

MDHS

*Methods for the Determination of
Hazardous Substances*
Health and Safety Laboratory



This method updates and replaces MDHS37 (ISBN 0 7176 0208 7, last published in March 1988) MDHS51/2 (ISBN 0 7176 02559, published in March 1988) and MDHS76 (ISBN 0 7176 0634 1, published in March 1994). The principal changes are (i) discussion of Fourier Transform Infrared spectroscopy (FTIR) as well as dispersive; (ii) changes, mostly in the section on analysis by X-ray diffraction, to the discussion of the crystalline content of quartz and cristobalite as a consequence of a single exposure limit being set in terms of crystalline silica; (iii) the inclusion of data on detection limits and uncertainty.

INTRODUCTION

Requirements of the COSHH Regulations

1 The Control of Substances Hazardous to Health Regulations (COSHH)¹ are designed to ensure that the exposure of people at work to substances which could cause health damage is either prevented or, where that is not reasonably practicable, adequately controlled. Employers are required to make an assessment of the health risk created by such work, and to prevent or control exposure to the substances involved. The COSHH Regulations also require that persons who could be exposed to substances hazardous to health receive suitable and sufficient information, instruction and training. Employers must therefore ensure that the requirements of the COSHH Regulations are fulfilled before allowing employees to undertake any procedure described in this MDHS.

2 Guidance is given in *Control of substances hazardous to health. The Control of Substances Hazardous to health Regulations 2002. Approved Code of Practice and guidance*.²

Occurrence, properties and uses

3 The occurrence, properties and uses of crystalline silica are summarised in HSE Guidance Note EH59.³

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Crystalline silica in respirable airborne dusts

Direct-on-filter analyses by infrared
spectroscopy and X-ray diffraction

February 2005

Health effects

4 The health effects of crystalline silica are summarised in EH59.³ The scientific evidence relating to the risks of silicosis and lung cancer are reviewed in Hazard Assessment Documents EH75/4⁴ and EH75/5⁵ respectively.

Health and safety precautions

5 Prevention and control of exposure, emergency procedures and health surveillance are described in HSE Guidance Note EH59.³

Exposure

6 Work activities which are likely to lead to exposure to crystalline silica are listed in HSE Guidance Note EH59.³ They include primary extraction or working of rocks containing quartz, especially tunnelling and quarrying; the drilling, cutting, dry grinding, scabbling, abrasive blasting and demolition of building and other materials containing quartz or cristobalite; the handling of finely ground material in ceramics manufacture and brick making; and the fettling of metal castings and earthenware. Additional information is contained in HSE guidance⁶⁻¹¹ relating to control of exposure to respirable silica in potteries, stonemasonry, heavy clay and refractory processes, and construction.

Exposure limits

7 Regulation 7 of the COSHH Regulations¹ lays down the requirements for using maximum exposure limits (MELs) and occupational exposure standards (OESs) for the purpose of achieving adequate control of worker exposure.

8 Schedule 1 of the COSHH Regulations¹ specifies a maximum exposure limit (MEL) of 0.3 mg/m³, 8-hour time-weighted average (TWA) reference period, for crystalline silica in respirable airborne dust. This limit is reproduced in HSE Guidance Note EH40¹² and the criteria on which it was based are documented in the 1994 supplement of

HSE Guidance Note EH64.¹³ HSE believes that in most cases it should be reasonably practicable to control exposure to 0.1 mg/m³ (8-hour TWA) or less by engineering or process control. Employers should aim to ensure that workers are not exposed to respirable crystalline silica dust concentrations above this level. If exposure cannot be controlled to 0.1 mg/m³ (8-hour TWA) or below by elimination or process or engineering controls, then exposure must be controlled by provision and use of suitable respiratory protective equipment.¹⁴

9 The MEL applies to the total amount of crystalline silica, quartz and cristobalite, and there are no longer separate exposure limits for those two forms of crystalline silica.

Analytical methods

10 There may be alternative methods available for the determination of a particular analyte. With the exception of a few cases where an exposure limit is linked to a specific method (eg rubber fume or asbestos), the use of methods not included in the MDHS series is acceptable provided that they have been shown to have the accuracy and reliability appropriate to the application.

11 This method has been validated to demonstrate that it complies with BS EN 482 *Workplace atmospheres - General requirements for the performance of procedures for the measurement of chemical agents*.¹⁵ If an alternative method is used it is necessary to carry out a similar assessment of its performance.

PRINCIPLE OF METHOD

12 A sample of respirable dust is collected on a membrane filter using a respirable dust sampler.¹⁶ The filter is then placed directly into the sample beam of either an infrared spectrophotometer or an X-ray diffractometer. The mass of crystalline silica on the filter is determined from the infrared or X-ray diffraction response, calibrated against filters loaded with known amounts of standard quartz or cristobalite. Since the volume of air sampled is known, the concentration of airborne crystalline silica is readily calculated.

13 The choice of analytical technique, ie infrared spectroscopy or X-ray diffractometry, depends largely on other materials present on the filter which may interfere in the analysis.

SCOPE OF METHOD

14 The method is suitable for the determination of quartz and cristobalite within the approximate range 20 µg to 1 mg. Both infrared and X-ray diffraction responses are linear over this range.

15 For a 500 litre air sample (corresponding to sampling for approximately four hours at 2.2 litre/min), a concentration of 0.3 mg/m³ corresponds to 150 µg of quartz/cristobalite on the filter. However, the concentration of airborne crystalline silica should be reduced to as low a value as is reasonably practicable and, accordingly,

airborne concentrations much lower than 0.3 mg/m³ will need to be measured. The mass of quartz/cristobalite on a typical filter is of the order of 50 µg.

