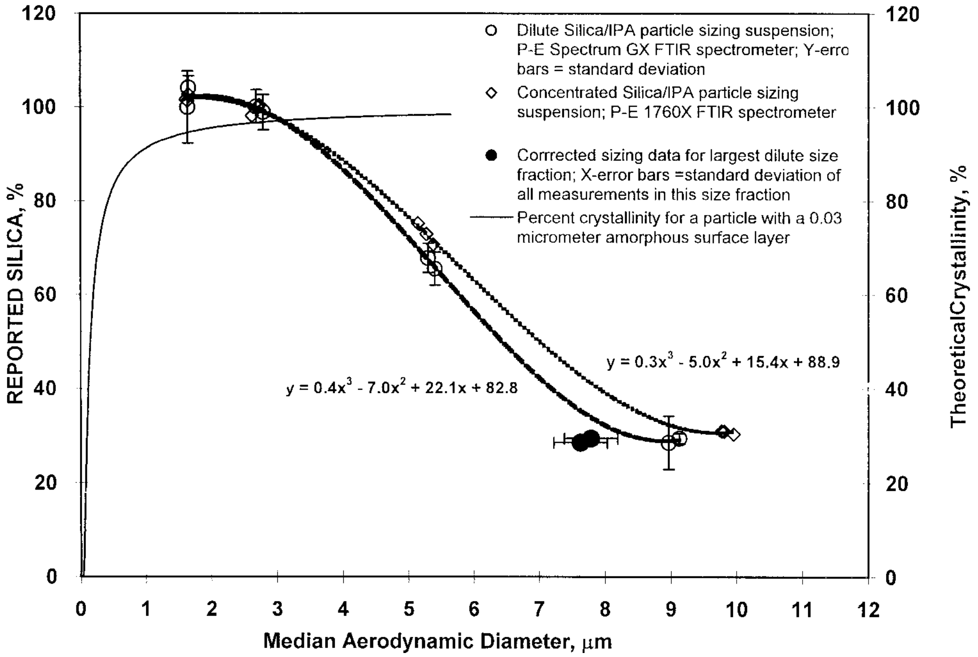

FIGURE 2. Reported silica as determined by the MSHA P7 Method

three independent samples of each size fraction at the concentrated and dilute silica suspensions used for particle sizing in the size range 1.5 to 10 μm. The error bars for reported silica based on the dilute silica particle sizing suspensions represent the standard deviation of nine measurements, comprised of triplicate measurements of three samples. The standard deviations for the concentrated silica particle sizing suspensions listed in Table III are not shown in Figure 2.

A cubic equation was chosen in this size range, based on previously published data by Foster and Walker,(14) to fit the data with an adjusted R-squared value of 0.99. A polynomial function can be justified on the basis that the reported silica from the infrared response is a superposition of surface area-to-volume ratios that change for each particle size. The present analysis closely mimics the results of the Foster and Walker infrared technique as a function of particle size at 799/cm wavenumber. It is reported by Dempster and Ritchie(27) that the absorbance decrease below approximately 1.5 μm is due to an amorphous quartz layer on the silica particles that becomes an appreciable volume percentage as the surface area-to-volume ratio increases at smaller particle sizes. Figure 2 also includes a function that represents a particle crystallinity percentage, based on a 0.03 μm amorphous layer on a 100% crystalline silica particle. The combination of the curves in Figure 2 provide the reader with some estimate of P7 performance at very small particle sizes.

It is apparent from Figure 2 that in the size range below approximately 3.5 μm, which is comparable to the median aerodynamic size of airborne dust classified by the 10-mm cyclone used for coal mine dust sampling, there is virtually no difference between the two spectrometers or any appreciable bias due to sample dilution effect in the particle size measurement. However, a bias is seen in the size range above 5 μm. Although in terms of relevance to airborne respirable dust as classified by the 10-mm cyclone this is of little concern, it is desirable to identify the possible sources of bias.

There are three possible sources of bias in Figure 2. The first bias, which has already been demonstrated, is the effect of particle sizing suspension concentration on the reported particle size. The implication of this result is that the dilute concentration data in Figure 2 is overestimating the median particle size in the largest size fractions, and this effect becomes less important with decreasing median size. Figure 2 shows the largest dilute size fraction corrected according to the results of Figure 1 and represented by the filled-in circles. The error bars for median size are the standard deviation determined from all measured sizes in that size fraction. The second possible source of bias could be the use of two different spectrometers. However, this is not likely because XRD analyses also shows the reported silica content in the two largest size fractions being slightly lower for the dilute suspensions than for the concentrated suspensions. The third possible source of bias is variability in suspension concentration and assuring homogeneous mixing when extracting samples. As previously mentioned, XRD analyses also show the reported silica content in the two largest size fractions being slightly lower for the dilute suspensions than for the concentrated suspensions used for particle sizing. These results suggest that the difference in reported silica is due to sample preparation.

