HSE
Health and Safety
Executive

Crystalline silica in respirable airborne dust

Direct-on-filter analyses by infrared spectroscopy or X-ray

MDHS101/2

Methods for the Determination of Hazardous Substances

Health and Safety Laboratory

Scope

1 This method describes a procedure for the determination of time-weighted average concentrations of respirable crystalline silica (RCS) either as quartz or cristobalite in airborne dust.

2 The method is suitable only when using air sample filters of 25 mm diameter or less.

Summary

3 A measured volume of air is drawn through a membrane filter mounted in a respirable dust sampler. The filter is then analysed directly by Fourier Transform infrared spectrometry (FTIR) or X-ray diffraction (XRD). The choice of analytical technique selected will depend largely on any potential interference present.

4 The method is suitable for the determination of quartz and cristobalite at a concentration of 20 µg to 1 mg on the 25 mm filter. Both FTIR and XRD responses are linear over this range.

5 The use of alternative methods not included in the MDHS series is acceptable provided they can demonstrate the accuracy and reliability appropriate to the application.

Recommended sampling

6 Long-term personal exposures: Maximum sampling time: 8 hours; Sampling flow rate and duration will depend on individual respirable sampler requirements and dust concentration (typically in the UK: 2.2 $l.min^{-1}$ for generic Higgins-Dewell type cyclone samplers); Sampled volume: up to 1056 litres.

7 Short-term exposures: This method is not suitable for the measurement of short-term exposures (15 minutes) when using samplers with flow rates of 2.2 $l.min^{-1}$ or less and high flow rate samplers (>4 $l.min^{-1}$) are required. High flow rate samplers often use collection filters with diameters larger than 25 mm to reduce back pressure on the pump. Air sample filters with diameters larger than 25 mm will require the use of an indirect method of analysis.[1,2]

8 A longer sampling time ensures a heavier deposit on the filter and therefore reduces the limit of detection. Sampling times should therefore be as long as is reasonably practical (preferably not less than four hours). General guidance on workplace monitoring is given in HSG173.[3]

9 To avoid sampler overloading where dust concentrations are high, several consecutive samplers should be employed. It is recommended that the collected dust deposits should be kept below 2 mg to avoid overloading that could lead to losses during transport and handling of the filter.

Prerequisites

10 Users of this method will need to be familiar with the content of MDHS14[4] and BS ISO 24095.[5]

Safety

11 Users of this method should be familiar with standard laboratory practice and carry out a suitable risk assessment. It is the user's responsibility to establish appropriate health and safety practices and to ensure compliance with regulatory requirements.

Equipment

Samplers

12 A respirable dust sampler that complies with the size fraction convention given in BS EN 481.[6] In the UK, a cyclone sampler of the generic Higgins-Dewell design with a 25 mm diameter filter is recommended for long-term sampling to obtain optimal agreement with the respirable convention. The sampler should be cleaned and operated according to the manufacturer's instructions.

13 Although the particle selection characteristics of commercial respirable samplers are tested to ensure they meet with the respirable convention in BS EN 4815, there may be significant differences in terms of the air concentration of respirable dust collected by each type.[7,8] Information on the comparability of sampler types with the Safety In Mines Personal Dust Sampler (SIMPEDS), which is used as a reference, is available from published literature.[8,9] The filter cassettes should be made of conductive material (metal or conductive plastic). The use of polycarbonate filter cassettes for respirable silica sampling must be avoided since this may lead to significant adherence of dust on the cassette walls.[10]

Filters

14 Polyvinyl chloride (PVC) filters (such as Gelman GLA5000) or PVC-acrylonitrile co-polymer filters (such as Gelman DM800) have suitable infrared characteristics. Silver filters are also suitable for X-ray diffraction analysis but not infrared spectroscopy and have a lower background for XRD than organic membrane filters, giving a better signal-to-noise ratio.

15 The filters used in the analysis should ideally be from the same batch and if necessary be pre-conditioned and weighed[4,5] (about 30 filters are required for calibration purposes plus sufficient filters for air monitoring). Silver filters require no pre-conditioning. PVC filters are more prone to collect static. If filters are susceptible to absorption of moisture, equilibrate them in their sample tins with lids left slightly ajar overnight in the balance room.

16 Weigh each filter to the nearest µg, record its weight and return to its tin.

17 Number the tins in ascending order of filter weights, and select several as laboratory blanks.

18 If analysing by FTIR, select the laboratory blanks such that each calibration filter has a blank filter within 200 µg of its mass to use for background correction. Alternatively, scan all the clean calibration filters and save the resulting spectra on disk so that each filter can be used for its own background correction.

Other equipment

19 Personal sampling pumps that meet the requirements of BS EN ISO 13137[11] operated according to the manufacturer's instructions. For cyclone samplers, pulsation damped flow is critical. Information for pulsations rates of some pumps and their effect on respirable dust sampling is available in published literature[12].

20 A portable flow meter calibrated against a primary standard, with a measurement uncertainty typically less than ±2%.

21 Flexible plastic tubing of a suitable diameter for making a leak-proof connection from the sampling head to the pump; for personal sampling, belts or harnesses to facilitate attachment of sampling apparatus to subjects.

22 Flat-tipped forceps for handling filters.

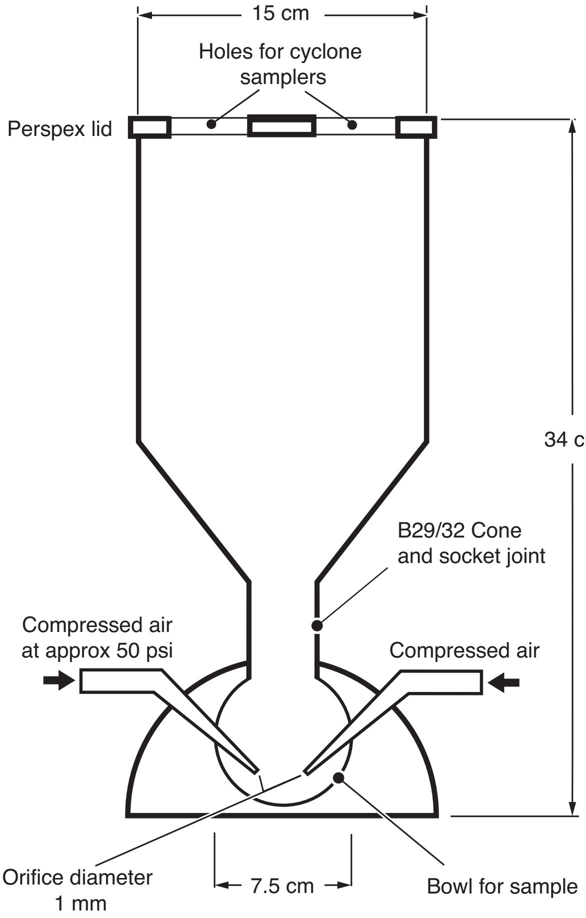
23 Filter transport tins or cassettes and transport container to transport samples from site to the analytical laboratory.

