The Determination of the Quartz Content of Gravimetric Mass Samples of Airborne Dust by an X-Ray Technique

By A. A. BRADLEY*

SYNOPSIS

The thin-film technique by which respirable airborne dust containing quartz is deposited on membrane filters (organic or silver) and then analyzed for quartz by X-ray diffraction, is now firmly established. For CuKα radiation, absorption effects are usually negligible for densities of deposition of less than 0,70 mg cm^{-2}, so that the X-ray response is proportional to the mass of quartz on the filter. If the density of deposition exceeds this value, absorption must be taken into account.

A method for measuring the absorption which occurs in specimens deposited on organic membrane filters is described. A correction factor which is calculated and applied extends the useful range of densities of deposition up to about 2,5 mg cm^{-2}. The potential of this type of sampling as a tool for the assessment and control of dusty environments is discussed.

INTRODUCTION

An empirical X-ray diffraction technique for analyzing small samples for quartz and cristobalite, in the form of thin films, was reported by Talvitie and Brewer[1] in 1962. Specimens vacuum-deposited onto organic membrane filters from air or water suspensions were used. The usefulness of this technique stems from the simplicity of the analytical procedure. If absorption effects are negligible, the X-ray response is proportional to the mass deposited on the filter.

These results were confirmed and it was demonstrated theoretically by Bradley,[2] in 1967, that, for quartzitic specimens, CuKα radiation and a Bragg angle of 13,3°, absorption effects should be negligible for densities of deposition of up to 0,7 mg cm^{-2}.

It was shown by Leroux and Powers[3] in 1969 that for many purposes porous silver filters are superior to organic membrane filters since a lower background and thus a better sensitivity are obtained. In 1973 a method was outlined by Leroux *et al*[4] for obtaining a corrected assessment of the mass of quartz on the filter by measuring the transmittance of specimens too thick for absorption to be neglected. This method is applicable to porous silver filters.

A similar method which was developed independently by the Chamber of Mines of South Africa involved the use of organic membrane filters and was, therefore, different in some respects from the method of Leroux.[4] In this paper a technique for determining the quartz content, corrected for absorption, of specimens deposited on organic membrane filters is described. Experimental confirmation of absorption corrections is shown for densities of deposition up to about 2,5 mg cm^{-2} using copper radiation and a Bragg angle of 13,3°.

EXPERIMENTAL CONDITIONS

Procedures for preparing specimens are described in detail elsewhere[1-6] and that used in the Chamber of Mines Laboratory has been described by Bradley.[2] Standard specimens used for control are prepared from aliquots taken from a standard suspension of quartz in water and deposited by vacuum filtration. Specimens used for analysis are prepared in the same way, or, in the case of airborne dust, are vacuum-deposited directly using one of the mass samplers now available. Sampling spots should be deposited evenly with clear sharp edges so that the area can be measured. Circular spots are particularly suitable.

A spinning specimen holder is used but is not essential if the dust is fine. The X-ray beam is collimated so that the beam section intercepted by the sampling spot falls completely within the spot. The whole of the X-ray beam but not all of the sampling spot area, therefore, is used.

Nickel oxide powder, mixed to a thick putty with epoxy resin, pressed into a sample holder and sanded flat after hardening, is used as a permanent external standard. The 200 NiO reflection from this standard is calibrated against the 101 quartz reflection obtained from at least 10 thick packings made of pure quartz powder. The quartz powder should be fine enough to give an inter-sample coefficient of variation of less than 4 per cent.

THEORETICAL

The calculations that follow are specifically for quartz analysis using the 101 reflection, CuKα radiation and the 200 NiO reflection from the permanent NiO standard as a reference. The method can readily be adapted to other conditions.

Absorption negligible

For a thin layer of pure quartz powder deposited on a membrane filter

$$I_q = I_Q\left(1 - e^{-2\mu x/\sin\theta}\right) \quad \ldots\ldots\ldots (1)$$

where μ = linear absorption coefficient of the specimen,
x = thickness of the specimen (cm),
θ = Bragg angle (13,3°),
I_q = intensity of the quartz reflection from the thin quartz specimen, and
I_Q = intensity of the quartz reflection at 13,3° from a pure quartz specimen effectively infinitely thick.

It should be noted that I_Q can be defined as a saturated reflection. For a sample having an absorption coefficient similar to that of quartz, a value of $x = 0{,}05$ cm is sufficient to give a saturated reflection. For pure quartz the slope at $x = o$ of the curve given by equation (1) is

$$I_q^1 = 2I_Q\mu x/\sin\theta \quad \ldots\ldots\ldots\ldots (2)$$

*Senior Research Officer, Metallurgy Division, Research Organisation, Chamber of Mines of South Africa.

and represents the response that would be obtained in the absence of absorption. Table I shows some points on these two curves calculated for pure quartz. For convenience the density of quartz powder has been assumed to be 1 g cm^{-3} so that μ is 34,9, the same as the mass absorption coefficient.

