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An International Comparison of the Crystallinity of Calibration Materials for the Analysis of Respirable α-Quartz Using X-Ray Diffraction and a Comparison with Results from the Infrared KBr Disc Method

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It is important that analytical results, produced to demonstrate compliance with exposure limits are comparable, to ensure controls are monitored to similar standards. Correcting a measurement result of respirable α-quartz for the percentage of crystalline material in the calibration dust is good analytical practice and significant changes in the values assigned to calibration materials will affect the interpretation of results by an analyst or occupational hygiene professional. The reissue of the certification for the quartz reference material NIST 1878a in 2005 and differences in comparative values obtained by other work created uncertainty about the values of crystallinity assigned to national calibration dusts for α-quartz. Members of an International Organization for Standardization working group for silica measurement ISO/TC146/SC2/WG7 collaborated to investigate the comparability of results by X-ray diffraction (XRD) and to reach a consensus.

This paper lists the values recommended by the working group for use with XRD analysis. The values for crystallinity obtained for some of the materials (NIST 1878, Min-U-Sil5 and A9950) were 6–7% lower than the original certification or estimates reported in other comparisons. Crystallinity values obtained by XRD gave a good correlation with BET surface area measurements ($r^2 = 0.91$) but not with mean aerodynamic particle size ($r^2 = 0.31$). Subsamples of two of the materials (A9950 Respirable and Quin 1 Respirable) with smaller particle size distribution than their parent material did not show any significant change in their values for crystallinity, suggesting that the area XRD measurement of these materials within the particle size range collected is more dependent on how the quartz is formed geologically or how it is processed for use. A comparison of results from laboratories using the infrared (IR) and KBr disc method showed that this method is more dependent than XRD on differences in the particle size within the respirable size range, whereas the XRD values were more consistent between the different measurement values obtained on each material. It was not possible to assign a value for percentage purity to each material for users of IR analysis.

This work suggests that differences are likely to exist between the results from XRD and IR analysis when measuring 'real' workplace samples and highlights the importance of matching the particle size of the calibration material to the particle size of the workplace dust for measurements of crystalline quartz.

Keywords: analysis; crystallinity; infrared; quartz; silica; x-ray diffraction

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INTRODUCTION

The reduction in the incidence of cases of silicosis is a priority for many countries and the assessment of an individual's exposure through measurement is key to the interpretation of epidemiological evidence for the establishment of workplace exposure limits. Some countries have recently lowered or are in the process of reviewing their workplace exposure limits for respirable crystalline silica (RCS) based on the evaluation of epidemiological studies. However, it is becoming increasingly difficult for the current methods and instruments to accurately measure the new exposure limits required by regulators. Variability of results from different methods or approaches adds to the uncertainty of the interpretation of these results by an occupational health professional, especially when the mass measured on the filter for analysis is small enough (<50 μg) to result in a relatively large measurement error ($>25\%$ at 2σ). The reliability of the current analytical methods when measuring RCS at the new or proposed exposure limits of 0.1, 0.05, or 0.025 mg m^{-3} is discussed in detail in a paper by Stacey (2005). A large analytical imprecision makes the identification of significant differences between the exposure of workers and the effectiveness of controls near or at the exposure limit difficult. The sensitivity of some measurements on samples of air with a concentration of <0.05 mg m^{-3}, using current sampling apparatus sampling at ~ 2 l min^{-1}, is poor. The analysis also becomes more problematic at this level (<50 μg mass on the filter) because the analyst cannot be confident about the presence of silica unless additional confirmatory evidence is available. As the exposure limit for quartz is lowered, the accurate determination of the sensitivity of analysis becomes more important. Work by Eller et al. (1999) has indicated that one of the major sources of variability in results between laboratories is difference in the calibration dust materials used for analysis.

This paper reports the work of members of the International Organisation for Standardization (ISO) working group for silica measurement ISO/TC146/SC2/WG7 to establish a consensus on the crystalline silica content of the measurement standards for α quartz. Quartz is the most commonly encountered polymorph of crystalline silica measured in the workplace and several different respirable dust calibration materials are available. Particles of quartz are not completely crystalline and have a disordered semi-crystalline surface associated with them. Traces of amorphous silica are present as very small particles and trace contaminants, such as kaolinite or feldspar minerals, are often associated with quartz, and are not easy to remove without altering the crystalline state of the material. The correction of results for the crystallinity of the calibration material is good analytical practice for the analysis of RCS (ISO, 2007).

