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Workplace air — Guidance for the measurement of respirable crystalline silica

Air des lieux de travail — Lignes directrices pour le mesurage de la fraction alvéolaire de la silice cristalline

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Contents

Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Respirable crystalline silica (RCS) is a hazard to the health of workers in many industries through exposure by inhalation. Industrial hygienists and other public health professionals need to determine the effectiveness of measures taken to control workers' exposure. Taking samples of air during a work activity and then measuring the amount of RCS present is often done to assess the exposure of an individual, the effectiveness of their respiratory protection or effectiveness of other controls. Studies have found that procedures to ensure the quality of RCS measurements must be followed to ensure results are fit-for-purpose. This is especially true if it is desired to accurately measure RCS at levels below applicable occupational exposure limit values where greater measurement variability can be observed. Reasonable measurement uncertainty can be achieved with proper controls to limit bias and measurement variability and the usefulness of RCS measurements to make informed decisions to protect worker health can be upheld. This document is intended to be of benefit to those involved in the determination of RCS in the workplace, e.g. agencies concerned with health and safety at work; industrial hygienists; safety and health professionals; analytical laboratories; industrial users and their workers. Readers should be aware that in some countries there are legal requirements for the quality assurance of these measurements.

Workplace air — Guidance for the measurement of respirable crystalline silica

1 Scope

This document gives guidelines for the measurements of respirable crystalline silica in air using direct on-filter or indirect X-ray diffraction and infrared analysis methods, including quality aspects of the measurements. The scope of this document includes the following crystalline silica polymorphs: quartz and cristobalite.

These guidelines are intended for use in conjunction with the following specific analytical methods under the jurisdiction of ISO TC 146 SC 2: ISO 16258-1, ISO 16258-2, and ISO 19087. When used with any of these documents, this guidance will help to ensure measurement procedures meet the uncertainty requirements stipulated in ISO 20581, to enable the results to be compared to occupational exposure limit values (OELV) in accordance with EN 689[40].

These guidelines are also relevant to the analysis of filters obtained from dustiness measurements in accordance with EN 15051[1] and EN 17289[35].

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 7708, *Air quality — Particle size fraction definitions for health-related sampling*

ISO 13137, *Workplace atmospheres — Pumps for personal sampling of chemical and biological agents — Requirements and test methods*

ISO 18158, *Workplace air — Terminology*

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

EN 13205, *Workplace atmospheres — Assessment of performance of instruments for measurement of airborne particle concentrations*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18158 and the following apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at https://www.electropedia.org/

3.1
respirable crystalline silica (RCS)
RCS
particles of crystalline silica that can penetrate to the unciliated airways

3.2
collection substrate

medium on which airborne chemical and/or biological agents are collected for subsequent analysis

Note 1 to entry: In RCS analysis, filters or polyurethane foams, alone or contained within capsules or cassettes are examples of collection substrates for airborne particles. Impinger solutions are not applicable.

[SOURCE: ISO 18158:2016, 2.2.3.7, modified for relevance to RCS measurement]

3.3
analysis filter

suitable filter used to carry out the RCS analysis

Note 1 to entry: For direct-on-filter analysis the collection substrate is the analysis filter.

Note 2 to entry: For the indirect analysis the dust is removed from the collection substrate and redeposited onto an analysis filter.

4 Principle

The aim of this document is to give information to select the most appropriate method for the analysis of RCS. In addition, information is provided to minimise the uncertainty in measurement. Therefore, sections in this document deal with the many factors that may influence the variability of a measurement around the true value. The uncertainty of an air measurement is the combination of the variation of measurements from the true value from both the sampling and chemical analysis. Within these two broad headings are other factors, some of which are illustrated below.

a) Organisational factors:
   1) strategy;
   2) method;
   3) training and experience.

b) Measurement factors:
   1) sampling instruments;
   2) calibration;
   3) sample preparation;
   4) instrumental variation;
   5) interferences.

The variability of these individual factors combines to add to the uncertainty of the measurement. At stages within the sampling and analysis process, the factors that contribute to the variance of a measurement can be monitored and controlled to reduce the expanded uncertainty. With such an approach, the variation of the measurements is minimised.

The quantifiable contributions to the uncertainty of crystalline silica in air measurement are illustrated in the classic cause and effect diagram often used as an aid to estimate uncertainty in measurement in Figure 1.

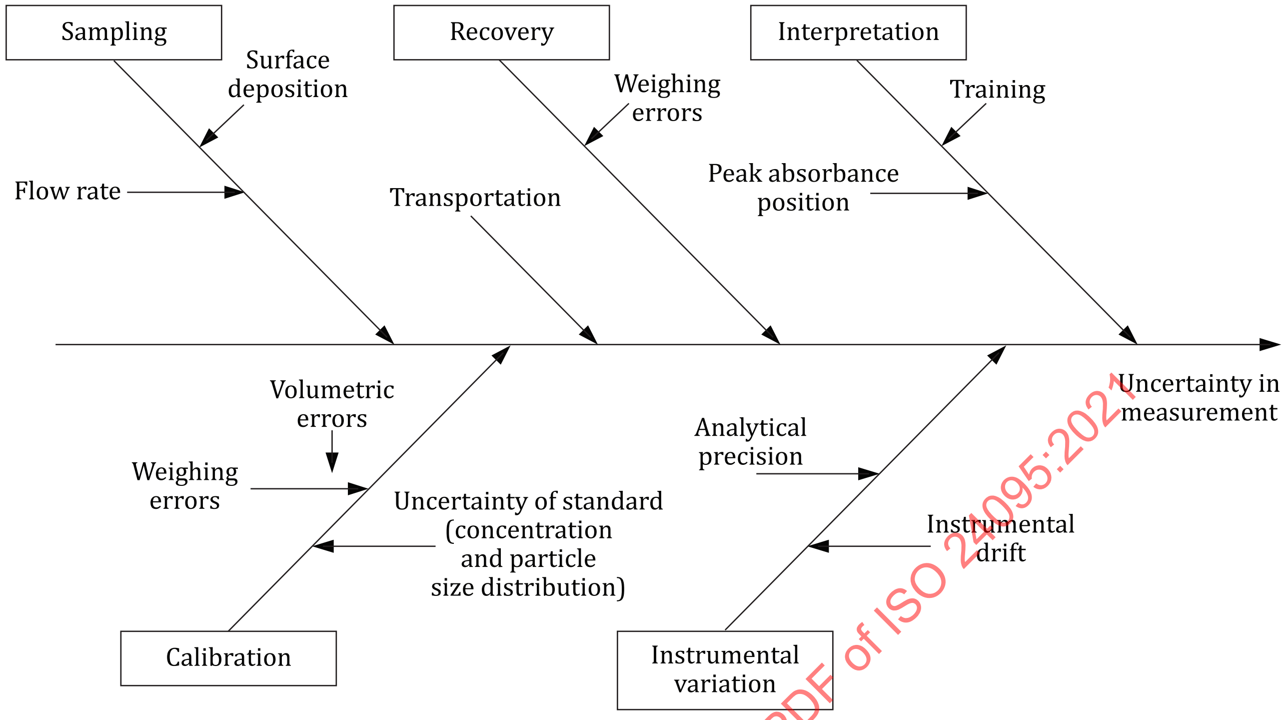


Figure 1 — Cause and effect diagram illustrating sources of uncertainty in the measurement of respirable crystalline silica

5 Analytical quality requirements

The level of analytical quality necessary for effective occupational hygiene monitoring should be considered before establishing requirements for a quality assurance program. Statistical quality control procedures can determine what is currently achievable in terms of intra- and interlaboratory precision and bias and may throw some light on the relative accuracy of different methods, but they do not determine what are desirable levels of trueness and precision.

The existence of legislative requirements to take corrective action when exposure limits are exceeded has a bearing on analytical quality requirements.

NOTE Performance criteria give limits to the expanded uncertainty in occupational hygiene analyses to reduce the potential for incorrect decisions due to the poor precision of results (ISO 20581). This uncertainty includes the imprecision in the sampling and analytical methods and is specified as a maximum of ± 30 % at the exposure limit value and ± 50 % at about half the limit value. The National Institute for Occupational Safety and Health (NIOSH) in the USA stipulates an expanded accuracy requirement of ± 25 % for its occupational hygiene methods based on laboratory tests[2]. The NIOSH accuracy requirement can be expanded to ± 35 % for accuracy determined using field comparison of methods[3]. The relationship between different approaches to determining uncertainty limits have been explored[4,5].

6 Administrative controls

ISO/IEC 17025 specifically addresses the establishment of a management system to ensure the traceability of measurements. In some countries, accreditation to ISO/IEC 17025 may be a legislative requirement.

Communication between those collecting the samples and those analysing them is encouraged in all cases but is especially important where the analyst does not prepare the sampling media.

Laboratory managers should consider whether analysts would benefit from training in mineralogy and/or advanced analytical techniques, such as peak profile fitting and spectral interferences.

7 Sampling

7.1 General

The sampling strategy shall be appropriate to the objectives of the survey.

NOTE EN 689[40] specifies one sampling strategy. Other examples include Reference [6] from the NIOSH and Reference [7] from the American Industrial Hygiene Association (AIHA).

Additional factors that should be considered are minimum sampling times for low concentrations and maximum sampling times for high concentrations.

Pumps conforming to the requirements of ISO 13137 are preferred, and the main requirement concerning pump pulsation from ISO 13137 shall be fulfilled for the pumps in use.

NOTE CEN/TR 15230[8] contains information regarding size-selective sampling procedures.

Sampling equipment and the associated collection substrate shall be compatible with the intended method of analysis. In some recommended or official methods, the sampling instrument is specified. Changes to official or recommended methods shall be validated to ensure they are appropriate and comparable.

7.2 Sampler

A specific sampler shall sample aerosol in accordance with the definition for respirable size-selective penetration given in ISO 7708, except where local regulation requires otherwise, and have a performance as required by EN 13205. Conventions for particle deposition[10] may also be considered. All connections included in the sampling trains shall be checked prior to use to avoid leaks.

Because of the range of sampler types available, practical aspects of their use require consideration. One of the most important is the flow rate required, both with respect to the size, mass, and cost of pump needed, the preferred sampling time-period, as well as with respect to the Limit of Detection (LOD) and Limit of Quantitation (LOQ), but conversely also the potential for overloading. There may be issues specific to certain samplers such as particles adhering to walls, orientation to the wind, ability to clean and re-use or even complexity of calibration and checking the flow rates. Refer to Annex E for information on the differences in performance of samplers. Consult the product information before use.

NOTE The most commonly used sampler for respirable size-selection is the miniature cyclone, and a wide variety of types are available. Many of these are designed for connection to a housing containing a filter to collect the separated, respirable particles. In recent years it has been shown that particles passing through the cyclone which should then be deposited on the filter can be attracted instead to the walls of the housing if it is made of non-conducting plastic[10]. These particles are intended to be part of the sample but are not included if only the filter catch is analysed. It is recommended to use conductive (static-dissipative) plastic cassettes for the purpose of housing filters instead of non-conductive plastic cassettes.

7.3 Filters and foams

Filters shall be of a diameter suitable for use in the selected sampler. The filter type selected for sampling shall have a filtration efficiency of not less than 95 % over the range of particle sizes to be collected (1 µm to 10 µm)[11]. Most polymer membrane filters, except polycarbonate filters, regardless of the nominal pore size, exhibit this characteristic over most flow rates. Foams are generally associated with a specific sampler and only the type of foams supplied for the sampler shall be used. A different type of filter than the foam or filter used for sampling may be preferred for analysis. Re-deposition of a collected foam or filter sample on another filter or other medium is generally referred to as an indirect analysis, rather than a direct analysis where the sampling filter is directly inserted in the analytical instrumentation. While it is possible to re-deposit the sample on to a different substrate from that used for sampling, this step may add to the uncertainty budget of the procedure. The advantage or disadvantage of re-deposition should be balanced against other considerations (evenness and thickness of deposit, removal of interfering species, etc.). Not all filters are suitable for all analytical methods. For example, silver membrane filters are suitable for X-ray diffraction (XRD) analysis but not infrared

(IR) spectroscopy. Polyvinylchloride (PVC), polypropylene, or PVC-acrylonitrile co-polymer filters have suitable IR characteristics[12], but a potassium bromide bead can also be created for indirect analysis[13]. Filter material may degrade if the sampling environment is particularly humid.