Table III shows that if the median d_{AED} of the silica particles in dust samples is between 1.6 and 2.8 μm, then P7 provides results that are reasonably accurate. Comparison of the median d_{AED} for the calibration materials shows that they are in close agreement with the P7 size range of accuracy. However, it is seen from Table III and Figure 2 that there is significant underestimation of the reported silica percentage for particle sizes greater than 4 μm. Previous research(9) has shown that MIN-U-SIL 5, MIN-U-SIL 15, and MIN-U-SIL 30 have median d_{AED} values of 1.16, 1.2, and 1.2 μm, respectively, after passing through a 10-mm nylon cyclone. This result is because these materials all contain a significant amount of very small material below 5 μm and the cyclone is very effective at uniformly removing the larger, nonrespirable silica particles. This suggests that it is unlikely one would

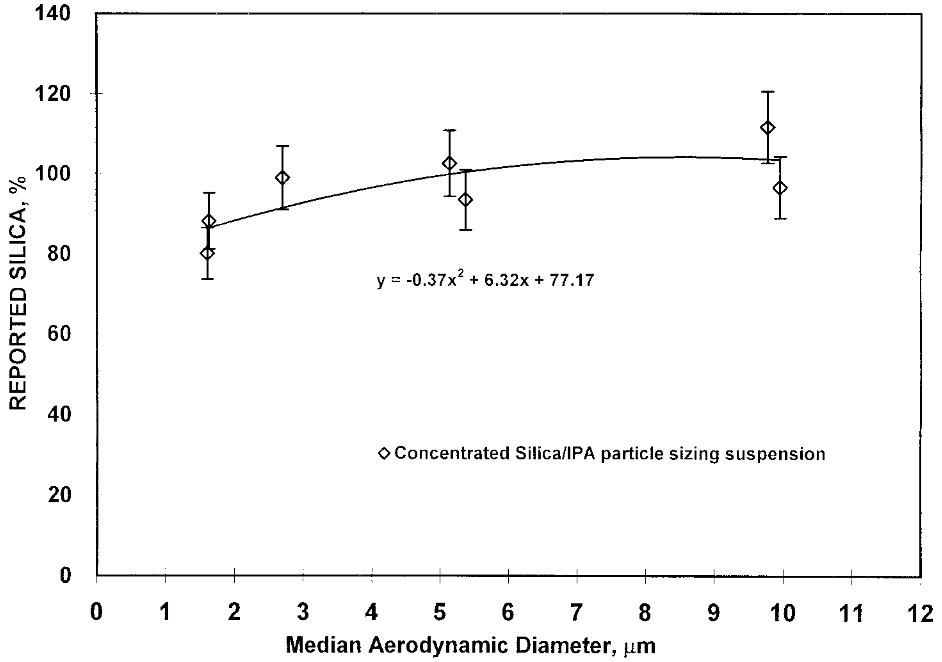

FIGURE 3. NIOSH XRD Analytical Method 7500 results on same samples analyzed by MSHA P7 Method and shown in Figure 2

obtain any significant error in P7 analysis of an airborne respirable dust sample that passes a 10-mm cyclone.

XRD Method

Table III and Figure 3 summarize the XRD analysis on the same MIN-U-SIL 10 size fractions that were prepared and analyzed by P7. However, the data using the dilute silica/IPA particle sizing suspension is omitted from Figure 3 because of the bias shown in Figures 1 and 2. When compared to Figure 2, it is immediately obvious in Figure 3 that XRD yields much less error than P7 in sizes above 4 µm median d_{AED}. However, one of the samples yielded a 111.7% silica content. This sample was scanned twice by XRD, yielding the same result, and it would appear that redeposition of the P7 deposit may be the source of the error. The error bars represent standard deviations calculated from the accepted value of 8% relative standard deviation(10) in the analysis method.