16 The upper limit of the analytical range is also governed by the total amount of dust on the filter. Experience has shown that heavy dust deposits may easily become dislodged during handling or transit of the samples and the total amount of dust on the filter is best kept below about 2 mg.

17 Further limitations to the scope of the method are discussed separately below for measurement by infrared and by X-ray diffraction.

18 HSG173¹⁷ advises employers about how they should conduct investigations into the nature, extent and control of exposure to substances hazardous to health which are present in workplace air. The objective of air monitoring is usually to determine worker exposure, and therefore the procedures described in this method are for personal sampling in the breathing zone. The method may also be used for background or fixed location sampling, but it should be recognised that, due to aerodynamic effects, samplers designed for personal sampling do not necessarily exhibit the same collection characteristics when used for other purposes.

SAMPLING EQUIPMENT

Samplers

19 Higgins-Dewell cyclone samplers with 25 mm diameter filters are the type most commonly used but any of the other types of respirable dust sampler described in MDHS14/3¹⁶ may be used. However, CIP10 samplers use a foam pad to collect the respirable dust and they are not suitable for the direct-on-filter method of measurement described here.

Filters

20 Filters should be of a diameter suitable for use in the selected sampler. The chosen filter type should have a capture efficiency of not less than 90% and be suitable for collection of samples of crystalline silica. PVC filters (such as Gelman GLA5000) or PVC-acrylonitrile co-polymer filters (such as Gelman DM800) have suitable infrared characteristics. Silver filters are suitable for X-ray diffraction analysis but not infrared spectroscopy: they have a lower background for XRD than organic membranes, giving a better signal-to-noise ratio, but are much more expensive and may have other disadvantages related to their high X-ray absorption.

Sampling pumps

21 Sampling pumps should comply with the provisions of BS EN 1232,¹⁸ have an adjustable flow rate, incorporate a flowmeter or a flow fault indicator, and be capable of maintaining the selected flow rate to within ±5% of the nominal value throughout the sampling period. When worn, the pump should not impede normal work activity.

22 For cyclone samplers, pulsation damped flow is particularly important and an external pulsation damper must be used if the pump does not contain an integral damper.

Flowmeter

23 The portable flowmeter used should be capable of measuring the appropriate flow rate to within $\pm 5\%$, and calibrated against a primary standard.¹⁶ Flowmeters incorporated in sampling pumps are not suitable for accurate measurement of the flow rate. However, they can be useful for monitoring the performance of samplers, provided they have adequate sensitivity.

LABORATORY APPARATUS

Infrared spectrophotometer

24 This method requires either an FTIR or a double beam dispersive instrument capable of at least x10 ordinate expansion on absorbance spectra.

25 A suitable filter holder, eg a rotatable polariser mount, is required so that the sample can be rotated in its own plane. This will allow the effect of non-uniform sample deposition to be reduced by taking absorbance measurements at several orientations.

X-ray powder diffractometer

26 An X-ray powder diffractometer with reflection geometry and X-ray generator are required. Diffractometers with Bragg-Brentano semi-focusing geometry with Cu- or Co- target X-ray tubes are in general use.

Dust cloud generator

27 A dust cloud generator of some kind is required for the generation of atmospheres containing quartz or cristobalite dust. Figure 1 shows a simple design constructed from 3 mm thick borosilicate glass, apart from the top which is made of 5 mm thick clear perspex. A 2 mm deep groove is machined into the top which mates with the rim of the main glass chamber to form a closed system. Four symmetrically spaced holes, through each of which a cyclone sampler can be suspended, are drilled in the top.

Balance

28 A micro-balance calibrated against a primary standard and capable of weighing to within $\pm 1 \mu\text{g}$ over the range 0-20 mg for the preparation of standard filters for calibration. An electrostatic eliminator for use when weighing filters.

REAGENTS

29 No 'reagents' in the strict sense are required in this method since the determination is carried out directly on the collected sample without chemical or physical treatment.

Standard reference materials

30 For both techniques, it is essential to have a standard quartz or cristobalite in which the percentage of crystalline quartz or cristobalite is known.

31 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 $1.5 \mu\text{m}$; below about $1.5 \mu\text{m}$, the response falls due to the presence of an amorphous surface layer. A standard reference sample for infrared analysis should therefore ideally have the same particle size distribution as the sample under consideration.

32 Only crystalline silica will give an XRD response, and particle size differences between the sample and the standard are much less important for that technique,²¹ although peak broadening and extinction effects are related to particle size.²¹⁻²³ But the effect of particle size on crystalline content may be a serious source of uncertainty in another way. Smaller particles contain a lower proportion of crystalline material because the amorphous surface layer makes up a higher proportion of the total.^{22, 23} The material on calibration filters is size-selected from the standard by the process of dispersal and sampling during filter preparation. As a consequence, it may not contain exactly the same proportion of crystalline