7.4 Sampling flow measurement devices and pumps

The device used to measure the flow through a sampling pump shall have its calibration traceable to national or international standards through an organization accredited for the purpose. Float-type flow meters (rotameters) are not traceable to national or international standards and can only be used to indicate the possibility that flow rates have deviated from the allowed range. Corrections to the flow rate readings from rotameters may be necessary to take account of changes in air density resulting from conditions of temperature and pressure and relative humidity which differ from those of the initial calibration of the rotameter. The reading of a rotameter used for this purpose shall be checked prior to use with a calibrator traceable to primary standards. Extreme conditions of temperature and pressure can have an influence on volumetric flow meters, and they should be calibrated to provide accurate measurements at the worksite conditions. Mass flow meters require correction for air density. Corrections are only necessary when the conditions at the site differ substantially from those where the flow rate check was originally made (e.g. using the universal gas law, a temperature change of 10 °C would change the volume sampled by about 3 %, but an altitude change of several thousand metres would have a much more profound effect). If the flow rate has been set away from the sampling site, a flow rate check of the sampling train should be made close to the site of the working operation to ensure the pump is functioning correctly and any necessary adjustments are made prior to sampling.

The battery for the sampling pump should be fully charged prior to the sampling exercise. When taking personal samples, sampling pumps worn by personnel should not impede normal work activity. Sampling pumps shall comply with the provisions of ISO 13137, or equivalent performance standard. Most pumps have an adjustable flow rate and a means for setting a specific flow rate. The sampler requires operation at a specific (nominal) flow rate to meet specified size-selective criteria in collecting a respirable size fraction. Excessive pulsation in flow will cause deviations from the required performance[14], therefore pumps for this purpose shall meet the requirements of the pulsation test in ISO 13137. Pumps shall maintain the nominal flow rate to within ± 5 % throughout the sampling period, and thus shall incorporate a flow fault indicator, or have their flow rate checked frequently throughout the sampling period to detect flow deviations. Prior to sampling, the flow rate value shall be set as close as possible to the nominal and in any case within a range of +/- 5 % of nominal. The pre-sampling flow rate shall be recorded. If flow rate through the sampler is checked at regular intervals during the sampling period by means of a rotameter, this device does not require a calibration traceable to national or international standards. If the flow rate during sampling is not within ± 5 % of the nominal value, the person recording the flow rate measurement shall inform the person responsible for communicating the results to note the observation in the final report. Flow rates can fall below 95 % of the nominal value when sampling very high concentrations, and the pressure drop resulting from build-up of dust on the filter exceeds the flow compensation capability of the pump. The sampler is removed from the pump at the end of the sampling period. The flow rate through the pump and the sampler used to set the pre-sampling flow rate shall be measured post-sampling and reported. When the post-sampling flow rate measurement is within 5 % of the pre-sampling value either the pre-sampling value, the average value, or the nominal value may be used to calculate the concentration, according to the standard procedure in use[15]. Where the post-sampling flow rate measurement is not within 5 % of the nominal value, the user of the results must consider that the size-selective performance of the sampler may have been compromised. Therefore, the results may have no validity, even if only the low or high flow rate value is used for calculating concentration.

7.5 Sampling period

7.5.1 Select a sampling period that is appropriate for the measurement task but ensure that it is long enough to enable RCS to be determined with acceptable uncertainty at levels of industrial hygiene significance. Many OELVs for RCS are couched in terms of an 8-hour shift average, and so sample numbers and/or sampling times should be sufficient to ensure appropriate coverage. If work-shifts are longer and exposure continues, longer sampling periods may be necessary, together with consequent adjustment of the OELV.

NOTE If the minimum sampling time required for analytical sensitivity is too long, consider the possibility of using a sampler designed to be used at a higher flow rate or modifying the analytical procedure to obtain greater sensitivity.

7.5.2 When high concentrations of airborne particles are anticipated, the sampling period may be reduced to not risk overloading the filter with particles (with subsequent additional samples as necessary where compliance with an OELV is being tested). While many published methods caution not to exceed 2 mg total deposit, this is a very conservative recommendation as loadings up to 4 mg have been circulated in round-robin studies without significant loss of sample[16]. However, it is also necessary to consider the matrix absorption effects from sample loading on the maximum allowable value. Table 4 of the Reference [17] shows that in a "worst case" standard sample, which was defined as 5 % quartz in a matrix with an x-ray absorption coefficient of 1 000 (hematite), the critical value where deviation from linear XRD calibration is 20 % is 2 mg on a 2,1 cm filter diameter, and so above this loading appropriate corrections should be applied to account for the non-linearity. If the sample is 80 % quartz the deviation will be much less (see Figure 17), and, since the effect also depends on the mass absorption coefficient of the interferent, a "typical" coefficient of 40 (with feldspar or calcite) would lead to a critical value for 80 % quartz of 2,4 mg.cm^{-2}. Over a 2,1 cm diameter filter this is greater than 4 mg loading before non-linearity.

7.5.3 When concentrations of RCS lower than 0,1 mg.m^{-3} are anticipated, or if measurements are being made to determine concentrations during short tasks or event, consider that insufficient sample for quantitation may be collected if the sampling flow rate is low. It may be necessary to consider using a sampler that operates at a higher flow rate for appropriate sensitivity.

7.5.4 Matrix effects in both IR and XRD procedures limit the possibility of analysis when RCS makes up less than 1 % of the collected dust. When concentrations of dust are high, and the silica content is low, and matrix reduction procedures cannot be applied, the silica content of the sampled dust cannot be quantified. Therefore, confirming the presence of RCS around an OELV will not be possible, even by sampling larger volumes of air.

NOTE For example, if the respirable dust concentration is greater than 2,5 mg.m^{-3}, it is not likely possible to detect RCS at a "1 %" level of 0,025 mg.m^{-3}, and, therefore, there can be no confidence of compliance with an OELV of 0,025 mg.m^{-3} when the analytical result for RCS is "none detected". Thus, there is value in measuring the aerosol collected gravimetrically to be able to detect and warn clients of this situation. Removal of matrix, e.g. by acid treatment or heating, can be used to decrease the quantity of aerosol and improve the ability to detect lower percentages of RCS in respirable dust. However, even with sample reduction it can still be difficult to confirm compliance where there is no detection. For example, if the dust concentration is 5 mg.m^{-3} and 50 % is calcite, removing the calcite only leads to the same situation as described above. Therefore, it is advisable to re-weigh samples after reduction to detect this situation.

7.6 Transportation

At most normal loadings (< 4 mg), the sample (of respirable dust) is safely contained on the filters specified in 7.3 and is not lost if the sample is handled with care. Test samples containing up to 4 mg of borax on glass fibre and PVC membrane filters have been sent through postal systems without significant losses in material from the filter[16].

NOTE For indirect methods the provision of sample losses in the cassette can be addressed during the sample preparation stage. However, sample losses in the cassette can be a source of bias for direct-on-filter analysis.

8 Procedures

8.1 Handling of filter cassettes

The user should refer to the manufacturer's handling instructions. For a cyclone selector, the respirable size selectors should be stored and opened with the grit pot for the non-respirable particles kept vertically below the cassette. Ensure that filter cassettes are firmly closed. Care should be taken upon opening the filter cassette to avoid loss of dust. The condition of the cassette should be visually checked and any deposition of dust on the walls of the cassette should be noted, if it is not intended to be analysed by procedure. However, fine dust particles are virtually invisible against most cassette materials, so that non-visibility cannot be taken as proof of absence of dust deposits. Static dissipative conductive cassettes can be useful in minimising wall deposition of dust[10].

8.2 Method validation

Laboratories shall use only published validated methods, or methods proven by validation to have comparable or better performance characteristics when compared with published methods. A Eurachem Guide[18] describes the method validation process. If deviations from a standard method are made, then the laboratory shall prove that the changes give comparable results and note the modifications when the results are reported.

8.3 Calibration

It is recommended to report the material used to prepare the calibration test samples. Treatment of the reference material during calibration may also change the particle size characteristics of the dust when they are sampled again and so lead to different absorbances for IR analysis and diffraction peak profiles.

The frequency of calibration depends on the stability of the instrument and the experience of the analysts. When using XRD, it is not necessary to recalibrate frequently, when a calibration is proved to achieve satisfactory results, provided the instrumental conditions and parameters are maintained for the method of analysis, an external monitor is used to correct the calibration for tube drift and quality control and/or external quality assurance programmes are in place to monitor the performance of the procedure.

The response from both XRD and IR analysis techniques is sensitive to the distribution of the size of the particles on the surface of the analysis filter and different standards may have a slightly different distribution of particle sizes, which may lead to differences in results between laboratories. Measurement of peak area shows less variability with particle size for XRD, because, as the median particle size decreases, the peak shape broadens, which decreases the height. Peak height is usually measured for IR analysis.

Where the uncertainty in a measurement contributes substantially to the expanded uncertainty, such measurements shall be traceable to national or international Standards. Weighing low microgram levels (< 200 µg) shall be done on a balance with a resolution of 1 µg. This also requires the use of E2 class certified check masses to verify the balance calibration. Humidity and electrostatic effects may affect the stability of the weighing (see ISO 15767). Weighing procedures for filters are given in ISO 15767.

Good practices use not less than six concentration levels of calibration test samples in order to reduce the standard error of the regression line to an appropriate level and use three replicates at each concentration level. Since many standard preparation procedures involve serial dilution from a single stock suspension, consider using two independently made stock solutions for verification. To reduce the uncertainty of the calibration line, at low measurement levels, some direct on-filter analysis methods for RCS recommend 30 calibration test samples because of the difficulty of producing replicates. The calibration test samples need to be equally spread across the analytical range to avoid a regression or other calibration model from being unduly weighted by isolated responses that may lead to significant differences between results. Where calibration produces data with standard deviation varying with mass of RCS (heteroscedastic), a weighted regression may be more appropriate for analysis. The calibration should be tested against some known sample such as a proficiency testing or spiked quality control sample.

To minimise bias, the preparation of the calibration standards needs to be fit for its intended purpose. For direct on-filter methods, the procedure for the preparation of the standards should match the sample collection methods. For deposition methods, the procedure for the preparation of the calibration standards should match the sample preparation methods.

If the calibration dust used in a laboratory is not a certified reference material (CRM) with a known amount of RCS, then the response of the calibration dust should be compared with these materials to determine any potential bias. It should be noted that even CRMs can have different crystallinity which can lead to different results when used to calibrate analysis of a sample. If the absorbance or diffraction peak profile is outside the repeatability precision of the measurement and is considered significant at the 95 % confidence level, a correction factor should be applied to the final result or calibration. The result reported to the customer should use the calibration corrected for purity and crystallinity of the calibration dust.

For example, if XRD is used and the difference between the area result for a sample of the bulk reference material is greater or less than 2,26 (Student *t*-distribution for nine degrees of freedom), standard deviations of 10 peak area measurements of the bulk dust used for calibration then the correction factor for crystallinity of the calibration dust is given in Formula (1):

$$\frac{\bar{A}_{\mathrm{CM}}}{A_{\mathrm{Ref}}} \frac{w}{100} \tag{1}$$

where

$\bar{A}_{\mathrm{CM}}$ is the average area, in counts per second, of the principal peak(s) of the calibration material;

A_{Ref} is the area, in counts per second, of the same principal peak(s) of CRM or secondary standard with a known concentration of RCS;

w is the mass fraction, expressed as a percentage, of crystalline silica in the CRM or secondary standard.

Alternatively, the correction values for common calibration dusts for α-quartz can be obtained from published work[19].

For more information on these techniques, refer to ISO 16258-1, ISO 16258-2, and ISO19807.