Table III shows that if the median d_{AED} of the silica particle size distribution in dust samples is between 2.5 and 10.0 µm, then XRD provides results that are reasonably accurate. An accepted 10% bias value occurs at approximately 2.5 µm. However, it is seen from Table III and Figure 3 that there is underestimation of the reported silica percentage for particle sizes smaller than approximately 2 µm. Although XRD is affected less by particle size than P7 over the size range less than 10 µm, it would appear that this method is likely to underestimate the silica content of an airborne respirable dust sample that passes a 10-mm cyclone. Comparison of the median d_{AED} for the calibration materials shows that they appear to fall somewhat below the XRD range of accuracy. Table IV shows that, for the underground respirable size distributions given, XRD can underestimate the silica content by as much as 17.4%. It should be pointed out that in metal and nonmetal mining dust sampling is performed at a sampler flow rate of 1.7 L/min, whereas in coal mining the sampler flow rate is 2.0 L/min. The impactor samples of Table IV also were obtained at a flow rate of 2.0 L/min. Because a cyclone operated at the lower flow rate will allow a somewhat greater penetration of larger particle sizes, the median d_{AED} of the sampled dust would be expected to be somewhat larger than shown in Table IV. However, the increase in median d_{AED} would not be expected to be large enough to appreciably reduce the potential underestimation of the silica content.

The observed decrease in response below 4 µm seen in Figure 3 could possibly be attributed to sample loss during sample preparation for the XRD analysis. However, this observed decrease is known to occur with XRD analysis.(12,19,28) The work of Edmonds et al.(19) showed the XRD intensity falling to nearly zero in the size range of 1–2 µm MIN-U-SIL 15 material, possibly indicating a significant fraction of noncrystalline material in this size range. However, Figure 3 suggests that the MIN-U-SIL 10 material fractionated in the present study does not have a significant fraction of noncrystalline silica in the 1–2 µm size range. XRD analysis would appear to be most appropriate for a dust sample that is representative of the total airborne dust, particularly because the mass fraction in the size range below 4 µm is a small percentage of the total airborne dust mass.

Impactor Sampling Data

To investigate a potential change in median size of underground coal mine dust, 83 impactor samples (group 1) were analyzed for the median d_{AED} of the respirable fraction according to the former ACGIH definition. The results are summarized in Table IV and the geometric standard deviations (GSD) reported in parentheses. The individual median d_{AED} values range from 0.9 to 3.6 µm. No discernable difference is noted in the size distributions from mines that used scrubbers for dust control. Using the polynomial regression equation from Figure 2, Table IV shows that P7 underestimates the silica content of the sample by at most 7.4% in the MMAD size range 0.9 to 3.6 µm. Although it is not known what the median d_{AED} of the silica component for these distributions is,

TABLE IV. Respirable Fraction Aerodynamic Equivalent Diameters of Underground Impactor Samples

Mine	Respirable Fraction Median d_{AED}, μm (GSD)												Mining Type	Scrubber
A	2.8 (1.48)	3.4 (1.34)	2.4 (1.67)	2.1 (1.65)	2.9 (1.49)								continuous miner	no
B	1.3 (2.32)	1.6 (2.37)	1.7 (2.26)	1.5 (2.23)	2.3 (2.23)								continuous miner	no
C	1.9 (2.33)	1.9 (2.32)	2.7 (1.67)	2.4 (2.33)	2.0 (2.33)								continuous miner	no
D	2.2 (1.77)	2.0 (1.72)	2.2 (1.75)	2.2 (1.76)	2.4 (1.82)	2.2 (1.77)							continuous miner	no
E	1.9 (2.16)	1.8 (1.96)	1.5 (2.27)	2.5 (1.70)	1.6 (1.93)								continuous miner	yes
F	3.6 (1.32)	1.3 (1.89)											continuous miner	no
G	1.8 (1.91)	1.8 (1.89)											longwall	no
H	2.5 (1.69)	2.3 (1.69)	2.6 (1.65)	2.6 (1.65)	2.3 (1.68)	2.5 (1.73)	2.4 (1.77)	2.4 (1.64)					longwall	no
I	2.6 (1.72)	2.1 (1.75)	1.6 (1.67)	2.3 (1.74)	2.2 (1.70)	2.1 (1.69)	2.2 (1.74)						longwall & continuous miner	no
J	2.2 (1.73)	1.5 (1.81)	1.2 (1.96)	1.0 (2.13)	1.3 (2.04)	1.2 (1.90)	1.4 (1.87)	1.7 (1.87)	1.1 (1.91)				continuous miner	yes
K	1.7 (1.82)	1.7 (1.81)	2.3 (1.67)	2.2 (1.68)	1.6 (1.82)	1.5 (1.75)	1.5 (1.80)	1.5 (1.79)	1.6 (1.90)	1.7 (1.82)	1.5 (1.88)	1.5 (1.92)	continuous miner	yes
L	1.8 (1.81)	1.5 (1.89)	2.1 (1.69)	1.8 (1.71)	2.3 (1.64)	2.6 (1.57)	2.1 (1.71)	0.9 (2.32)	1.2 (2.07)	2.5 (1.66)	1.8 (1.77)		continuous miner	yes
M	2.2 (1.60)	2.2 (1.65)	2.0 (1.58)	2.2 (1.63)	2.3 (1.60)	2.3 (1.64)							continuous miner	no
					Analytical Method =								P7[A]	XRD[B]
Low value =	0.9 μm;				percentage underestimation =								1.1	17.4
High value =	3.6 μm;				percentage underestimation =								7.4	4.9