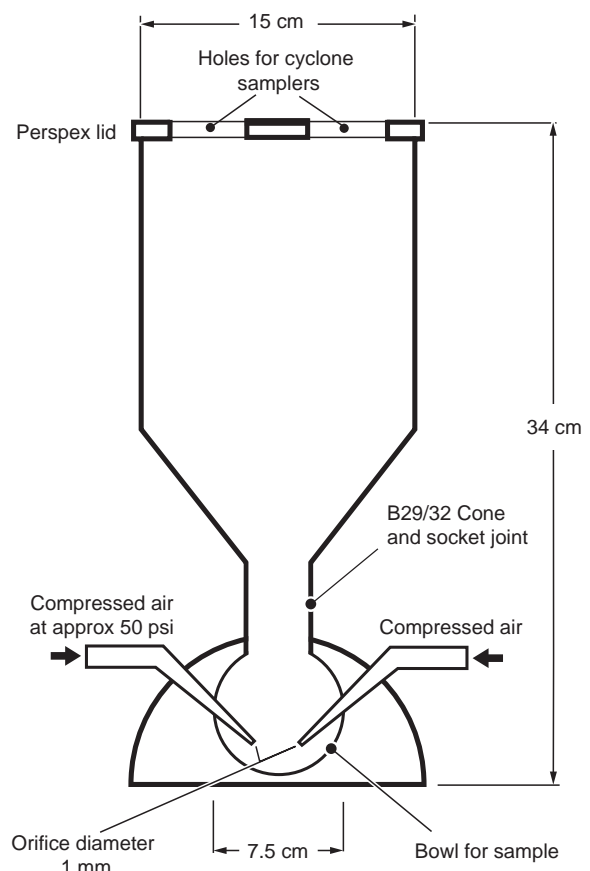


Figure 1: Glass chamber for the preparation of calibration standards

material as the untreated standard. An ideal standard for XRD would be such that its crystalline content is unaltered in the preparation of calibration filters or is modified to a known extent. In practice, no such information is available for current standards and it is necessary to assume that the crystalline content of material on calibration filters is the same as in the bulk standard. The analytical results may be subject to bias to the extent that this assumption is uncertain.

33 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.

34 The US National Institute of Standards and Technology (NIST) offers a certified respirable α -quartz standard (Standard Reference Material (SRM) 1878) of known crystalline quartz content which is suitable for calibration when analysing by infrared spectroscopy or X-ray powder diffraction. Sikron F600 (HSE standard quartz A9950) is also a suitable standard and this can be obtained from the Health and Safety Laboratory. It does not differ significantly from SRM 1878 when used to calibrate for direct on-filter analysis by XRD.²⁴ Alternatively, it is permissible to use any other documented standard or a secondary standard which has been compared with a primary standard using the same analytical method.

35 The US National Institute of Standards and Technology (NIST) offers a certified respirable α -cristobalite standard (Standard Reference Material (SRM) 1879) of known crystalline cristobalite content which is suitable for calibration when analysing by infrared spectroscopy or X-ray powder diffraction. Alternatively, it is permissible to use any other documented standard or a secondary standard which has been compared with a primary standard using the same analytical method.

Drift correction sample

36 In X-ray diffraction, 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.

SAMPLING

37 Personal samples for respirable crystalline silica are collected as described in MDHS14/3.¹⁶

Preparation of sampling equipment

38 Clean the samplers before use. Dismantle the parts that come into contact with dust (referring to the manufacturer's instructions where necessary), soak in detergent solution, rinse thoroughly with water, and allow to dry before reassembly.

39 Using clean flat-tipped tweezers, load each sampler with a filter (pre-weighed, in order to match blanks, when

using dispersive IR; pre-scanned when using FTIR), and label each sampler with a unique identification number.

40 Set the volumetric flow rate on each sampler to the appropriate value (see MDHS14/3¹⁶), to an accuracy of $\pm 5\%$.

Collection of samples

41 Attach the sampler to the wearer, preferably on the lapel, and as close to the mouth and nose as possible.¹⁷ Cyclone samplers are not generally sensitive to orientation, but should be attached to the wearer with the grit-pot at the base. Attach the pump to a suitable belt or harness so that it causes minimum inconvenience to the wearer, and safely secure any tubing connecting the pump and sampler.

42 For each sampler, carefully record the sample identity and all relevant sampling data (see Appendix A, page 13).

43 To begin sampling, remove the protective cover (if any) from the sampler and switch on the pump. Record the time and volumetric flow rate at the beginning of the sampling period. Where the pump is fitted with an integral timer, ensure that this is reset to zero.

44 At the end of the sampling period, again record the volumetric flow rate and the time, and calculate the duration of the sampling period. If the pump is fitted with an integral timer, check that the indicated period agrees with the calculated period. Consider the sample to be invalid if the two sampling times differ by more than 5% or if the volumetric flow rate at the end of the sampling period differs from that at the beginning by more than 0.1 litre/min.

45 Retain as blanks one unused loaded sampler from each batch of ten prepared; a minimum of three blanks should always be kept. Treat these as far as possible in the same manner as those actually used for sampling, but do not draw air through them.

Background (fixed position) sampling

46 In use, the personal samplers should be mounted at approximately head height, away from obstructions, fresh air inlets or strong winds. The sampling procedures are otherwise the same as for personal sampling. It is not appropriate to compare fixed point (background) samples with the exposure limit. Fixed-position samples may be useful in identifying the main source(s) of crystalline silica exposure. Comparison of airborne concentration measurements from personal and fixed point samples may give some indication of the extent to which exposure arises from local or general conditions.

Sampling time

47 A long sampling time ensures a heavier deposit of dust on the filter, thus reducing measurement inaccuracies. Sampling times should therefore be as long as is reasonably practicable (preferably not less than four hours), and should be representative of the working periods of the individuals being monitored. If the dust

concentration is so high that a single filter would be overloaded, several filters may be used consecutively.

48 Further advice on sampling procedure is given in Guidance Note HSG173.¹⁷

Transport

49 Remove the filter from the sampler using flat-tipped tweezers, place it in an airtight tin and close with a lid. Take particular care to prevent material being dislodged from the filter. Transport the samples to the laboratory in a container capable of preventing damage in transit, and labelled to ensure proper handling. In some types of sampler, the filter is in a cassette whose inlet and outlet openings are closed with a plastic clip for transport to the laboratory where the filter may then be removed.

CALIBRATION

Preparation of calibration standards

50 Take 30 filters, ideally from the same box, and place separately on a clean surface in an oven at 50°C for two hours.

51 Leave overnight in sample tins with lids left slightly ajar in the balance room to equilibrate with the atmosphere. Remove each filter in turn, weigh to the nearest μg , record the weight and return the filter to its tin.

