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On-Filter Analysis of Quartz in Respirable Coal Dust by Infrared Absorption and X-Ray Diffraction

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An infrared spectrometric and an independent X-ray diffraction method were developed for the analysis of α-quartz in airborne respirable coal dust. Sensitivity is such that the procedures can be used for analysis of the material from a single membrane filter such as is used for personal samplers by the Mining Enforcement and Safety Administration (MESA) in its enforcement program. Sensitivity down to less than 10 μg of quartz is obtainable. The methods are reasonably precise with good agreement between them. Their accuracy is limited by the unavailability of a true quartz standard. In both procedures dust is transferred ultarsonically from the collection filter to a small area of a second filter which is relatively infrared-transparent and has a weak X-ray background. This technique provides a substantial increase in area concentration and attendant sensitivity. Both methods, in principle, are capable of use with a wide variety of solid materials.

Introduction

THE ANALYSIS OR RESPIRABLE DUST is of importance to industrial hygienists because of the tendency of this form of dust to produce various types of pulmonary disease[1] such as silicosis or coal workers' pneumoconiosis (commonly known as black lung disease). Quartz and other free silica polymorphs are of particular interest because of their toxicity.[2]

At MESA, coal mine dust samples are spot-checked for quartz concentration using a Bureau-developed infrared halide pellet procedure which requires the combining of several samples to provide adequate sensitivity. This method is time-consuming and high individual exposures to quartz can be overlooked due to composite sampling. A procedure with sufficient sensitivity to provide for the analysis of 100 μg or less of quartz collected on a single membrane filter was sought. A rapid procedure is required, since it is anticipated that over 100 samples per day will be analyzed.

Other methods available did not appear adequate. Wet chemical procedures such as the well-known Talvitie Method employing phosphoric acid, differential thermal analysis, optical microscopy, and petrographic analysis are inaccurate, insensitive, and time consuming.[3,4]

As is common with many solids, it is difficult to determine quartz accurately by molecular spectroscopy for physical rather than chemical reasons. This and the difficulty of obtaining reproducible standards will be explained subsequently. Infrared and X-ray diffraction appear to be the best techniques available.[5,6] The samples are pelletized in a relatively inert matrix material such as potassium bromide for infrared or starch for X-ray diffraction.

The concept of using the collection filter itself as a matrix is not new. The use of silver membrane filters was investigated by Leroux and Powers.[7] Samples collected on silver membrane filters were analyzed for quartz using X-ray diffraction. This technique was subsequently tried by Bumsted[8] and by Knight *et al.*[9] Knight noted that the

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reported accuracy is low particulary at low quartz concentrations. The use of an internal standard is generally recommended for X-ray diffraction analysis of bulk samples in view of the lack of uniformity of mass absorption coefficients of components of various specimens.[10] However, correction for mass absorption for very thin layers should be quite small.[7]

An on-filter infrared technique useful for analysis of many solids, has previously been described by Toma and Goldberg[11] for the analysis of respirable-size pure quartz dust. The latter gave well-defined spectra when deposited on transmissive organic filters in the pure state. Respirable coal dust also yielded fairly good quartz spectra in the 800 cm^{-1} region. Superimposition of the quartz and coal dust filters yielded spectra which were quantitatively additive in quartz response.

In preliminary work done at the Bureau since development of the on-filter technique, it was found that ultrasonic redeposition of the dust in isopropanol from the collection filters onto smaller filter areas was advantageous. The original deposit is usually not homogeneous, but the dust redeposited onto the small filter areas is evenly distributed. The latter condition is desirable for infrared or X-ray diffraction analysis. In addition, when the dust is redeposited from a 37-mm dia. collection filter onto a 10.4-mm dia. filter, a concentration effect of about 13 times is achieved. This provides adequate sensitivity for analysis with the very small amounts of dust collected on single filter samples. The filter material selected for redeposition must be relatively free of infrared absorbers of X-ray scatterers in the band regions of interest.

In the work reported here, samples of respirable pure quartz and collected respirable coal dust samples are analyzed by infrared spectrophotometric procedures and by X-ray diffraction on-filter procedures; the results are compared.

Experimental Procedure

Airborne respirable coal dust is collected in mines by company personnel and Federal inspectors. Samples are prepared for analysis by redeposition onto membrane filters with high infrared transmittance and low X-ray scattering using the concentrating technique. Samples are examined by infrared methods and then they are ashed and redeposited for comparative analysis by infrared and X-ray diffraction using the same redeposited filter. Ashing reduces interferences in the infrared and X-ray spectra.