The National Bureau of Standards [now the National Institute of Standards and Technology (NIST)] in the USA produced a reference material in 1983, Standard Reference Material (SRM) 1878, that was certified as 95.5 ± 1.1% crystalline α quartz. The certified crystalline purity was determined using X-ray diffraction (XRD) and a modified 'spiking' technique for the amorphous content. Since then several national institutes have compared the standards they developed with the NIST SRM 1878 and its certified value for crystallinity. Different approaches to the assessment of the percentage crystallinity in these materials have produced different results. Papers by Chisholm (2005) and Verma and Shaw (2005) both propose explanations for these differences. When stocks of NIST SRM 1878 were exhausted, it was replaced in 1999 with the material NIST SRM 1878a and certified as containing 100% crystalline quartz. The certified crystalline purity was determined using a Rietveld analysis of neutron time-of-flight (TOF) powder diffraction data. Rietveld analysis (Young 2003) is a way of determining the crystallinity of a material from the difference between the profile of the material analysed under specified conditions and the ideal profile obtained from information about the materials crystal structure. The homogeneity of NIST SRM 1878a was determined using Rietveld analyses of X-ray powder diffraction data. The certification method utilized NIST SRM 676 (Alumina Internal Standard for Quantitative Analysis by X-Ray Powder Diffraction). However, this certification was retracted in 2006 and replaced with a certificate stating 93.7 ± 0.21%. The revised percentage crystalline material in NIST SRM 1878a was determined subsequent to the revision of the certification for the Alumina Internal Standard, NIST SRM 676 using a Rietveld type data processing approach and neutron activation analysis (NIST, 2005).

Verma and Shaw (2005) compared NIST SRM 1878 with NIST SRM 1878a using the KBr disc infrared (IR) method and found that NIST SRM 1878 had a less sensitive calibration response by ~3%. This would indicate that the two standards were very similar. XRD analysis is usually preferred for this type of analysis because, strictly, the crystallinity of materials can only be determined using this instrumental technique and in most countries RCS is specified in occupational exposure limits. The certification for NIST SRM 1878 has not been changed or withdrawn, and this SRM may still be in use. In 2006, members of the ISO working group agreed to participate in a laboratory comparison by XRD to assess the crystallinity of the calibration materials that are available for quartz analysis in order to reach an agreement on the crystallinity in each material and investigate the comparability of results.

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APPROACH

The analysis approach agreed upon by members of the working group is based on a method published by Altree-Williams *et al.* (1977). The approach is described in Kauffer *et al.* (2002) and the procedure involves preparing test samples of known amounts of powder on 0.45 μm pore size polycarbonate filters. Each laboratory developed a calibration line within the range 1.5–6 mg for each powder using XRD, corrected each result for absorption and drift, and compared the value for the slope of the relationship between response and mass of each powder to that of the chosen reference material, NIST SRM 1878a. The powders involved in the study are listed in Table 1.

In addition to the powders listed in Table 1, two other materials were studied. The Instituto Nacional de Silicosis (NIS) in Spain examined the reference material BCR66, which is used by some laboratories as a calibration standard for quartz, although it is sold as a particle size analysis reference material. The Health and Safety Laboratory (HSL) in the UK examined the crystallinity of the fraction of A9950 obtained when sampled by a Higgins-Dewell type cyclone operating at $2.2\ \mathrm{l\,min^{-1}}$.

RESULTS

Quartz has four reflections in its XRD pattern that are commonly used by laboratories for quantification. When using copper $K\alpha$ radiation, these are as follows: (i) the 100 reflection (20.9 degrees 2θ) with a relative intensity of $\sim$25%, (ii) the 101 reflection (26.6 degrees 2θ) with a relative intensity of 100%, (iii) 112 reflection (50.1 degrees 2θ) with a relative intensity of $\sim$14–9%, and (iv) the 211 reflection (60.1 degrees 2θ) with a relative intensity of $\sim$9–7%. The different analytical instruments and instrumental parameters used by each laboratory produced calibration lines with different sensitivities for each of the reflections. In order to combine these data, the results from each participating laboratory were normalized by determining the average slope for each X-ray reflection for NIST SRM 1878a and then applying a factor to each result for each participating laboratory. Tables 2–5 summarize the results obtained from the regression lines for all the reflections to highlight the slight differences in response for each reflection. The estimate of the uncertainty of the prediction of the relative crystallinity of each material obtained from the ratio of the slopes $\frac{b_\mathrm{m}}{b_\mathrm{ref}}$ was quantified from the standard error of each slope and calculated as $\sqrt{s_\mathrm{m}^2 + s_\mathrm{ref}^2}$, where s_m *i*s the standard error of the slope of the regression of a test material b_m and s_ref is the standard error of the slope of the regression of NIST SRM 1878a, b_ref. The values of crystallinity recommended by the working group for each material are listed in Table 6. The values

Table 1. Calibration test materials involved in the laboratory comparison

Powder	Donor	Origin	Details
NIST SRM 1878a	NIST	US Defense Stockpile, Brazilian quartz	Crushed, jet milled and acid washed (HF)
NIST SRM 1878	NIST	Min-U-Sil5	Not known
Min-U-Sil5	NIOSH	US Silica	Ground, not acid washed
A9950	HSL	Quartzwerke Germany, Sikron F600	Sedimentation
Quin 1 Bulk	INRS	Moulin des Près, Saint Aubin sur Scie, France	Not known
Quin 1 Respirable (Res)	INRS	Moulin des Près, Saint Aubin sur Scie, France	Quin 1 Bulk separated using a Dorr-Oliver cyclone
DQ12	HSL	Old German Standard; tertiary quartz sand from Dörentrup	Centrifugal separation in air

HF, hydrofluoric acid.