52 Number the tins in ascending order of filter weights, and select five or six filters as reference blanks such that each standard has a reference blank filter within 200 μg of its weight. If using a Fourier Transform InfraRed spectroscopy (FTIR), scan the clean filters and save the resulting spectra on disk so that each filter can later be used as its own reference.

53 Use the remaining filters to prepare a series of standards by sampling from an airborne cloud of standard quartz or cristobalite generated in a dust cloud chamber (Figure 1). **Safety note:** Adequate means must be provided to prevent the glass chamber becoming dangerously pressurised during use when compressed air is applied to the side arms. The dust cloud generator must be placed inside a fume cupboard while atmospheres of quartz or cristobalite are being produced and sampled.

54 Place about 0.1 g of the standard quartz or cristobalite in the 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 one minute for the coarser particles to settle out from the dust cloud. Run each sampling pump for sufficient time, typically 5-20 sec, to obtain filters loaded with the required amounts of standard covering the range 20-500 μg by trial and error. A minimum of five or six filters is required to give a reliable calibration.

55 When the required filters have been loaded with standard, allow them and the blanks to equilibrate in the balance room and re-weigh. Use the weights of the blank filters to determine a 'blank correction' for adsorption/desorption of moisture and apply it to the weight increases of the loaded filters to obtain the mass of standard on each.

Calibration of spectrophotometer/diffractometer

56 Calibration of the infrared spectrophotometer and X-ray diffractometer are discussed separately below.

ANALYSIS BY INFRARED SPECTROSCOPY

Scope

57 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.

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

Interferences

59 Several minerals which may occur in conjunction with quartz and cristobalite absorb infrared radiation in the region of the quartz absorbances at 800 and 780 cm^{-1} and the cristobalite absorbances at 800 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 absorbances assessed. Using software techniques, it is possible to subtract any interfering bands from the infrared spectrum of a sample.

Re-radiation effects

60 Some dark-coloured samples (eg those containing graphite or magnetite) can act as black body radiators while in the spectrophotometer beam. In older dispersive instruments, this re-radiation effect²⁵ could result in up to 75% attenuation of the quartz absorbances at 800 and 780 cm^{-1} . This problem could be overcome by the use of a spectrophotometer equipped with an asynchronously double chopped optical system, or, in lower-cost single chopped instruments, by the use of germanium cut-on/blocking filters in the sample and reference beams.²⁵ 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 unmodulated and not detected.

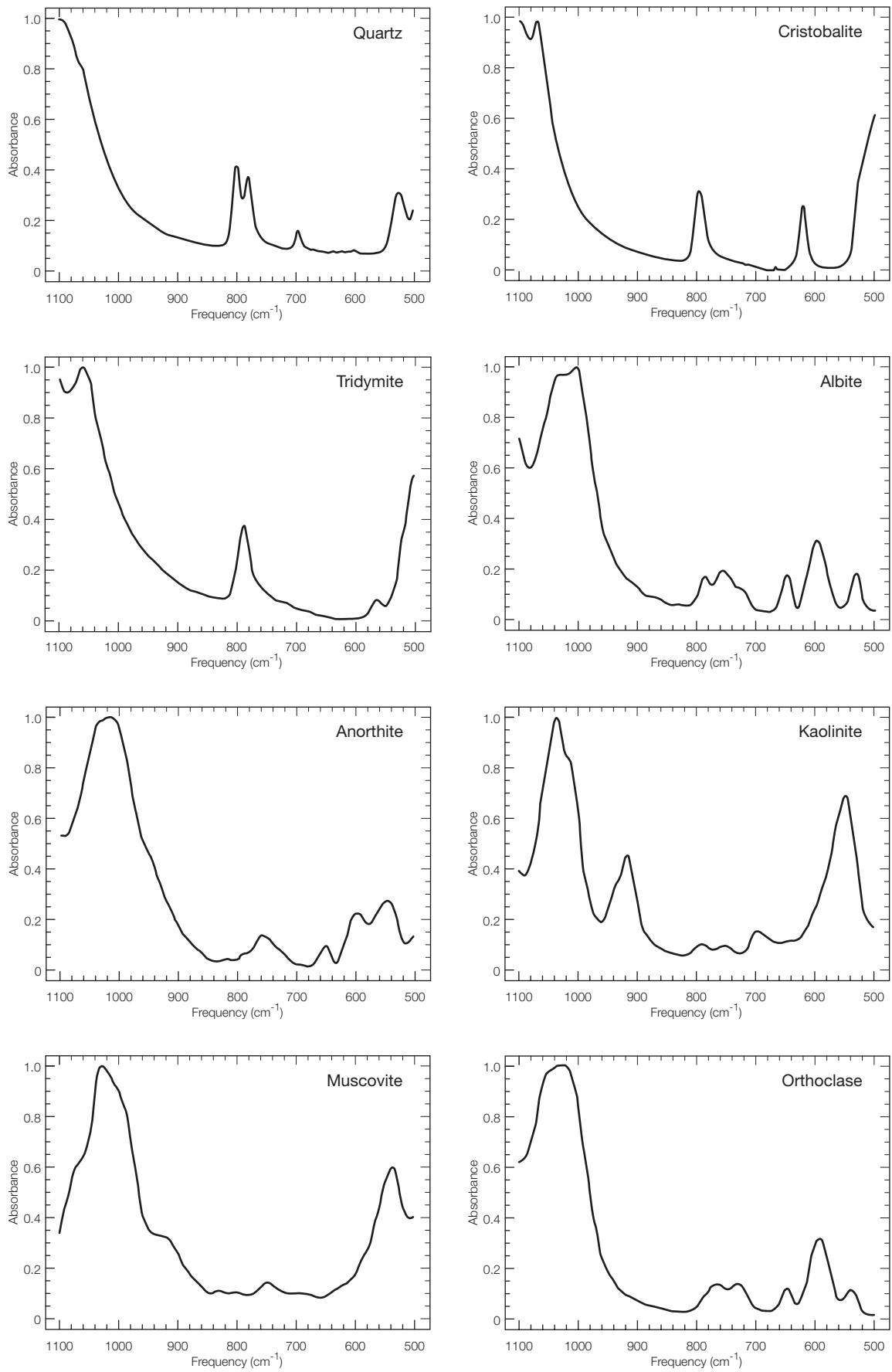


Figure 2: Infrared spectra of quartz, cristobalite and interfering phases

Other limitations

61 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 α -cristobalite standard.