Laboratory apparatus

24 Infrared spectrophotometer: A Fourier Transform infrared spectrometer (FTIR) with a suitable filter holder, eg a rotatable polariser mount, is required so that the sample can be rotated in its own plane. This will enable the effect of non-uniform sample deposition to be reduced by taking absorbance measurements at several orientations.

25 X-ray powder diffractometer (XRD) with reflection geometry and X-ray generator: Diffractometers with Bragg-Brentano semi-focusing geometry with Cu- or Co- target X-ray tubes are in general use.

26 Dust cloud generator: For suspending quartz or cristobalite dust in air for preparation of calibration standards for use in both IR and XRD techniques. Figure 1 shows a simple design of dust cloud generator constructed from thick borosilicate glass with a thick clear Perspex lid. A groove machined into the top of the lid mates with the rim of the main glass chamber to form a closed system. Four symmetrically spaced holes are drilled in the top through which a cyclone sampler can be suspended. Adequate means must be provided to prevent the glass chamber becoming dangerously pressurised during use when compressed air is applied. The dust cloud generator must be placed inside a fume cupboard while atmospheres of quartz or cristobalite are being produced and sampled. It is recommended that the glass chamber be earthed via a cable during aerosol generation to reduce static charging.



Glass chamber for the preparation of calibration standards

27 Microbalance: Calibrated against a primary standard, capable of weighing to within ±1 µg over the range 0–20 mg for the preparation of calibration filters. The accuracy of the balance should be checked with a calibrated standard weight at the intervals recommended by the balance manufacturer.

28 Electrostatic eliminator for use when weighing filters.

29 Calibration materials: Both FTIR and XRD techniques require materials with known concentrations of quartz or cristobalite for the preparation of calibration samples (see Appendix 1 for further details). A list of calibration materials and their consensus values for crystallinity have been published.[13]

30 XRD drift correction sample: An aluminium plate or any other suitable stable robust material can be used as an external standard to correct for the gradual decline in X-ray tube emission. Such a standard should be fine-grained, free from marked texture and have a strong X-ray diffraction peak in roughly the same 2Θ range as the quartz or cristobalite peaks being used for analysis.

Preparation and sampling

Sampler preparation

31 Personal samples for respirable crystalline silica should be collected as described in MDHS14.[4]

32 Set the volumetric flow rate in a clean area.

33 Connect each sampler equipped with an appropriate filter substrate to a sampling pump, ensuring that no leaks occur.

34 Switch on the sampling pump and attach the calibrated flow meter to the inlet of the sampler so that it measures the flow through the inlet orifice.

35 Allow the pump to stabilise before measuring and adjusting the flow.

36 Set the required volumetric flow rate (± 0.1 l.min^{-1}) and switch off the pump. Extreme conditions of temperature and pressure have relatively small influence on the volume of air sampled. Generally they have no significant effect but the temperature and pressure in mines can vary because of the depth, presence of machinery and ventilation or air extraction rates. Corrections would only be necessary when the conditions at the site differ substantially from those where the flow rate check was originally made (eg a temperature change of 10 °C would change the volume sampled by typically 3%).

37 Retain as a field blank one unused loaded sampler from each batch of ten prepared, with a minimum of three blanks overall. Treat these as far as possible in the same manner as those actually used for sampling, but draw no air through them.

Sampling

38 Attach the sampler in the worker's breathing zone on the upper chest or lapel, not more than 30 cm away from the nose-mouth region. Cyclone samplers are not generally sensitive to orientation, but should be attached with the grit-pot at the base.

39 Attach the pump to a belt or harness so that it causes minimum inconvenience to the worker, and safely secure any tubing used to connect the sampler to the pump.

40 When ready to begin sampling, switch on the pump.

41 Record the time and volumetric flow rate at the beginning of the sampling period. Record the sample identity and all relevant sampling data. Check the sampler and pump periodically during sampling.

42 At the end of the sampling period record the final sampling flow rate, switch off the pump, record the sampling time and carefully dismount the sampling equipment from the worker without inverting the grit pot.

43 Carefully remove the sampling equipment to a clean, dust-free area such as that used for sampler preparation. Cyclones must be retained upright when switched off until the filter has been removed.

44 Calculate the duration of the sampling period and the average measured sampling flow rate.

45 Remove the filter from each sampler using flat-tipped forceps and place in a labelled container capable of preventing damage to the filter during transport to the laboratory. Take particular care to prevent dust being dislodged from heavily loaded filters.

46 Guidance on assessing uncertainties due to sample transport errors can be found elsewhere.[14]

Preparation of calibration standards

47 Use the pre-conditioned, pre-weighed filters to prepare a series of calibration filters by sampling an aerosol of quartz or cristobalite calibration material generated in the dust cloud chamber (Figure 1) as described below. The calibration samples need to be equally spread across the analytical range to avoid the calibration model being unduly weighted by isolated responses that may lead to significant calibration errors. The calibration filters must also be prepared using the same type of cyclone sampler as the samples.

48 Place a small amount (about 0.1–0.5 g) of the standard quartz or cristobalite in the chamber bowl. Attach a sampling pump to each of four cyclone samplers and set their volumetric flow rates to the required value. Fix the cyclone samplers to the lid of the chamber and place it on top. Apply a jet of compressed air to the side arms of the bowl for a few seconds. Allow approximately 30–60 sec for the agglomerates to settle out from the dust cloud. Run each sampling pump for sufficient time, typically 1–5 sec, to obtain filters loaded with the required amount of standard, covering the range 20–500 µg. A minimum of six filters are required for reliable calibration.

49 Reweigh the filters to determine the loading.

Sample analysis

Infrared spectroscopy

50 Place each calibration filter in turn in the sample beam, using a defocused beam so that the beam covers the sample area on the filter. Where the spectrometer has a moveable stage on which to mount the sample holder, it is essential that the stage is placed in the same position for all calibration and sample filters.

51 Scan the calibration and blank filters in absorbance mode between 1000 cm^{-1} and 500 cm^{-1}, using typical settings of 32 scans at 4 cm^{-1} resolution.

52 Take the infra-red spectra obtained from the calibration filters and blank correct by subtracting the spectrum obtained from a suitable weight-matched blank filter (see paragraph 17).

53 For quartz, draw baselines on the blank corrected spectra tangential to the absorbance minima at about 730 cm^{-1} and 830 cm^{-1} on either side of the quartz doublet (see Figure 2). The baselines should be straight and as horizontal as possible. For each spectrum, measure the heights of the 780 cm^{-1} and 800 cm^{-1} peaks from the baseline. Rotate the standard through 90° and repeat the absorbance measurements. (Note that rotation of the sample is not necessary where the infrared beam has a circular cross-section).