Table 2. Summary of results for the 101 diffraction peak (26.6 degrees 2θ)

Material	Number of laboratories participating	Slope	Correlation coefficient	Ratio with NIST SRM 1878a	Percentage relative crystallinity	Uncertainty of the prediction (1σ)
NIST SRM 1878a	4	731	0.994	1	93.7	1.17
Quin 1 Bulk	4	753	0.991	1.030	96.6	2.17
Quin 1 Res	4	720	0.998	0.985	92.3	2.43
A9950 Res	1	707	0.999	0.968	90.7	1.99
A9950	4	704	0.995	0.963	90.2	1.97
Min-U-Sil	3	697	0.999	0.953	89.3	1.55
NIST SRM 1878	4	689	0.995	0.942	88.2	2.09
BCR66	1	626	0.985	0.856	80.3	1.92
DQ12	4	575	0.999	0.787	73.7	2.90

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Table 3. Summary of results for the 100 diffraction peak (20.9 degrees 2θ)

Material	Number of laboratories participating	Slope	Correlation coefficient	Ratio with NIST SRM 1878a	Percentage relative crystallinity	Uncertainty of the prediction (1σ)
NIST SRM 1878a	3	106.3	0.995	1	93.7	1.37
Quin 1 Bulk	3	105.6	0.982	0.993	93.1	2.98
Quin 1 Res	3	107.8	0.991	1.014	95.0	2.34
A9950 Res	1	103.4	0.998	0.972	91.1	2.69
A9950	3	99.8	0.993	0.939	88.0	2.11
Min-U-Sil	3	99.7	0.997	0.938	87.9	1.76
NIST SRM 1878	3	98.3	0.997	0.924	86.7	2.21
BCR66	1	90.5	0.997	0.851	79.8	2.18
DQ12	3	86.5	0.996	0.814	76.2	1.86

Table 4. Summary of results for the 112 diffraction peak (50.1 degrees 2θ)

Material	Number of laboratories participating	Slope	Correlation coefficient	Ratio with NIST SRM 1878a	Percentage relative crystallinity	Uncertainty of the prediction (1σ)
NIST SRM 1878a	3	61.0	0.998	1	93.7	0.81
Quin 1 Bulk	3	62.1	0.997	1.016	95.2	2.78
Quin 1 Res	3	62.0	0.992	1.018	95.4	1.96
A9950 Res	1	58.2	0.995	0.955	89.5	3.7
A9950	3	58.3	0.996	0.956	89.6	1.51
Min-U-Sil	3	58.2	0.999	0.954	89.4	1.37
NIST SRM 1878	3	57.6	0.998	0.944	88.5	1.60
BCR66	1	51.4	0.998	0.843	78.9	2.35
DQ12	3	47.9	0.979	0.785	73.6	3.02

Table 5. Summary of results for the 211 diffraction peak (60.0 degrees 2θ)

Material	Number of laboratories participating	Slope	Correlation coefficient	Ratio with NIST SRM 1878a	Percentage relative crystallinity	Uncertainty of the prediction (1σ)
NIST SRM 1878a	2	51	0.997	1	93.7	1.3
Quin 1 Bulk	2	52.1	0.998	1.02	95.7	2.05
Quin 1 Res	2	52.6	0.988	1.03	96.6	2.85
A9950	2	48.6	0.997	0.953	89.3	1.80
Min-U-Sil	2	47.8	0.998	0.937	87.8	1.72
NIST SRM 1878	2	47.1	0.999	0.924	86.5	1.90
BCR66	1	41.0	0.997	0.804	75.3	2.77
DQ12	2	36.7	0.977	0.719	67.4	3.75

in Table 6 are the average of the four reflections weighted for the number of laboratories contributing data to each reflection. For comparison, HSL, NIS, and the Institut National de Recherche et de Sécurité (INRS) analysed the calibration dusts using an IR and a KBr disc analytical procedure similar to the National Institute for Occupational Safety and Health (NIOSH) method 7602 (NIOSH, 2005). The results for the IR KBr disc method for five absorbance bands at 798, 780, 695, 398, and 374 cm^{-1} are shown in Tables 8–12.

DISCUSSION

Crystallinity values

The values of crystallinity for the individual XRD reflections for each material in Tables 2–5 are generally consistent and within the expanded uncertainty (2σ). The occasional small difference between a value obtained for a particular reflection and the consensus value listed in Table 6 for a specific material is explained by the variability of these data, rather than preferred orientation of the crystals in

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Table 6. Recommended values for crystallinity and their uncertainty

Material	Percentage crystallinity	Uncertainty of the prediction (%) (1σ)
NIST SRM 1878a	93.7	0.21[a]
Quin 1 Bulk	95.2	2.51
Quin 1 Res	94.5	2.36
A9950	89.3	1.86
Min-U-Sil5	88.7	1.60
NIST SRM 1878	87.6	1.97
BCR66	78.6	2.31
DQ12	73.3	2.81

[a]From the NIST certification.

the mount. No data points were excluded in the determination of the values for crystallinity. The average values listed in Table 6 are weighted towards the number of laboratories contributing data to each reflection. As the majority of participating laboratories analysed the most sensitive reflections of 101, 100, and 211, this weights the values in Table 6 towards those reflections that are visible when measuring <50 μg of crystalline silica on the filter. The silica measurement group WG7 is confident that the values reported in Table 6 provide an accurate indication of the crystallinity of each material.