8.4 Sample preparation

Some analysis methods require the dust to be recovered from the original air sample filter to allow for sample treatment to remove interferences and then the recovered dust is re-deposited on to another filter. The best practice is to prepare several standards from a calibration solution and involve these in the sample preparation process to test the recovery. If the difference between the target value and the results obtained from the recovery samples are significantly more than the expected precision of the procedure, then a correction factor for recovery should be applied. For example, if the target value is more than two standard deviations from the expected precision (determined from experience of proficiency testing, quality control, published or method validation data) of the recovered values.

For re-deposition methods, it is recommended that laboratories choose the most appropriate "clean-up" technique for the mineral matrix in the sample. This will also raise the silica percentage in the dust which can be helpful in detecting low concentrations (see 7.5.4). Ashing in a furnace can remove carbonaceous materials (use fresh crucibles each time for ashing in muffle furnaces) and dilute acids can remove carbonates[20]. If carbonates are not removed then reaction with silica to form silicates can take place at elevated temperatures. There may be matrix interferences such as silicates that could be handled best by a sample clean-up step prior to analysis. This can be accomplished by an acid digestion[21]. This procedure does not successfully remove some silicates (e.g., feldspars, clays) and may cause the loss of very small particles of RCS and the formation of amorphous silica.

During the re-deposition process, care should be taken that there is a complete seal around the filter when filtering the crystalline silica suspension to prevent leakage leading to sample loss. Ultrasound should be used before the filtration to overcome the agglomeration of particles in suspension and to ensure homogeneity. Placing about 2 ml of solvent in the filtration funnel before pouring the sample provides a cushion for the suspension and contributes to a homogenous surface.

XRD parameters related to sample preparation include sample homogeneity, size distribution of the particles, size of the sample surface exposed to the X-ray beam, thickness of the sample deposition, and choice of internal standards if any. Silver filters for sample collection or re-deposition or metal base plates like silver, zinc or aluminium used in sample analysis can correct for matrix absorption.

8.5 Sample measurement

8.5.1 Limit of Detection

Many analysis procedures require laboratories to calculate an LOD by multiplying the standard deviation of measurements of a number (typically 10) of blank samples by a factor of three. Users of this Standard should note that there is some doubt about the relationship between signal and the mass when RCS is measured at very low masses and a specific formula to determine the LOD using statistics based on a normal distribution is not given in this document. The test samples used for calibration are not matrix matched and reporting an LOD based on three standard deviations of the background noise may give an optimistic impression of the capability of method when analysing “real” samples. Analysts should take this into consideration when analysing samples for RCS.

8.5.2 X-ray diffraction

XRD is a technique where X-rays are reflected from the surface of the sample and most methods assume the sample deposit is a thin layer and so does not need any correction for any absorption or depth effects. Some methods use a silver filter or a silver, zinc or aluminium base plate to help correct for any matrix absorption. Measurement of the response of the reflections from a metal helps correct the intensity of the signal when the relationship between response and intensity is no longer linear because of the absorption or depth of the sample. Since crystalline silica often occurs in a matrix with other silicate minerals, some of which exhibit X-ray spectra that overlap with the primary quartz diffraction peak, the use of alternative peaks for quantification may be necessary. Annex A gives a list of potential mineral interferences. Good practice includes a qualitative XRD scan to characterise the environmental matrix for a set of samples from a given site. The use of secondary, tertiary, and even quaternary peaks results in decreased sensitivity. A determination revealing the correct peak ratios for the three largest peaks can be taken as an indicator of lack of interferences; otherwise, a clean-up procedure may be needed prior to analysis.

Sample spinning during XRD analysis allows the beam to cover a larger area and increases the precision of the analysis.

8.5.3 Infrared analysis

For IR, matrix effects from interferences with other polymorphs of crystalline silica and silicates, such as kaolinite, present analysis problems. There is a potential for bias when correcting for matrix absorption effects, with the bias increasing at low levels of quartz. In coal mining, the assumption is made that quartz is the only polymorph present due to the geological processes involved in coal formation. It is sometimes assumed that the only mineral interference found in coal dust samples after acid-washing is kaolinite. Spectral correction is possible to eliminate IR interference from kaolinite in coal.

For direct-on-filter IR analyses, good practice requires that samples be rotated, and multiple measurements taken and averaged in order to minimise possible differences in deposition across the filter.

8.6 Instrumental variation

8.6.1 X-ray diffraction

8.6.1.1 Intensity

For optimum XRD instrument performance, the X-ray source should be aligned and monitored routinely for stability. An estimate of instrumental drift should be performed whenever measurements are made. For XRD, the intensity of the radiation deteriorates over time and a correction should be applied to correct for the instrumental drift. An aluminium plate or any other suitable stable robust material can be used as an external standard to correct a measurement for the gradual decline in X-ray tube emission from the calibration. Such a standard should be fine-grained, free from marked texture and have a strong XRD peak in the same range as the quartz or cristobalite peaks being used for analysis.

8.6.1.2 Stability of intensity distribution over 2θ range

In a diffractometer with Bragg-Brentano geometry, the diffracted intensity measured should be reproducible at any 2θ position. Displacement of the slit assemblies changes the semi-focusing geometry and may lead to intensity becoming slightly dependent on 2θ. Because the ratios of the intensities of peaks in different positions are used both for identification and quantitative analysis, such a displacement would lead to erroneous results, although a displacement large enough to have a serious effect is unlikely. Checking the intensity ratio of diffraction peaks from a reference sample is a method of detecting serious errors.

8.6.1.3 Line position

It is appropriate to use a standard reference material such as US National Institute of Standards and Technology (NIST) 640c (silicon powder) to check the instrument after service or to use other characterised material such as Arkansas stone that gives reproducible line positions.

8.6.2 Infrared analysis

A check sample, previously analysed proficiency testing sample or known standard should be used to check instrumental drift and resolution.

8.6.2.1 Absorbance

As necessary, laser intensity (energy) should be checked periodically for deterioration.

8.6.2.2 Resolution

Instruments employ their own checks for wavelength drift and the absorbance of silica is a relatively broad peak. It is recommended that the resolution for analysis should be set at no more than 8 cm^{-1}.

9 Internal quality control

The analytical precision is dependent on the particular conditions employed for the analysis. The aim of a quality control scheme is to check every stage of an analysis. One way to check that an analytical procedure is functioning correctly is to take a matrix-matched sample of known value through the entire analytical procedure in the same way as the field samples. If an indirect analysis procedure is employed then the samples for quality control should be included with the samples during the preparation stage of the method, so that both accuracy and precision are evaluated. Any untoward losses or contamination experienced by the field samples during the analytical process is likely to be experienced by the quality control sample also and the analyst may be alerted to any deviation and take it into account.

It is recommended that for analyses, which are determined frequently, a batch quality control material should be prepared. A suitable quality control material might be a filter spiked with a known amount of crystalline silica added to it, or a past proficiency-testing sample.

A good practice is to plot the value obtained for the quality control sample on a chart. The simplest form is the Shewhart chart that is described in more detail in Annex C. A Shewhart chart with simple rules, i.e. warning at ± 2 *s*, action at ± 3 *s*, where *s* is standard deviation, is probably sufficient for a laboratory starting up a quality control scheme. A more complex set of rules can be employed once analysts are familiar with quality control procedures.

A good practice is to check the standard deviation of the method at intervals and revise the warning and action limits if necessary. The data used to calculate the initial standard deviation may not be representative and the application of a quality control scheme may result in an improvement in the precision of the results obtained, so that the old warning limits may no longer be appropriate.

10 External verification and assessment of uncertainty

A laboratory may be able to control its precision, but still report inaccurate results if the bias between the true value and the results it obtains is not assessed. An internal quality control scheme helps a laboratory control its precision but does not include potential bias from the calibration standards, preparation of calibration samples, unaccounted factors in recovery and interpretation of data. Proficiency testing (PT) is a requirement of laboratory accreditation, and accreditation services rely on PT providers for this service. Participation in PT programmes helps a laboratory to compare the results it obtains on almost identical samples with the results from other laboratories and laboratory clients can use records of laboratory proficiency performance to determine the ability of the laboratory to produce measurements of consistent quality.

A laboratory should select a PT program that is appropriate for its method of analysis. Of the several schemes which exist (such as the AIR PT scheme originating in the UK), the American Industrial Hygiene Association Proficiency Analytical Testing, LLC scheme provides blind quartz on PVC filter samples that also include calcite, talc, coal mine dust, and talc with coal mine dust as potentially interfering dusts. However, while proficiency testing is highly recommended, national methods may not be compatible with the particular requirements of any PT scheme. In such case, an internal assessment protocol is essential for monitoring the quality of the data. Proficiency test data has been used to evaluate the performance of XRD and IR methods in the presence of interferences (Annex F).

For interpretation of analytical measurements, good practice includes an assessment of the uncertainty of the measurements. ISO/IEC Guide 98-3[22] describes an approach for estimating the uncertainty associated with measurement. An uncertainty range should be reported with the results to aid in the interpretation of data. An example of the ISO/IEC Guide 98-3[22] approach to estimate the uncertainty of results is shown in Annex D.

11 Test report

11.1 Minimum report requirements

The test report shall contain the minimum information required by ISO/IEC 17025, and the laboratory shall have the following information available on request:

a) the condition of the sampling medium such as damage, overloading and any residual dust in the container used for transport;

b) the dust standard used for the calibration;

c) the estimated expanded uncertainty;

d) the LOD and if appropriate the LOQ;

e) the name and the model of the instrument used for the analysis, and functional parameters;

f) the known other phases present during the analysis of the sample;

g) analytical range of the calibration standards;

h) the storage period of the samples;

i) all laboratory operating details not specified in this document, or regarded as optional, together with details of any incident that may have influenced the result(s).

In addition, relevant environmental factors or operating details of the sampling, including type(s) of sampler and ancillary equipment, together with details of any incident during sampling that may have influenced the result(s) shall able to be appended to the analytical result(s).

11.2 Data to be archived by the laboratory

The laboratory shall ensure the management of technical records in accordance with ISO/IEC 17025 The following is the minimum information that should be archived by the laboratory:

a) a copy of the report sent to the customer;

b) a copy of the scans and parameters of the instrument;

c) the source of the dust standard and the date on which the calibration standards were prepared;

d) the calibration curve;

e) the samples for a period of time to allow analyses to be verified;

f) a copy of the written procedures used to perform the analysis and the results from any tests used to demonstrate the comparability of any changes from the standard method.

Annex A
(informative)

Polymorphs of crystalline silica and their interferences

A.1 Interferences in the XRD and IR spectra of RCS

Industrial hygiene samples for RCS are often taken in environments that include mineral matrices such as graphite in the iron and steel industry and various silicates in agriculture and ceramics. The presence of mineral compounds that have characteristic peaks in close proximity to the peaks of the crystalline silica polymorphs can interfere with the measurement of the RCS. It is important to characterise the composition of the dust that was collected in order for the analyst to have a good understanding of any suspected interfering compounds. When the sampled dusts are submitted to the laboratory for analysis, it is advisable to provide all available information relating to the industrial process, including raw materials, extraction processes, transformation products and packaging of the final product.

A.1.1 X-ray diffraction

In XRD, interferences can be detected with the analytical technique. Most XRD reference methods call for a qualitative analysis of a representative bulk sample in order to investigate the presence of interfering minerals (NIOSH Method 7500[3], US Occupational Safety and Health Administration (OSHA) Method ID-142[23], UK Methods for the Determination of Hazardous Substances (MDHS) 101[24], ISO 16258-1 and ISO 16258-2). In this case, the interfering minerals can be identified in corroboration with any information provided by the hygienist who collected the bulk sample. If interferences are found, sample clean-up can be performed prior to analysis of the respirable samples or a secondary peak can be used with an associated loss in sensitivity. Interferences on the peaks used for quantitative analysis of each crystalline silica polymorph can be evaluated by measuring the (three or four) principal peaks of RCS, calculating the relative ratios of their diffraction intensities, and comparing them with their reference values (ISO 16258-1, ISO 16258-2). In XRD, the diffraction peaks of the main polymorphs may be subject to overlap, changes in intensity or distortion of peak shape. It is possible to obtain a reference profile from the calibration material and to use software to compare the relative intensity, peak width, and peak symmetry with the peak profile of the sample to estimate the amount of silica present. However, it may be simplest to reject results from peaks with interference and use a different silica 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. It is to the advantage of the analyst and the hygienist to have a working knowledge of the common interferences that are found in various industrial environments.