TABLE I

ABSORPTION EFFECTS CALCULATED FOR SOME THIN QUARTZ SPECIMENS

$x/\sin 13{,}3°$ (cm)	mg cm^{-2} on filter for $\theta = 13{,}3°$	I_q/I_Q (normal case)	$I_q{}^1/I_Q$ (No absorption)	$\frac{100\,(I_q{}^1-I_q)}{I_q}$ (% low)
0,003 20	0,736	0,20	0,223 1	10,3
0,001 51	0,347	0,10	0,105 3	5,0
0,000 754	0,169	0,05	0,051 2	2,3

It will be seen that as x increases the value of I_q deviates further and further from that of $I_q{}^1$. I_q is 10,3 per cent lower than $I_q{}^1$ when the density of deposition is 0,736 mg cm^{-2}. A good compromise would be to use a line through the points (0;0) and (0,347;0,1) for assessing specimens as follows

$$\text{mg quartz on filter} = 0{,}347AI_q/0{,}1I_Q \quad \ldots\ldots (3)$$

where A = area of the sampling spot in cm^2.

I_Q can be replaced by I_s/C

where I_s = intensity of the 200 NiO reflection at 21,6° from the permanent standard.

$$C = I_s/I_Q$$

For a fixed size of sampling spot all the constants can be consolidated to a single constant K_1 so that

$$\text{mg quartz on filter} = K_1 I_q/I_s \quad \ldots\ldots\ldots (4)$$

It can be shown that this equation is valid for specimens of mass of up to 0,7 mg containing only a portion of quartz, provided the mass absorption coefficient does not greatly exceed that of quartz. Samples at the bottom of the range will be over-estimated by about 5 per cent and samples at the top of the range will be under-estimated by about 5 per cent, but the analytical procedure is very simple and rapid.

Absorption not negligible

Consider the reflection $I_s{}^1$ from the NiO reference standard after the beam has passed twice through a thin specimen of pure quartz, as shown in Fig. 1, ignoring for the present the filter:

$$I_s{}^1 = I_s e^{-2\mu x/\sin\theta_1}$$

that is,

$$I_s{}^1/I_s = e^{-2\mu x/\sin\theta_1}$$

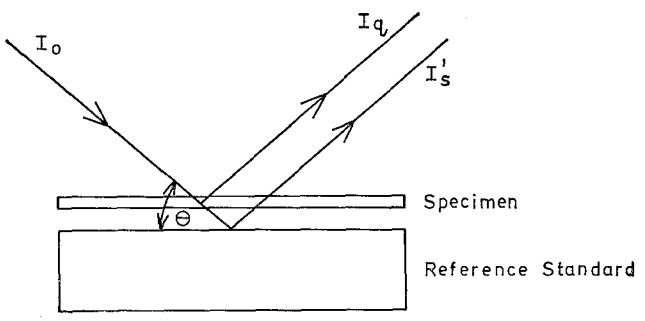

Fig. 1. Arrangement for measuring the amount of absorption present in the case of a Bragg reflection from a thin specimen.

Similarly for the thin quartz specimen, from equation (1)

$$I_q/I_Q = 1 - e^{-2\mu x/\sin\theta_2}$$

therefore,

$$I_q/I_Q = 1 - (I_s{}^1/I_s)^{\sin\theta_1/\sin\theta_2}$$

For $\theta_1 = 21{,}6°$ and $\theta_2 = 13{,}3°$

$$I_q/I_Q = 1 - (I_s{}^1/I_s)^{1,6} \quad \ldots\ldots\ldots (5)$$

Therefore, by measuring $I_s{}^1$ and I_s the value of I_q/I_Q for this particular specimen can be determined. If the term $1 - (I_s{}^1/I_s)^{1,6}$ is greater than 0,2 equation (4) cannot be used, and an absorption correction must be made. This is done by using equations (1) and (2) to find $I_q{}^1/I_q$, the correction factor, as shown in Table II.