54 Plot the baseline corrected peak heights at 780 cm^{-1} and 800 cm^{-1} against the mass of quartz, in µg. Determine the lines of best fit for each plot (which should be linear and pass close to the origin). The slopes of these lines are the response factors (R_F) for quartz at 780 cm^{-1} and 800 cm^{-1}. Examine the scatter of the data points from the regression line and re-examine any outliers to determine the cause.

55 For cristobalite, follow the same procedures as described for quartz, but measure the peak heights at 800 cm^{-1} and 620 cm^{-1}. The peak at 620 cm^{-1} requires a second baseline to be drawn (again straight and as horizontal as possible) tangential to the trace minima at approximately 650 cm^{-1} and 590 cm^{-1}. Plot the baseline corrected peak heights and determine the lines of best fit and response factors for cristobalite at the two frequencies.

Determination of quartz in respirable dust samples

56 Scan the sample filters using the same instrumental conditions as used for the calibration filters and blank correct by subtracting the spectrum obtained from a suitable weight-matched blank filter.

57 Draw a baseline on each blank corrected sample spectrum, in the same way as for the calibration samples (see paragraph 52), and measure the heights of the 780 cm^{-1} and 800 cm^{-1} peaks from this baseline. If more than one spectrum is recorded, calculate the mean peak height at each frequency.

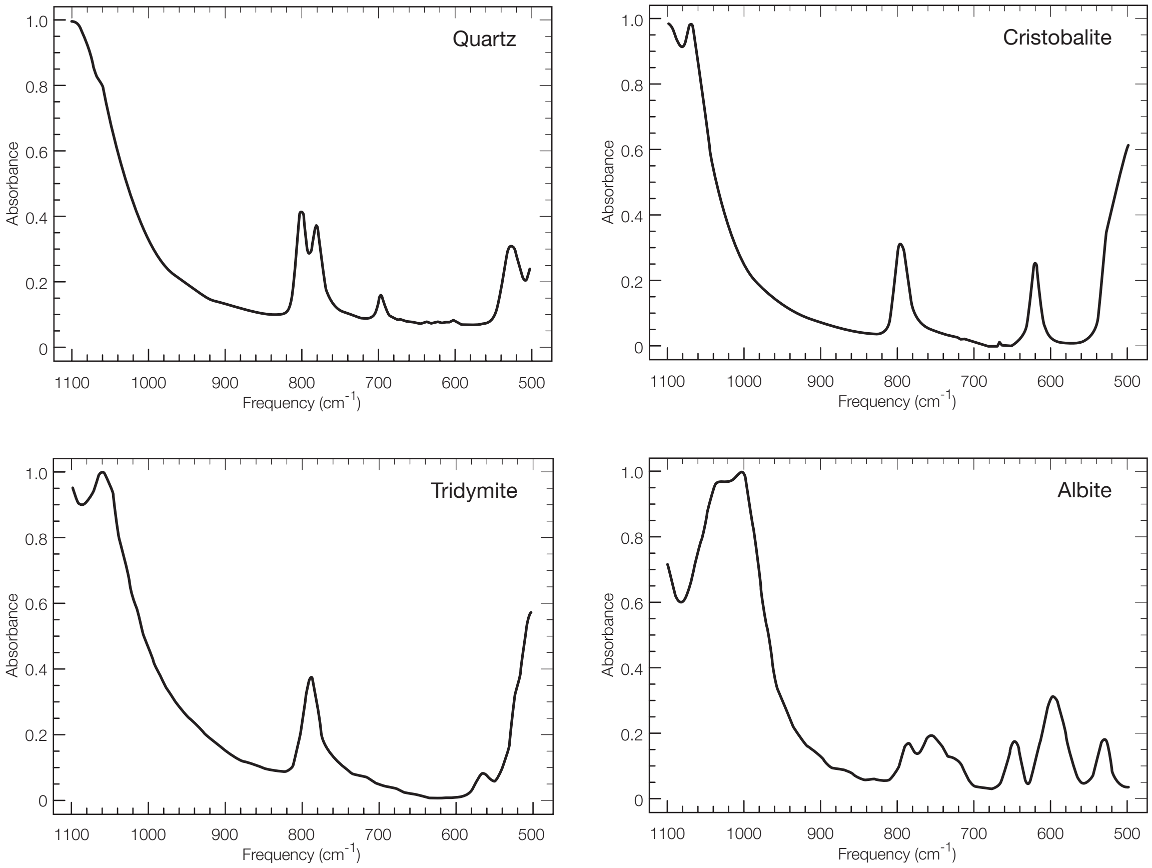


Figure 2 Infrared spectra of quartz, cristobalite and interfering phases.

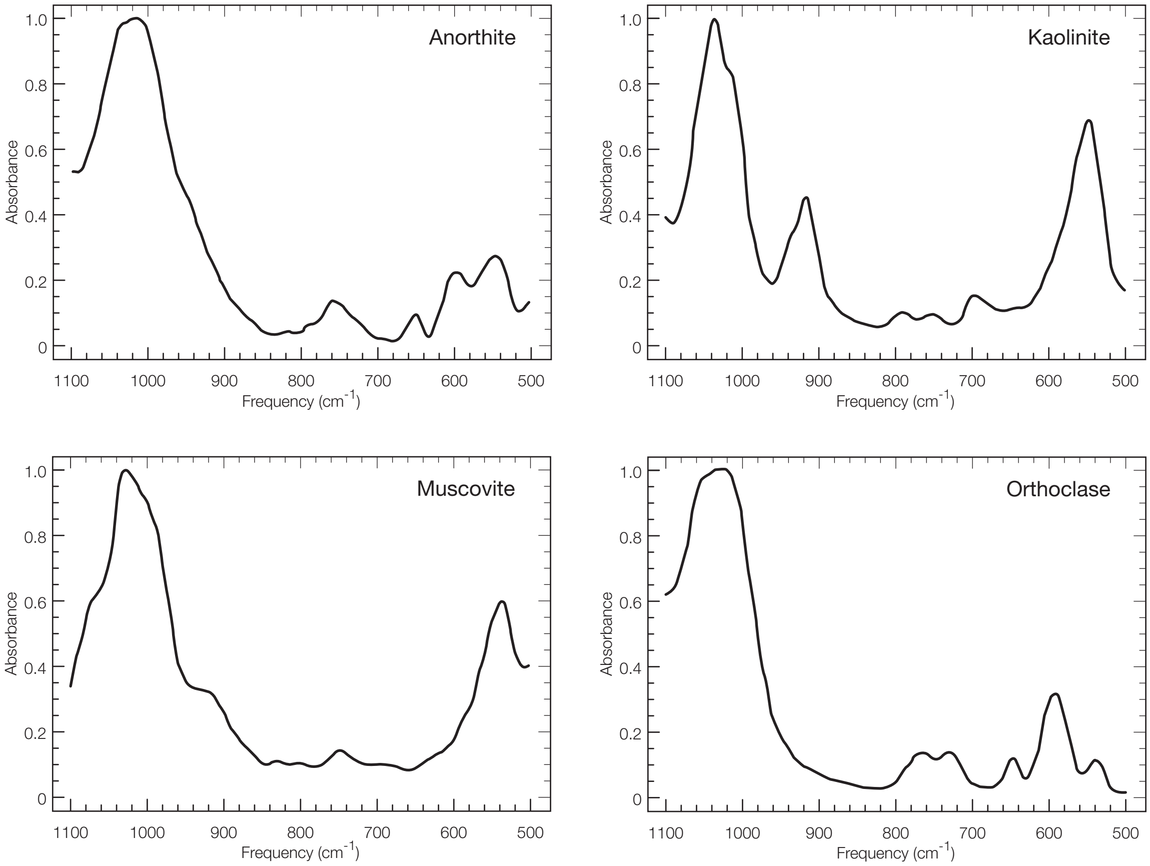


Figure 2 Infrared spectra of quartz, cristobalite and interfering phases.