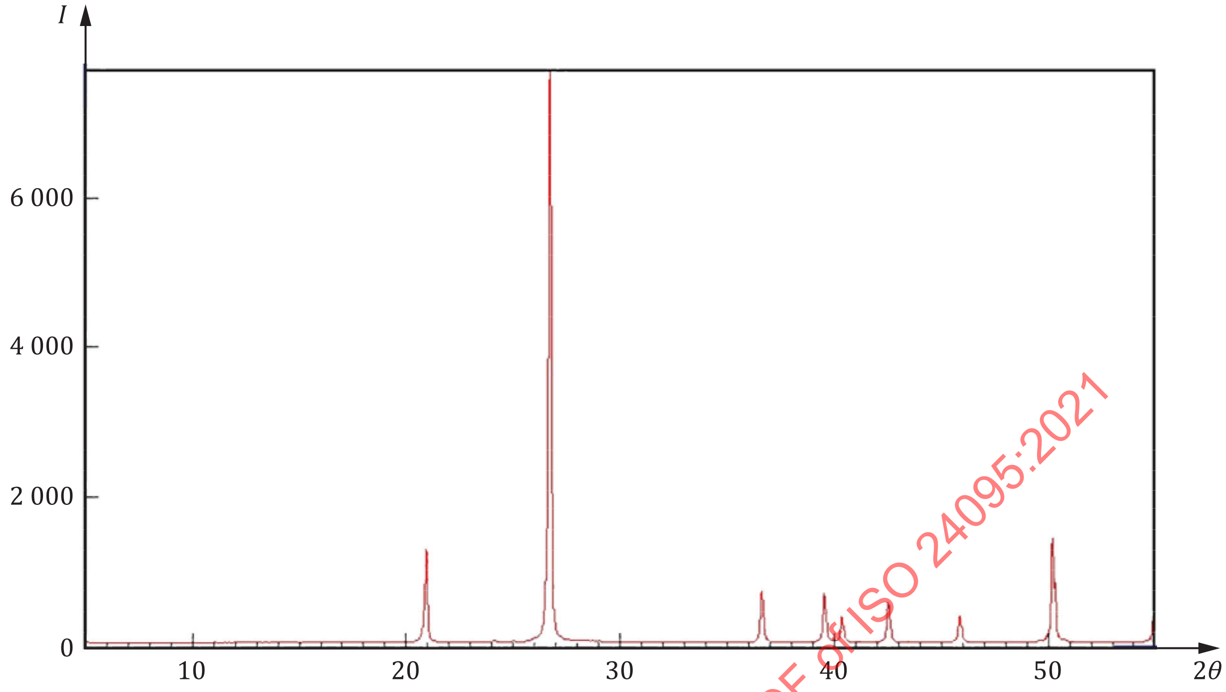
The four main peaks of α-quartz are given in Table A.1 along with several known mineral interferences.

Table A.1 — Peaks and intensities of α-quartz (fixed divergence slit mounted on the incident beam, Cu Kα radiation) and known mineral interferences[24]

Analysis reflection	(100)	(101)	(112)	(211)
Relative intensity	22	100	14	9
d (Å)	4,26	3,34	1,82	—
Angle of diffraction (2θ) Cu K$_\alpha$	20,85	26,65	50,17	59,96
Interferences				
Albite		X	X	X
Anorthite			X	X
Aragonite	X	XX	X	X
Barite		XX	XX	
Biotite		XX		X
Cristobalite				X
Graphite		XX		
Gypsum	XX		X	X
Kaolinite	X	X	X	X
Maghemite	X	X	X	
Microcline	X	XX		
Mullite		XX		X
Muscovite		XX		
Orthoclase	XX	XX	X	
Sillimanite		XX	X	X
Tridymite	XX		X	X
Wollastonite		XX	X	X
Wüstite				X
Zircon		XX		X
X indicates a partial overlap XX indicates a possibly complete overlap, this line may not be suitable for quantitation in the presence of this interference				

A.1.2 Typical X-ray diffraction scans of α-quartz and potential interferences

For an XRD scan (Cu Kα radiation) of crystalline α-quartz, see Figure A.1. For an XRD scan (Cu Kα radiation) of a sample containing a feldspar and α-quartz, see Figure A.2. Figure A.3 shows an XRD scan (Cu Kα radiation) of a sample containing gypsum and a trace amount of feldspar showing the potential for interference with α-quartz.



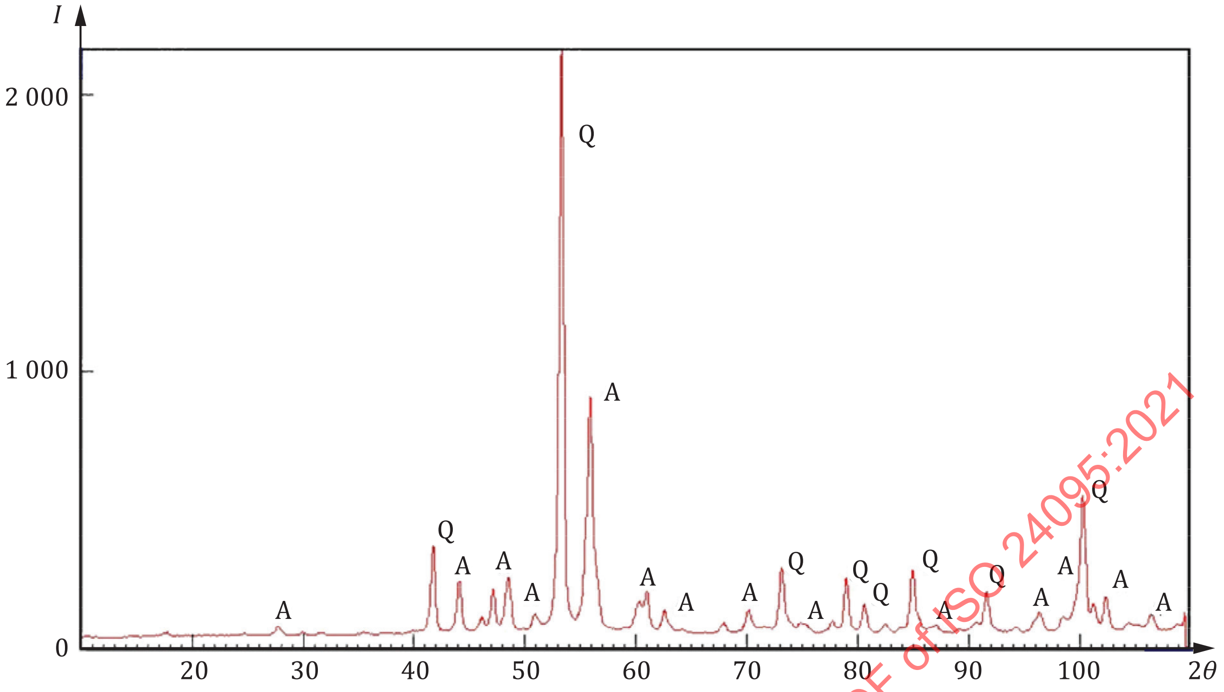
Key

2θ diffraction angle

I intensity/counts

NOTE A scan of cristobalite is shown in Annex B.

Figure A.1 — An X-ray diffraction scan of crystalline α-quartz

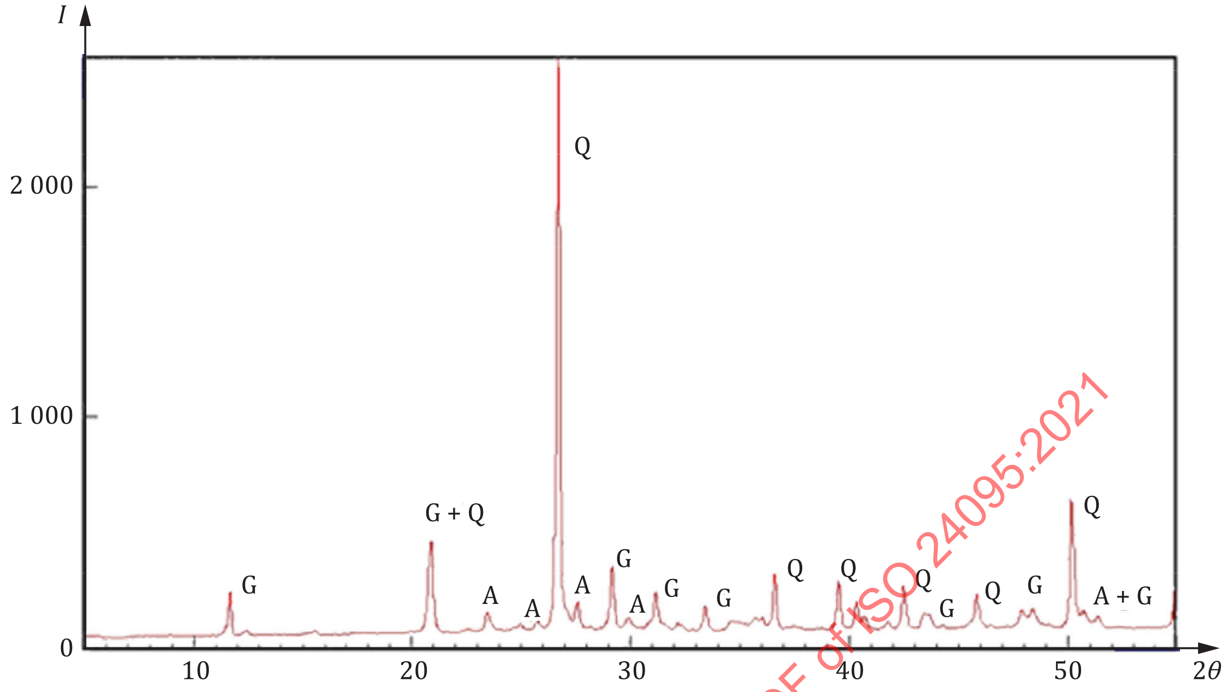


Key

2*θ*	diffraction angle
I	intensity/counts
A	feldspar mineral
Q	α-quartz

NOTE The scan shows potential interference with the 26,65° and 50,1° 2*θ* reflections of α-quartz.

Figure A.2 — An X-ray diffraction scan of a sample containing a feldspar (low temperature albite) and α-quartz



Key

2*θ*	diffraction angle
I	intensity/counts
A	feldspar mineral
G	gypsum
Q	α-quartz

Figure A.3 — An X-ray diffraction scan of a sample containing gypsum and a trace amount of feldspar (low temperature albite) showing the potential for interference with α-quartz

A.1.3 Infrared analysis

Different polymorphs of crystalline silica exhibit distinct absorption patterns. α-Quartz exhibits a characteristic doublet at 798 cm^{-1} to 790 cm^{-1} and 779 cm^{-1} to 780 cm^{-1} (Figure A.4) and secondary peaks at 694 cm^{-1}, 512 cm^{-1}, 460 cm^{-1}, 397 cm^{-1}, and 370 cm^{-1}. The 694 cm^{-1} peak can be used for quantification in cases where mineral interferences overlap with the primary doublet. α-Quartz may be quantified in the presence of amorphous silica by using the 694 cm^{-1} peak or, alternatively, a phosphoric acid digestion may be used prior to analysis. If the phosphoric acid digestion procedure is used, the analyst should take care not to prolong the contact between acid and particles because the acid may dissolve the smaller sized particles of crystalline silica. Cristobalite exhibits characteristic peaks at 798 cm^{-1}, 623 cm^{-1}, 490 cm^{-1}, 385 cm^{-1}, 297 cm^{-1}, and 274 cm^{-1}. The 623 cm^{-1} peak may be used for quantification in cases where mineral interferences overlap with the customarily used 798 cm^{-1} peak. Tridymite exhibits characteristic peaks at 793 cm^{-1}, 617 cm^{-1}, and 476 cm^{-1}. It may not be possible to quantify tridymite in the presence of α-quartz or cristobalite.

