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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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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).

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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.

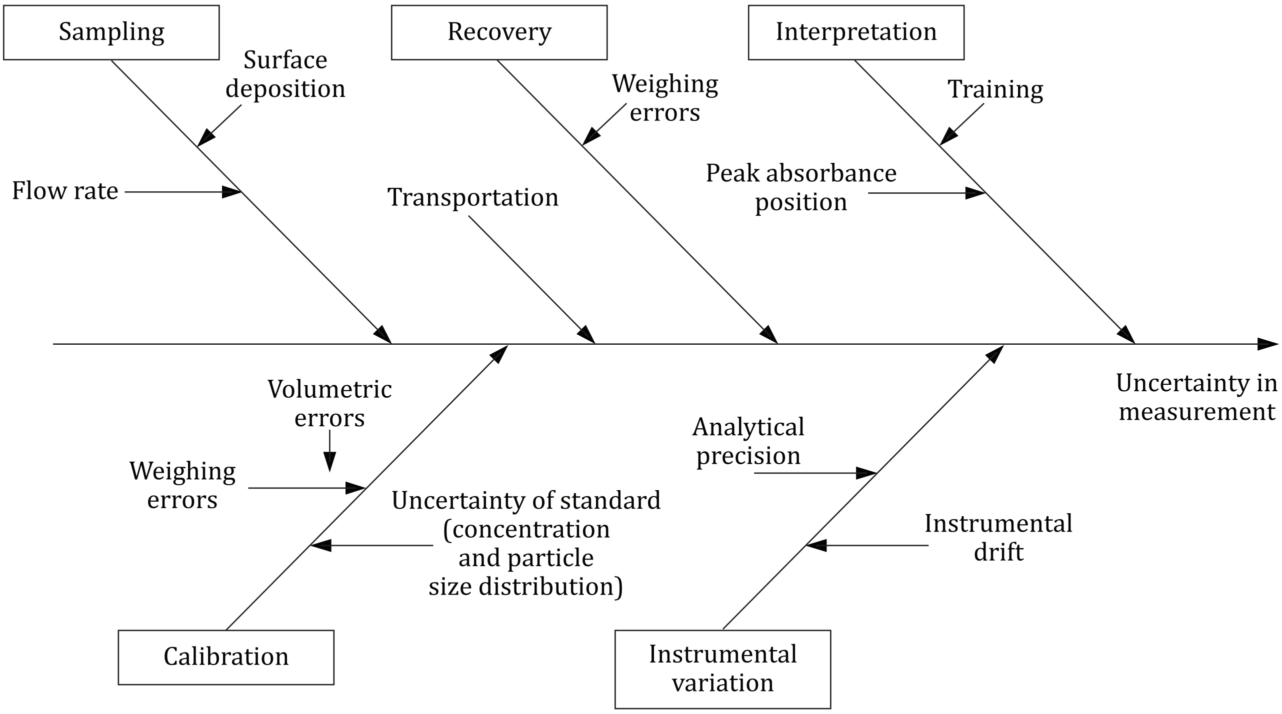

Figure 1 — Cause and effect diagram illustrating sources of uncertainty in the measurement of respirable crystalline silica

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):

$$\frac{\bar{A}_{\mathrm{CM}}}{A_{\mathrm{Ref}}}\,\frac{w}{100} \qquad (1)$$

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