58 Calculate the amount of quartz on the sample filter, in µg, by dividing the peak height at each frequency by the R_F value for that frequency obtained from the calibration standards and then averaging the two results. If the ratio of the peak height at 800 cm^{-1} to that at 780 cm^{-1} is outside the range 1.0 to 1.4, the sample spectrum should be examined for the presence of interferences, in particular cristobalite at 620 cm^{-1} and kaolinite at 915 cm^{-1} (see Figure 2).

Determination of cristobalite in respirable dust samples

59 Follow the same procedures as described for quartz, but using the peaks at 800 cm^{-1} and 620 cm^{-1}.

Determination of mixtures of quartz and cristobalite

60 Follow the procedure for cristobalite and measure the peak heights at 800 cm^{-1} and 620 cm^{-1}. The cristobalite content of the sample can be determined from the peak height at 620 cm^{-1}. The quartz content of the sample can be then be determined from the peak height at 800 cm^{-1}, after first subtracting the contribution of the cristobalite to this peak (this is calculated by multiplying the cristobalite content determined at 620 cm^{-1} by the R_F value of cristobalite at 800 cm^{-1}). Alternatively, the peak at 800 cm^{-1} can be used to determine the total crystalline silica content (ie quartz + cristobalite) since in practice both quartz and cristobalite have similar IR responses at this frequency.

X-ray diffractometry

61 The diffractometer operating conditions should be chosen to maximise intensity and to reduce errors arising from counting statistics, even if this leads to

some loss of resolution. (Largest practicable divergence and receiving slits; sample spinner).

62 Collect the diffraction data for the calibration standards for quartz and cristobalite in the same way as for samples. Since no interfering phases will be present on the calibration standard filters a qualitative scan is unnecessary.

63 As a minimum, measure the net peak area of the selected diffraction peak of the drift correction sample before and after analysing a batch of filters. If there is a difference between the two results (eg >4% within a batch) the reasons for the difference in performance should be investigated.

64 Mount each sample filter in the diffractometer and make a rapid qualitative scan; an example of typical data collection conditions is given in Table 1. Identify as many as possible of the phases present and in particular note any evidence of possible line overlaps on the quartz and/or cristobalite peaks used for analysis. For a set of dust samples taken in the same industrial environment, experience may show that the dust is very similar each time sampling is done and qualitative scans will not then be required for all filters.

65 Collect diffraction data for each peak required for analysis using a step scan extending at least 1° either side of the expected peak position (Table 2). The data should be sufficiently smooth and the noise level low enough for the peak limits and background to be set with reasonable ease and reproducibility.

66 If quartz is determined, collect diffraction data at least for the most intense quartz peak and preferably for two other principal quartz peaks. Similarly, if cristobalite is to be determined, collect data for at least the most intense cristobalite peak and preferably also for the other two principal peaks. The peaks, their approximate d-spacings and 2Θpositions for CuKΘradiation are given in Table 2.

67 Identify the peak position and minima either side of the diffraction peak to define the limits of the area and the background intensity below it. Most XRD software will calculate the net peak area once these limits have been defined. The net peak area is the sum of all the counts when the background is subtracted. The background is the sum of all the counts under the straight line joining the minima on either side of the peak. The net peak area is expressed as raw counts, counts.sec^{-1} or the counts.sec^{-1} may be multiplied by the step size in degrees to express it as counts.sec^{-1}.deg^{-1}. Using counts.sec^{-1}.deg^{-1} allows the step size to be changed with the calibration unaltered.

68 Use the observed net peak area of the drift correction sample, D_o, to normalise the observed net peak area for the sample, A_o, relative to a chosen value, of the peak area, D_r, (the peak area of the drift correction monitor the first time it was measured under the same analysis conditions) for the drift correction sample:

Normalised sample peak area $A_s = A_o.Dr/D_o$

69 For each quartz and cristobalite peak of the calibration standards, plot the diffracted intensity, ie the normalised net peak area, A_s, against the mass of quartz or cristobalite on the filter. Determine the lines of best fit for each plot (which should be linear and pass close to the origin). The slopes of these lines are the response factors (R_F) for that particular analyte and diffracted intensity. Examine the scatter of the data points from the regression line: if there are any extreme outliers, re-examine the data for those points to try to identify the cause.

Determination of quartz and/or cristobalite in respirable dust samples

70 If quartz is present, select one or more quartz peaks which appear to be free from peak overlap for quantitative analysis. For each peak, measure the normalised net peak area, A_s, and use the appropriate R_F value obtained from the calibration standards to calculate the mass of quartz, in µg, on the filter. If more than one quartz line is measured, report an average value for the mass of quartz, using the most consistent results free from interference. If cristobalite is present, repeat the process for cristobalite peaks free from interference. It is not good practice to calculate two calibrations within the analytical range 0–1000 µg (for low and high loadings). Such an action would suggest the inappropriate selection of instrumental parameters eg not irradiating the whole filter area.

71 For some samples it is difficult to be sure that diffraction peaks are free from overlap on the basis of the information provided by the qualitative scans. In these cases the mass should be calculated for all the diffraction lines for which there is no visible splitting or distortion of the peak. If significant peak overlap occurs, it will lead to an overestimate of the mass present. Ideally the sample should be re-analysed using another diffraction peak, but this will also involve additional calibration work and result in lower analytical precision. Confirmatory analysis using infrared spectroscopy should also be considered in such cases.

Calculation of results

Volume of air sampled

72 Calculate the volume, in litres, of each air sample by multiplying the average measured sampling flow rate, in $l.min^{-1}$, by the sampling time, in minutes.

Concentration of respirable crystalline silica in air

73 Calculate the airborne concentrations of quartz and/or cristobalite, in $mg.m^{-3}$, by dividing the mass of each component collected on the sample filter, in µg, by the volume of the air sample, in litres.

74 Calculate the airborne concentration of respirable crystalline silica by summing the airborne concentrations of quartz and cristobalite (if both are present).