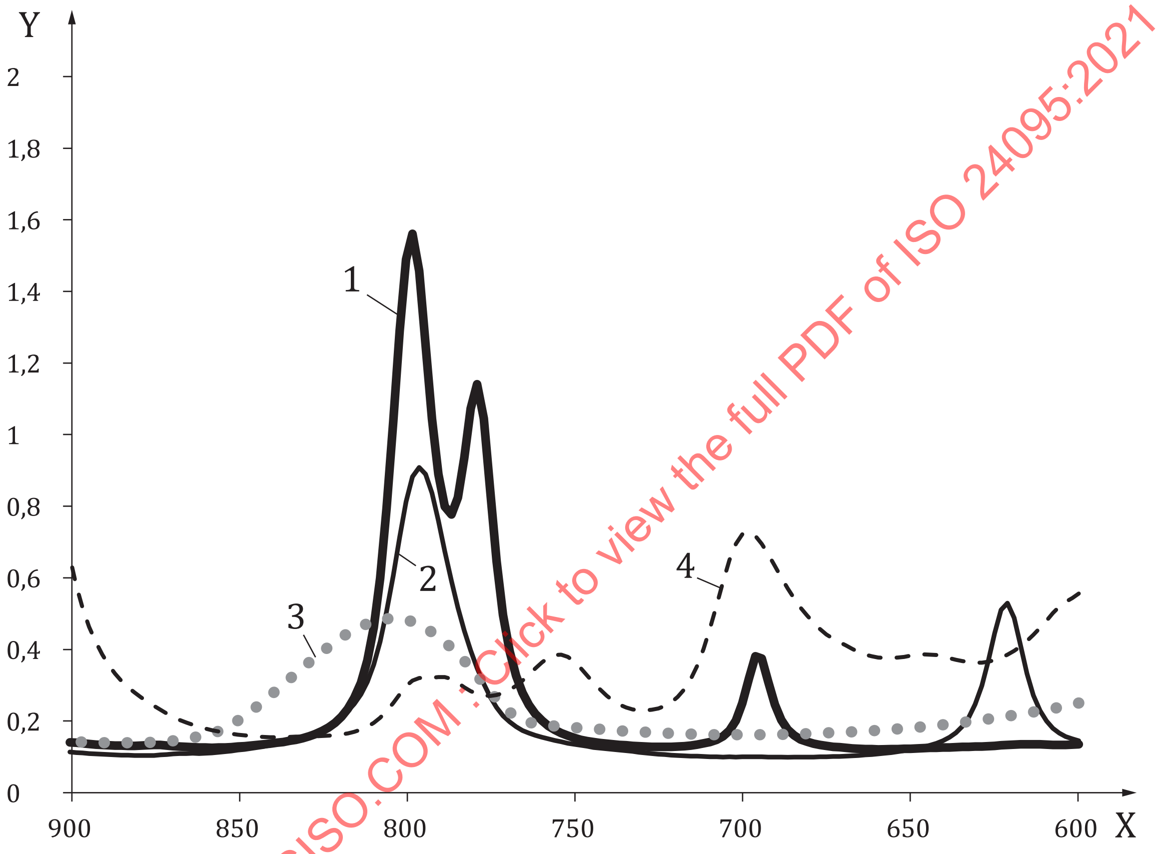
Matrix effects from interferences with other silicates present analysis problems. The following are examples of minerals groups that can cause interference:

a) clays e.g. kaolinite, dickite;

b) feldspars e.g. albite, anorthite, orthoclase;

c) micas e.g. muscovite.

The list is not exhaustive, since any mineral with a Si-O vibration stretch might contribute to absorbance in the same area as the principal absorbances of the silica polymorphs. There is a potential for bias when correcting for matrix absorption effects, with the bias increasing at low levels of quartz. In coal mining, the assumption is made that α-quartz is the only polymorph present due to the geological processes involved in coal formation. Generally, the only significant mineral interference found in coal is kaolinite. The analytical method of the US Mine safety and Health Administration (MSHA) P-7[25] gives a spectral correction procedure for eliminating IR interference from kaolinite. Although most analytical chemists are familiar with the IR technique as applied to organic analyses, mineralogical samples require additional knowledge of geology and mineralogy to correctly interpret data for the laboratory client. The example shown in Figure A.4 gives the absorbance spectra of quartz, cristobalite, amorphous silica and kaolinite.



Key

X wavenumber [cm^{-1}]
Y absorbance
1 quartz
2 cristobalite
3 amorphous silica
4 kaolinite

Figure A.4 — FT-IR transmission spectra of quartz, cristobalite, amorphous silica and kaolinite

Annex B
(informative)

The quantification of cristobalite using X-ray diffraction

B.1 Quantification of cristobalite

The quantification of cristobalite is difficult because of the variations of position and intensity of the diffraction maxima of both α- and β-cristobalite. The intensity of the diffraction lines has been shown to vary by a factor of three in some samples. It is possible that some of this variation is due to the two distinctly different forms of cristobalite.

The high temperature β-cristobalite is stable at temperatures above 1 470 °C but undergoes rapid conversion to the α-form when reaching about 200 °C on cooling. Therefore, it is assumed that workplace samples contain the α-form. See Figure B.1. However, studies of devitrified aluminosilicate ceramic insulation material have shown that the β-form can exist. If the β-cristobalite is analysed using the α-cristobalite calibration standard, the result has significant bias.

B.2 Quantification of cristobalite in the presence of opal and amorphous silica

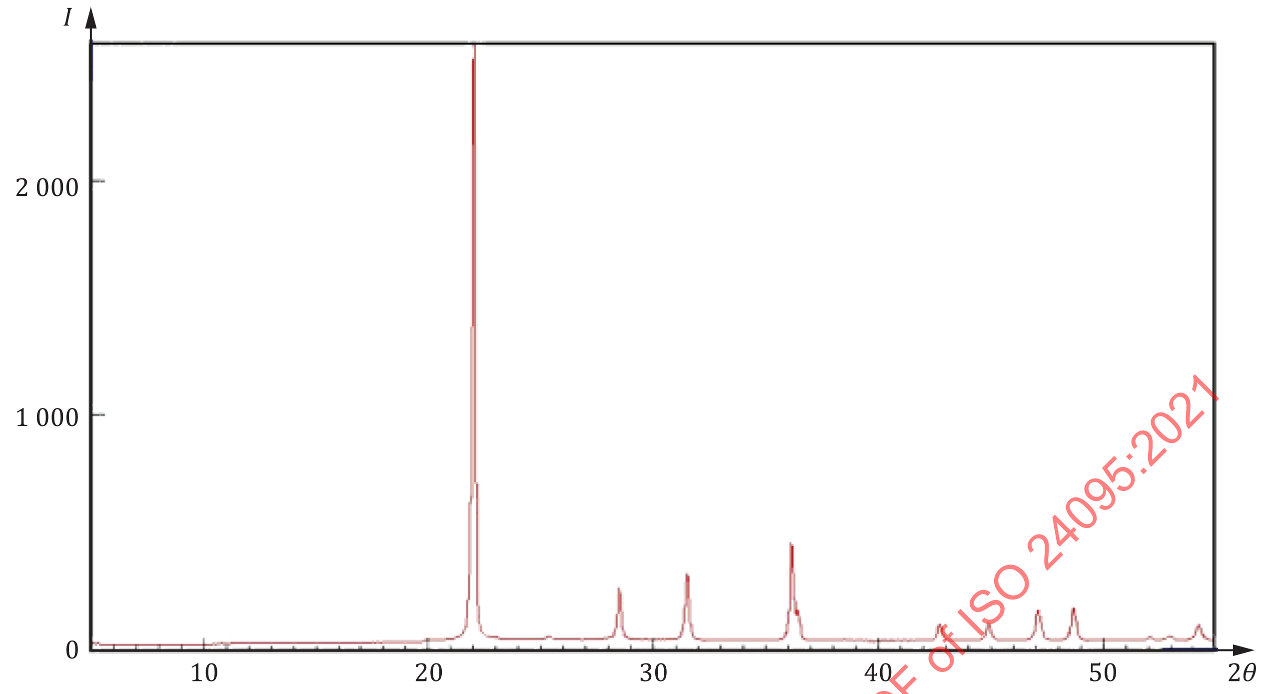
Some cristobalite samples show a diffuse scattering under the cristobalite maxima, either from the diffuse scattering of amorphous material with localised areas of arrangement such as silica glass or from some disordered structure within the crystalline silica. The question for the analyst is where to set the baseline to quantify the crystalline material. This is a subjective judgement by the analyst since, in some samples, the inclusion of some of the broadening of the base of the cristobalite peak may increase the area counted by 30 % to 50 %. The essential requirement for occupational hygiene is the measurement of the crystalline component, since this is thought to cause the most serious health problems. Therefore, it is reasonable to quantify the sharp crystalline maximum since this represents the most crystalline material. Profile fitting or Rietveldt analysis may be a useful software tool to separate the crystalline from the amorphous or poorly crystalline material.

Samples of opal show a full range of crystalline behaviour from highly ordered cristobalite (opal-C and some samples of opal-CT) through to a broad amorphous peak in the region of the α-cristobalite maxima (opal-A).

B.3 Quantification of cristobalite in the presence of tridymite

Some samples of cristobalite show a broadening of the diffraction maxima and occasionally tridymite stacking is also observed with the cristobalite peak. In a sample with a mixture of cristobalite and tridymite, the tridymite should also be quantified or reported as present, since it is a crystalline silica. Several of the tridymite peaks coincide with the principal cristobalite peak and the reported result needs careful interpretation. In the absence of a calibration for tridymite, best practice is to report the value obtained for cristobalite and note it as a minimum value due to the presence of tridymite.

Figure B.2 shows an XRD scan of crystalline tridymite, while Figure B.3 depicts the combined XRD scans of cristobalite, quartz, and tridymite.

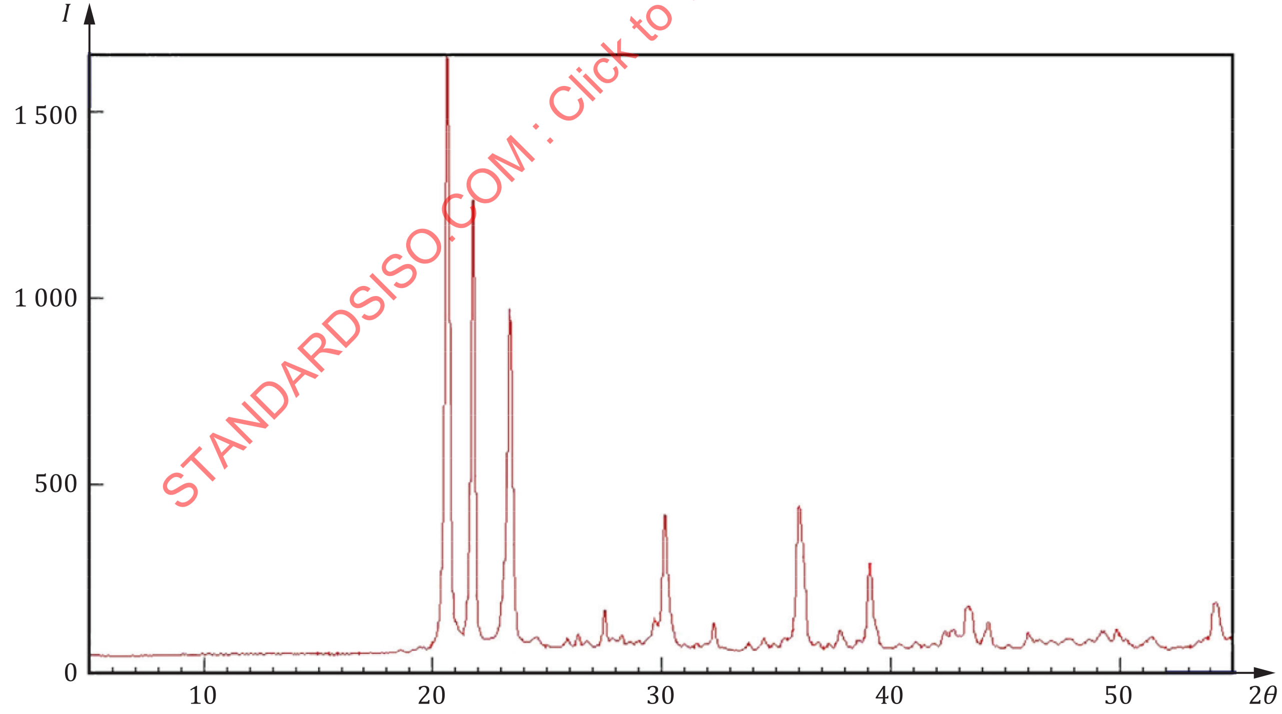


Key

2θ diffraction angle

I intensity/counts

Figure B.1 — An X-ray diffraction (Cu Kα radiation) scan of crystalline α-cristobalite