Particle size differences

Figure 1 shows particle size data, collected at HSL, for eight of the materials tested using an AeroSizer and AeroDisperser [Amherst Process Instruments Inc., (API), Minneapolis, MA, USA], an aerodynamic particle sizer incorporating a TOF aerosol beam spectrometer. Data from the certificate on NIST SRM 1878a are also plotted in Fig. 1 and exhibit a good match for the results obtained on the same material at HSL. The revised certificate for NIST SRM 1878a states that the particle size distribution measurements were obtained by laser scattering. There are some differences between the order of cumulative curves for particle size shown in Fig. 1 and the order of the values assigned for the crystallinity of each material in Table 6. The particle size results comparing A9950 with the dust collected when sampled by a Higgins-Dewell cyclone (A9950 Res) and comparing Quin 1 with the same dust separated using a Dorr-Oliver cyclone (Quin 1 Res) shown in Fig. 1 confirm that a further size separation effect occurs when these calibration materials of respirable dust are sampled through a cyclone. It is expected that the larger number of smaller particles will increase the proportion of non-crystalline silica in the material and reduce the magnitude of the XRD response. However, the additional size separation has no significant effect on the area response of the XRD instrument. Quin 1 (bulk) and Quin 1 Res (respirable) have different particle size distributions but show very similar values for crystallinity, while A9950 Res has a similar particle size distribution to Quin 1 Res but a different value for crystallinity. These comparisons suggest that the difference in XRD area measurement of the crystallinity of A9950 and Quin 1 bulk when further separated by a size selection device is not significantly influenced by the particle size, although there might be changes in the shape of the reflections. It suggests that for these materials, the XRD area measurement is more dependent on the crystallinty of the material as a consequence of its geological formation and its chemical or physical treatment than by its particle size.

Figure 2 shows the relationship between the percentage crystallinity determined by XRD and the average number aerodynamic diameter calculated by the API instrument. The error bars plotted with the individual values for crystallinity in Fig. 2 are taken from the values of uncertainty for the prediction in Table 6. The poor correlation value of $r^2 = 0.31$ of the linear trend line shown on the chart for XRD in Fig. 2 is mainly due to the low result obtained for the DQ12 material. This material has a small particle size compared with the other test materials and it is likely that the smaller particle size includes a larger proportion of non-crystalline particles or that some other contaminant is present. Other work (Page, 2003) reports an underestimation of the XRD value for particle sizes <2 μm when determined by a Horiba LA-920 instrument (equivalent API values ~1.2 μm). Although it would be incorrect to consider this, an underestimation since the proportion of non-crystalline or structurally disordered content for particles of this size is expected to become a significant proportion of material present (Foster and Walker, 1984) and legislation is generally in terms of monitoring the crystalline silica.

Early studies examining a single material, for example Gordon and Harris (1955), Edmonds *et al.* (1977), and Bhaskar *et al.* (1994), have shown a more pronounced decrease in XRD response with decreasing particle size. However, some previous studies have used peak height, which is more sensitive to changes in particle size than peak area because as the particle size reduces the profile of the XRD peak broadens (Chisholm, 2005). Indeed, the profile of the peak shape from an XRD scan can be used to calculate the mean particle size of a given sample.

For verification, these materials were also tested at Particle Analysis Ltd (Hatton, Derbyshire, UK) using a Horiba LA-930 laser instrument. The results are compared with these from the API Aerosizer in Table 7. The fundamental differences between the two techniques are that the API instrument uses energy to disperse the material as an aerosol and counts the number of particles of a particular size and the Horiba instrument disperses the material as a suspension in a liquid and measures the volume of particles within specific size criteria. The results from the API

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Table 7. Comparison of particle size data

Sample	Horiba LA-390 (volume)	API number (geometric diameter)	API number (aerodynamic diameter)	API volume (geometric diameter)	API volume (aerodynamic diameter)
Mean size (μm)					
NIST SRM 1878a	2.9	0.99	1.67	2.11	3.5
Quin 1 Bulk	7.2	1.82	3.00	4.35	6.88
Quin 1 Res	Not available	0.77	1.30	1.31	2.17
A9950 Res	Not available	0.79	1.33	1.18	1.95
A9950	4.85	1.01	1.70	3.47	5.56
MIN-U-SIL5	3.34	0.90	1.52	1.75	2.9
NIST SRM 1878	2.54	0.85	1.44	1.82	3.02
DQ12	0.52	0.59	1.03	0.96	1.57
Median size (μm)					
NIST SRM 1878a	2.27	0.93	1.52	2.23	3.72
Quin 1 Bulk	7.2	1.94	3.24	4.55	7.16
Quin 1 Res	Not available	0.72	1.21	1.38	2.28
A9950 Res	Not available	0.76	1.29	1.17	1.92
A9950	4.2	0.85	1.39	3.77	6.04
MIN-U-SIL5	3.02	0.85	1.40	1.85	3.11
NIST SRM 1878	2.25	0.78	1.30	1.94	3.24
DQ12	0.45	0.59	1.03	0.94	1.49