Calibration of spectrophotometer

62 Place each standard sample in turn in the sample beam, using a defocused beam so that the beam covers the sample area on the filter.

63 When using FTIR, scan each standard sample filter in absorbance mode between 900 cm^{-1} and 500 cm^{-1} , using typical settings of 32 scans at 4 cm^{-1} resolution, and reference the resulting spectrum against that obtained from the pre-scanned blank filter.

64 When using dispersive IR, place the reference blank filter nearest in weight (ideally within $200\text{ }\mu\text{g}$) to the sample filter weight in the reference beam. Scan the sample filter in absorbance mode from 900 cm^{-1} to 500 cm^{-1} using a suitable scale expansion.

65 For both instrument types, determine the absorbance for the infrared bands at 780 cm^{-1} and 800 cm^{-1} for quartz or 800 cm^{-1} and 620 cm^{-1} for cristobalite. Rotate the standard through 90° and repeat the absorbance measurements. (Note that rotation of the sample may not be necessary if the infrared beam in the instrument has a circular cross-section.)

66 Take the mean of the two measurements for each standard sample and prepare a graph of absorbances at 780 cm^{-1} and 800 cm^{-1} against mass for quartz, or absorbances at 800 cm^{-1} and 620 cm^{-1} against mass for cristobalite. The points should lie on a straight line passing close to the origin for each peak.

67 Calculate the slope and intercept of each calibration line as a linear regression ($y = mx + c$) with diffracted intensity as the dependent variable (y) and mass as the independent variable (x). 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.

68 Divide the slope, m , by the fraction of crystalline quartz or cristobalite in the standard to express it and the results derived from it in terms of crystalline quartz or cristobalite.

Determination of quartz in respirable dust samples

69 Condition, say, 30 filters from the same box. If using a dispersive instrument, retain five or six of these filters for use as reference blanks (covering the weight variation range at approximately $400\text{ }\mu\text{g}$ intervals) and use the rest as sample filters. With FTIR, all 30 filters are pre-scanned and can therefore all be used as sample filters. After sampling, the sample and reference filters are presented directly to the spectrophotometer for analysis.

70 When using FTIR, the instrument should be set up to collect sufficient scans to reduce the signal-to-noise ratio to an acceptable level. Typically, 32 scans are adequate.

71 When using a double beam dispersive instrument, a low resolution scan from 1500 cm^{-1} to 400 cm^{-1} should be carried out using a wide-slit setting. This allows checking for filter mismatch and gives a warning of the presence of other interfering phases. It also gives an idea of the degree of scale expansion that is required for the quantitative scan.

72 If a single-chopped dispersive instrument is being used, fit the matched 9 mm cut-on/blocking filters in the sample and reference filter holders. These are placed between the infrared source and the membrane filters, using suitable spacer rings. Reset the gain of the instrument if necessary. The qualitative scan is carried out between 900 and 500 cm^{-1} , repeating the scan after rotating the sample through 90° .

73 The baseline is drawn as a straight line tangential to the trace minima on either side of the quartz doublet. These minima occur at about 730 and 830 cm^{-1} , as shown in Figure 2. Measure the heights of the 780 and 800 cm^{-1} peaks from this baseline and, if more than one spectrum is recorded, calculate the mean absorbances.

74 The amount of quartz on the filter is calculated separately from the infrared absorbances at 780 and 800 cm^{-1} by reference to their individual calibration lines. The two results are then averaged to produce the mass of quartz on the filter. If the ratio of the absorbance at 800 cm^{-1} to that at 780 cm^{-1} is outside the range 1.0 to 1.4, the spectrum should be examined for interferences, in particular cristobalite.

Determination of cristobalite in respirable dust samples

75 Follow the same procedures as described for quartz, and measure the peaks at 800 and 620 cm^{-1} . For the peak at 620 cm^{-1} , draw a second baseline using the trace minima at approximately 650 and 590 cm^{-1} .

Determination of mixtures of quartz and cristobalite

76 Follow the same procedures as described for quartz, and measure the peaks at 800 and 620 cm^{-1} . The cristobalite content is determined from the peak at 620 cm^{-1} . The quartz content is determined from the peak at 800 cm^{-1} after first subtracting the contribution of the cristobalite to this peak. 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 wave number.

CALCULATION OF RESULTS

Volume of air sample

77 Calculate the volume, V_s , in litres of each air sample as the product of the average measured sampling flow rate (litres/min) and the sampling time (min).

Concentration of respirable crystalline silica in air

78 Calculate the airborne concentration of quartz or cristobalite (mg/m^3 or its equivalent $\mu\text{g}/\text{litre}$) as the mass on the filter (μg) divided by the air volume (litres). Calculate the airborne concentration of respirable crystalline silica by adding the concentrations of quartz and cristobalite if both are present.