Method performance

Detection limit: FTIR

75 The qualitative and quantitative detection limit for crystalline silica, when defined as three times and ten times the standard deviation of the blank determination, are typically around 3 µg and 10 µg per sample respectively. For a 500 litre air sample, these figures correspond to qualitative and quantitative detection limits of 0.006 $mg.m^{-3}$ and 0.02 $mg.m^{-3}$ respectively.

Detection limit: XRD

76 The estimation of limits of detection for quartz and cristobalite is problematic because it is dependent on the sample matrix, instrumental parameters and performance of the respirable sampler. It is important that the instrument parameters are arranged so that the whole filter area is irradiated, otherwise a sample may have a positive mass but no X-ray response, which may cause a positive or curved intercept at low measurement masses. Automatic slits set as

wide as possible, to cover the area of the filter but avoid scattered radiation from the sample holder can mitigate this. It is recommended that the limit of detection be estimated from 3 times the standard deviation of the count rate of the background over an appropriate scan range of a clean sample filter.

77 The LOD can also be established empirically by adding low levels of RCS to a clean filter to determine the smallest detectable mass. Alternatively, filters loaded with silica-free quantities of the matrix of interest (eg 200–500 µg of calcite or clay) can be used to determine an estimate of the limit of detection that includes the anticipated sample matrix.

78 The qualitative limit of detection on 'clean' filters is probably about 5–10 µg for the strongest quartz peak[15] and around 10–20 µg for the strongest cristobalite peak.[16,17] For a 500 litre air sample (approximately four hours at 2.2 $l.min^{-1}$), these correspond to 0.02 $mg.m^{-3}$ quartz and 0.04 $mg.m^{-3}$ cristobalite. In practice, on 'real' samples it is often necessary to be able to observe the presence of the secondary peak to confirm the presence of quartz or cristobalite since there are several common interferences on the main diffraction peak, which may define the practical limit of detection.

79 The qualitative limit of detection is poorer for the weaker diffraction peaks: about 15 µg, 20 µg and 40 µg for the 100, 112 and 211 quartz peaks respectively, corresponding to 0.03, 0.04 and 0.08 $mg.m^{-3}$ quartz for a 500 litre air sample; and about 40 µg and 30 µg for the 101 and 200+112 cristobalite peaks, corresponding to 0.08 and 0.06 $mg.m^{-3}$ cristobalite for a 500 litre air sample.

80 It is probably reasonable to base quantitative limits of detection on a standard deviation of ten measurements made on blank filters and a linear calibration, which gives roughly 25 µg for the strongest quartz and cristobalite peaks, which for a 500 litre air sample corresponds to 0.05 $mg.m^{-3}$ in each case. The corresponding estimates for the weaker diffraction peaks are: about 30 µg, 50 µg and 70 µg for the 100, 112 and 211 quartz peaks respectively, equivalent to 0.06, 0.10 and 0.14 $mg.m^{-3}$ for a 500 litre air sample; and about 70 µg and 60 µg for the 101 and 200+112 cristobalite peaks, equivalent to 0.14 and 0.12 $mg.m^{-3}$ for a 500 litre air sample.

Expanded uncertainty: FTIR

81 The expanded uncertainty for the analysis of crystalline silica by FTIR is typically around ±50% when measuring an airborne concentration in the range 0.02 $mg.m^{-3}$ to 0.05 $mg.m^{-3}$ and around ±20% when measuring an airborne concentration in the range 0.05 $mg.m^{-3}$ to 0.2 $mg.m^{-3}$.

Expanded uncertainty: XRD

82 The expanded uncertainty when measuring quartz on calibration type filters was assessed following the guidance in ISO 24095[5] and EN 482.[18] EN 482 requires the expanded uncertainty including sampling when measuring long term exposure limits to be less than ±30% when measuring 0.5 to 2 x the limit value and less than ± 50% when measuring 0.1 to <0.5 x the limit value.

83 Table 5 lists the lowest masses measured with an expanded uncertainty of 30% and 50% when using reproducibility data to assess the analytical variability. These values were achieved with the analytical conditions listed in Table 1 for the array detector and using a fixed estimate for the sampling variability using values published in ISO 24095.[5]

84 The values in Table 5 indicate that the method is compliant for a limit value 0.1 mg.m^{-3} and suitable for half shift sampling when using a respirable sampler at a flow rate of 2.2 l.min^{-1} and measuring the strongest quartz peak at 26.6 degrees free from interference.

85 As the principle source of error when measuring test samples of RCS is the analytical variability, it is reasonable to suggest that the uncertainty is related to the area intensity measurement. For the strongest diffraction peak of cristobalite the expanded uncertainty estimate for a particular mass would be comparable to the value obtained for a quartz peak of the same magnitude of intensity.

Stability

86 Crystalline silica is stable indefinitely but the organic membrane filters of quality control samples may gradually discolour and become brittle with repeated exposure to X-rays.

Quality control measures

87 A record of the diffraction peak position and intensity of the drift correction sample may be used as a more sensitive check on the performance of the X-ray diffractometer.

88 As an additional check, filters prepared in the same way as the calibration standards with loadings of 100–200 µg are suitable for internal quality control.

89 It is strongly recommended that all laboratories undertaking the determination of hazardous substances in workplace air should participate in an external quality assurance scheme.

Appendix 1 Calibration dusts

1 The infrared absorption response of both quartz and cristobalite is particle size dependent.[19,20] The response increases as the particle size decreases to about 1.5 µm; below about 1.5 µm, the response falls due to the presence of an amorphous surface layer. A calibration sample for infrared analysis should therefore ideally have the same particle size distribution as the workplace sample for analysis.

2 Only crystalline silica will give an XRD response, and particle size differences between the sample and the standard are much less important for this technique,[21] although peak broadening and extinction effects are related to particle size.[19-22]

3 For comparability with other calibration materials used in laboratories it is important to use a calibration material of known crystallinity and to correct the reported value for the crystallinity of the calibration dust.

4 A satisfactory calibration procedure is to generate an atmosphere containing the standard quartz or cristobalite and sample from this through the respirable dust sampler onto filters.

5 The US National Institute of Standards and Technology (NIST) certified respirable ϴ-quartz standard (SRM 1878), of known crystalline quartz content, is suitable for calibration when analysing by infrared spectroscopy or X-ray powder diffraction. Sikron F600 (HSE standard quartz A9950, available from the Health and Safety Laboratory) is also a suitable standard. Quartz calibration dusts and their

values of crystallinity when compared with the NIST certified reference material SRM1878a are listed in published work.[7]

6 NIST certified respirable Θ-cristobalite standard (SRM 1879), of known crystalline cristobalite content, is suitable for calibration by infrared spectroscopy or X-ray powder diffraction. Alternatively, it is permissible to use other suitably documented standards or secondary standards calibrated against a primary standard using the same analytical method.

Appendix 2 Limitations of infrared spectroscopy

1 The infrared method is suitable for the determination of quartz/cristobalite over the range 10 µg to 1 mg on a 25 mm filter. Over this range, there is a linear relationship between infrared response and quartz/cristobalite content of the sample.