Equipment and Materials

A high resolution, double beam, infrared spectrophotometer—such as a Perkin Elmer Model 180—is employed. Infrared sample holders consist of 75 mm x 50 mm x 3 mm (thick) brass plates with a center hole corresponding to the diameter of the circular sample deposit. Spring clips hold the membrane filters in place. Filters with high infrared transmittance such as Gelman DM 450 are required.

An X-ray diffractometer with a copper-target tube, a proportional counter, a pulse height analyzer, a scaler and a recorder (General Electric XRD-6) is used. The sample holder for X-ray is the regual powder sample holder modified with a mask to hold a membrane filter in position. The mask consists of a thin piece of brass or aluminum with a center rectangular hole about the size of the holder window. One edge of the mask is hinged to the holder with pressure sensitive tape. After the filter is positioned, the opposite edge is taped to the holder also. The quartz external standard used for X-ray diffraction is Novaculite, a mass of microcrystalline quartz also known as Permaquartz.

An ultrasonic bath of at least 0.5-gallon capacity is used for transferring filter deposits. The filtration apparatus is a Millipore XX1002514 Filter Holder with a clamp modified by replacing the upper part with a flared funnel having a stem of accurately known internal diameter as shown in Figure 1. Several interchangeable funnels are prepared with stem internal diameters ranging from 7 to 18 mm to cover the anticipated range of sensitivities.

Preparation of Samples

Deposits from single collection filters or pure quartz (as reference material) are slurried ultransonically in isopropanol and redeposited by filtration through DM450 membrane filters. For single filter samples, 15 ml of isopropanol is used in a 50-ml beaker for a maximum of 2 min in the ultrasonic bath. The quartz is added most conveniently and accurately by pipetting in an aliquot of a larger amount of quartz slurried in isopropanol. Filtration to yield a homogeneous deposit is done as follows:

Apply a slight vacuum, insert a glass fiber filter into the holder as a backing, cut a DM450 filter in half and mount the superimposed halves on top of the glass fiber filter. (This is done to provide a blank reference filter, which will be exposed to the same solvent action as the half containing the sample spot.) Clamp the top half of the holder (funnel part) in place, remove the vacuum and add the ultrasonically dispersed sample slurry. Then, reapply the vacuum and immediately transfer the remaining sample with small portions of isopropanol; keep the liquid level to within 2.5 cm of the top of the funnel to avoid disturbing the deposit. When the depth of the liquid in the funnel reaches 4 cm, gently rinse down the sides of the funnel with solvent. After filtration, make four holes around the circumference of the deposit to locate this area on both the sample and blank filters. (A scriber is convenient for this purpose.) Allow both filter halves to air-dry.

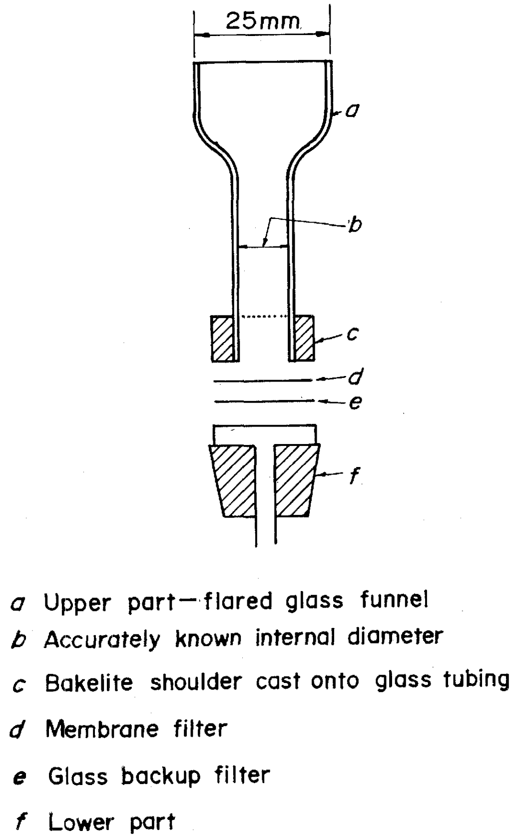

Figure 1. Funnel assembly.

Ashing of Filters

Filter halves containing deposits are held with tweezers and about 2 mm of the outside edge is trimmed off with scissors. The filter is placed in a 10-ml platinum crucible face down. The crucible is placed in a cold muffle and heated to 650 ±25° for 10 to 30 min. About 5 ml of isopropanol is added to the cooled crucible, is dispersed ultrasonically for 1 min and is redeposited on a DM450 filter.