ANALYSIS BY X-RAY DIFFRACTION

Scope

79 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. 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. In practice, for dust samples from typical industrial environments, no significant deviation from linearity is found for dust loadings up to about 2 mg. Occasionally, samples with a high mass absorption coefficient for the radiation used may be encountered, eg an iron oxide matrix with $\text{CuK}\alpha$ radiation, 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^{26, 27} but they make the analysis more complicated and may introduce significant overcorrection.²⁸

80 Empirical observation suggests that the linear relationship between diffracted intensity and mass may not hold when the mass of dust is very low, ie close to the origin. The extrapolated straight line calibration does not usually pass through the origin (Figure 3) leading to uncertainty in the detection limit and measurements close to it.

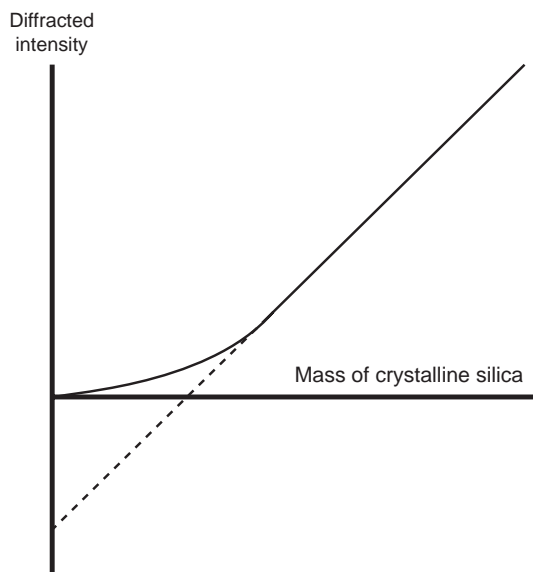


Figure 3: Supposed behaviour of the XRD calibration line near the origin

X-ray diffractometry

81 The diffractometer operating conditions should be chosen:

- to maximise intensity even if this leads to some loss of resolution;
- to minimise errors arising from particle statistics (largest practicable divergence and receiving slits; sample spinner). An example of suitable operating conditions is given in Table 1.

Table 1: Example of operating and data collection conditions for X-ray diffractometry

Diffractometer operating conditions

2.7kW broad focus copper anode X-ray tube run at 50kV, 45mA

1° divergence and scatter slits (used over whole range to avoid changes during data collection)

(An automatic divergence slit is suitable if fitted)

Receiving slit: 0.3 mm

Diffracted-beam graphite monochromator

Sample spinner

Automatic sample changer

Data collection

Qualitative scan	6 to 70 °2 θ continuous scan at 1°/min or 0.02°/sec
Quartz	25.65 to 27.65 °2 θ in 0.05° steps, counting for 10 sec at each step or 0.02° steps, counting for 4 sec at each step
Quartz	19.90 to 21.90, 49.10 to 51.10 and 59.00 to 61.00 °2 θ in 0.05° steps, counting for 30 sec at each step or 0.02° steps, counting for 12 sec at each step
Cristobalite	21.00 to 23.00, 30.45 to 32.45 and 35.10 to 37.10 °2 θ in 0.05° steps, counting for 30 sec at each step or 0.02° steps, counting for 12 sec at each step

System calibration

82 Diffraction data are collected for the calibration standards for quartz and cristobalite in the same way as for sample analysis (see below). Since no interfering phases will be present on the calibration standard filters, a qualitative scan is unnecessary.

Samples

83 Before and after measuring a batch of filters, measure the net peak area of the selected reference peak of the drift correction sample. If there is a significant difference between the two results, all results should be discarded and the reasons for the apparent change in diffractometer performance investigated.

84 Mount each sample filter in turn in the diffractometer and make a rapid qualitative scan; an example of 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 group 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.

85 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 low enough for the peak limits and background to be set with reasonable ease and reproducibility. Satisfactory results can be obtained using the data collection conditions in Table 1.

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 (CuKα)
101	100	3.343	26.67 (CuKα)
112	17	1.8178	50.15 (CuKα ₁) 50.28 (CuKα ₂)
211	15	1.5420	59.94 (CuKα ₁) 60.10 (CuKα ₂)
Cristobalite			
100	100	4.05	21.95 (CuKα)
102	14	2.841	31.49 (CuKα)
200	20	2.485	36.15 (CuKα)
112	6	2.465	36.45 (CuKα)
2θ calculated for λ 1.54186 Å (CuKα); 1.54060 Å (CuKα ₁); 1.54439 Å (CuKα ₂)			

86 If quartz is to be determined, collect diffraction data at least for the most intense quartz peak and preferably also for the other three 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 2θ positions for CuKα radiation are listed in Table 2. For samples of a particular type or from a particular industrial environment, experience may show that it is not worth collecting data for certain peaks as they are almost always subject to interference and therefore unsuitable for analysis.

Interferences

87 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.

88 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.

Table 3: Line overlap for phases commonly found in association with quartz

α-quartz diffraction lines

Interfering phase	(100)	(101)	(112)	(211)
Albite	-	✓	✓	✓
Anorthite	✓	✓	-	-
Aragonite	✓	✓	✓	✓
Biotite	-	✓	-	✓
Graphite	-	✓	-	✓
Gypsum	✓	-	✓	-
Kaolinite	✓	✓	✓	✓
Maghemite	✓	✓	✓	-
Nucricline	✓	✓	-	-
Mullite	-	✓	-	✓
Muscovite	-	✓	-	-
Sillimanite	-	✓	✓	✓
Vaterite	✓	✓	✓	✓
Wollastonite	-	✓	✓	✓
Wustite	-	-	-	✓
Zircon	-	✓	-	✓

✓ indicates a potential line overlap on the quartz diffraction line indicated

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.

Table 4: Line overlap for phases commonly found in association with cristobalite

α -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 cristobalite diffraction line indicated

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.

89 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 non-silicates, analysis by infrared spectroscopy may be preferable.

90 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° 2 θ CuK α) is partially overlapped by the 311 cristobalite peak at d 1.533 Å (60.47° 2 θ CuK α) 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° 2 θ

CuK α) and 112 at d 2.465 Å (36.45° 2 θ CuK α). 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 CuK α).