2 The limit of detection and accuracy of the method are dependent upon a number of parameters, for example: particle size, other constituents of the sample and type of spectrophotometer used.

Interferences

3 Several minerals which may occur in conjunction with quartz and cristobalite absorb infrared radiation in the region of the quartz absorbance at 800 cm^{-1} and 780 cm^{-1} and the cristobalite absorbance at 800 cm^{-1} and 620 cm^{-1}, giving rise to positive interferences. Infrared spectra of quartz and cristobalite and the most common of these interfering phases are shown in Figure 2. Positive identification, however, can only be made by comparison with a standard reference spectrum of the mineral suspected to be an interfering phase. On-filter mixtures containing the mineral and quartz/cristobalite can be prepared using the same technique as for standard quartz/cristobalite samples, and the effect of the interference on the quartz/cristobalite absorbance assessed. Using software techniques, it is possible to subtract any interfering bands from the infrared spectrum of a sample.

Re-radiation effects

4 The response of an FTIR instrument is unaffected by re-radiation. Here, the sample is placed between the modulated source radiation and the detector; re-radiation is un-modulated and not detected.

Other limitations

5 The infrared method for the determination of cristobalite is subject to some uncertainty if metastable forms of cristobalite are present in the sample. The infrared absorbance responses of these metastable forms may differ from that of the Θ-cristobalite standard.

Appendix 3 Limitations of X-ray diffraction

1 The X-ray diffraction method is suitable for the determination of quartz and cristobalite in respirable dust samples weighing up to about 2 mg when deposited on a 25 mm diameter filter. If the layer of dust on the surface of the filter is thin enough for X-ray absorption to be negligible, the diffracted intensity is directly proportional to the mass of quartz/cristobalite on the filter.

2 At high dust loadings the layer of dust is thicker, the observed diffracted intensity is reduced by absorption effects and the linear relationship no longer holds. The limit of linearity with a deviation of 10% for a sample containing 5% quartz in a highly absorbing matrix (100 $g.cm^2$) for copper radiation is 0.938 mg for filter deposit diameter of 2.1 cm[23]. Occasionally, samples with a very high mass absorption coefficient for the radiation used may be encountered, eg an iron oxide matrix with CuKΘradiation, and the deviation from linearity may begin at filter loadings as low as 0.5 mg. In such cases, the dust loading on the filter should be reduced by sampling for a shorter time. Methods exist to correct for these matrix absorption effects[1,24] using the silver filter as a reference.

Interferences

3 Diffraction peaks from phases which commonly occur in association with quartz and cristobalite in industrial environments may overlap one or more of the principal quartz or cristobalite diffraction peaks. Such overlap may give an erroneously high or low result depending on the relative positions of the interfering peak and the quartz or cristobalite peak. Direct overlap will generally make the measured intensity higher than the true value. If the interfering peak is displaced to one side of the quartz/cristobalite peak, the background level will be set too high and the measured intensity will be lower than the true value.

4 The general approach to this problem is to identify the other phases present on the filter and check for possible overlap of their diffraction peaks and those which might be used for analysis. Examples of commonly occurring phases whose diffraction peaks may overlap the most intense peaks of quartz and cristobalite are listed in Tables 3 and 4 respectively. For complete diffraction data on the phases listed refer to the Powder Diffraction File (PDF) published by the Joint Committee on Powder Diffraction Standards (JCPDS), International Center for Diffraction Data (ICDD), 1601 Park Lane, Swarthmore, Pennsylvania 19081, USA.

5 Interference resulting from diffraction peak overlap can often be recognised by looking at the diffraction peak which may show the two components partially resolved or may be distinctly unsymmetrical in appearance (eg with a shoulder). It may be simplest to reject the results from such peaks and use a different quartz or cristobalite peak for analysis. Alternatively, if the interfering phase is known, it may be possible to make a simple correction by measuring the intensity of another line of the interfering phase and then making an appropriate adjustment to the intensity. For some interfering phases, particularly coal and furnace dust, analysis by infrared spectroscopy may be preferable.

6 Peak overlaps occur if both quartz and cristobalite are present in the same sample although this is not a particularly common occurrence. The 211 quartz peak at d 1.541 Å (60.04° 2ΘCuKΘ) is partially overlapped by the 311 cristobalite peak at d 1.533 Å (60.47° 2ΘCuKΘ) and should not be used for analysis if cristobalite is present. The second most intense cristobalite peak is actually composed of two peaks, 200 at d 2.485 Å (36.15° 2ΘCuKΘ) and 112 at d 2.465 Å (36.45° 2 ΘCuKΘ). It should not be used for analysis if quartz is present as it may be subject to interference from the 110 quartz peak at d 2.458 Å (36.56° 2 Θ CuKΘ).

Other limitations

7 The X-ray diffraction method for the determination of cristobalite is subject to some uncertainty because variations have been shown to occur in the positions, relative intensities and widths of the diffraction lines of samples of cristobalite from different sources.[25,26] These variations are probably related to the presence of Θ -cristobalite which normally occurs at high temperatures and transforms rapidly into

Θ-cristobalite on cooling. The Θ-form may, however, be stabilised in the presence of small amounts of some oxides and so persist after cooling.[27,28] Other metastable forms may also be encountered.[29,30] These and Θ-cristobalite have diffraction peaks in positions very close to those of the Θ-form but with different intensities. Analyses using Θ-cristobalite as standard may therefore be grossly in error if other metastable forms are present, but there seems to be no alternative until well-characterised standards for all the forms of cristobalite become available.

8 The secondary diffraction peaks of cristobalite are relatively weak and their analytical sensitivity correspondingly poor. At low levels, it will probably be necessary to rely on the most intense peak alone and it is then essential to take account of possible interference with that line. Measurements using the second and third strongest lines may still be worthwhile as confirmation of high concentrations and a check on interference with the primary diffraction peak.

9 Differences in the particle size distribution between the workplace dust sample and the standard quartz or cristobalite used for calibration were of great importance in XRD analysis when the exposure limits were set in terms of quartz and cristobalite. Diffracted intensity comes solely from the crystalline material but quartz and cristobalite contain amorphous material as a surface layer. This amorphous layer makes up a higher proportion of the smaller particles and the proportion of crystalline material is correspondingly reduced.