Infrared Calibration and Analysis

A calibration curve is prepared from pure quartz using a series of filter deposits prepared from pipetted aliquots of a weighed batch of quartz in a measured volume (50 ml) of isopropanol. A convenient concentration range is 25 to 150 $\mu g/cm^2$ deposited on 10 to 18-mm dia. filter areas. Absorbance, A, is plotted as the ordinate versus concentration, C ($\mu g/cm^2$) to give a straight line passing close to the origin and having a slope, A/C, equal to the absorptivity. A slope of 1.4×10^{-3} is used for analysis.

For infrared analysis, the quartz or respirable dust samples are scanned versus blank filters in the double beam-absorbance mode from 850 to 700 cm^{-1}. The 800-cm^{-1} peak of the quartz doublet is selected for measurement. Where baseline measurement is visually difficult (as may be the case with unashed dust), a minimum to maximum measurement is made by measuring the vertical distance between a tangent to the top of the 800-cm^{-1} peak and a tangent to the valley minimum of the leading edge of that peak. In either case, quartz concentration is read from the calibration curve.

If 10 or more samples are determined, the total time per sample for analysis by the infrared procedure is about 7-8 min without ashing, or about 16-18 min with ashing.

X-Ray Diffraction Calibration and Analysis

Typical settings of the X-ray spectrometer are 45 kvp at 25 ma; a medium resolution Soller slit and 1° beam slit are employed. Dectector voltage (adjusted daily) is typically 1.5 kv. The pulse height selector cutoff EL = 2V and the window with $\triangle E = 6V$ are used.

For calibration of the instrument, select a 0.008-mm nickel filter (half the thickness recommended by Klug and Alexander[12]) to provide stronger Cu Kα intensity. Choose a 0.1° receiving slit and adjust the pulse height selector to provide the maximum signal-to-background ratio. Set the goniometer angle close to 26.65° to maximize quartz response using the Novaculite external standard. Obtain the net peak height by taking three 90-sec counts (a background count on each side of the peak and a peak maximum count). Determine the net peak height by subtracting the average of the background counts from the peak count. (Typically for quartz deposits of 100 $\mu g/cm^2$, peak counts of 300 cps, and background counts of 80 cps are measured.)

To obtain a calibration curve, use the infrared filter standards directly. Determine the net peak heights and plot a calibration curve of net peak heights versus concentration. Determine silica concentrations of unknown samples using this curve after applying the daily external standard correction factor.

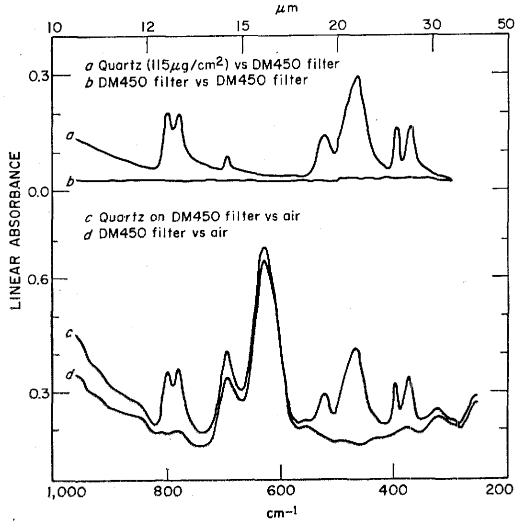

Figure 2. Absorbance spectra of pure quartz on DM450 filters.

Results

In Figure 2, the infrared absorbence spectrum of the DM450 filter, d, is compared directly with that of quartz deposit, c, on a similar filter (both measured versus air). The distinctive quartz peaks are observable. The double beam spectrum, b, of the filter (filter in both sample and reference beams) provides an adequate base line and spectrum, a, shows the double beam response of about 115 $\mu g/cm^2$ of quartz. Supersil, a commercially available quartz, screened to minus 5 μm, was employed.

The X-ray background of the DM450 filter is relatively smooth and horizontal in the vicinity of the quartz peak used ($2\theta = 26.65°$), as contrasted with the background characteristics found by Bumsted[8] for other types of membrane filters. The interference of clay minerals such as muscovite, illite, and kaolinite in this region is well known to X-ray crystallographers. In addition, other inorganic materials such as dolomite and pyrite interfere.

