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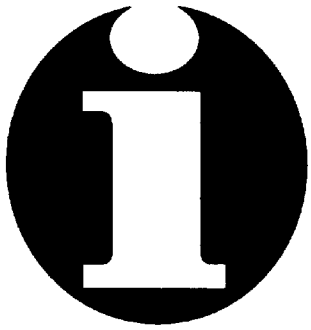

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COMPARISON OF INFRARED ABSORBANCES FOR STANDARD SAMPLES PREPARED FROM SIEVED AND NONSIEVED QUARTZ REFERENCE MATERIALS

by

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ABSTRACT

The Mine Safety and Health Administration (MSHA) analyzes respirable coal mine dust samples for quartz content as part of their program to enforce environmental dust levels as mandated by the Federal Mine Health and Safety Act of 1977. Under the Act, the amount of respirable coal mine dust to which miners can be exposed is dependent on the percentage of quartz in the mining atmosphere. Currently, MSHA uses infrared spectrophotometry for the quartz analysis. A quartz reference material, comparable in crystalline structure and particle size distribution to the quartz found in coal mine dust, is necessary to prepare the calibration curves for the quantitative measurement of the mineral.

A National Institute for Occupational Safety and Health report in 1989 stated that the standard quartz reference material (SRM 1878) used in the calibration of instrumentation utilized for quartz analysis contains particles greater than 10 micrometers in diameter (examined by optical microscope with polarized light). This report further stated that the calibration of X-ray diffraction (XRD) instrumentation was found to be significantly different after the particles larger than 10 micrometers in size were removed from the reference material.

Because of these reported results, a similar study was conducted by MSHA to determine if the same effect occurred with the calibration of infrared spectrophotometers. This study consisted of wet sieving two quartz reference materials (SRM 1878 and minus 5 micrometer MINUSIL) through a 10 micrometer size sieve, preparing calibration standards with masses ranging from 20 to 200 micrograms from both the sieved and unsieved materials, and comparing the infrared absorbances obtained for the standards. The particle size distribution of sieved and unsieved fractions of the reference materials was determined by Coulter Counter analysis. In addition, sieved and unsieved suspensions of the materials were examined by optical microscopy.

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The results of this study indicate that there is no significant difference in calibration curves derived for the infrared spectrophotometer using reference standards prepared from sieved or unsieved minus 5 micrometer MINUSIL or SRM 1878. Sieving caused no significant effect in the particle size distributions of the reference materials, and less than a half percent of particles greater than 10 micrometers in size were detected in either of the materials. Therefore, either SRM 1878 or minus 5 micrometer MINUSIL may be used without sieving for the calibration of infrared spectrophotometers for the analysis of coal mine dust samples for quartz content.

INTRODUCTION

The National Institute for Occupational Safety and Health reported the results in May, 1989 from a study that showed that the standard quartz reference material available from the National Institute for Standards and Technology (NIST, formerly National Bureau of Standards), SRM 1878, contains particles greater than 10 micrometers as measured by light microscopy.[4,5] The study further showed that these particles have an effect on the peak intensity obtained by X-ray diffraction analysis which significantly affects the calibration curve for the instrument. Based on these results, NIOSH modified its analytical procedure for quartz analysis, Method 7500, in May, 1989 to include wet sieving of the reference material prior to the preparation of calibration standards. The purpose of this study was to determine if sieving of the standard materials also affected infrared absorbance measurements and to determine if the standard materials, SRM 1878 and minus 5 micrometer MINUSIL, contained particles greater than 10 micrometers.

It is well documented in the literature that particle size has an effect on infrared absorbance.[6,7,8] For this reason, work was done in the past to determine the best choice of a reference material to use for the calibration of infrared instrumentation for the quantification of quartz in coal mine dust samples. Under contract with NIOSH and the U.S. Bureau of Mines (BOM), SRI International conducted a study of X-ray diffraction and infrared methods for silica analysis in 1983.[9] An evaluation was made on the size distributions of several quartz materials, including MINUSIL, for the purpose

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[4] SRM 1878 is obtained from the purification of minus 5 micrometer MINUSIL.

[5] Palassis, J.; Jones, W.: Particle Size Effects on the Accuracy of Respirable Silica Analyses by X-Ray Powder Diffraction. AIHA Conference, St. Louis, MO (1989).

[6] Tuddenham, W.M.; Lyon, R.J.P.: Infrared Techniques in the Identification and Measurement of Minerals. Analytical Chemistry 32:1630-1634 (1960).