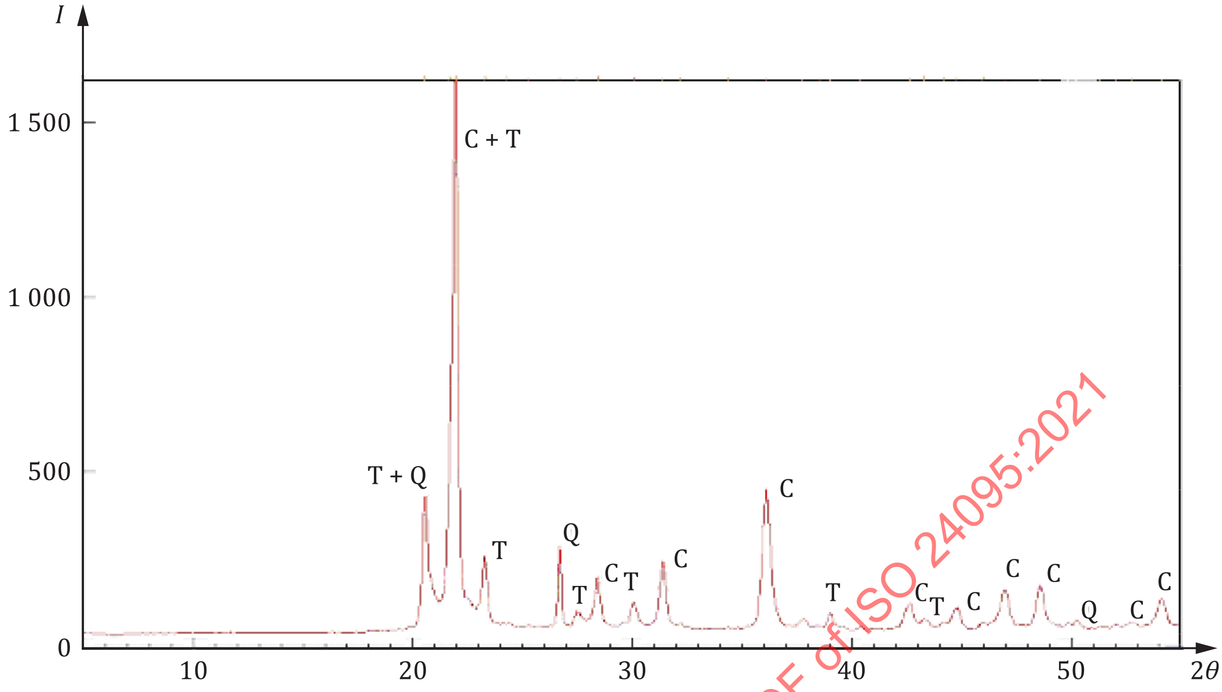


Key

2θ diffraction angle

I intensity/counts

Figure B.2 — An X-ray diffraction (Cu Kα radiation) scan of crystalline tridymite



Key

2*θ* diffraction angle
I intensity/counts
C cristobalite
Q quartz
T tridymite

NOTE The cristobalite in this example came from an industrial source and contained a trace amount of quartz.

Figure B.3 — An X-ray diffraction (Cu Kα radiation) scan of a sample containing cristobalite, quartz and tridymite

B.4 XRD interferences on cristobalite

The three main peaks of α-cristobalite are given in Table B.1 along with several known mineral interferences.

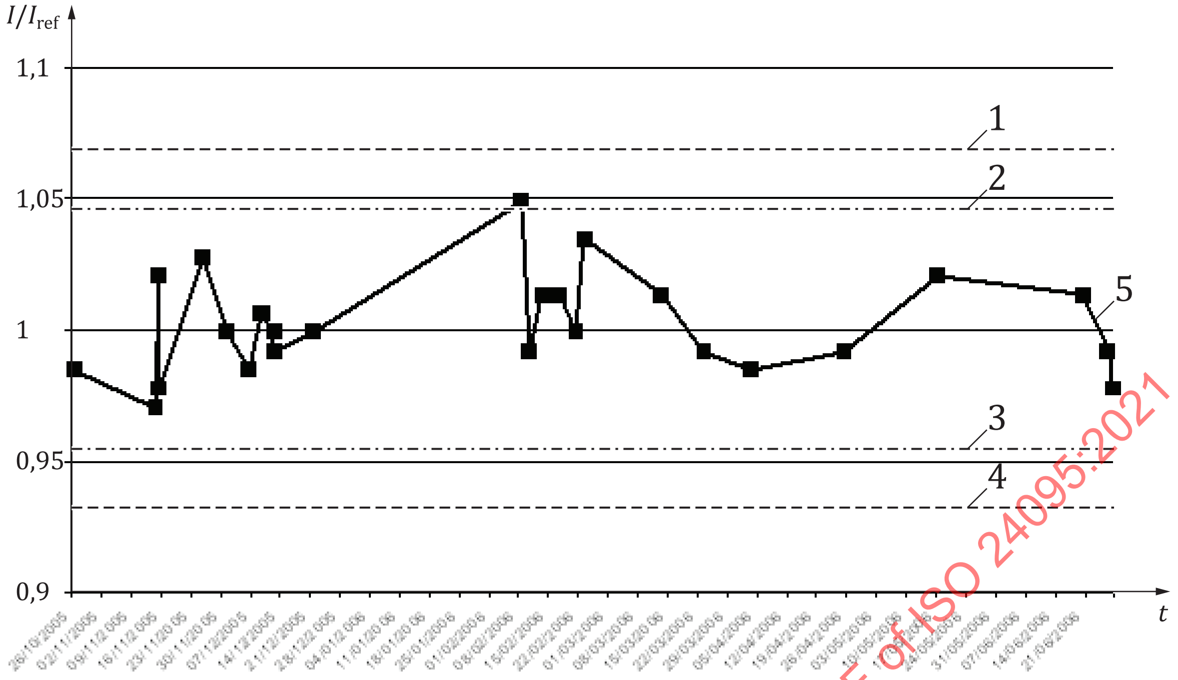
Table B.1 — Peaks and intensities of α-cristobalite (fixed divergence slit mounted on the incident beam, Cu Kα radiation) and known mineral interferences[24]

Analysis reflection	(100)	(101)	(200)
Relative intensity	100	14	20
d (Å)	4,05	2,841	2,485
Angle of diffraction (2θ) Cu Kα	21,95	31,49	36,15
Interferences			
Quartz	X		X
Tridymite	X		X
Albite (low)	X	X	X
Anorthite	X	X	X
Orthoclase	X	X	X
Calcite		X	X
Cordierite	X		X
Corundum			X
Kaolinite	X		X
Mullite			X
Muscovite	X	X	X
Talc	X		X
Zircon			X

Annex C
(informative)

Example of quality control charting for respirable crystalline silica

It is useful to record or plot the result obtained by each individual X-ray reflection or IR absorbance used in analysis because differences in background or peak position when analysing the same sample may produce an unexpected result on one of the reflections/absorbances and bias an average value. Unexpected values may be the object of an investigation and corrective action indicated by the quality system of the laboratory in accordance with ISO/IEC 17025. The example in Figure C.1 shows the variation of the measurements of the primary XRD 26,6° 2θ peak (Cu Kα radiation) on a sample containing about 100 µg of α-quartz. Similar plots can be created for IR analysis. The ratio between the results obtained and the value of the quality control material is plotted against the date of analysis. The value of the quality control material can be a theoretical or known value determined from the mass loaded on to a filter or an assigned or participant value from a proficiency-testing sample. If these values are used, the ratio of the result obtained with the assigned value may also provide an indication of potential bias. The ratio rather than absolute difference from the quality control value is often plotted so that samples with slightly different values can be included on the same chart. Before the ratio is calculated, diffraction intensity of quartz measured at each point in time must be corrected for the instrumental drift (radiation deterioration over time, see 8.6.1.1). This function may be included in the operation of the instrumentation. When using XRD, membrane or PVC filters become dry and brittle after repeated measurement. A slight trend towards larger values is not unexpected when measuring RCS with X-rays on these types of filter materials.



Key

t	date of analysis
I/I_{ref}	ratio of result and target value
1	upper action limit
2	upper control limit
3	lower control limit
4	lower action limit
5	quality control ratio value

Figure C.1 — A quality control chart for X-ray diffraction measurement

Annex D
(informative)

Estimation of expanded uncertainty for measurements of respirable crystalline silica

D.1 Uncertainty estimation

Uncertainty is quoted on measurement reports so that occupational health professionals can assess the reliability of a measurement value when interpreting data. If the exposure limit value (LV) is within the stated uncertainty of the result, further measurements may have to be taken to increase confidence that the LV is not exceeded. Knowing the expected uncertainty of the measurement is especially important if LVs are established at masses that approach the LOQ of the measurement methods, since the relative precision of measurements decreases as the amount of analyte measured is reduced. Performance requirements, such as ISO 20581 and Chapter E of the *NIOSH Manual of Analytical Methods*[26], describe the maximum allowable uncertainty or inaccuracy of occupational hygiene measurement methods in terms of relative error. ISO 20581 states that the relative expanded uncertainty of a measurement, including sampling and analysis, should not be greater than 50 % in the concentration range 0,1 to <0,5 times the LV and not greater than 30 % in the concentration range 0,5 to 2 times the LV. NIOSH have a method accuracy requirement for laboratory tests of ± 25 %, which may be expanded to ± 35 % for accuracy determined using field comparison of methods. Therefore, it is important that, when measurements are taken to assess compliance with an LV, information about the expanded uncertainty or variability of RCS measurements is available and that the method selected is demonstrated to meet the performance requirements of ISO 20581 or NIOSH at the appropriate occupational exposure limit. This annex provides guidance about how to calculate the uncertainty of RCS measurements to comply with ISO/IEC Guide 98-3[22] and gives an example of the uncertainty associated with a reported value. Other approaches may still be valid if it can be demonstrated they provide a “realistic” assessment of the variability of results.

D.2 Uncertainty of measurement

This method of calculating the uncertainty requires the analyst to examine the analytical procedure and identify each individual component that may add to the variability of a measurement. Estimates of the precision of each component are then calculated as a standard deviation or relative error and combined. According to ISO/IEC Guide 98-3[22], the n single components of uncertainty of type A and the m components of type B uncertainty can be estimated or calculated and then properly added to obtain a combined uncertainty, $u_{(c)}$. The final expanded uncertainty, U, is calculated at the end, multiplying $u_{(c)}$ by an approximate coverage factor, k = 2, if the degrees of freedom are at least 30. See Formula (D.1), Formula (D.2) and Formula (D.3):

$$u_{(c)A} = \sqrt{\sum_{1}^{n} u_{sA}^{2} + \sum_{1}^{n} u_{aA}^{2}} \tag{D.1}$$

$$u_{(c)B} = \sqrt{\sum_{1}^{m} u_{sB}^{2} + \sum_{1}^{m} u_{aB}^{2}} \tag{D.2}$$

$$u_{(c)} = \sqrt{u(c)_{A}^{2} + u(c)_{B}^{2}} \qquad U = 2\,u_{(c)} \tag{D.3}$$

where

u_{sA} is the sampling uncertainty of type A;

u_{sB} is the sampling uncertainty of type B;

u_{aA} is the analysis uncertainty of type A;

u_{aB} is the analysis uncertainty of type B.