Generally, several clay minerals such as koalinite[13] are present in coal mine dust samples and interfere with infrared analysis. Much of the spectral response appears to be destroyed by ashing. Spectra of samples showing kaolinite prior to ashing show a disappearance of kaolinite peaks in the 800 cm^{-1} region after ashing. Quartz peaks, however, remain relatively unchanged under these conditions. Figure 3 shows the effect of ashing on coal mine dust. The 800 cm^{-1} quartz peak in spectrum b, before ashing, is larged than the corresponding peak in spectrum a, after ashing. This indicates the apparent elimination of a small amount of an impurity, possibly kaolinite, which has a moderately strong absorption band in this region. A glance at each 800 cm^{-1} region provides an indication of why baseline measurement is less appropriate before ashing than afterward. Unashed spectra such as b can best be measured by the minimum-to-maximum technique, which we have found to be reproducible. Larsen *et al.*[6] have also found this type of measurement to be accurate as is evident from their Figure 1 (p. 369).

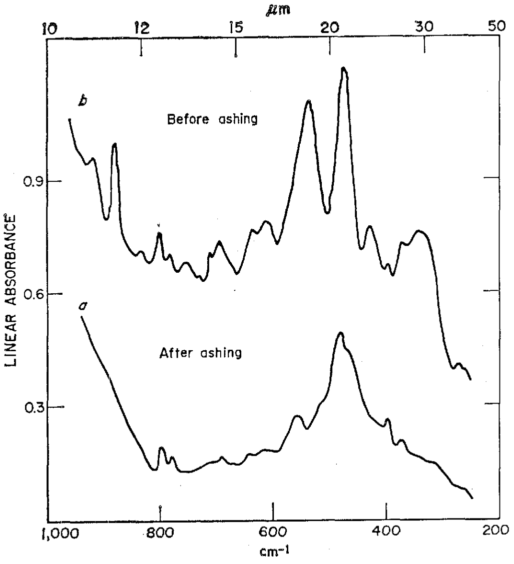

Figure 3. Effect of ashing on coal mine dust.

The efficiency of redeposition of dust from the collection filter onto a second filter was investigated using infrared measurement. First, several new 37-mm MSA filters (commonly used for dust collection by the Bureau) were ashed and redeposited individually on 10.4-mm dia. areas of DM450 filters. No quartz was found. Then, 12 field samples of respirable coal mine dust collected on MSA filters were treated by the redeposition procedure, using 10.4 mm diameter DM450 deposits, and the quartz weights were determined. The denuded MSA filters were then ashed and redeposited in a similar manner and quartz readings were obtained. A linear regression of quartz removed (X) versus quartz remaining (Y) over a dust deposit range of 0.5 to 3.0 mg was calculated yielding excellent correlation ($r = 0.969$). The slope of the regression line was 0.095 with small scatter ($Sy/x = \pm 1.75 \mu g$). A correction for residual quartz can be made by adding 10 µg to the weight of each 100 µg of quartz found in the redeposited sample. However, no correlation was observed between the total dust weight and the fraction of quartz remaining on the filter.

When quartz was analyzed by infrared or X-ray diffraction to determine precision, values close to $\pm 5\%$ were obtained either by repetitive analysis at the same concentration level or by linear regression over a range of concentrations. For example, 14 pure quartz samples containing 150 µg/cm^2 had a relative standard deviation of $\pm 5.2\%$ when they were measured at 800 cm^{-1} and were redeposited on 10.4-mm and 17.7-mm filter areas. Similar precision was obtained by repetitive analysis of a composite sample prepared by removal of dust from a large number of respirable coal mine dust-covered filters.

Forty seven field samples of respirable coal mine dust were redeposited from collection filters and the quartz content determined by infrared analysis. These samples were then ashed, redeposited, analyzed by in-

TABLE I
Intercomparison of Quartz Methods.

Comparison	N (No. samples)	Correlation coefficient (r)	Slope	Sy/x (standard error of estimate) (±μg)	y Intercept (μg)
X ashed IR Y unashed IR	44	0.966	1.07	20.5	1.63
X ashed IR Y ashed x-ray	47	0.976	0.92	14.6	0.62

frared, and finally by X-ray diffraction. The ashed samples gave the best defined peaks, and, for comparison, these results were arbitrarily taken as refernce values. Corresponding quartz weights obtained by each of the other two techniques were then compared with the reference weights by linear regression. Results are given in Tables I and II. The weights of quartz per sample ranged from 8 μg to 267 μg. The slopes and correlation coefficient are close to 1.00 and the Y axis intercepts are small. The values for standard error of estimate, Sy/x, represent vertical scatter (in μg) about the regression lines.