[7] Dodgson, J.; Whittaker, W.: The Determination of Quartz in Respirable Dust Samples By Infrared Spectrophotometry-I. Ann. Occup. Hyg. 16:373-387 (1973).

[8] Lorberau, C.D.; Carsey, T.; Fischbach, T.; Mulligan, K.: Evaluation of Direct-on-Filter Methods for the Determination of Respirable α-Quartz. Appl. Occup. Environ. Hyg. 5:27-35 (1990).

[9] Anderson, C.C., SRI International: Collaborative Tests of Two Methods for Determining Free Silica in Airborne Dust. Contract No. 210-79-0059 prepared for NIOSH, BOM (1983).

of selecting a bulk reference material that has a size distribution that most closely resembles the size distribution of materials passing particle size classifiers which are used to collect respirable particulate samples. The size distribution data and scanning electron micrographs presented in that report showed that there were no particles larger than 10 micrometers (equivalent spherical diameter) in size in minus 5 micrometer MINUSIL.

In 1984, MSHA compared calibrations of a dispersive infrared spectrophotometer obtained using different quartz reference materials. Both minus 5 micrometer MINUSIL and SRM 1878 were part of the comparison. The results of this comparison showed that there was no significant difference in the infrared calibration equations determined from minus 5 micrometer MINUSIL and SRM 1878.[10]

The Bureau of Mines (BOM), in 1985, looked at the particle size distributions, measured by scanning electron microscopy, of several quartz materials and compared them to the size distributions of samples collected in surface and underground coal mines.[11] The particle size distributions of the minus 5 micrometer MINUSIL and SRM 1878 were among those determined. The data from these distributions, presented in Table 1, show that 0.25 percent (one particle of approximately 400 counted) of the particles of minus 5 micrometer MINUSIL was larger than 9.6 micrometers and that the largest particles in SRM 1878 were in the 10.2 to 10.5 micrometer size interval and accounted for 0.5 percent of its particles. BOM concluded that both SRM 1878 and minus 5 micrometer MINUSIL were acceptable as reference standards for quartz analysis by X-ray diffraction or infrared spectrometry.

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[10] Kacsmar, P.; Tomb, T.: Comparison of Alpha Quartz Materials Used as Calibration Standards. Coal Mine Dust Conference Proceedings, S.S. Peng, Ed., Morgantown, pp. 144-150 (1984).

[11] Huggins, C.W.; Johnson, S.N.; Segreti, J.M.; Snyder, J.G.: Determination of Alpha Quartz Particle Distribution in Respirable Coal Mine Dust Samples and Reference Standards. BOM RI 8975 (1985).

TABLE 1. Bureau of Mines' Size Distribution Data

Quartz Length, μm	-5 μm MINUSIL	NBS 1878
0.0 - 0.3	ND	ND
0.3 - 0.6	6.25	4.71
0.6 - 0.9	18.75	13.40
0.9 - 1.2	25.75	18.63
1.2 - 1.5	15.00	11.66
1.5 - 1.8	8.00	11.17
1.8 - 2.1	7.50	10.17
2.1 - 2.4	5.00	6.95
2.4 - 2.7	4.00	6.45
2.7 - 3.0	2.25	3.47
3.0 - 3.3	1.50	3.72
3.3 - 3.6	1.50	1.49
3.6 - 3.9	0.75	1.74
3.9 - 4.2	0.75	3.23
4.2 - 4.5	0.25	0.99
4.5 - 4.8	0.25	0.99
4.8 - 5.1	0.25	0.50
5.2 - 5.4	0.50	0.25
5.4 - 5.7	0	0.50
5.7 - 6.0	0.25	0.25
6.0 - 6.3	0	0
6.3 - 6.6	0	0
6.6 - 6.9	0.25	0.50
6.9 - 7.2	0	0.25
7.2 - 7.5	0.50	0
7.5 - 7.8	0.25	0
7.8 - 8.1	0	0
8.1 - 8.4	0	0
8.4 - 8.7	0	0
8.7 - 9.0	0.25	0
9.0 - 9.3	0	0.25
9.3 - 9.6	0	0
9.6 - 9.9	0	0
9.9 - 10.2	0	0
10.2 - 10.5	0	0.50
10.5 - 10.8	0	0
10.8 - 11.1	0	0
11.1 - 11.4	0	0
11.7 - 12.0	0	0
12.0 - 12.3	0	0
12.3 - 12.6	0	0
12.6 - 12.9	0	0
12.9 - 13.2	0	0
13.2 - 13.5	0.25	0
13.5 - 13.8	0	0
13.8 - 14.1	0	0
14.1 - 14.4	0	0
14.4 - 14.7	0	0
14.7 - 15.0	0	0
15.0 - 15.3	0	0
Quartz Frequency, 4.2 - 9.6 μm	2.75	4.48
Mean Quartz Length....μm	1.26	1.65
Mean Quartz Diameter....μm	0.97	1.31

ND - not determined.