The single components of the uncertainty of sampling can mainly be those linked to:

a) volume of sampled air;

b) efficiency of the sampler;

c) transportation and storage of samples.

The single components of the uncertainty of analysis can mainly be those linked to:

1) analytical variation, e.g. matrix absorption can be a significant uncertainty factor for a heavy dust sample, if variation is estimated only from pure CS samples;

2) correction for the recovery or bias of the method;

3) instrumental drift.

D.3 and D.4 give guidelines on how laboratories can quantify each of these components.

D.3 Sampling

The analyst can only assess the variation of the measurement itself rather than the sampling environment. The precise characterisation of the sampling environment is the responsibility of the individual supervising the collection of the sample, who is not always the same person that measures the sample. If the purpose of the uncertainty estimate is to assess if the method complies with ISO 20581, then it should include the estimate of the contribution from the sampling procedure directly influencing the measurement. Many of these sampling components are not easily estimated within a laboratory and it is common practice, in these circumstances, to include a value taken from published standards (see guidelines in ISO 20581).

The sampling components and typical values associated with the sampling process and how they are determined are shown in Table D.1.

The dust on the filter material should not suffer any degradation or loss if it is stored under normal laboratory conditions. Sample loss occurs if pressure is applied against the sample surface or if the sample is too heavily loaded (> 6 mg for 25 mm diameter filters). At most normal loadings (< 4 mg), the respirable dust is safely contained on the filter and is not lost if the sample is handled with care. The filter material degrades if the sampling environment is particularly humid. In most circumstances, transportation and storage can be ignored for crystalline silica measurement uncertainty estimation.

D.4 Analysis

The processes in D.4.1 to D.4.3 are associated with the analysis. A summary of typical values for each process is shown in Table D.2.

Table D.1 — Summary of major uncertainty contributions and typical values for RCS sampling

Variable	Determination method	Typical values
Master flow meter calibration (bubble flow meter)	Test certificate	0,6 %
Pump rate reading	10 repeat measurements	1,9 %
Sampling time	Estimation from ISO 20581 assuming 4 h sampling period	0,24 %
Sampling instrument		
Calibration of sampler test system	Listed as a typical value in EN 13205	1 % to 2 %
Estimation of sampled concentration	Listed as a typical value in EN 13205	1 % to 2 %
Bias relative to sampling convention	Listed as a typical value in EN 13205	5 % to 10 % for well optimised samplers 10 % to 25 % otherwise
Individual sampler variability	Listed as a typical value in EN 13205	3 % to 7 %
Excursion from nominal flow rate	Listed as a typical value in EN 13205	2 % to 5 % if the concentration is calculated from the nominal flow rate 5 % to 9 % if the concentration is calculated from the average flow rate
Sampling uncertainty taking mid-range values listed in EN 13205		11,8 % from average flow rate 10,1 % from nominal flow rate

NOTE Some countries recommend using the nominal flow rate for cyclones or impactors as the sampling instrument is able to self-compensate in terms of the mass, because the separation efficiency is dependent on the pump performance.

Table D.2 — Summary of major uncertainty contributions and typical values for RCS analysis

Variable	Determination method	Typical values[a] Method A	Typical values[a] Method B
Certified standard	From certification	1,4 % to 0,4 %	1,4 % to 0,4 %
Analytical precision	Within laboratory reproducibility	9 %	
Instrumental precision	Repeat measurements		5 %
Calibration (including weighing)	Residual error		7 %
Recovery/method bias	Recovery tests/proficiency test results	See D.4.2	See D.4.2
Instrument drift	Variation of differences	2 %	2 %
Analysis uncertainty		9 %	9 %

[a] For a 100 µg sample.

Method A — Uncertainty estimation from an intermediate reproducibility exercise where the test samples are included in the whole analytical procedure including recovery

Method B — Uncertainty estimation from a repeatability exercise where calibration is traceable to primary standards.

D.4.1 Analytical precision

D.4.1.1 Method A — Determining analytical variation from intermediate reproducibility

This component comprises both the instrumental and calibration error and can be determined from a within-laboratory exercise; measuring replicate samples at different measurement levels across the analysis range on different days and calculating the reproducibility using analysis of variance (ANOVA). The relationship between reproducibility and the mass measured should be characterised across the analytical range and the equation used in the calculation of the reported uncertainty since the precision is not expected to be constant at all measurement levels. It is difficult to accurately produce replicate samples using aerosol deposition methods and, in these circumstances, laboratories may choose to calculate the uncertainty from repeatability and calibration data (Method B) or use within-laboratory precision results from interlaboratory comparisons (subject to certain considerations). This procedure can be used when laboratories are using methods that are able to produce replicate test samples. Alternatively, those laboratories using direct on-filter methods may prepare pairs of test samples with similar loadings, normalise the results obtained for each pair with their average and calculate the reproducibility of the normalised results.

D.4.1.2 Method B — Determining analytical precision from repeatability data

The components described in D.4.1.2.1 to D.4.1.2.2 should be considered for RCS analysis.

D.4.1.2.1 Instrumental precision

This precision is derived by the repeated measurement of samples loaded with different masses of crystalline silica within the expected analysis range. The relationship between precision and mass measured should be characterised and used in the calculation of the reported uncertainty. In XRD analysis, instrumental precision may vary depending on the diffraction peak or peaks selected for reporting and this should be taken into consideration.

D.4.1.2.2 Calibration precision

The uncertainty of weighing and volumetric procedures involved in making the calibration test samples are small when using methods where the test samples are prepared by pipetting known aliquots of suspension, such as NIOSH Method 7500[3]. If weighing is used to prepare the calibration test samples, then this factor should be carefully controlled because it may become an important contribution to the uncertainty of the calibration line[27].

The uncertainty of the calibration line is determined from the square root of the sum of squares of the residual errors. This is the sum of the differences in the value of the mass on the standard compared with the value calculated from the intensity obtained when measuring the standard and calibration coefficients. The uncertainty of the calibration line, u_c, is given by Formula (D.4) (see Eurachem/CITAC Guide[28]).

$$u_\mathrm{c} = \frac{s_\mathrm{c,\,res\,err}}{b_\mathrm{c}} \sqrt{\frac{1}{n_\mathrm{p}} + \frac{1}{n_\mathrm{c}} + \frac{(m_\mathrm{obs} - \bar{m})^2}{\sum (m_i - \bar{m})^2}} \qquad \text{(D.4)}$$

where

b_c is the calibration slope co-efficient;

$s_\mathrm{c,res\,err}$ is the standard deviation of the residual error of the calibration line;

n_c is the number of calibration standards;

n_p is the number of measurements;

m_obs is the observed value;

$\bar{m}$ is the average mass of the calibration standards;

m_i is the mass of calibration standard i.

where Formula (D.6) applies

$$s_{\mathrm{c,\,res\,err}} = \sqrt{\frac{\sum\left(I_{\mathrm{pred}} - I_i\right)^2}{\left(n_{\mathrm{c}} - 2\right)}} \tag{D.5}$$

in which

I_i is the intensity of calibration standard i;

I_{pred} is the observed value of the intensity.

The root mean square (RMS), $s_{\mathrm{c,res\,err}}$, should be calculated taking into account the degrees of freedom ($n_{\mathrm{c}} - 2$).

The term given in Formula (D.6)

$$\frac{\left(m_{\mathrm{obs}} - \bar{m}\right)^2}{\sum\left(m_i - \bar{m}\right)^2} \tag{D.6}$$

allows for an increase in uncertainty at the extreme masses of the calibration and is almost zero in the centre of the calibration range.

The reported masses of most measurements of RCS are at the lower end of the calibration range so the formula should not be simplified. The value obtained from the calculation is in terms of mass and has to be compared with the predicted mass to obtain a relative value to use in the expanded uncertainty calculation. If the amount of analyte on the calibration test samples is traceable to a primary standard, the residual error also includes an estimate of method bias.

Table D.3 is an example of the XRD calibration line of the primary quartz peak at 26,6°.

In the example given in Table D.3, the uncertainty in the calibration line is small in terms of micrograms but in terms of relative error it makes an impact on the expanded uncertainty when measuring masses of 25 µg or less (see Table D.4).

D.4.2 Method bias

D.4.2.1 RCS calibration standard

Either the calibration or the reported results should be corrected for the known crystallinity of the respirable crystalline silica standard used for calibration to prevent potential bias[19]. The certified value for crystallinity has a known variability that can be included in the uncertainty estimation. However, the variability of the certified value for α-quartz is likely to be very small (0,4 % to 1,4 %) and does not influence the expanded estimate.

D.4.2.2 Recovery

This is a major source of potential bias. A separate estimate for this is not needed if the samples used in the intermediate precision exercise are involved in the whole analytical process, otherwise it should be determined separately by measuring the mass recovered from loaded filters included in the sample preparation process. It is important to gain an estimate of the loss of analyte at the LV and half the LV for full and half-shift sampling. The reader should be aware that some procedures might not permit half-shift sampling.

D.4.2.3 Certified reference material

The method bias can be determined by using a suitable CRM or by participation in proficiency testing programmes. Suitable CRM for the direct-on-filter method is available from the UK Health and Safety Laboratory (HSL). Suitable CRM for the indirect method is available from NIST(29). If a CRM is used the reported uncertainty of the method bias u_{mb} should be a combination of the uncertainty of the assigned value and the variation of the error of the measurement results compared with the assigned value of the CRM. See Formula (D.7)

$$u_{\text{mb}} = \sqrt{u_{\text{CRM}}^2 + s_m^2} \quad \text{(D.7)}$$

where

u_{CRM} is the uncertainty of the CRM taken from the certificate;

s_m is the standard deviation of measurements on the certified reference value.

Table D.3 — Example for an X-ray diffraction calibration

Calibration points $-m_i$ µg	$(m_i - \bar{m})$	$(m_i - \bar{m})^2$	**Intensity** I_i counts/s	I_{pred} **from calibration formula**	**Difference** $I_{\text{pred}} - I_i$	$(I_{\text{pred}} - I_i)^2$
74	−97,17	9 442,01	8,438	9,336	0,898	0,806
31	−140,17	19 647,63	3,622	3,561	−0,061	0,004
145	−26,17	684,87	17,87	18,871	1,001	1,002
155	−16,17	261,47	20,21	20,214	0,004	0,000
143	−28,17	793,55	19,00	18,603	−0,397	0,158
146	−25,17	633,53	19,49	19,005	−0,485	0,235
347	175,83	30 916,19	44,97	46,000	1,030	1,060
214	42,83	1834,41	28,45	28,138	−0,312	0,097
264	92,83	8 617,41	35,12	34,853	−0,267	0,071
212	40,83	1 667,09	28,64	27,869	−0,771	0,594
173	1,83	3,35	24,31	22,632	−1,679	2,817
150	−21,17	448,17	18,42	19,543	1,123	1,260
	Sum	74 949,67			Sum	8,11
From equation of regression line						
	8,11	Sum of differences squared of $\sum(I_{\text{pred}} - I_i)^2$				
	0,900	RMS, $s_{\text{c,res err}}$				
	0,134 3	Slope, b, from the equation				
	6,704	sc,res err /b				
	171,17	Average calibration point mass, $\bar{m}$				
	74 949,67	Sum of squares $\sum(m_i - \bar{m})^2$				

Table D.4 — Predicted uncertainties in the RCS analysis due to the XRD calibration

Mass measured m_{pred}	$(m_{\text{pred}} - \bar{m})^2$	**Uncertainty** u_{c} µg	**Relative uncertainty** %
25	21 364,69	7,842	31,37
50	14 682,17	7,582	15,16
100	5 065,17	7,192	7,19
150	448,17	6,997	4,66
300	16 597,17	7,658	2,55

D.4.2.4 Proficiency testing schemes

Alternatively, long-term participants in proficiency testing schemes can obtain estimates of method bias from their results. To estimate the uncertainty of the method bias value, the standard deviation of differences of the laboratories' results from the values assigned by the proficiency-testing provider should be calculated. To provide a realistic estimate, loadings nearest the EL or towards the lower third of the analytical range supplied by the proficiency testing provider should be considered in preference to those at the higher end of the analytical range[30]. The variation in laboratories' results should be combined with the uncertainty of the assigned value.

$$u_{\mathrm{mb}} = \sqrt{s_{\mathrm{PT}}^2 + \sigma_m^2} \tag{D.8}$$

where

σ_m is the standard deviation of measurements from the proficiency testing assigned value;

s_{PT} is the uncertainty of the assigned values.