Table 8. IR 798 cm^{-1} absorption band

Material	Number of laboratories participating	Slope	Correlation coefficient	Ratio with NIST 1878a	Percentage relative purity	Error slope	Uncertainty of the prediction (%)
NIST 1878a	3	1.18	99.78	1.00	93.70	0.011	
Quin 1 Bulk	3	0.74	98.62	0.62	58.54	0.017	3.19
Quin 1 Respirable	3	1.14	97.01	0.96	90.40	0.039	6.78
A9950	3	0.96	99.57	0.81	76.31	0.012	2.56
Min-U-Sil	3	1.17	99.49	0.99	92.36	0.017	3.39
NIST 1878	3	1.09	99.53	0.92	86.26	0.015	3.06
BCR66	1	1.22	99.96	1.03	96.80	0.008	2.40
DQ12	3	1.10	99.12	0.93	86.74	0.022	4.06

Table 9. IR 780 cm^{-1} absorption band

Material	Number of laboratories participating	Slope	Correlation coefficient	Ratio with NIST 1878a	Percentage relative purity	Error slope	Uncertainty of the prediction (%)
NIST 1878a	3	0.86	99.78	1.00	93.70	0.008	
Quin 1 Bulk	3	0.65	95.47	0.76	70.88	0.028	6.75
Quin 1 Respirable	3	0.83	96.77	0.97	91.02	0.030	7.20
A9950	3	0.75	99.88	0.88	82.49	0.005	2.06
Min-U-Sil	3	0.85	99.30	1.00	93.58	0.014	3.87
NIST 1878	3	0.81	99.73	0.94	88.29	0.008	2.64
BCR66	1	0.84	99.97	0.98	91.47	0.005	2.19
DQ12	3	0.78	98.06	0.91	85.44	0.023	5.62

have been converted by the instrument to give comparable results in terms of volume of particles measured. A good correlation between the two techniques of mean size in terms of volume aerodynamic diameter of particles counted was obtained ($r^2 = 0.91$). The relationship between these two instruments for this parameter is as follows: result Horiba = 0.8354 × (result API) + 0.9323. This work

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Table 10. IR 695 cm^{-1} absorption band

Material	Number of laboratories participating	Slope	Correlation coefficient	Ratio with NIST 1878a	Percentage relative purity	Error slope	Uncertainty of the prediction (%)
NIST 1878a	3	0.27	99.82	1.00	93.70	0.002	
Quin 1 Bulk	3	0.24	99.60	0.88	82.39	0.003	2.69
Quin 1 Respirable	3	0.25	98.15	0.93	87.04	0.007	5.25
A9950	3	0.24	99.88	0.89	83.62	0.002	1.94
Min-U-Sil	3	0.26	99.75	0.95	88.92	0.003	2.51
NIST 1878	3	0.25	99.72	0.91	85.17	0.003	2.44
BCR66	1	0.23	99.98	0.86	80.15	0.001	1.67
DQ12	3	0.19	99.48	0.72	67.07	0.003	2.49

Table 11. IR 398 cm^{-1} absorption band

Material	Number of laboratories participating	Slope	Correlation coefficient	Ratio with NIST 1878a	Percentage relative purity	Error slope	Uncertainty of the prediction (%)
NIST 1878a	3	1.07	98.63	1.00	93.70	0.027	
Quin 1 Bulk	3	0.62	83.32	0.58	54.68	0.058	11.28
Quin 1 Respirable	3	0.88	84.90	0.83	77.38	0.076	14.81
A9950	3	0.80	94.06	0.75	69.92	0.038	8.02
Min-U-Sil	3	0.99	97.23	0.92	86.67	0.033	7.78
NIST 1878	3	0.79	94.72	0.73	68.84	0.036	7.74
BCR66	1	0.85	99.63	0.79	74.15	0.017	5.13
DQ12	3	0.77	97.91	0.72	67.62	0.024	5.70

Table 12. IR 374 cm^{-1} absorption band

Material	Number of laboratories participating	Slope	Correlation coefficient	Ratio with NIST 1878a	Percentage relative purity	Error slope	Uncertainty of the prediction (%)
NIST 1878a	2	0.86	99.12	1.00	93.70	0.020	
Quin 1 Bulk	2	0.54	98.99	0.63	58.68	0.014	4.35
Quin 1 Respirable	2	0.93	98.07	1.08	101.30	0.031	8.86
A9950	2	0.66	98.24	0.77	72.58	0.022	6.27
Min-U-Sil	2	0.80	98.03	0.94	88.09	0.029	7.93
NIST 1878	2	0.82	98.54	0.96	90.18	0.023	6.94
BCR66	1	0.90	96.69	1.05	98.24	0.074	17.99
DQ12	2	0.70	99.62	0.82	77.07	0.012	4.71

indicates that the Horiba instrument will generally give higher values for particle size than the API.