TABLE II

CORRECTION FACTORS CALCULATED FOR VARIOUS VALUES OF MEASURED ABSORPTION

$I_s{}^1/I_s$	$(I_s{}^1/I_s)^{1,6}$	I_q/I_Q	$I_q{}^1/I_Q$	Correction factor $I_q{}^1/I_q$
1,0	1,0	0,00	0,00	1,00
0,9	0,844	0,156	0,169	1,09
0,8	0,700	0,300	0,357	1,19
0,7	0,565	0,435	0,571	1,32
0,6	0,441	0,559	0,819	1,47
0,5	0,330	0,670	1,110	1,65
0,4	0,230	0,769	1,467	1,91

The mass of quartz on the filter would be estimated as follows, using equation (2) and the points (0;0), (0,347;0,1053) from Table I:

$$\text{mg quartz on filter} = 0{,}347AI_qFC/0{,}105\,3I_s \quad \ldots (6)$$

where F = correction factor.

As before, all the constants can be consolidated into one constant, K_2, so that

$$\text{mg quartz on filter} = K_2 F I_q/I_s \quad \ldots\ldots\ldots (7)$$

The correction factor is conveniently obtained from the curve in Fig. 2.

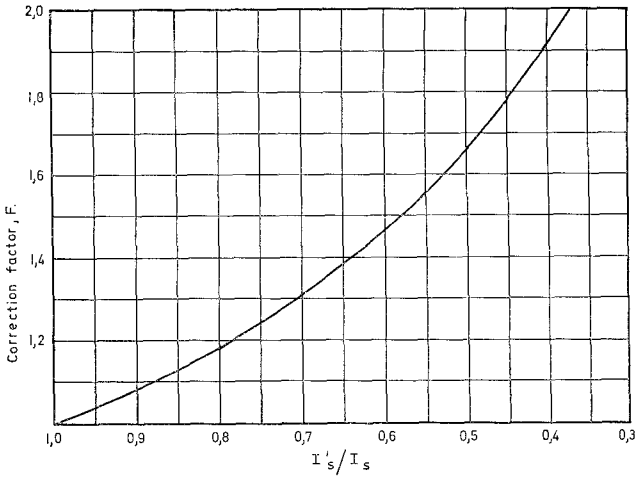

Fig. 2. Absorption correction factor, F, for the quartz reflection at $\theta = 13{,}3°$ obtained from $I_s{}^1/I_s$ measured at $\theta = 21{,}6$.

Two points require to be clarified. First, $I_s{}^1$ is necessarily measured with the specimen on a filter. I_s should be measured with the standard covered by a clean filter of the same weight.

The correct ratio of I_s^1/I_s will thus be obtained. Alternatively, I_s can be measured with the standard uncovered and the effect of the filter estimated by means of a curve such as that in Fig. 3.

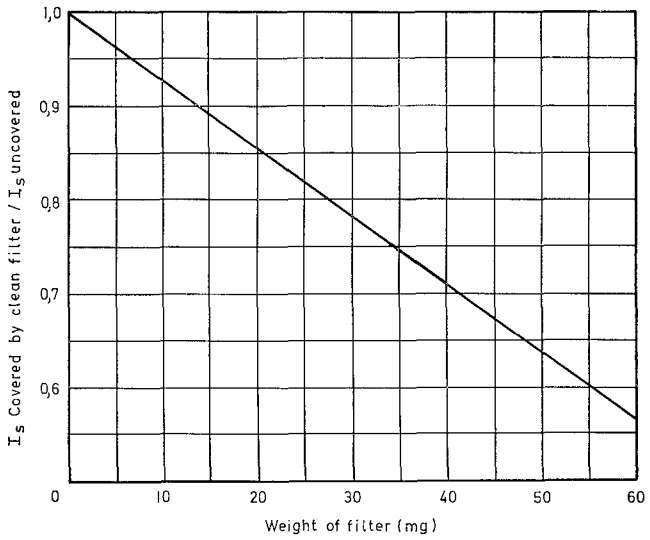

Fig. 3. Curve for estimating the absorption contributed by the filter.

Second, it can be shown that the same procedure can be used for specimens of mixed composition of which only a fraction is quartz.

RESULTS

Test specimens were made up using pure quartz powder and a mixture of equal masses of quartz and Fe_2O_3. The masses on the filters were determined by depositing from aliquots taken from standard suspensions of quartz in water and were not weighed on the filters. The quartz reflection was measured by scanning over 2° (2θ) and peak heights were used. The apparatus used was a Hilger and Watts diffractometer with a power of 150W. Four minutes were required to draw one peak using a chart recorder. A 22-mm sampling spot was used. The results obtained are shown in Table III. In some cases the corrections applied are large.