Other limitations

91 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.^{29,30} These variations are probably related to the presence of β -cristobalite which normally occurs at high temperatures and transforms rapidly into α -cristobalite on cooling. The β -form may, however, be stabilised in the presence of small amounts of some oxides and so persist after cooling.^{31,32} Other metastable forms may also be encountered.^{33,34} These and β -cristobalite have diffraction peaks in positions very close to those of the α -form but with different intensities. Analyses using α -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.

92 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.

93 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.²² This amorphous layer makes up a higher proportion of the smaller particles and the proportion of crystalline material is correspondingly reduced. Laboratory studies show a fall of up to 50% in diffracted intensity in the smallest size fractions,^{22,35-39} almost all of which resulted from the fall in the proportion of crystalline material. Since the MEL is for 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

Derivation of net peak area intensity

94 Derive the net peak area from the data collected covering each diffraction peak. The raw data may be used or a smoothing algorithm applied before processing. The

data may be handled either as raw counts or the count at each step may be divided by the count time to convert it to counts/sec. The latter procedure has the advantage that a different count time may be used with the calibration unaltered.

95 Identify the peak position and minima either side of it to define the limits of the peak and the background intensity below it. Most X-ray diffraction software will calculate the net peak area once these limits have been defined. The net peak area is the sum of all the counts between the limits with the background 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 may be expressed as raw counts, counts/sec or the counts/sec may be multiplied by the step size in degrees to express it as counts/sec.deg. Using counts/sec.deg allows the step size to be changed with the calibration unaltered.

96 Use the observed net peak area for the drift correction sample, D_o , to normalise the observed net peak area for the sample, A_o , relative to a chosen reference value, D_r , of the peak area for the drift correction sample:

$$\text{normalised sample peak area } A_s = A_o \cdot D_r / D_o$$

Calibration

97 For each quartz and cristobalite peak, plot the diffracted intensity, ie the normalised net peak area, A_s , against the mass of quartz or cristobalite on the filter. The points should lie on a straight line passing close to the origin.

98 Calculate the slope and intercept of each calibration line as a linear regression ($y = mx + c$) with diffracted intensity as the dependent variable (y) and mass as the independent variable (x). 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.

99 Divide the slope, m , by the fraction of crystalline quartz or cristobalite in the standard to express it and the results derived from it in terms of crystalline quartz or cristobalite.

Concentration of quartz and/or cristobalite in air

100 If quartz is to be determined, select one or more quartz peaks which appear to be free from peak overlap for quantitative analysis. For each peak, take the normalised net peak area, A_s , and use the slope m and intercept c to calculate the mass of quartz on the filter as $(A_s - c)/m$. If more than one quartz line has been measured calculate an average figure for quartz weight, though results should be rejected if interference is suspected. If cristobalite is to be determined, repeat the process for cristobalite peaks free from interference.

101 For some samples it may be difficult to be sure that diffraction peaks are free from overlap on the basis of the information provided by the qualitative scans. In such 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 in such cases, it will lead to an overestimate of the mass present. The lowest of the results may be reported as the best estimate obtainable. 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. Infrared spectroscopy should also be considered in such cases.

CALCULATION OF RESULTS

Volume of air sample

102 Calculate the volume, V_s , in litres of each air sample as the product of the average measured sampling flow rate (litres/min) and the sampling time (minutes).

Concentration of respirable crystalline silica in air

103 Calculate the airborne concentration of quartz or cristobalite (mg/m^3 or its equivalent $\mu\text{g/litre}$) as the mass on the filter (μg) divided by the air volume (litres). Calculate the airborne concentration of respirable crystalline silica by adding the concentrations of quartz and cristobalite if both are present.

METHOD PERFORMANCE

Detection limits: Infrared

104 The qualitative and quantitative detection limits for crystalline silica, defined as three times and ten times the standard deviation of a blank determination, are typically around $3 \mu\text{g}$ and $10 \mu\text{g}$ 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 limits: XRD

105 The estimation of detection limits for quartz and cristobalite is problematical because the linear relationship between diffracted intensity and mass does not appear to hold near the origin. Theoretically the calibration line should pass through the origin and zero diffracted intensity should correspond to zero mass. However, it is almost always found that the calibration line has a negative intercept on the diffracted intensity axis, ie zero diffracted intensity appears to require a small mass already present. Of course this cannot actually be the case and the supposed behavior near the origin is shown schematically in Figure 3.

106 Taking an intensity at three times the standard deviation of a blank determination and applying the linear calibration leads to an unrealistically high estimate of the limit of detection (LOD), around 20-25 μg for the strongest quartz and cristobalite peaks. This estimate of the LOD is determined predominantly by the intercept of the calibration line on the mass axis. In the past, attempts have been made to overcome this difficulty by taking a calibration line constrained to pass through the origin. The slope of this line differs very little from that of the unconstrained line and the resulting estimates of the LOD

are much lower but equally unrealistic, around 5 µg for the strongest quartz peak³⁹ and around 10 µg for the strongest cristobalite peak.^{29,40} The most one can say is that the true qualitative LOD lies between these two estimates, probably about 10 µg for the strongest quartz peak and around 20 µg for the strongest cristobalite peak. For a 500 litre air sample (approximately four hours at 2.2 litres/min), these correspond to 0.02 mg/m³ quartz and 0.04 mg/m³ cristobalite.

107 The qualitative LOD is poorer for the weaker diffraction peaks: about 20 µg, 30 µg and 50 µg for the 100, 112 and 211 quartz peaks respectively, corresponding to 0.04, 0.06 and 0.10 mg/m³ 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/m³ cristobalite for a 500 litre air sample.