10 Laboratory studies show a fall of up to 50% in diffracted intensity in the smallest size fractions,[15,23,31-34] almost all of which resulted from the fall in the proportion of crystalline material. Since exposure standards are based on crystalline silica, it is not necessary to consider the amorphous surface layer and the effect of particle size is much less significant. Particle-size broadening of the diffraction peaks has no effect on peak area intensities whose use is recommended in this method. In a sample of respirable dust, there will be very few particles coarse enough to be subject to extinction, which is believed to reduce the diffracted intensity from coarser size fractions.[21,22]

Table 1 Typical operating and data collection conditions for X-ray diffractometry

Diffractometer operating conditions	
Point Detector	**Array detector**
2.7kW broad focus copper anode x-ray tube run at 50 kV, 45 mA	
1° divergence and scatter slits (used over whole range to avoid changes during data collection, an automatic divergence slit is suitable if fitted)	18 mm automatic divergence slits 20 mm mask
Receiving slit: 0.3 mm	Detector window set at 2.12 degrees 2 Θ
Diffracted-beam graphite monochromator	Nickel filter (detector side)
Sample spinner 1 rev/min	

Examples of data collection conditions		
Detector	Proportional/Scintillation	Array
Continuous scan	6 to 65 degrees 2Θat 10/min or 0.020/ sec	6 to 65 degrees 2Θfor a minimum of 15 seconds per step
Silver reference or aluminium plate 101 reflection at 38.3 degrees 2Θ	36.4 ± 0.3 ° 2Θ– 39.5 ± 0.3 ° 2Θin 0.02 ° 2Θsteps for 4 seconds per step	36.4 ± 0.3 ° 2Θ– 39.5 ± 0.3 ° 2Θin 0.02 ° 2Θsteps for 120 seconds per step
Quartz 101 reflection at 26.6 degrees 2Θ	From 25.6 ± 0.3 ° 2Θto 27.6 ± 0.3 ° 2Θ in 0.05 steps for 10 seconds or in 0.02 steps for 4 seconds at each step.	From 25.6 ± 0.3 ° 2Θto 27.6 ± 0.3 ° 2Θin 0.05 or 0.03 steps for 120 seconds
Quartz 100 reflection at 20.9 degrees 2Θ	From 19.9 ± 0.3 ° 2Θto 21.9 ± 0.3 ° 2Θ in 0.05 steps for 30 seconds or in 0.02 steps for 12 seconds at each step.	From 19.9 ± 0.3 ° 2Θto 21.9 ± 0.3 ° 2Θin 0.05 or 0.03 steps for 240 seconds
Quartz 112 reflection at 50.1 degrees 2Θ	From 49.1 ± 0.3 ° 2Θto 51.1 ± 0.3 ° 2Θ in 0.05 steps for 30 seconds or in 0.02 steps for 12 seconds at each step.	From 49.1 ± 0.3 ° 2Θto 51.1 ± 0.3 ° 2Θin 0.03 steps for 240 seconds
Cristobalite 100 reflection at ~ 21.7 degrees 2Θ	From 21.00 ± 0.3 °2Θto 23.00 ± 0.3 °2Θin 0.05 steps for 30 seconds or in 0.02 steps for 12 seconds at each step.	From 21.00 ± 0.3 °to 23.00 ± 0.3 ° 2Θin 0.05 or 0.03 steps for 240 seconds
Cristobalite 200 & 112 reflection at ~ 36.4 degrees 2Θ	From 35.1 ± 0.3 °2Θto 37.1 ± 0.3 ° 2Θin 0.05 steps for a minimum of 30 seconds or in 0.02 steps 12 seconds at each step.	From 35.1 ± 0.3 ° 2Θto 37.1 ± 0.3 °2Θin 0.05 or 0.03 steps for 240 seconds

Table 2 Data for the most intense diffraction peaks of quartz and cristobalite

Indices	Relative Intensity	D(Å)	2Θ(radiation)
Quartz			
100	35	4.257	20.87 (CuKΘ)
101	100	3.343	26.67 (CuKΘ)
112	17	1.8178	50.15 (CuKΘ1)
50.28 (CuKΘ2)			
211	15	1.5420	59.94 (CuKΘ1)
60.10 (CuKΘ2)			
Cristobalite			
100	100	4.05	21.95 (CuKΘ)
102	14	2.841	31.49 (CuKΘ)
200	20	2.485	36.15 (CuKΘ)
112	6	2.465	36.45 (CuKΘ)
2Θcalculated for Θ1.54186 Å (CuKΘ); 1.54060 Å (CuKΘ1); 1.54439 Å (CuKΘ2)			

Table 3 Line overlap for phases commonly found in association with quartz (Θ-quartz diffraction lines)

Interfering phase	(100)	(101)	(112)	(211)
Albite	-	✔	✔	✔
Anorthite	✔	✔	-	-
Aragonite	✔	✔	✔	✔
Biolite	-	✔	-	✔
Graphite	-	✔	-	✔
Gypsum	✔	-	✔	-
Kaolinite	✔	✔	✔	✔
Maghemite	✔	✔	✔	-
Nucricline	✔	✔	-	-
Mullite	-	✔	-	✔
Muscovite	-	✔	-	-
Sillimanite	-	✔	✔	✔
Vaterite	✔	✔	✔	✔
Wollastonite	-	✔	✔	✔
Wustite	-	-	-	✔
Zircon	-	✔	-	✔
✔ indicates a potential line overlap on the quartz diffraction line indicated				

Table 4 Line overlap for phases commonly found in association with cristobalite (Θ-cristobalite diffraction lines)

Interfering phase	100	101	200/112
Quartz	✔	-	✔
Tridymite	✔	-	✔
Albite (low)	✔	✔	✔
Anorthite	✔	✔	✔
Orthoclase	✔	✔	✔
Calcite	-	✔	✔
Cordierite	✔	-	✔
Corundum	-	-	✔
Kaolinite	✔	-	✔
Mullite	-	-	✔
Muscovite	✔	✔	✔
Talc	✔	-	✔
Zircon	-	-	✔
✔ indicates a potential line overlap on the quartz cristabolite line indicated			

Table 5 Minimum mass with expanded uncertainty of ±30% or ±50% for quartz analysis by XRD

XRD peak degrees 2 Θ	Expanded uncertainty	
	±30%	±50%
26.6 (101)	25 µg	5 µg
20.9 (100)	~ 60–75 µg	25–30 µg
50.1 (112)	~ 60–75 µg	25–30 µg

References

1 NIOSH 2003 National Institute for Occupational Safety and Health Manual of Analytical Methods (NMAM). *Silica, Crystalline, by XRD (filter redeposition) Method* 7500. Issue 4. Available from http://niosh.cihcsp.com/pdfs/7500.pdf last viewed 20/08/13

2 NIOSH 2003 Manual of Analytical Methods (NMAM) *Silica, Crystalline by Infra-Red (KBr pellet) 760 Method 7602 Issue 4* www.niosh.cihcsp.com/pdfs/7500.pdf

3 Monitoring strategies for toxic substances HSG173 (Second edition) HSE Books 2006 www.hse.gov.uk/pubns/books/hsg173.htm

4 *General methods for sampling and gravimetric analysis of respirable, thoracic and inhalable aerosols* MDHS14/4 HSE 2014
www.hse.gov.uk/pubns/mdhs/index.htm

5 BS ISO 24095:2009 *Workplace air: Guidance for the measurement of respirable crystalline silica* British Standards Institution