EXPERIMENTAL

Minus 5 micrometer MINUSIL and SRM 1878 were each dispersed in isopropanol and wet sieved through a 10 micrometer Buckbee Mears[12] sieve using MSHA Standard Method A2.[13] The sieved materials were recovered by evaporation of the alcohol in a vacuum oven and then dried for several hours at 110°C. Suspensions (10 milligrams per liter in isopropanol) of each of the four materials (sieved and unsieved MINUSIL and SRM 1878) were prepared following MSHA Standard Method P7.[14] Samples were prepared by pipetting known volumes of the suspensions onto Gelman DM-450 filters. The suspensions were vacuum filtered into a 10 millimeter diameter spot using the procedure described in Standard Method P7. Sets of 15 samples, consisting of groups of three samples each of 20, 30, 50, 100 and 200 micrograms, were prepared from each of the four alcohol suspensions.

The filters were then scanned on a Perkin-Elmer Model 1750 FTIR spectrophotometer and the absorbance at 800 cm^{-1} was measured. The infrared absorbance and the absorbance per microgram for each sample and the standard deviation and relative standard deviation for the average absorbance per microgram values were determined. The respective data are shown in Tables 2 and 3. To determine if the reference materials contained particles larger than 10 micrometers in size, sieved and unsieved fractions of the materials were analyzed using an electro-zone sensing technique (Coulter Counter) and optical microscopy. For electro-zone sensing analysis, the respective materials were dispersed in approximately 100 milliliters of isopropanol. About one half of each of the suspensions was wet sieved using a 10 micrometer Buckbee Mears sieve. Aliquots of the sieved and unsieved materials were analyzed for particle size distributions using a Model TA II Coulter Counter, following MSHA Standard Method P-5,[15] which includes ultrasonic agitation of the suspension. Unsieved material was also analyzed without the ultrasonic agitation of the suspension. Equivalent spherical volume diameters (ESVD) determined from the analyses were classified into 16 size ranges. Using a 50 micrometer diameter aperture sampling tube, particles from 0.79 to greater than 20 micrometers were classified. The relative frequency of particles in the respective size intervals were graphed and empirically compared.

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[12] Reference to specific equipment, trade names, manufacturers or companies does not imply endorsement by MSHA.

[13] MSHA: A Rapid Method for Separating Dust into Discrete Fractions Down to Less than 10 Micrometers. Standard Method No. A2 (1971).

[14] MSHA: Infrared Determination of Quartz in Respirable Coal Mine Dust. Standard Method P7 (1989).

[15] MSHA: Particle Size Determination Using the Model TA II Coulter Counter. Standard Method P5 (1989).

TABLE 2. Comparison of Quartz Infrared Absorbances for Sieved and Unsieved Minus 5 Micrometer MINUSIL

Mass (μg)	MINUSIL		Sieved MINUSIL	
	Abs.	Abs./μg	Abs.	Abs./μg
20	0.02541	0.00127	0.02420	0.00121
20	0.02463	0.00123	0.02547	0.00127
20	0.02354	0.00118	0.02551	0.00128
30	0.03554	0.00118	0.03756	0.00125
30	0.03606	0.00120	0.03615	0.00121
30	0.03471	0.00116	0.03782	0.00126
50	0.06109	0.00122	0.06028	0.00121
50	0.06086	0.00122	0.06178	0.00124
50	0.06229	0.00125	0.06286	0.00126
100	0.11850	0.00118	0.12321	0.00123
100	0.12396	0.00124	0.12491	0.00125
100	0.11998	0.00120	0.12364	0.00124
200	0.23499	0.00117	0.24595	0.00123
200	0.23935	0.00120	0.23775	0.00119
200	0.23336	0.00117	0.24436	0.00122
Mean		0.00120		0.00124
SD		0.00003		0.00003
%RSD		2.7		2.1

For microscopic analysis, aliquots of the sieved and unsieved materials were examined at 10,000X and at 1,000X using procedures described by Anderson.[16] For examination at 10,000X, a portion of the suspensions containing the sieved and unsieved reference materials were deposited on Millipore AA, 0.8 micrometer pore size membrane filters. Fifty 0.0005 mm^2 microscopic fields, containing an average of 25 particles per field, were examined for particles greater than 10 micrometers in size. For analysis at 1,000X, portions of the sieved and unsieved suspensions were placed in Sedgewick-Rafter cells. Particles in the cells were allowed to settle for 30 minutes prior to the examination of twenty-five 0.05 mm^2 microscopic fields for particles greater than 10 micrometers in size.