Surface area

The relationship between crystallinity and BET surface area measurements obtained using a Micromeritics TriStar 3000 gas adsorption analyser at Elkem Materials (Kristiansand, Norway) is shown in Fig. 3. The results for BET analysis of the surface area of the solid powder correlated well with the results for surface area obtained by calculation from the particles size distribution of each powder using the API particle sizing instrument ($r^2 = 0.78$) where the particles are dispersed in air and assumed to be spherical. This study shows a good correlation between surface area measured by BET and percentage crystallinity ($r^2 = 0.91$). One of the two points not close to the trend line plotted on the graph can also be explained since the reference material NIST SRM 1878a in Fig. 4 is expected to give slightly more intensity than the other materials because it has been treated with acid, which is thought to remove or etch some of the disordered structure on the surface of the crystalline material. This is a significant finding because some of the mechanisms proposed for the toxicity of crystalline silica are thought to be dependent on the nature of the surface (Donaldson and Borm, 1998).

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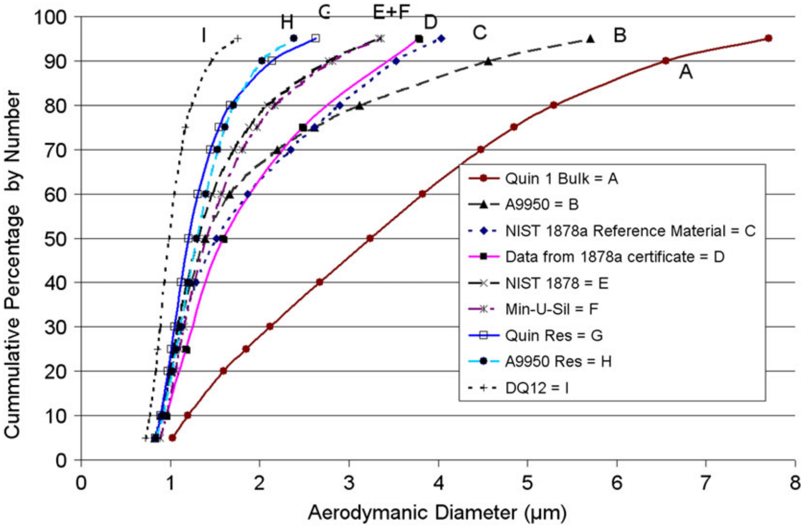

Fig. 1. Particle size distributions.

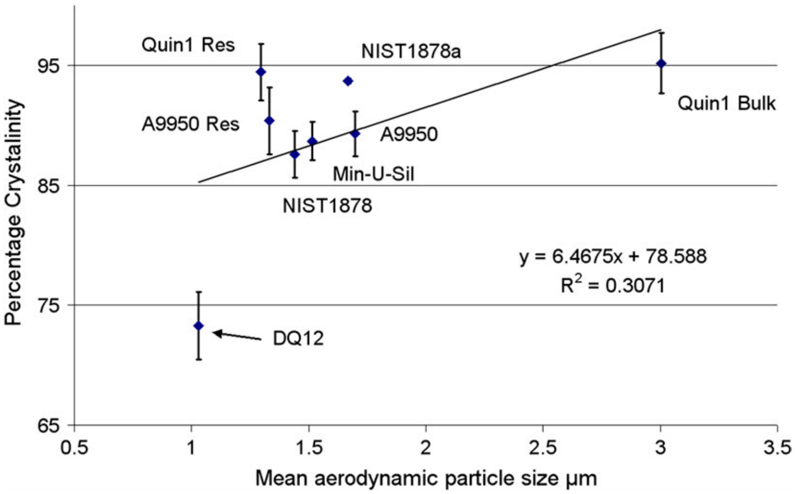

Fig. 2. Relationship between crystallinity and mean aerodynamic diameter.

Comparison with Infrared analysis (KBr disc method)

The most common technique used to measure quartz is infrared analysis, because of the lower relative cost, maintenance of the instrument compared with XRD and because of the more specialized training needed for XRD methods. The differences between the reported values of crystallinity and purity for XRD and IR and the analytical approaches for each material used in this study are shown in Figs. 4a and b. The term purity rather than crystallinity is used on the chart in Fig. 4a for IR analysis because the absorbance of the IR band is not thought to be completely related to the crystallinity of the sample. Figure 4a shows differences in the sensitivities of each of the five IR absorbance bands for each calibration material. Of particular note is the range of values obtained for the materials with the largest particle sizes (Quin 1 Bulk and A9950) and for the smallest particle size material (DQ12).

It is evident from Fig. 4a that the variation between each IR absorbance is greater than the variation between XRD lines Fig. 4b and that XRD is more consistent than IR for the measurement of respirable crystalline quartz. The different relative sensitivities of the less sensitive (695, 398, and 374 cm^{-1}) absorbance bands would put into question the reliability of their use. These observed differences are probably because the infrared absorbance has a greater dependency on the particle size of the quartz. The dependence of IR on the particle size of the quartz within the respirable dust range is described in previous work (Foster and Walker, 1984) (Page, 2003) and has implications when measuring workplace samples.