6 BS EN 481:1993 *Workplace atmospheres: Size fraction definitions for measurement of airborne particles* British Standards Institution

7 Stacey P, Mecchia M, Verpaele S, Pretorius C, Key-Schwartz, R, Mattenklott M, Eypert-Blaison C, Thorpe A, Roberts P and Frost G Differences Between Samplers for Respirable Dust and the Analysis of Quartz - An International Study, Silica and Associated Respirable Mineral Particles, STP 1565, Lee, Ed., 2013 1–30, doi:10.1520/STP156520120188, ASTM International, West Conshohocken, PA

8 Lee T, Lee EG, Kim S et al. Quartz measurement in coal dust with high-flow rate samplers: laboratory study, *Ann Occup Hyg* 2012 56: 413–25

9 Stacey P, Lee T, Thorpe A, Roberts P, Frost G and Harper M Collection Efficiencies of High Flow Rate Personal Respirable Samplers When Measuring Arizona Road Dust and Analysis of Quartz by X-ray Diffraction *Ann Occup Hyg* 2014 met075 first published online January 27, 2014 doi:10.1093/annhyg/met075

10 Soo J, Lee T, Kashon M, Kusti M and Harper M Quartz in coal dust deposited on internal surface of respirable size selective samplers, *J Occup Environ Hyg* 2014 11(12), D215-9. doi: 10.1080/15459624.2014.960575

11 BS EN ISO 13137:2013 *Workplace atmospheres: Pumps for personal sampling of chemical and biological agents. Requirements and test methods* British Standards Institution

12 Lee E, Lee T, Kim S, Lee L, Flemmer M, Harper M Evaluation of pump pulsation in respirable size-selective sampling: Part II. Sampling efficiency shift *Annals of Occup Hyg* 2014 58 (1): 74-84

13 Stacey P, Kauffer E, Moulut JC, Dion C, Beauparlant M, Fernandez P, Key-Schwartz R Friede B, Wake D 'An international comparison of the crystallinity of calibration materials for the analysis of respirable Θ-quartz using x-ray diffraction and a comparison with results from the infrared KBr disc method' *Ann occup Hyg* **53** (6) 2009 639–649

14 EN 13205-6:2012 *Workplace exposure: Assessment of sampler performance for measurement of airborne particle concentrations: Part 6: Transport and handling tests* British Standards Institution

15 Pickard KJ, Walker RF, West NG 'A comparison of X-ray diffraction and infra-red spectrophotometric methods for the analysis of Θ-quartz in airborne dusts' *Ann Occup Hyg* 1985 **29** 149-167

16 Jeyaratnam M, West NG 'The determination of Θ-cristobalite in airborne dust by X-ray diffraction – theory and practice' *Advances in X-ray Analysis* 1989 32 585-592

17 Chisholm JE 'Determination of cristobalite in respirable airborne dust using X-ray diffraction' *Anal Chim Acta* 1994 286 87-95

18 BS EN 482:2012 *Workplace exposures. General requirements for the performance of procedures for the measurement of chemical agents Standard* British Standards Institution

19 Foster RD, Walker RF 'Quantitative determination of crystalline silica in respirable-size dust samples by infrared spectrophotometry' *Analyst* 1984 **109** 117–1127

20 Shinohara Y 'Direct quantitative analysis of respirable cristobalite on filter by infrared spectrophotometry' *Industrial Health* 1996 **34** 25–34

21 Elton NJ, Salt PD, Adams JM 'Determination of quartz in kaolins by X-ray powder diffractometry' *Anal Chim Acta* 1994 **286** 37–47

22 Gordon RL, Harris GW 'Effect of particle size on the quantitative determination of quartz by X-ray diffraction' *Nature* 1955 **176** 1135

23 Mecchia M, Pretorius C, Stacey P, Mattenklott M and Incocciati E X-Ray Absorption Effect in Aerosol Samples Collected on Filter Media, in Silica and Associated Respirable Mineral Particles, ASTM International, STP 1565, Martin Harper and Taekhee Lee, Eds. 2013 139–168 doi:10.1520/STP156520130035.

24 Altree-Williams S, Lee J, Mezin NV 'Quantitative X-ray diffractometry on respirable dust collected on Nucleopore filters' *Ann Occup Hyg* 1977 **20** 109–126

25 Jeyaratnam M, West NG 'The determination of Θ-cristobalite in airborne dust by X-ray diffraction – theory and practice' *Advances in X-ray Analysis* 1989 **32** 585–592

26 Biggins PDE *The selection of a suitable cristobalite standard to be used in the analysis of airborne dust for cristobalite* Report No X.191 (Revised) British Cast Iron Research Association 1986

27 Perrotta AJ, Grubbs DK, Martin ES, Dando NR, McKinstry HA, Huang C-Y 'Chemical stabilisation of Θ-cristobalite' *J Am Ceram Soc* 1989 **72** 441–447

28 Young J, Rea MS, Briggs G 'The non-formation of Θ-cristobalite in devitrified commercial-grade aluminosilicate refractory ceramic fibre' *Br Ceram Trans J* 1989 **88** 58–62

29 Butler MA, Dyson DJ 'The quantification of different forms of cristobalite in devitrified aluminosilicate ceramic fibres' *J Appl Cryst* 1997 **30** 467–475

30 Dyson DJ, Butler MA, Hughes RJ, Fisher R, Hicks GW 'The de-vitrification of alumino-silicate ceramic fibre materials – the kinetics of the formation of different crystalline phases' *Ann Occ Hyg* 1997 **41** 561–590

31 Nagelschmidt G 'Inter-laboratory trials on the determination of quartz in dusts of respirable size' *Analyst* 1956 **81** 210–219

32 Edmonds JW, Henslee WW and Guerra RE 'Particle size effects in the determination of respirable Θ-quartz by X-ray diffraction' *Anal Chem* 1977 **49** 2196–2203

33 Kohyama N 'A new X-ray diffraction method for the quantitative analysis of free silica in the airborne dust in working environment' *Industrial Health* 1985 **23** 221–234

34 Bhaskar R, Li J and Xu L 'A comparative study of particle size dependency of IR and XRD methods for quartz analysis' *Amer Ind Hyg Assoc J* 1994 **55** 605–609

You should use the current edition of any standards listed.

Further information

For information about health and safety, or to report inconsistencies or inaccuracies in this guidance, visit www.hse.gov.uk/. You can view HSE guidance online and order priced publications from the website. HSE priced publications are also available from bookshops.

This guidance is issued by the Health and Safety Executive. Following the guidance is not compulsory, unless specifically stated, and you are free to take other action. But if you do follow the guidance you will normally be doing enough to comply with the law. Health and safety inspectors seek to secure compliance with the law and may refer to this guidance.

This MDHS is available at: www.hse.gov.uk/pubns/mdhs/index.htm.

For further information about this method or other MDHS methods, please visit HSL's website: www.hsl.gov.uk or email: hslinfo@hsl.gov.uk

First published 09/14.