DISCUSSION

The infrared absorbance and absorbance per microgram values measured for the sieved and unsieved samples of MINUSIL and SRM 1878 are shown in Tables 2

[16] Anderson, F.G.: A Technique for Counting and Sizing Dust Samples with a Microprojector. Am. Ind. Hyg. Ass. Journal. 23:330-336 (1962).

TABLE 3. Comparison of Quartz Infrared Absorbances for Sieved and Unsieved SRM 1878

Mass (μg)	SRM 1878		SIEVED SRM 1878	
	Abs.	Abs./μg	Abs.	Abs./μg
20	0.02301	0.00115	0.02543	0.00127
20	0.02343	0.00117	0.02550	0.00127
20	0.02491	0.00125	0.02563	0.00128
30	0.03534	0.00118	0.03843	0.00128
30	0.03728	0.00124	0.03728	0.00124
30	0.03575	0.00119	0.03878	0.00129
50	0.05916	0.00118	0.05747	0.00115
50	0.06011	0.00120	0.05942	0.00119
50	0.06056	0.00121	0.06015	0.00120
100	0.11664	0.00117	0.11837	0.00118
100	0.11592	0.00116	0.11637	0.00116
100	0.12227	0.00122	0.12018	0.00120
200	0.23075	0.00115	0.23096	0.00115
200	0.23524	0.00118	0.23180	0.00116
200	0.23569	0.00118	0.23802	0.00119
Mean		0.00119		0.00121
SD		0.00003		0.00005
%RSD		2.5		4.3

and 3, respectively. Also shown in Tables 2 and 3 are the relative errors (%RSD) associated with the infrared absorbance per microgram values for the respective material fractions. This error is less than one half the intralaboratory precision determined during the collaborative testing of the infrared method for measuring free silica in airborne dust, which was between 7 and 10 percent.[17] This reduction in relative error of the analysis is expected since the error in the transmittance measurement is lower for the FTIR than for older dispersive instruments. The error in the infrared absorbance measurement (ΔA/A) can be calculated from the equation

$$\frac{\Delta A}{A} = \left(\frac{0.434}{\log T}\right)\frac{\Delta T}{T}$$

where T is the transmitted energy of a beam of radiation passing through the sample, A is the absorbance, defined as -log T, and ΔT is the error in the transmittance measurement.

[17] Work cited in Footnote 9.

The reported error in the transmittance measurement for the FTIR is less than 0.1 percent. For MSHA's quartz analysis, where the absorbance for most samples is generally between 0.02 and 0.5 absorbance units, the error in the absorbance due to the error in the transmittance measurement is less than 2 percent.

The total error for the standard sample analysis (CV_{cal}) can be estimated from the equation

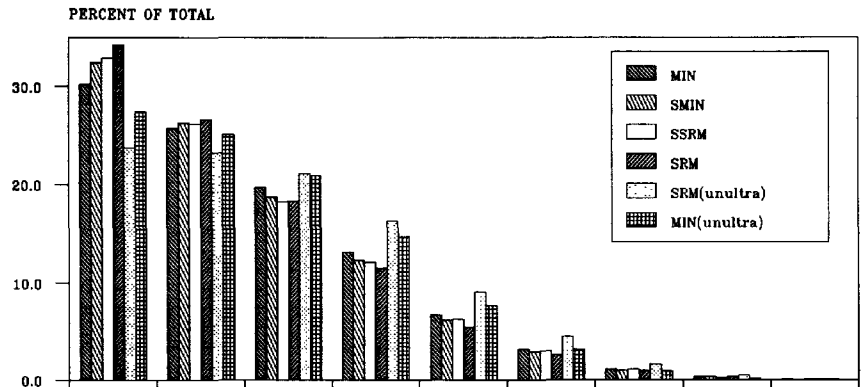
$$(2) \qquad CV_{cal} = [(CV_{abs})^2 + (CV_{mass})^2 + (CV_{vol})^2]^{½}$$

where CV_{abs} is the error in the infrared absorbance, CV_{mass} is the error in the weighing of the material for the preparation of the suspension and CV_{vol} is the error in the volume measurement, which is greatly effected by temperature and includes dilution to volume in the preparation of the suspension and pipetting of the samples.