Discussion

Accuracy and Standards

Various sources of error have been investigated but little has been said about the accuracy of the quartz methods. Accuracy refers to the difference between a measured value and what is believed to be the true value.[14] To obtain the true value we must have reproducible standards. However, when measuring by molecular spectroscopy, such "standards" for solids often vary from batch to batch, even when materials of accurately-known chemical purity are used. This may result from variations in physical condition, such as the effects of mechanical and thermal treatment[15] which form a damaged surface layer of vitreous silica. Other physical parameters, such as particle size, particle size distribution, aspect ratio and lattice distortions, produce differing infrared or X-ray diffraction response. Physical differences in chemically similar materials make it very difficult to select reproducible standards for solids such as quartz. We must, therefore, measure our results with respect to a reference batch of material rather than to an artificial standard. In respirable coal mine dust itself, some variation in spectral response may occur due to the physical characteristics of the quartz present.

Inferences

Spectral interferences due to the presence of other molecular species should be considered. Other crystalline polymorphs of silica, such as cristobalite and tridymite, interfere with the infrared determination of quartz. However, they have not been detected in coal. Noncrystalline (amorphous) or vitreous) silica, if present, would be difficult to determine due to its weak spectral response. Organic material in the coal and several clay minerals such as illite, kaolinite, and muscovite interfere with infrared or X-ray diffraction analyses. Much of this interference appears to be eliminated by ashing the sample.

Effects of Particle Size

As mentioned earlier, particle size and size distribution have a marked effect on spectral response. In the respirable range, infrared response increases with decreasing particle size,[16] and X-ray response decreases or levels off with decreasing particle size.[17] The sharply differing particle size effects of infrared and X-ray diffraction would accentuate any differences in size distribution of individual respirable dust samples. The fact that our comparison values were close to-

TABLE II
Regression of IR Ashed versus IR Unashed and X-ray Ashed Weights (μg).

X	Y	
IR Ashed	IR Unashed	X-ray Ashed
9.	7.	8.
37.	43.	45.
67	79	60
49	67	49
37	43	26
43	58	31
12	6	14
25	31	28
21	15	14
25	46	12
49	60	31
21	25	24
9	3	10
43	60	31
79	88	73
39	39	40
49	49	34
52	49	47
85	88	85
116	158	100
31	18	28
12	—	9
110	122	80
116	137	87
27	—	26
70	79	46
17	17	20
17	17	10
262	262	267
71	71	76
17	10	25
235	297	213
123	174	142
201	230	221
61	105	34
44	44	56
150	123	113
245	279	245
27	—	37
65	51	78
34	10	49
218	174	184
61	44	66
113	157	105
245	235	194
17	—	22
85	88	85

gether is an indirect indication that the size distributions did not vary greatly from sample to sample. This may be due to the classification that results from the use of the 10-mm nylon cyclone employed for size-selection.

Significance of Comparison Data

Correlation coefficients close to 1.00 indicate a high degree of correlation of the alternate methods with the reference method. Slopes close to 1.00 are an indication of reasonable equivalence of the procedures. Also, concentration-dependent interferences, such as the response from other chemical species, are small or, if significant, affect all the methods equally. The small y intercepts indicate reliability of the methods down to low quartz concentrations.

Advantages of the Methods

The independent on-filter methods agree well with each other. In addition, quantitative transfer of quartz has been experimentally demonstrated. The methods are rapid as compared with others available. Clear-cut advantages of the on-filter methods are sensitivity and quantitative analysis of single filter samples. These are important in terms of supplying data for enforcement laws that protect the health of the miner.

The difficulty in obtaining true values is related to the difficulty of obtaining reliable standards for quartz and to the unknown physical characteristics of the silica in the coal mine dust samples. We have seen variations of roughly ±20% in infrared response of various batches of pure quartz which we have analyzed.

These procedures are potentially applicable to any solid that gives a significant infrared or X-ray diffraction response and has small filter matrix or other interference in the appropriate band regions.

Additional work should be done in acquiring true standards, evaluation of interferences, and effect of ashing. Careful examination of the silica in the coal itself is also in order.

Summary

An infrared spectrometric and an X-ray

diffraction procedure were developed for rapid analysis of microgram quantities of quartz deposited on a single field filter sample of respirable coal mine dust. Good agreement was obtained between the two independent methods for the quartz content in 47 respirable coal dust samples collected in mines by size-selective samplers. A reliable quartz standard is required because of the varied spectral response of different batches of quartz. The methods are shown to be reliable for the kinds of samples studied.

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American Occupational Medical Association

The name of the organization formerly known as the Industrial Medical Association has been changed to American Occupational Medical Association. The name change was voted by the membership at its annual business meeting in Bal Harbour, Florida, on May 1, 1974. The headquarters office is 150 North Wacker Drive, Chicago, Illinois 60606. Telephone: (312) 782-2166.