If the uncertainties of the assigned values are not provided by the proficiency testing provider, they can be estimated from the between-laboratory standard deviation and number of participants using Formula (D.9)

$$s_{\mathrm{PT}} = \frac{s_{\mathrm{T}}}{\sqrt{n}} \tag{D.9}$$

where

s_{T} is the average between-laboratory standard deviation of participants results obtained from literature or from proficiency testing reports;

n is the average number of participants involved in the rounds.

However, in RCS analysis, a between-laboratory standard deviation of about 15 % can reasonably be achieved at about 50 µg. If 15 laboratories are involved in the scheme, σ_m would have to be about 5 % or less before s_{PT} would contribute more than 1 % to the method bias uncertainty.

D.4.3 Instrumental drift

Instrumental drift is calculated from the variation of the differences of the value of a monitor measured before and after the analyses of samples. For IR instruments, the calibration is not expected to change during the analysis of a typical set of samples and for most XRD instruments the change in monitor is often 2 % or less. However, the instrumental drift can be poorer on older types of instrument, when the IR calibration has not been checked for some time or when the intensity of the X-ray tube is substantially reduced from its initial value.

D.5 Uncertainty estimated from the Horwitz equation

The Horwitz equation for between-laboratory precision data is proposed as a method to estimate the uncertainty RCS measurements may achieve. The Horwitz equation is an empirical expectation for the median spread of results based on data obtained from a wide range of collaborative testing programmes in the Association of Official Analytical Chemists in the USA. Collaborative testing and proficiency testing may differ in the precision achieved because proficiency testing often permits different methodologies. The Horwitz equation for the coefficient of variation (CV), C_V, as a percentage, in this document is expressed as given in Formula (D.10)

$$C_V = A\,m^B \tag{D.10}$$

where

A, B are constants;

Im is the concentration level, expressed as the mass of the analyte sampled.

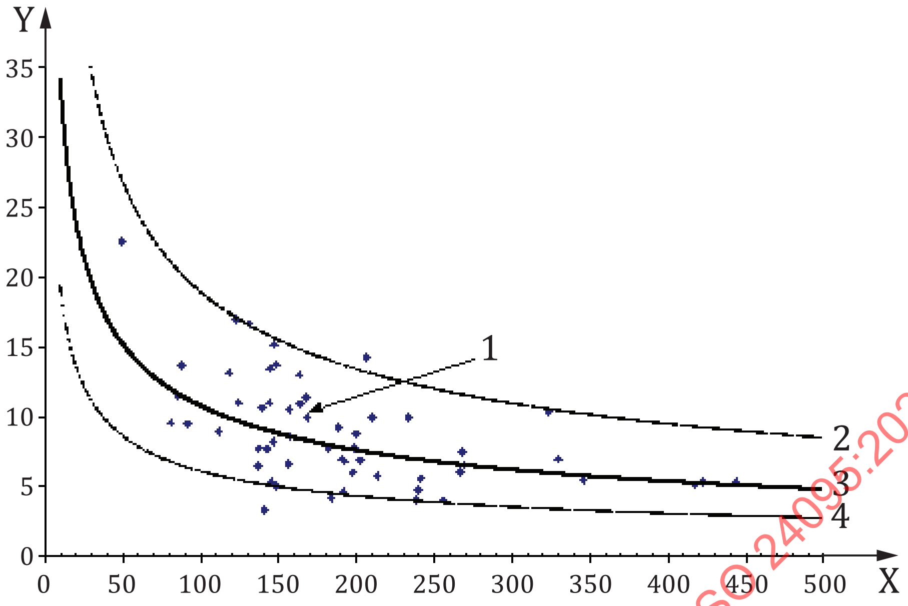
Reference [30] suggests the least-squares fitting of a linearized form of the Horwitz equation as a useful tool to explore analytical systems. The Horwitz equation is linearized by taking the logarithm of both sides. See Formula (D.11)

$$\log C_V = B \log m + \log A \tag{D.11}$$

The linearized equation has the added convenience of allowing the use of the analytical unit of measurement rather than the mass fraction required by the standard approach using the Horwitz equation; if the constants in the equation are consistent with the analytical unit of measure used to derive them, the equation returns the median CV value. When the constants A and B are fitted to data from the United Kingdom proficiency testing programme the Workplace Analysis Scheme for Proficiency (WASP) (WASP rounds 36 to 49, 70) the resulting empirical Horwitz equation is given in Formula (D.12)

$$C_V = 109{,}01\,m^{-0{,}503\,6} \tag{D.12}$$

where m is the mass, in micrograms. See Figure D.1.



Key

X	mass
Y	coefficient of variation $C_V = 109{,}01\ m^{-0{,}503\,6}$
1	interlaboratory standard deviation of results from WASP participants using direct on-filter analysis methods
2	upper 97,5 % confidence level
3	linearized Horwitz curve
4	lower 97,5 % confidence level

Figure D.1 — Coefficient of variation, as a percentage, predicted using the coefficients obtained from the linearized Horwitz equation for results from laboratories using direct on-filter analysis methods

The two-sided 90 % confidence interval is calculated based on the standard error in the estimate (SEE), $(s/\sqrt{n_p})_{\log m,\log CV}$ obtained from the linearized equation. For these data, $(s/\sqrt{n_p})_{\log m,\log CV} = 0{,}150\,2$, see Formula (D.13) and Formula (D.14)

$$C_V = 109{,}01(m^{-0{,}503\,6}) \times 10^{1{,}645(0{,}150\,2)} \text{ upper 5 % boundary} \qquad \text{(D.13)}$$

$$C_V = 136{,}34(m^{-0{,}503\,6})/10^{1{,}645(0{,}150\,2)} \text{ lower 5 % boundary} \qquad \text{(D.14)}$$

The empirical Horwitz equation fits data from WASP quite well, but the extrapolated curve can be sensitive to outliers at high and low masses and Horwitz-like equations are known to easily overestimate the CV at low concentrations. However, the derived empirical equation is similar to the Poisson counting error formula, familiar to XRD measurements, where the counting error is the primary contributor to the analytical error, see Formula (D.15)

$$C_V = 100\,K\,m^{-0{,}5} \qquad \text{(D.15)}$$

where K is a constant that includes the statistical sampling of the calibration slopes of the laboratories involved in the study. The close similarity to the Poisson error prediction indicates that the equation fitted to the WASP data may be useful within the analytical range where the background noise is a minor consideration. Other work has observed that about 120 ppb (ng/g) the measured CV of results tends to fall in the range 20 % to 25 % even though the Horwitz equation may predict higher values. Within-laboratory CV is often one-half to two-thirds the between-laboratory precision measured in collaborative tests. Therefore, when the between-laboratory CVs are close to about 22 % (about 25 µg based on the fitted Horwitz-like equation) the within-laboratory CVs are approaching their LOQ.

D.6 Proficiency test results

Proficiency testing results can contribute to the estimation of uncertainty and can also be used to assess if the uncertainty estimates obtained are valid. There are however several considerations.

a) The lowest mass in the analytical range of a proficiency-testing sample is often higher than the masses measured on routine samples.

b) Extrapolation of the standard deviation of measurements below the lowest proficiency test sample mass is not recommended unless additional precision tests can verify the predicted relationship.

D.7 Reporting

It is best practice to report the expanded uncertainty with the analysis result in terms of mass. If the sampling volume is known this can be reported in terms of mgm^{-3}. For RCS analysis, many laboratories may not have control over the calibration of the sampling apparatus used to collect the samples, so it may not be appropriate to report a value combining the uncertainties from sampling and analysis in these circumstances. When appropriate, the uncertainty statement should indicate whether an estimate has been included for the uncertainty associated with the sampling apparatus or give an indication of the magnitude of this uncertainty separately. If laboratories have used the same procedure detailed in this document, they may wish to indicate that many of the estimates for the sampling instrument were obtained from international standards.

In RCS measurements, the uncertainty is usually determined by taking measurements on filter samples with a pure crystalline silica dust standard. In samples with significant interferences, the uncertainty reported is smaller than the true range of analysis results. Possible interferences should be noted in the report and if appropriate, the laboratory should add a statement about how the reported uncertainty is affected.

The reported results should be corrected for the percentage crystalline silica in the powder used to prepare the calibration test samples.

Annex E
(informative)

Differences between samplers (cyclones and other types)

It is not uncommon, even within the same company, to discover that several different sampler types were used to assess the same task. Some national methods or practices allow the use of alternative samplers. Most samplers were not designed to conform to the ISO 7708 sampling penetration curve, but their flow rates can be modified to provide a reasonable match. However, samplers do not match the penetration curve exactly and nor does their performance exactly match that of other sampler types. Even within a sampler type there is a unit-to-unit variation in performance. As differences in performance affect the mass of dust collected by the sampler this can cause differences in the mass of analyte measured and hence results for RCS obtained by laboratories. The table below compares the performance of respirable samplers in common use with the analysis of RCS when sampling dust in a calm air chamber with low wind speeds (0,3 m.s^{-1} or less). The differences are related to the consensus value of all the samplers in the test run. The results are based on the sampling of ultra-fine and medium Arizona road dust, which contains a significant percentage of quartz. Generally, the performance of samplers is dependent on wind speed and the median and the standard deviation of the particle size range. Therefore, these results are indicative.

Table E.1 — Differences of samplers (cyclones and other types) from an average air concentration in calm air[31]

Variable	Flow rate# (l/min)	Difference	95 % Confidence level	Difference	95 % Confidence level
Sampler		Medium ARD		Ultra fine ARD	
FSP10	10,2	+13,6 %	± 14,1 %	+16,7 %	± 9,2 %
PPI2	2,0	+5,6 %	± 26,3 %	+12,7 %	± 12,5 %
SKC “non corrosive”	2,2	+5,5 %	± 13,1 %	+3,1 %	± 8,1 %
Envirocon GX-1	2,2	+4,0 %	± 7,8 %	+1,5 %	± 8,0 %
SIMPEDS	2,2	+3,5 %	± 9,2 %	−6,1 %	± 4,7 %
BCIRA	2,2	−0,6 %	± 10,2 %	−3,6 %	± 8,0 %
CIP 10-R	10	−4,6 %	± 6,9 %	−6,9 %	± 15,7 %
GS3	2,75	−10,5 %	± 8,8 %	−9,2 %	± 4,8 %
GK2.69	4,2	−17,5 %	± 14,9 %	+1,9 %	± 7,1 %
IOM with PUF Insert	2,0	−19,0 %	± 7,0 %	−17,9 %	± 5,8 %
SKC Al cyclone	2,7	−22,5 %	± 8,6 %	−14,2 %	± 7,9 %
Dorr Oliver*	1,7	−27,2 %	± 9,8 %	−22,1 %	± 10,2 %

NOTE 1 Some of the samplers were used with a non-conductive cassette but none of the dust collected on the inside walls of the cassette was recovered prior to the analysis.

NOTE 2 Flow rate used in the experimental study. Different flow rates may be required for workplace monitoring.

The samplers listed in this table are not exhaustive. The samplers used should comply with the requirements of EN 13205, but not all these samplers have been tested in accordance with the requirements of EN 13205 by an organization accredited to perform such testing. These results are applicable to the flow rates specified by the supplier of the sampler at the time of the study and may be different if another flow rate is used. Please note that these results are applicable to calm air conditions