TABLE III

RESULTS UNCORRECTED AND CORRECTED FOR ABSORPTION USING TEST SAMPLES

Sample	mg material on filter	mg quartz assessed by X-ray	
		Uncorrected	Corrected
Pure quartz	1,5	1,51	1,62
	3,0	2,87	3,27
	4,5	3,46	4,26
	6,0	4,38	5,65
	10,0	6,66	9,76
50% quartz +50% Fe_2O_3	1,5	0,72	0,81
	3,0	0,99	1,34
	4,5	1,27	1,92
	6,0	1,52	2,71

DISCUSSION

Although care may be taken during a dust survey to choose a sampling period to ensure that a reasonable density of deposition can be expected, specimens will sooner or later be obtained which are excessively heavy because of unusually bad dust conditions. It is important to assess such samples accurately. This can now be done for samples on either organic or silver membranes without the necessity for ashing and re-depositing the dust which is a time-consuming procedure.

The mass of silver filters is very stable so that the total mass of the specimen can be determined more accurately than that of a specimen on an organic filter. If the mass of only the quartz is required, this advantage is not so marked. If high sampling rates are required, organic filters are superior because the necessarily larger pore size can lead, in the case of silver filters, to entry losses, that is, dust is drawn into the filter where it is shielded from the X-ray beam.

It is fortunate that quartz is particularly easy to analyze by X-ray diffraction. Preferred orientation effects which are so troublesome with mica and asbestos, are absent. Interference with the 101 quartz reflection is the most serious problem. Some aspects of this problem were reported by Knight,[5] in 1972, who used three different quartz reflections. The only mineral in samples from the South African gold mines likely to cause interference is muscovite. Tests with artificial samples have shown that if the mass of muscovite present exceeds 25 per cent of the mass of the quartz present a significant enhancement of the quartz peak can occur because of overlapping of the 006 muscovite reflection and the 101 quartz reflection. The presence of muscovite can be established by scanning the 002 muscovite reflection at a Bragg angle of 4,4° which operation is part of the analytical routine used at this laboratory. It is likely that a satisfactory correction can be made by subtracting a proportion of this reflection from the quartz reflection, but this is still being investigated. At the moment the presence of muscovite is merely noted.

The sensitivity of this method of analysis is remarkable. A limit of detection of 0,015 mg cm^{-2} has been achieved in this laboratory using a low-power diffractometer. No difficulty was experienced when a sampling spot 12 mm in diameter and an area of approximately one cm^2 was used. Much better sensitivities have been obtained with modern high-power diffractometers.

Results published by Beadle and Bradley[6] in 1970 were obtained using the Corner House Laboratories gravimetric sampler and organic membrane filters. This apparatus had a sampling rate of 10 litres per minute for a sampling spot 22 mm in diameter. If a maximum permissible mass of 0,1 mg of quartz per m^3 is assumed it would be necessary to sample for 100 minutes to determine this with reasonable precision. If a 12-mm spot was used the sampling rate would be 2,5 litres per minute.

It is conceivable that with a modern diffractometer and a slightly higher sampling rate a sample could be taken in 30 minutes or less which would indicate whether or not the concentration of quartz in the air was above the threshold limit, so that it would be possible to use this technique for routine sampling as well as for dust surveys. If the mass of only the quartz, and not the total mass, were acceptable, it should be possible to design a sampler taking a 55-mm filter, on which, say, six 12-mm spots could be deposited, while the filter holder is rotated 60° after each spot in a manner similar to sampling with a konimeter.

There appears to be ample incentive to explore the full potential of this type of sampling.

ACKNOWLEDGEMENTS

The co-operation of Miss E. F. Peter and Mr. J. H. Quilliam and colleagues and the permission of the Chamber of Mines of South Africa to publish this paper are gratefully acknowledged.

REFERENCES

1. TALVITIE, N. A., and BREWER, L. W. Separation and analysis of dust in lung tissue. *Amer. Ind. Hyg. Ass. J.*, vol. 23, 1962, pp. 58-61.
2. BRADLEY, A. A. The determination of quartz in small samples by an X-ray technique. *J. Sci. Instrum.*, vol. 44, 1967, pp. 287-288.
3. LEROUX, J., and POWERS, C. A. Direct X-ray diffraction quantitative analysis of quartz in industrial dust films deposited on silver membrane. *Staub Reinhalt. Luft* 29: No. 5 (1969) (English translation).
4. LEROUX, J., DAVEY, A. B. C., and PAILLARD, A. Proposed standard methodology for the evaluation of silicosis hazards. *Amer. Ind. Hyg. Ass. J.*, vol. 34, 1973, pp. 409-417.
5. KNIGHT, G. X-ray diffraction analysis of quartz in respirable dust: brief description and procedure. Proceedings Roundtable discussion, Dec. 6-7, 1972. Analytical techniques for quartz. American Conference of Governmental Industrial Hygienists.
6. BEADLE, D. G., and BRADLEY, A. A. The composition of airborne dust in South African gold mines. Pneumoconiosis. Proceedings of the International Conference, Johannesburg, 1969, pp. 426-466 (1970).