Assuming the estimated errors in the concentration measurement, mass and volume are 0.02, 0.05 and 0.05, respectively, then the total sample analysis error is on the order of 7 percent. Removing the mass error from the equation gives the expected error for one standard suspension, which is approximately 5 percent. The results from this study are within the expected precision of the analysis.

Student's t tests were performed on the data to determine if the mean absorbance per microgram values (calibration constants) established for the MINUSIL, sieved MINUSIL, SRM 1878 and sieved SRM 1878 were statistically different from the mean absorbance per microgram determined from previous work with minus 5 micrometer MINUSIL. The expected, "population" absorbance per microgram from previous work for 79 samples from eight standard suspensions is 0.00124 with a standard deviation of 0.00010. Results of the t tests show there is no significant difference in the absorbance per microgram values between the test materials and this "population" value.

Figure 1 shows a comparison of the size distribution data obtained from the Coulter Counter analyses. The comparison shows that there is no significant difference in the size distribution of the sieved fraction and the SRM 1878 (ultrasonicated). However, the unsieved MINUSIL (ultrasonicated) material has a lower percentage of particles in the size interval below 1.25 micrometers. This is probably due to the fact that the MINUSIL material has not been subjected to any additional treatment (which would tend to remove larger particles and cause a higher percentage for the smaller particles which remain) while all the other fractions have been treated. No particles with equivalent spherical volume diameters greater than 10 micrometers in size were measured using this analysis method. In addition, analysis without ultrasonic agitation of the sample shows differences in the size distributions. Visual inspection of the non-ultrasonicated suspensions reveal material too large to remain in suspension long enough to be analyzed. This indicates that large



	0.8	1.0	1.3	1.6	2.0	2.5	3.2	4.0	5.0
MIN	30.2	25.7	19.7	13.1	6.7	3.2	1.1	0.3	0.1
SMIN	32.4	26.2	18.7	12.3	6.2	2.9	1.0	0.3	0.0
SSRM	32.9	26.1	18.2	12.1	6.3	3.0	1.1	0.2	0.1
SRM	34.2	26.6	18.3	11.5	5.5	2.6	1.0	0.3	0.1
SRM(unultra)	23.7	23.2	21.1	16.3	9.0	4.5	1.6	0.5	0.1
MIN(unultra)	27.4	25.1	20.9	14.6	7.7	3.2	0.9	0.2	0.0

AVERAGE EQUIVALENT VOLUME DIAMETER, um

FIGURE 1. Comparison of Size Distributions

"particles" reported by procedures not including ultrasonic agitation are most likely attributable to agglomerations of smaller particles.

The results of the microscopic analyses are shown in Tables 4 and 5. At 10,000X, no particles larger than 10 micrometers in size were observed in either the sieved or unsieved reference materials. At 1,000X, a few particles

TABLE 4. Microscopic Analysis at 10,000X

Material	Particles/Field (Average)	Total Particles Counted	Particles > 10 μm
MINUSIL	22.6	1,180	None
Sieved MINUSIL	13.6	680	None
SRM 1878	25.6	1,280	None
Sieved SRM 1878	23.6	1,180	None

larger than 10 micrometers in size were observed in both the sieved and unsieved fractions of the reference materials. It could not be determined from the microscopic analysis alone if these particles were, in fact, silica particles. The number of greater than 10 micrometer particles observed at 1,000X constituted approximately 0.25 percent of the particles counted.

TABLE 5. Microscopic Analysis at 1,000X

Material	Particles/Field (Average)	Total Particles Counted	Particles > 10 μm
MINUSIL	45.6	2,260	5 *
Sieved MINUSIL	35.7	1,786	1
SRM 1878	47.3	2,363	3 **
Sieved SRM 1878	46.1	2,306	3

* One particle approximately 27 μm in diameter.
** One particle approximately 20 μm in diameter.
All other particles > 10 μm were between 10 and 15 μm.

CONCLUSIONS

The results of this investigation show that the minus 5 micrometer MINUSIL and SRM 1878 used in this study contained few (less than a half of a percent) particles greater than 10 micrometers in size (ESVD), confirming previously referenced work of the Bureau of Mines and SRI. The results also show that infrared absorbances obtained using the sieved and unsieved MINUSIL and SRM 1878 were not different from the "population" value determined from previous work.

Based on the results obtained during this investigation, it is recommended that if these reference materials are to be sieved before use, data should be gathered to demonstrate that sieving does not alter the characteristics of the minus 10 micrometer fraction of the material. It is also recommended that suspensions of reference material in isopropanol be ultrasonicated before use.