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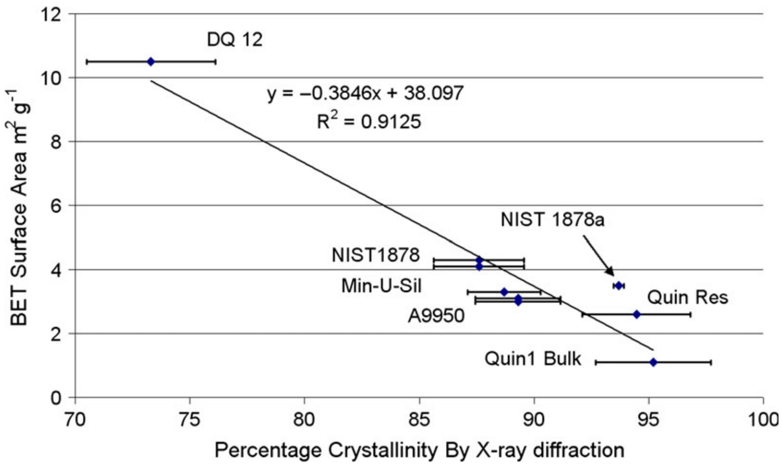

Fig. 3. Relationship between surface area and crystallinity.

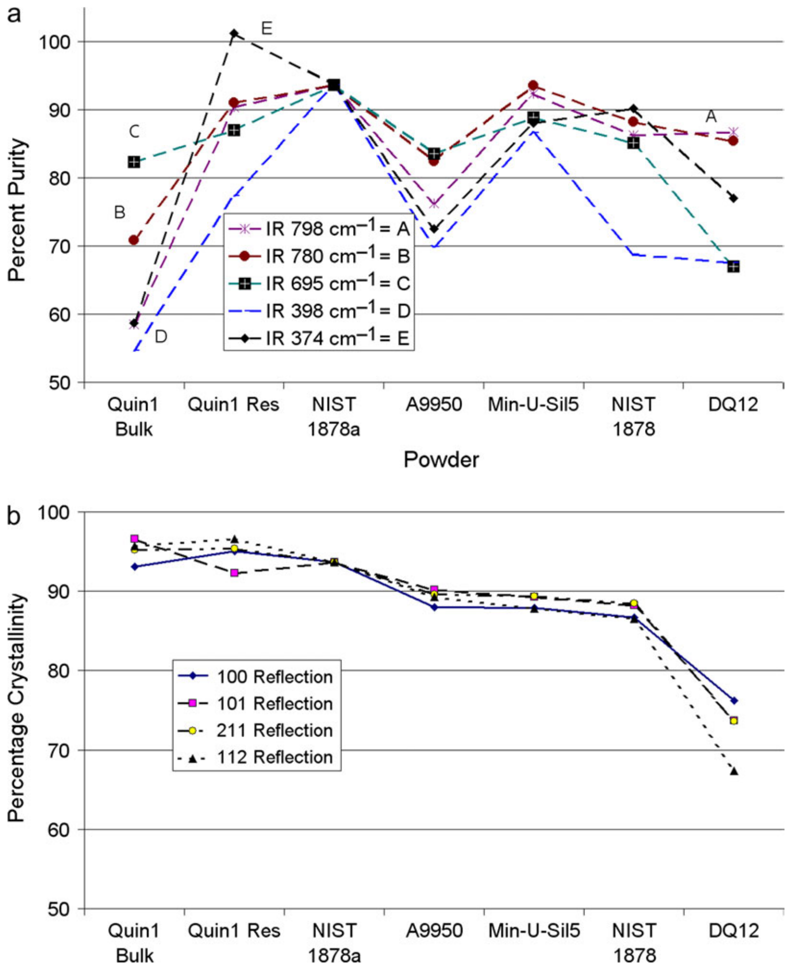

Fig. 4. (a) Variability of the IR response for each material. (b) Variability of the XRD measurement for each material.

Figure 5 plots the values of purity of the calibration materials obtained for the three most sensitive absorption bands at 798, 780, and 695 cm^{-1} using IR and the KBr disc method with mean number aerodynamic size of each calibration material. The infrared absorbance bands of 798 and 780 cm^{-1} are generally used for quantification and the other absorbance bands are usually only measured if interferences are present. The chart shows the individual values for each of the absorption bands, rather than the

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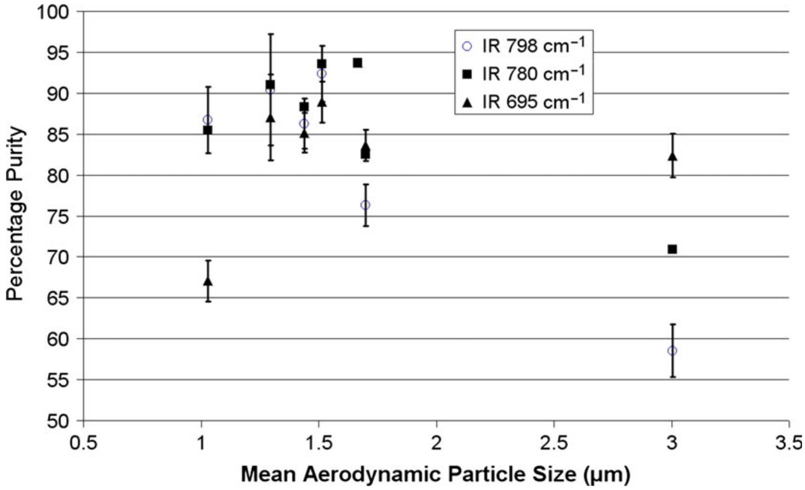