108 Estimation of quantitative detection limits based on a diffracted intensity ten times the standard deviation of a blank determination presents the same problem but in less acute form. It is probably reasonable to base quantitative detection limits on the (unconstrained) 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/m³ 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/m³ 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/m³ for a 500 litre air sample.

Overall uncertainty

109 The overall uncertainty for a measuring procedure is defined in BS EN 482 as 'the quantity used to characterise as a whole the uncertainty of the result given by a measuring procedure', and is quoted as a percentage combining bias and precision using the following equation:¹⁵

where:

$$\text{overall uncertainty} = \frac{|\bar{x} - x_{ref}| + 2s}{x_{ref}} \times 100$$

\bar{x} is the mean value of results of a number n of repeated measurements;

x_{ref} is the true or accepted reference value of concentration;

s is the standard deviation of measurements.

110 An additional 5% is usually added to the overall uncertainty percentage calculated using this equation, to allow for the variability of the pump flow rate. The performance requirements quoted in BS EN 482 for overall uncertainty, where the task is 'measurement for comparison with limit values' are ± 50% for samples in the range 0.1 to 0.5 LV and ± 30% for samples in the range 0.5 to 2.0 LV (LV = Limit Value).¹⁵

111 The overall uncertainty of the method was determined to be less than ± 50% for samples in the range 0.2 to 0.5 LV and less than ± 20% for samples in the range 0.5 to 2.0 LV for analysis by infrared.

112 The overall uncertainty of the method was determined to be less than ± 50% for samples in the range 0.2 to 0.5 LV and less than ± 20% for samples in the range 0.5 to 2.0 LV for analysis by XRD using the strongest diffraction peaks of quartz and cristobalite. Estimates for analysis by XRD using the weaker diffraction peaks are listed in Table 5.

Table 5: Estimates of overall uncertainty for analysis by XRD

Strongest quartz peak

Quartz 101 ±50% in the range 0.2 to 0.5 LV ±20% in the range 0.5 to 2.0 LV

Weaker quartz peaks

Quartz 100 ±50% in the range 0.2 to 0.5 LV ±20% in the range 0.5 to 2.0 LV

Quartz 112 ±50% in the range 0.4 to 0.7 LV ±20% in the range 0.7 to 2.0 LV

Quartz 211 ±50% in the range 0.5 to 1.0 LV ±20% in the range 1.0 to 2.0 LV

Strongest cristobalite peak

Cristobalite 101 ±50% in the range 0.2 to 0.5 LV ±20% in the range 0.5 to 2.0 LV

Weaker cristobalite peaks

Cristobalite 102 ±50% in the range 0.5 to 1.0 LV ±20% in the range 1.0 to 2.0 LV

Cristobalite 200 + 112 ±50% in the range 0.5 to 1.0 LV ±20% in the range 1.0 to 2.0 LV

Stability

113 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. Note also that sample filters have to be handled carefully at all times to prevent the dust from being dislodged.

TEST REPORT

114 Appendix A (page 13) gives recommendations for information to be included in the test report.

QUALITY CONTROL MEASURES

115 An appropriate level of quality control is required when using this method. Analytical quality requirements, guidance

on the establishment of a quality assurance programme and details of internal quality control and external quality assessment schemes are fully described in MDHS71.⁴¹

116 Filters prepared in the same way as the calibration standards with loadings of 100-200 µg are suitable for internal quality control. One or more such quality control filters should be included with each batch of samples to be analysed and the results recorded and monitored.

117 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 itself.

118 It is strongly recommended that all laboratories undertaking the determination of hazardous substances in workplace air should participate in an external quality assessment scheme such as HSE's Workplace Analysis Scheme for Proficiency (WASP). Details of WASP are given in MDHS71.⁴¹

ADVICE

Advice on this method and the equipment used can be obtained from the Health and Safety Executive, Health and Safety Laboratory, Harpur Hill Industrial Estate, Harpur Hill, Buxton, Derbyshire SK17 9JN (Tel: 01298 218000, Fax: 01298 218986, email: hslinfo@hsl.gov.uk).

The Health and Safety Executive wishes, where possible, to improve the methods described in this series. Any comments that might lead to improvements would therefore be welcome and should be sent to the above address.

APPENDIX A: RECOMMENDATIONS FOR THE TEST REPORT

It is recommended that the test report should include the following information:

- (a) a complete identification of the air sample, including the date of sampling, the place of sampling, either the identity of the individual whose breathing zone was sampled or the location at which a fixed point measurement was made, a very brief description of the work activities that were carried out during the sampling period, and a unique sample identification code;
- (b) a reference to this MDHS, including information about which analytical technique was used, and a description of any deviation from the procedures described;
- (c) the make and type of sampler used;
- (d) the make, type and diameter of filter used;
- (e) the make and type of sampling pump used, and its identification;
- (f) the type of flowmeter used, the primary standard against which the calibration of the flowmeter was checked, and the range of flow rates over which the calibration of the flowmeter was checked;
- (g) the time at the start and end of the sampling period, and the sampling time in minutes;
- (h) the mean flow rate during the sampling period, in litres per minute;
- (i) the volume of air sampled, in litres;
- (j) the name of the person who collected the sample;
- (k) the time-weighted average mass concentration of crystalline silica found in the air sample, in milligrams per cubic metre;
- (l) the analytical variables used to calculate the result;
- (m) the type(s) and instrument(s) used for sample analysis;
- (n) the name of the analyst; and
- (o) any inadvertent deviations, unusual occurrences or other notable observations.

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British Standards are available from BSI Customer Services, 389 Chiswick High Road, London W4 4AL
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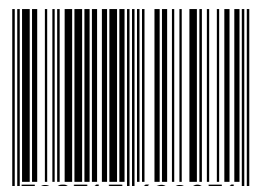
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