[A] Based on equation from Figure 2.

[B] Based on equation from Figure 3.

the fact that these are aerodynamic estimates of the respirable fraction suggests that the median d_{AED} of the silica component should be in approximately the same size range.

Group 2 impactor samples (Table V) were analyzed for total dust and silica content in three size ranges R_1=21.3 to 9.8 μm, R_2=6.0 to 1.55 μm, and R_3=0.93 to 0.1 μm. Twenty-three of 29 samples have larger percentages of silica in the combined ranges of R_2 and R_3 compared with the total dust in these ranges. It is apparent that the largest contributor to this result is the percentage of silica in the size range 6.0 to 1.55 μm. Although the values of the median d_{AED} of the dust sample and silica content are not known, it is possible to do a Student's t-test for paired two-sample means analysis (Microsoft™ Excel™ 2000) on the values of (R_2 + R_3) in Table V. The rationale for this choice is that the median d_{AED} of a respirable dust sample is likely to be in this range. A two-tailed analysis yields $t_{data}=1.98<t_{critical}=2.05$ with 28 degrees of freedom at the 5% significance level. These results suggest that the median d_{AED} of the dust sample silica content is not statistically different from the median d_{AED} of the total dust sample.

A significant error could be introduced into P7 analysis of a respirable coal sample if the silica dust being sampled contains relatively few particles in the 1–2 μm size range. The result of this would be an increase in the median size of the cycloned material, and it is reasonable to ask under what circumstances this might occur. Among the changes in coal mining technology is a significant increase in the power delivered by mining machinery to mine the coal. Because coal mining frequently involves cutting the much harder rock material, which is usually the source of silica, it is possible that there has been a decrease in the amount of grinding and an increase in the actual breakage of this rock material due to these more powerful machines. On this basis, it would appear reasonable to suspect some change in the median size of the airborne respirable silica compared with that of the early 1980s when the MIN-U-SIL 5 material was chosen as the best representation of airborne respirable silica dust in underground coal mines. However, the results of this work suggest that the median d_{AED} of the respirable silica component of coal mine dust still remains within the size range in which P7 is calibrated.

It must be pointed out that the P7 results describe performance only for dust samples that have been classified according to a respirable definition similar to the penetration of a 10-mm cyclone or, at a minimum, samples that have a median d_{AED} in the size range mentioned. Therefore, application of P7 to impactor stage samples that possess 50% cut points outside of the approximate size range 0.9 to 3.6 μm is likely to produce significant underestimation errors due to the particle size sensitivity of P7.

CONCLUSIONS

The effect of particle size on the MSHA P7 IR and NIOSH XRD Analytical Method 7500 was measured using size fractions of MIN-U-SIL 10 silica. Although the effect of particle size on these measurement techniques has been studied and presented previously, the objective of this work was to compare particle size distributions of underground coal mine dust with the particle size

TABLE V. Comparison of Total Dust and Silica Dust Weight Distributions Among Composited Impactor Stages