Fig. 5. Relationship between absorbance and particle size for infrared analysis.

standard deviation for uncertainty as is seen in Fig. 2 for XRD analysis, to emphasize the variability of these values with increasing particle size. These results are not very different from the work of Page (2003) and Foster and Walker (1984). The differences between the XRD and IR techniques are more pronounced at the extremes of the particle size range. For example, the differences between the two techniques range from 36% at 798 cm^{-1}, for a material like Quin 1 Bulk that has particles with mean volume aerodynamic diameter of about 7 µm, to about 13% for the 798 and 780 cm^{-1} absorbance bands for a material such as DQ12 with particles with a mean volume aerodynamic diameter of about 1.6 µm. However, for materials such as Min-U-Sil5, NIST 1878, and Quin 1 Res differences in XRD values of crystallinity and the IR values of purity for the absorbances of 798, 780, and 695 cm^{-1} are relatively small and are not likely to be significant.

Sampling instruments will standardize the particle size distribution collected in the workplace since they generally collect a proportion of different fractions of the respirable aerosol present and this may reduce any differences between the techniques or introduce a consistent bias. Work at NIOSH (1994) has shown that dust of different particle sizes Min-U-Sil5, Min-U-Sil10, and Min-U-Sil15 have a median particle size of 1.16, 1.2, and 1.2 µm, respectively, when passed through a 10-mm nylon cyclone. Data from Proficiency Testing (PT) programmes have shown no significant difference between the results given by laboratories using XRD and laboratories using IR analysis (Stacey, 2005). This is possibly because, in some PT programmes, all the laboratories are using the same calibration test material. Alternatively, the variability of the measurement result due to particle size is masked by some other possibly larger factor such as the variability of sample recovery.

On workplace samples, the accuracy of these methods will also depend on the procedure used for calibration and how well the particle size of the calibration test material matches the workplace samples. It is probable that work tasks using tools with low energy will tend to produce larger respirable particles and tools with high energy will produce small particles. The particle size of the quartz in the original material may also be a factor. For example, clays contain many particles of ~2 µm, while sandstones have much larger grains. In practice, particle sizes of about 0.5 µm or less generated as a result of a mechanical force on a bulk material are considered rare (Baron and Willeke 2001), so XRD may generally be a better indication of 'dose' than IR analysis, especially if the distribution of particles is not uniform or has a mean number aerodynamic diameter of >2 µm.

The particle size distribution of RCS from various industrial processes is not generally known and may depend on the tool used and the crystalline size of the silica in a material, which may vary from sample to sample in a geological material depending on the way the material was formed. In a recent work of Kauffer *et al.* (2005) on the comparison of direct (XRD and IR spectroscopy) methods for the analysis of α quartz, it was noticed that the agreement between the two direct methods was close on average (on 241 samples) but that, on the basis of a comparison of the individual results, differences existed. In the study by Kauffer *et al.* (2005), all the samples were sampled with a Dorr-Oliver cyclone and the standard used for calibration was the same for both XRD and IR, but the quartz sampled was probably different from sample to sample. This may be a possible explanation of the differences on an individual basis as the response of the different quartz may be different by XRD and IR. A more complete interpretation of an exposure measurement for RCS may also

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need information on the particle size distribution of the RCS present in the workplace.

CONCLUSIONS

The percentage of crystalline quartz in the calibration materials tested has been overestimated in previous work.

The working group recommends that, to ensure comparability, laboratories should use the values listed in Table 6 to correct analysis results for crystallinity of the calibration material.

A subsample of a given calibration test material can be obtained by dispersing the dust in air and using a cyclone to collect a portion of dust on a filter. Although this procedure alters the particle size of the calibration material, there is no resulting significant effect on the area XRD measurement of the materials tested. Furthermore, the value of crystallinity for the bulk material can be used without significantly affecting the uncertainty of the analysis.

For the calibration materials tested, there is a significant correlation between crystallinity and surface area measured by BET analysis.

It is not possible to assign a single value of relative purity to each of these materials for IR analysis when using the KBr disc method because of the variability in sensitivity of the absorbance bands.

This work shows that differences are likely to exist between results from XRD and IR analysis when measuring 'real' workplace samples and highlights the importance of matching the particle size of the calibration material to the particle size of the workplace dust for measurements of crystalline silica. It is also important to note that in most cases, a difference will also subsist between the origin of the quartz used for calibration and the origin of the quartz used in the workplace.

Although this work places some suspicion on the reliability of the IR technique using the KBr disc method, the debate about which analytical method is most appropriate will remain. The cost of the instrumentation and its maintenance limit the widespread use of XRD for this analysis, especially in countries attempting to establish systems of control and monitoring. IR analysis may also have advantages in particular industrial environments, e.g. coalmines, and it may be possible to correct for differences in the sensitivities of the different IR absorbance bands when continually monitoring one particular process from one type of environment. The health debate about the mechanism of the silicosis disease has not been resolved conclusively and this debate may have an influence on the instrument of choice for future work. In particular, a comprehensive interpretation of an exposure measurement for RCS may need information about the particle size emitted from a process or work task as well as the concentration present in the air.

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