		Percentage of Total Dust Weight in Impactor Size Ranges (μm)				Percentage of Silica Dust Weight in Impactor Size Ranges (μm)			
Mine	Sample Location	R_1 21.3–9.8	R_2 6.0–1.55	R_3 0.93–0.1	$(R_2 + R_3)$ 6.0–0.1	R_1 21.3–9.8	R_2 6.0–1.55	R_3^A 0.93–0.1	$(R_2 + R_3)$ 6.0–0.1
N	intake	71.8	17.0	11.2	28	79.7	17.9	2.4	20
	return	89.1	7.1	3.7	11	83.5	14.7	1.8	16
	return	64.3	25.9	9.8	36	33.8	64.3	1.9	66
	lab crusher	76.0	22.3	1.7	24	66.2	32.6	1.1	34
	lab crusher	65.1	30.8	4.1	35	55.2	43.7	1.1	45
	lab crusher	43.0	45.6	11.4	57	32.6	59.6	8.4	68
O	intake	34.2	20.4	45.3	66	24.2	32.3	43.5	76
	return	50.3	38.5	11.2	50	50.4	41.7	7.9	50
	return	49.8	45.7	4.5	50	52.0	43.9	4.2	48
	return	60.2	34.6	5.2	40	55.2	37.5	7.1	45
	lab crusher	61.2	38.8	0.0	39	60.5	39.5	0.0	40
	lab crusher	63.6	36.4	0.0	36	61.1	38.9	0.0	39
P	lab crusher	67.4	32.6	0.0	33	66.8	33.2	0.0	33
	lab crusher	57.2	42.8	0.0	43	54.8	45.2	0.0	45
	lab crusher	57.6	42.4	0.0	42	63.8	36.2	0.0	36
	lab crusher	50.4	49.6	0.0	50	53.8	46.2	0.0	46
	lab crusher	58.1	41.9	0.0	42	69.3	30.7	0.0	31
	lab crusher	57.8	42.2	0.0	42	54.4	45.6	0.0	46
	lab crusher	60.1	39.9	0.0	40	55.0	45.0	0.0	45
Q	intake	39.3	46.4	14.3	61	27.8	55.6	16.7	72
	return	38.2	30.6	31.2	62	19.2	57.7	23.1	81
	return	38.3	38.3	23.3	62	39.0	50.8	10.2	61
	return	40.6	43.0	16.4	59	31.6	59.6	8.8	68
	lab crusher	57.2	38.3	4.5	43	56.0	42.0	1.9	44
	lab crusher	64.6	31.6	3.8	35	68.7	29.5	1.7	31
	lab crusher	61.3	35.6	3.1	39	61.1	36.7	2.2	39
R	lab crusher	73.9	23.9	2.2	26	75.6	20.4	4.6	25
	lab crusher	71.1	24.1	4.8	29	74.2	21.5	4.3	26
	lab crusher	69.8	26.9	3.3	30	76.2	19.6	4.2	24

^{A}Values of R_3 reported in Table IV are 20% higher than reported by laboratory analysis to correct for the underestimation at 0.5 μm midpoint.
Note: Twenty-three of twenty-nine samples $(R_2 + R_3)_{silica}/(R_2 + R_3)_{total} \geq 1$, allowing for an assumed 8% RSD error propagation in the silica determination $R_2 + R_3$.

dependency of these two silica analysis techniques using Berkeley 5 and SRM 1878 calibration standard materials.

Impactor sampling data for various locations on continuous mining and longwall mining operations from 13 underground mines were analyzed for the respirable fraction and the resulting median d_{AED}. The individual median d_{AED} ranged from 0.9 to 3.6 μm. It appears that P7 will underestimate the silica content of the sample by at most 7.4% in the median d_{AED} size range 0.9 to 3.6 μm and that it is unlikely one would obtain any significant error in P7 analysis of an airborne respirable dust sample that passes a 10-mm cyclone when the method uses Berkeley 5, MIN-U-SIL 5, or SRM 1878 as a calibration standard material.

XRD appears to be more appropriate for a dust sample that is representative of the total rather than the respirable airborne dust, particularly because the mass fraction in the size range below 4 μm is a small percentage of the total airborne dust mass. However, the results of this study indicate that XRD may not be as suitable as P7 for respirable dust samples. Comparison of underground respirable size distributions indicate that XRD could underestimate the silica content by as much as 17% if the respirable aerodynamic equivalent diameter is 0.9 μm and as little as 5% if the respirable aerodynamic equivalent diameter is 3.6 μm. Because it is not common to find mine environments with respirable mass median aerodynamic diameters as low as 0.9 μm, the NIOSH Analytical Method 7500 is likely to underestimate the silica content of an airborne respirable dust sample by only 5 to 10%.

The results of this study suggest that any changes that may have occurred in the median respirable size of airborne coal mine dust are not enough to cause any appreciable error in the current methods used for respirable crystalline silica analysis. Although the crystalline purity of the standard calibration materials used is not known, the differences reported in this work cannot be attributed to a significant noncrystalline component.

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